Powder Diffraction and Rietveld Refinement School 2026

Session 0 “Welcome”

Prof. John S.O. Evans

Durham University, Department of Chemistry

Teachers, tutors, tutorials

- Jeremy Cockcroft, UCL
- Robert Dinnebier, Max Planck Stuttgart
- John Evans, Durham Chemistry
- Andy Fitch, ESRF
- Arnt Kern, Bruker
- Emma McCabe, Durham Physics

- Anders Baek Borup, Aarhus
- Sam Thompson, Aarhus

- Esther Curtis, Durham
- George Marshall, Durham
- Oliver Wagstaff, Durham

Tutorials etc

topas.webspace.durham.ac.uk/rietveld_school_tutorials/

[typo apology…..]

Thanks

- Teachers/tutors for their time
- Sponsors for cash
- Alan Coelho/Bruker for TOPAS software
- Bob von Dreele/Brian Toby for GSAS-II
- Juan Rodriguez-Carvajal for FullProf

Welcome formalities

- Health and Safety/Fire procedures
- We have a plan for the week, but tell us if there are things you'd like covered – special topics on the final morning?
- e.g. use the pre-course questionnaire for this
- Make use of the experts who will be here for the school

Legalities

- By using CIS account you're agreeing to University policy on use of the internet

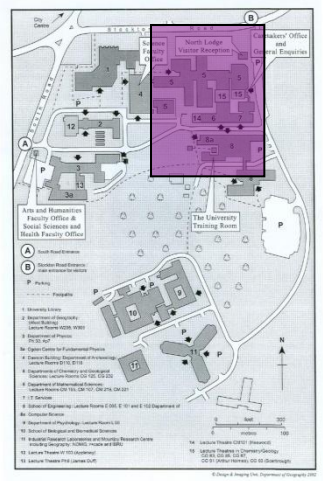
- You each have your own login id. Don't change the password!!!
- Password: Ws1Q84PLmb42!

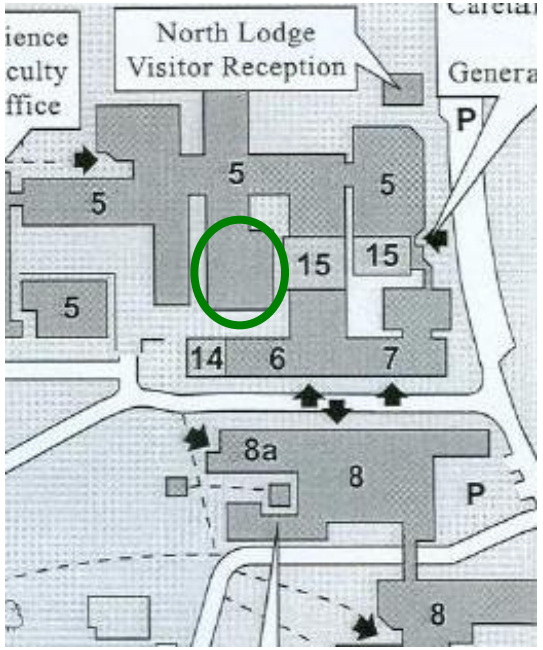
- TOPAS controlled by license server "codemeter" which is installed on your CIS computer
- TOPAS license is time-limited

- All timetabled sessions are compulsory
- Always wear a name badge
- No email during lectures/classes (teachers behind you!)
- Phones to silent
- Please don't record lectures

House keeping/arrangements

- Morning sessions will be lectures/small group tutorials in Calman Learning Centre 406/407
- Afternoon sessions will be in computer classrooms near Chemistry – CG66 and CG68
- Most lunches in Calman Learning Centre
- Most dinners in Collingwood college
- Evening events in Collingwood, Durham City and Castle





The school isn't meant to be…..

- How to use TOPAS
- How to use GSAS-II
- How to use FullProf

- Linear in its organisation
  - 3 days of theory lectures + 1 day hands-on = bad
  - Sometimes you'll be doing problems "blind" – trust us!
  - Some practicals will come before the relevant theory
  - There IS value in plugging numbers into equations!
  - You'll learn by mistakes
  - Confusion can be good

The school is meant to…..

- Provide understanding of how to think when collecting (powder) diffraction data
- Provide understanding of what Rietveld packages are doing
- Allow you to practice Rietveld refinement
  - Different instruments
  - Different sample types
  - Different problems
- Teach you to be critical/creative
  - How far you can push data?
  - When you should start to be suspicious?
  - How to spot problems
  - How to do novel types of analysis
- Be interactive and supportive
  - Don’t worry if (when) you don’t finish all problems, nobody every has
  - Don’t worry if you don’t understand everything in lectures, there’s time in tutorials and hands-on exercises to talk to teachers one-to-one

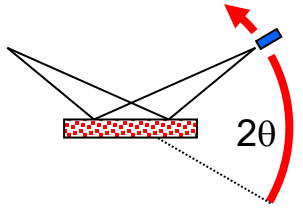
Approximate timetable – special topics requests?

	Sunday 12/4/26	Monday 13/4/26	Tuesday 14/4/26	Weds 15/4/26	Thursday 16/4/26
09:00		3. Intro to (powder) diffraction	9. Structure factors, peak intensities & Rietveld refinement	16. Peak shapes & microstructure	22. Q&A/special topics
09:45		4. Peak positions tutorial	10. Data collection lecture	17. Restraints, constraints & rigid bodies	23. Multiple data sets, structure solution, other software
11:00		Coffee	Coffee	Coffee	Coffee
11:30		5. Least squares lecture	11. Synchrotrons & neutrons	18. Intro to GSAS/Fullprof	24. Spot the errors
		6. Least squares tutorial	12. Tutorials on morning topics	19. Tutorials on morning topics.	
13:00		Lunch	Lunch	Lunch	Lunch
13:45	14.00 onwards Registration in Collingwood College	7. Least squares tutorial – excel (lines, Rietveld, cells and indexing)	13. Interactive Rietveld /Software intro	20. Rietveld problems – empirical peak shapes, microstructure, fund'l parameters	
	15:15 Welcome/Intro		14. Rietveld problems - simple		
15:45	1. Symmetry	Tea	Tea	Tea	
16:15	2. Symmetry tutorial	8. Peak fitting and indexing	15. Rietveld problems – neutron, synch, combined	21. Rietveld problems – restraints, rigid bodies, combined, structure solution	
18:00	Dinner – Collingwood	Rest time	Dinner - Chemistry	Beautification time	
18:30		Dinner – Collingwood	"Fun" Tutorial (you'll need outside clothes)		
19:00	19.00 Symmetry tutorial			19:00 Castle bar opens	
19:30		School Quiz		19.30 School Banquet, Castle	

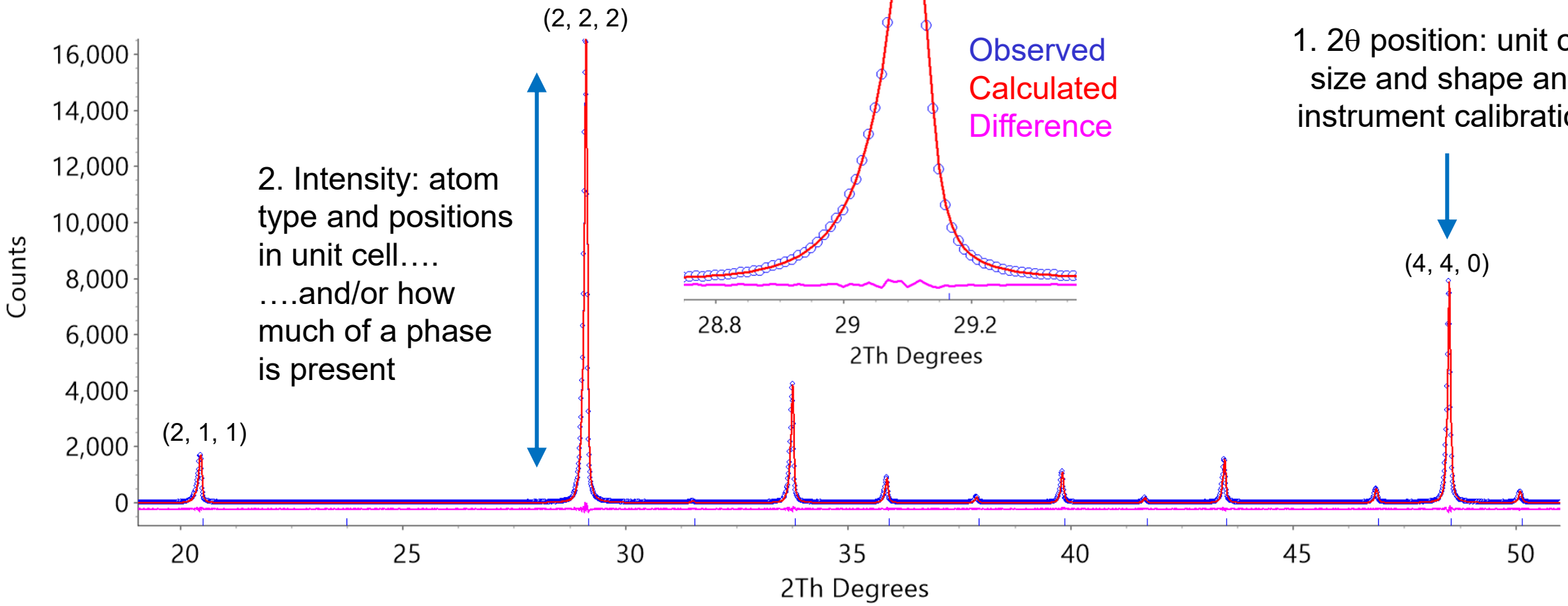
Key:	Computer exercise	Lecture	Social	By-hand tutorial

Powder diffraction / Whole Pattern Powder Fitting

"Rietveld refinement in Excel", Evans and Evans, *J. Chem. Educ.*, 2021, **98**, 495−505



3. Shape/fwhm: instrument and sample contributions



Powder diffraction / Whole Pattern Powder Fitting

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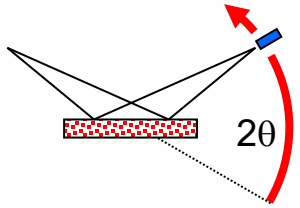
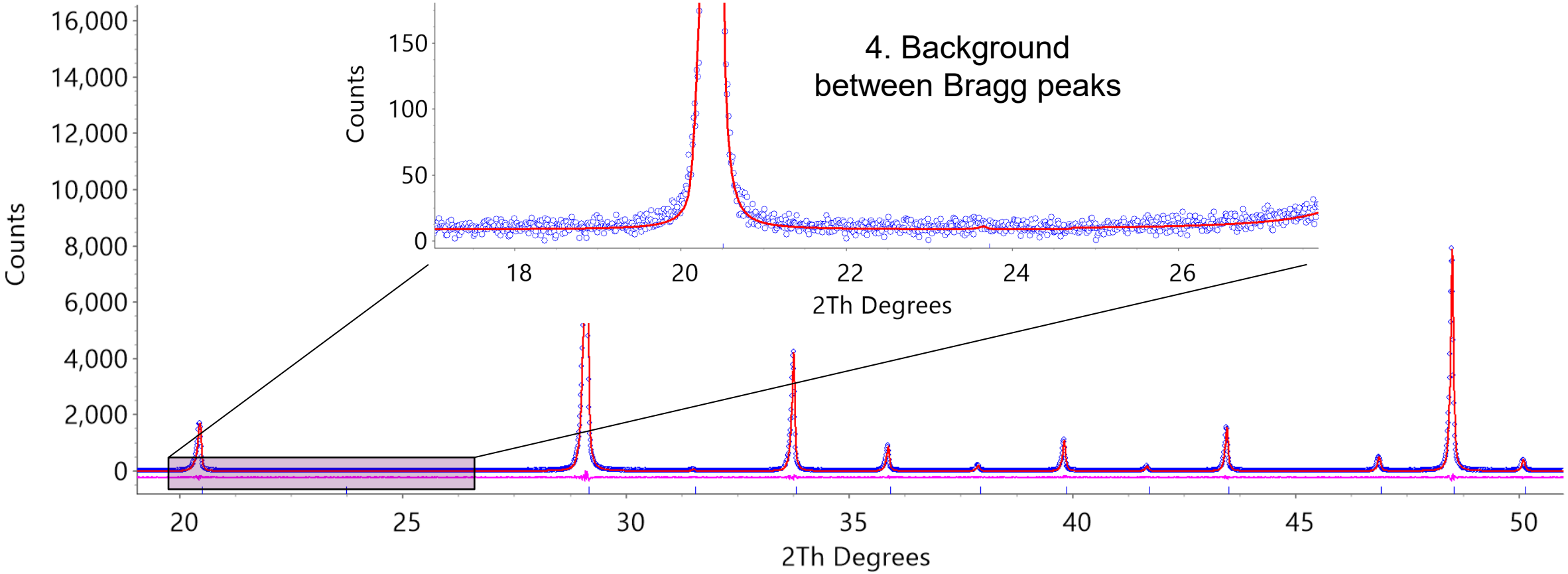
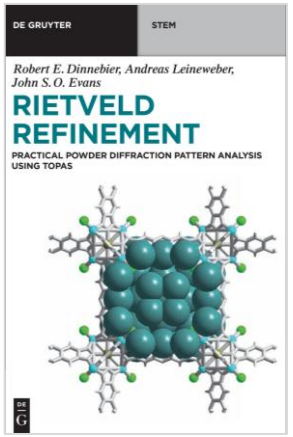


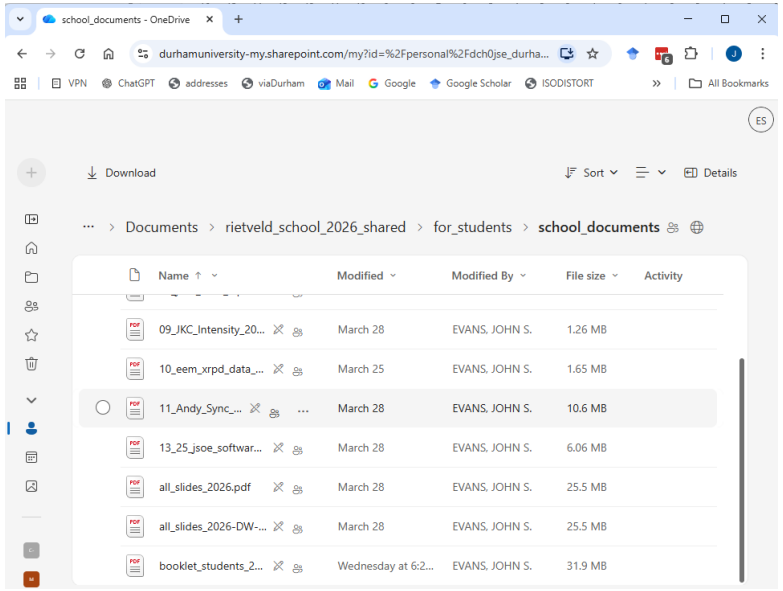


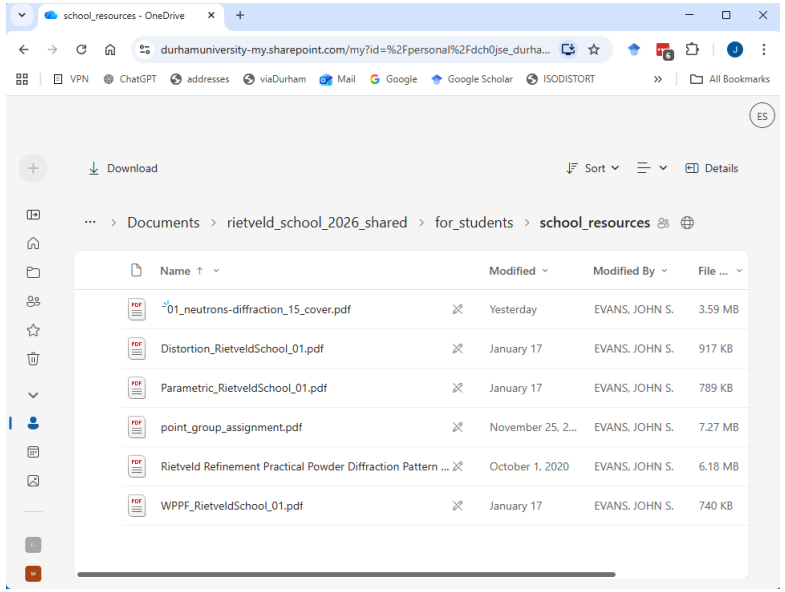
School resources

- Booklet contains lecture slides, classroom problems
- Other files linked from main tutorial page
- Sharepoint folder: for_students
  - school_documents: booklet, colour pdf of slides, etc
  - school_resources: Rietveld book, neutron chapter, notes, etc
- Answers to problems after school



Tutorials etc





Actions, questions, group bonding

- Homework
  - Complete the pre-course questionnaire
  - Complete the “Session 0: Matrix Homework” questions in booklet (10 minutes?)
  - Matrix reminders on P79 of booklet
- Questions?
- Group introductions

Tutorials etc

Questionnaire

Session 1: Crystallographic Symmetry

Jeremy Karl Cockcroft

Department of Chemistry, UCL

Why bother?

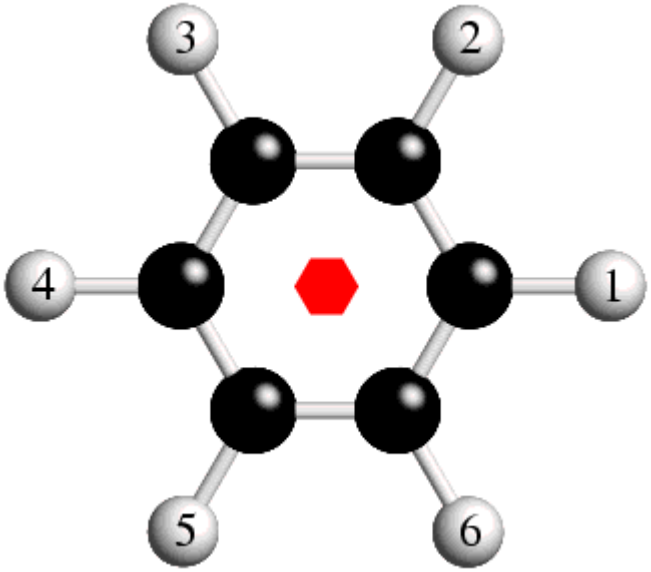
- To describe crystal structures
  - Simplifies the description, e.g. NaCl structure
    - » Requires coordinates of just 2 ions + space group symmetry to describe a crystal made up of trillions of ions!
- To solve crystal structures
  - Relate diffraction (reciprocal-space) symmetry to crystal (real-space) symmetry
- To relate crystal structures
  - Phase transitions
- To index a powder pattern
  - Exploit symmetry of the unit cell

Types of Symmetry

- Rotational symmetry about a line
- Rotary-inversion symmetry about a line
- Translational symmetry
- Screw symmetry
- Glide symmetry

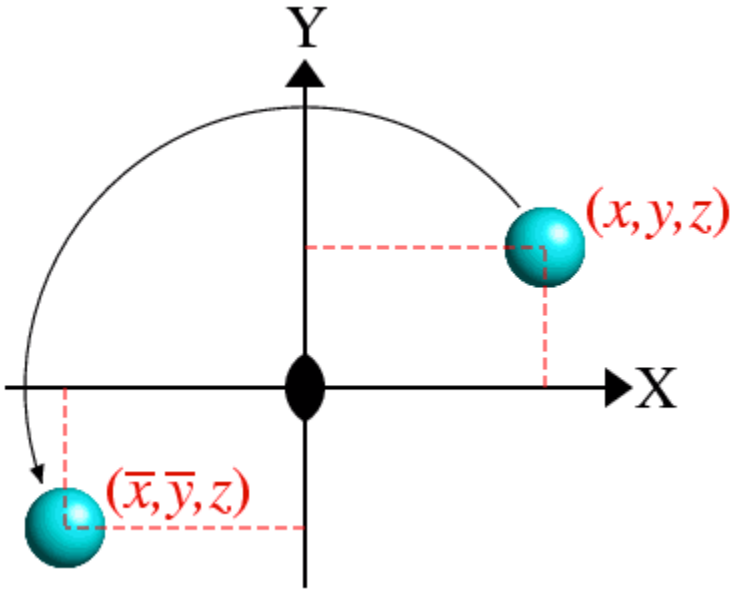
Rotational Symmetry

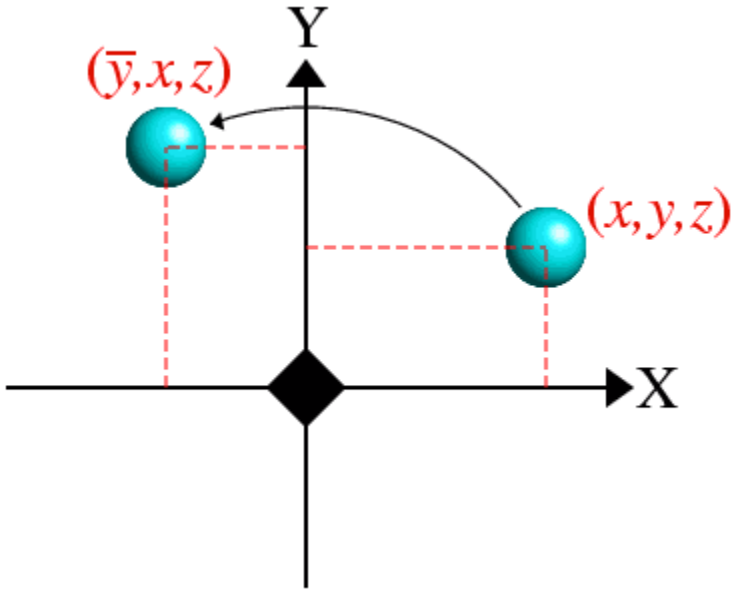
- Rotation anticlockwise 360° / n
  - Symbols: 1, 2, 3, 4, 6



Symmetry Operators

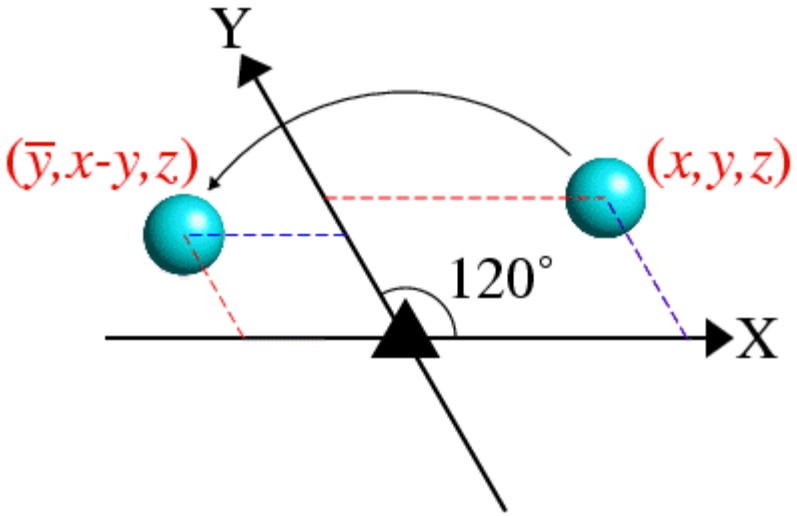
- Need to distinguish between symmetry elements, symmetry operators, & coordinates





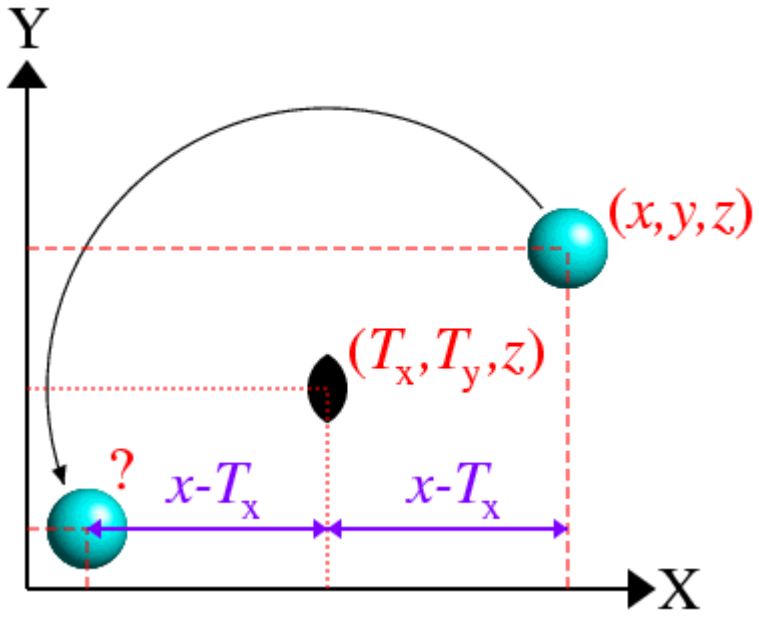
Symmetry Operators

- Advantage of non-orthogonal axes



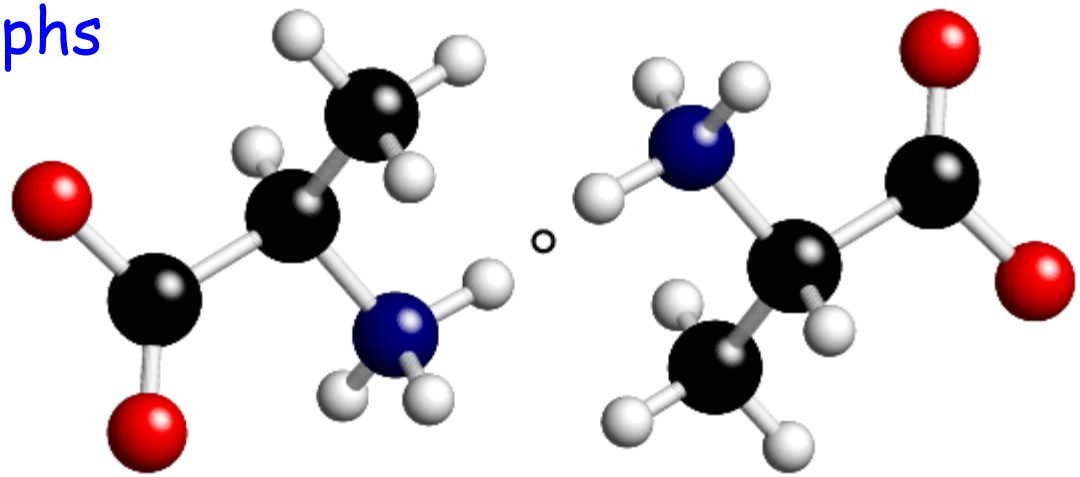
Symmetry Operators

- Off-centre (non-origin) axes



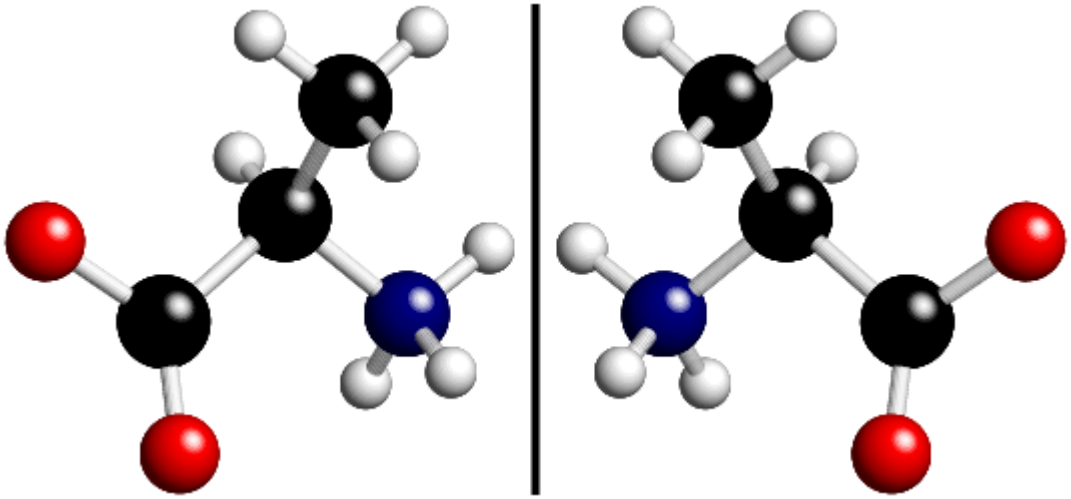
Rotary-inversion Symmetry

- Rotation anticlockwise 360° / n + Inversion
  - Symbols: -1, -2, -3, -4, -6
    - » written with bar $\bar{\ }$ above digit
    - » n = 1
    - » enantiomorphs



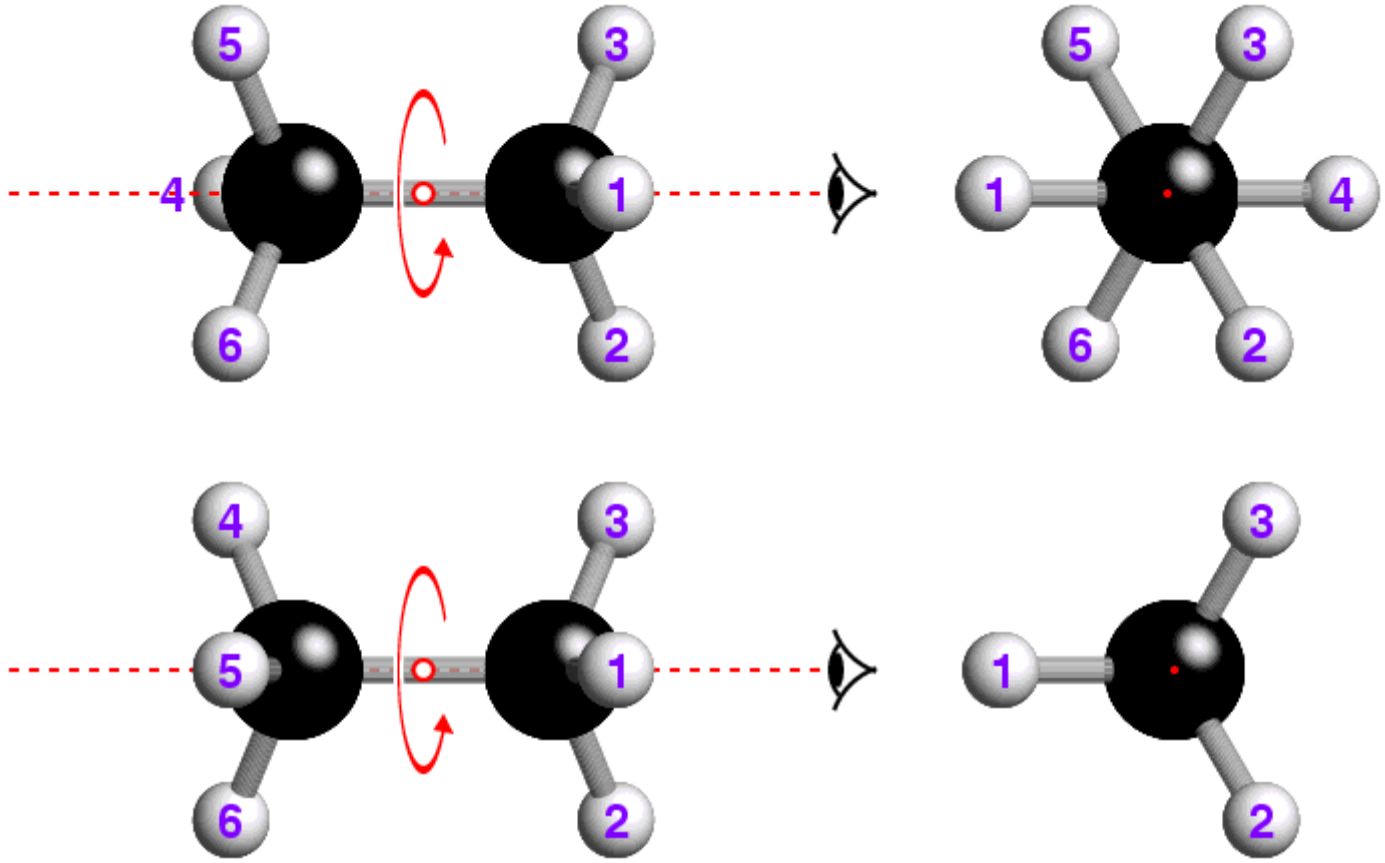
Mirror Symmetry

- Rotary-inversion axis with n = 2

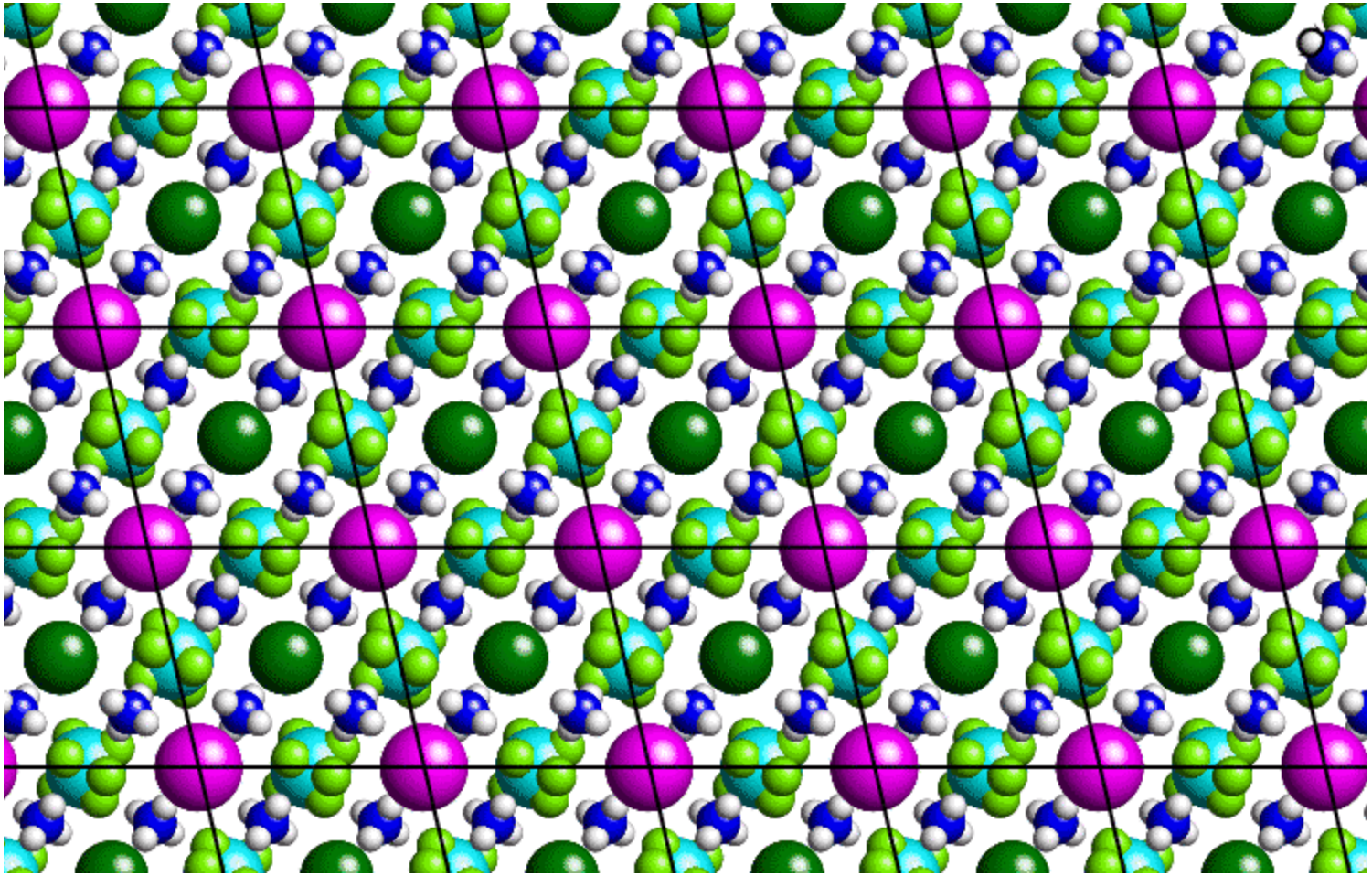


Higher-order Rotary-inversion

- Staggered v. eclipsed C_2H_6 –3 and –6



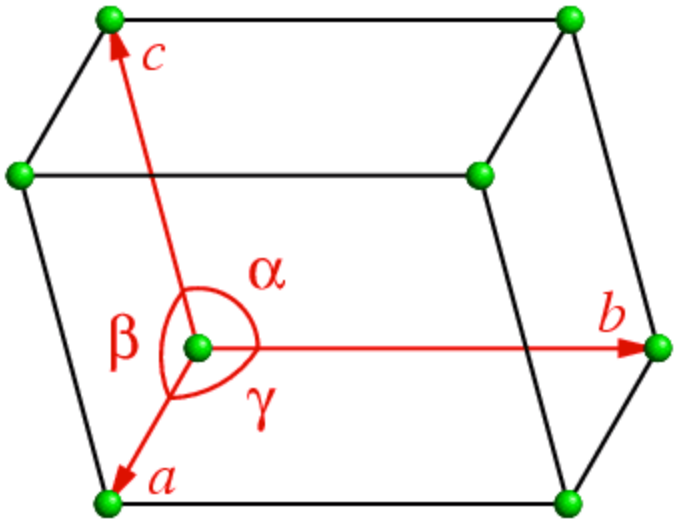
Translation Symmetry



Translation Symmetry

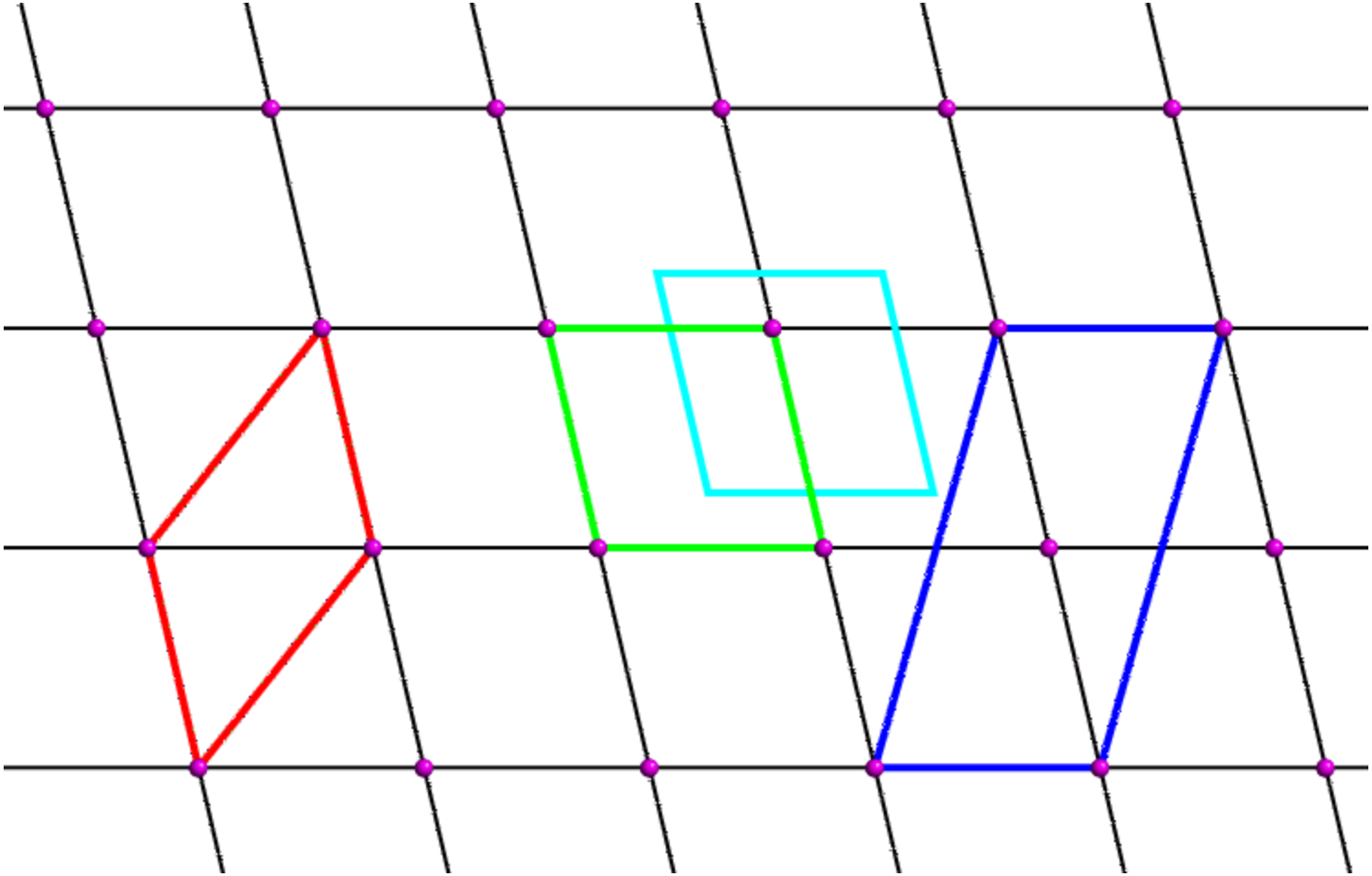
Unit Cell & Lattices

- Define unit cell (6 parameters)



- Lattice obtained by adding unit translations in x, y, and z

Choices



Coordinate Systems

- Cartesian: X, Y, Z

$$\mathbf{r} = X\mathbf{i} + Y\mathbf{j} + Z\mathbf{k}$$

- Fractional real space: x, y, z

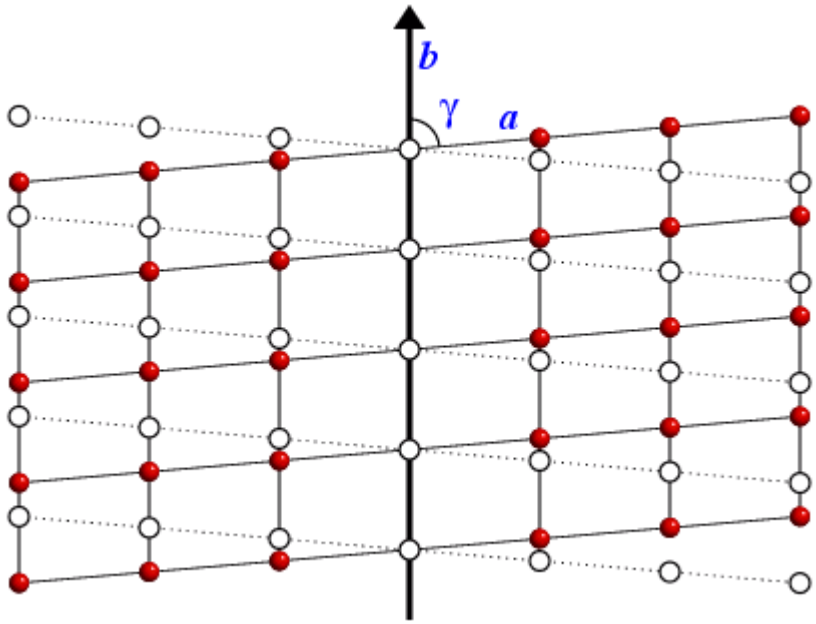
$$\mathbf{r} = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}$$

- Integer reciprocal space: h, k, l

$$\mathbf{r^*} = h\mathbf{a^*} + k\mathbf{b^*} + l\mathbf{c^*}$$

7 Crystal Systems

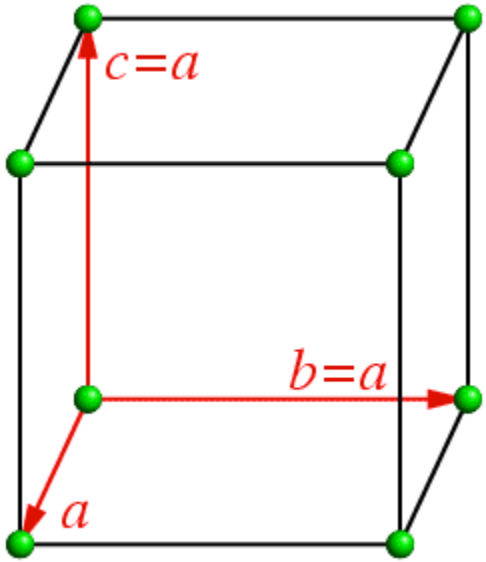
- Combination of rotational (or rotary-inversion) symmetry with a lattice

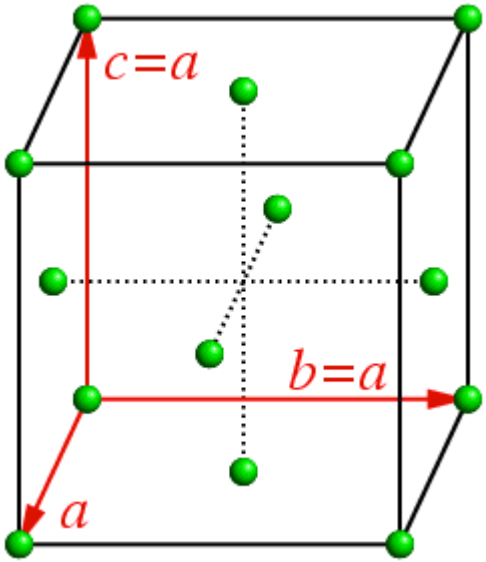


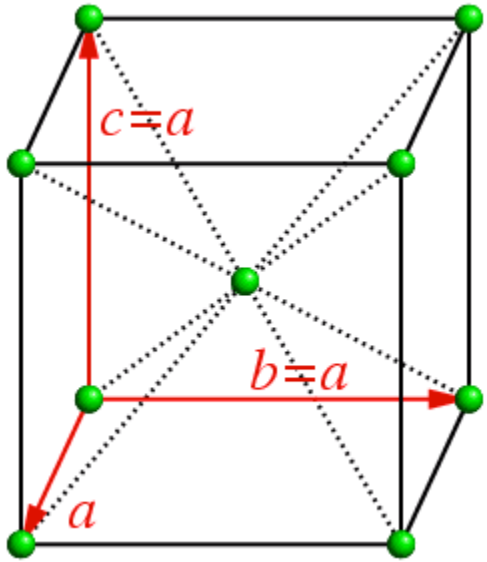
Triclinic	1×	1-fold
Monoclinic	1×	2-fold
Orthorhombic	3×	2-fold
Tetragonal	1×	4-fold
Trigonal	1×	3-fold
Hexagonal	1×	6-fold
Cubic	4×	3-fold

14 Bravais Lattices

- Combination of 7 crystal systems with lattice centring operation
  - P, A, B, C, I, F, R

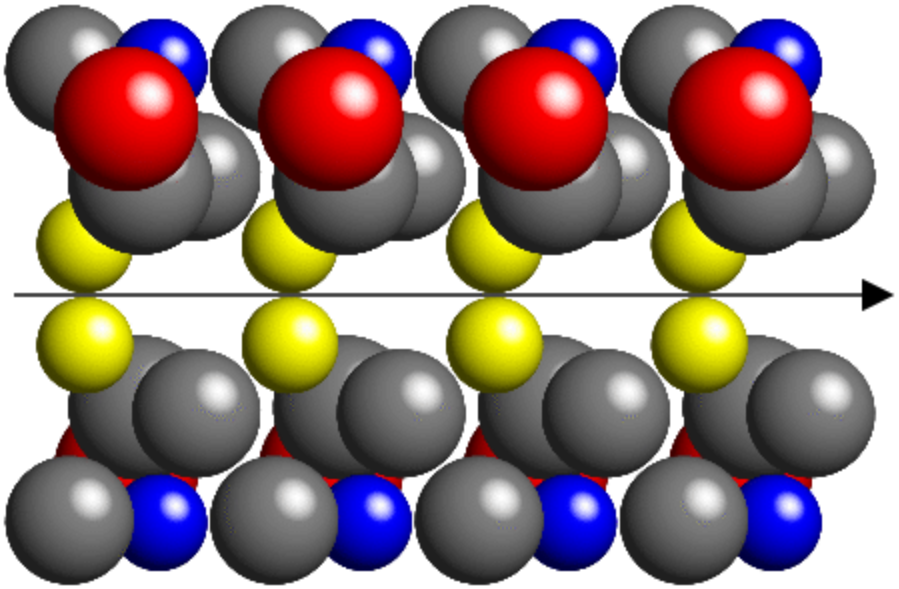


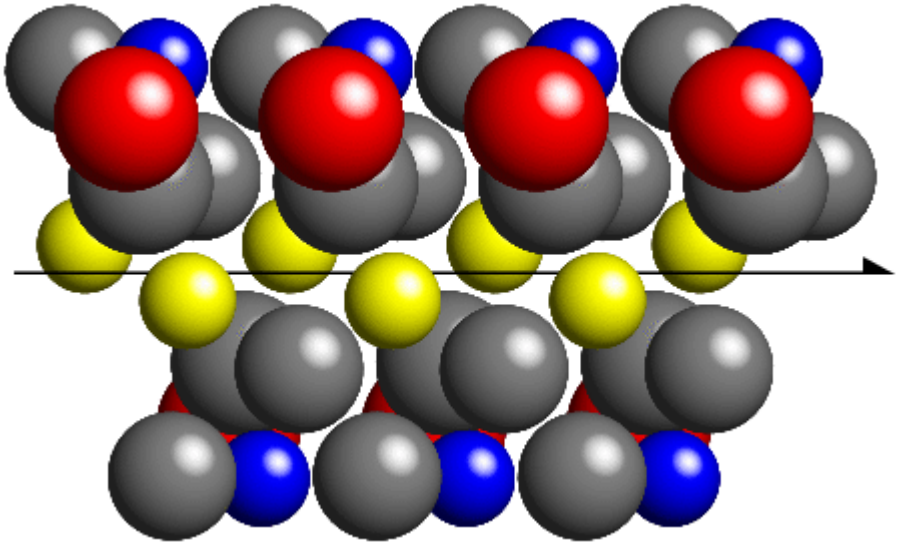




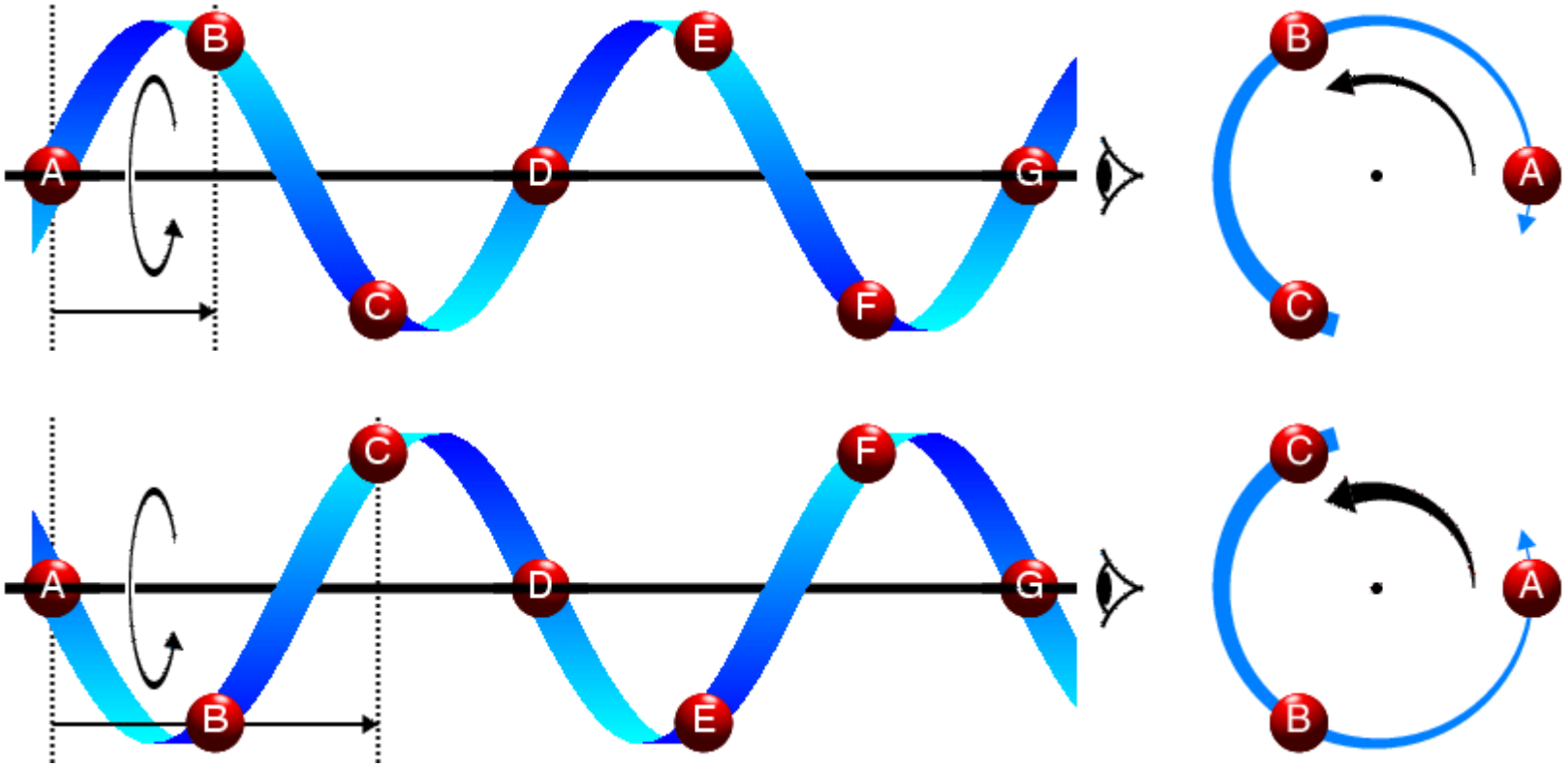
Screw Symmetry

- Combination of rotational symmetry with translational: n_m (360°/n R + m/n T)
  - Enables efficient packing of atoms/molecules





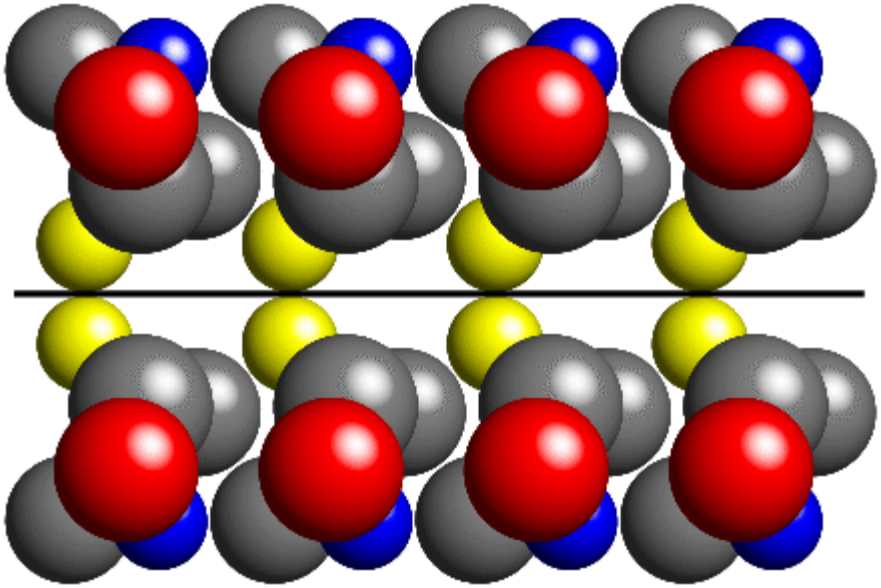
Helical Symmetry e.g. 3_1 v. 3_2

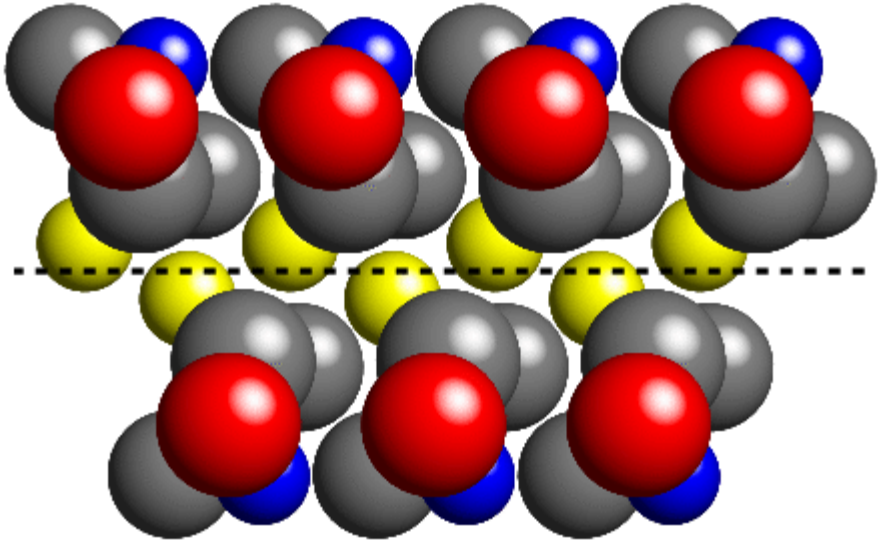


- Others 4_1 and 4_3, 6_1 and 6_5, 6_2 and 6_4
  - Note 2_1, 4_2, 6_3 are not helical

Glide Symmetry

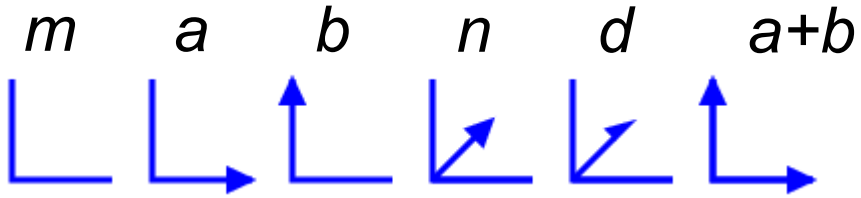
- Combination of 2-fold rotary-inversion (m) with translation: a, b, c, n, d
  - Also enables efficient packing of atoms/molecules



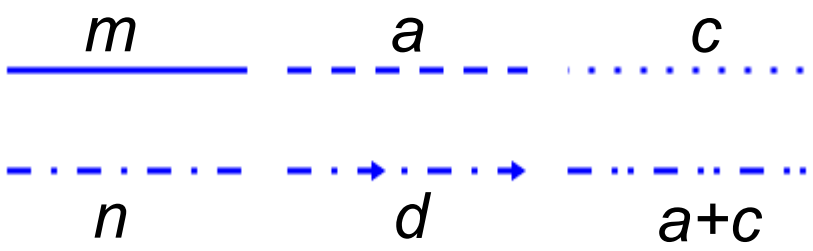


Symmetry Symbols

- Planes parallel to the screen plane

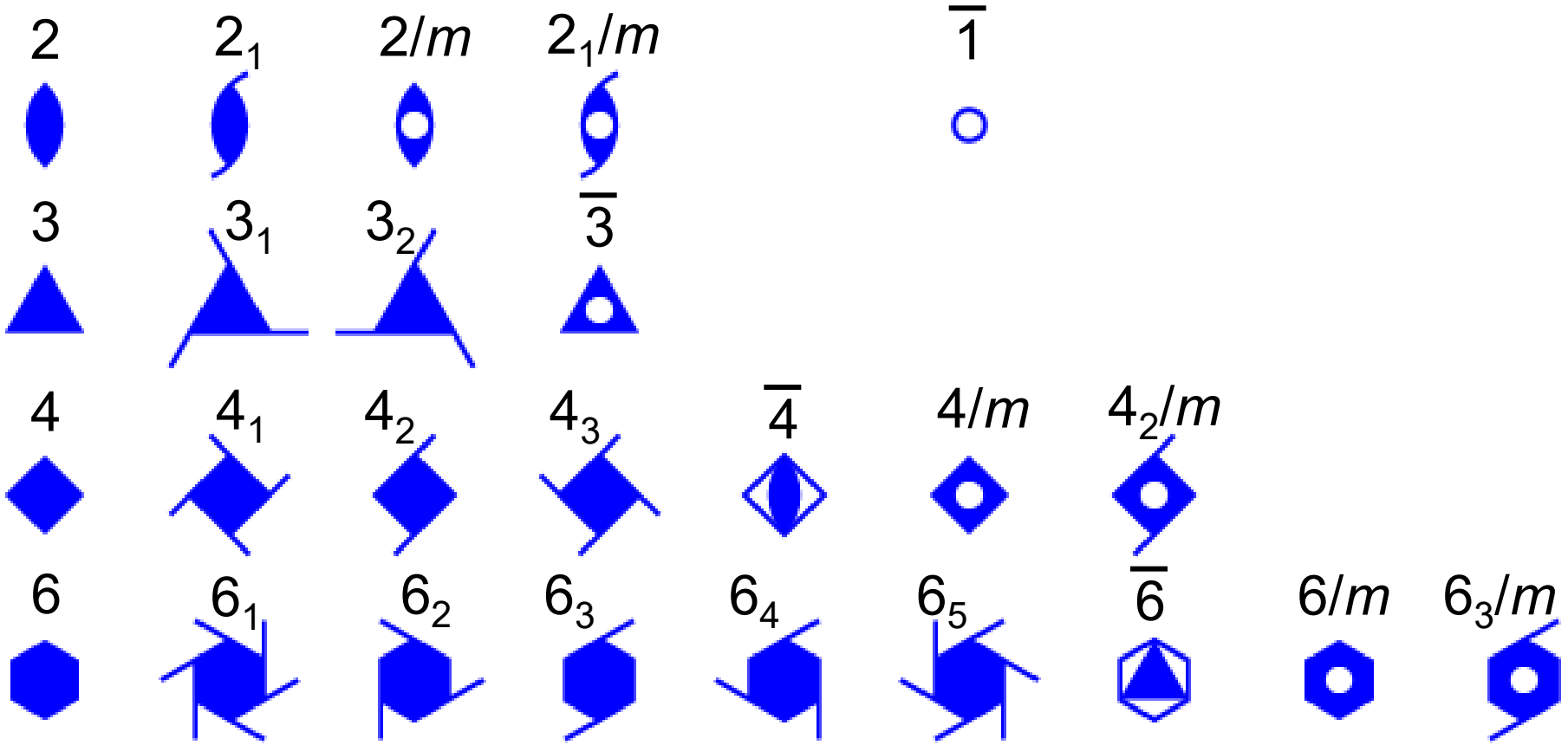


- Planes perpendicular to the screen plane



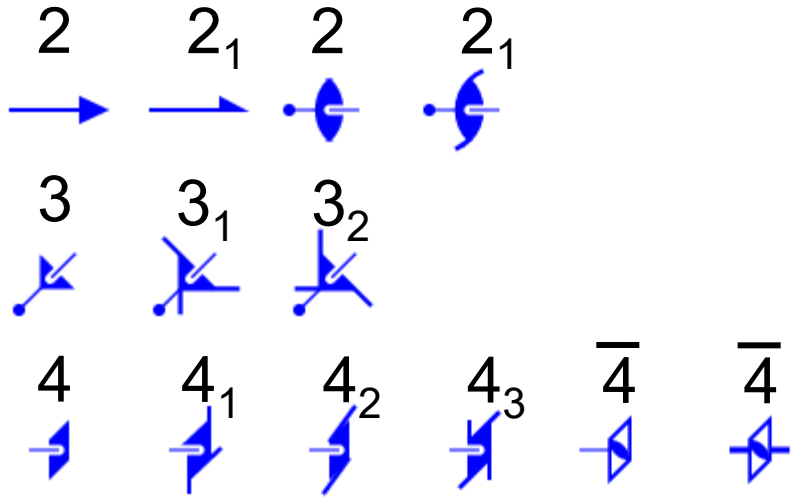
Symmetry Symbols

- Axes perpendicular to the plane



Symmetry Symbols

- Axes parallel or inclined to the plane of the screen



Point Groups

- Local symmetry at a point in space
- Combination of rotation and rotary-inversion axes to form a mathematical group
  - Only use 1, 2, 3, 4, 6 and –1, –2, –3, –4, –6
  - 32 crystallographic point groups
    - 11 centrosymmetric
      - Diffraction symmetry
      - Laue classes

Point Groups

- 11 centrosymmetric point groups

  -1 $2/m$ mmm $4/m$ $4/mmm$

  -3 $-3m$ $6/m$ $6/mmm$ $m-3$ $m-3m$

- 11 enantiomorphic point groups
  - Rotation axes only

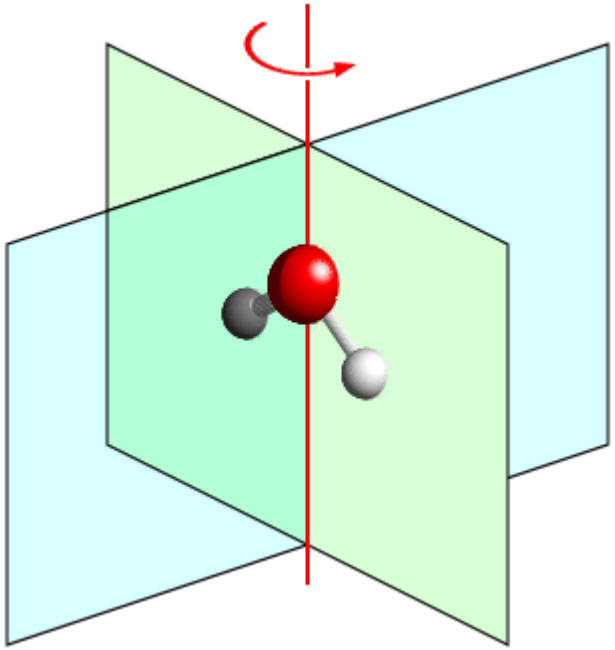
    1 2 222 4 422 3 32 6 622 23 432

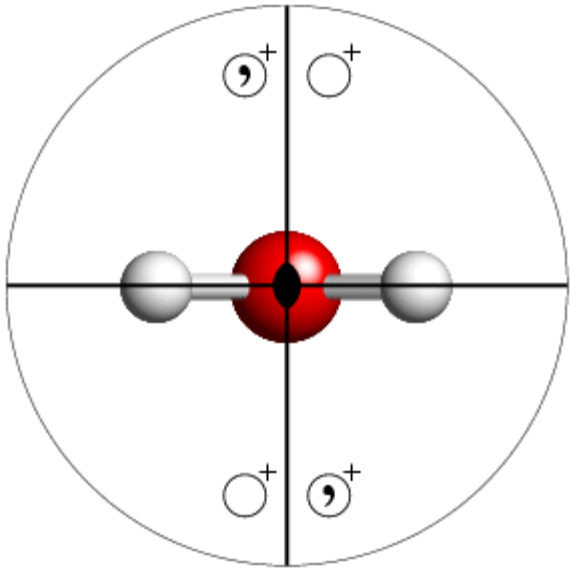
- 10 polar point groups
  - » Leave more than one common point unchanged

    1 2 m $mm2$ 4 $4mm$ 3 $3m$ 6 $6mm$

Example

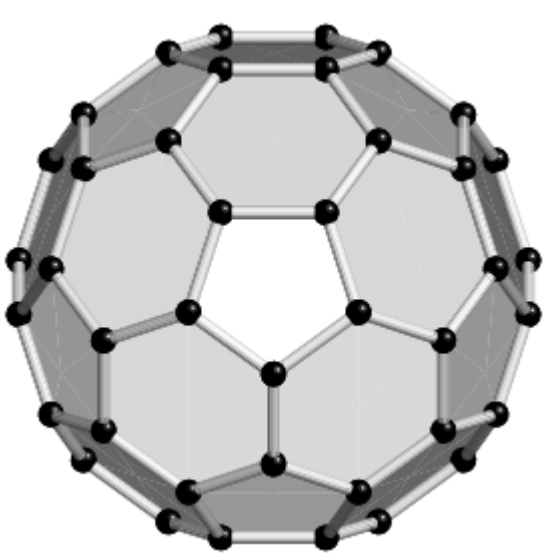
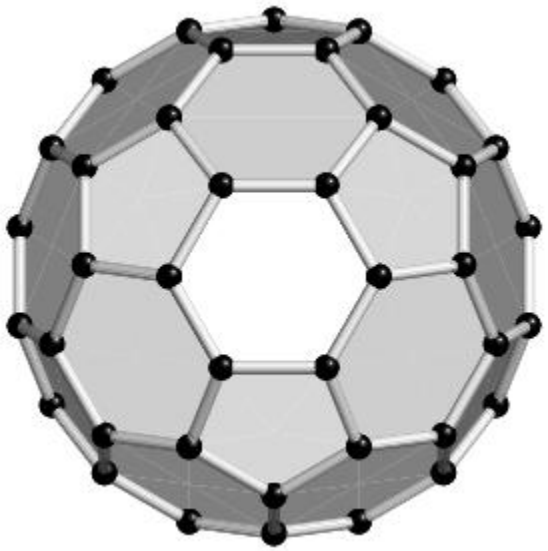
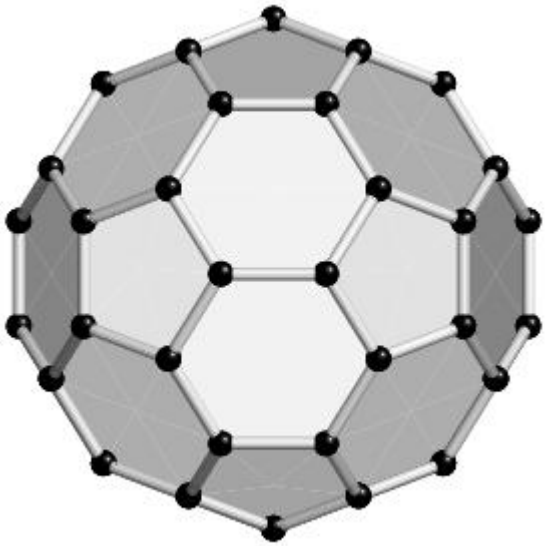
- Combination of m_x, m_y, and 2_z gives $mm2$





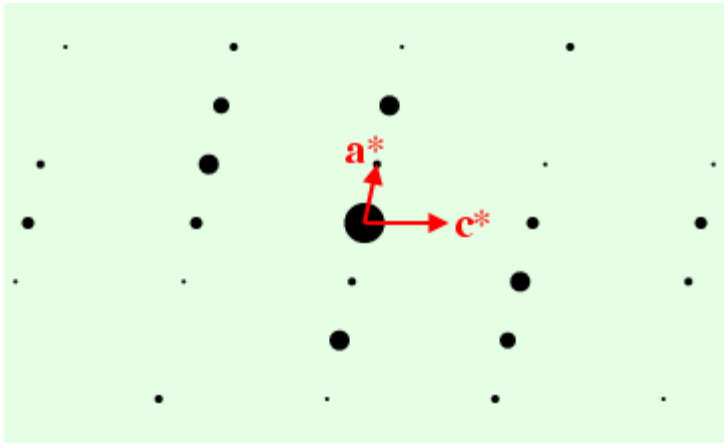
Molecular Symmetry

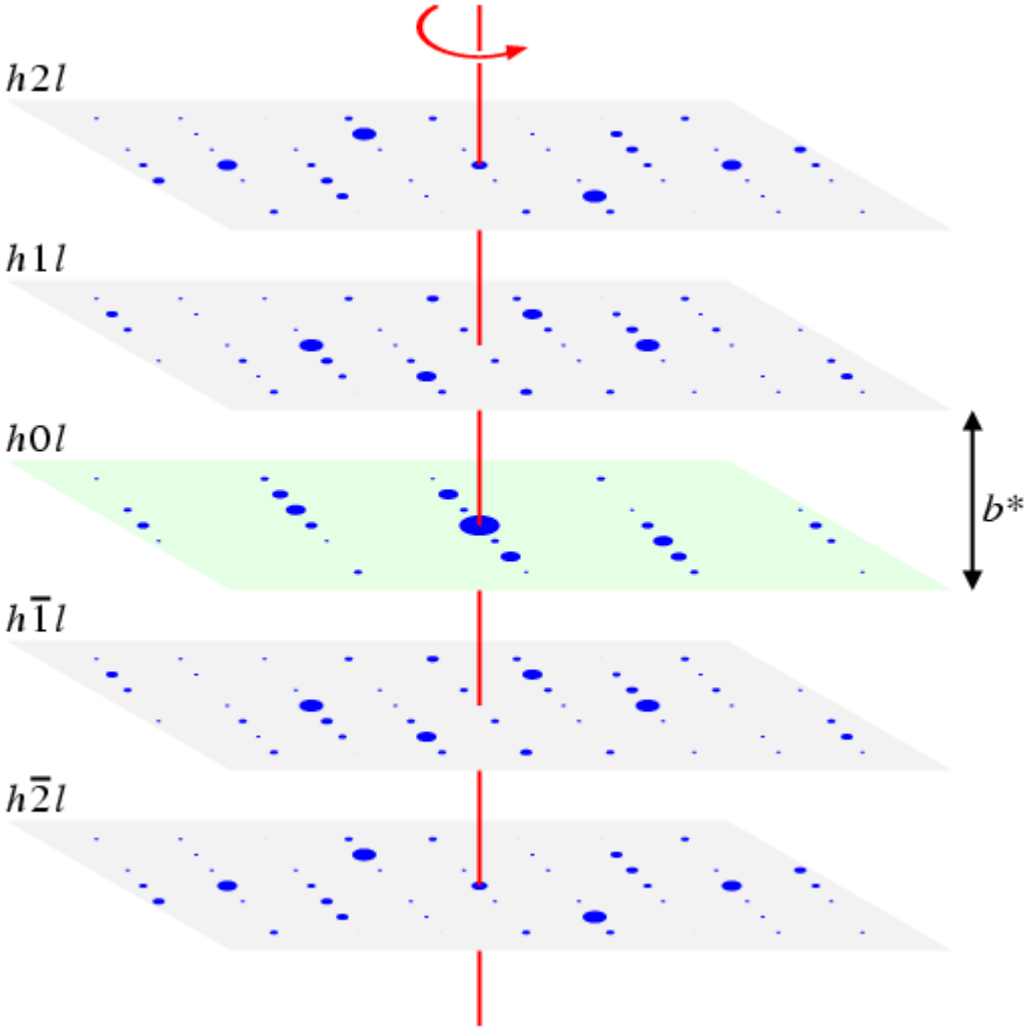
- May be higher than crystallographic point group symmetry e.g. C_{60}
  - Point group 5 –3 2/m

Diffraction Symmetry

- e.g. 2/*m*

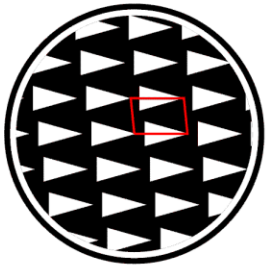




Optical Demonstration

- Not practical to show in 3D, but easy to show in 2D using diffraction from simple "wall paper patterns" (17 possibilities)
  - Objects photographically reduced to μm size on 35 mm slides
  - Similar in size scale to red or green laser light
    - » Expect optical diffraction to occur
      - Recall school experiment where a 1D set of parallel slits -> 1D set of spots with "orders" of diffraction

The 17 Two-Dimensional (Plane) Groups



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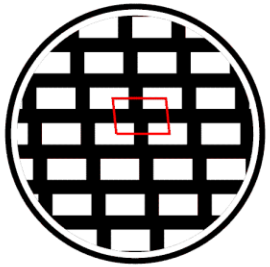

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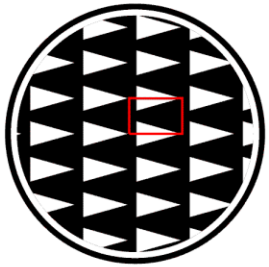

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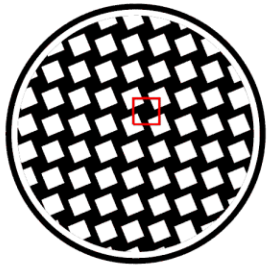
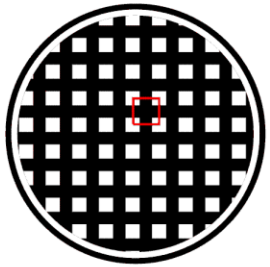
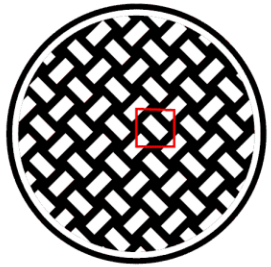


p4 (No.10)

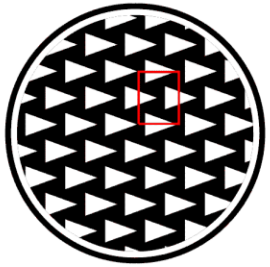


p4mm (No.11)



p4gm (No.12)

pg (No.4)



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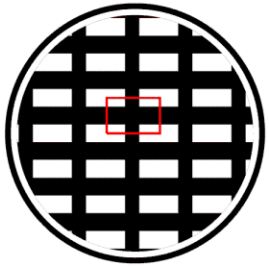
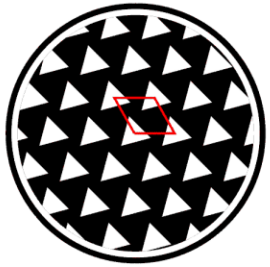


p2mm (No.6)



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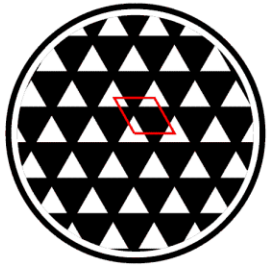

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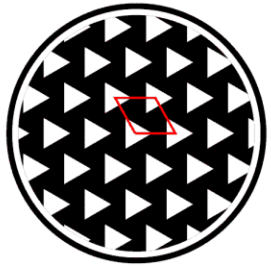

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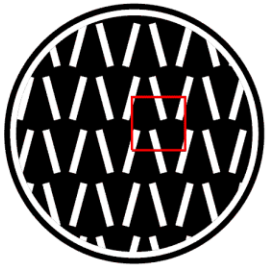
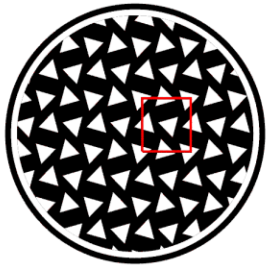
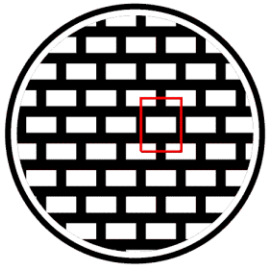


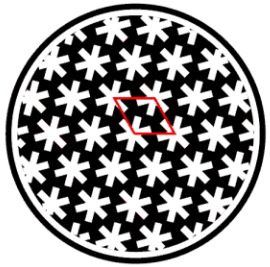
p2mg (No.7)



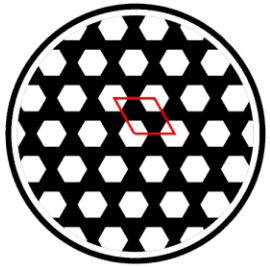
p2gg (No.8)



c2mm (No.9)

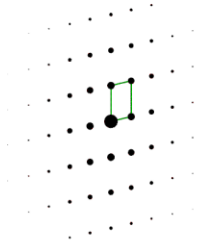


p6 (No.16)



p6mm (No.17)

Diffraction Symmetry of the 17 Plane Groups



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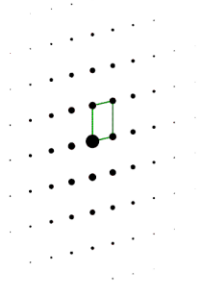

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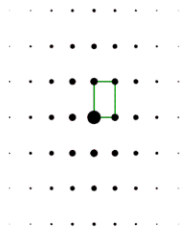

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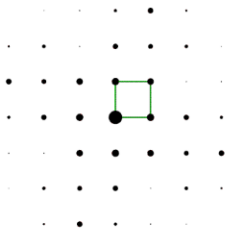

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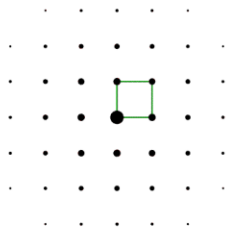

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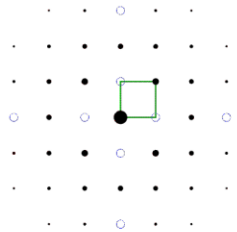

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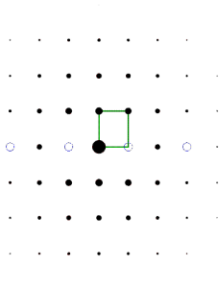
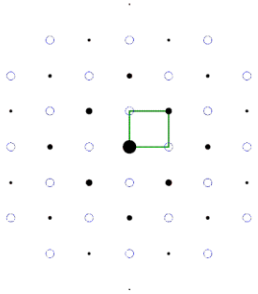
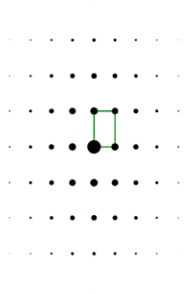


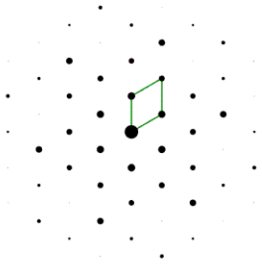
pg (No.4)



cm (No.5)



p2mm (No.6)



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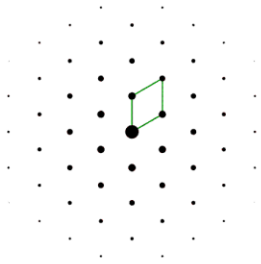
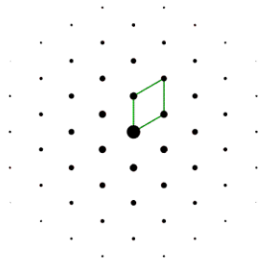


p3m1 (No.14)



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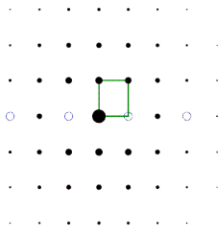

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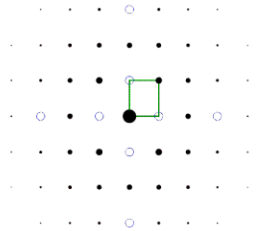

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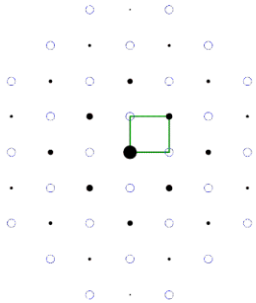

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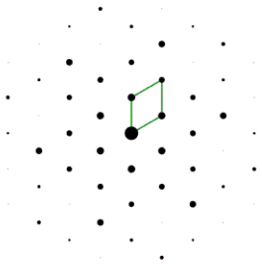

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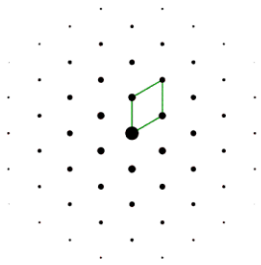

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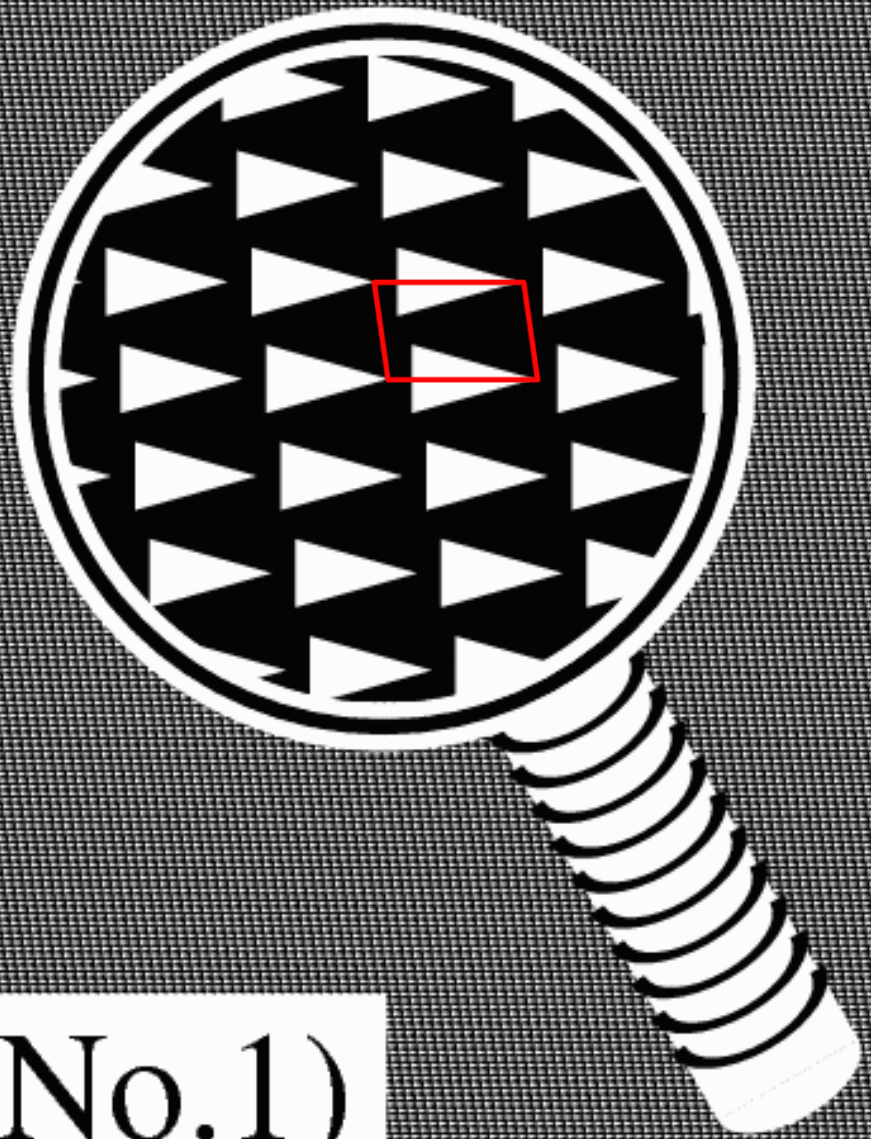
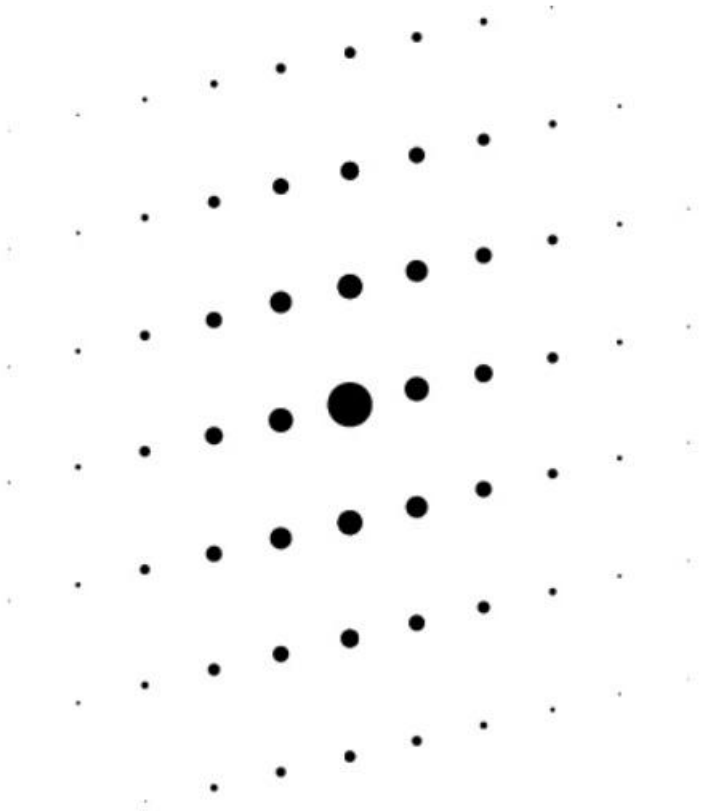


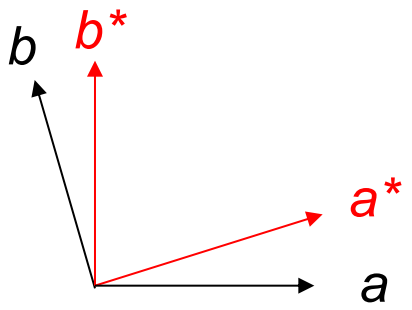
p1 (No.1)

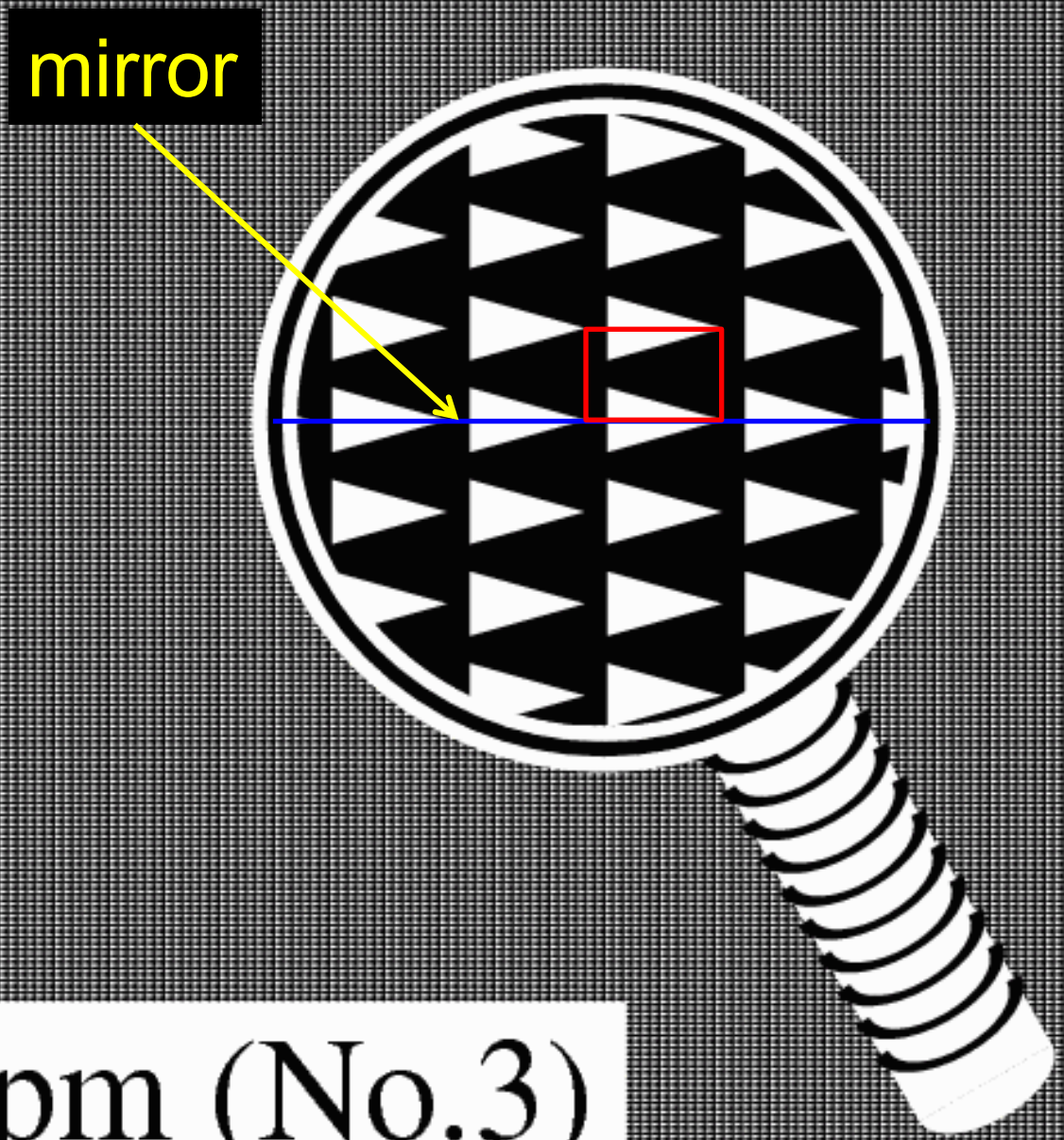
Diffraction Symmetry



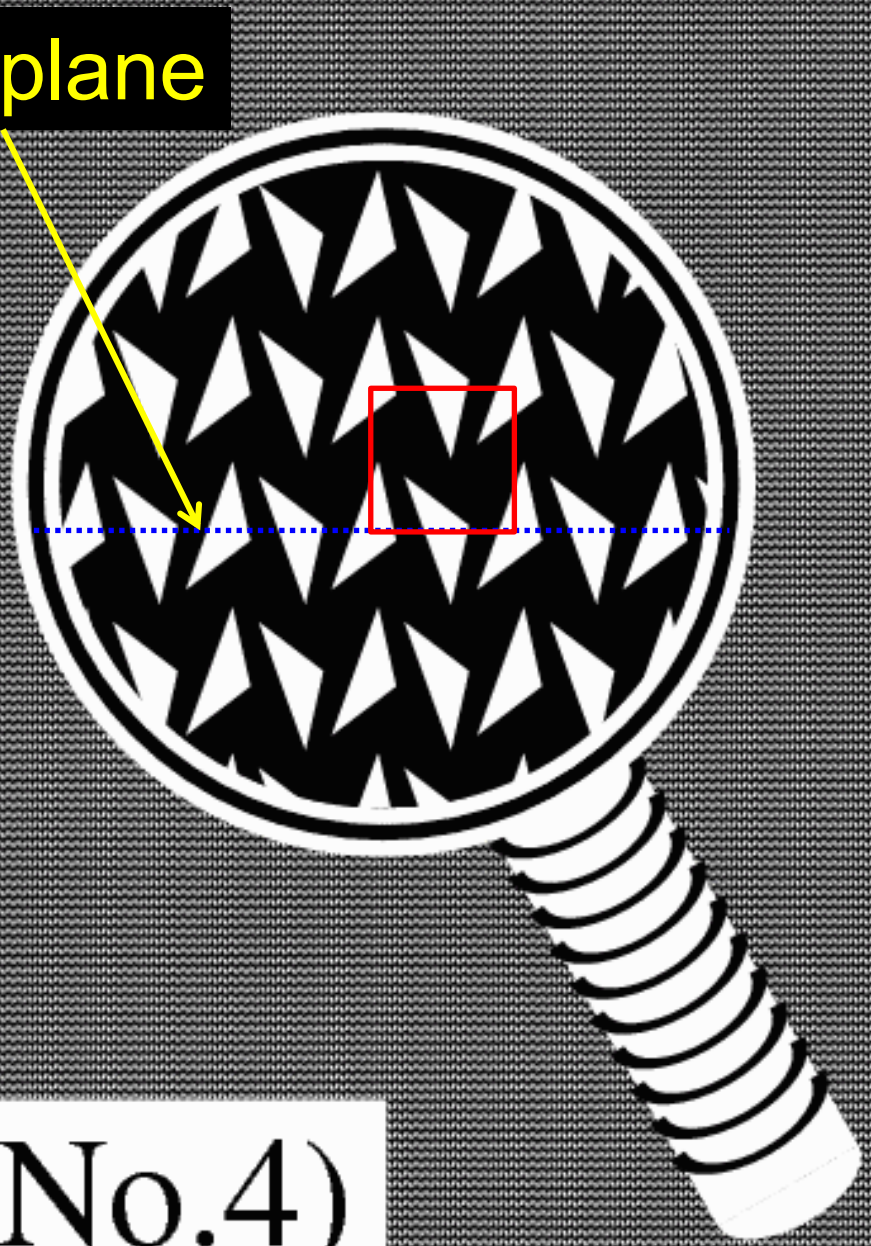
Optical Demonstration

- Note the following points:
  - Inversion symmetry is added during the process of diffraction
    - » Not exact as object itself has no inversion symmetry but very close to centre of symmetry
  - Diffraction space unit cell vectors are in a different direction to real space ones when angle is non 90°





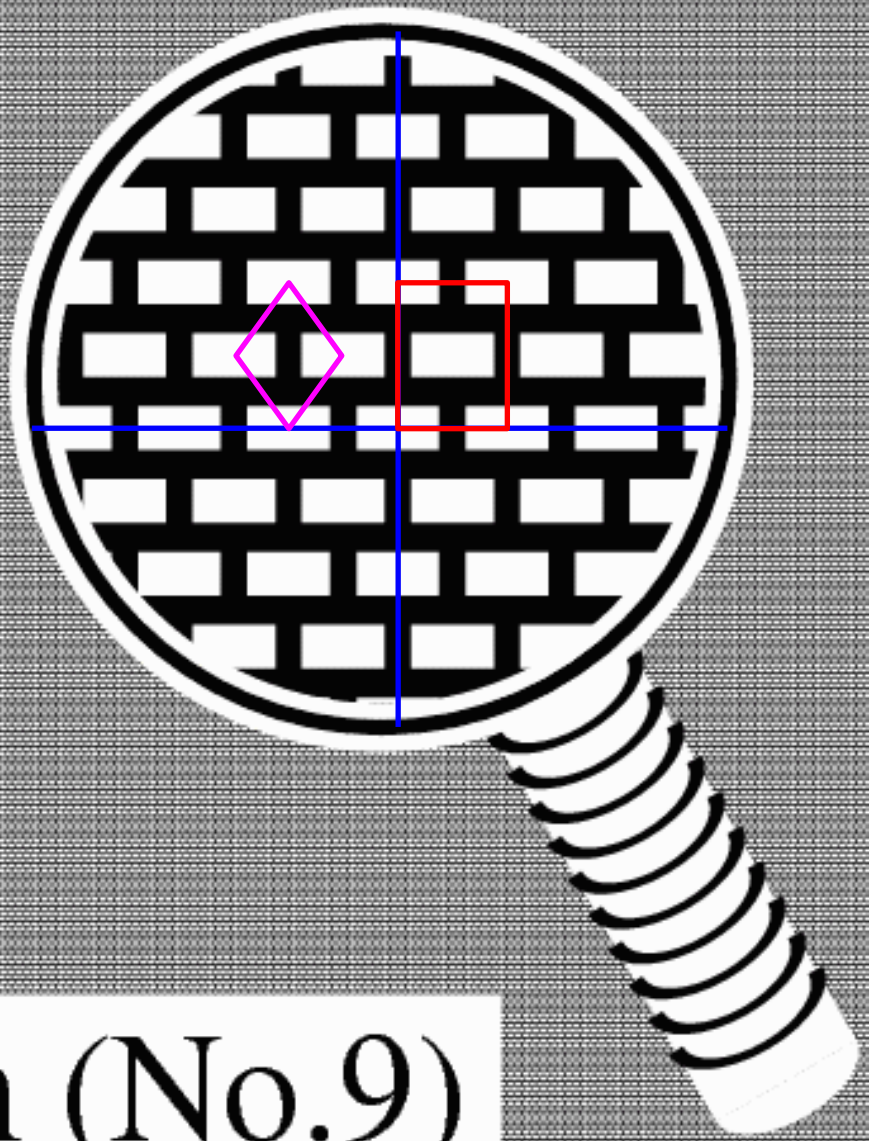
pm (No.3)



pg (No.4)

Optical Demonstration

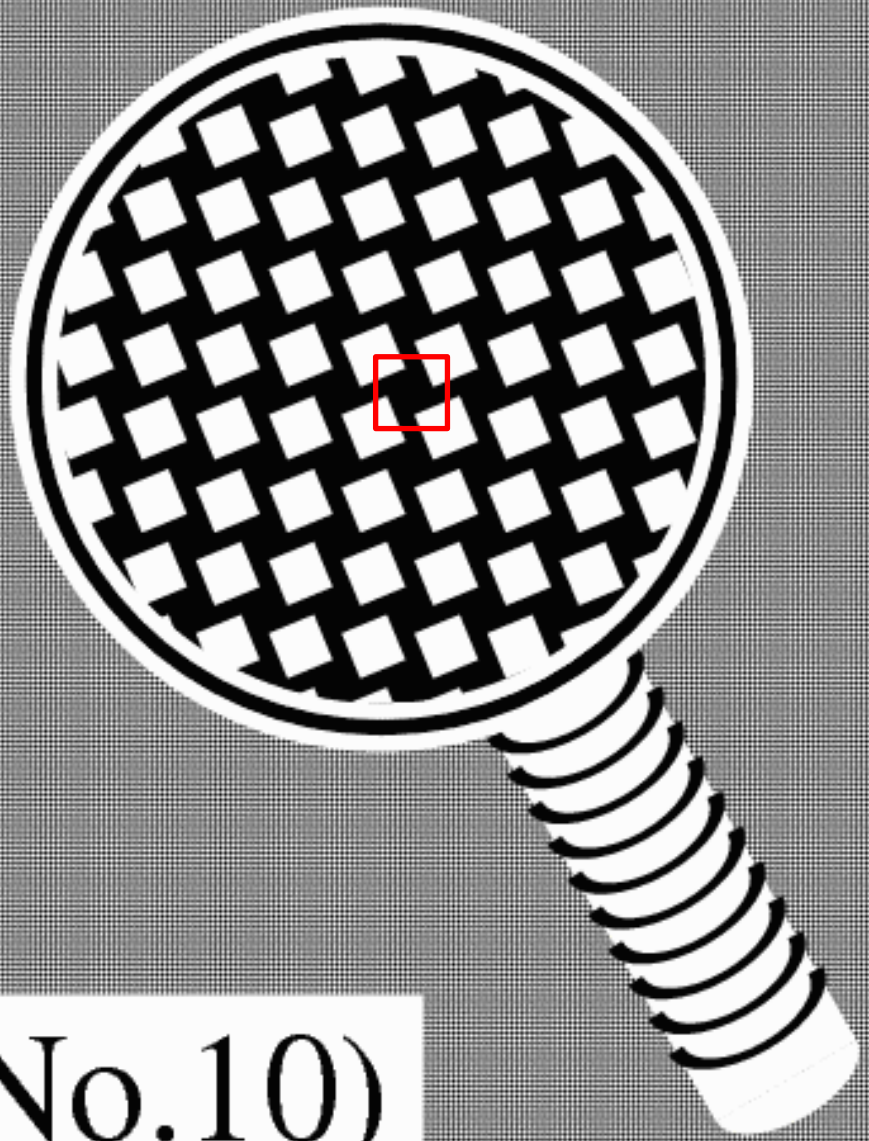
- Note the following point:
  - Translational symmetry along a line leads to missing intensity spots in a systematic manner along a line in diffraction space



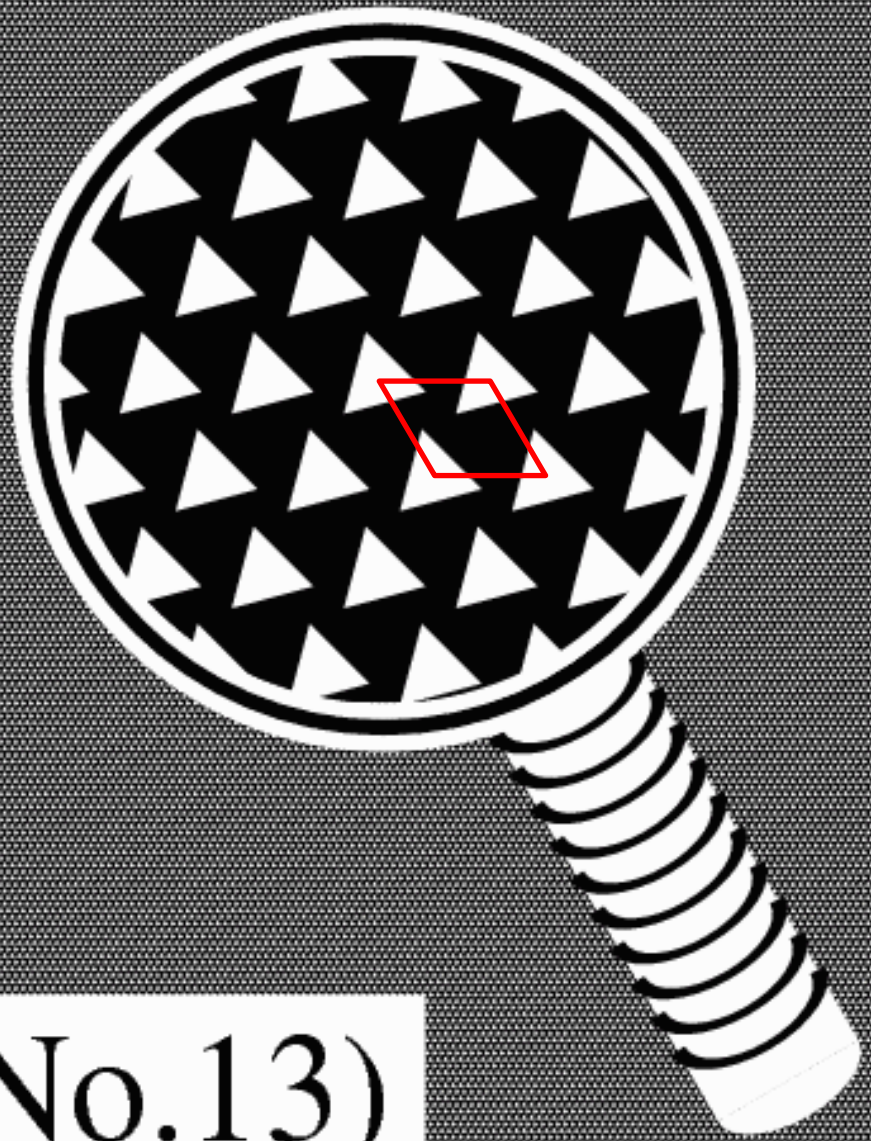
c2mm (No.9)

Optical Demonstration

- Note the following point:
  - Translational symmetry in two dimensions leads to missing intensity spots in a systematic manner in a plane in a diffraction space



p4 (No.10)



p3 (No.13)

Optical Demonstration

- Note the following point:
  - 3-fold symmetry gives many problems in crystallography especially with powder diffraction as it can look like 6-fold symmetry

Diffraction Symmetry

- Crystalline objects diffract
  - Symmetry relationship between crystal ("real") space with 3D symmetry across all space and diffraction ("reciprocal") space with 3D symmetry at a point (h,k,l = 0,0,0)
    - » Not a 1:1 relationship!
- Are diffracting objects (i.e. ones that produce sharp spots) crystalline?

Reflection Multiplicity

- Single-crystal diffraction
  - Individual reflections measured
- Powder diffraction
  - Reflections related by point group symmetry are superimposed
  - Multiplicity (J) is the number of symmetry equivalent reflections
    - » Depends on diffraction symmetry
    - » Depends on class of reflection
      - Most programs can calculate it

Space Groups

- Combination of symmetry elements to form a mathematical group
  - All must contain at least the identity (1) operation plus the unit translations:
    - » $t(1,0,0)$, $t(0,1,0)$, $t(0,0,1)$
      - "Mother of All Space Groups" is $P1$
- 230 combinations
  - Classified by crystal system & crystal class

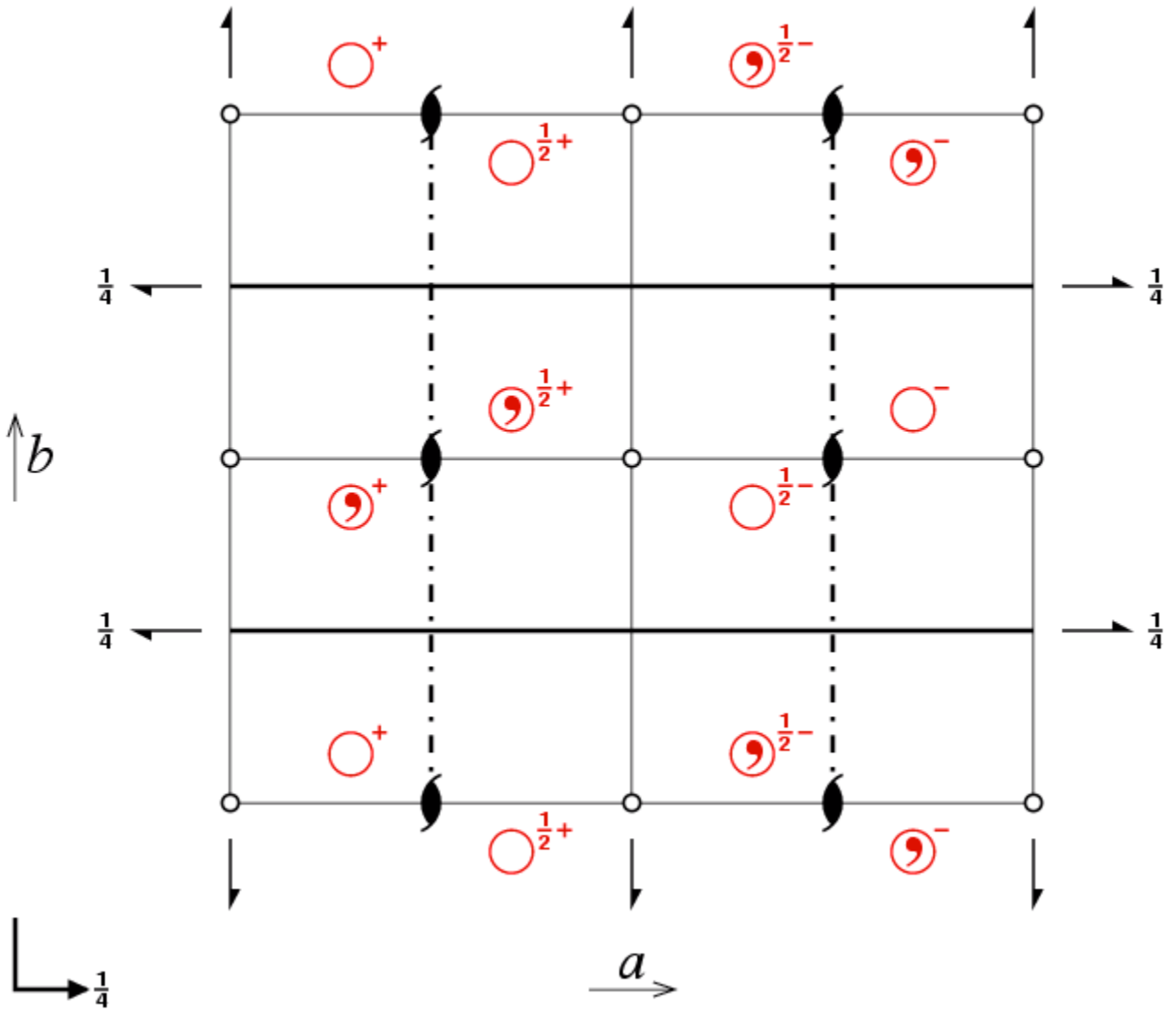
Crystal Class

- Point group derived from a space group by setting all the translation components of the symmetry operators to zero
  - e.g. $2_1 \rightarrow 2$, $a \rightarrow m$, ...
- Crystal class + Inversion symmetry

  $\rightarrow$ Diffraction symmetry

Space Group Diagrams

Pnma $P\,2_1/n\,2_1/m\,2_1/a$ *mmm* No. 62



1 x, y, z

2 $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$

3 $x, \frac{1}{2} - y, z$

4 $\frac{1}{2} + x, y, \frac{1}{2} - z$

5 $\bar{x}, \bar{y}, \bar{z}$

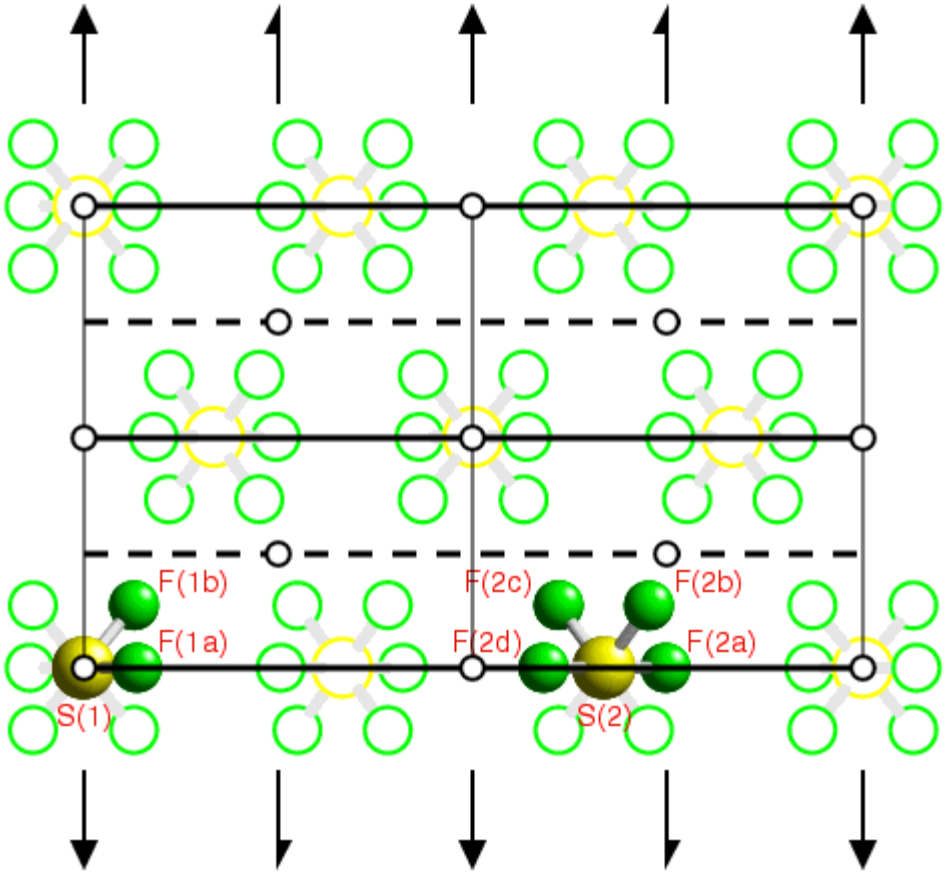
6 $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$

7 $\bar{x}, \frac{1}{2} + y, \bar{z}$

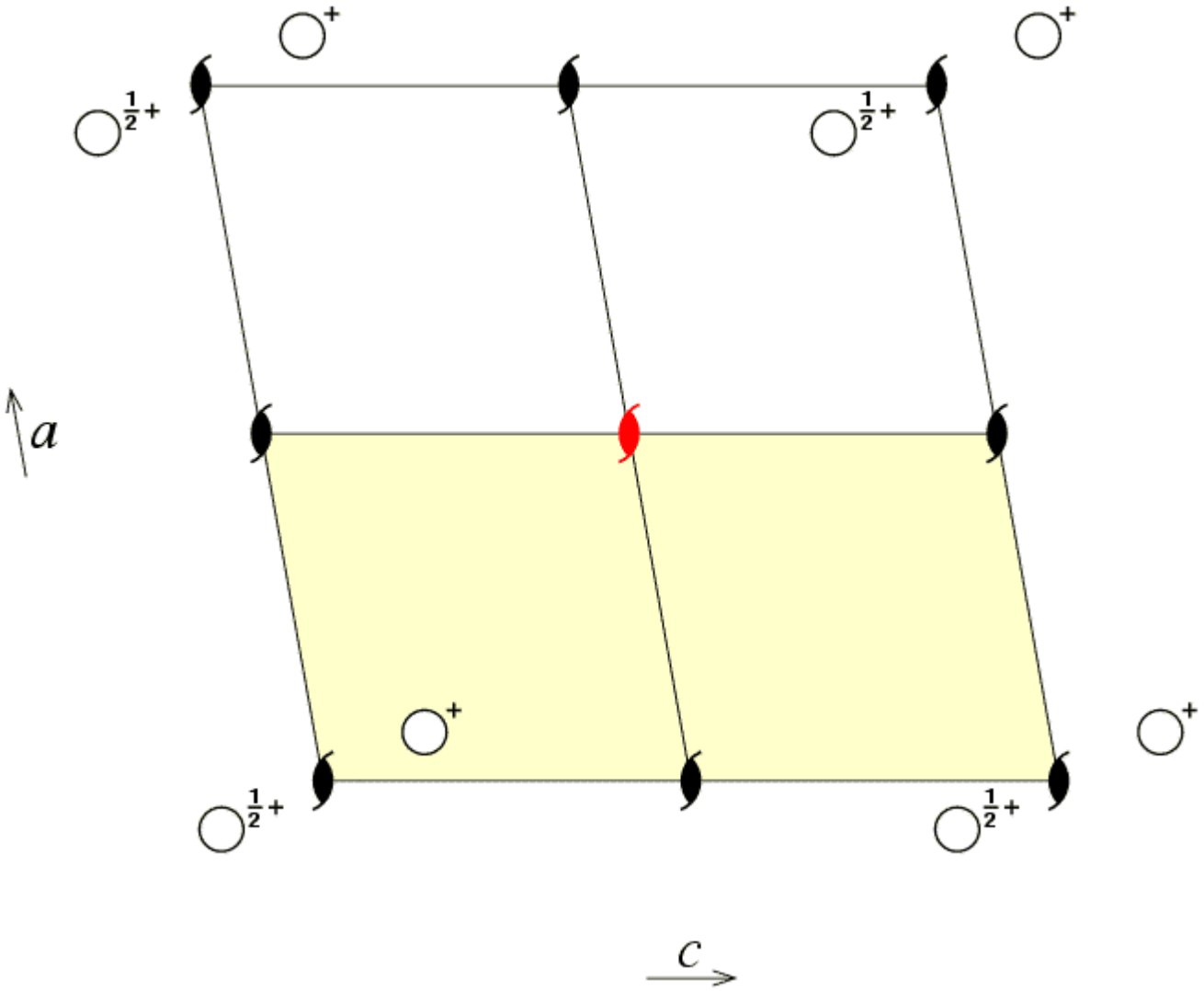
8 $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$

Special Positions

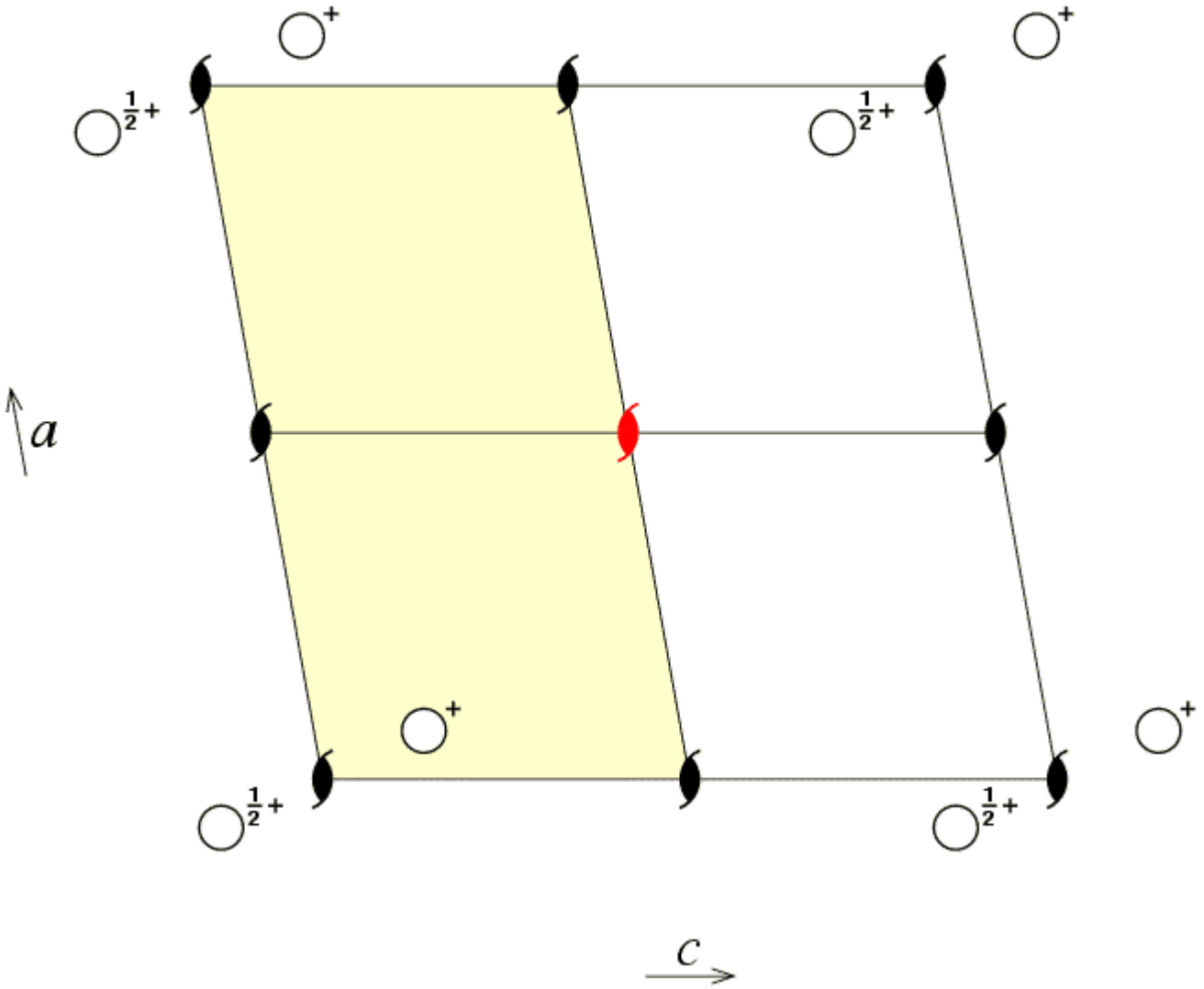
- Points in space where the symmetry is higher than 1
  - e.g. SF_6



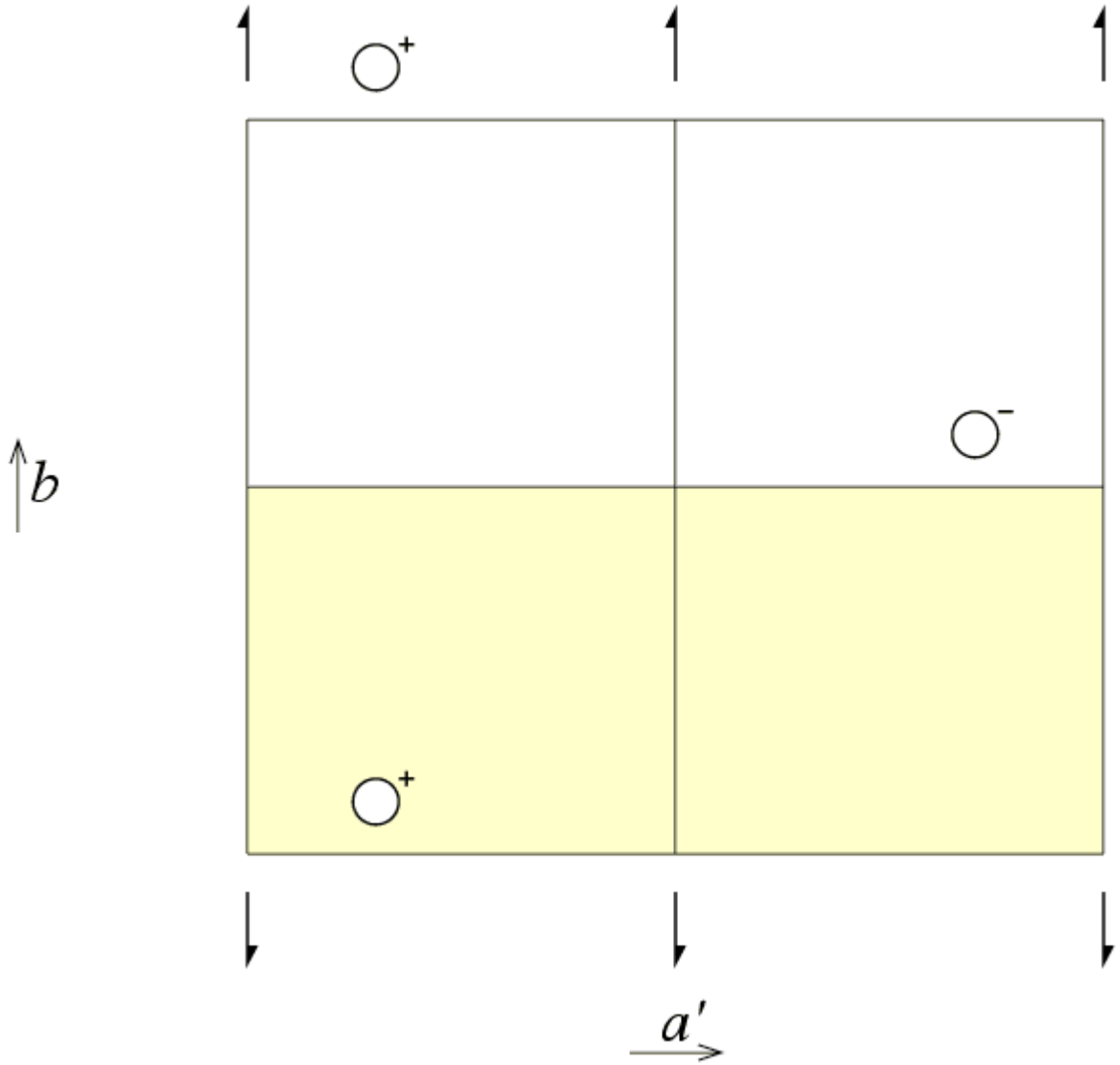
Asymmetric Units



Asymmetric Units

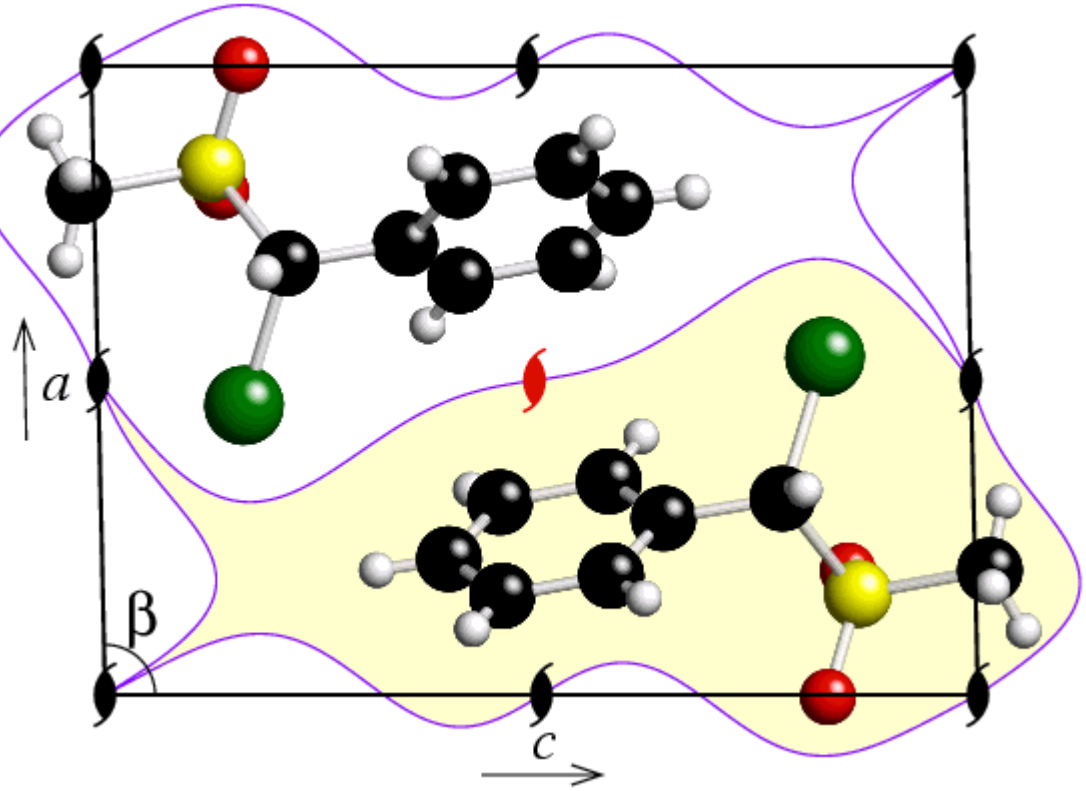


Asymmetric Units

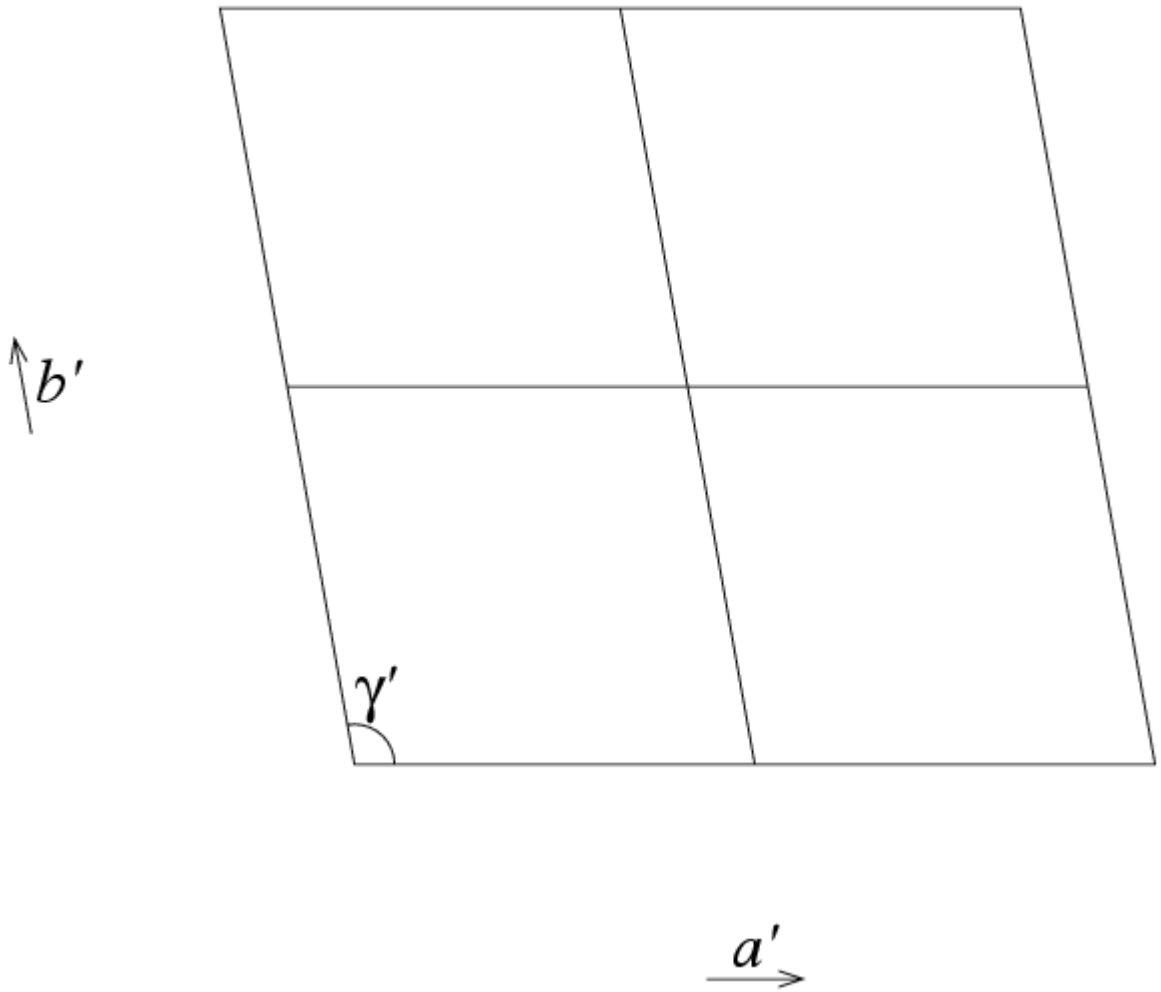


Asymmetric Units

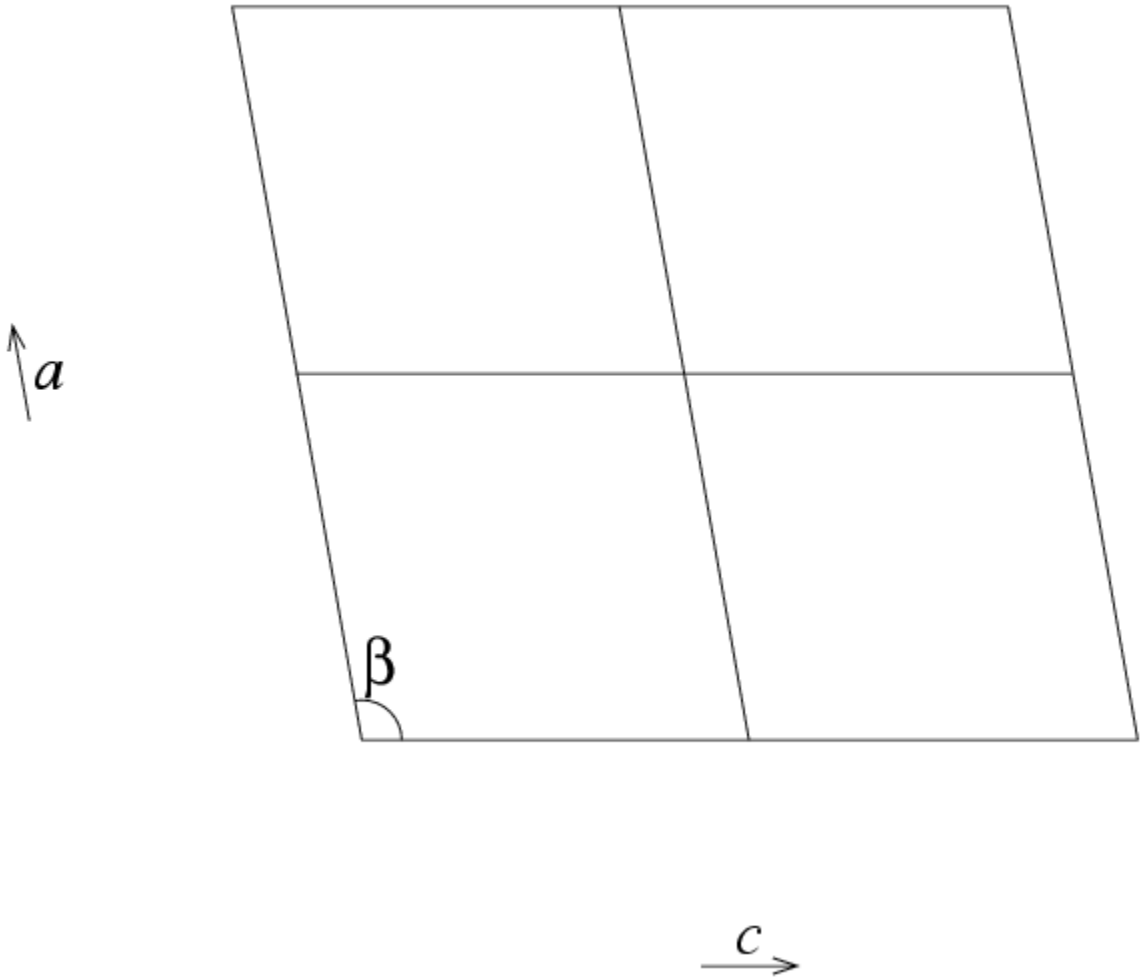
- Space occupied by molecule can be used!



Triclinic Space Groups



Monoclinic Space Groups

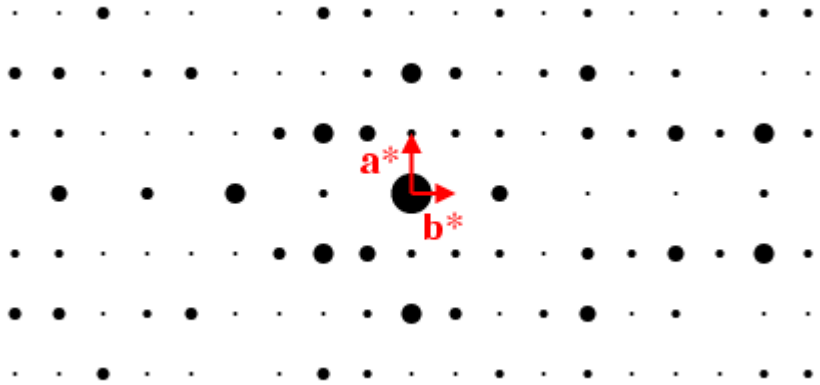


Space Group Determination

- Geometrical implications, e.g.
  - $a \neq b \neq c,\ \alpha \neq \beta \neq \gamma \neq 90°$ → triclinic
  - $a \neq b \neq c,\ \alpha = \gamma = 90°,\ \beta \neq 90°$ → monoclinic
  - $a \neq b \neq c,\ \alpha = \beta = \gamma = 90°$ → orthorhombic
  - $a = b \neq c,\ \alpha = \beta = \gamma = 90°$ → tetragonal
  - $a = b = c,\ \alpha = \beta = \gamma = 90°$ → cubic
- Beware of experimental error
  - Symmetry may be lower than expected

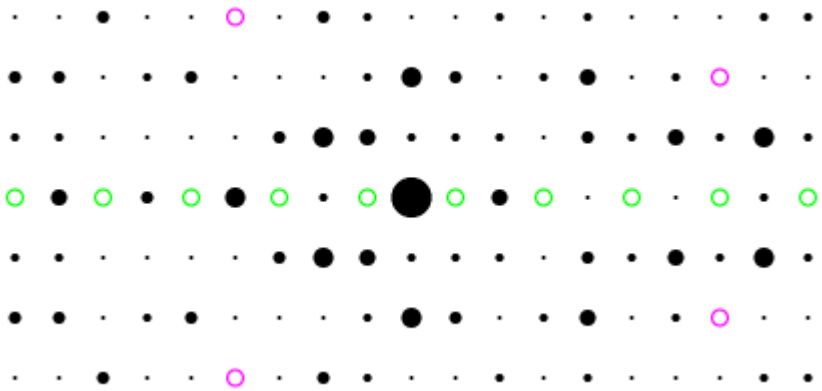
Systematic Absences

- Random v. systematic zero intensity



Systematic Absences

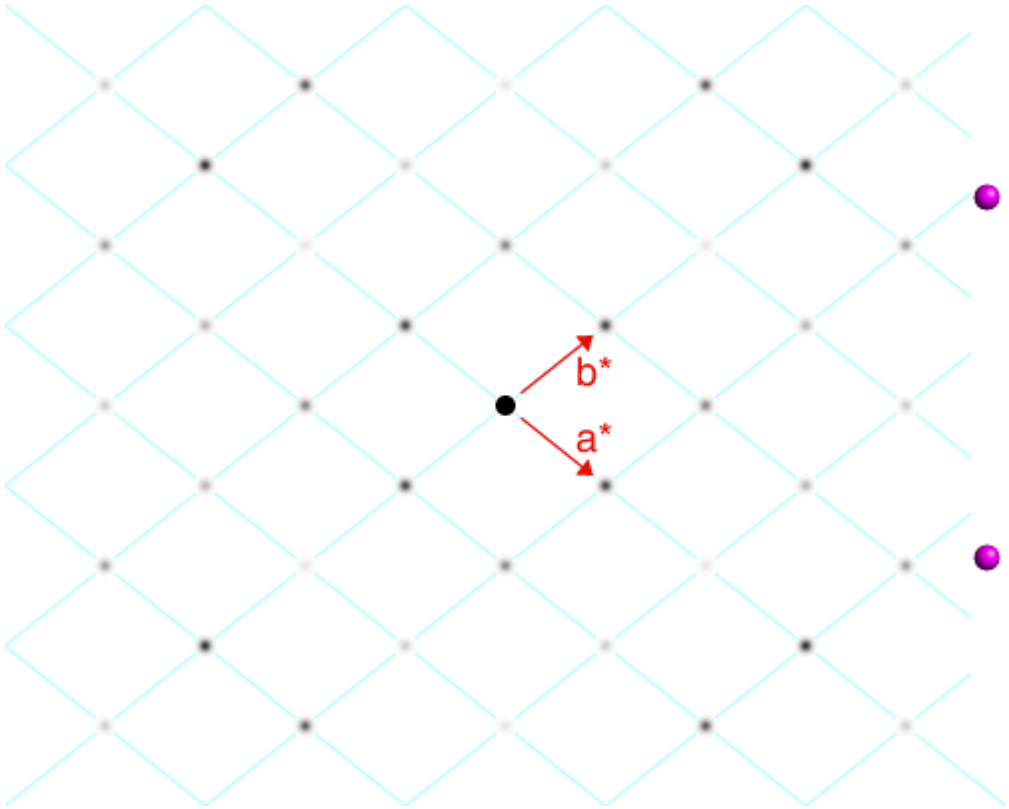
- Random v. systematic zero intensity

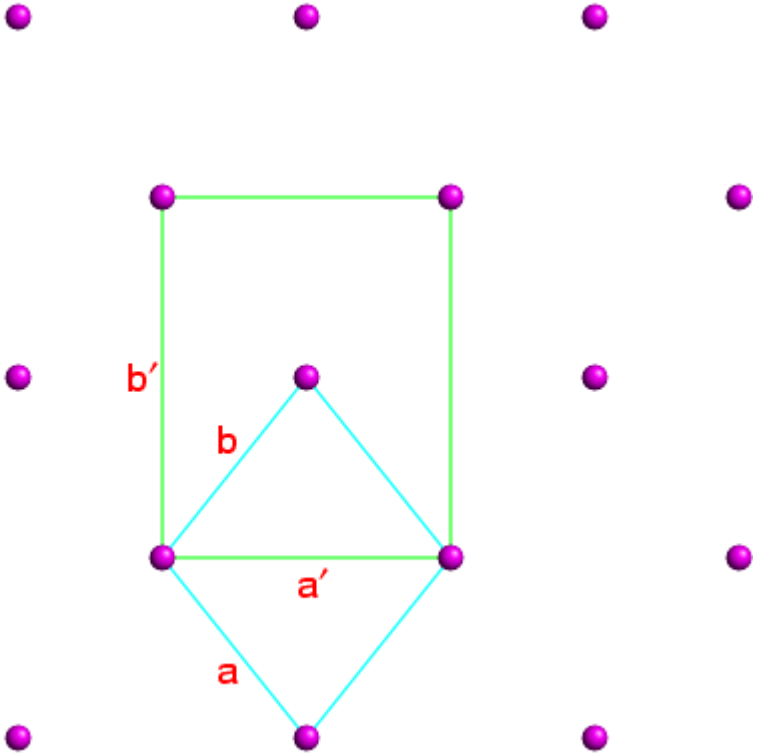


  - $I(h00) = 0$ when $h = 2n + 1$ (i.e. h odd)
- Reflection Conditions
  - $I(h00) \neq 0$ when $h = 2n$ (i.e. h even)

Centred Lattices

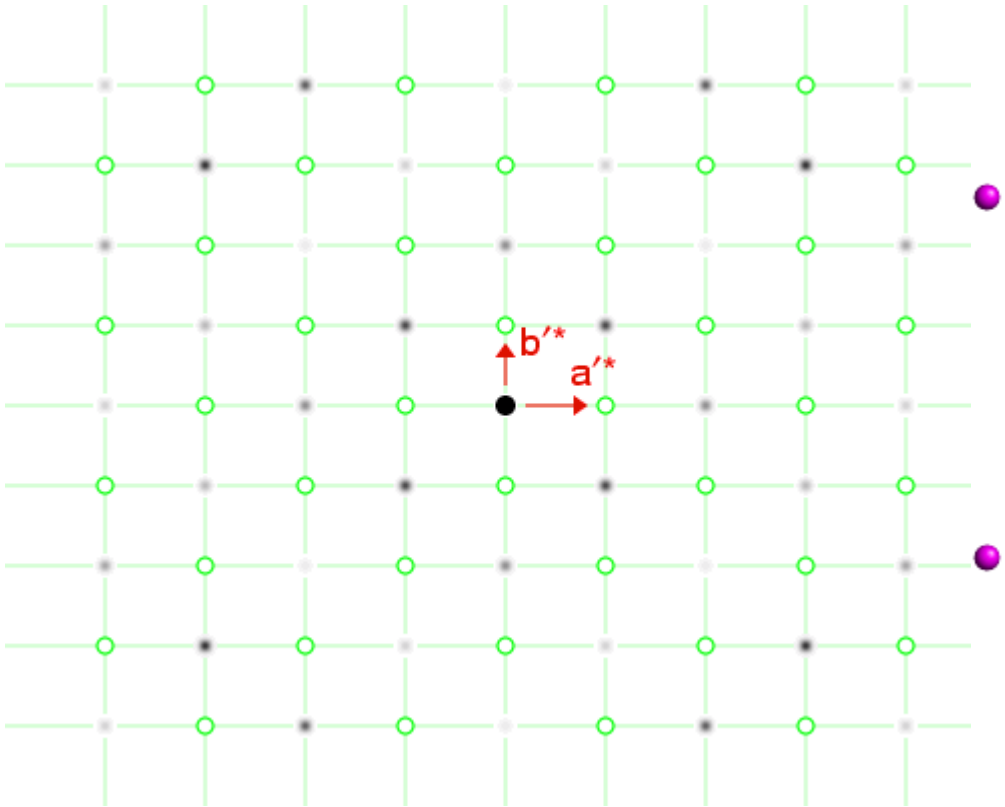
- Reciprocal Space v. Real Space

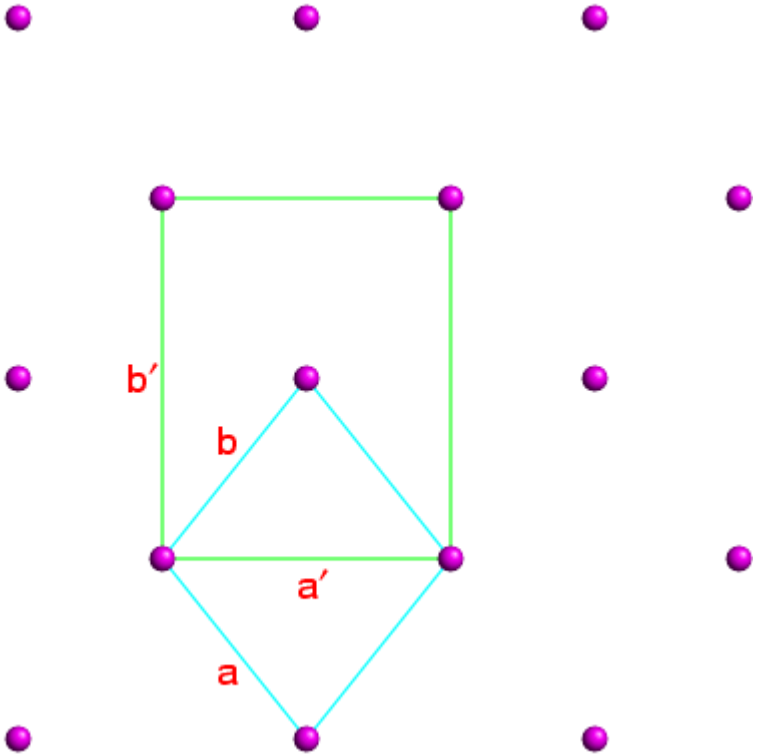




Centred Lattices

- Reciprocal Space v. Real Space





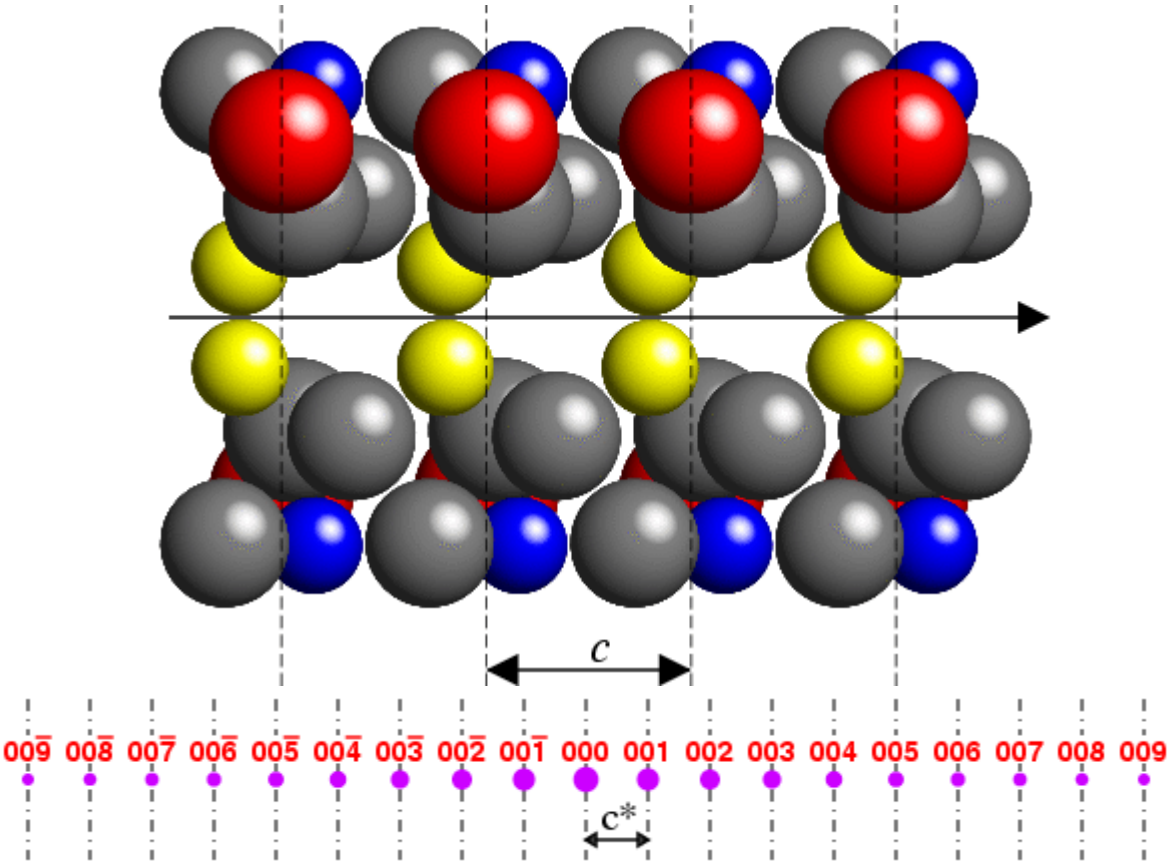
Centred Lattices

- Translation in 3 dimensions gives rise to reflection condition in 3 dimensions

P	*none*	*none*
A	$x, \frac{1}{2}+y, \frac{1}{2}+z$	$hkl: k + l = 2n$
B	$\frac{1}{2}+x, y, \frac{1}{2}+z$	$hkl: h + l = 2n$
C	$\frac{1}{2}+x, \frac{1}{2}+y, z$	$hkl: h + k = 2n$
I	$\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}+z$	$hkl: h + k + l = 2n$
F	$= A + B + C$	$hkl: h + k = 2n, h + l = 2n,$ $\& \; h + k = 2n$

Translation Along an Axis

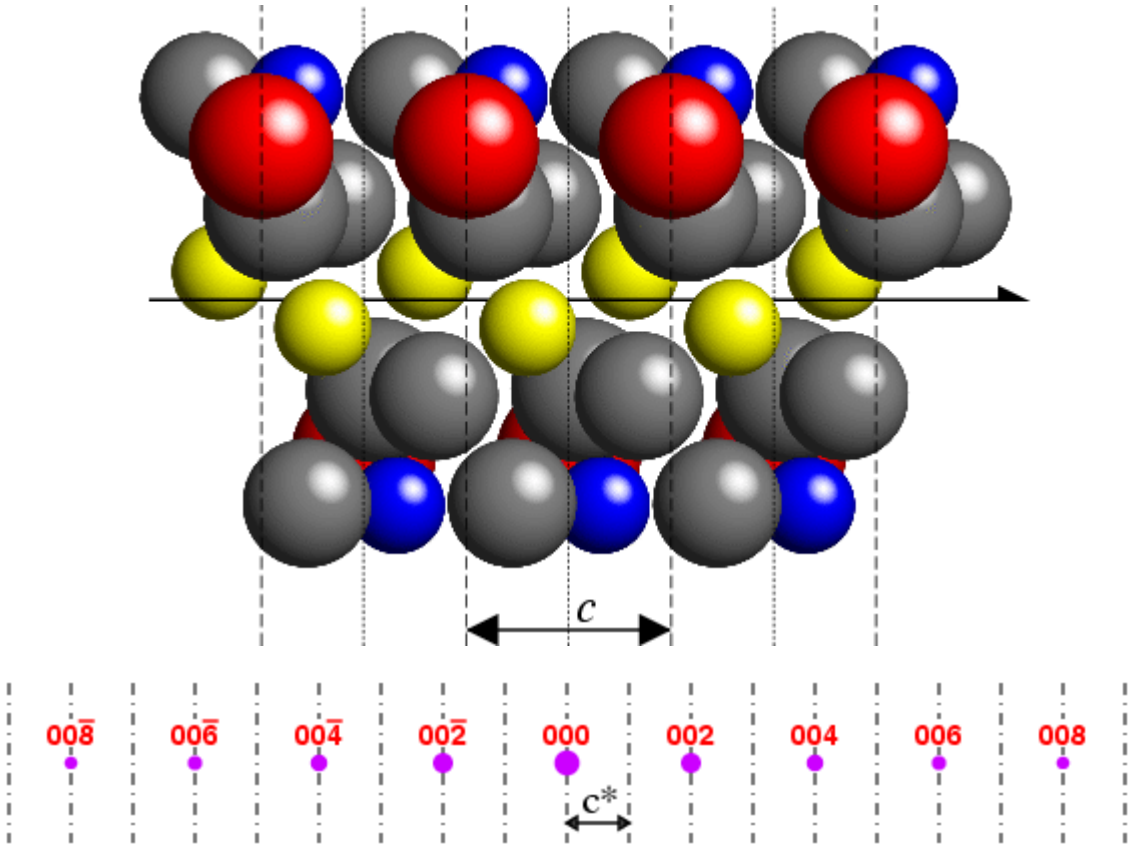
- No translation, e.g. 2 axis



- No reflection condition

Translation Along an Axis

- With translation, e.g. 2_1 axis



- Reflection condition 00l: $l = 2n$

Screw Axes

- Translation in 1 dimension gives rise to reflection conditions in 1 dimension:

2_1 (x) $h00$: $h = 2n$; (y) $0k0$: $k = 2n$; (z) $00l$: $l = 2n$

3_1 or 3_2 (z) $00l$: $l = 3n$

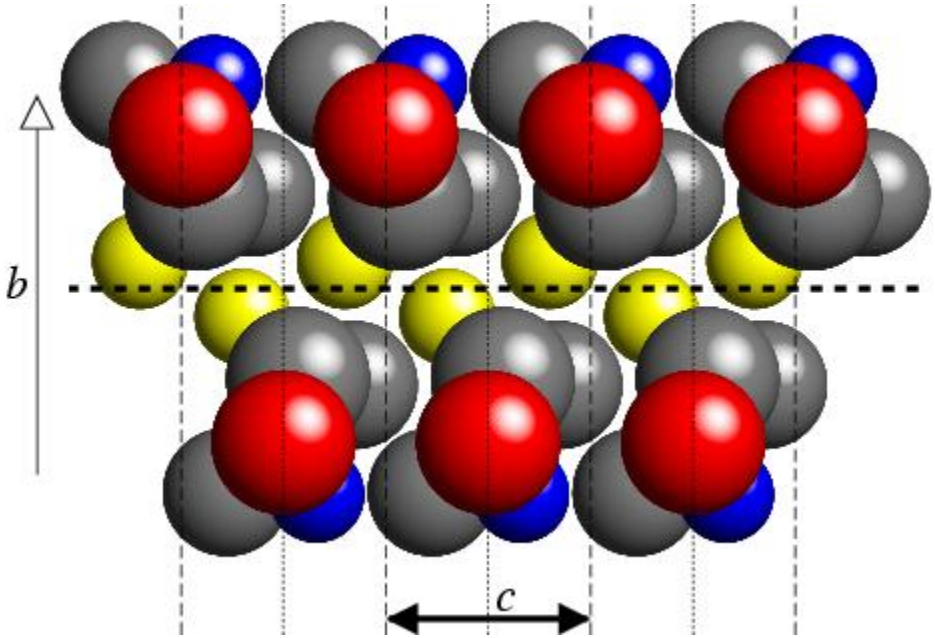
4_1 or 4_3 (z) $00l$: $l = 4n$; 4_2 (z) $00l$: $l = 2n$

6_1 or 6_5 (z) $00l$: $l = 6n$; 6_2 or 6_4 (z) $00l$: $l = 3n$;

6_3 (z) $00l$: $l = 2n$

Glide Planes

- Translational component gives rise to reflection conditions in a diffraction plane



- Reflection condition $h0l$: $l = 2n$

Glide Planes

- Translation in 2 dimensions gives rise to reflection conditions in 2 dimensions:

	x	y	z	
a	N/A	$h0l$: $h = 2n$	$hk0$: $h = 2n$	
b	$0kl$: $k = 2n$	N/A	$hk0$: $k = 2n$	
c	$0kl$: $l = 2n$	$h0l$: $l = 2n$	N/A	
n	$0kl$: $k+l=2n$	$h0l$: $h+l=2n$	$hk0$: $h+k=2n$	etc.
d	$0kl$: $k+l=4n$	$h0l$: $h+l=4n$	$hk0$: $h+k=4n$	etc.

Single-Crystal v Powder Diffraction

- Single crystal (3-D data)
  - Lattice reflection conditions very obvious
  - Glide plane reflection conditions very obvious
  - Screw axis reflection conditions often obvious
- Powder (1-D data)
  - Lattice reflection conditions often obvious
  - Glide plane reflection conditions less obvious
  - Screw axis reflection conditions very tricky

Space Groups & Standards

- 230 Space Groups for 3 Dimensions
- BUT
  - Crystallographer chooses unit cell
  - Crystallographer chooses an origin
    - » Consequence is that many sets of symmetry operators can represent the same space group
      - Number is finite (but may still be very large) if a sensible origin is chosen

Example: Space Group No.7

$x, y, z \;\&\; x, -y, \frac{1}{2}+z$

$x, y, z \;\&\; x, \frac{1}{2}-y, \frac{1}{2}+z$

$x, y, z \;\&\; \frac{1}{2}+x, -y, z$

$x, y, z \;\&\; \frac{1}{2}+x, -y, \frac{1}{2}+z$

$x, y, z \;\&\; \frac{1}{2}+x, \frac{1}{2}+y, -z$

$x, y, z \;\&\; -x, \frac{1}{2}+y, \frac{1}{2}+z$

$x, y, z \;\&\; -x, \frac{1}{2}+y, z$

$x, y, z;\ \frac{1}{2}+x, y, \frac{1}{2}+z;\ \frac{1}{2}+x, -y, z;\ \&\ x, -y, \frac{1}{2}+z$

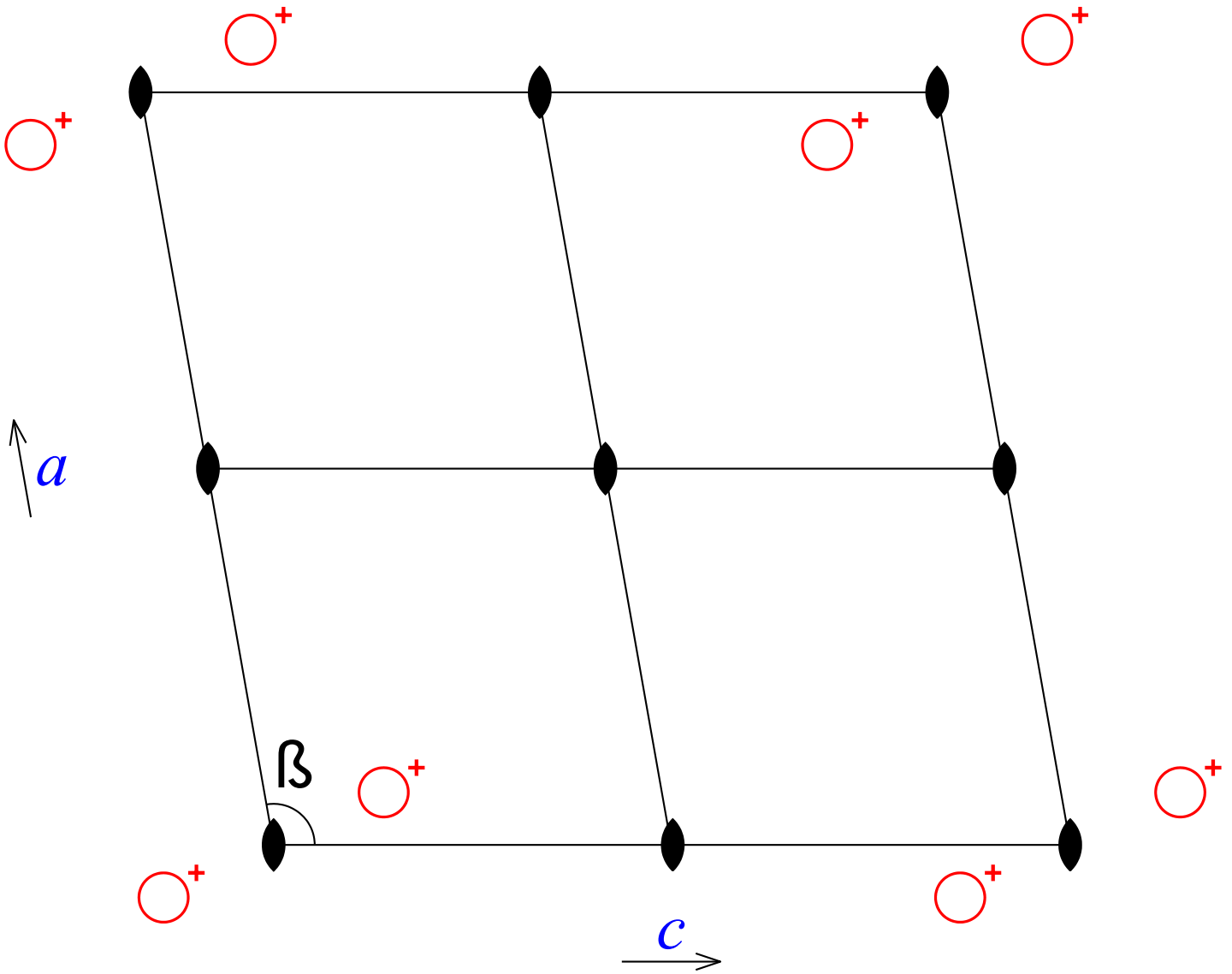
$x, y, z;\ \frac{1}{2}+x, y, \frac{1}{2}+z;\ \frac{1}{4}+x, -y, \frac{1}{4}+z;\ \&\ \frac{3}{4}+x, -y, \frac{3}{4}+z$

- All have lattice translations plus glide plane

Need for Standards

- Comparison of crystal structures
  - Is ones structure a new structure?
  - Differences are easy to spot
    - e.g. if space group number is different then new structure is obviously different
      - Unless one has made a mistake!
  - Similarities may be harder to spot
    - The higher the symmetry, the easier it is to make a comparison since symmetry axes provide unique directions
      - Hardest with triclinic structures

Comparison Problems



Non-Standard Space Groups

- Why bother with non-standard space group settings?
  - Make comparison of crystal structures in different space groups easier
  - To help solve crystal structures that change as a result of a phase transition
- Are there lots of non-standard settings of space groups?
  - YES

Triclinic

(For the enlarged unit cells, click here)

1. $P\ 1$ 2. $P\ \bar{1}$

Monoclinic

(For a fuller list with alternative unique axes, origins, or enlarged unit cells click here)

3. $P\ 1\ 2\ 1$ 4. $P\ 1\ 2_1\ 1$ 5. $C\ 1\ 2\ 1$ 6. $P\ 1\ m\ 1$ 7. $P\ 1\ c\ 1$

8. $C\ 1\ m\ 1$ 9. $C\ 1\ c\ 1$ 10. $P\ 1\ 2/m\ 1$ 11. $P\ 1\ 2_1/m\ 1$ 12. $C\ 1\ 2/m\ 1$

13. $P\ 1\ 2/c\ 1$ 14. $P\ 1\ 2_1/c\ 1$ 15. $C\ 1\ 2/c\ 1$

Orthorhombic

(For a fuller list with alternative axes and origins click here)

16. $P\ 2\ 2\ 2$ 17. $P\ 2\ 2\ 2_1$ 18. $P\ 2_1\ 2_1\ 2$ 19. $P\ 2_1\ 2_1\ 2_1$ 20. $C\ 2\ 2\ 2_1$

21. $C\ 2\ 2\ 2$ 22. $F\ 2\ 2\ 2$ 23. $I\ 2\ 2\ 2$ 24. $I\ 2_1\ 2_1\ 2_1$ 25. $P\ m\ m\ 2$

26. $P\ m\ c\ 2_1$ 27. $P\ c\ c\ 2$ 28. $P\ m\ a\ 2$ 29. $P\ c\ a\ 2_1$ 30. $P\ n\ c\ 2$

x-axis unique

3. (i) *P* 2 1 1 (ii) *A* 2 1 1

4. (i) *P* 2_1 1 1 (ii) *A* 2_1 1 1

5. (i) *B* 2 1 1 (ii) *C* 2 1 1 (iii) *I* 2 1 1 (iv) *F* 2 1 1

6. (i) *P m* 1 1 (ii) *A m* 1 1

7. (i) *P b* 1 1 (ii) *P c* 1 1 (iii) *P n* 1 1 (iv) *A b* 1 1 (v) *A d* 1 1

8. (i) *B m* 1 1 (ii) *C m* 1 1 (iii) *I m* 1 1 (iv) *F m* 1 1

9. (i) *B b* 1 1 (ii) *C c* 1 1 (iii) *I b* 1 1 (iv) *F d* 1 1

10. (i) *P* 2 / *m* 1 1 (ii) *A* 2 / *m* 1 1

11. (i) *P* 2_1 / *m* 1 1 (ii) *A* 2_1 / *m* 1 1

12. (i) *B* 2 / *m* 1 1 (ii) *C* 2 / *m* 1 1 (iii) *I* 2 / *m* 1 1 (iv) *F* 2 / *m* 1 1

13. (i) *P* 2 / *b* 1 1 (ii) *P* 2 / *c* 1 1 (iii) *P* 2 / *n* 1 1 (iv) *A* 2 / *b* 1 1 (v) *A* 2 / *d* 1 1

14. (i) *P* 2_1 / *b* 1 1 (ii) *P* 2_1 / *c* 1 1 (iii) *P* 2_1 / *n* 1 1 (iv) *A* 2_1 / *b* 1 1 (v) *A* 2_1 / *d* 1 1

15. (i) *B* 2 / *b* 1 1 (ii) *C* 2 / *c* 1 1 (iii) *I* 2 / *b* 1 1 (iv) *F* 2 / *d* 1 1

Non-Standard Space Groups

- Different choice of unit cell vectors
- Origin at different locations
  - See space group $I4_1/a$ on UCL web pages
    - *http://pd.chem.ucl.ac.uk/sgp/large/088a.htm*
- Use of enlarged unit cells
  - e.g. $F\ 1\ 2/d\ 1$

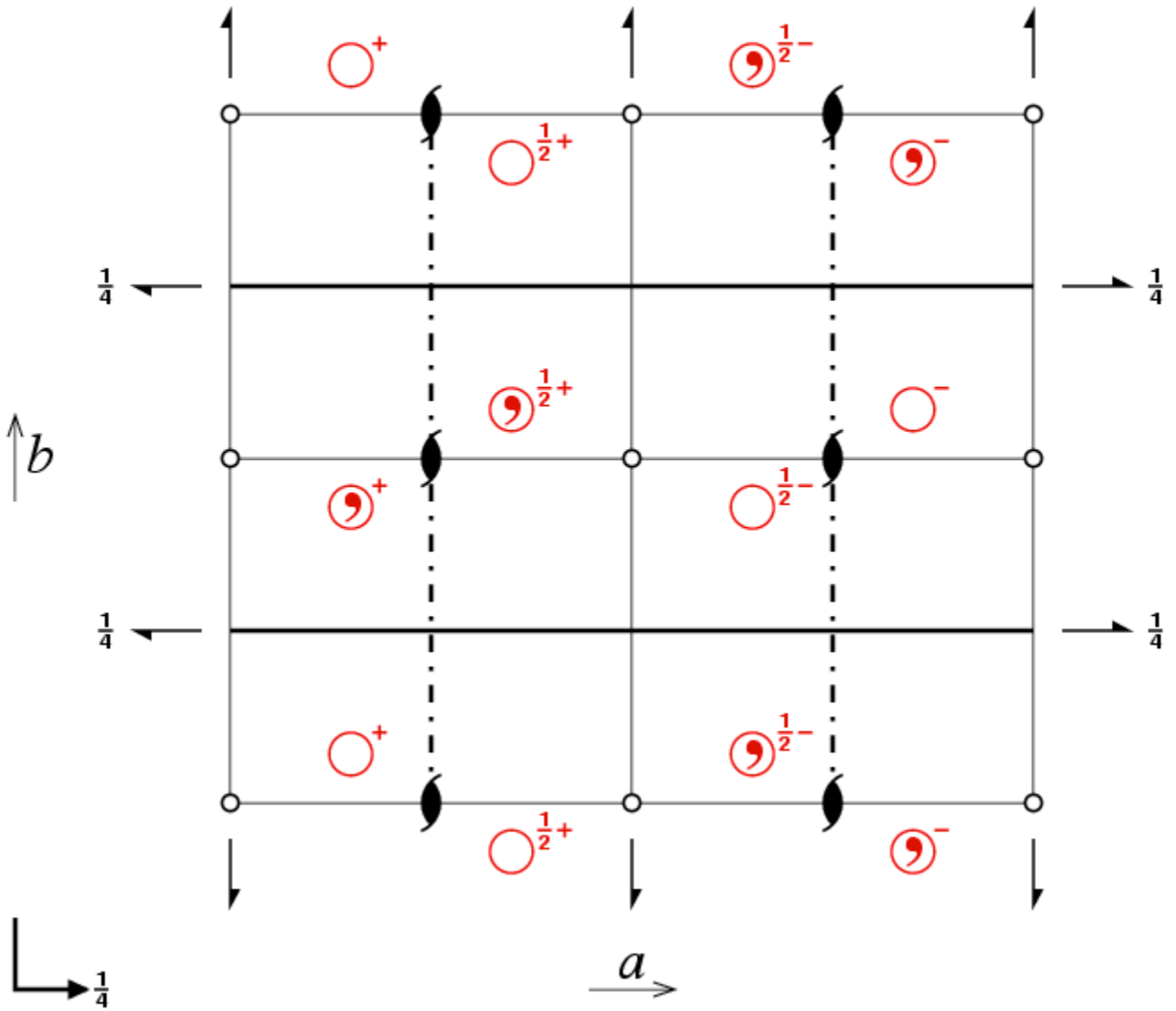
- Unacceptable reasons
  - Too lazy to convert to standard setting

Web Info

- **3-D Symmetry Elements**
  - *http://pd.chem.ucl.ac.uk/pdnn/symm1/symindex.htm*
- **Point Groups**
  - *http://pd.chem.ucl.ac.uk/pdnn/symm2/indexpnt.htm*
- **Space Groups**
  - *http://pd.chem.ucl.ac.uk/pdnn/symm3/spgindex.htm*
- **Space-Group Determination**
  - *http://pd.chem.ucl.ac.uk/pdnn/symm4/condex.htm*
- **Space Groups Diagrams & Tables**
  - *http://pd.chem.ucl.ac.uk/sgp/*

Example

Pnma $P\,2_1/n\,2_1/m\,2_1/a$ *mmm* No. 62



1 x, y, z

2 $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} + z$

3 $x, \frac{1}{2} - y, z$

4 $\frac{1}{2} + x, y, \frac{1}{2} - z$

5 $\bar{x}, \bar{y}, \bar{z}$

6 $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$

7 $\bar{x}, \frac{1}{2} + y, \bar{z}$

8 $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$

Session 3: Introduction to (powder) diffraction

Dr Emma E. McCabe

Durham University, Department of Physics

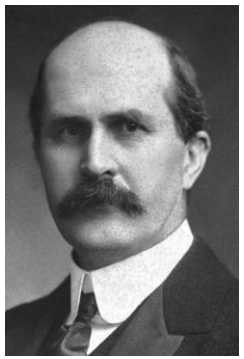
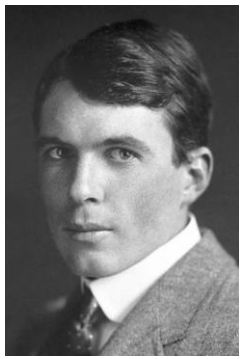
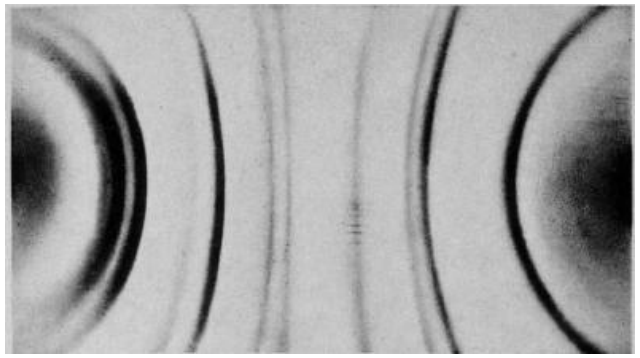
Lecture Contents

1. Diffraction
2. Bragg’s Law and Laue equations
3. Reciprocal lattice
4. Ewald construction
5. Atomic scattering factor
6. Information in a powder pattern

Historical background

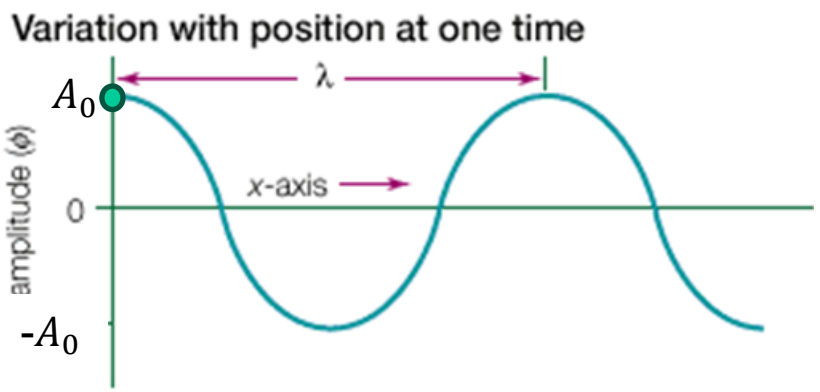
- 1895: Röntgen discovers X-rays
- 1912: von Laue discovers X-ray diffraction on crystals
- 1913: Bragg & Bragg discover structure analysis by XRD
- 1916: Debye & Scherrer discover powder X-ray diffraction
- 1941: Joint Commission on Powder Diffraction and Standards (JCPDS)
  - 1978 International Centre for Diffraction data (ICDD)
- 1943: $BaTiO_3$ studied by Helen Megaw
- 1948: neutron powder diffraction
- 1967: The Rietveld method
- 1990: direct space approaches to structure solution
- 2000: work on proteins, 100+ atom structures
- 2005: XRPD on the Mars rover!

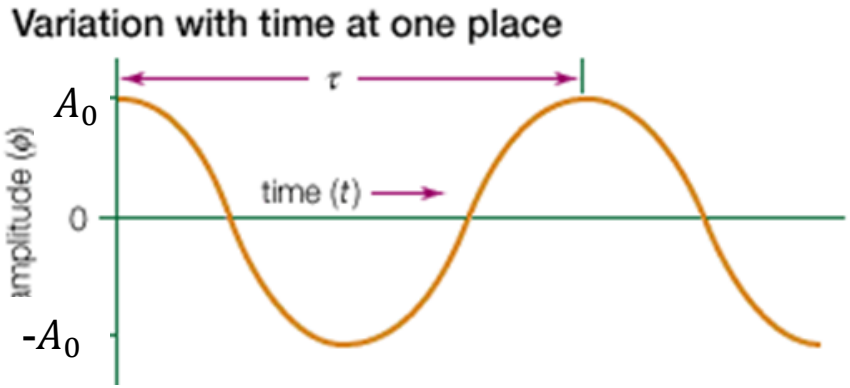



Waves

- Characteristics of periodic waves
  - amplitude A
  - wavelength λ
  - period τ $\quad \tau = \frac{1}{\nu} = \frac{2\pi}{\omega}$
  - frequency f
  - angular frequency ω $\quad \omega = 2\pi f$

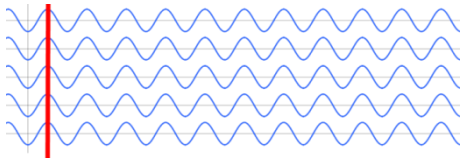




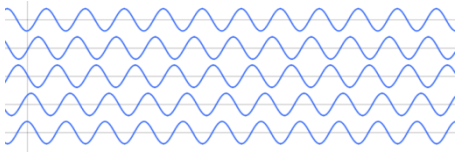
- wavenumber k $\quad k = \frac{2\pi}{\lambda}$ $\qquad \omega = \nu k$ $\qquad A = A_0 \cos(kx - \omega t)$
- phase ϕ $\quad \phi = (kx - \omega t)$

- Coherent waves
  - constant phase relationship
- Superposition of waves:

constructive interference

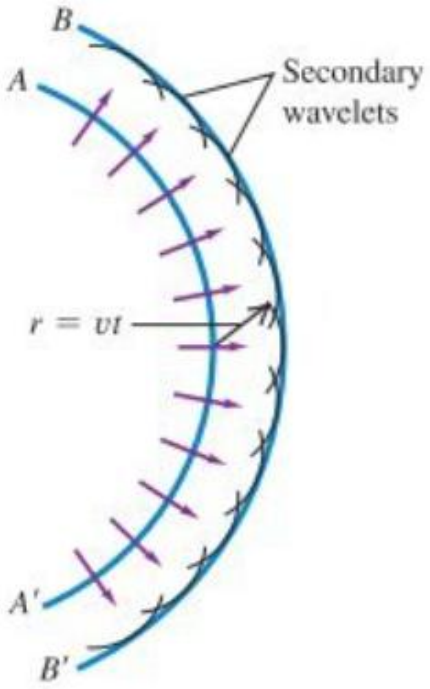


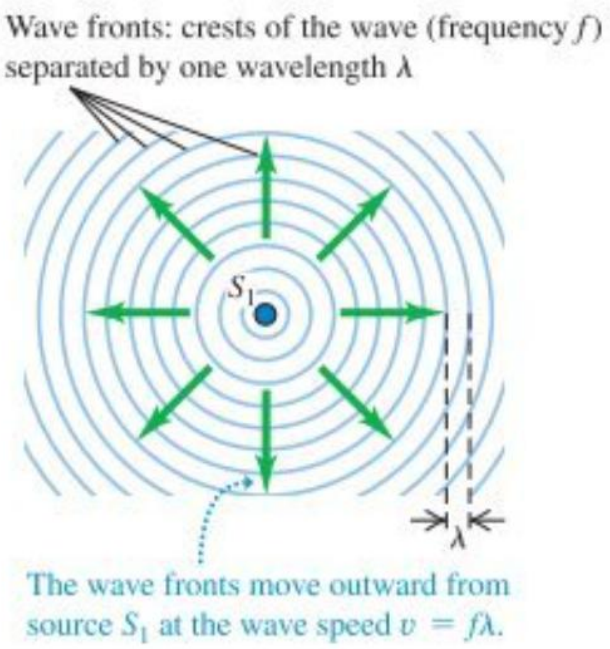
destructive interference

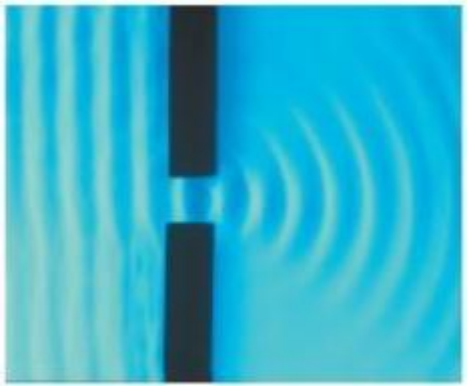


Huygen's principle

- Propagation of waves:
  - every point on a wavefront is a source of spherical wavelets
  - developing wavefront is an envelope of these wavelets
  - propagation direction is tangential to this envelope

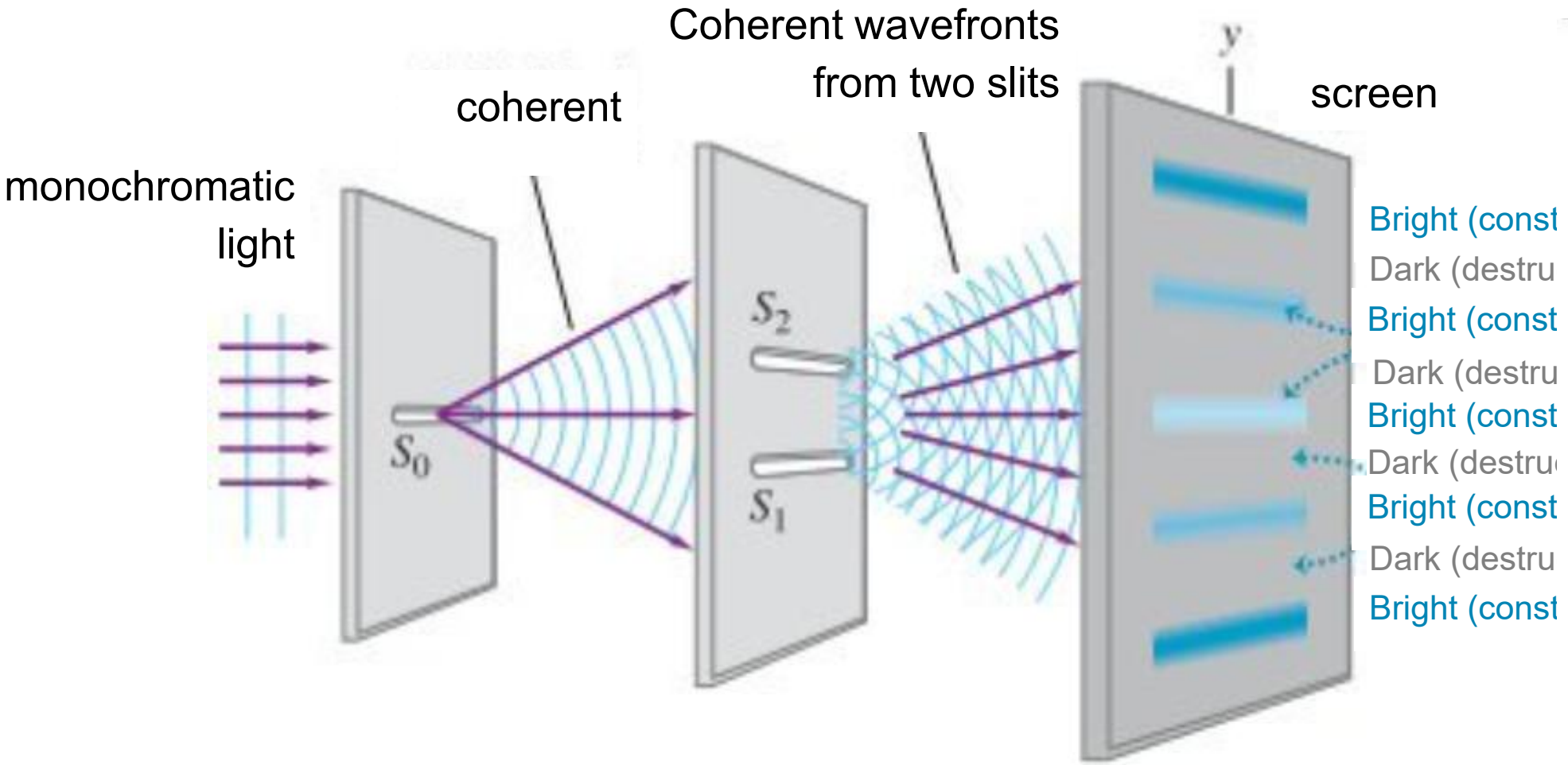


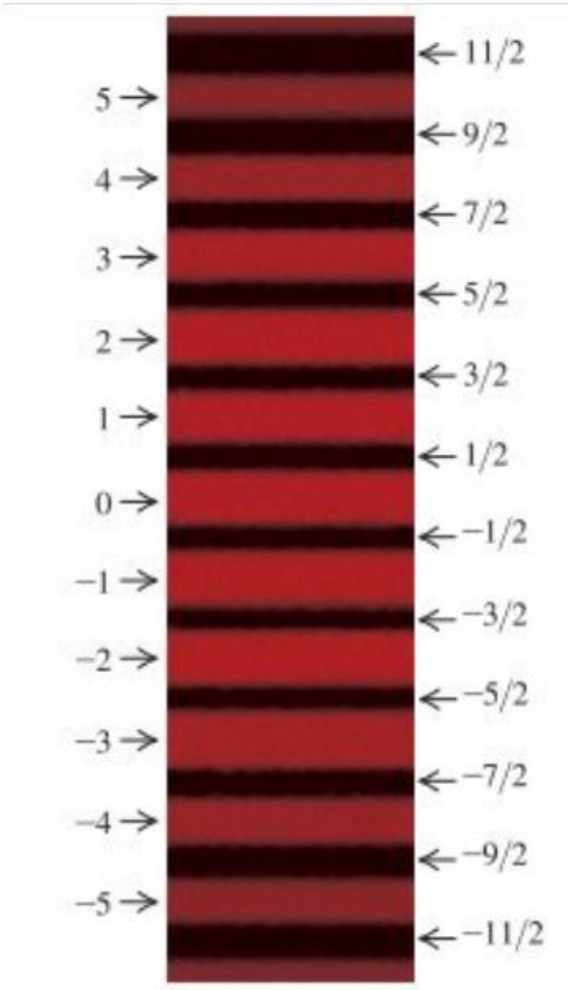




University Physics, Young and Freedman, Pearson Education 2015

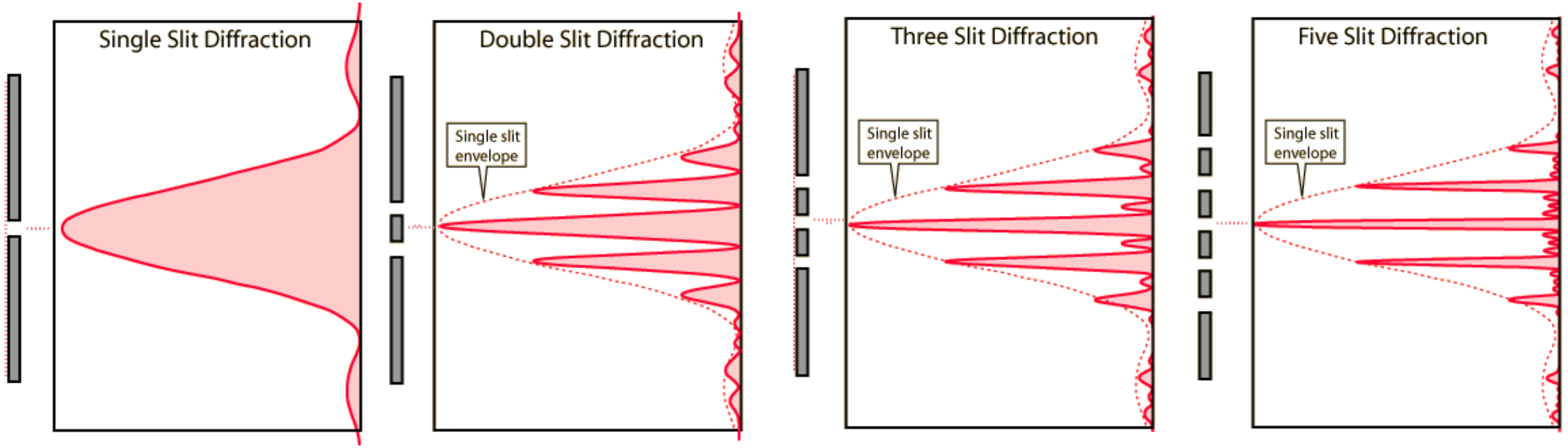
Young's double slit experiment





University Physics, Young and Freedman, Pearson Education 2015

Multiple slits

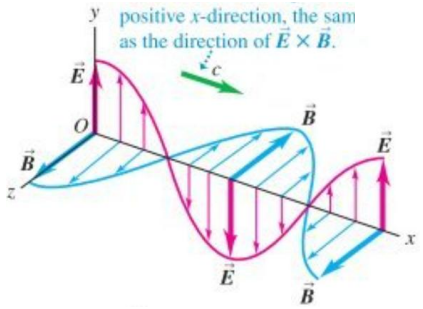


Diffraction by crystalline solids

- Crystalline solids:

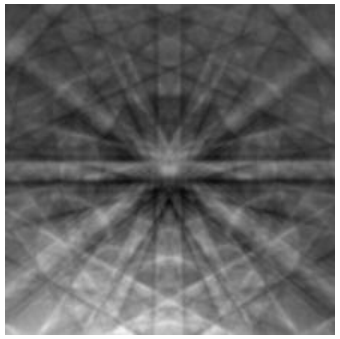
*"A solid is a crystal if its atoms, ions and/or molecules form, on average, a long-range **ordered** arrangement. In most crystals the arrangement is a periodic array that is governed by the rules of translational symmetry."*

- Diffraction probes for crystalline solids:



X-rays
- electromagnetic radiation
- $\lambda = 0.1 - 100$ Å

Neutrons
- $\lambda = \frac{h}{mv}$

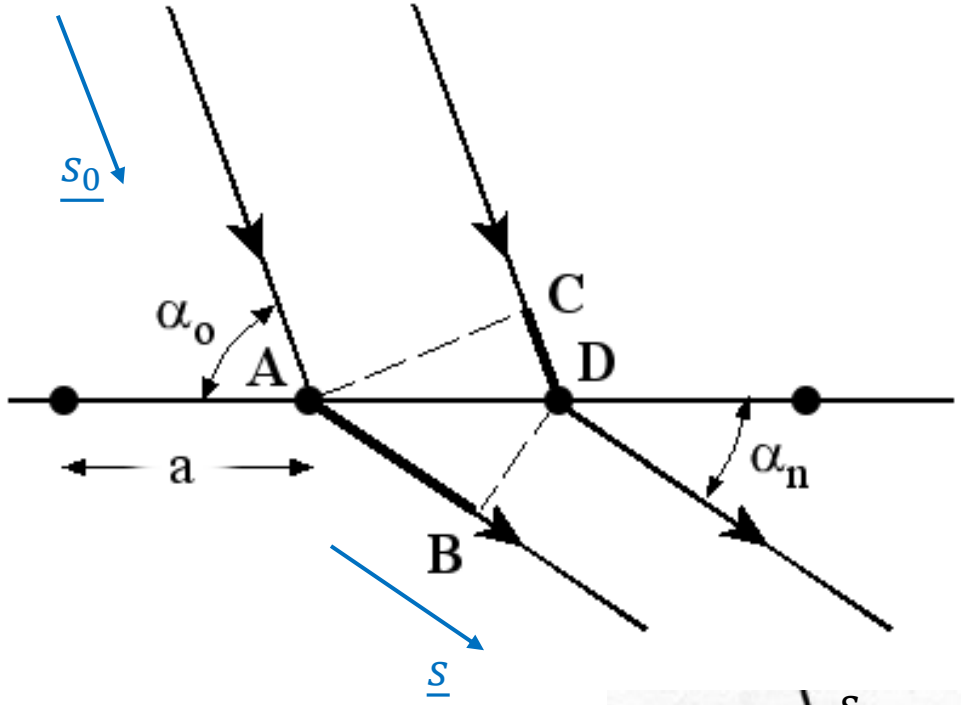


Electrons
- $\lambda = \frac{h}{mv}$

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

University Physics, Young and Freedman, Pearson Education 2015 *https://dictionary.iucr.org/Crystal*

Diffraction from a 1D array of atoms



- Using vector notation:

  lattice vector $\underline{a}$

  unit incident wavevector $\underline{s_0}$

  unit scattered wavevector $\underline{s}$

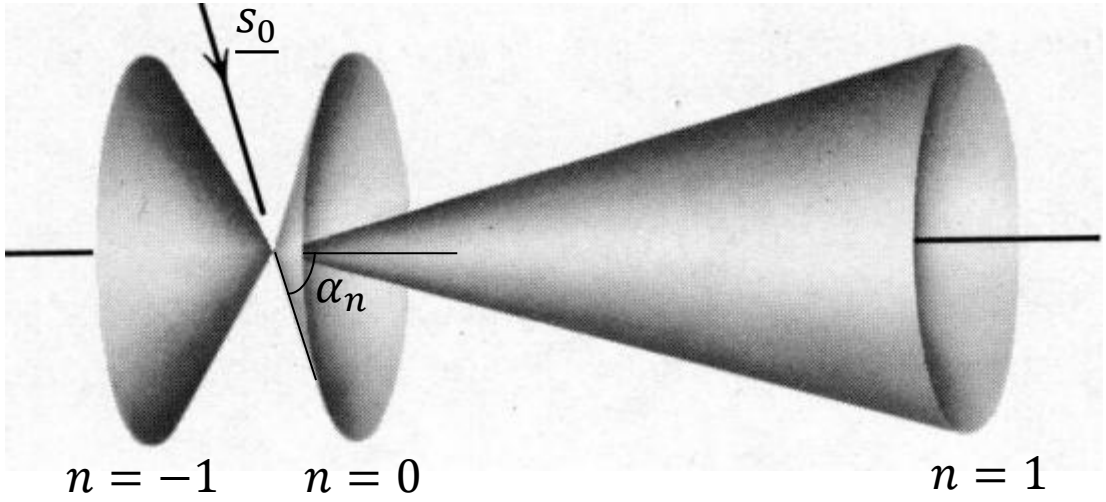
  $a \cos \alpha_n = a \cdot \underline{s}$

- Constructive interference:

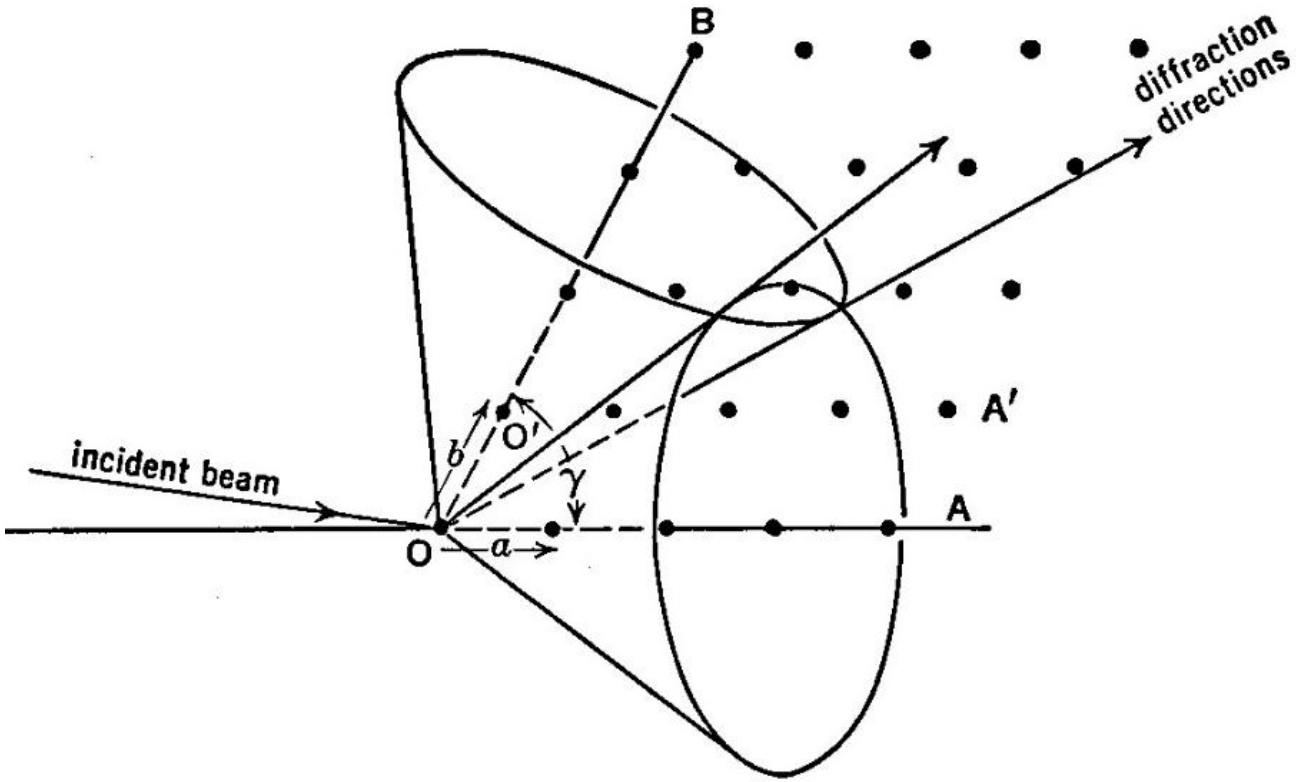
$$\mathrm{AB} - \mathrm{CD} = a(\cos \alpha_n - \cos \alpha_0) = h\lambda$$

- Laue equation:

$$\underline{a}\left(\underline{s} - \underline{s_0}\right) = h\lambda$$



Diffraction from 2D arrays of atoms



- Laue equations:

$$\underline{a}\left(\underline{s}-\underline{s_0}\right)=h\lambda$$

$$\underline{b}\left(\underline{s}-\underline{s_0}\right)=k\lambda$$

- maxima in intensity along two directions

Diffraction from 3D arrays of atoms

- Laue equations:

$$\underline{a}\left(\underline{s}-\underline{s_0}\right)=h\lambda$$

$$\underline{b}\left(\underline{s}-\underline{s_0}\right)=k\lambda$$

$$\underline{c}\left(\underline{s}-\underline{s_0}\right)=l\lambda$$

- maxima in intensity along a single direction

The reciprocal lattice

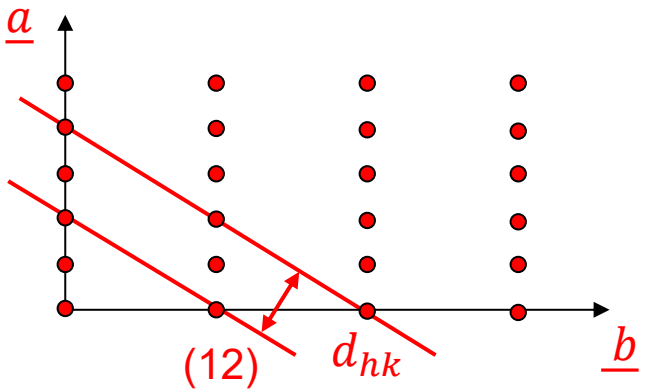
For a set of direct lattice vectors $\underline{a}$, $\underline{b}$ and $\underline{c}$, a set of reciprocal lattice vectors $\underline{a}^*$, $\underline{b}^*$ and $\underline{c}^*$ are defined:

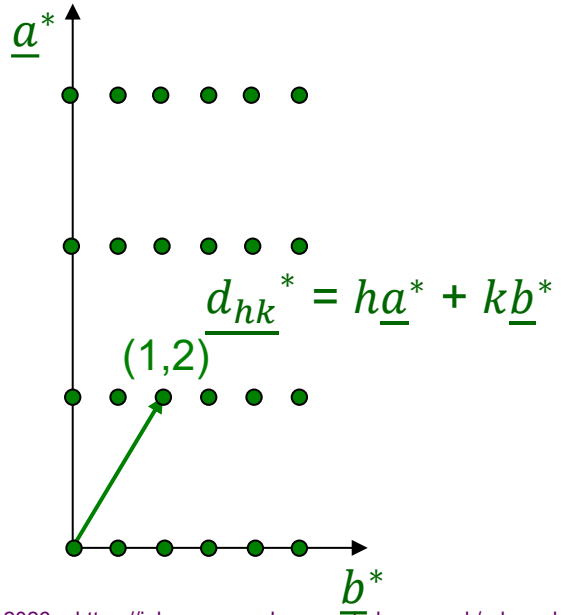
$$\underline{a}^* = \frac{\underline{b}\times\underline{c}}{V_{cell}} \qquad \underline{b}^* = \frac{\underline{c}\times\underline{a}}{V_{cell}} \qquad \underline{c}^* = \frac{\underline{a}\times\underline{b}}{V_{cell}} \qquad \text{(and } \underline{a}^* = \frac{1}{\underline{a}},\ \underline{b}^* = \frac{1}{\underline{b}},\ \underline{c}^* = \frac{1}{\underline{c}}\text{)}$$

$\underline{a}^*$, $\underline{b}^*$ and $\underline{c}^*$ define another lattice, in "reciprocal space", the set of points defined by

$$\underline{d_{hkl}}^* = h\underline{a}^* + k\underline{b}^* + l\underline{c}^*$$

where h, k and l are integers and $\underline{d_{hkl}}^*$ is a reciprocal lattice vector associated with a set of planes d_{hkl} in real space which are normal to $\underline{d_{hkl}}^*$ and separated by $d_{hkl} = \frac{1}{\left|\underline{d_{hkl}}^*\right|}$.





Note that $\underline{a}\cdot\underline{a}^* = \underline{b}\cdot\underline{b}^* = \underline{c}\cdot\underline{c}^* = 1$, and $\underline{a}\cdot\underline{b}^* = \underline{a}\cdot\underline{c}^* = \underline{b}\cdot\underline{c}^* = \cdots = 0$.

Diffraction from 3D arrays of atoms

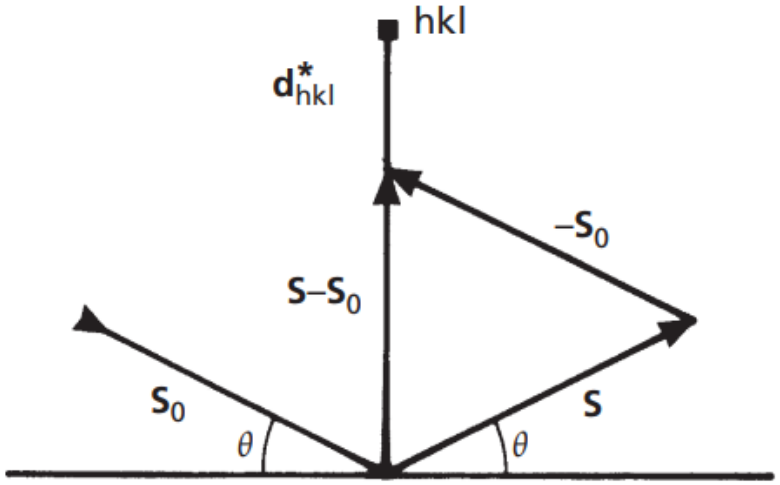
- Laue equations:

$$\underline{a}\left(\underline{s}-\underline{s_0}\right)=h\lambda$$

$$\underline{b}\left(\underline{s}-\underline{s_0}\right)=k\lambda$$

$$\underline{c}\left(\underline{s}-\underline{s_0}\right)=l\lambda$$

$$\left|\underline{s}-\underline{s_0}\right|=2\sin\theta \qquad \frac{\left(\underline{s}-\underline{s_0}\right)}{\lambda}=\underline{d_{hkl}}^{*}$$



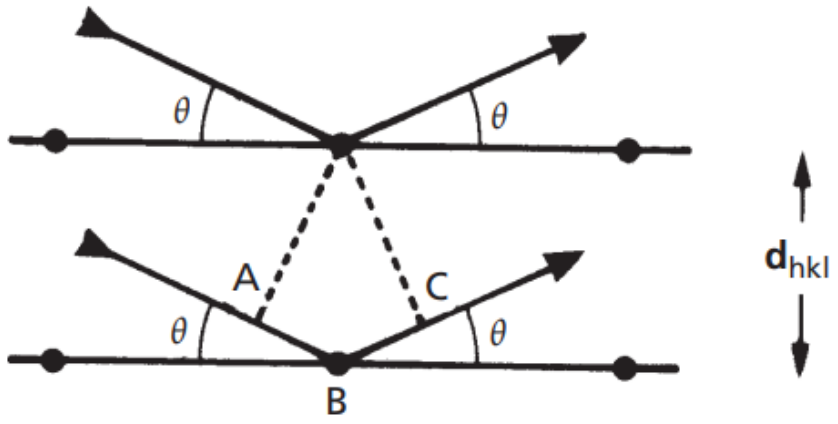
$$\frac{\left(\underline{s}-\underline{s_0}\right)}{\lambda}=\underline{d_{hkl}}^{*}=\left(h\underline{a}^{*}+k\underline{b}^{*}+l\underline{c}^{*}\right)=\frac{1}{d_{hkl}}$$

$$\left(\underline{s}-\underline{s_0}\right)=\lambda\left(h\underline{a}^{*}+k\underline{b}^{*}+l\underline{c}^{*}\right)=\frac{\lambda}{d_{hkl}}$$

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

- Bragg's law

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



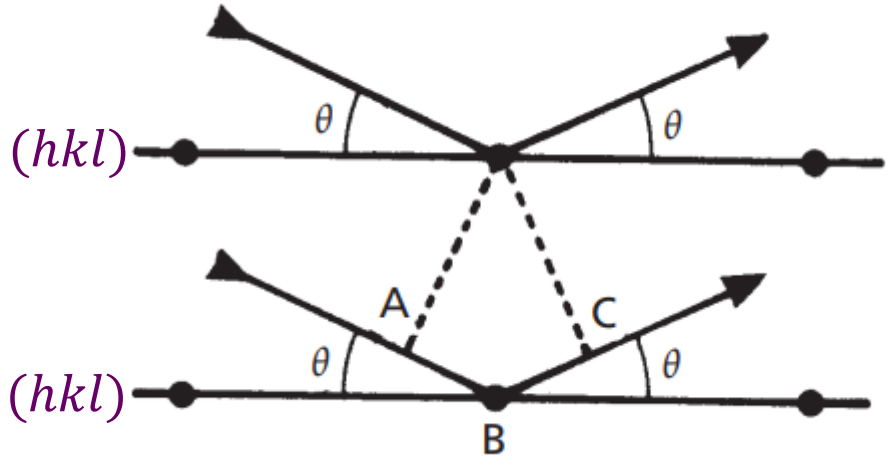
The basics of crysrtallography and diffraction, Hammond, IUCr Oxford University Press, 2012

Bragg's Law

- Simplistic, but useful view of diffraction:
  - Consider parallel planes hkl of atoms in a crystal;
  - Semi-transparent mirrors: incident X-rays reflected off these planes;
  - Peaks in diffraction pattern referred to as "reflections".

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

n = order of diffraction



d_{hkl} Interplanar spacing, d spacing

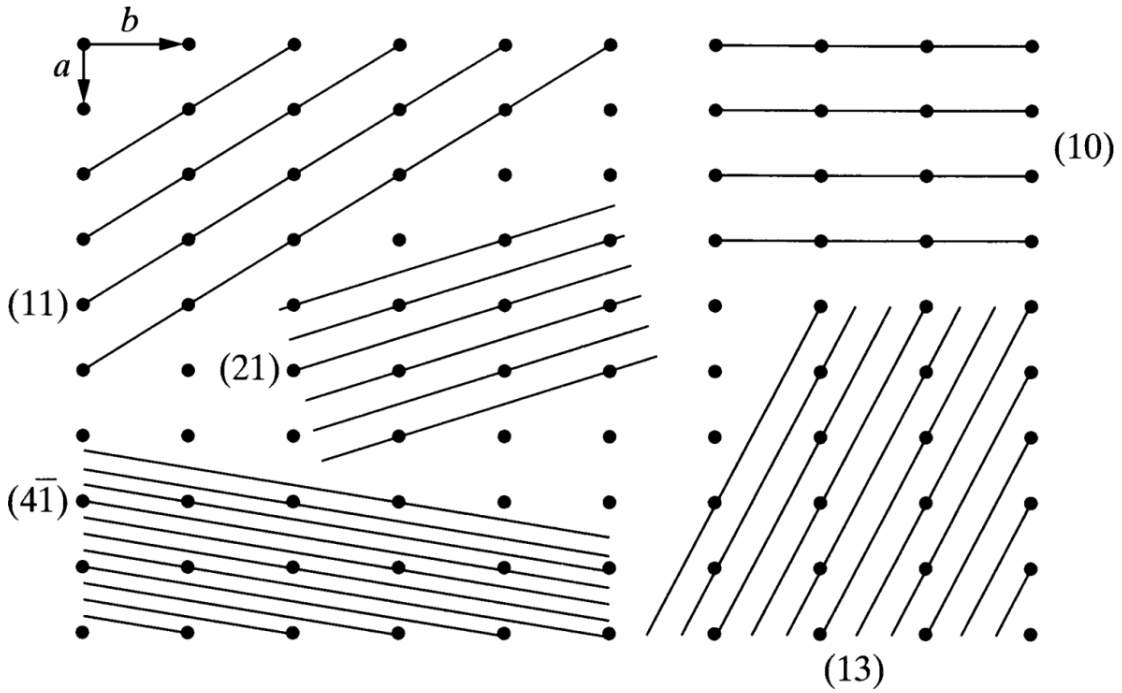
Miller indices (hkl)

The basics of crysrtallography and diffraction, Hammond, IUCr Oxford University Press, 2012

Miller indices

- For each set of parallel planes in crystals, hkl:
  - Take the plane closest to the one that passes through origin;
  - Write the intercepts with the crystallographic axes as fractions of the edges: $^1/_h$, $^1/_k$, $^1/_l$ (for planes parallel to a crystallographic axis, intercept is ∞)

- 2D examples:



d spacings and unit cell parameters

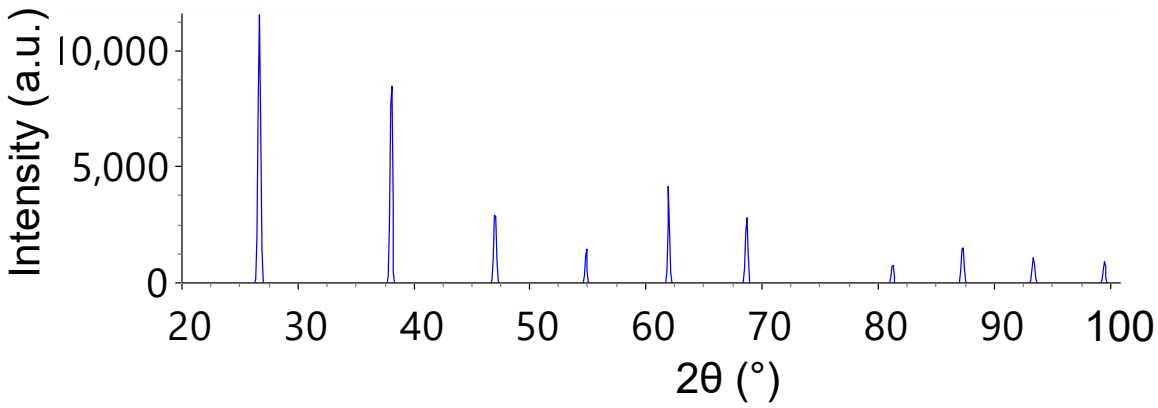
- d spacings between planes in crystals are related to the unit cell parameters a, b, c:
  - for orthogonal systems:

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

- Applications:
  - From known unit cell parameters we can predict peak positions in diffraction patterns;
  - From observed peak positions we can determine unit cell parameters.

Bragg's Law: application

- Predicting the positions of diffraction peaks:
- e.g. Po:
  - Space group $Pm\bar{3}m$ (primitive cubic)
  - $a = 3.352$ Å
  - $\lambda = 1.54056$ Å (Cu $K_{\alpha 1}$)

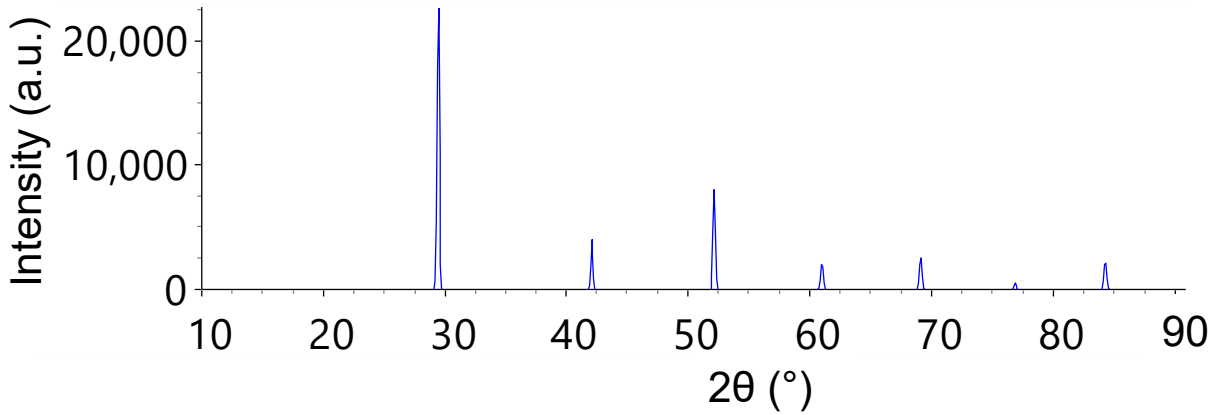


a (Å)	h	k	l
3.352	1	0	0
3.352	1	1	0
3.352	1	1	1
3.352	2	0	0
3.352	2	1	0
3.352	2	1	1
3.352	2	2	0
3.352	2	2	1
3.352	3	0	0
3.352	3	1	0

Bragg's Law: application

- Determining the unit cell parameters i.e. indexing the pattern:
- e.g. unknown element 1
  - cubic
  - $\lambda = 1.54056$ Å (Cu $K_{\alpha 1}$)
  - 2θ values for the first 7 reflections:

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



2θ (°)	θ (°)	θ (rad)	d (Å) = λ/2sinθ
29.4	14.7	0.256	3.039
42.0	21.0	0.367	2.148
52.1	26.1	0.455	1.754
60.9	30.5	0.532	1.519
69.1	34.5	0.603	1.359
76.8	38.4	0.670	1.240
84.3	42.1	0.735	1.148

Ewald sphere: geometrical expression of Bragg's law

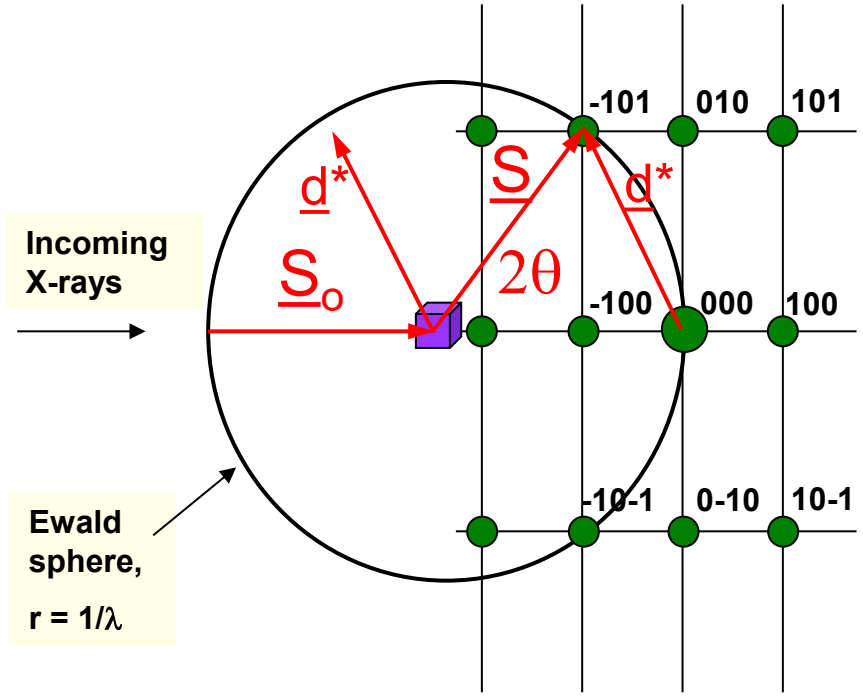
- Back to reciprocal space: $\left|\underline{d_{hkl}}^*\right| = \frac{1}{d_{hkl}}$

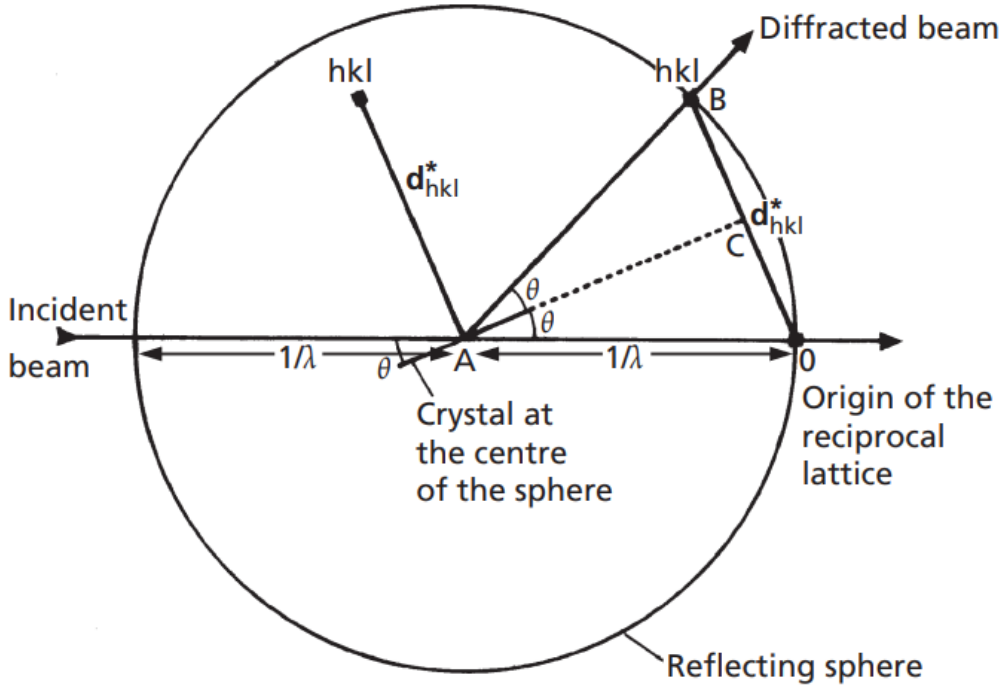
$$OC = \frac{d_{hkl}^*}{2} = \frac{1}{\lambda}\sin\theta$$

$$\frac{1}{2d_{hkl}} = \frac{1}{\lambda}\sin\theta$$

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

- Diffraction condition is satisfied when the reciprocal lattice point for plane hkl intersects the Ewald sphere.

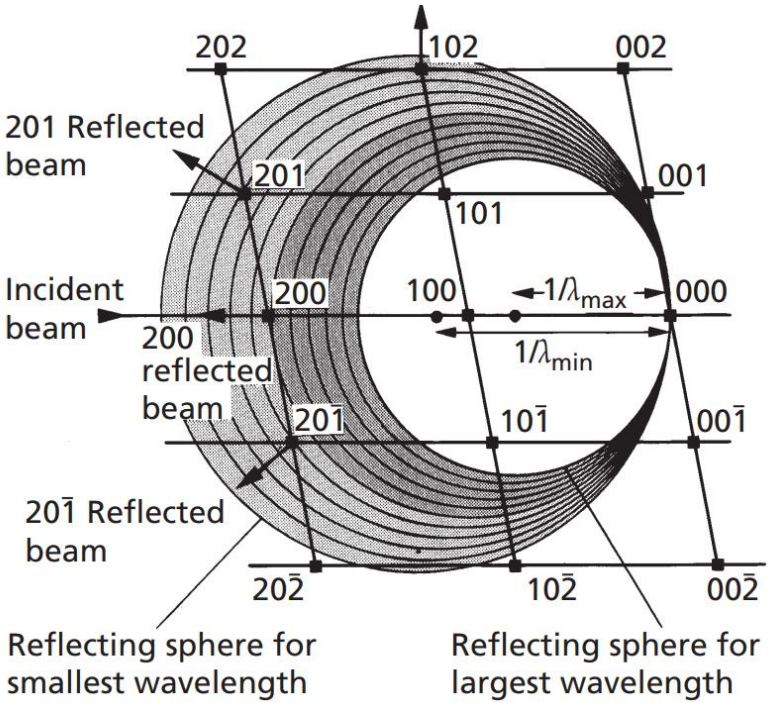


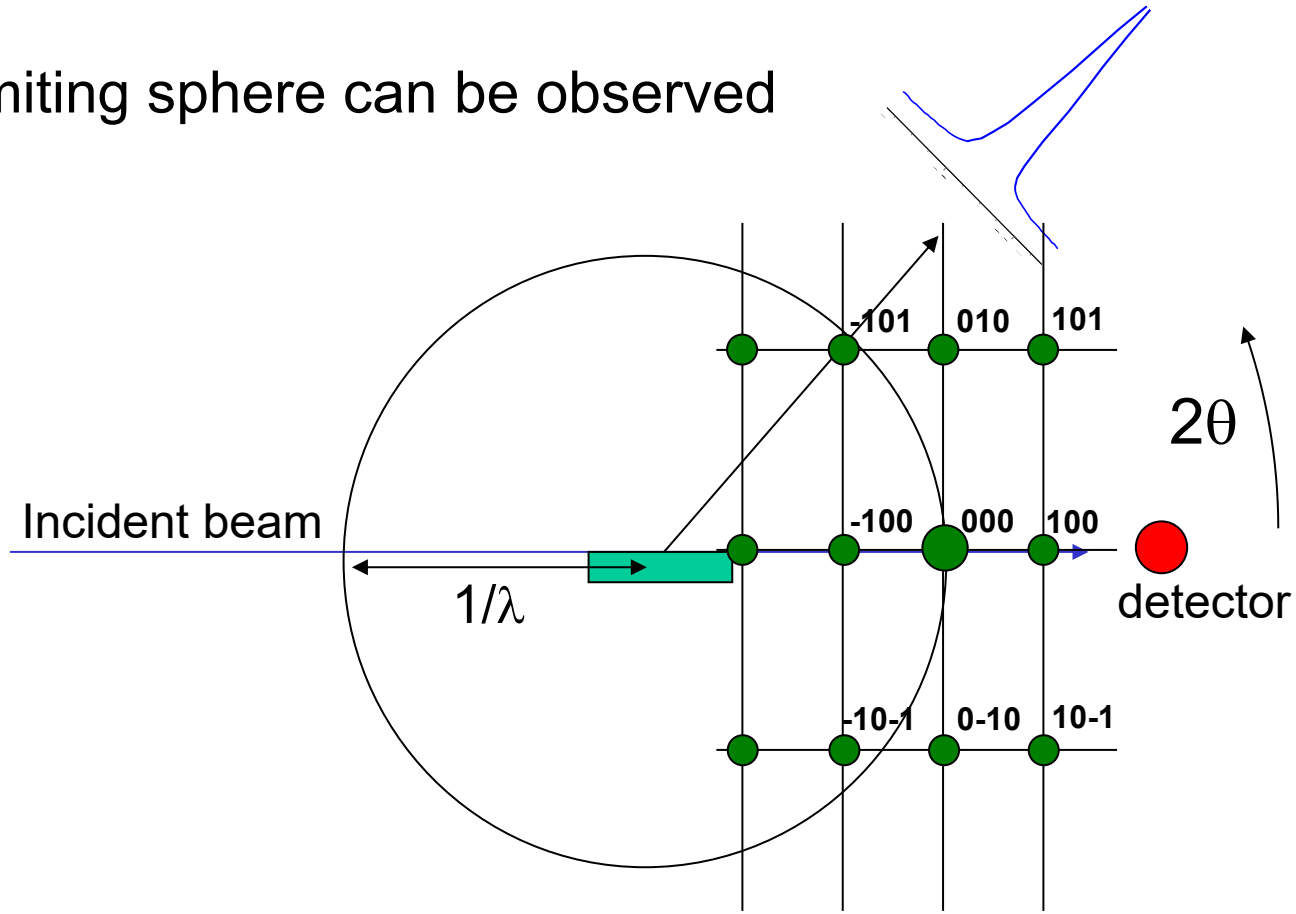


The basics of crysrtallography and diffraction, Hammond, IUCr Oxford University Press, 2012

Ewald sphere and Laue diffraction

- Move detector or rotate crystal to find diffraction peaks
- Laue diffraction: use polychromatic radiation
  - limiting sphere: radius 2/λ
  - only reciprocal lattice points within limiting sphere can be observed



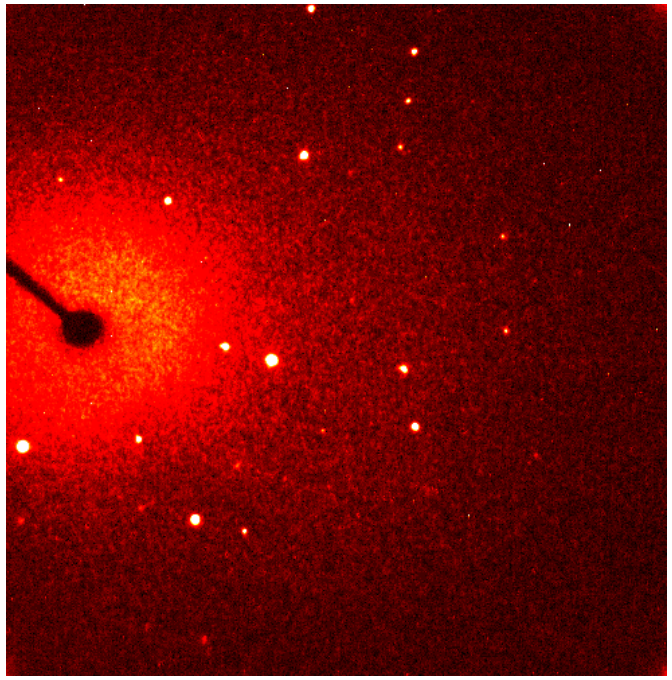


The basics of crysrtallography and diffraction, Hammond, IUCr Oxford University Press, 2012

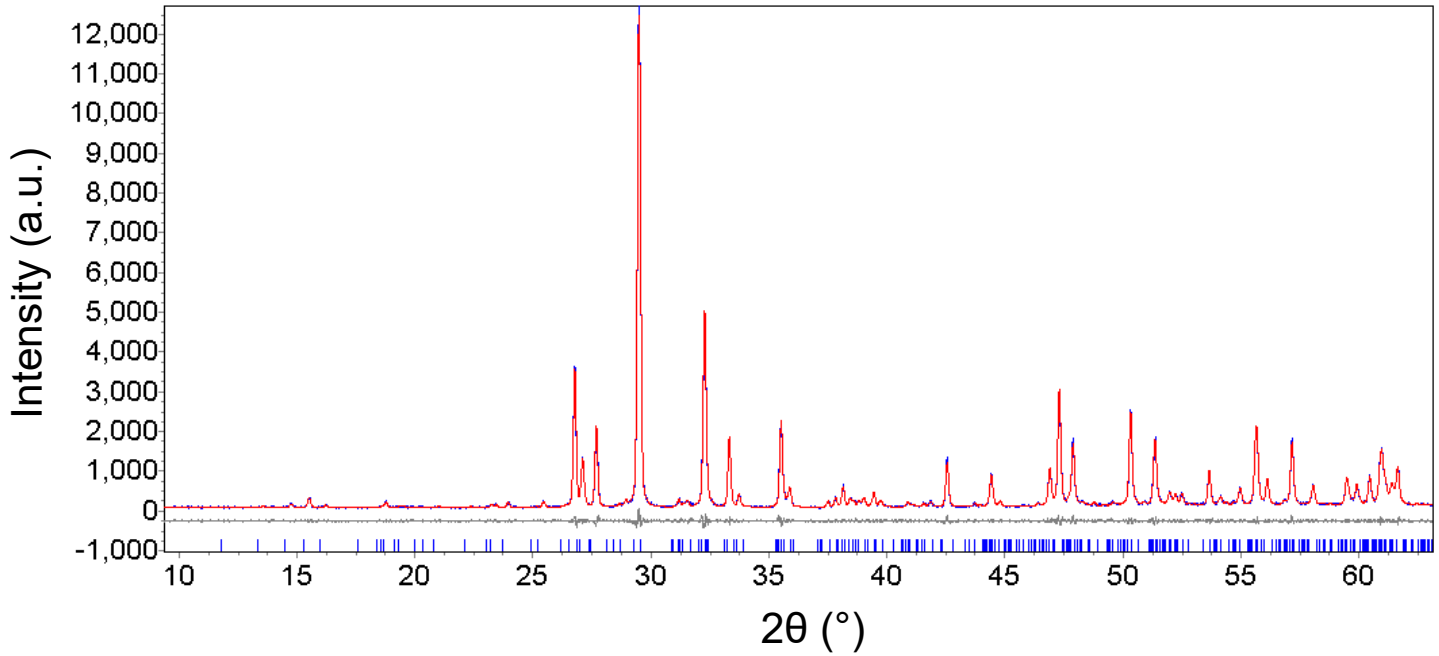
Diffraction patterns

- Experimentally observed X-ray diffraction patterns

Single crystal diffraction

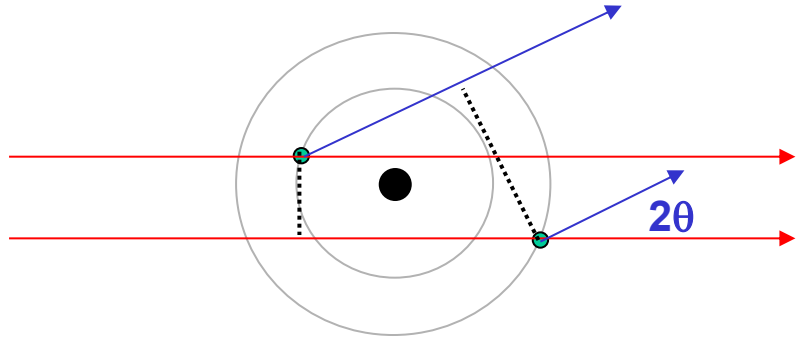


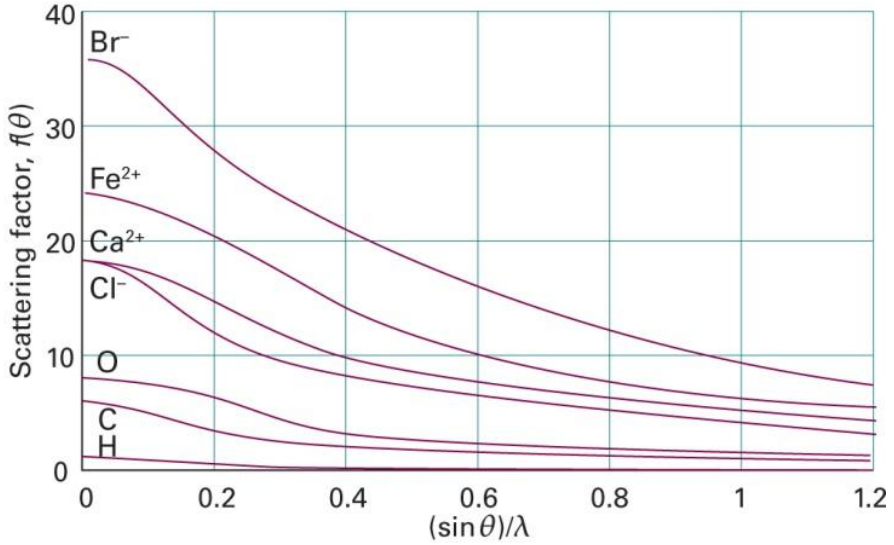
Powder diffraction

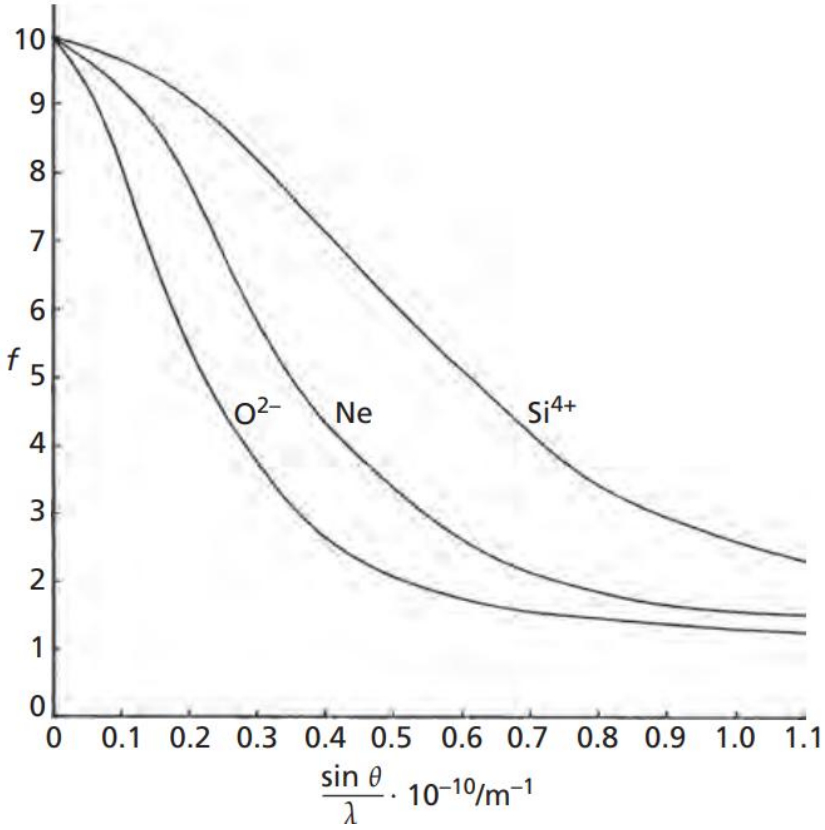


Peak intensities: scattering of X-rays by atoms

- Atomic scattering factor, or “form factor”, f
- $f = Z$ for X-rays scattered in forwards direction
  - f decreases with increasing θ
  - decreases more rapidly for more diffuse electron clouds
  - f calculated using quantum mechanics







Physical chemistry, Atkins, Oxford University Press, 2018

The basics of crysrtallography and diffraction, Hammond, IUCr Oxford University Press, 2012

Peak intensities: scattering of X-rays by the unit cell

- Peak intensities I_{hkl}:

$$I_{hkl} \propto |F_{hkl}|^2$$

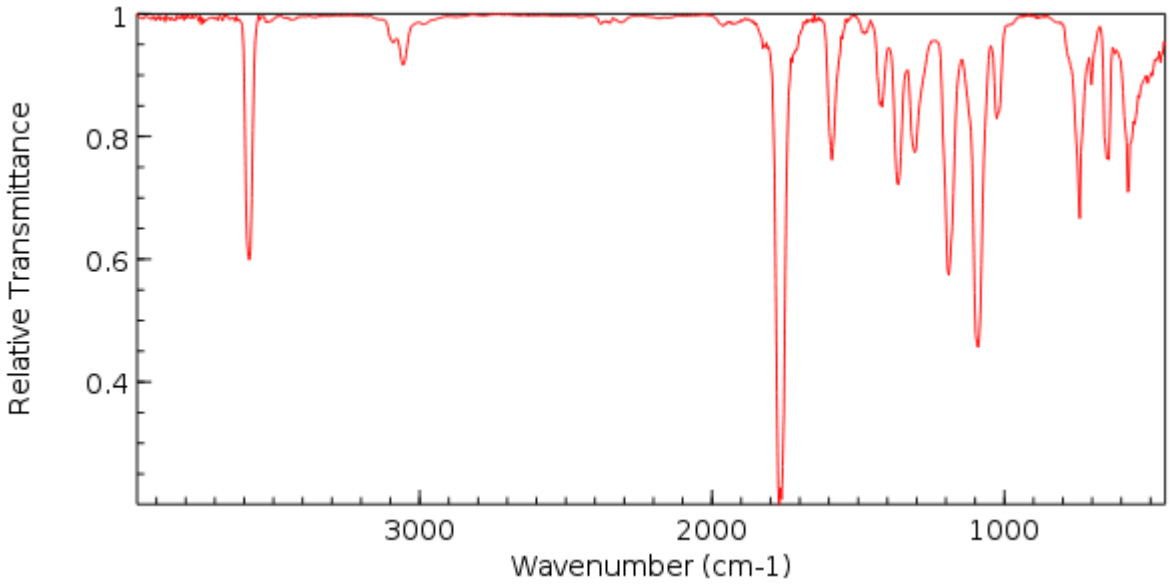
  - F_{hkl}: the collective scattering power of the atoms in the unit cell
  - Other factors: diffractometer optics, absorption, thermal vibrations, site occupancies

- Structure factor F_{hkl}:

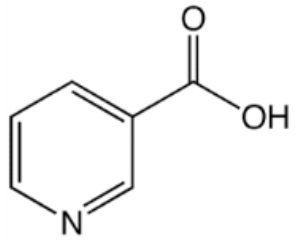
$$F_{hkl} = \sum_j f_j(Q) e^{2\pi i(hx_j + ky_j + lz_j)}$$

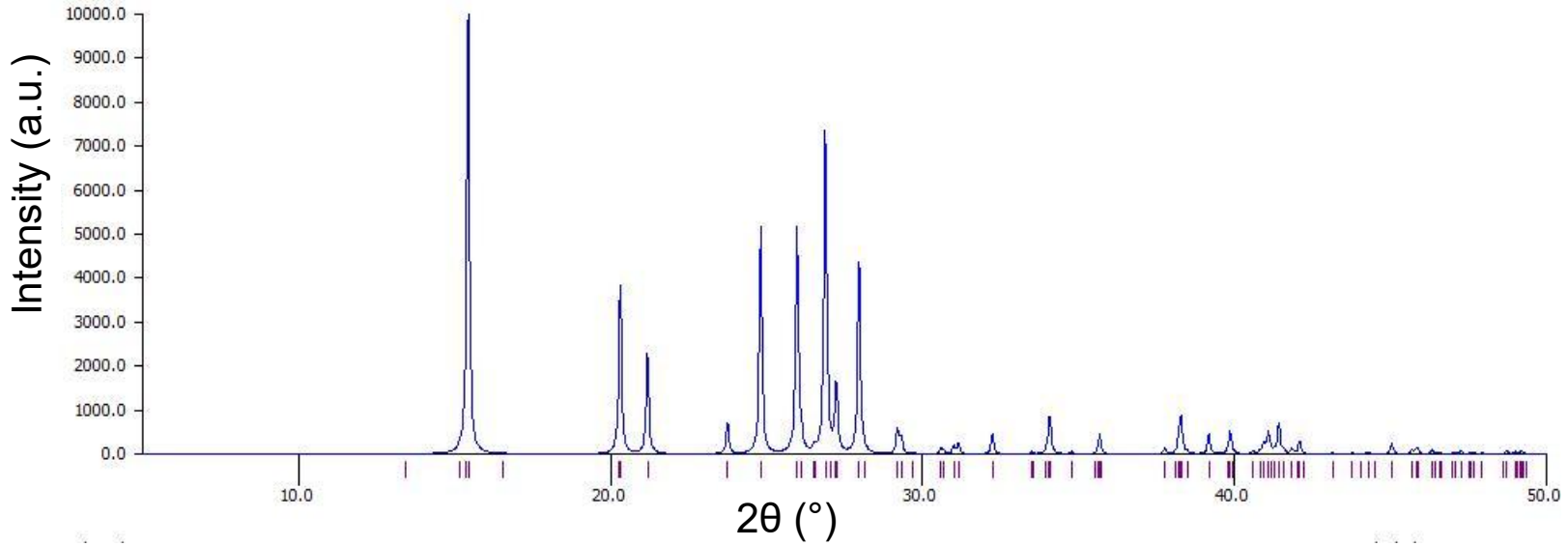
  - $f_j(Q)$: atomic scattering factor of atom j (information about atom types)
  - $e^{2\pi i(hx_j + ky_j + lz_j)}$: structural arrangement within unit cell (information about positions of atoms)

Powder diffraction: what it isn't…



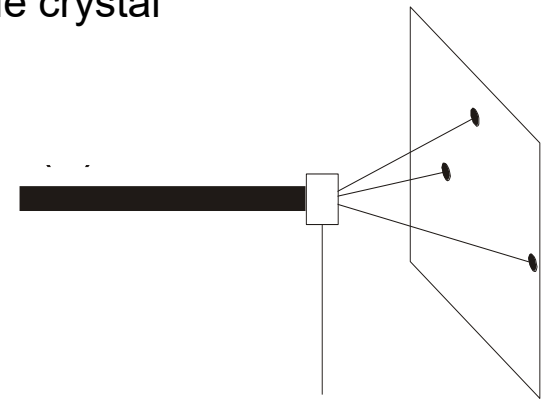
Pyridine-3-carboxylic acid
Niacin
Nicotinic acid
Vitamin B3



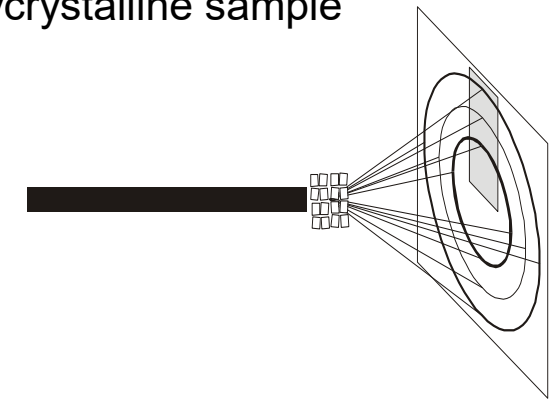


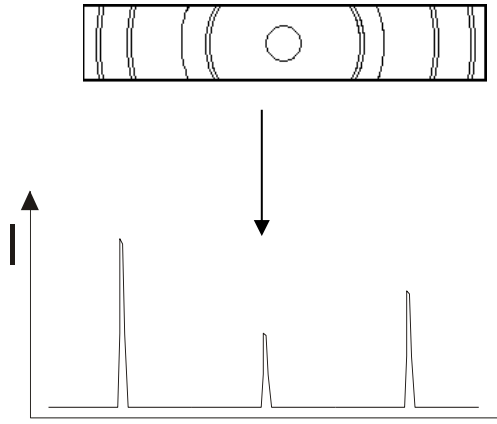
Single crystal vs powder diffraction

Single crystal

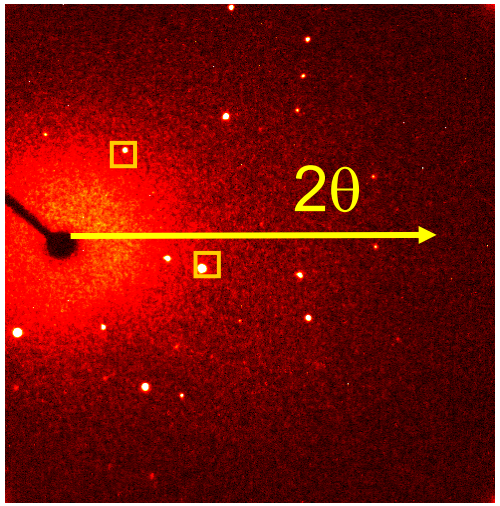


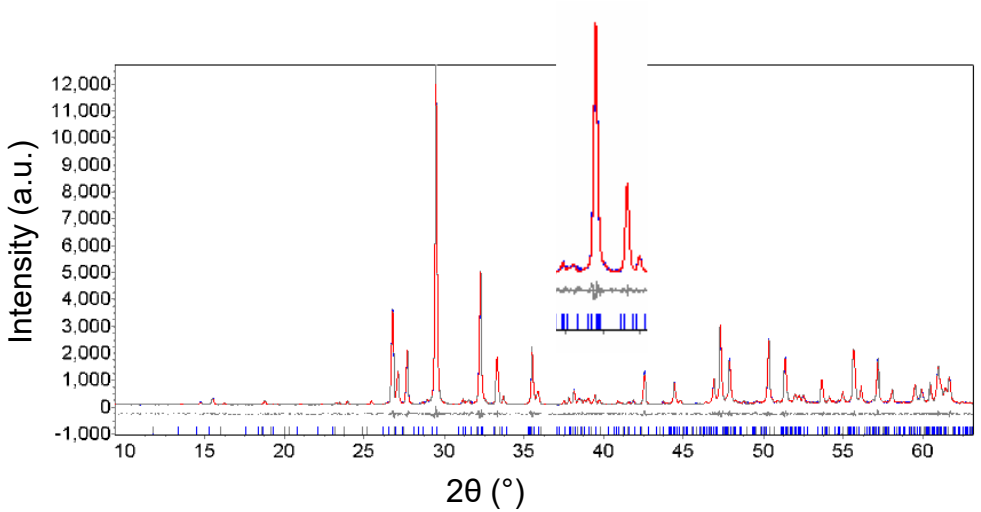
Polycrystalline sample



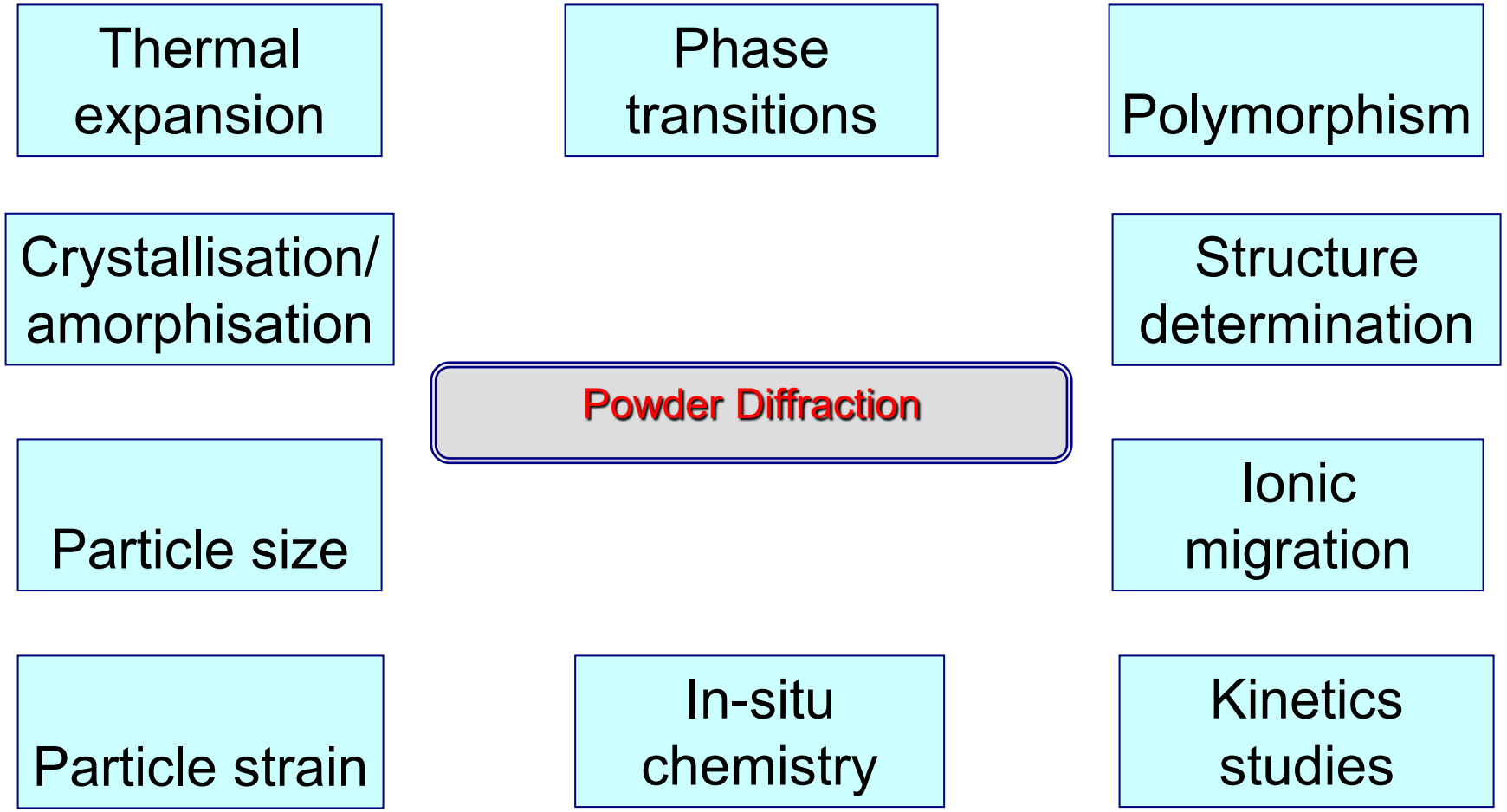


- Powder diffraction: data compressed into one dimension





What can powder diffraction do for you?



Lecture notes

Lecture notes

Session 6: Introduction to Least Squares

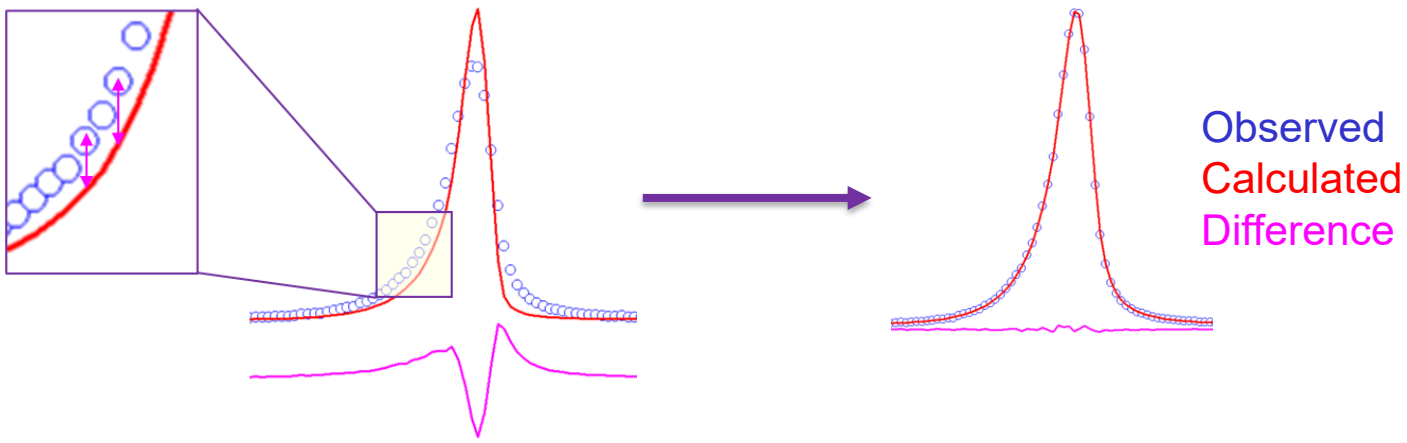
Prof. John S.O. Evans

Durham University, Department of Chemistry

What is whole powder pattern fitting (WPPF) or Rietveld refinement?

"*At its core, WPPF is a constrained mathematical fitting challenge. The aim is to develop a model which describes all aspects of the powder diffraction pattern (background, peak positions, peak shapes and peak intensities) such that the information of interest can be extracted.*"

John, Robert, Bill David, Whole Powder Pattern Fitting School notes, 2026; from Erice notes



Lecture content

- Matrix revision
- Simple data analysis
  - Averages, uncertainties, weighting
- Linear least squares
  - How to fit a straight line to experimental data
  - How to work out standard uncertainties
  - The correlation matrix
  - Constraints, restraints and how they're applied
  - Thinking critically about least squares refinements
- Non-linear least squares

- Tutorials
  - Least squares by hand
  - Least squares in excel
  - Least squares in TOPAS

Warning!

- There will be equations
- Watch/listen now, work through later

Matrix reminders: definitions

Matrix: $\mathbf{A} = \begin{pmatrix} a & b \\ c & d \end{pmatrix}$

Inverse: $\mathbf{A^{-1}} = \frac{1}{ad - bc}\begin{pmatrix} d & -b \\ -c & a \end{pmatrix}$ $\mathbf{AA^{-1}} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = \mathbf{I}$

Transpose: $\mathbf{A} = \begin{pmatrix} a & d \\ b & e \\ c & f \end{pmatrix}$ $\mathbf{A^T} = \begin{pmatrix} a & b & c \\ d & e & f \end{pmatrix}$ $\mathbf{AA^T} = (square)$

Multiplication: $\mathbf{B} = \begin{pmatrix} e & f \\ g & h \end{pmatrix}$ $\mathbf{AB} = \begin{pmatrix} a & b \\ c & d \end{pmatrix}\begin{pmatrix} e & f \\ g & h \end{pmatrix} = \begin{pmatrix} ae + bg & af + bh \\ ce + dg & cf + dh \end{pmatrix}$

Matrix reminders: 3×3×3 matrix inversion recipe

Matrix: $\mathbf{A} = \begin{pmatrix} a & b & c \\ d & e & f \\ g & h & i \end{pmatrix}$

Minors: $\begin{pmatrix} \det\begin{pmatrix} e & f \\ h & i \end{pmatrix} & \cdot\cdot & \cdot\cdot \\ \cdot\cdot & \cdot\cdot & \cdot\cdot \\ \cdot\cdot & \cdot\cdot & \cdot\cdot \end{pmatrix}$

Determinant: $(aei + bfg + cdh) - (gec + dbi + ahf)$

Matrix of cofactors: $\begin{pmatrix} + & - & + \\ - & + & - \\ + & - & + \end{pmatrix} * \begin{pmatrix} \text{minors} \end{pmatrix}$

Inverse: $\frac{1}{\text{determinant}} \times \begin{pmatrix} \text{cofactors} \end{pmatrix}^{\mathrm{T}}$

5 Minute matrix homework practice

$$\begin{pmatrix} 3 & 1 \\ 4 & 6 \end{pmatrix} \times \begin{pmatrix} 2 & 5 \\ 3 & 2 \end{pmatrix} =$$

$$\begin{pmatrix} 3 & 1 \\ 4 & 6 \end{pmatrix} \times \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} =$$

$$\begin{pmatrix} 30 & 10 \\ 10 & 4 \end{pmatrix} \times \begin{pmatrix} 0.2 & -0.5 \\ -0.5 & 1.5 \end{pmatrix} =$$

$$\begin{pmatrix} 1 & 2 & 3 & 4 \\ 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 2 & 1 \\ 3 & 1 \\ 4 & 1 \end{pmatrix} =$$

Matrix manipulation can store and compress useful information?

- Imagine we were doing some maths on an experiment with n different observations at n different x_i observation points and we needed to sum the x_i values and sum the squares x_i^2
- The product $\mathbf{A^T A}$ might be useful

$$\begin{pmatrix} x_1 & x_2 & x_3 & x_4 \\ 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} x_1 & 1 \\ x_2 & 1 \\ x_3 & 1 \\ x_4 & 1 \end{pmatrix} = \begin{pmatrix} \sum x_i^2 & \sum x_i \\ \sum x_i & n \end{pmatrix}$$

$$\begin{pmatrix} 1 & 2 & 3 & 4 \\ 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 2 & 1 \\ 3 & 1 \\ 4 & 1 \end{pmatrix} = \begin{pmatrix} 30 & 10 \\ 10 & 4 \end{pmatrix}$$

Determining one parameter

- Assume we've got somebody to measure male delegates' height and get the following answers:
  - 1.75, 1.79, 1.80, 1.77, 1.82, 1.60, 1.85 m
- We might decide to take an average ($\bar{x}$) of these measurements
- We might work out the variance (σ^2) and therefore the standard deviation (σ) and standard deviation of the mean ($\sigma(\bar{x})$)

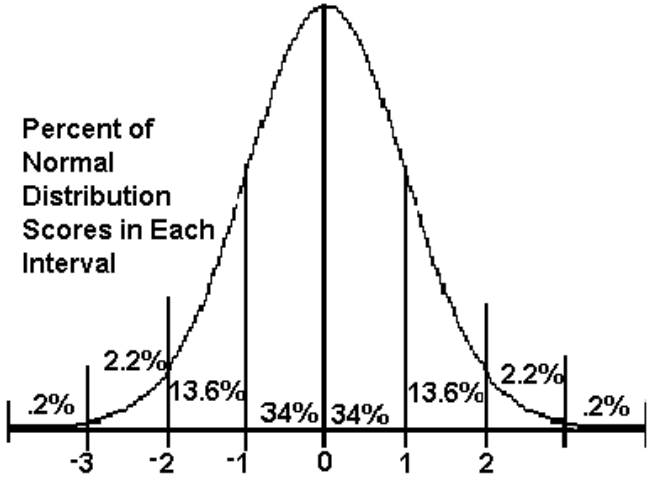
$$\bar{x} = 1.77$$

$$\sigma^2 = \frac{1}{n-1}\sum_{1}^{n}(x_i - \bar{x})^2 = 0.0066$$

$$\sigma = 0.08$$

$$\sigma(\bar{x}) = \frac{\sigma}{\sqrt{n}} = 0.03$$

$$\bar{x} = 1.77(3)$$



http://www.mathnstuff.com/math/spoken/here/2class/90/normal.htm

±1σ 68%
±2σ 95%
±3σ 99%

Weighted averages: minimise variance

- Male delegates' height measurements:
  - 1.75, 1.79, 1.80, 1.77, 1.82, 1.60, 1.85 m
- Let's assume that the last 2 measurements are less reliable than the first 5 (×2 uncertainty)

- Take a weighted average to find the "best" answer
- One way to define "best" is the value of $\bar{x}$ which minimises the variance
- The weights to use are then inversely proportional to the variance of each individual measurement, σ_i^2 (here ×¼ for less reliable measurements)

$$\bar{x} = \frac{\sum_1^n w_i x_i}{\sum_1^n w_i}$$

$$weight = w_i = \frac{1}{\sigma_i^2}$$

$$\sigma^2 = \frac{n}{n-1} \frac{\sum_1^n w_i (x_i - \bar{x})^2}{\sum_1^n w_i}$$

(for independent measurements)

Least squares

$$\bar{x} = \frac{\sum_1^n w_i x_i}{\sum_1^n w_i} \qquad weight = w_i = \frac{1}{\sigma_i^2} \qquad \sigma^2 = \frac{n}{n-1}\frac{\sum_1^n w_i (x_i - \bar{x})^2}{\sum_1^n w_i}$$

- Minimise variance ≡ sum of the squares of the deviations from mean
- "Least Squares" result is:

$$\bar{x} = 1.78 \qquad \sigma^2 = 0.0015 \qquad \sigma = 0.038 \qquad \sigma(\bar{x}) = \frac{\sigma}{\sqrt{n}} = 2$$

$$\bar{x} = 1.78(2)$$

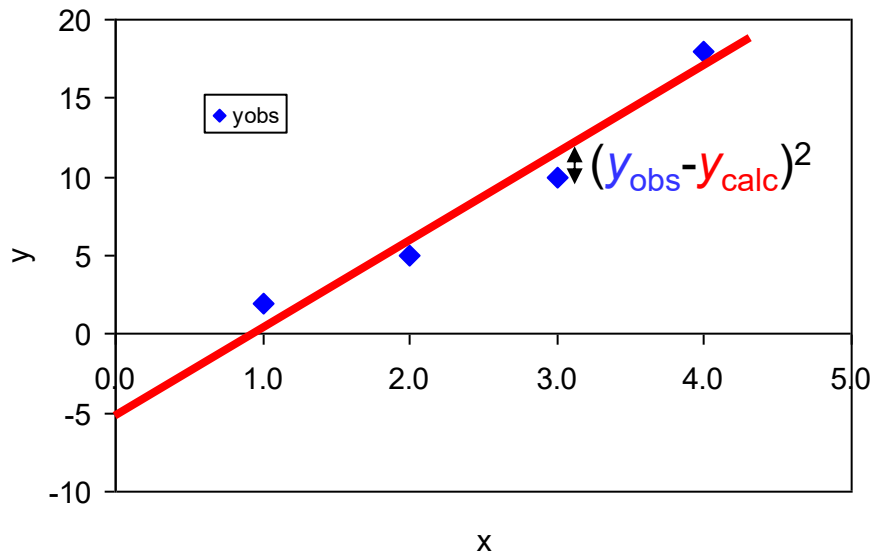
- Previous $\bar{x}$ value (all the data) was smaller with larger variance:

$$\bar{x} = 1.77(3) \qquad \sigma^2 = 0.0066 \qquad \sigma = 0.08$$

Determining two parameters

- Assume we've done an experiment which yielded the following data points for (x_i, y_i)
  - (1, 2), (2, 5), (3, 10), (4, 18)
- E.g. number of daffodils in flower outside
- We might plot the data to have a look at it
- We might then try and fit a straight line $y = mx + c$ (e.g. to extrapolate to day 5 or give rate of appearance as single number)
- How do we get the best fit?

$$y_{calc} = mx + c$$



Determining two parameters from two equations

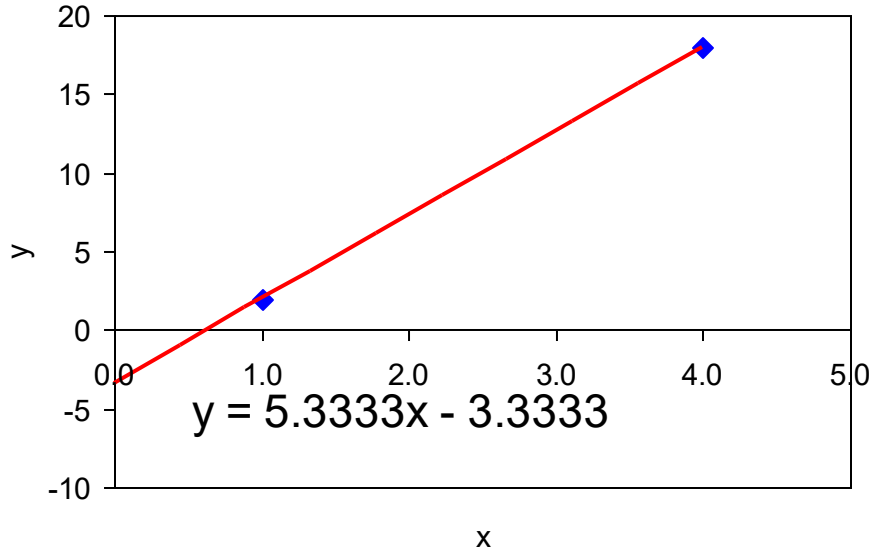
- Two points only, line $mx + c = y$
  - (1, 2), (4, 18)
- Observational equations

$$m \times x + c = y$$

$$m \times 1 + c = 2$$
$$m \times 4 + c = 18$$

← 2 equations, 2 unknowns

- Solve simultaneous equations
- m = 5.33, c = -3.33



4 observations, 2 unknowns

- We can express our measured data as a series of equations $mx + c = y$

$$m \times x + c = y$$

$$m \times 1 + c \approx 2$$
$$m \times 2 + c \approx 5$$
$$m \times 3 + c \approx 10$$
$$m \times 4 + c \approx 18$$

Problem: 4 equations, 2 unknowns
Want: 2 equations, 2 unknowns

- Each equation will be obeyed approximately when best values for m and c are found
- Least squares says minimise the variance of y or minimise the objective function S:

$$objective\ function = S = \sum_{i=1}^{n} \left(y_{i,obs} - y_{i,calc}\right)^2$$

Method 1: do some maths

1. Data and the observational equation are:

$$(x_1, y_{1,obs}), (x_2, y_{2,obs}), \ldots, (x_n, y_{n,obs})$$

$$y_{i,calc} = mx_i + c$$

2. Calculate the residuals r_i and the sum of squares of residuals ≡ objective function S:

$$r_i = (y_{i,obs} - y_{i,calc}) = y_{i,obs} - (mx_i + c)$$

$$S = \sum_{i=1}^{n} \left(y_{i,obs} - (mx_i + c)\right)^2$$

3. Differentiate S with respect to m and c and set equal to zero to find minimum:

$$\frac{\partial S}{\partial m} = -2\sum_{i=1}^{n} x_i(y_{i,obs} - mx_i - c) = 0$$

$$\frac{\partial S}{\partial c} = -2\sum_{i=1}^{n} (y_{i,obs} - mx_i - c) = 0$$

4. Rearrange to give two simultaneous equations – the normal equations of least squares:

$$\sum_{i=1}^{n} x_i y_{i,obs} = m\sum_{i=1}^{n} x_i^2 + c\sum_{i=1}^{n} x_i$$

$$\sum_{i=1}^{n} y_{i,obs} = m\sum_{i=1}^{n} x_i + nc$$

5. Solve the two simultaneous equations to find expressions for *m* and c:

$$m = \frac{n\sum x_i y_{i,obs} - \sum x_i \sum y_{i,obs}}{n\sum x_i^2 - (\sum x_i)^2}$$

$$c = \frac{\sum y_{i,obs} - m\sum x_i}{n}$$

Best line fit plugging in numbers

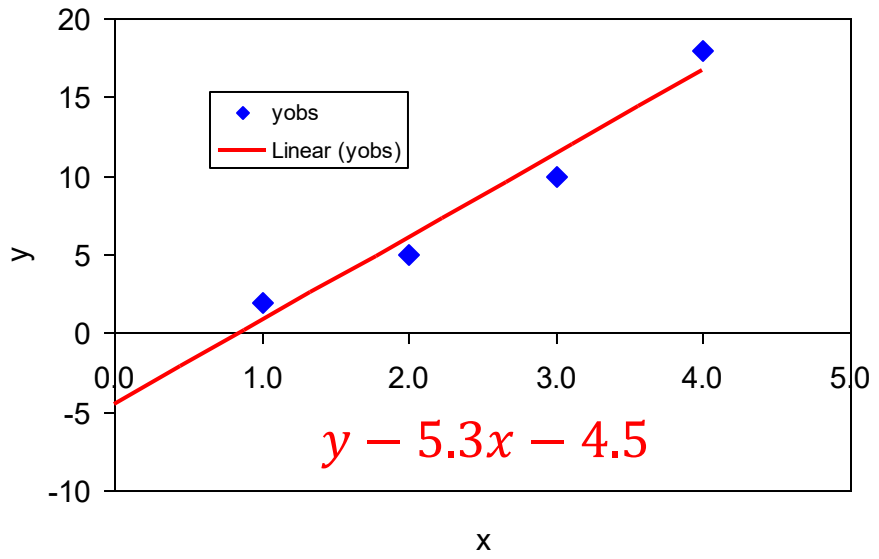
$$m = \frac{n\sum x_i y_{i,obs} - \sum x_i \sum y_{i,obs}}{n\sum x_i^2 - (\sum x_i)^2}$$

$$c = \frac{\sum y_{i,obs} - m\sum x_i}{n}$$

	x_i	$y_{i,obs}$	$x_i * y_{i,obs}$	x_i^2
	1	2	2	1
	2	5	10	4
	3	10	30	9
	4	18	72	16
sums	10.0	35.0	114.0	30.0

n	4
nsumxiyi	456
sumx*sumy	350
nsumx^2	120
(sumx)^2	100.0

gradient, m	5.3
intercept, c	-4.5



Method 2: use matrices

- We can express our measured data as a series of equations $m \times x + c = y$

$$m \times x + c = y$$

$$\begin{aligned} m \times 1 + c &\approx 2 \\ m \times 2 + c &\approx 5 \\ m \times 3 + c &\approx 10 \\ m \times 4 + c &\approx 18 \end{aligned}$$

Problem: 4 equations, 2 unknowns
Want: 2 equations, 2 unknowns

- Express they equations in matrix format:

$$\begin{pmatrix} 1 & 1 \\ 2 & 1 \\ 3 & 1 \\ 4 & 1 \end{pmatrix} \begin{pmatrix} m \\ c \end{pmatrix} = \begin{pmatrix} 2 \\ 5 \\ 10 \\ 18 \end{pmatrix} \longrightarrow \begin{pmatrix} 1 \times m + c \\ 2 \times m + c \\ 3 \times m + c \\ 4 \times m + c \end{pmatrix} = \begin{pmatrix} 2 \\ 5 \\ 10 \\ 18 \end{pmatrix}$$

$$\mathbf{A} \quad \mathbf{x} = \mathbf{y}$$

Design matrix

Vector of unknowns

Vector of observations

Method 2: do some matrix maths

1. Set up model eq'n, data, vector of unknowns $\mathbf{x}$ and vector of observations $\mathbf{y}$ in matrix form:

$$\mathbf{A}\,\mathbf{x} = \mathbf{y}$$

$$\mathbf{A} = \begin{pmatrix} x_1 & 1 \\ x_2 & 1 \\ \vdots & \vdots \\ x_n & 1 \end{pmatrix} \quad \mathbf{x} = \begin{pmatrix} m \\ c \end{pmatrix} \quad \mathbf{y} = \begin{pmatrix} y_{1,obs} \\ y_{2,obs} \\ \vdots \\ y_{n,obs} \end{pmatrix}$$

2. Calculate residual and sum of squares of residuals ≡ objective function S:

$$\mathbf{r} = \mathbf{y} - \mathbf{A}\,\mathbf{x}$$

$$S = \mathbf{r}^{\mathrm{T}}\mathbf{r} = (\mathbf{y} - \mathbf{A}\mathbf{x})^{\mathrm{T}}(\mathbf{y} - \mathbf{A}\mathbf{x})$$

3. Expand S then differentiate with respect to $\mathbf{x}$ and set to zero for minimum:

$$S = \mathbf{r}^{\mathrm{T}}\mathbf{r} = \mathbf{y}^{\mathrm{T}}\mathbf{y} - 2\mathbf{x}^{\mathrm{T}}\mathbf{A}^{\mathrm{T}}\mathbf{y} + \mathbf{x}^{\mathrm{T}}\mathbf{A}^{T}\mathbf{A}\mathbf{x}$$

$$\frac{\partial S}{\partial \mathbf{x}} = -2\mathbf{A}^{\mathrm{T}}(\mathbf{y} - \mathbf{A}\mathbf{x}) = 0$$

4. Rearrange to give the normal equations in compact matrix form:

$$\mathbf{A}^{\mathrm{T}}\mathbf{A}\mathbf{x} = \mathbf{A}^{\mathrm{T}}\mathbf{y}$$

5. If $\mathbf{A}^{\mathrm{T}}\mathbf{A}$ is invertible the solution is:

$$\mathbf{x} = \left(\mathbf{A}^{\mathrm{T}}\mathbf{A}\right)^{-1}\mathbf{A}^{\mathrm{T}}\mathbf{y}$$

6. Check consistency with non-matrix approach by expressing (4) explicitly then multiply out:

$$\begin{pmatrix} \sum x_i^2 & \sum x_i \\ \sum x_i & n \end{pmatrix} \begin{pmatrix} m \\ c \end{pmatrix} = \begin{pmatrix} \sum x_i y_{i,obs} \\ \sum y_{i,obs} \end{pmatrix}$$

Many observations, 2 unknowns

Design matrix

Vector of unknowns

Vector of observations

1. Set up model equations in matrix form:

$$\mathbf{Ax} = \mathbf{y}$$

$$\begin{pmatrix} 1 & 1 \\ 2 & 1 \\ 3 & 1 \\ 4 & 1 \end{pmatrix} \begin{pmatrix} m \\ c \end{pmatrix} = \begin{pmatrix} 2 \\ 5 \\ 10 \\ 18 \end{pmatrix}$$

4. Write the normal equations in compact matrix form:

$$\left(\mathbf{A}^{\mathbf{T}}\mathbf{A}\right)\mathbf{x} = \mathbf{A}^{\mathbf{T}}\mathbf{y}$$

$$\begin{pmatrix} 1 & 2 & 3 & 4 \\ 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 2 & 1 \\ 3 & 1 \\ 4 & 1 \end{pmatrix} \begin{pmatrix} m \\ c \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 & 4 \\ 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 2 \\ 5 \\ 10 \\ 18 \end{pmatrix}$$

$$\Rightarrow \begin{pmatrix} 30 & 10 \\ 10 & 4 \end{pmatrix} \begin{pmatrix} m \\ c \end{pmatrix} = \begin{pmatrix} 114 \\ 35 \end{pmatrix}$$

5. Premultiply both sides by $\left(\mathbf{A}^{\mathbf{T}}\mathbf{A}\right)^{-1}$ to solve for $\mathbf{x}$:

$$\mathbf{x} = \left(\mathbf{A}^{\mathbf{T}}\mathbf{A}\right)^{-1}\mathbf{A}^{\mathbf{T}}\mathbf{y}$$

$$\begin{pmatrix} m \\ c \end{pmatrix} = \begin{pmatrix} 0.2 & -0.5 \\ -0.5 & 1.5 \end{pmatrix} \begin{pmatrix} 114 \\ 35 \end{pmatrix} = \begin{pmatrix} 5.3 \\ -4.5 \end{pmatrix}$$

Solving equations simultaneously or graphically

- Matrix approach gave normal equations as below, could have multiplied them out to solve:

$$(\mathbf{A}^{\mathbf{T}}\mathbf{A})\mathbf{x} = \mathbf{A}^{\mathbf{T}}\mathbf{y}$$

$$\begin{pmatrix} 30 & 10 \\ 10 & 4 \end{pmatrix}\begin{pmatrix} m \\ c \end{pmatrix} = \begin{pmatrix} 114 \\ 35 \end{pmatrix}$$

$$30m + 10c = 114$$
$$10m + 4c = 35$$

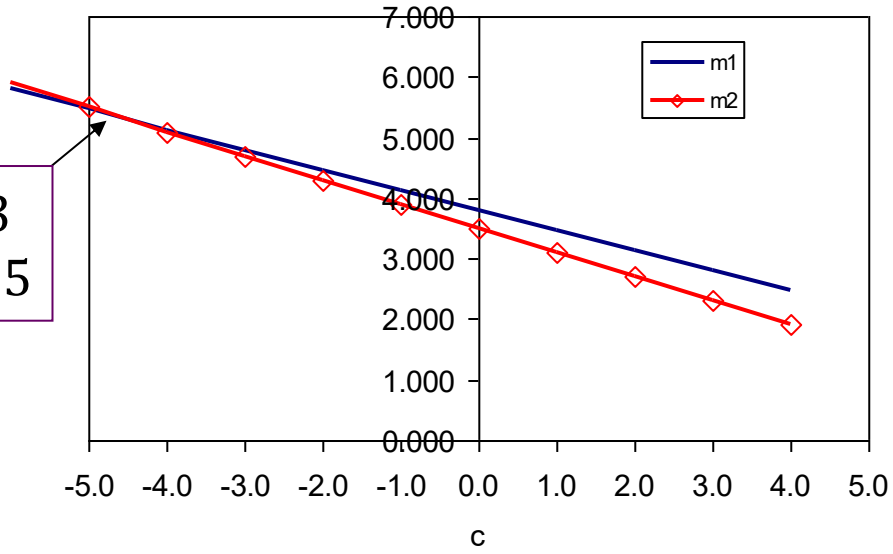
← 2 equations, 2 unknowns

- Or each equation could be rewritten in $y = mx + c$ format and solved graphically:

$$\text{line 1: } m_1 = -\frac{10c_1}{30} + \frac{114}{30}$$

$$\text{line 2: } m_2 = -\frac{4c_2}{10} + \frac{35}{10}$$

$m = 5.3$
$c = -4.5$



Standard uncertainties on estimated values

- To calculate uncertainty σ_y we need to propagate errors:

$$y = mx + c$$

$$\sigma_y^2 = \sigma_m^2 x^2 + \sigma_c^2 + 2x\sigma_m\sigma_c\mu_{mc}$$

$\sigma_m\sigma_c\mu_{mc}$ = covariance

μ_{mc} = correlation coefficient

- The quantities we need appear in the variance-covariance matrix $\mathbf{M}$:

$$\mathbf{M} = \begin{pmatrix} \sigma_m^2 & \sigma_m\sigma_c\mu_{mc} \\ \sigma_m\sigma_c\mu_{mc} & \sigma_c^2 \end{pmatrix}$$

Variance-Covariance Matrix

$$\mathbf{M} = \frac{n}{n-p} \frac{\sum_1^n w_i(obs - calc)^2}{\sum_1^n w_i} \left(\mathbf{A^T W A}\right)^{-1}$$

Number observations

Number parameters

Weights

Standard uncertainties

$$\mathbf{M} = \frac{n}{n-p} \frac{\sum_1^n w_i (obs - calc)^2}{\sum_1^n w_i} \left(\mathbf{A^T W A}\right)^{-1}$$

$$\left(\mathbf{A^T W A}\right)^{-1} = \begin{pmatrix} 30 & 10 \\ 10 & 4 \end{pmatrix}^{-1} = \begin{pmatrix} 0.2 & -0.5 \\ -0.5 & 1.5 \end{pmatrix}$$

$n = 4$ observations
$p = 2$ parameters

$= 4$ if unit weights

x	yobs	ycalc	yobs-ycalc	$(yobs-ycalc)^2$
1.0	2	0.800	-1.200	1.440
2.0	5	6.100	1.100	1.210
3.0	10	11.400	1.400	1.960
4.0	18	16.700	-1.300	1.690
				6.300

$$\sum_1^n w_i (obs - calc)^2$$

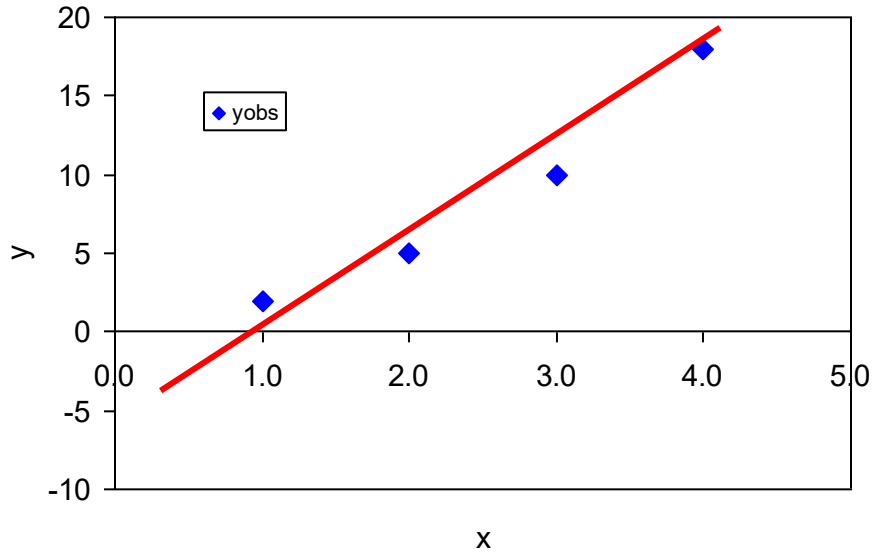
$$\mathbf{M} = \frac{4}{2} \times \frac{6.3}{4} \times \begin{pmatrix} 0.2 & -0.5 \\ -0.5 & 1.5 \end{pmatrix} = \begin{pmatrix} 0.63 & -1.575 \\ -1.575 & 4.725 \end{pmatrix} = \begin{pmatrix} \sigma_m^2 & \sigma_m \sigma_c \mu_{mc} \\ \sigma_m \sigma_c \mu_{mc} & \sigma_c^2 \end{pmatrix}$$

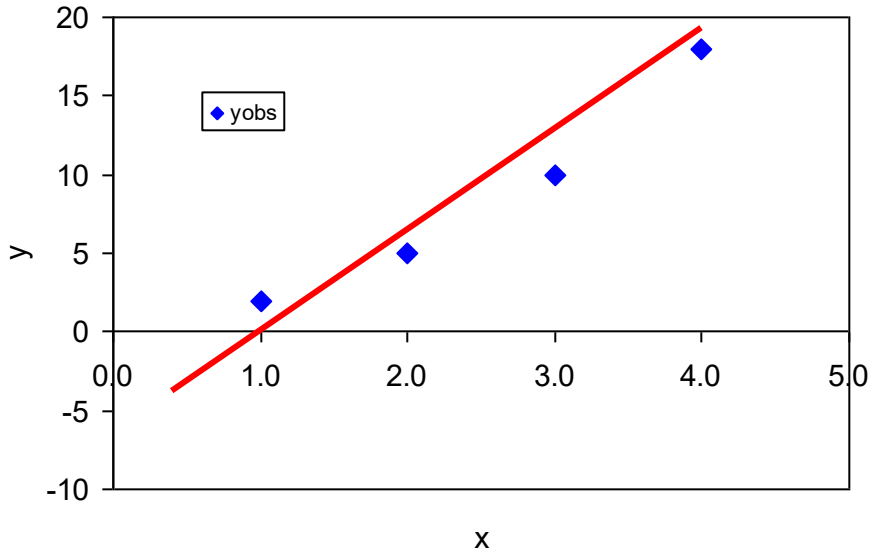
$\sigma_m = 0.79$
$\sigma_c = 2.17$
$\mu_{mc} = -0.91$

$m = 5.3(8)$
$c = -4.5(20)$

Correlations in least squares

- Gradients and intercepts will show a negative correlation
- As gradient decreases intercept will increase





Constraints and restraints

- Constraints are pieces of information your model must obey mathematically
- Restraints are “soft” information you’d like your model to obey

- [how to upset teachers/tutors: “I’ve refined the data…..”]

Constraint: line must pass through origin

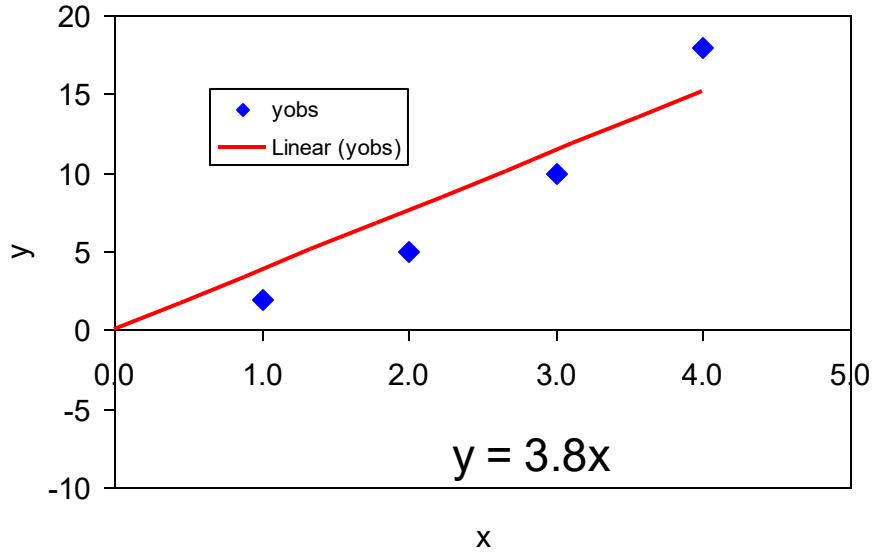
- Assume line must pass through origin: $m \times x + 0 = y$

$$\left(\mathbf{A}^{\mathbf{T}}\mathbf{A}\right)\mathbf{x} = \mathbf{A}^{\mathbf{T}}\mathbf{y}$$

$$\begin{aligned} m \times 1 &= 2 \\ m \times 2 &= 5 \\ m \times 3 &= 10 \\ m \times 4 &= 18 \end{aligned}$$

$$\begin{pmatrix} 1 & 2 & 3 & 4 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \\ 3 \\ 4 \end{pmatrix} (m) = \begin{pmatrix} 1 & 2 & 3 & 4 \end{pmatrix} \begin{pmatrix} 2 \\ 5 \\ 10 \\ 18 \end{pmatrix}$$

$$\begin{aligned} 30m &= 114 \\ m &= 3.8(5) \end{aligned}$$



Constraint: intercept = –gradient

- Assume line intercept = −gradient, i.e. $m = -c$

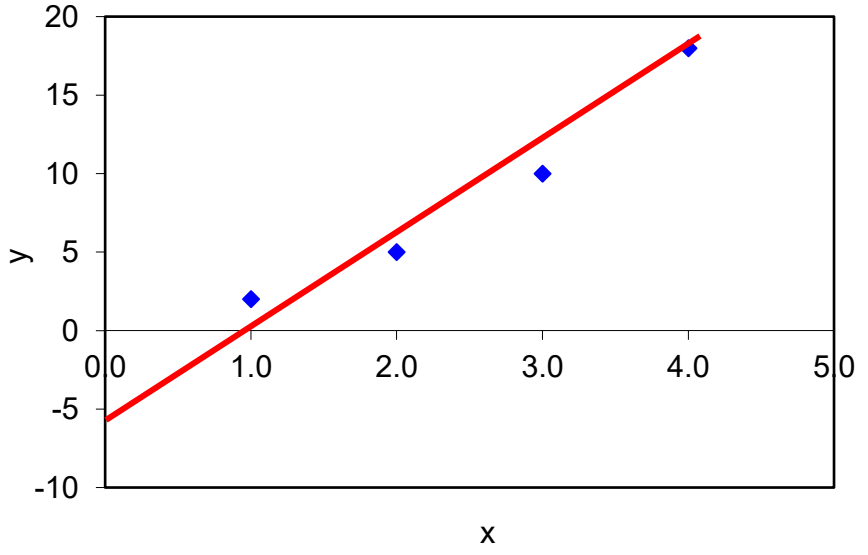
$$mx - m = y$$
$$m(x-1) = y$$

$$\mathbf{(A^T A)x = A^T y}$$

$$m \times 0 = 2$$
$$m \times 1 = 5$$
$$m \times 2 = 10$$
$$m \times 3 = 18$$

$$\begin{pmatrix} 0 & 1 & 2 & 3 \end{pmatrix} \begin{pmatrix} 0 \\ 1 \\ 2 \\ 3 \end{pmatrix} (m) = \begin{pmatrix} 0 & 1 & 2 & 3 \end{pmatrix} \begin{pmatrix} 2 \\ 5 \\ 10 \\ 18 \end{pmatrix}$$

$$14m = 79$$
$$m = 5.6(4)$$
$$\longrightarrow \quad c = -5.6(4)$$



Restraint: line should pass through origin

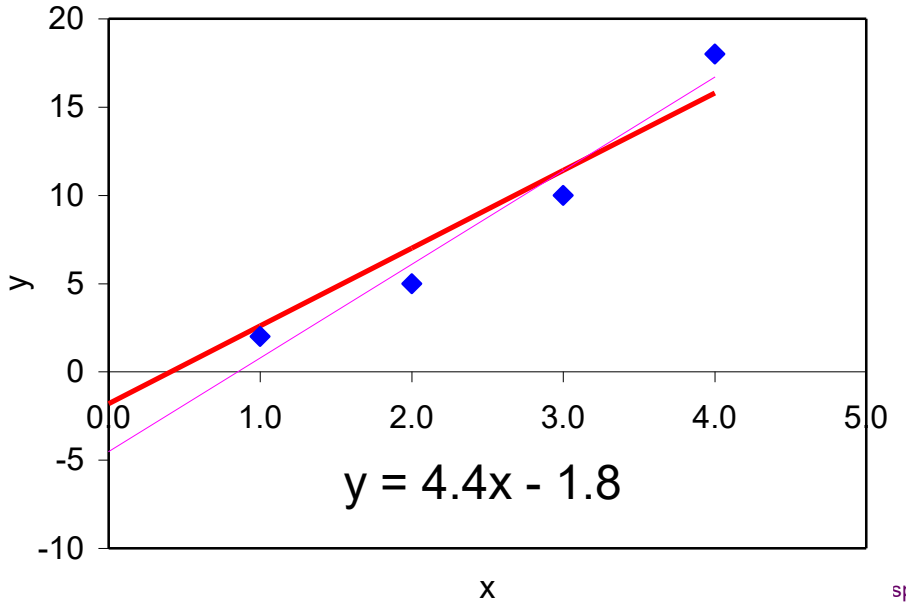
- Treat $x = 0$, $y = 0$ as an extra observation

$$\begin{pmatrix} 1 & 2 & 3 & 4 & \boxed{0} \\ 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 2 & 1 \\ 3 & 1 \\ 4 & 1 \\ \boxed{0} & 1 \end{pmatrix} \begin{pmatrix} m \\ c \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 & 4 & 0 \\ 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 2 \\ 5 \\ 10 \\ 18 \\ \boxed{0} \end{pmatrix}$$

$$\begin{pmatrix} 30 & 10 \\ 10 & 5 \end{pmatrix} \begin{pmatrix} m \\ c \end{pmatrix} = \begin{pmatrix} 114 \\ 35 \end{pmatrix}$$

$$30m + 10c = 114$$
$$10m + 5c = 35$$

$$m = 4.4$$
$$c = -1.8$$



Restraint: “I really, really want” the line to pass through origin

- Treat $x = 0$, $y = 0$ as an extra observation, but give a high weight

$$\mathbf{WAx} = \mathbf{Wy}$$

$$\left(\mathbf{A}^{\mathbf{T}}\mathbf{WA}\right)\mathbf{x} = \left(\mathbf{A}^{\mathbf{T}}\mathbf{W}\right)\mathbf{y}$$

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 0 \\ 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 100 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 2 & 1 \\ 3 & 1 \\ 4 & 1 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} m \\ c \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 & 4 & 0 \\ 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 100 \end{pmatrix} \begin{pmatrix} 2 \\ 5 \\ 10 \\ 18 \\ 0 \end{pmatrix}$$

Restraint: “I really, really want” the line to pass through origin

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 0 \\ 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 2 & 1 \\ 3 & 1 \\ 4 & 1 \\ 0 & 100 \end{pmatrix} \begin{pmatrix} m \\ c \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 & 4 & 0 \\ 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 2 \\ 5 \\ 10 \\ 18 \\ 0 \end{pmatrix}$$

$$\begin{pmatrix} 30 & 10 \\ 10 & 104 \end{pmatrix} \begin{pmatrix} m \\ c \end{pmatrix} = \begin{pmatrix} 114 \\ 35 \end{pmatrix}$$

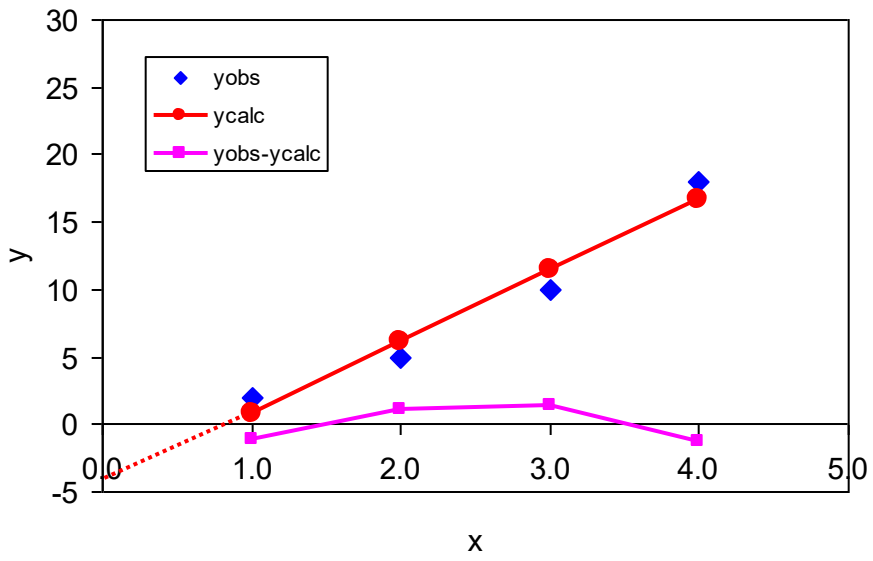
$$30m + 10c = 114$$
$$10m + 104c = 35$$

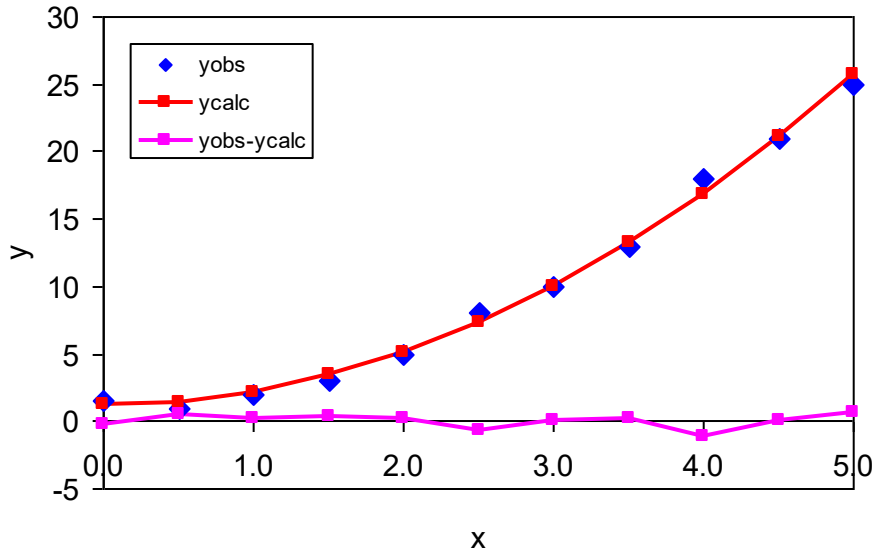
$$m = 3.81$$
$$c = -0.03$$

Standard uncertainties = ????

Impacts of data quality and model choice

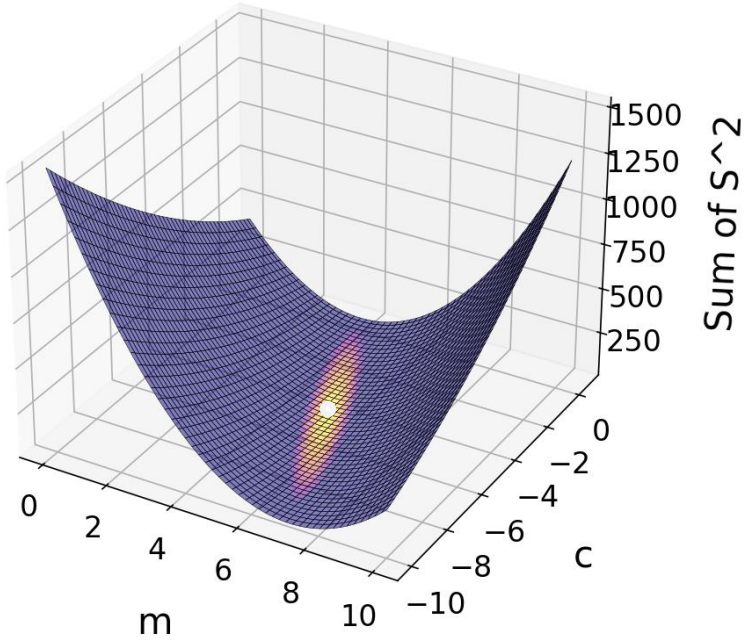
- Feynman's rule: first and last data points
- Need good quality data but also data that defines the problem you're trying to answer





Linear least squares

- Recipe works for linear equations where you have a smooth hyperbolic surface with a single minimum



- e.g. these equations are all linear in the parameters a, b, c:

$$y = ax + c$$

$$y = ax^2 + bx + c$$

$$y = a\sin(x) + b\cos(x)$$

- Recipe won't work for the many non-linear equations in crystallography:

$$y = a\sin(bx)$$

$$y = ae^{bx}$$

Non-linear least squares

- We have a recipe for linear least squares for simple expressions like $y = mx + c$
- In crystallography equations will be more complex, e.g. calculated intensity Y_C

$$Y_C = lots\ of\ things \times \left(\sum_{j=1}^{N} f_j \exp\left[2\pi i\left(hx_j + ky_j + lz_j\right)\right] \right)^2$$

- How do we cope with non-linearity?
- Let's assume that calculated intensity, Y_C, is a function of many variables x_i

$$Y_C = f\left(x_1, x_2, x_3, \ldots\ldots, x_{np}\right)$$

- If we guess values for x_n and calculate the intensity Y_C it probably won't match observed intensity, Y_O :

$$Y_O - Y_C \neq 0$$

Non-linear least squares

$$Y_O - Y_C \neq 0$$

- If we knew how much to change each x_n guess by (shift δx_n) in order to make $Y_O - Y_C$ zero we could just apply these shifts to the initial guesses and the calculated intensity would be correct

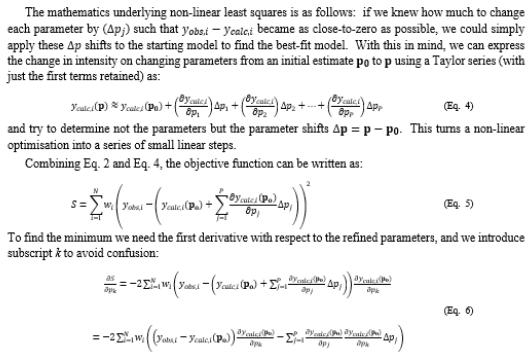
- We can express this as a Taylor series that just retains the first terms:

$$\left(\frac{\partial Y}{\partial x_1}\right)\delta x_1 + \left(\frac{\partial Y}{\partial x_2}\right)\delta x_2 + \ldots + \left(\frac{\partial Y}{\partial x_{np}}\right)\delta x_{np} = Y_O - Y_C$$

- Equation is linear in the shifts δx_n, one equation for each intensity
- We can use linear least squares methods to find the shifts

Non-linear least squares

- The maths is a bit more complex with huge matrices (see the school notes for details)



The mathematics underlying non-linear least squares is as follows: if we knew how much to change each parameter by (Δp_j) such that $y_{obs,i} - y_{calc,i}$ became as close-to-zero as possible, we could simply apply these Δp shifts to the starting model to find the best-fit model. With this in mind, we can express the change in intensity on changing parameters from an initial estimate $\mathbf{p_0}$ to $\mathbf{p}$ using a Taylor series (with just the first terms retained) as:

$$y_{calc,i}(\mathbf{p}) \approx y_{calc,i}(\mathbf{p_0}) + \left(\frac{\delta y_{calc,i}}{\delta p_1}\right)\Delta p_1 + \left(\frac{\delta y_{calc,i}}{\delta p_2}\right)\Delta p_2 + \cdots + \left(\frac{\delta y_{calc,i}}{\delta p_P}\right)\Delta p_P \quad \text{(Eq. 4)}$$

and try to determine not the parameters but the parameter shifts $\Delta\mathbf{p} = \mathbf{p} - \mathbf{p_0}$. This turns a non-linear optimisation into a series of small linear steps.

Combining Eq. 2 and Eq. 4, the objective function can be written as:

$$S = \sum_{i=1}^{N} w_i \left(y_{obs,i} - \left(y_{calc,i}(\mathbf{p_0}) + \sum_{j=1}^{P} \frac{\delta y_{calc,i}(\mathbf{p_0})}{\delta p_j}\Delta p_j \right) \right)^2 \quad \text{(Eq. 5)}$$

To find the minimum we need the first derivative with respect to the refined parameters, and we introduce subscript k to avoid confusion:

$$\frac{\delta S}{\delta p_k} = -2\sum_{i=1}^{N} w_i \left(y_{obs,i} - \left(y_{calc,i}(\mathbf{p_0}) + \sum_{j=1}^{P} \frac{\delta y_{calc,i}(\mathbf{p_0})}{\delta p_j}\Delta p_j \right) \right) \frac{\delta y_{calc,i}(\mathbf{p_0})}{\delta p_k} \quad \text{(Eq. 6)}$$

$$= -2\sum_{i=1}^{N} w_i \left(\left(y_{obs,i} - y_{calc,i}(\mathbf{p_0}) \right) \frac{\delta y_{calc,i}(\mathbf{p_0})}{\delta p_k} - \sum_{j=1}^{P} \frac{\delta y_{calc,i}(\mathbf{p_0})}{\delta p_j} \frac{\delta y_{calc,i}(\mathbf{p_0})}{\delta p_k}\Delta p_j \right)$$

Since $\frac{\partial S}{\partial p_k} = 0$ at the minimum, it follows that:

$$\sum_{i=1}^{N} w_i \sum_{j=1}^{P} \frac{\delta y_{calc,i}(\mathbf{p_0})}{\delta p_j} \frac{\delta y_{calc,i}(\mathbf{p_0})}{\delta p_k}\Delta p_j = \sum_{i=1}^{N} w_i \left(y_{obs,i} - y_{calc,i}(\mathbf{p_0}) \right) \frac{\delta y_{calc,i}(\mathbf{p_0})}{\delta p_k} \quad \text{(Eq. 7)}$$

Changing the summations on the left side leads to:

$$\sum_{j=1}^{P} \sum_{i=1}^{N} w_i \frac{\delta y_{calc,i}(\mathbf{p_0})}{\delta p_j} \frac{\delta y_{calc,i}(\mathbf{p_0})}{\delta p_k}\Delta p_j = \sum_{i=1}^{N} w_i \left(y_{obs,i} - y_{calc,i}(\mathbf{p_0}) \right) \frac{\delta y_{calc,i}(\mathbf{p_0})}{\delta p_k} \quad \text{(Eq. 8)}$$

This equation is linear in the parameter shifts $\Delta\mathbf{p}$. There will be one equation for each p_k and the set of equations can be concisely expressed in matrix notation as:

$$\mathbf{A}\Delta\mathbf{p} = \mathbf{Y} \quad \text{(Eq. 9)}$$

with the components of the $P \times P$ matrix $\mathbf{A}$ (each k corresponds to a matrix row and each j corresponds to a column) given by:

$$A_{kj} = A_{jk} = \sum_{i=1}^{N} w_i \frac{\delta y_{calc,i}(\mathbf{p_0})}{\delta p_j} \frac{\delta y_{calc,i}(\mathbf{p_0})}{\delta p_k} \quad \text{(Eq. 10)}$$

and the P components of the vector $\mathbf{Y}$ by:

$$Y_p = \sum_{i=1}^{N} w_i \left(y_{obs,i} - y_{calc,i}(\mathbf{p_0}) \right) \frac{\delta y_{calc,i}(\mathbf{p_0})}{\delta p_k} \quad \text{(Eq. 11)}$$

The equations in Eq. 9 are called the normal equations of least squares and can be solved by pre-multiplying each side of the equation by $\mathbf{A}^{-1}$ to give the parameter shifts $\Delta\mathbf{p}$ which should be applied to the model.

$$\mathbf{A}^{-1}\mathbf{A}\Delta\mathbf{p} = \Delta\mathbf{p} = \mathbf{A}^{-1}\mathbf{Y} \quad \text{(Eq. 12)}$$

- Each entry in the $\mathbf{A}$ and $\mathbf{y}$ matrices contains sums over all observations involving at least one partial derivative
- We end up with familiar looking equations from which we can determine parameter shifts:

$$\left(\mathbf{A}^{\mathbf{T}}\mathbf{A}\right)\boldsymbol{\delta}\mathbf{x} = \mathbf{A}^{\mathbf{T}}\mathbf{y} \qquad \boldsymbol{\delta}\mathbf{x} = \left(\mathbf{A}^{\mathbf{T}}\mathbf{A}\right)^{-1}\mathbf{A}^{\mathbf{T}}\mathbf{y}$$

- We apply the shifts to each parameter x_i in order to change Y_C to be the same as Y_O

$$\mathbf{x_{new}} = \mathbf{x_{old}} + \boldsymbol{\delta}\mathbf{x}$$

Non-linear least squares: summary

- If we have an initial set of guesses for parameters we can determine how much to change them such that Y_C and Y_O become equal
- Recipe only works exactly for infinitesimally small shifts
- We will have to repeat the process multiple times
- We need good starting values to ensure convergence
- The maths is tedious and slow – use a computer

- This is structure refinement

ill-conditioned least squares

- Consider the following equations which are just like the equations we came across earlier for fitting a straight line through data
- Values $m = 5.3$, $c = -4.5$ are exact solutions to the equations

$$30.0m + 10.0c = 114.0$$
$$10.0m + 3.34c = 37.7$$

$$m = 5.3$$
$$c = -4.5$$

- Imagine we repeat the measurement and find that 114.0 in the first equation changes to 114.1
- A very small change:

$$30.0m + 10.0c = 114.1$$
$$10.0m + 3.34c = 37.7$$

$$m = 20.5$$
$$c = -50$$

- Solve the equations again m = 20.5, c = -50
- Oh dear!

Solving equations simultaneously or graphically

- Matrix approach gave normal equations as below, could have multiplied them out to solve:

$$(\mathbf{A}^{\mathrm{T}}\mathbf{A})\mathbf{x} = \mathbf{A}^{\mathrm{T}}\mathbf{y}$$

$$\begin{pmatrix} 30 & 10 \\ 10 & 4 \end{pmatrix}\begin{pmatrix} m \\ c \end{pmatrix} = \begin{pmatrix} 114 \\ 35 \end{pmatrix}$$

$$30m + 10c = 114$$
$$10m + 4c = 35$$

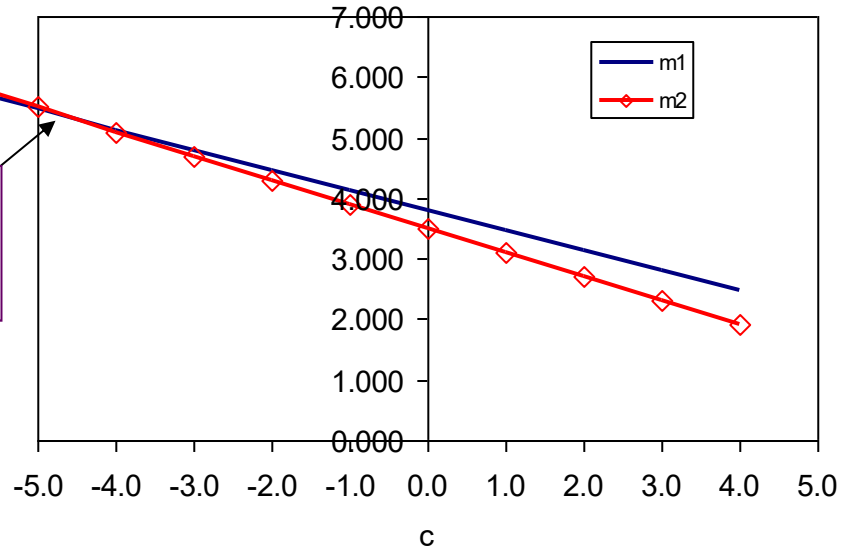
← 2 equations, 2 unknowns

- Or each equation could be rewritten in $y = mx + c$ format and solved graphically:

$$\text{line 1: } m_1 = -\frac{10c_1}{30} + \frac{114}{30}$$

$$\text{line 2: } m_2 = -\frac{4c_2}{10} + \frac{35}{10}$$

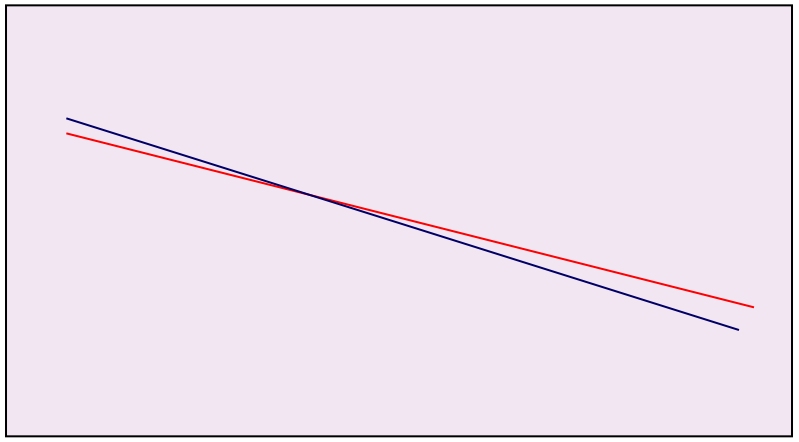
$m = 5.3$
$c = -4.5$

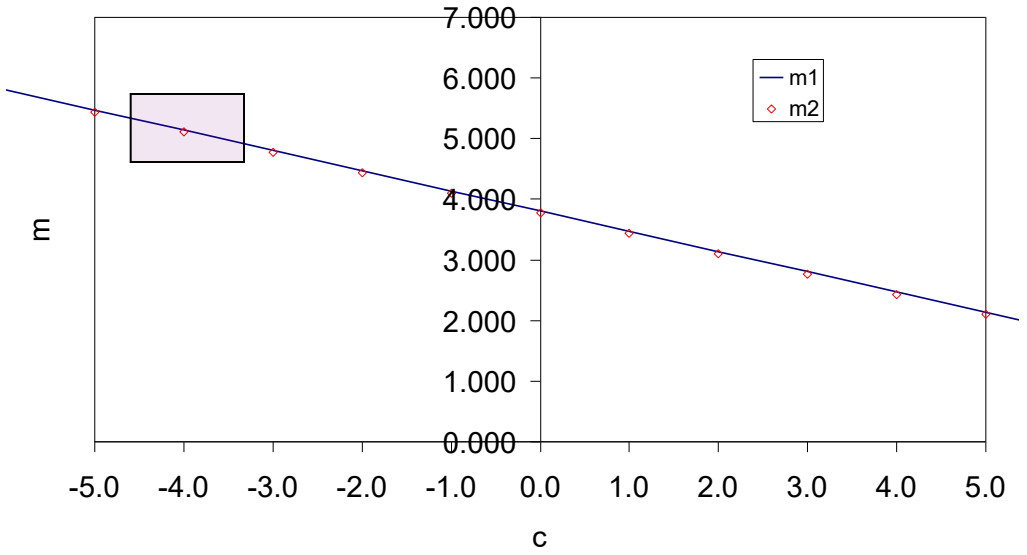


ill-conditioned least squares

$$30.0m + 10.0c = 114$$
$$10.0m + 3.34c = 37.7$$

$$m_1 = -\frac{10.0}{30.0}c_1 + \frac{114}{30}$$
$$m_2 = -\frac{3.34}{10.0}c_2 + \frac{37.7}{10}$$





ill-conditioned least squares

$$\mathbf{M} = \begin{pmatrix} \sigma_m^2 & \sigma_m\sigma_c\mu_{mc} \\ \sigma_m\sigma_c\mu_{mc} & \sigma_c^2 \end{pmatrix}$$

$$\mathbf{M} = \frac{n}{n-p}\frac{\sum_1^n w_i(obs-calc)^2}{\sum_1^n w_i}\left(\mathbf{A^T W A}\right)^{-1}$$

$$\left(\mathbf{A^T W A}\right)^{-1} = \begin{pmatrix} 30.0 & 10.00 \\ 10.00 & 3.34 \end{pmatrix}^{-1} = \frac{1}{100.2-100}\begin{pmatrix} 3.34 & -10 \\ -10 & 30 \end{pmatrix} = \begin{pmatrix} 16.7 & -50 \\ -50 & 150 \end{pmatrix}$$

$$\begin{pmatrix} a & b \\ c & d \end{pmatrix}^{-1} = \frac{1}{ad-bc}\begin{pmatrix} d & -b \\ -c & a \end{pmatrix}$$

- Determinant is 0.2 – small compared to contents of normal matrix
- Large errors
- Either an infinite number of solutions or no solution
- Determinant = 0 means a singular matrix

Correlation matrix

- Many software packages will give you a graphical representation of the correlation matrix
- Beware values >80% if you're interested in those parameters

Correlation matrix from software →

		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
1	bkq1F871651788	100	49	45	10	23	-1	3	4	10	5	21	-2	35	-1	-3	-5	2	13	-15	13	-38	17
2	bkq1F871651830	49	100	33	43	13	25	-2	0	18	2	21	-9	32	-5	-1	-9	1	4	-6	3	-35	24
3	bkq1F8716518D8	45	33	100	24	45	9	-4	-2	12	-1	9	-12	9	1	-4	-6	-4	-10	8	-8	-6	10
4	bkq1F871651980	10	43	24	100	23	44	4	3	-7	2	2	-3	-11	-6	-5	-10	-2	-7	6	-4	13	-12
5	bkq1F871651A28	23	13	45	23	100	20	-2	-1	1	0	4	-4	-5	-1	-6	-6	2	-4	6	-6	-1	5
6	bkq1F871651AD0	-1	25	9	44	20	100	0	0	-2	0	2	-4	-8	0	-6	-4	4	-1	3	-4	5	-2
7	axial	3	-2	-4	4	-2	0	100	58	-5	36	-1	2	-2	-1	0	0	0	-6	5	-4	20	-35
8	zero	4	0	-2	3	-1	0	58	100	-4	82	-1	2	-2	0	1	0	-1	-13	13	-13	7	-17
9	scale1F8715DBAE8_	10	18	12	-7	1	-2	-5	-4	100	-3	35	-2	61	4	2	0	15	0	-1	-1	-15	15
10	lpa	5	2	-1	2	0	0	36	82	-3	100	0	1	-1	0	0	0	-1	-11	12	-13	-1	-7
11	beq1F8715DBDB8_	21	21	9	2	4	2	-1	-1	35	0	100	17	-3	-9	9	-2	9	5	-5	4	-17	10
12	x1F8715DBE48_	-2	-9	-12	-3	-4	-4	2	2	-2	1	17	100	-9	-14	2	-5	5	2	-2	2	2	-5
13	beq1F8715DC088_	35	32	9	-11	-5	-8	-2	-2	61	-1	-3	-9	100	8	2	3	2	9	-9	7	-31	20
14	x1F8715DC118_	-1	-5	1	-6	-1	0	-1	0	4	0	-9	-14	8	100	-29	5	-2	0	0	0	1	0
15	y1F8715DC1A8_	-3	-1	-4	-5	-6	-6	0	1	2	0	9	2	2	-29	100	-8	-32	0	0	0	-1	2
16	z1F8715DC238_	-5	-9	-6	-10	-6	-4	0	0	0	0	-2	-5	3	5	-8	100	-5	2	-1	1	1	-1
17	beq1F8715DC358_	2	1	-4	-2	2	4	0	-1	15	-1	9	5	2	-2	-32	-5	100	2	-2	2	-2	1
18	pku	13	4	-10	-7	-4	1	-6	-13	0	-11	5	2	9	0	0	2	2	100	-95	87	-24	-11
19	pkv	-15	-6	8	6	6	3	5	13	-1	12	-5	-2	-9	0	0	-1	-2	-95	100	-97	20	19
20	pkw	13	3	-8	-4	-6	-4	-4	-13	-1	-13	4	2	7	0	0	1	2	87	-97	100	-9	-30
21	pky	-38	-35	-6	13	-1	5	20	7	-15	-1	-17	2	-31	1	-1	1	-2	-24	20	-9	100	-83
22	pkx	17	24	10	-12	5	-2	-35	-17	15	-7	10	-5	20	0	2	-1	1	-11	19	-30	-83	100

Correlation between parameter 13 (beq) and 9 (scale) = 61%

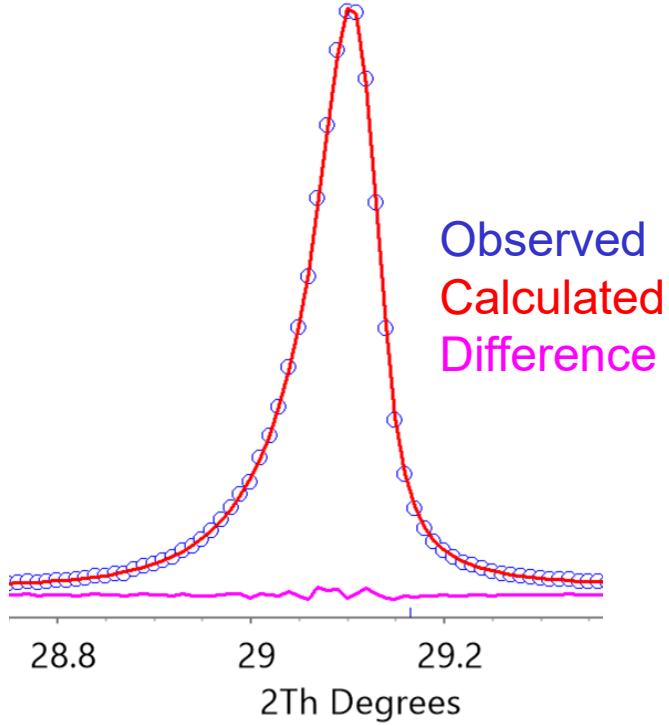
Diagonal = parameter *n* with parameter *n*

Whole Powder Pattern Fitting (WPPF) or Rietveld refinement

- Minimise the difference between an observed and a calculated powder diffraction pattern using non-linear least squares

- Flavours of WPPF
  - Structural model (Rietveld)
  - Cell-parameter constrained structure-independent fit (Pawley/Le Bail)
  - Free fitting
  - A combination of the above

- Model must contain all the relevant information
  - Cell parameters to predict positions
  - Structural model *x*, *y*, *z*, *uiso*/*adps*
  - Model to fit observed peak shapes
  - Functions to describe instrumental effects
  - Functions to correct systematic effects (LP, Absorption)



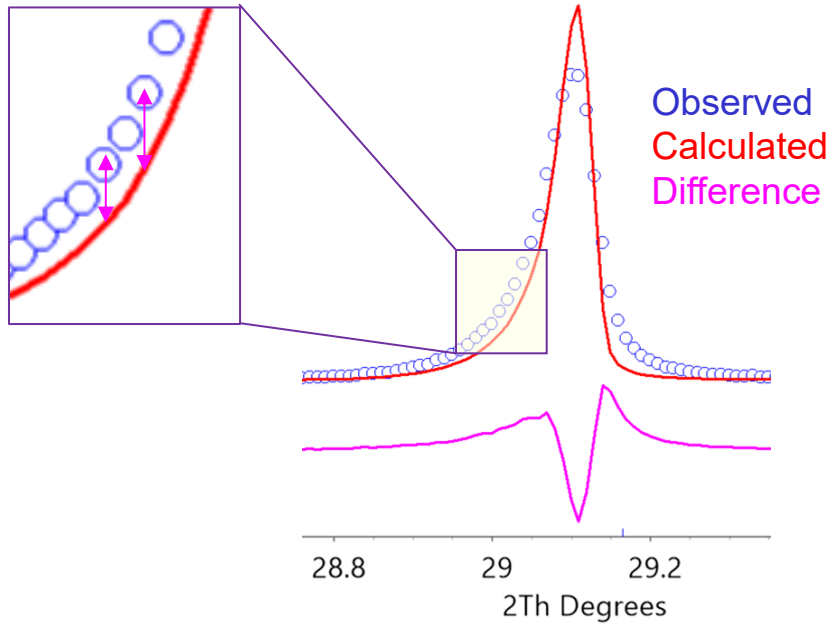
Minimisation, R-factors, etc

Minimise: $\sum_{i=1}^{N} w_i \left(y_{obs,i} - y_{calc,i}\right)^2$

Monitor: $R_{\mathrm{wp}} = \sqrt{\frac{\sum_{i=1}^{N} w_i \left(y_{obs,i} - y_{calc,i}\right)^2}{\sum_{i=1}^{N} w_i {y_{obs,i}}^2}}$

Monitor: $GoF = \sqrt{\chi^2} = \frac{\mathrm{R_{wp}}}{\mathrm{R_{exp}}} = \sqrt{\frac{\sum_{i=1}^{N} w_i \left(y_{obs,i} - y_{calc,i}\right)^2}{N - P}}$

Consider: $R_{\mathrm{Bragg}} = \frac{\sum_{hkl} |I_{hkl}('obs') - I_{hkl}(calc)|}{\sum_{hkl} I_{hkl}('obs')}$



N: number of data points; P: number of parameters. Least-squares uses $1/\sigma(y_{obs,i})^2$ weighting, where $\sigma(y_{obs,i})$ is the experimental uncertainty in $y_{obs,i}$.

Weighting in Rietveld refinement

- Old data formats were 2θ, Intensity
- Assume Poisson statistics $\sigma(I) = I^{0.5}$ and weight accordingly
- For many PSD/neutron/tof/other measurements this will not hold
- Always use 2θ, *Intensity*, $\sigma(I)$ format
- .xye file or equivalent gsas/fullprof
- Never e.g. convert from gsas to xy format in fullprof in a way that loses errors
- Particularly for time of flight data
- If you manipulate a file (e.g. variable to fixed slit correction) always correct errors accordingly

Least squares in Excel

- Demonstration

- Fit our function using “chart/add trendline”
- Fit using solver
- Change to a quadratic function

Least Squares in TOPAS

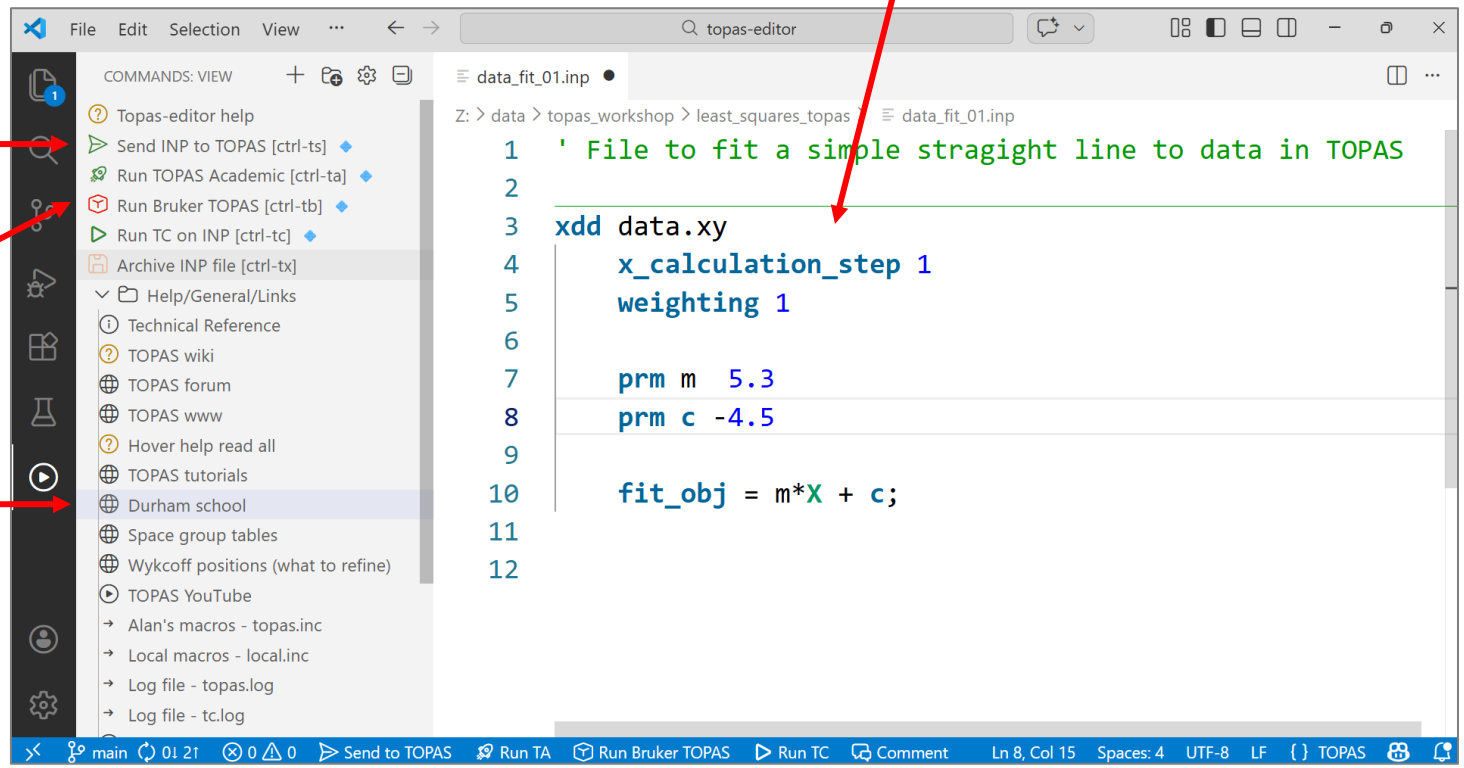
- e.g. fit data.xy using a simple linear equation
- Calculate esd's and correlation
- Identical to values calculated by hand
- Much easier!!

TOPAS instructions for straight line fit

Click here to send to TOPAS

Click here to run TOPAS

Click here for tutorials



Topas graphics and windows

Fixing parameters – using !

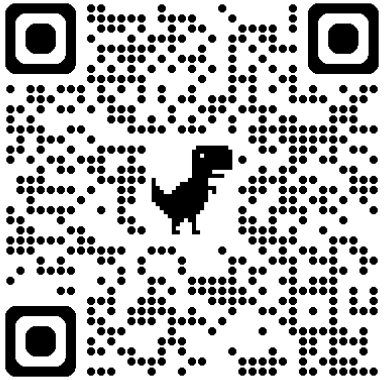
```
prm   m   5.3
prm  !c  -4.5

fit_obj = m*X + c;
```

- Gradient defined as parameter `m` (refining)
- Intercept defined as parameter `c` (not refining)

Initial software setup

- Go to main school tutorial page
  - You can start the excel-based tutorials straight away
  - If you don't have excel solver in the data tab, go to Tutorial 0.1 – Setting up software

Tutorials



- For TOPAS/topas-editor tutorials
  - Go to Tutorial 0.1 – Setting up software
  - Follow the instructions there
  - It might take a few minutes to copy software if everybody does simultaneously
  - Ask a tutor over the first couple of hours for help

Software setup

Problem session

- Problems (Excel)
  - Tutorial 1.1: Fit a linear function as in lecture
  - Tutorial 1.1: Fit a Gaussian peak shape
  - Tutorial 1.4: Perform a Pawley refinement in Excel
  - Tutorial 1.4: Perform a full Rietveld refinement in Excel
  - Tutorial 1.3: Refine unit cells from the morning's tutorials

$$\frac{C_0^{1/2}}{H_K \pi^{1/2}} \exp\left(\frac{-C_0(2\theta_i - 2\theta_K)^2}{H_K^2}\right)$$

- Problems (TOPAS)
  - Tutorial 1.2: Perform the same fits as in excel to compare results
  - Do it mechanically today – explanations tomorrow!

End of Slides

Session 9: Peak Intensities in Powder Diffraction

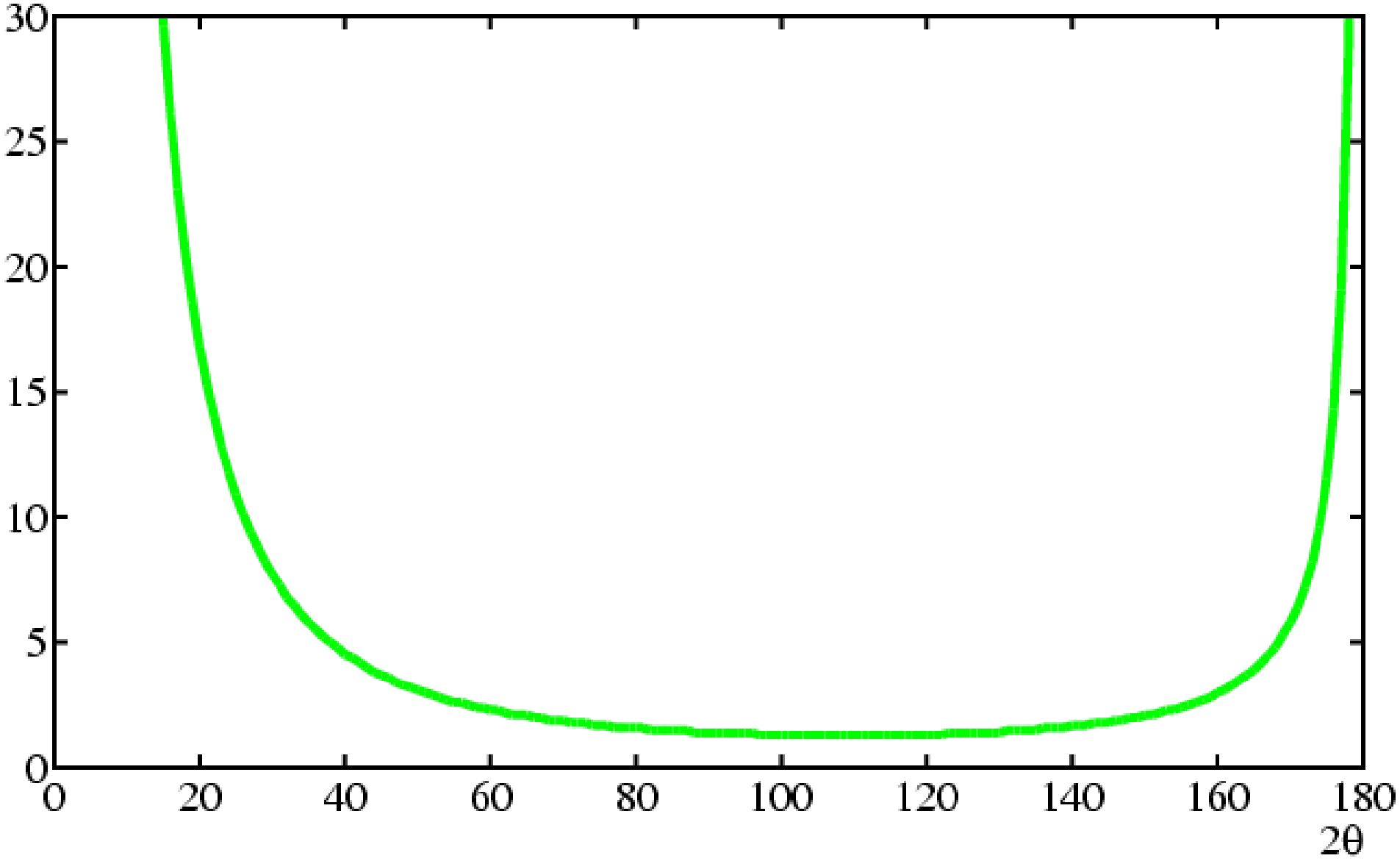
Jeremy Karl Cockcroft
Department of Chemistry, UCL

Peak Intensities

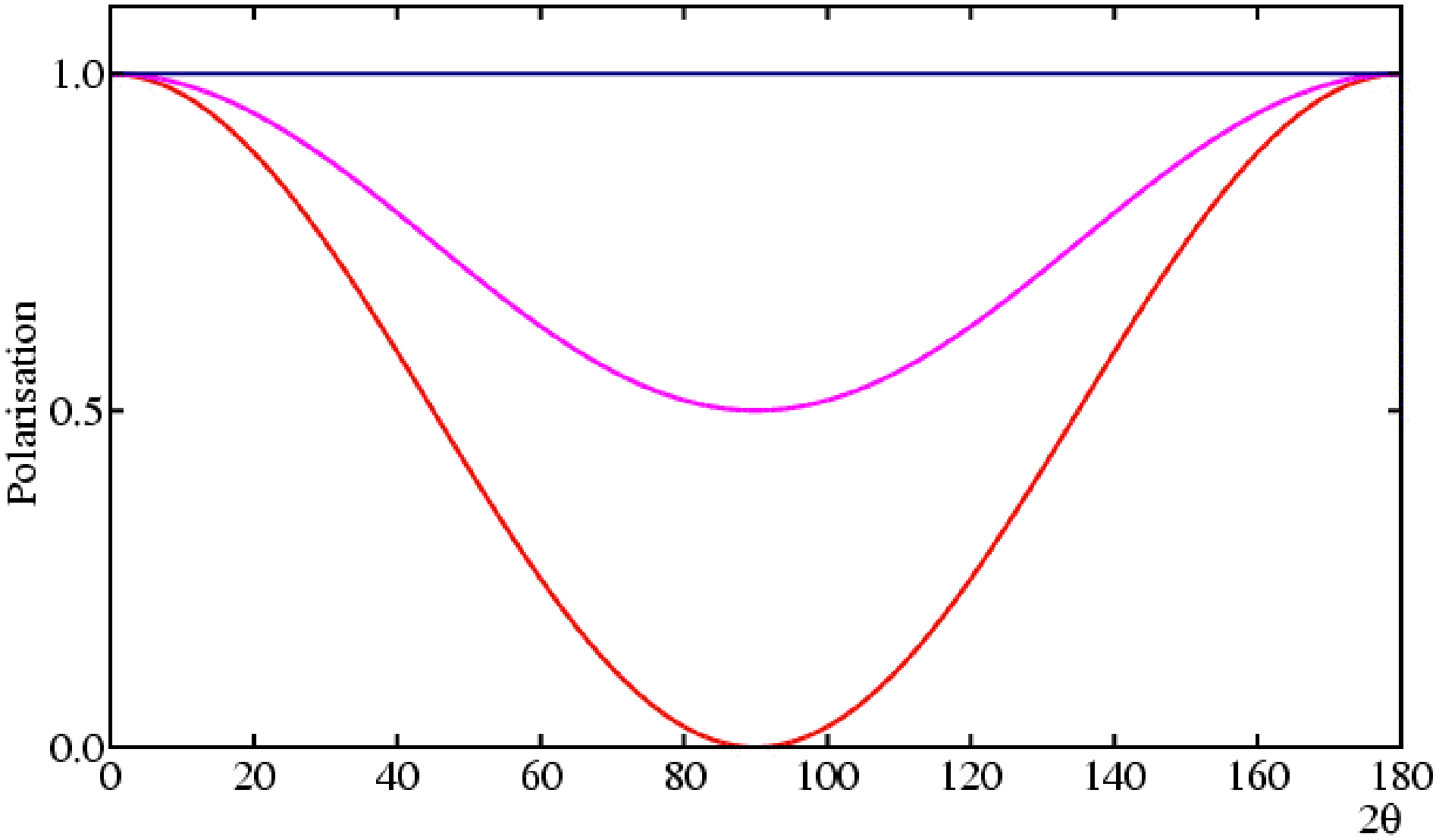
- For an ideal powder sample:

$$I(hkl) = c\ \mathrm{L}(2\theta)\ \mathrm{P}(2\theta)\ \mathrm{A}(2\theta)\ j_{\mathrm{hkl}}\ |\mathbf{F}(hkl)|^2$$

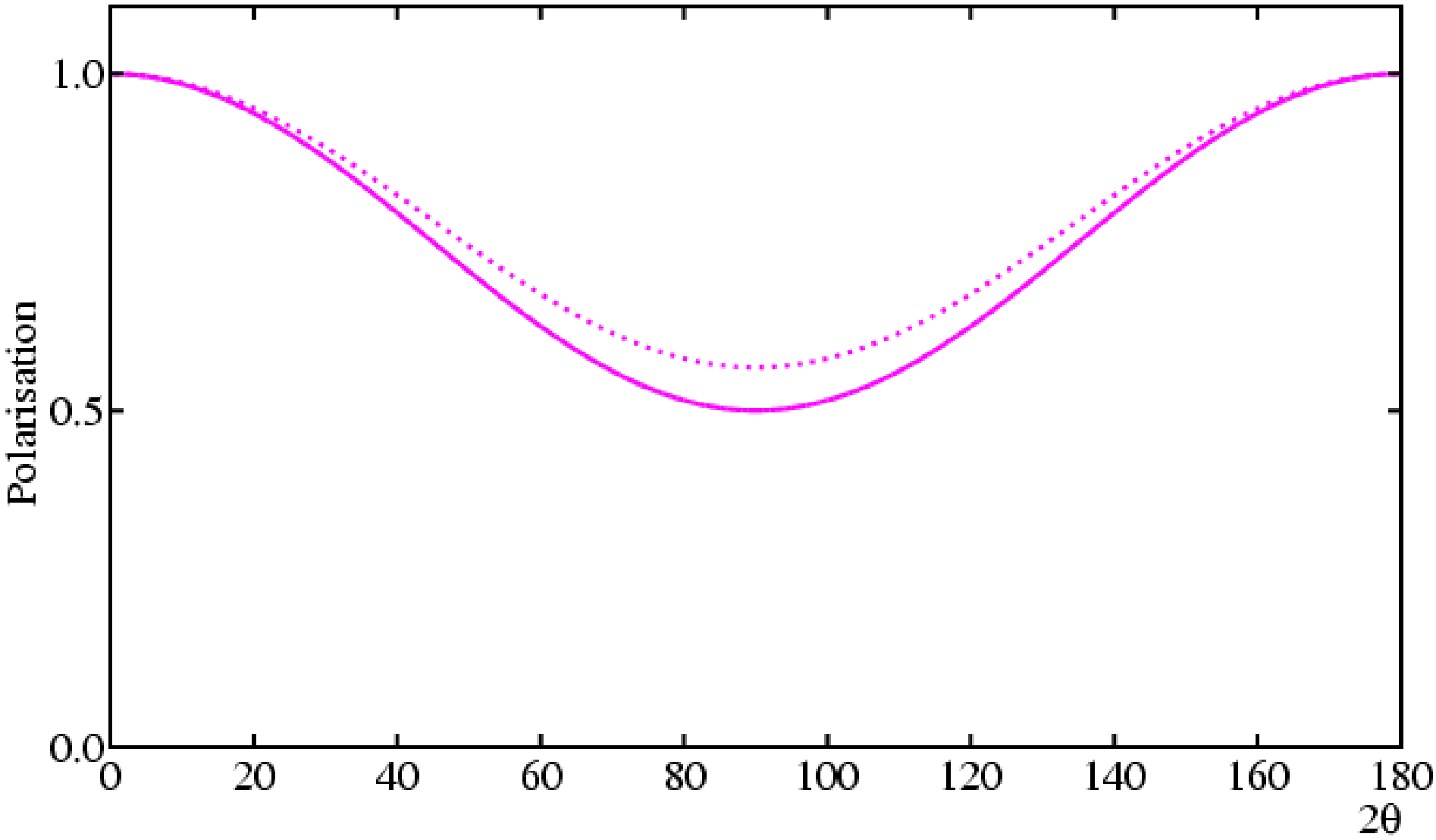
Lorentz Factor



Polarisation

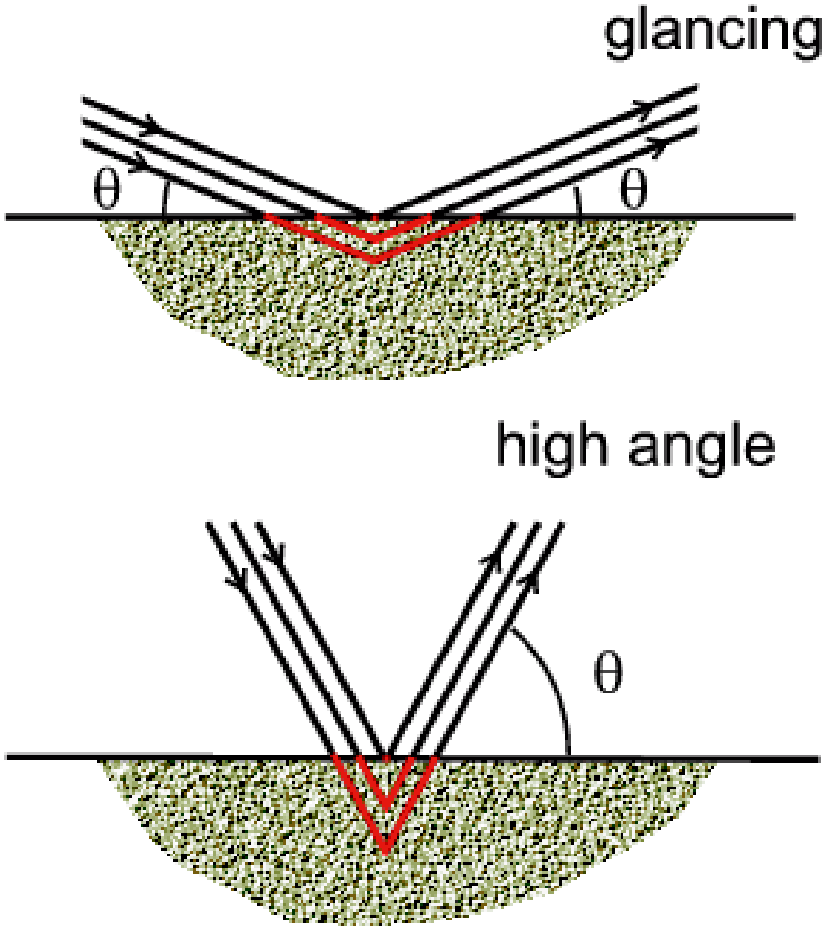


Polarisation

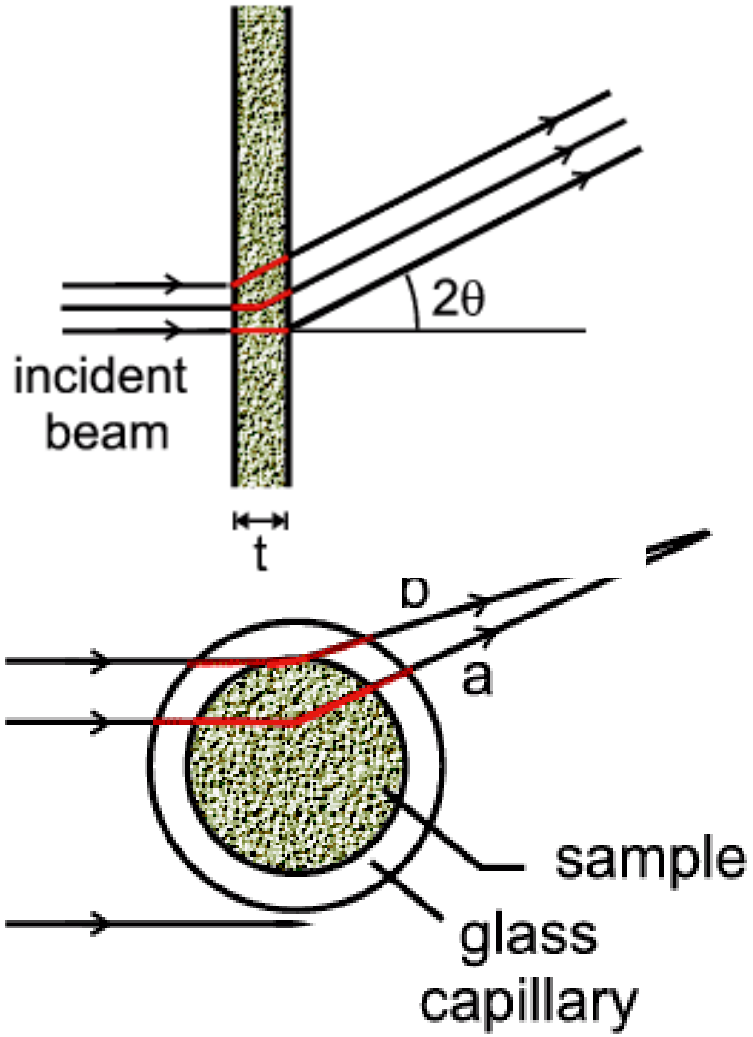


Absorption

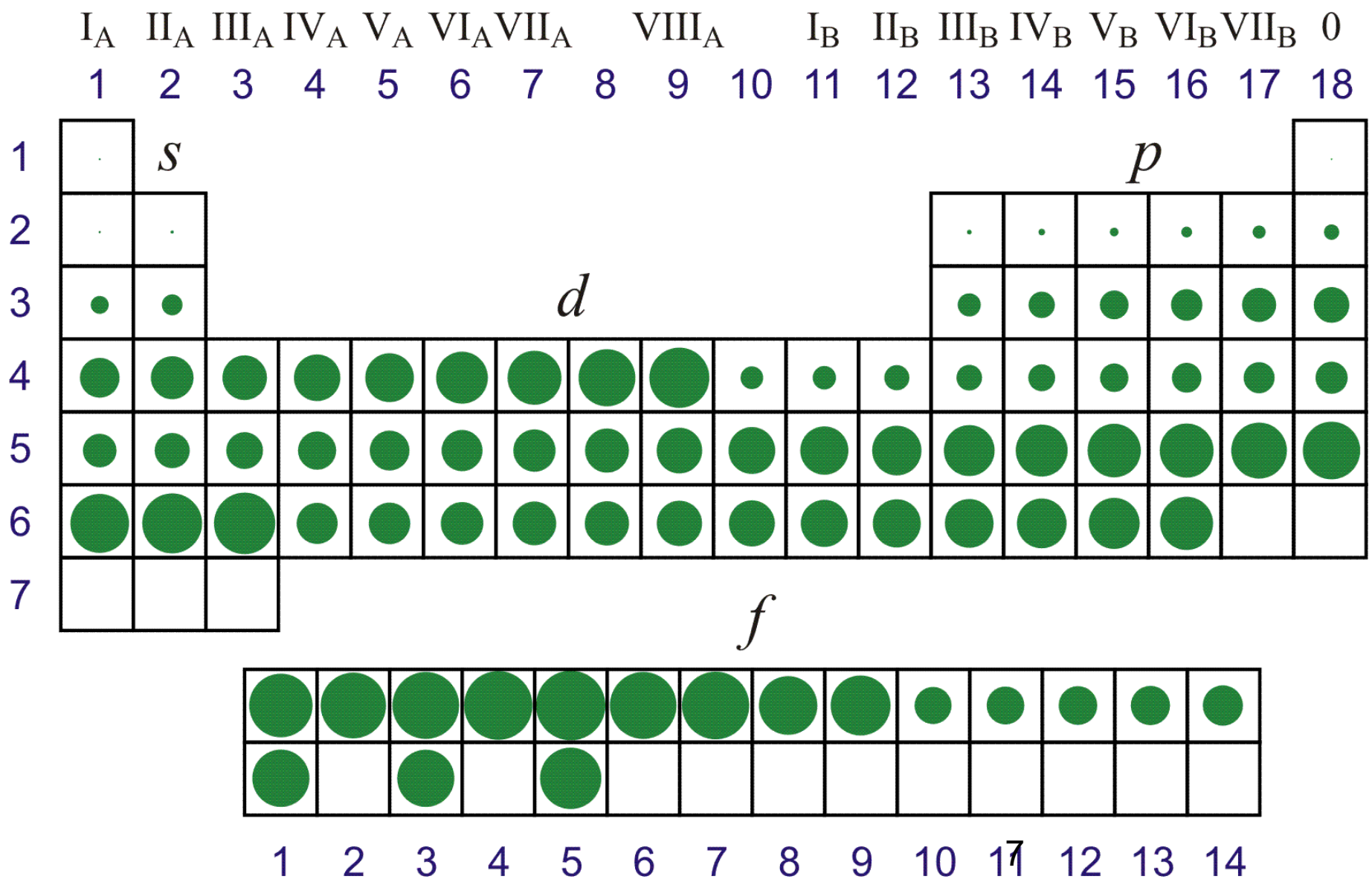
- Reflection



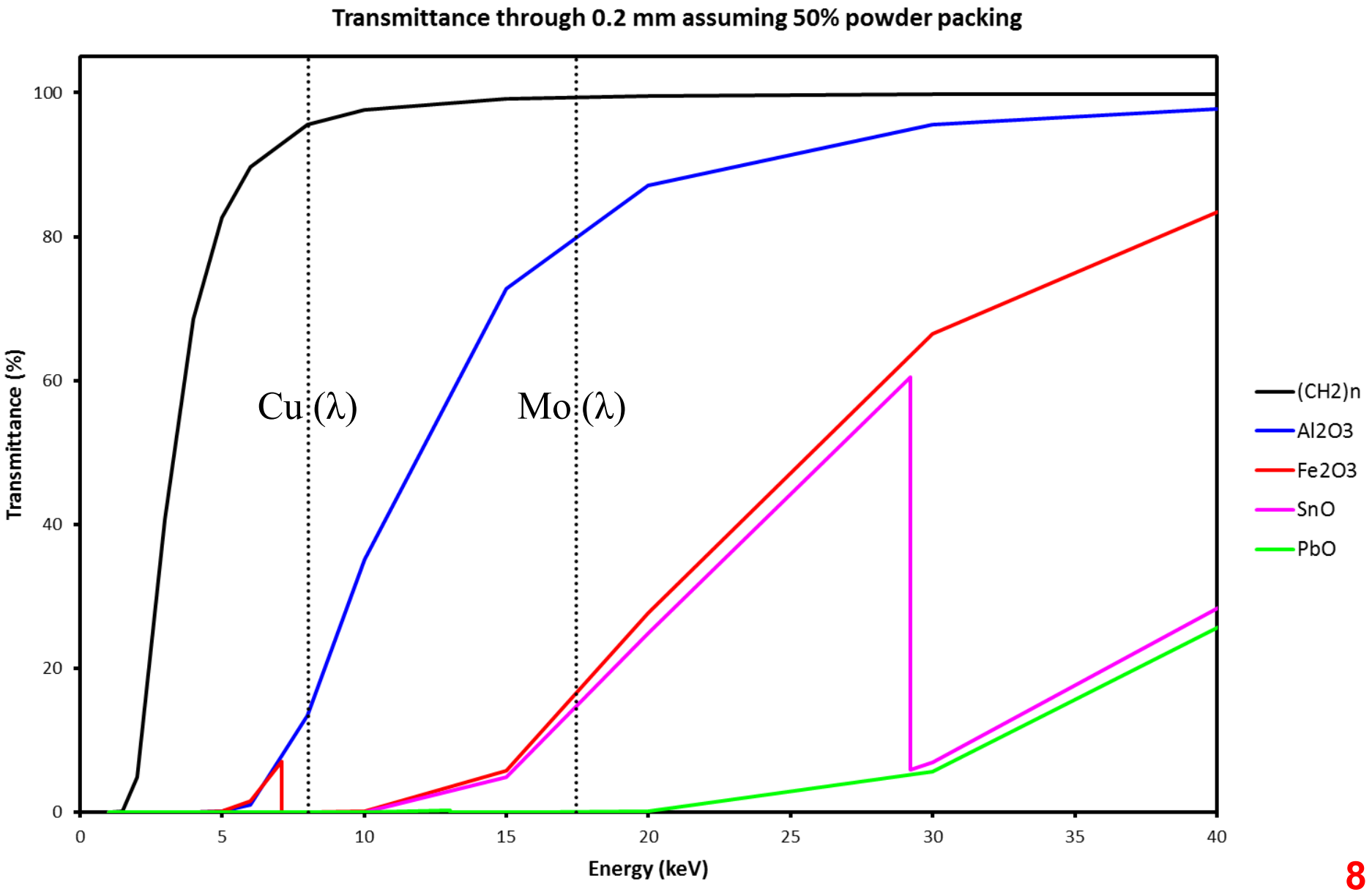
- Transmission



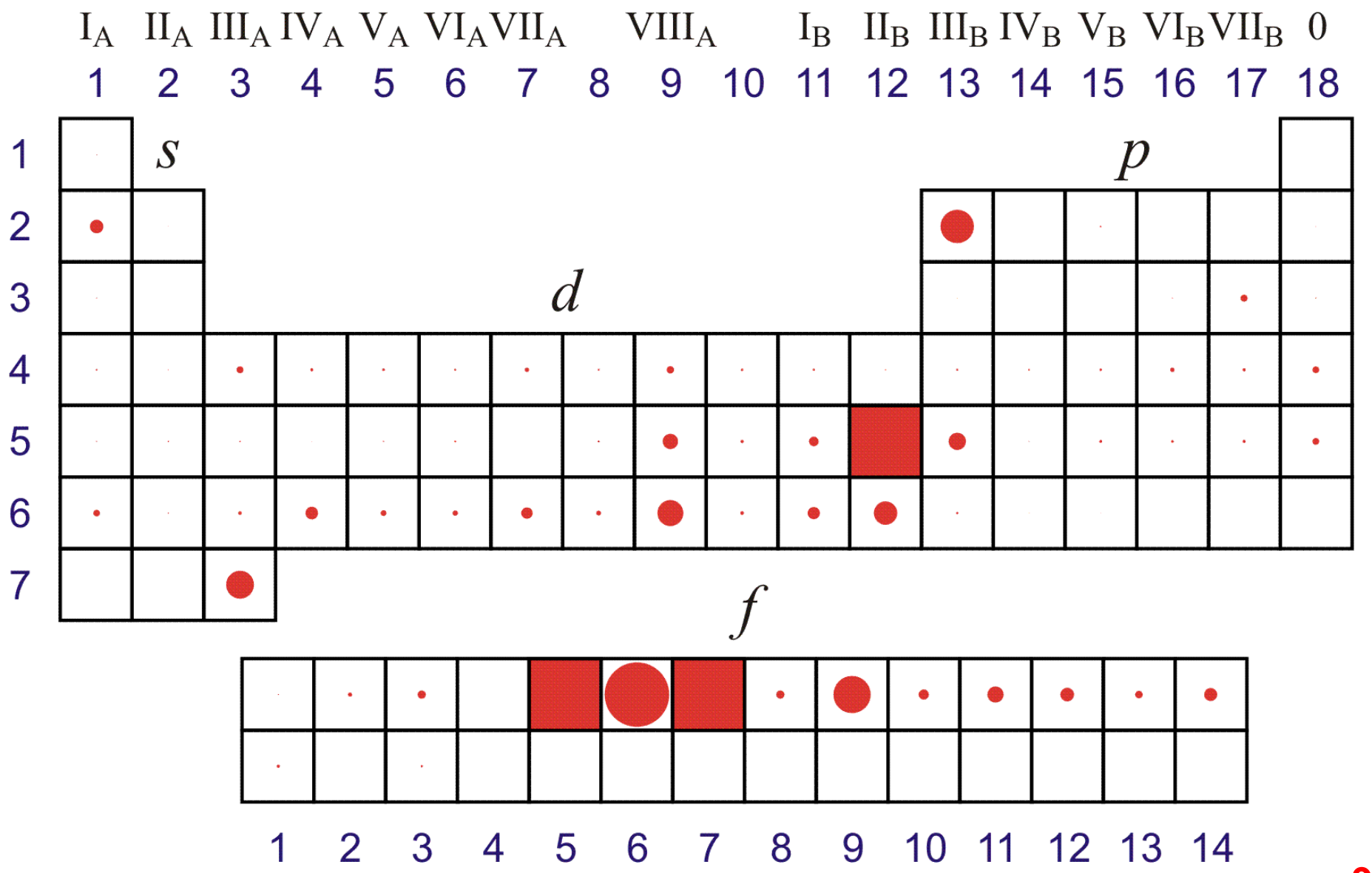
X-Ray Mass Absorption (Cu)



X-Ray Transmittance



Neutron Absorption X-Section



Structure Factors

$$I(hkl) = k\,|\mathbf{F}(hkl)|^2$$

$$\mathbf{F}(hkl) = \sum s_n\, o_n \exp(2\pi i\{hx + ky + lz\}) \exp(-W_n)$$

- Vector quantity (magnitude F & phase φ)
  - atomic scattering length s_n
  - atomic occupation number o_n
  - wave interference term: $\exp(2\pi i\{hx + ky + lz)$
  - Debye-Waller factor W_n
- Summation over all atoms in 1 unit cell

Structure Factors

$$\mathbf{F}(hkl) = \sum s_n o_n \exp(2\pi i\{hx + ky + lz\}) \exp(-W_n)$$

Real Space (Crystal)		Reciprocal Space (Diffraction)
=		=
Atoms	⟺	Scattering Factor
⊗	*Fourier Transform*	×
Lattice	⟺	Interference Term
⊗		×
Atomic Displacements	⟺	Debye-Waller Factors

- Fourier transform of **F** is simply the electron density (for X-ray **F** values)

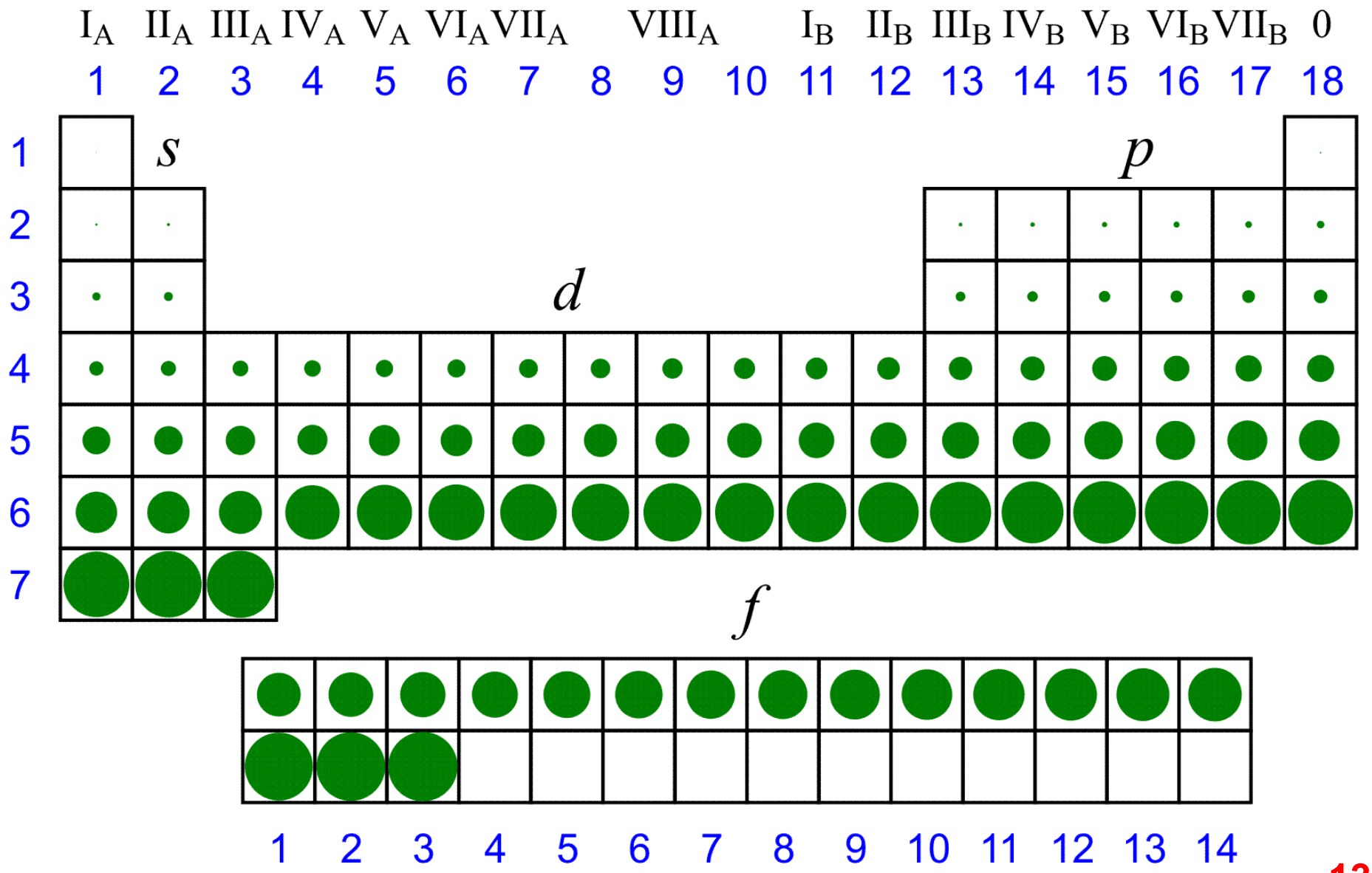
Atomic Scattering Length s_n

- X-rays:
  - Scattering factor f
    - Scattering length divided by r_e

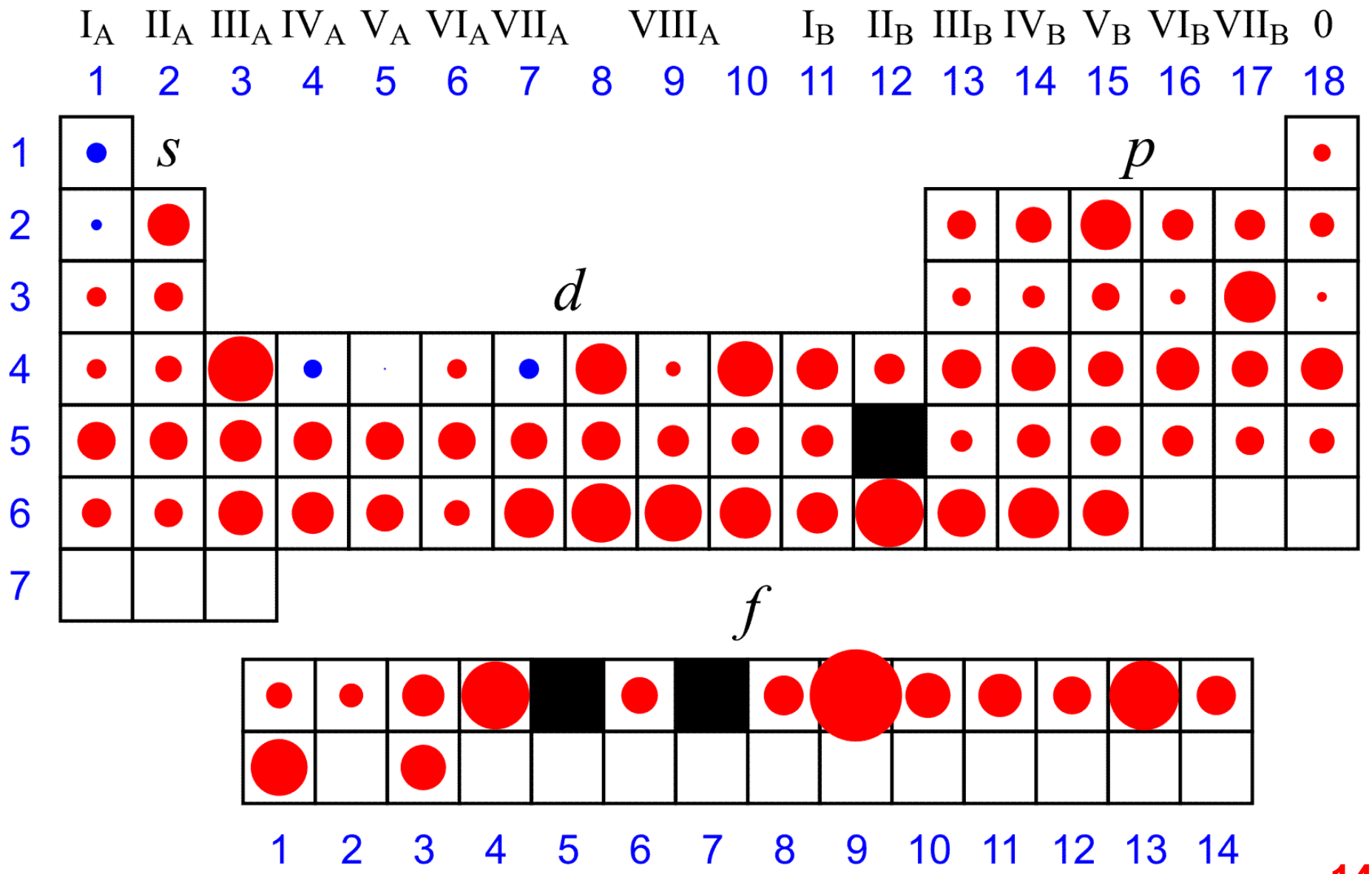
      where r_e classical electron radius = 2.818 fm

- Neutrons:
  - Scattering length b

X-ray Scattering Factors *f*



Neutron Scattering-Lengths b



Scattering-Length Comparison

Element	H	D	U	Fe	Co
X-ray f (0°) (Z)	1	1	92	26	27
Neutron b (fm)	−3.74	6.67	8.42	9.45	2.78

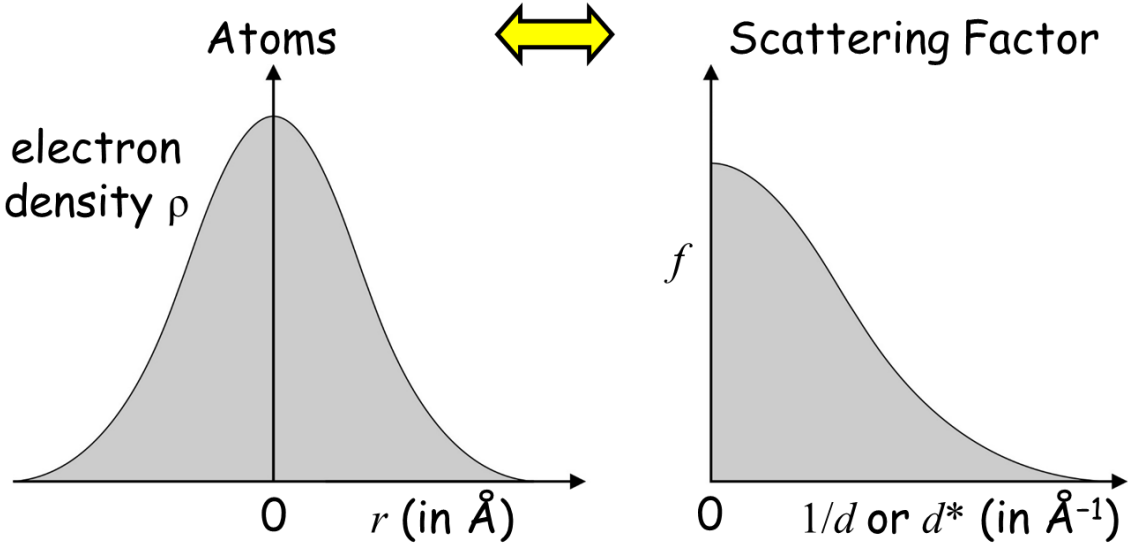
Element	Ba	O	V	Ti	Zr
X-ray f (0°) (Z)	56	8	23	22	40
Neutron b (fm)	5.28	5.81	−0.38	−3.44	5.28

Absolute comparison: $f(2\theta = 0°) \times r_e$

where r_e = 2.818 fm

Scattering as a Function of 2θ

- X-ray interacts with electron cloud
  - Atoms are similar in size to wavelength
  - Fourier transform of the electron cloud corresponds to the X-ray form factor
    - e.g. F.T. Gaussian (broad) → Gaussian (narrow)
      - Usually tabulated as a sum of 4 Gaussians + c

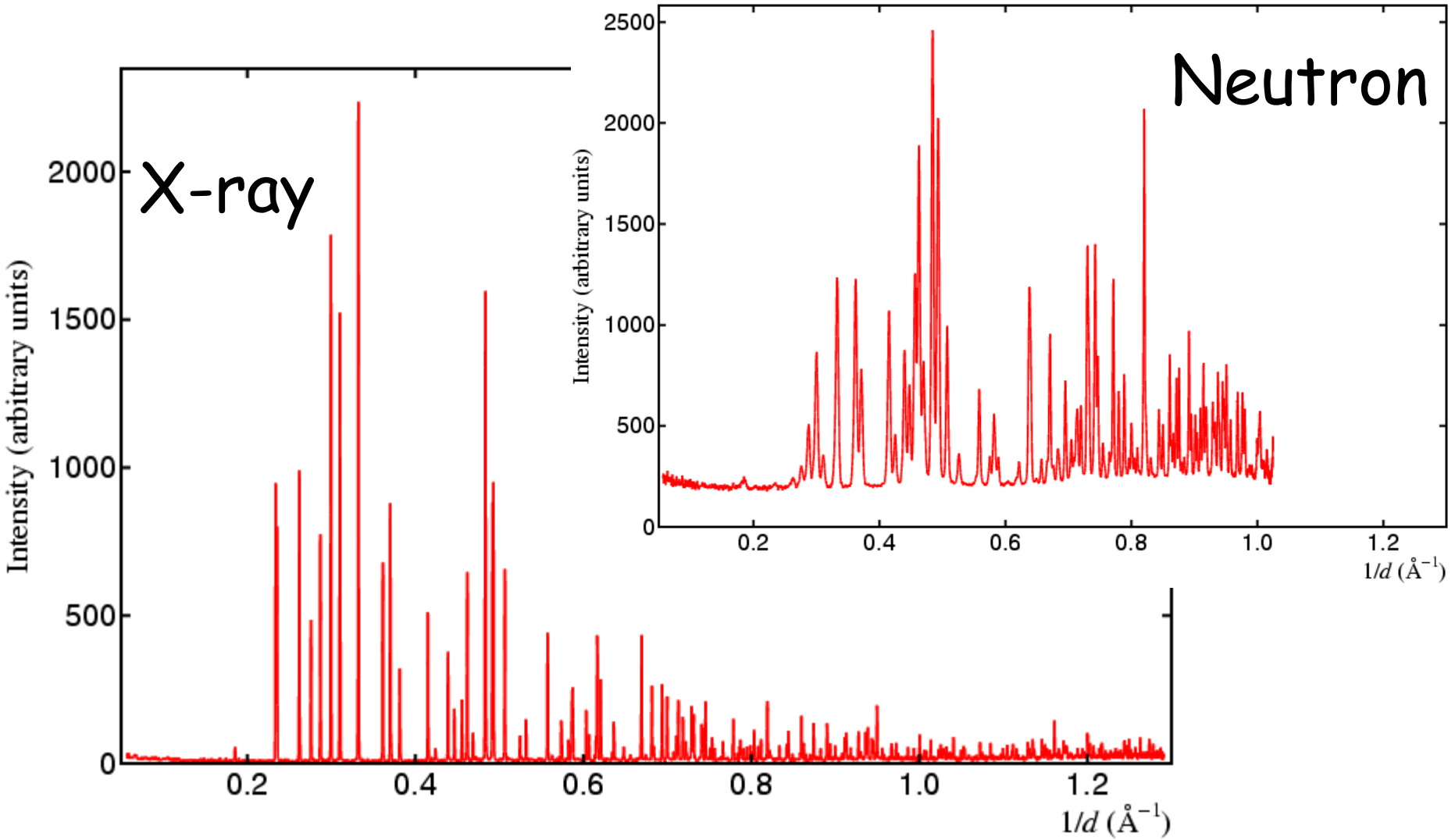


Scattering as a Function of 2θ

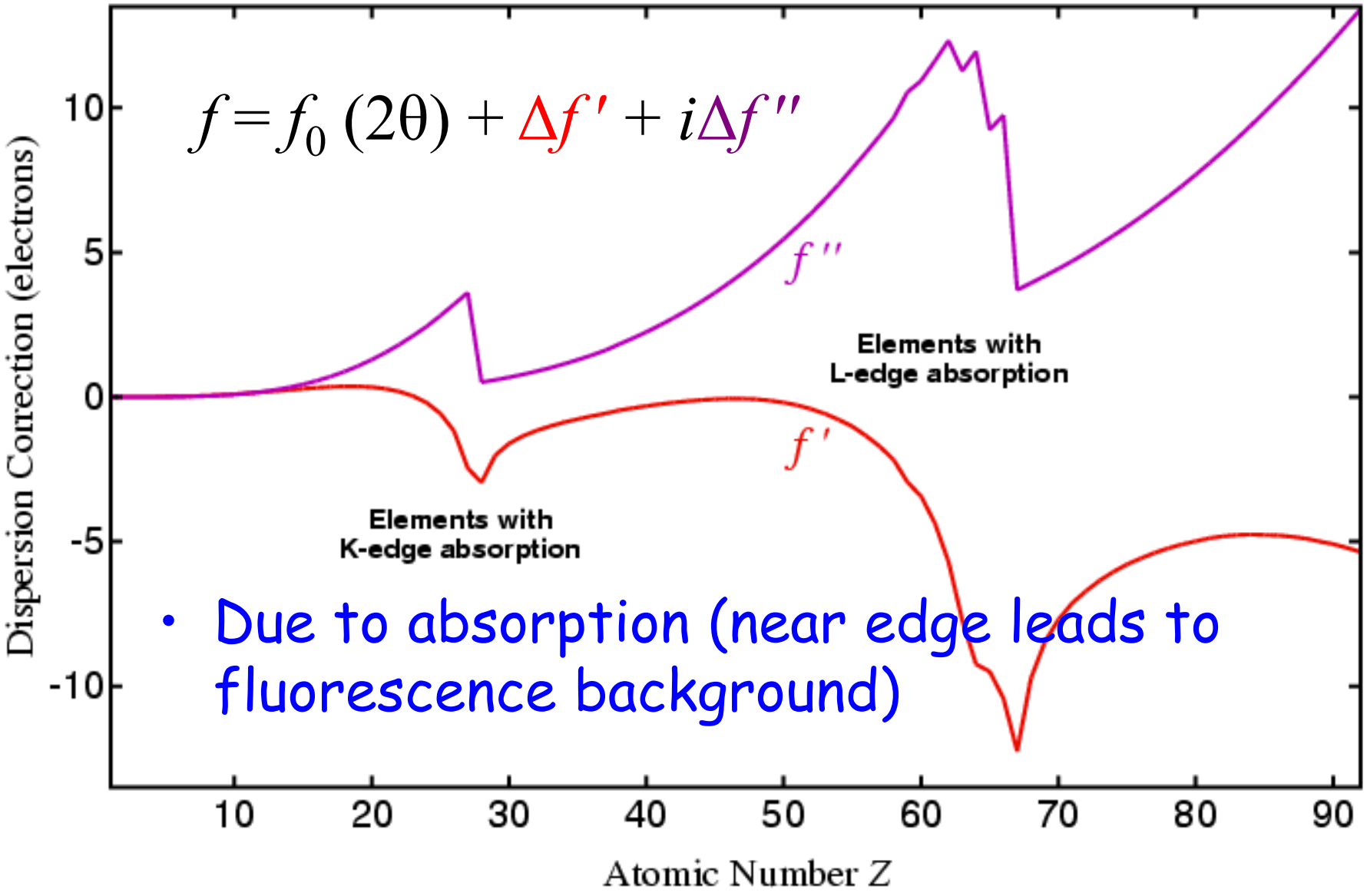
- Neutron interacts with nucleus
  - Nucleus is very small (point scatterer) compared to λ
  - Fourier transform of a delta function is a horizontal line

    → No form factor for neutrons
  - Exception: interaction with unpaired electron(s)
    - Form factor for magnetic cations (e.g. Fe^{3+}, Ni^{2+}, Ho^{3+}) in magnetic crystallography
      - Differences in shape between TM and Ln/An elements due to differences in *d* and *f* orbitals

Scattering as a Function of 2θ



Anomalous Scattering



- Due to absorption (near edge leads to fluorescence background)

Site Occupation o_{n}

- Structure: list of atoms in asymmetric unit
- Summation performed by all applying symmetry operators to all hkl
  - Mathematically equivalent to applying them to all atoms
  - o_{n} compensates for atoms on special positions since calculation assumes general position x,y,z
  - o_{n} takes into account atomic disorder

Interference Term $e^{2\pi i(hx+ky+lz)}$

- Vector dot product between real- and reciprocal-space vectors:
  - $(h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*) \bullet (x\mathbf{a} + y\mathbf{b} + z\mathbf{c})$
- Effected by translational symmetry
  - Leads to reflection conditions & systematic absences
- Not a smooth function of 2θ
  - Reflections with similar d spacings may have large or small interference terms

Interference Term $e^{2\pi i(hx+ky+lz)}$

- May be written as a sum of cosine and sine terms:

$$\exp(2\pi i\{hx+ky+lz\}) = \cos 2\pi(hx+ky+lz) + i \sin 2\pi(hx+ky+lz)$$

- If atom on x,y,z and on $-x,-y,-z$, then the cosine terms double and sine terms vanish
  - Use of centrosymmetric origin
    - Reduces calculation time by 50%
      - Historically very important when done by hand!!!!

Structure Factor for NaCl

Na^+ at 0,0,0; $\frac{1}{2},\frac{1}{2},0$; $\frac{1}{2},0,\frac{1}{2}$; $0,\frac{1}{2},\frac{1}{2}$

Cl^- at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$; $\frac{1}{2},0,0$; $0,\frac{1}{2},0$; $0,0,\frac{1}{2}$

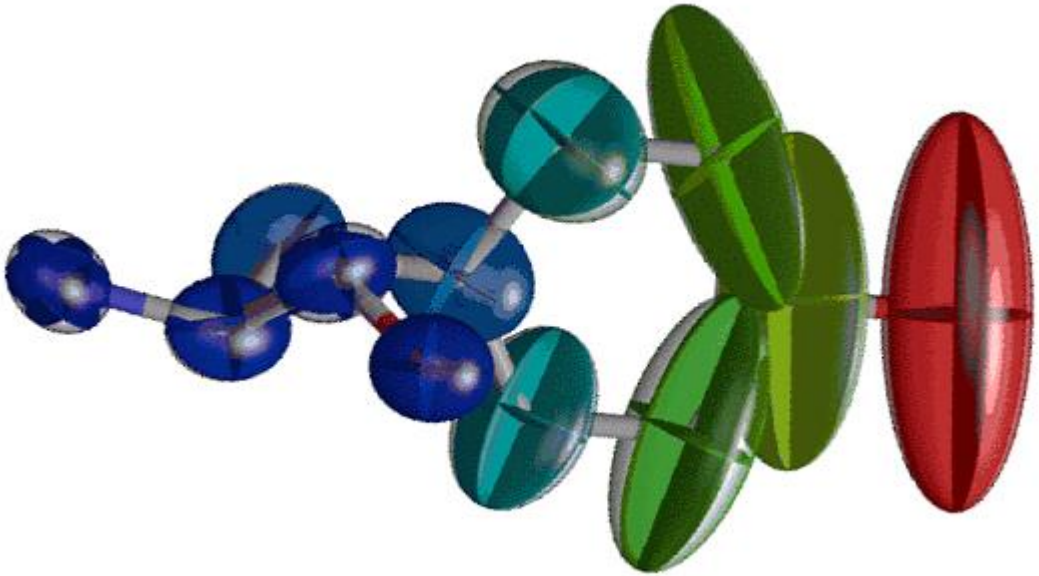
$$f_{Na}\{\cos 2\pi(h0+k0+l0) + \cos 2\pi(h\tfrac{1}{2}+k\tfrac{1}{2}+l0) + \cos 2\pi(h\tfrac{1}{2}+k0+l\tfrac{1}{2}) + \cos 2\pi(h0+k\tfrac{1}{2}+l\tfrac{1}{2})\} +$$

$$f_{Cl}\{\cos 2\pi(h\tfrac{1}{2}+k\tfrac{1}{2}+l\tfrac{1}{2}) + \cos 2\pi(h\tfrac{1}{2}+k0+l0) + \cos 2\pi(h0+k\tfrac{1}{2}+l0) + \cos 2\pi(h0+k0+l\tfrac{1}{2})\}$$

Note: $i \sin 2\pi(hx+ky+lz) = i \sin(n\pi) = 0$

Debye-Waller Factors

- Atomic displacement parameters (ADPs)
- "Temperature factors"



Functions

- Isotropic (spheroid)

  $\exp(-B_n \sin^2\theta / \lambda^2) = \exp(-B_n / 4d^2) =$

  $\exp(-2\pi^2 U_n / d^2)$

  - U_n is mean-square atomic displacement
  - B_n often liked since values are around 1
    - but now rarely used for SXD

Functions

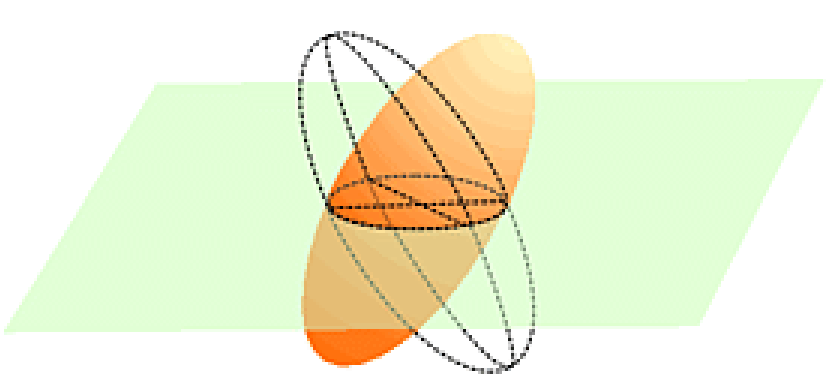
- Anisotropic (ellipsoid)

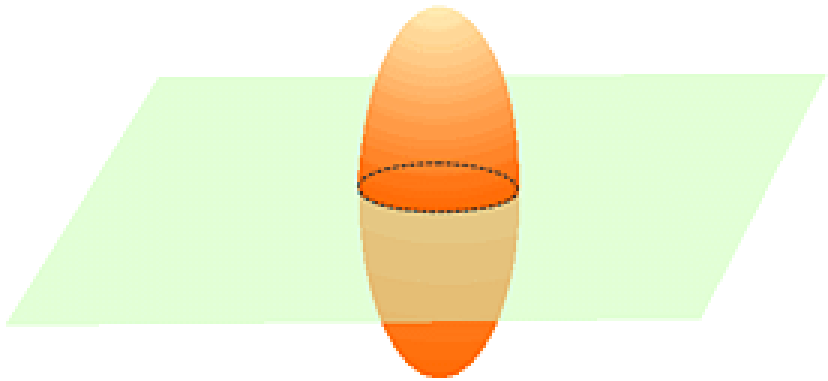
$\exp(-\{\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{23}kl + 2\beta_{13}hl + 2\beta_{12}hk\})$

  - Tensor quantity with 6 parameters
  - β used for speed of calculation but doesn't easily relate to atomic displacements
    - contain terms relating to cell parameters
  - Use of b_{11} and u_{11} etc. (similar to B and U)
    - $b_{11} = 8\pi^2 u_{11}$
    - independent of lattice parameters

Symmetry Constraints

- Only effected by point-group symmetry elements





  - $u_{13} = u_{23} = 0$
  - should always be applied by software!

Rietveld Refinement

- Objective is to refine a model structure against a measured powder diffraction pattern
- Peak intensities provide the information about the crystal structure
  - Peak positions provide unit cell information
  - Peak widths and shape provide information on instrument and crystallinity of sample

Agreement Tests

- Need to monitor progress of fit
- Need to compare different model fits
- Need to measure data quality
- Solution:
  - Visualisation (XY plot)
  - Numeric quantity (popular for working blind!)
  - Monitor chemical parameters
    - bond lengths, angles, etc.

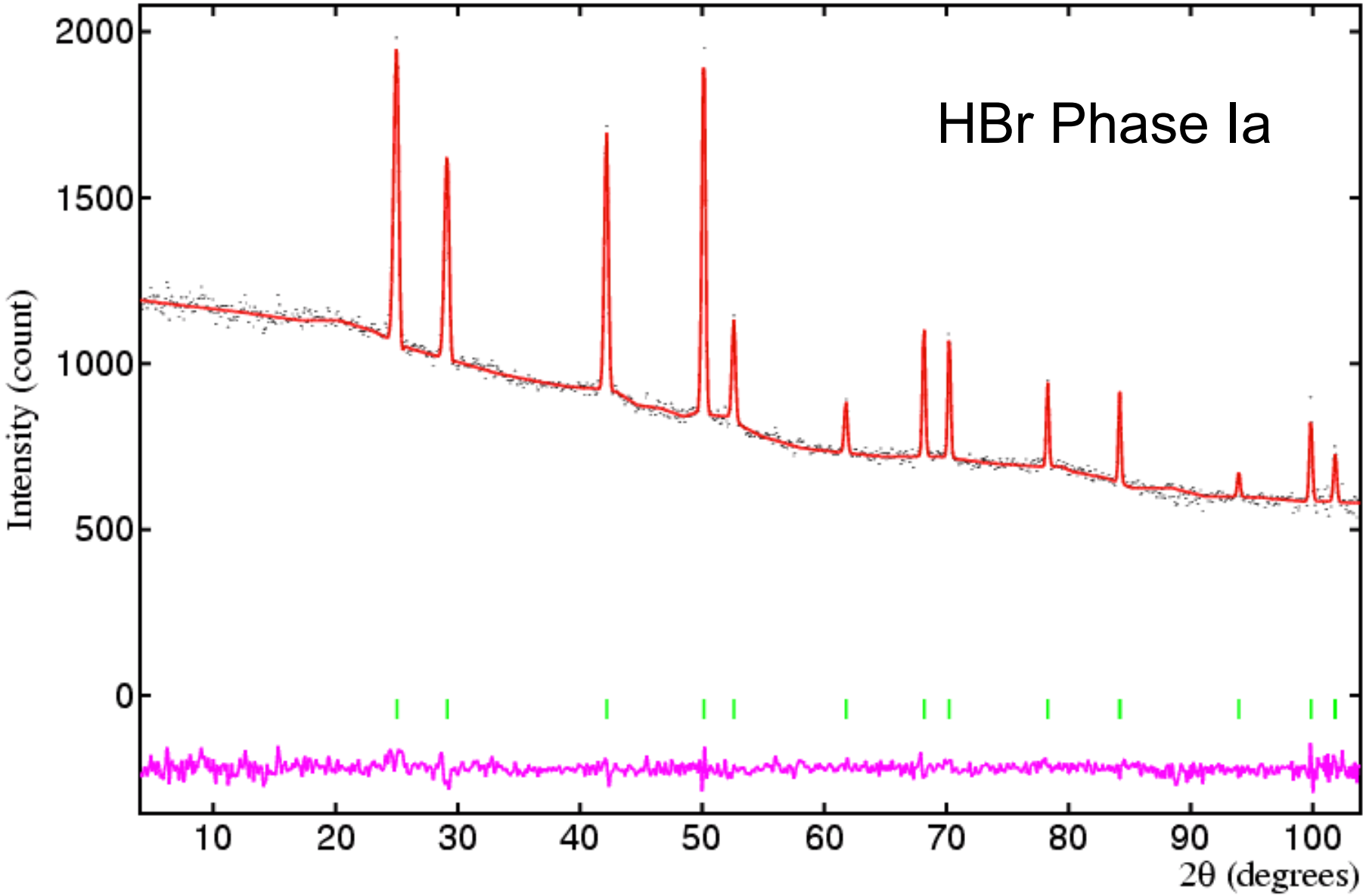
R-factors

$$R_{\mathrm{wp}} = [\ \Sigma\, w_{\mathrm{i}} \{\ y_{\mathrm{i}}(\mathrm{obs}) - y_{\mathrm{i}}(\mathrm{calc})\}^2 / \Sigma\, w_{\mathrm{i}}\, y_{\mathrm{i}}(\mathrm{obs})2]^{½}$$

One formula, but many interpretations 

$$R_{\mathrm{exp}} = [(\ N - P + C\ ) / \Sigma\, w_{\mathrm{i}}\, y_{\mathrm{i}}(\mathrm{obs})^2]^{½}$$

- Other R-factors similar to R_{wp} in format:
  - $I(hkl)$ [or even $I(hkl)^2$]
  - $|\mathbf{F}(hkl)|^2$
  - $|\mathbf{F}(hkl)|$ etc.
    - All use derived "observed" values



R_{wp} = 8.1% or 2.5% or 1.8%!

Simple Example

- $PbSO_4$ at RT (powder neutron diffraction)
  - Simple structure & a model example
- Structure:

  Space group *Pbnm*

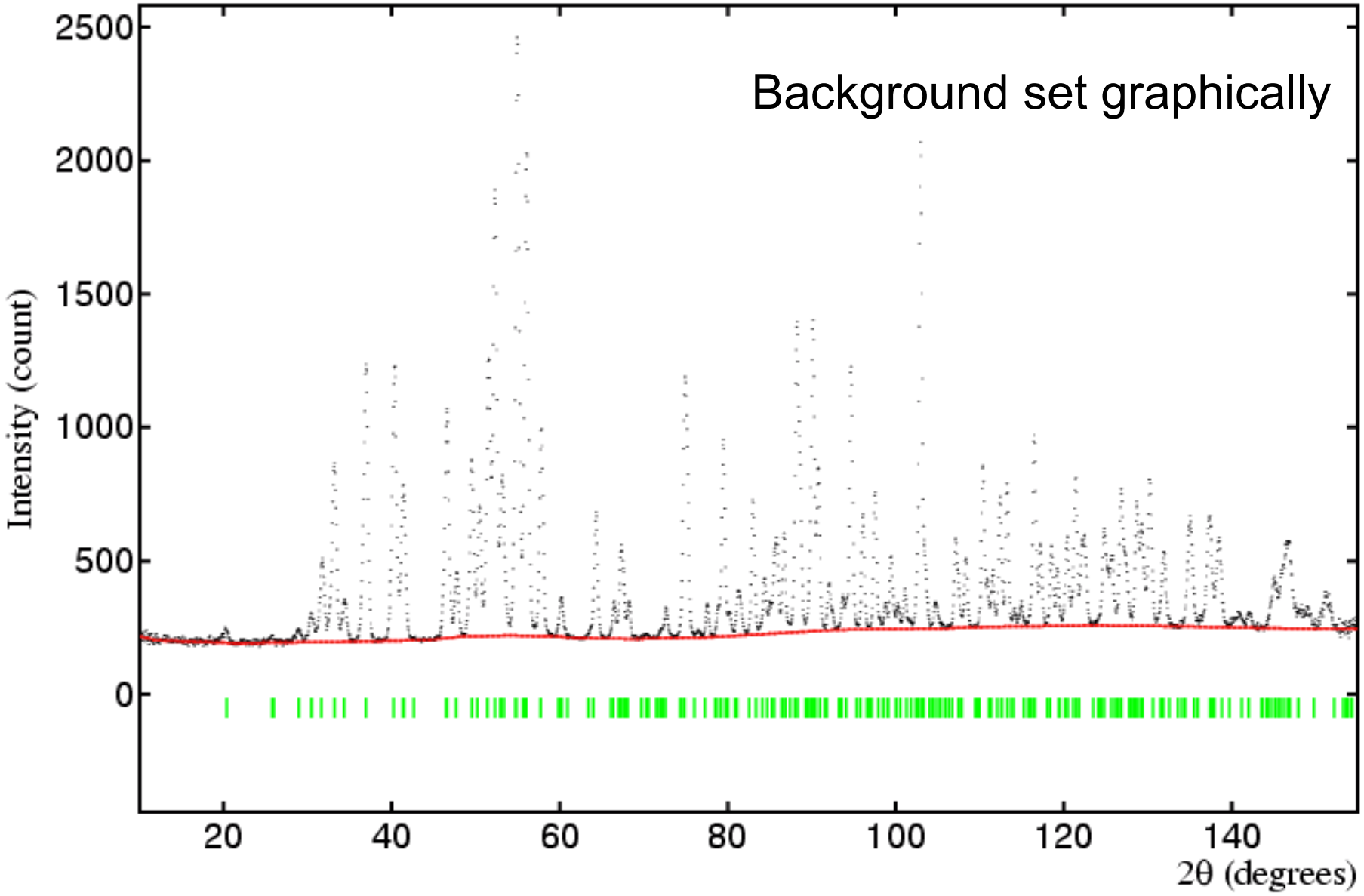
  a = 7.0 Å, b = 8.5 Å, c = 5.4 Å

  4 Pb (0.15,0.20,$\frac{1}{4}$); 4 S (0.20,0.50,$\frac{3}{4}$);

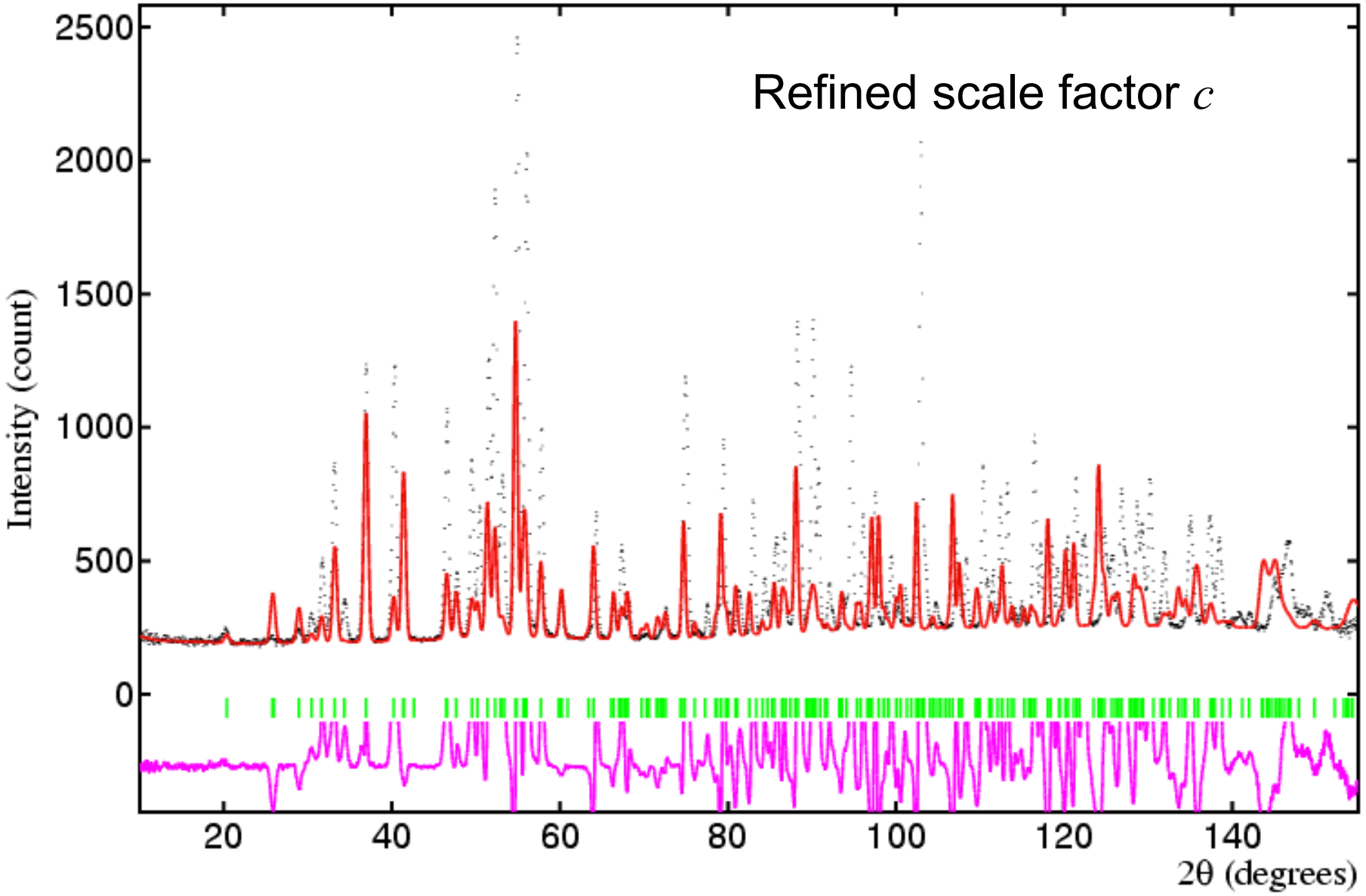
  4 O(1) (0.10,0.60, $\frac{3}{4}$); 4 O(2) (0.00,0.30,$\frac{3}{4}$);

  4 O(3) (0.30,0.40,0.98)

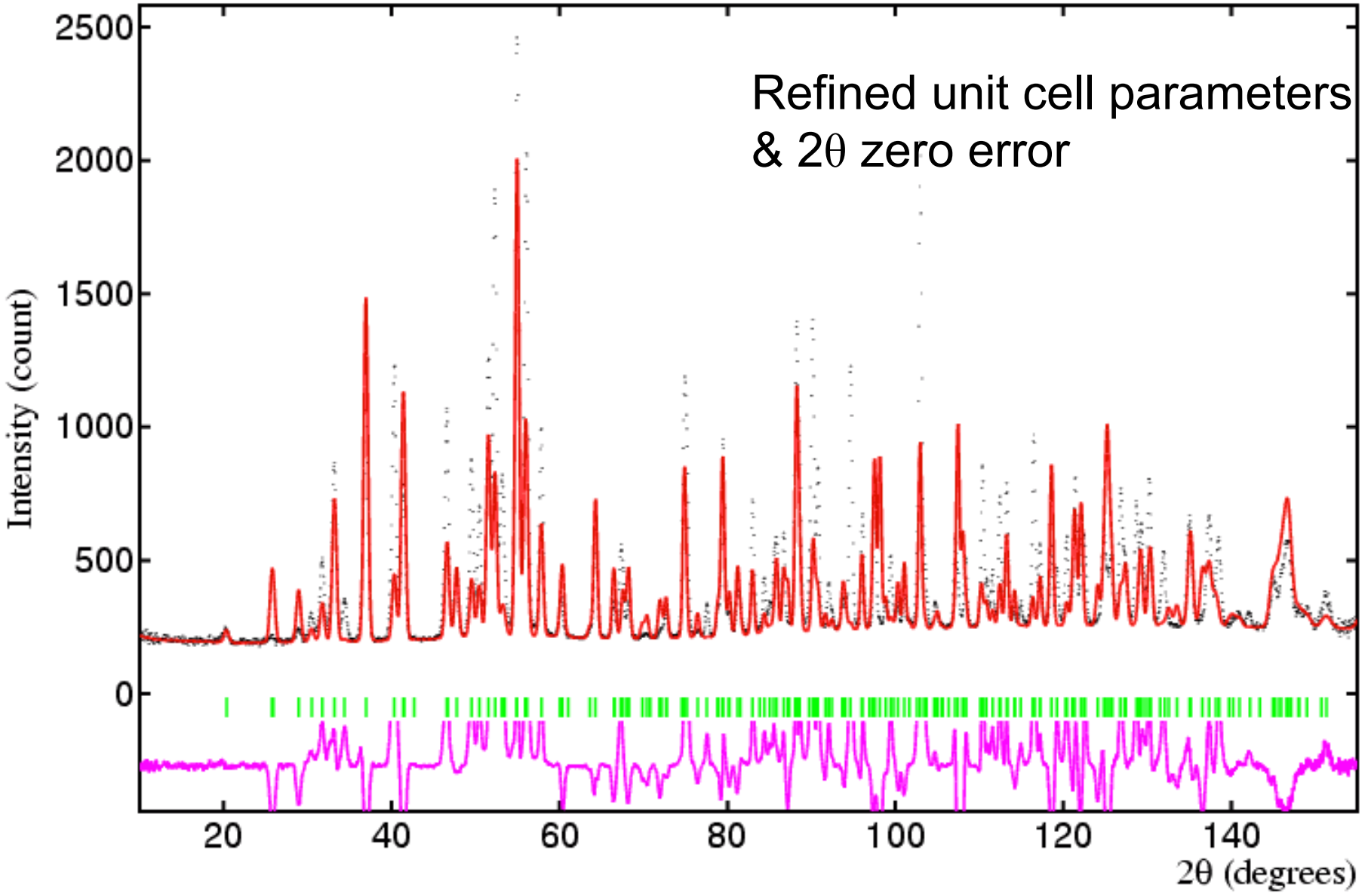
  λ = 1.909 Å, U = 0.2°^{2}, V = –0.5°^{2}, W = 0.5°^{2}


Background set graphically
Intensity (count)
2500
2000
1500
1000
500
0
20
40
60
80
100
120
140
2θ (degrees)

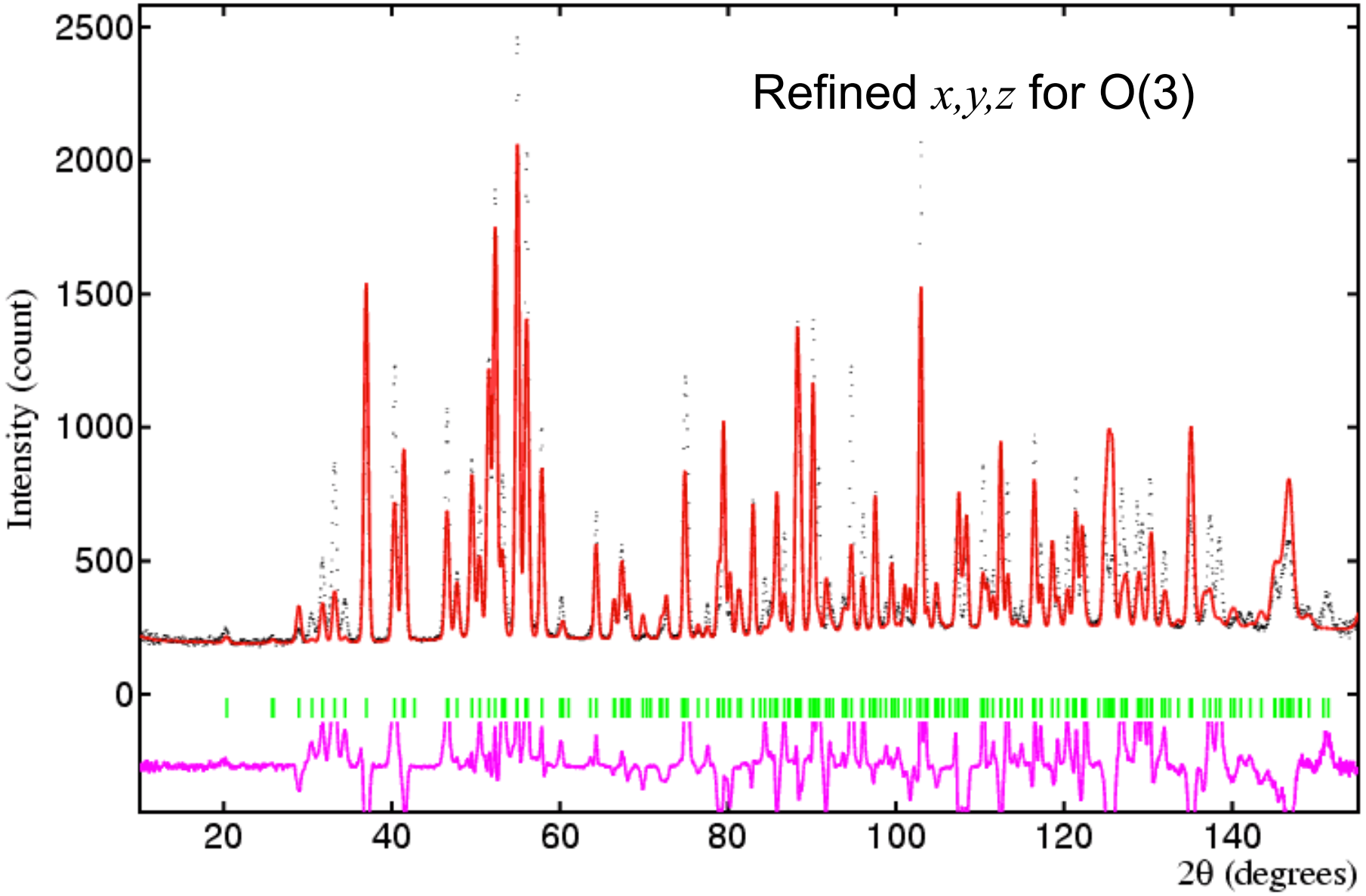
R_{wp} = 100%


Refined scale factor c
Intensity (count)
2500
2000
1500
1000
500
0
20
40
60
80
100
120
140
2θ (degrees)

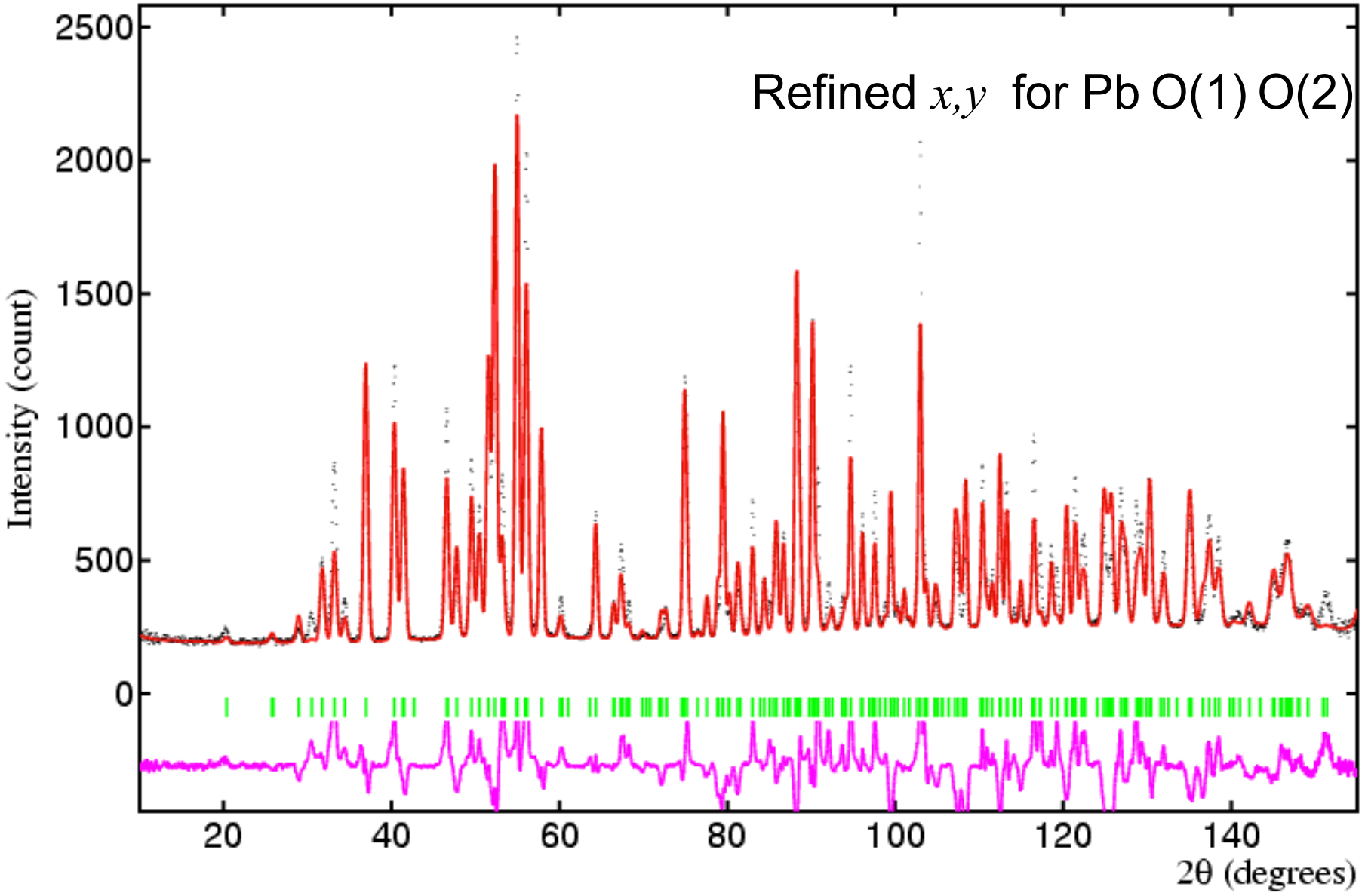
R_{wp} = 81%


Refined unit cell parameters
& 2θ zero error
Intensity (count)
2500
2000
1500
1000
500
0
20
40
60
80
100
120
140
2θ (degrees)

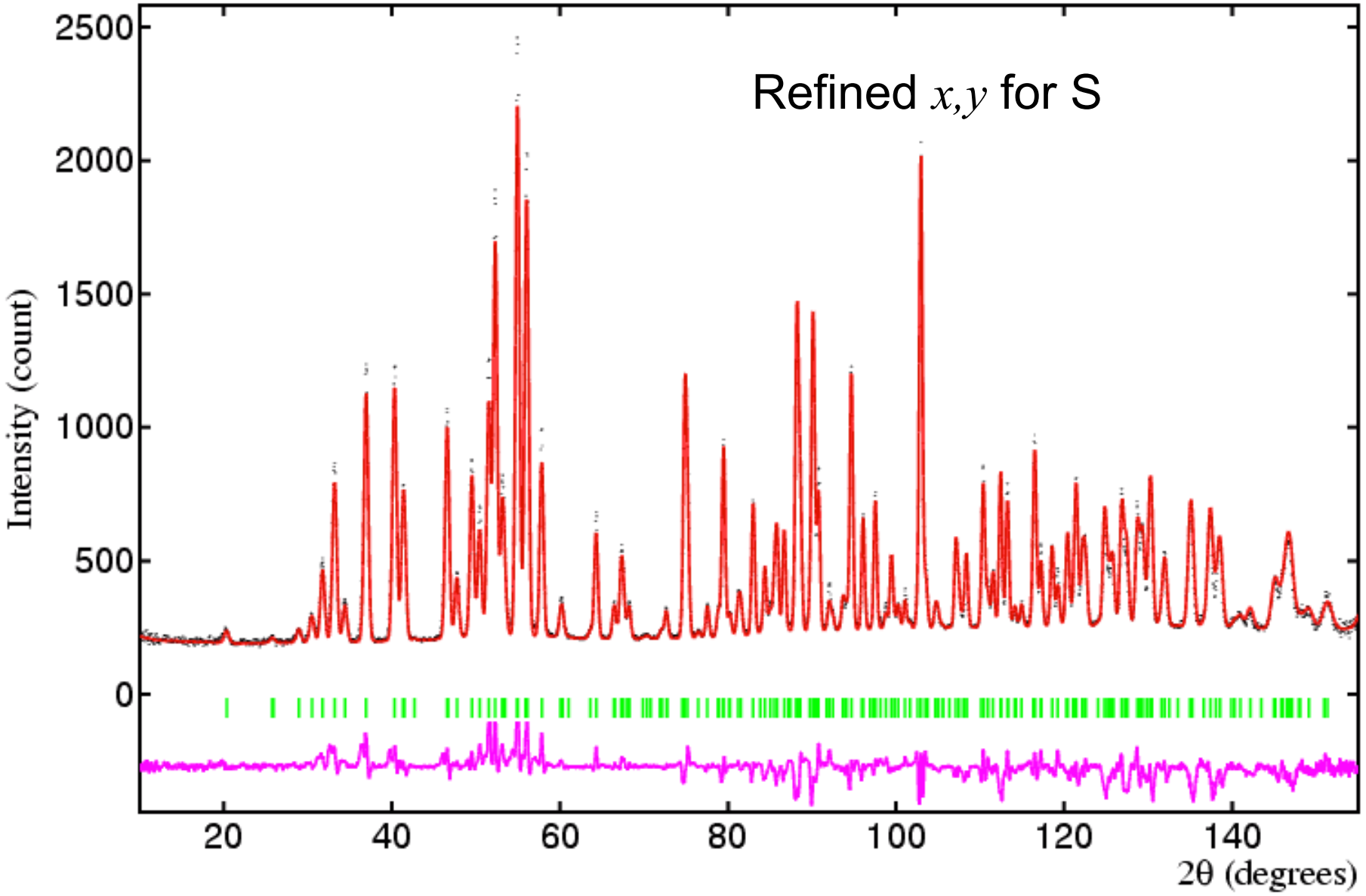
R_{wp} = 61%


Refined x,y,z for O(3)
Intensity (count)
2500
2000
1500
1000
500
0
20
40
60
80
100
120
140
2θ (degrees)

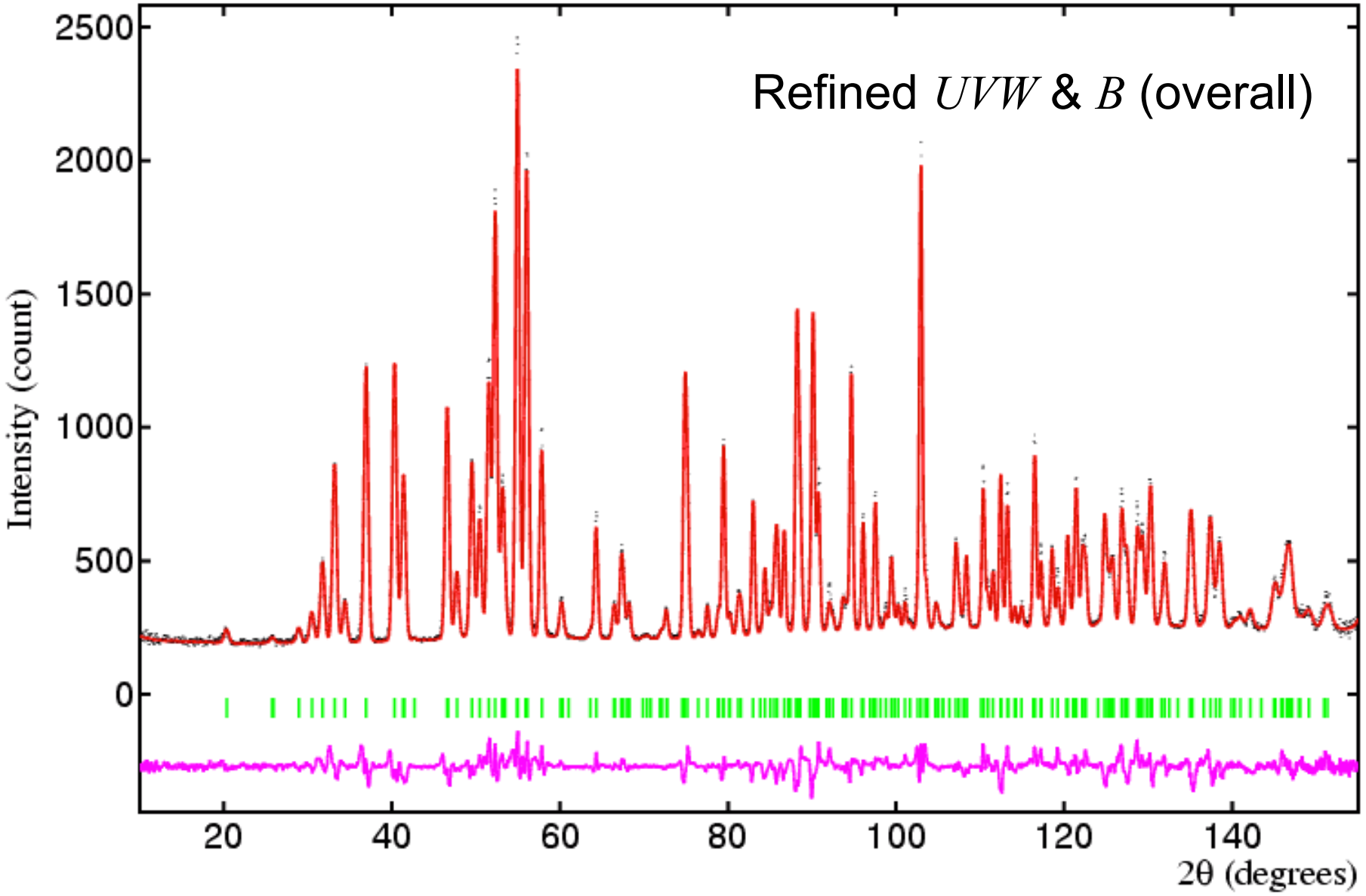
R_{wp} = 42.4%


Refined x,y for Pb O(1) O(2)
Intensity (count)
2500
2000
1500
1000
500
0
20
40
60
80
100
120
140
2θ (degrees)

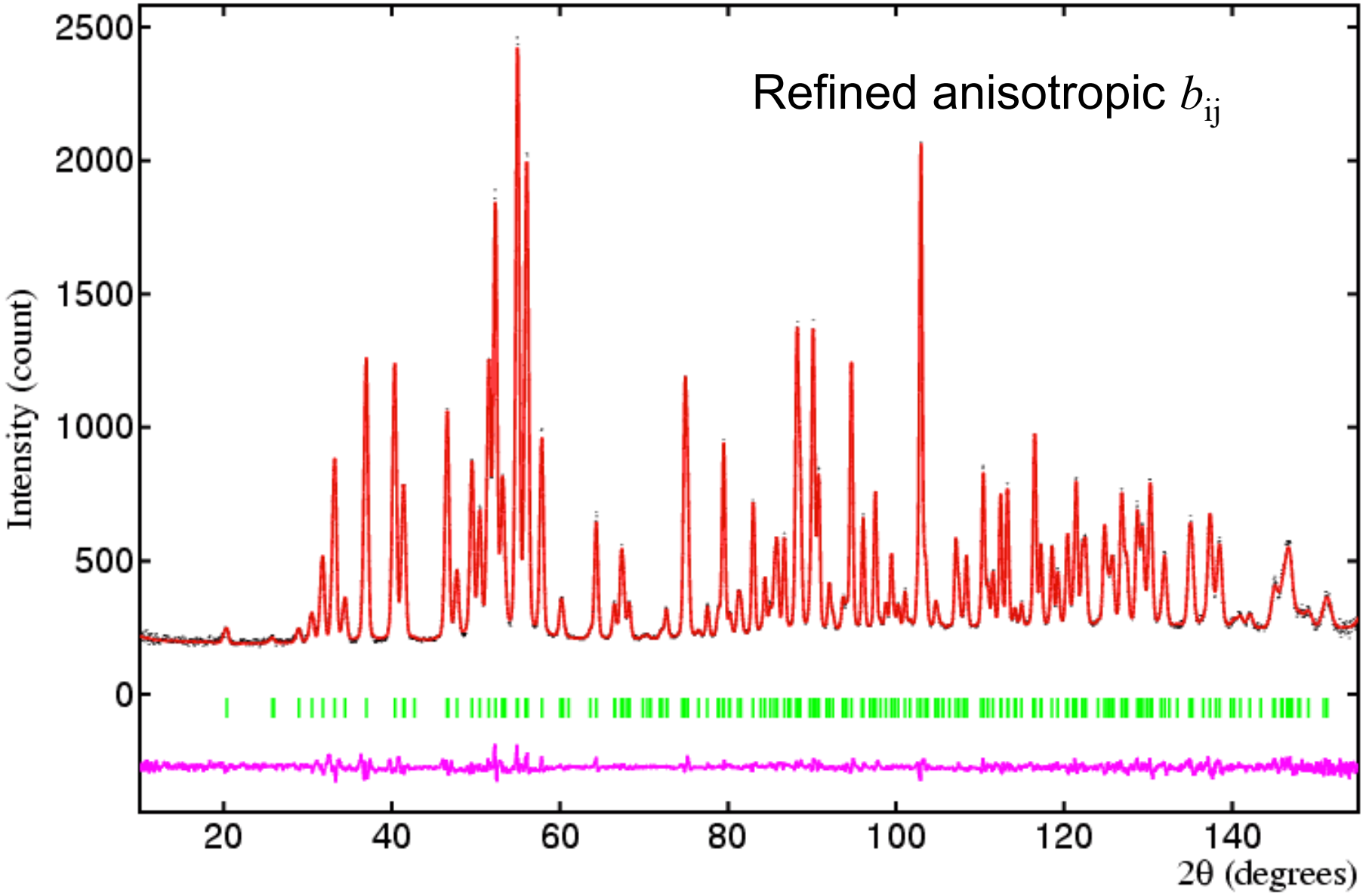
R_{wp} = 29.4%


Refined x,y for S
2500
2000
1500
1000
500
0
Intensity (count)
20
40
60
80
100
120
140
2θ (degrees)

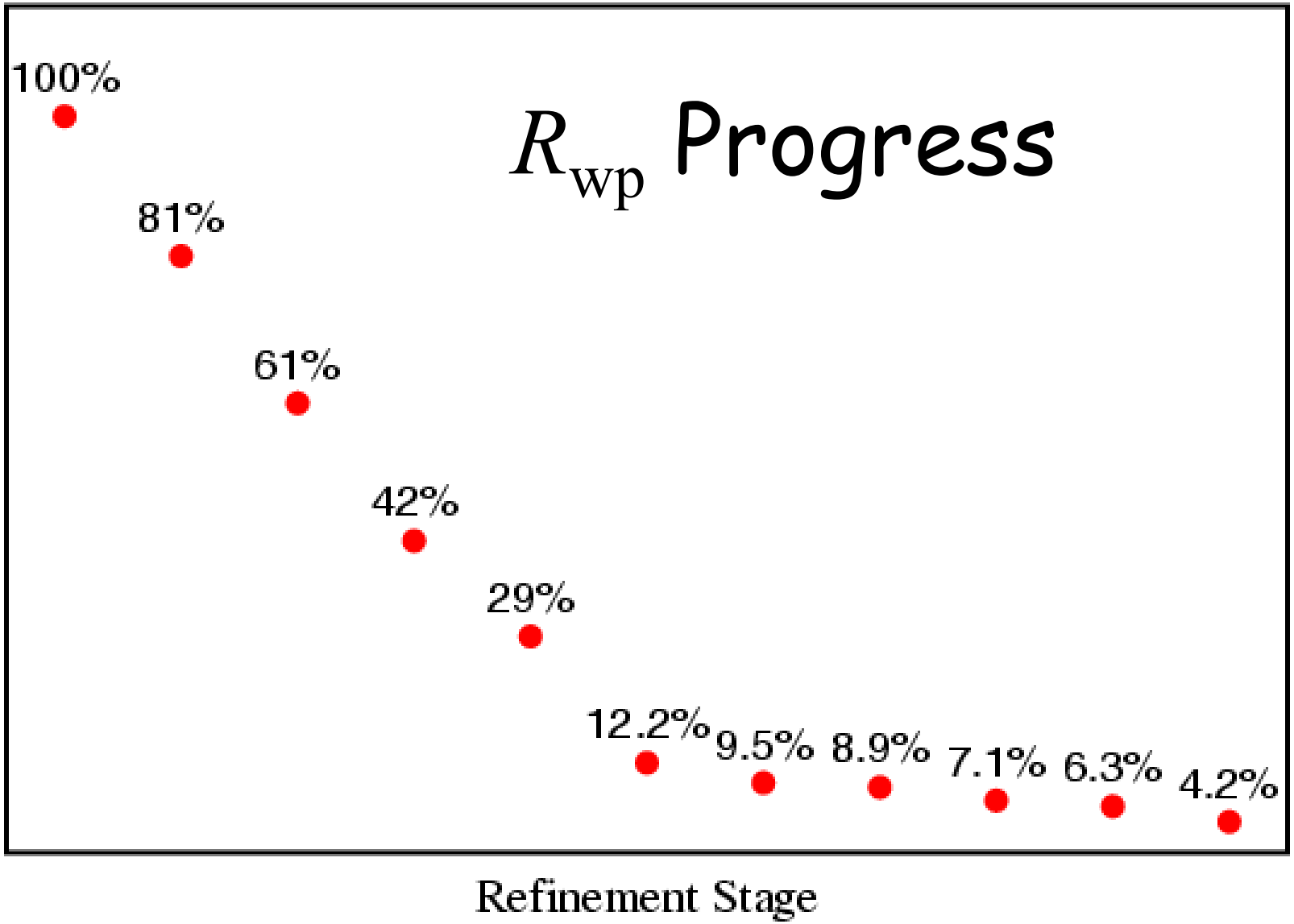
R_{wp} = 12.2%


Refined UVW & B (overall)
Intensity (count)
2500
2000
1500
1000
500
0
20
40
60
80
100
120
140
2θ (degrees)

R_{wp} = 6%


Refined anisotropic b_{ij}
Intensity (count)
2500
2000
1500
1000
500
0
20
40
60
80
100
120
140
2θ (degrees)

R_{wp} = 4.2%


R_{wp} Progress
100%
81%
61%
42%
29%
12.2%
9.5%
8.9%
7.1%
6.3%
4.2%
R-factor
Refinement Stage

Final Message

- Be very self critical about the quality of your powder diffraction data fits
  - Are you getting the most out of your data?
  - Is your model correct?
- Peak positions
  - Unit cell shape and size
- Peak intensities
  - Unit cell contents
- Peak shape
  - Instrumental and sample effects

Lecture Notes

Lecture Notes

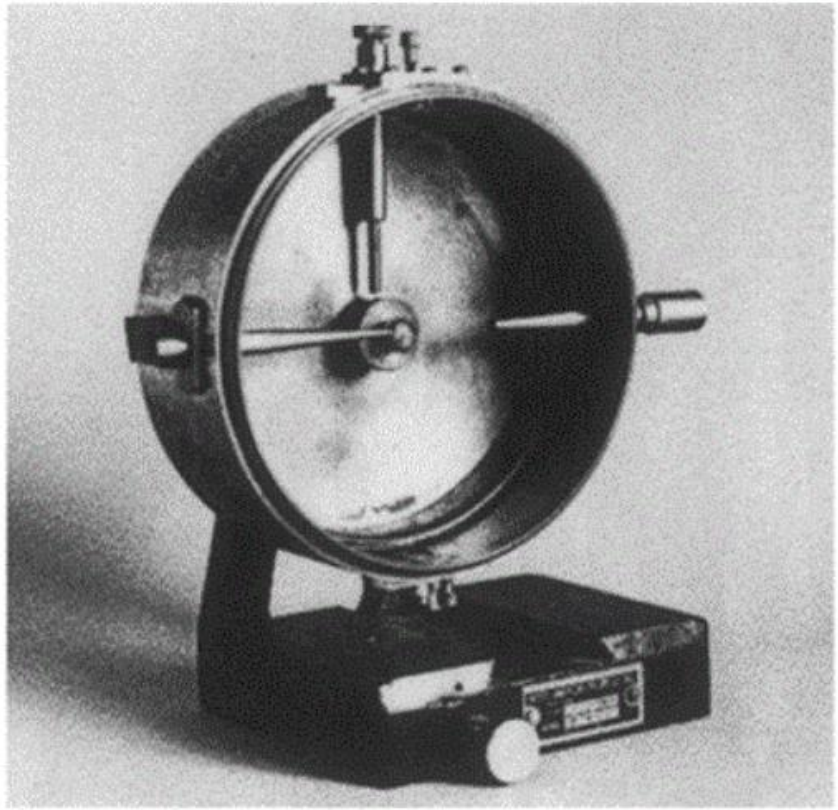
Session 10: Collecting XRPD data

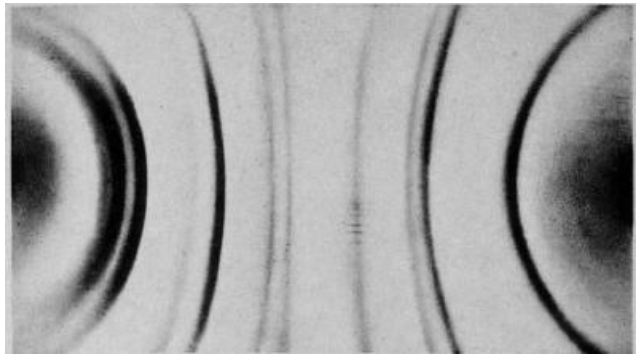
Dr Emma E. McCabe

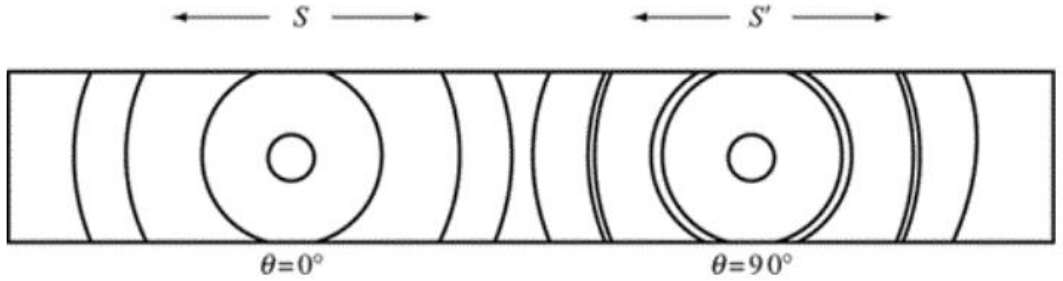
Durham University, Department of Physics

Lecture Outline

1. Common laboratory configurations
2. How to collect (laboratory) data
3. Sample preparation
4. Factors that affect peak positions
5. Factors that affect peak intensities
6. XRPD and sample preparation “crimes” 😱

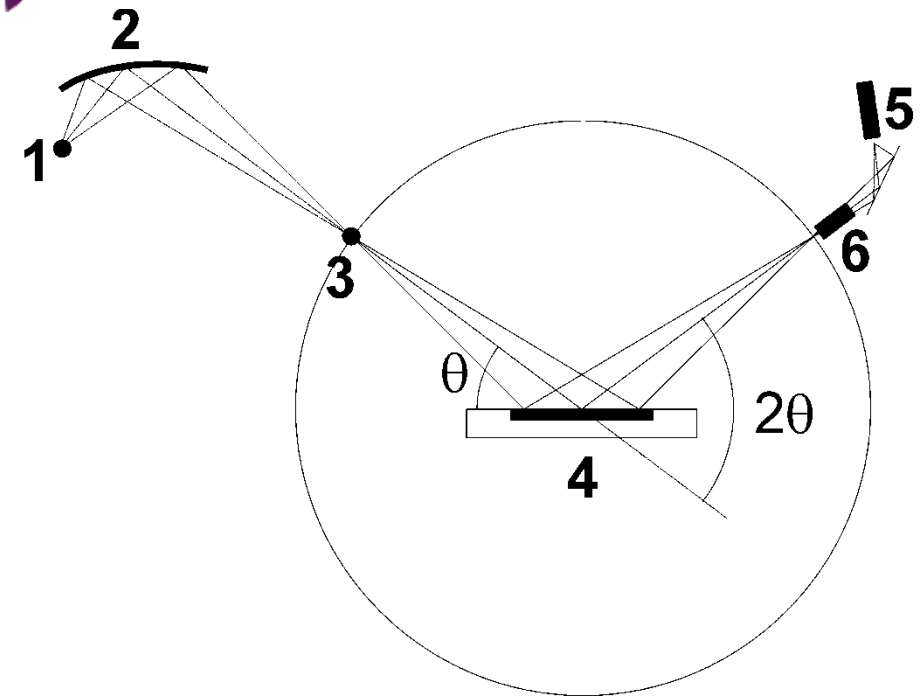






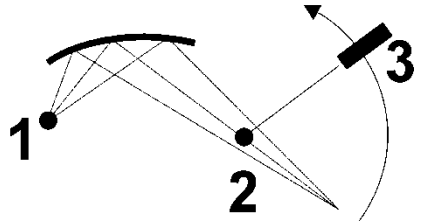
Fundamentals of Crystallography, editor: Giacovazzo, IUCr Oxford Science Publications, 2008

Laboratory XRPD configurations: focusing/parafocusing diffractometers



Reflection geometry

1: Source
2: incident beam monochomator
3: tube focal point
4: sample
5: detector (with diffracted beam monochromator)
6: detector (without diff. beam mono.)

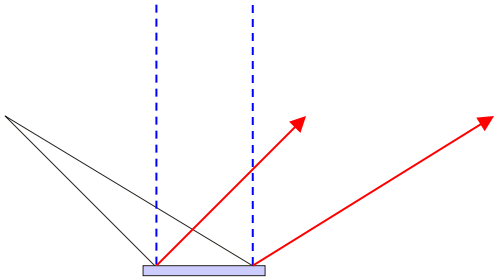


Transmission geometry

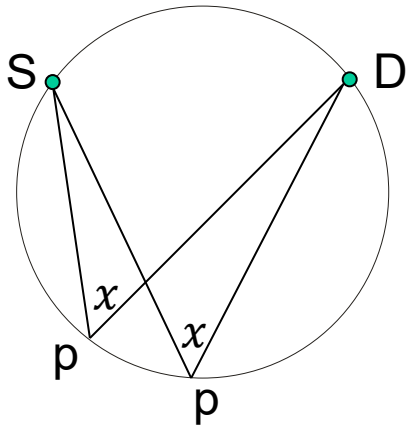
1: Source
2: sample
3: detector (without diff. beam mono.)

Laboratory XRPD configurations: reflection geometry

- Why does reflection geometry work?

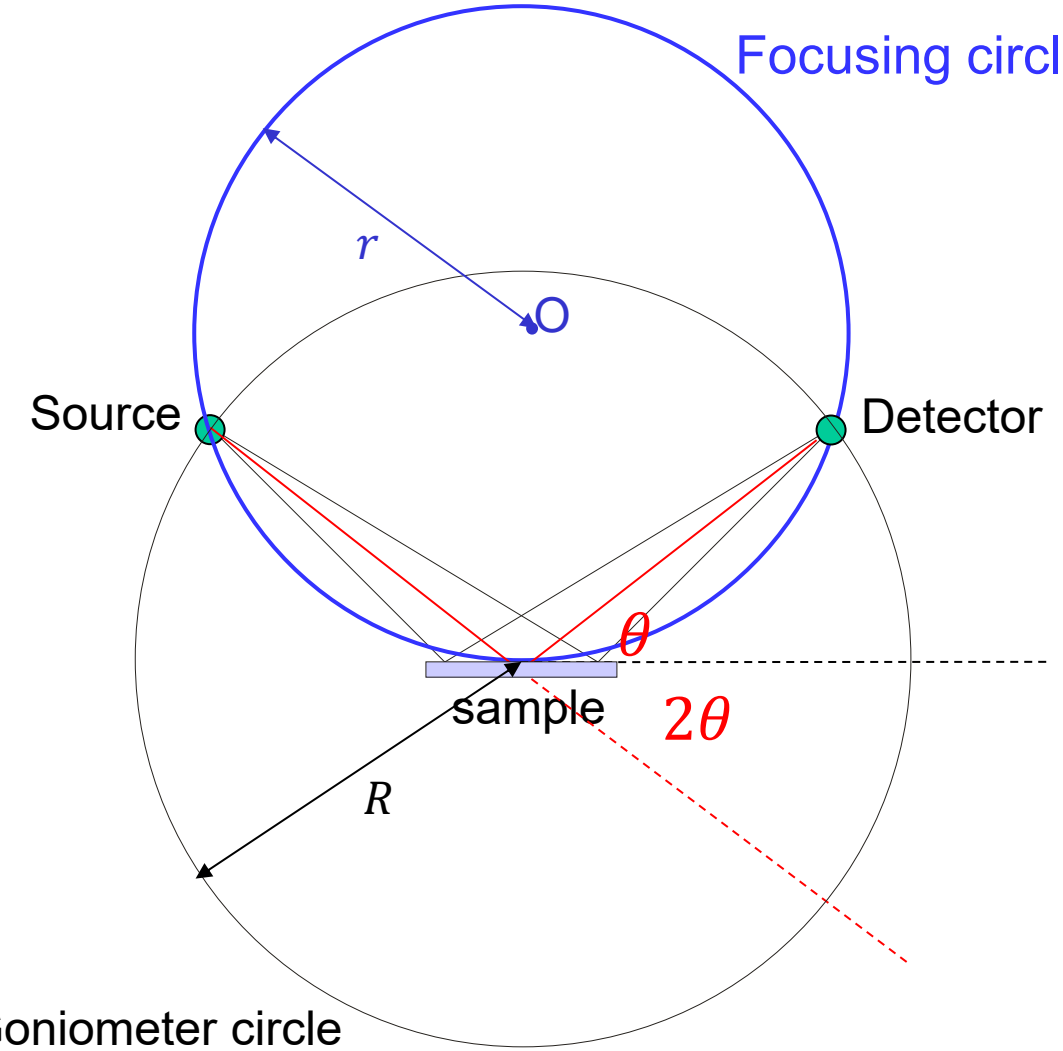


the law of reflection



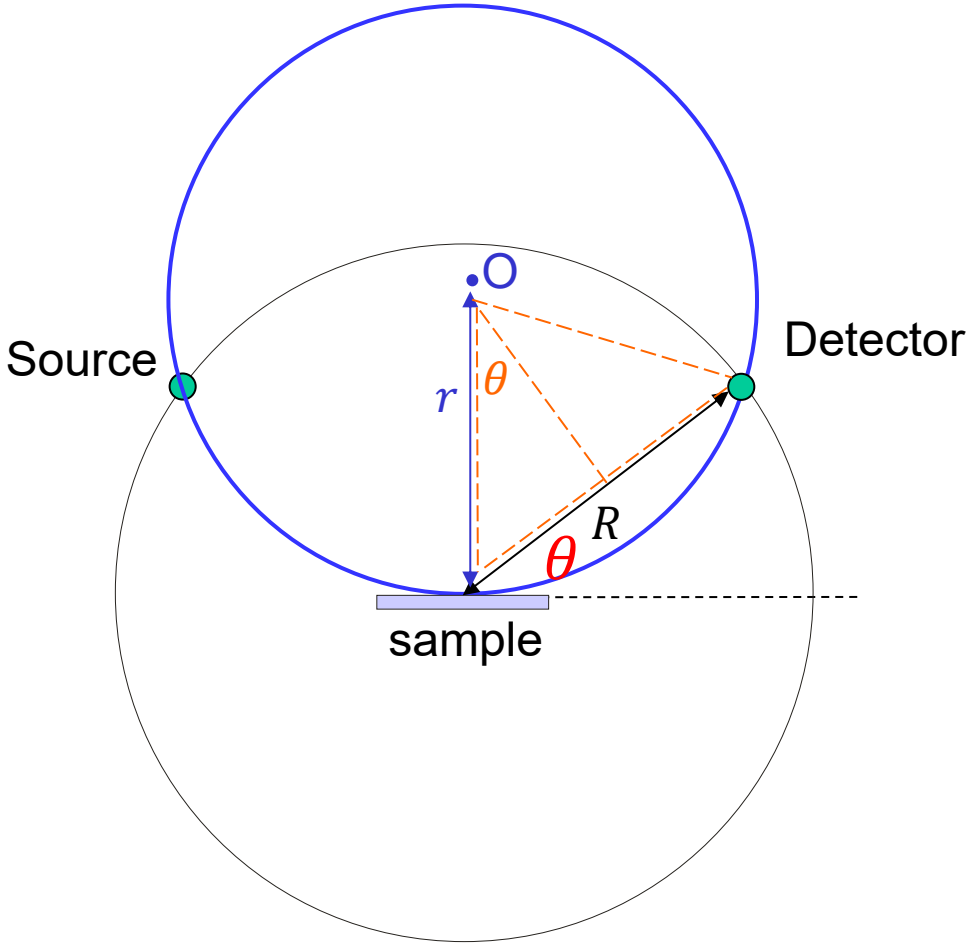
Euclid's "The Elements", Book III

"the angles in the same segment of a circle are equal to one another"



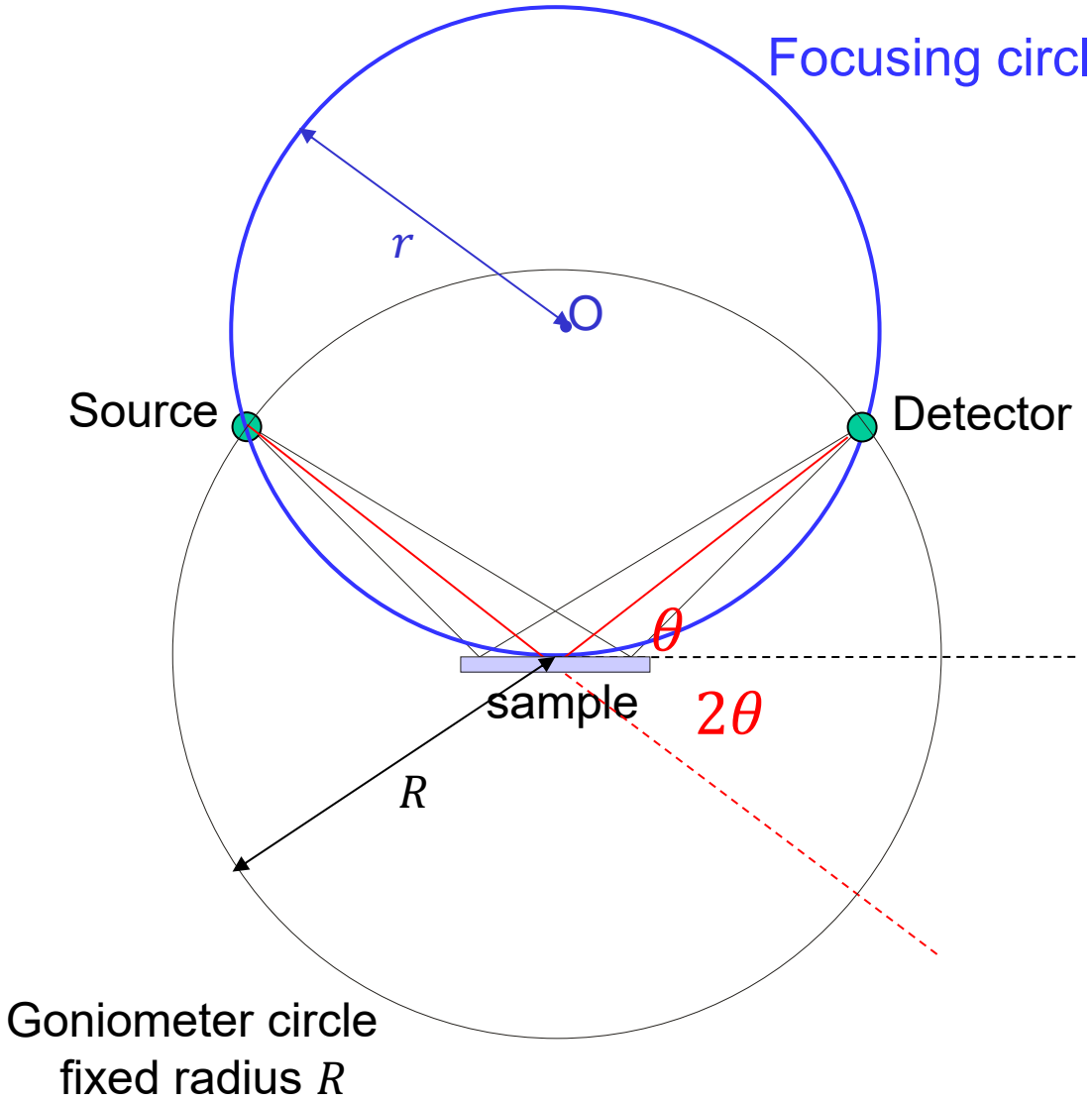
Goniometer circle
fixed radius R

Laboratory XRPD configurations: reflection geometry



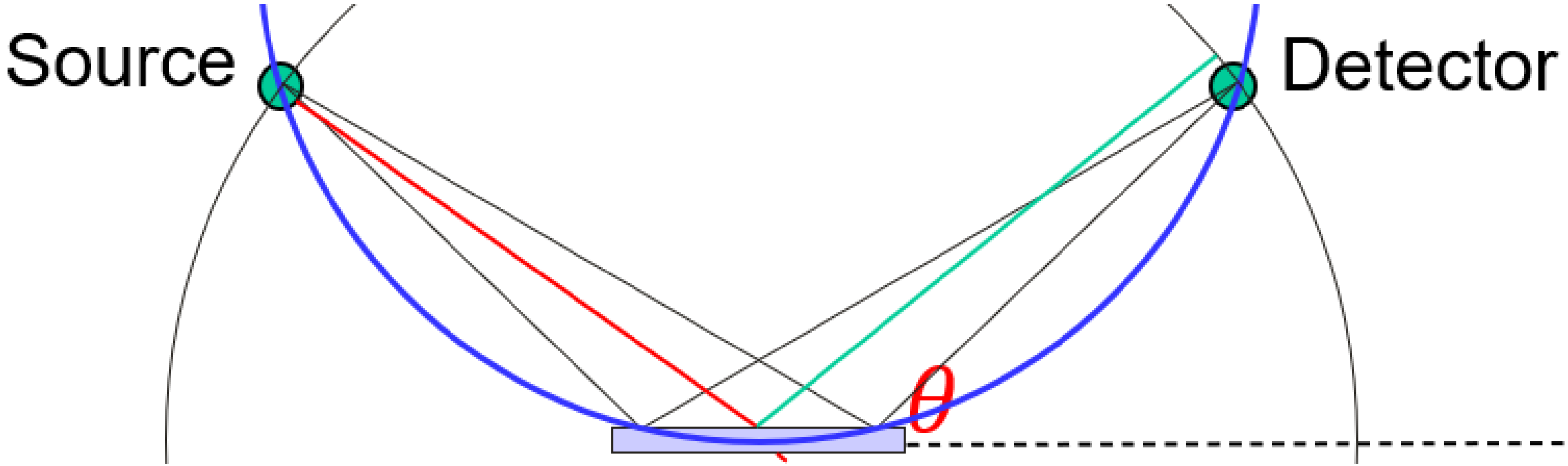
$$r \sin\theta = \frac{R}{2} \quad \therefore \quad r = \frac{R}{\sin\theta}$$

radius $r = \infty$ for $2\theta = 0°$;
$r = {}^{R}/_{2}$ for $2\theta = 180°$.



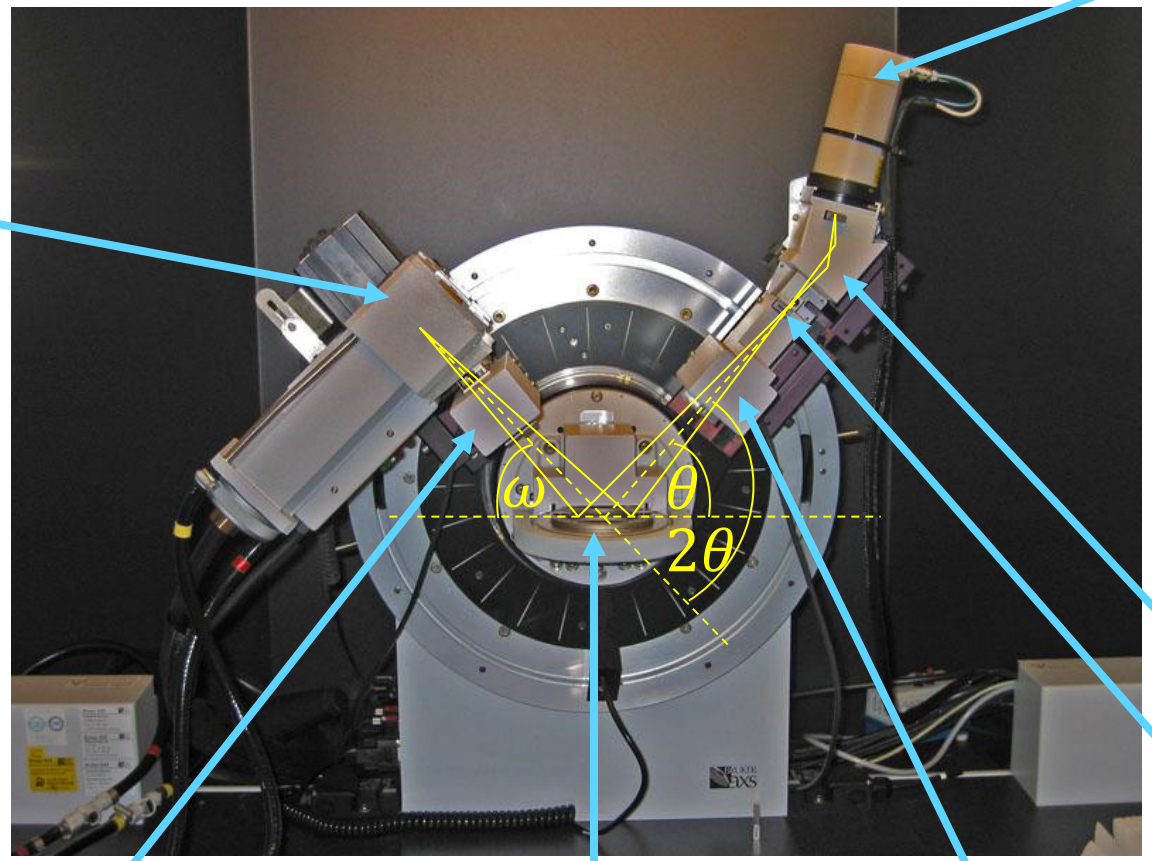
Laboratory XRPD configurations: reflection geometry

- Parafocusing geometry



Laboratory XRPD configurations: Bragg-Brentano

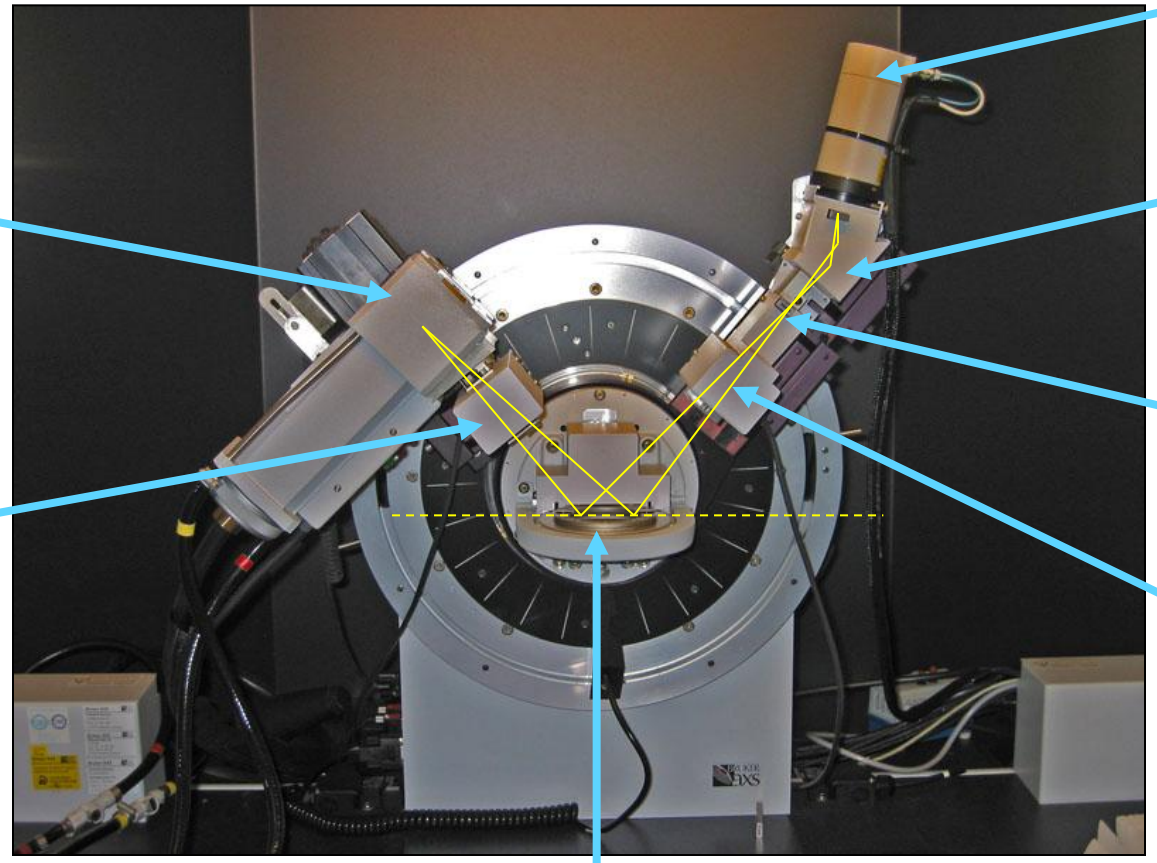
- Parafocusing geometry: Bragg-Brentano



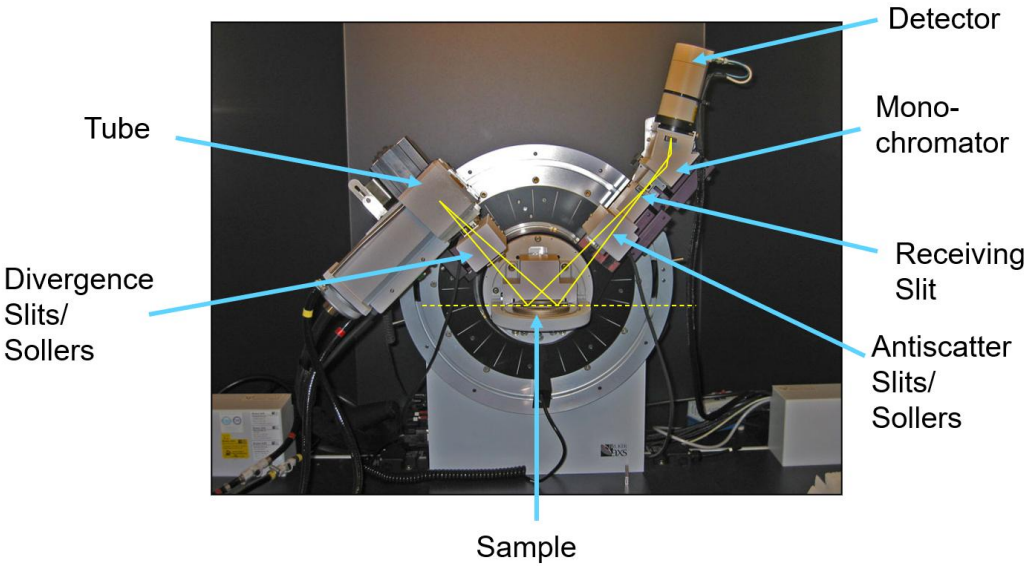
- $\theta - \theta$ scan:
  - sample fixed horizontal
  - tube and detector move
- $\theta - 2\theta$ or $\omega - 2\theta$ scan:
  - X-ray tube fixed
  - sample tilts such that ω is half of detector angle

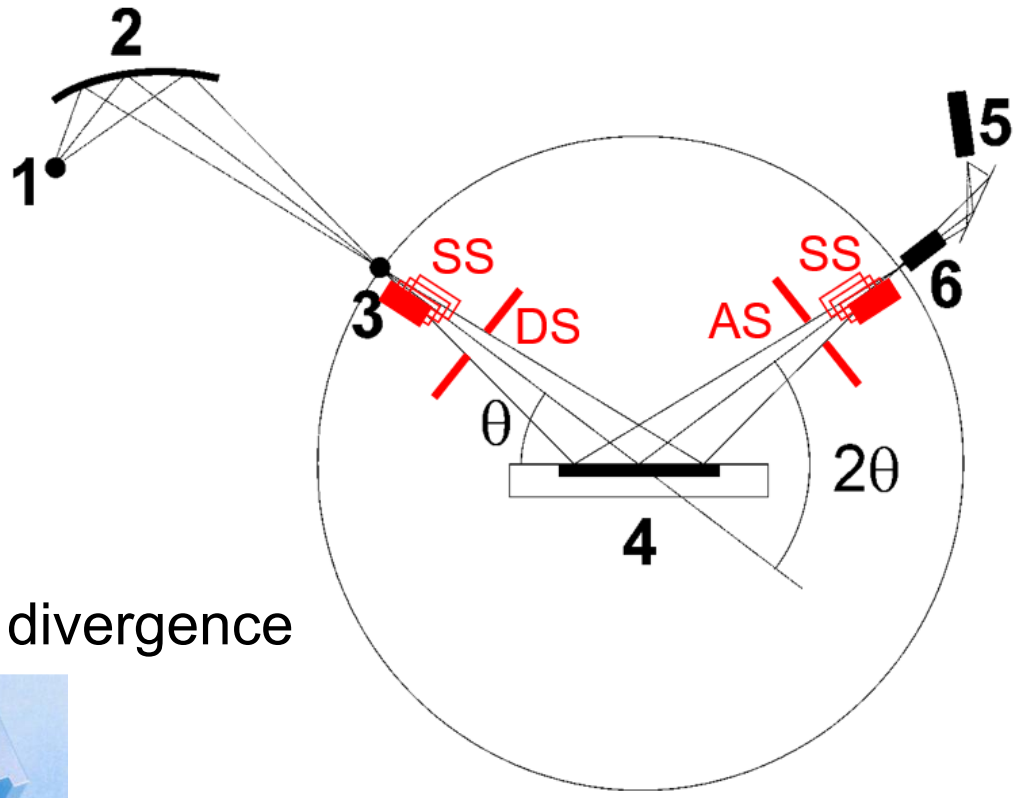
Laboratory XRPD configurations: Bragg-Brentano

- Parafocusing geometry: Bragg-Brentano



Laboratory XRPD configurations: Bragg-Brentano





Optics:

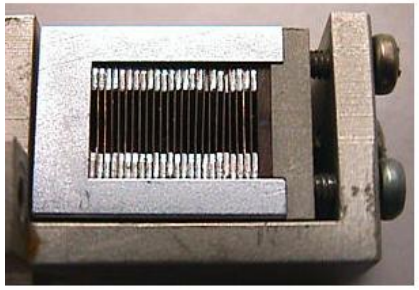
DS: divergence slits

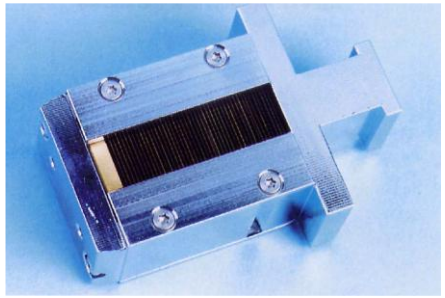
SS: Soller slits

AS: anti-scatter slits

RS: receiving slits

- Soller slits: reduce out-of-plane (axial) divergence

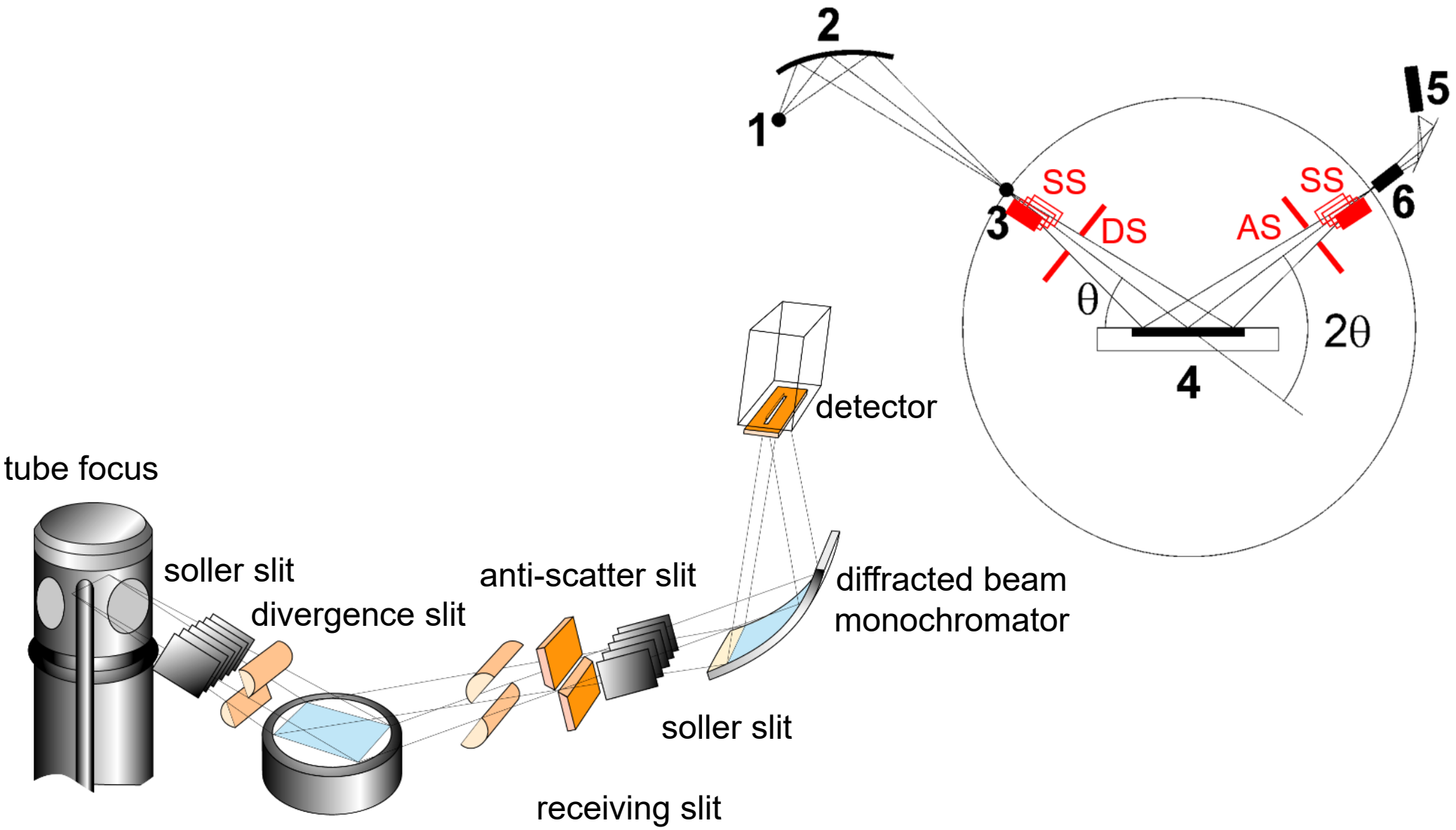




- Divergence, antiscatter slits: reduce in-plane (equatorial) divergence

1: Source
2: incident beam monochomator
3: tube focal point
4: sample
5: detector (with diffracted beam monochromator)
6: detector (without diff. beam mono.)

Laboratory XRPD configurations: Bragg-Brentano



Optics:

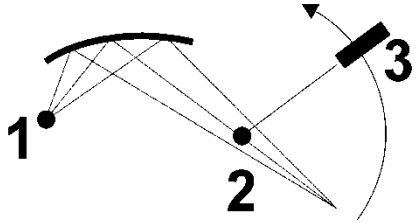
DS: divergence slits

SS: Soller slits

AS: anti-scatter slits

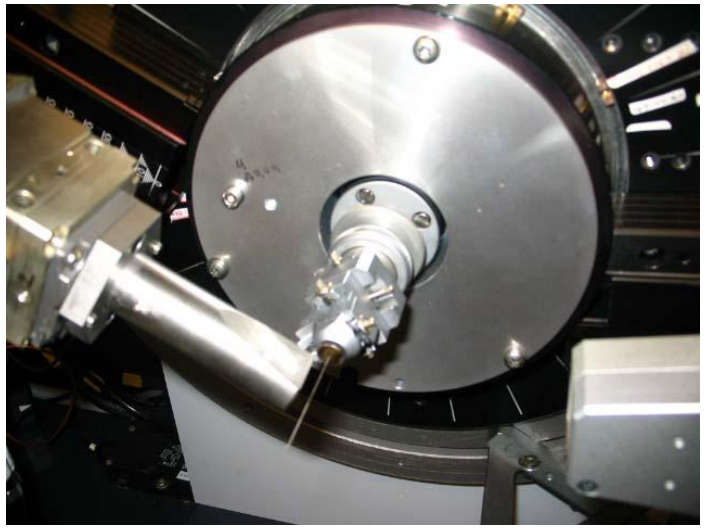
RS: receiving slits

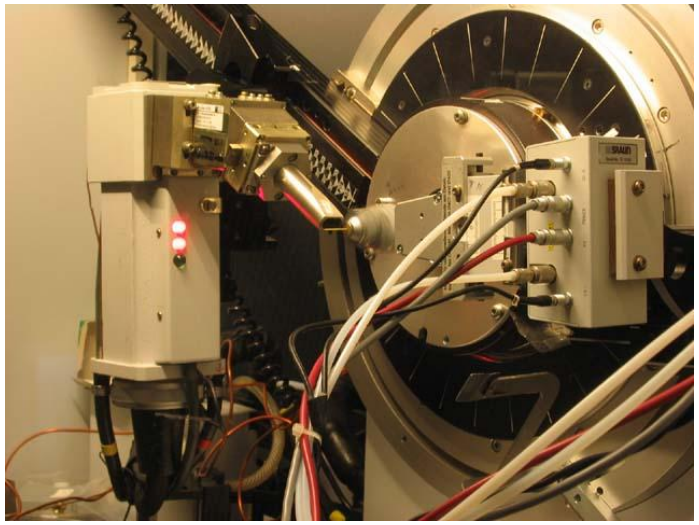
Laboratory XRPD configurations: transmission capillary



Transmission geometry

1: Source
2: sample
3: detector (without diff. beam mono.)





- Capillary size:
  - Impacts resolution
  - Absorption: https://11bm.xray.aps.anl.gov/absorb/
    - mass attenuation coefficient (or mass absorption coefficient) $\mu_m = \frac{\mu}{\rho}$ is quoted (cm^2/g)
    - $\mu_{sample\ in\ capillary} = \left[\rho_{sample\ in\ capillary} \sum_i \left(\frac{\mu}{\rho}\right)_i \omega_i\right] \times packing\ fraction$
    - want $\mu_m r < 1.5$, r = capillary radius

μ = linear absorption coefficient

ρ = density

ω_i = mass % of element i

Powder diffraction: experiment aims and set-up

- Powder diffraction sample must be:
  - An ensemble of an “infinite” number of randomly oriented crystallites;
  - Representative of the bulk of the sample.

- Experiment aims inform sample preparation, instrument configuration & data collection:
  - Phase identification: rapid data collection, less need for higher angles (lower d-spacing).
  - Indexing: lower angle (higher d-spacing) peaks important; consider internal standard.
  - Structure solution: wide d-spacing range; high resolution; high intensity.
  - Rietveld refinement: highest quality data in time available.

Data collection

- Depends on the instrument:
  - Is the configuration and set-up suitable for your aims?

- Statistics and count rate:
  - Are the statistics good enough for your aims?
  - Consider counting for longer at higher 2θ to account for decrease in form factor.
  - Do you have sufficient points to define a peak (e.g. 10 across FWHM)?

- First guess on a lab instrument might be:
  - 5-90° 2θ, 0.02° step, 1 second per step, ~1 hour
  - 8-68° 2θ, 0.01° step, 2.2° min^{-1}, ~30 mins to monitor synthesis

Sample preparation

- Grinding the powder:
  - ensures homogeneity;
  - decreases particle size.

agate mortar & pestle

McCrone micronizing mill

ball mill

- Possible concerns:
  - Structural phase transitions or reactions (small organics);
  - Strain-induced peak broadening;
  - (partial) amorphisation.

- Flat plate sample holders:
  - bulk;
  - sprinkled;
    - wafers of Si single crystal for low background.

https://www.bruker.com/en/products-and-solutions/diffractometers-and-x-ray-microscopes/x-ray-diffractometers/davinci-components/specimen-holders.html

Factors that affect peak positions

$$2\theta_{obs} = 2\theta_{obs} + \Delta 2\theta$$

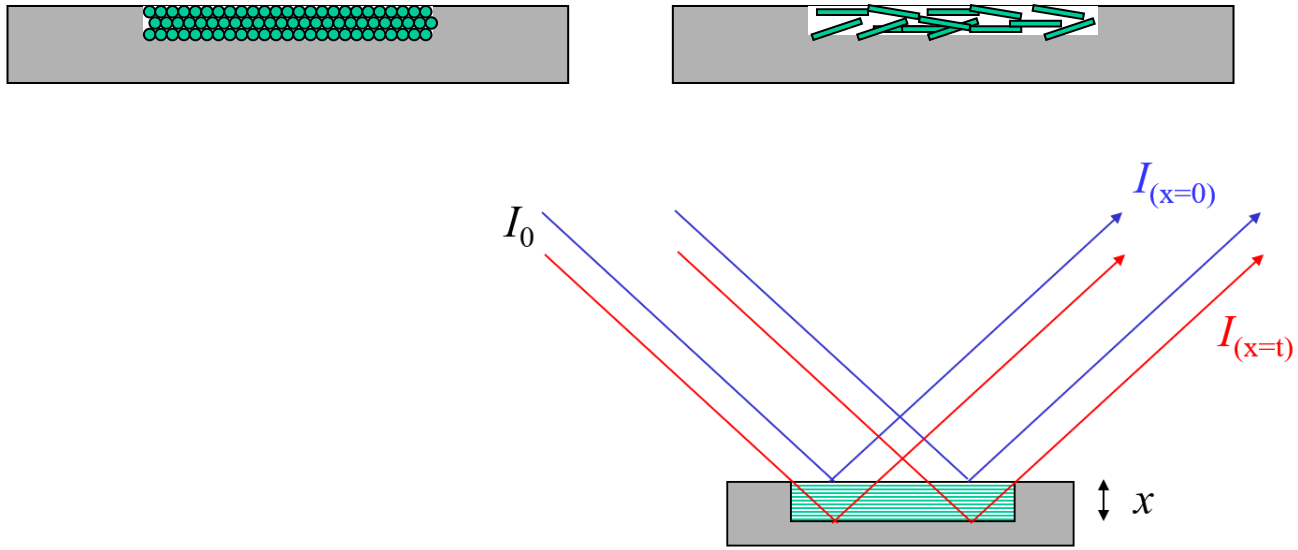
$$\Delta 2\theta = \frac{p_1}{\tan 2\theta} + \frac{p_2}{\sin 2\theta} + \frac{p_3}{\tan \theta} + p_4 \sin\theta + p_5 \cos\theta + p_6$$

- p_1, p_2 : incident beam axial divergence; peak asymmetry (p_1)
  - Correct axial divergence using Soller slits
  - Some asymmetry due to finite detector receiving slit width
- p_3: incident beam in-plane divergence (small effect, due to sample curvature)
- p_4: absorption (transparency shift error)
  - Due to X-rays penetrating sample, $p_4 = \left(2\mu_{eff}R\right)^{-1}$
  - Important for thick (>50-1000 μm) samples with low absorption coefficients
- p_5: sample displacement (displacement off goniometer axis)
- p_6: zero error (instrument misalignment, error in source/detector zero angles)

Factors that affect peak intensities

$$I_{hkl} = K \times |F_{hkl}|^2 \times P_{hkl} \times E_{hkl} \times T_{hkl} \times (LP)_\theta \times A_\theta \times DW_\theta$$

- K: scale factor
- F_{hkl}: structure factor
- P_{hkl}: multiplicity
- E_{hkl}: extinction
- T_{hkl}: preferred orientation
- $(LP)_\theta$: Lorentz-polarisation factor
- A_θ: absorption
- DW_θ: Debye-Waller factor



$$f_T = f \exp\left(\frac{-B \sin^2 \theta}{\lambda^2}\right)$$

$B = 8\pi^2\langle u^2 \rangle$ $\langle u^2 \rangle$ = root mean square displacement of atom from average position

XRPD and sample preparation “crimes” 😢

Factors that affect peak positions

$$2\theta_{obs} = 2\theta_{obs} + \Delta 2\theta$$

$$\Delta 2\theta = \frac{p_1}{\tan 2\theta} + \frac{p_2}{\sin 2\theta} + \frac{p_3}{\tan \theta} + p_4 \sin\theta + p_5 \cos\theta + p_6$$

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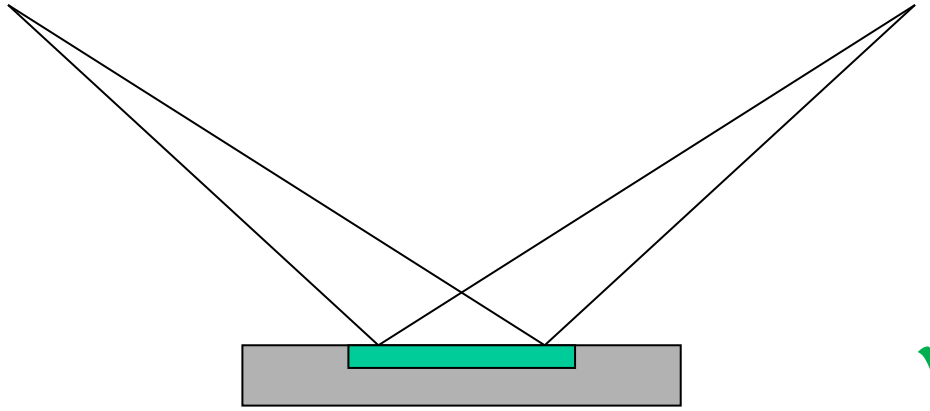
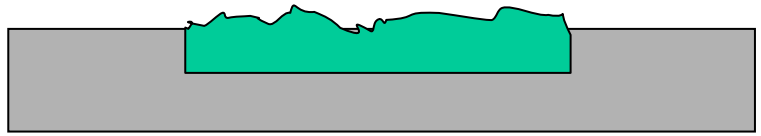
- Sample height:
  sample displaced off goniometer axis

```
2θ offset = zero - 2*Δheight*cos(θ)/radius;
```





XRPD and sample preparation ~~"crimes"~~ 😷

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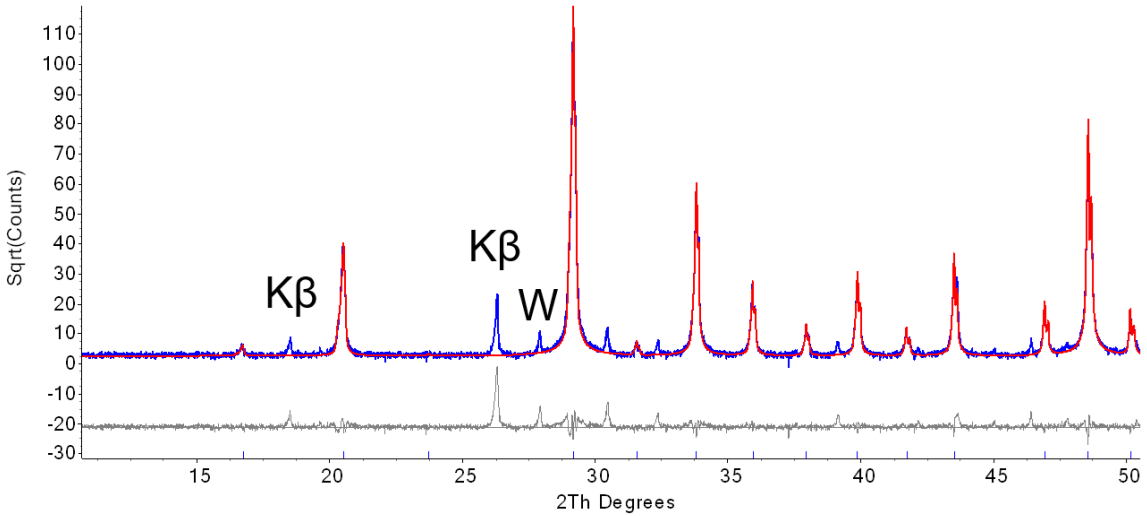


- Additional wavelengths:
  - $K_{\alpha 1}$ and $K_{\alpha 2}$ if monochromator not aligned.
  - Cu K_β ($\lambda = 1.392$ Å) if Ni foil too thin.
  - Old X-ray tubes can give W L_α ($\lambda = 1.476$ Å) from tungsten filament.

XRPD and sample preparation “crimes” 😢

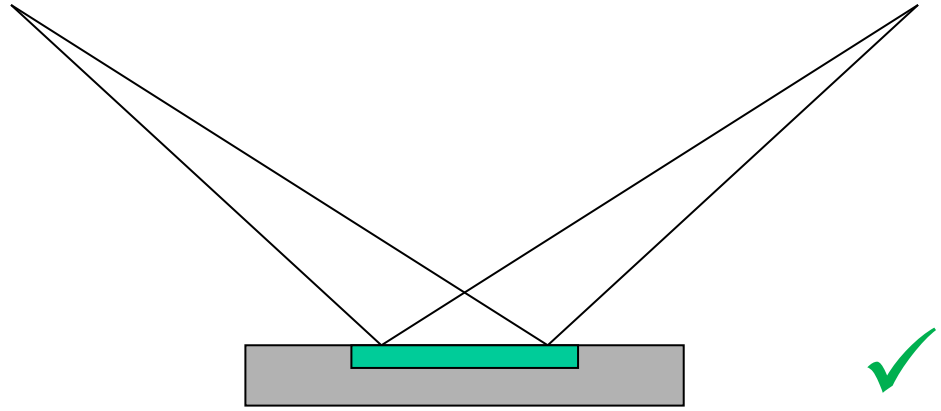
Factors that affect peak intensities

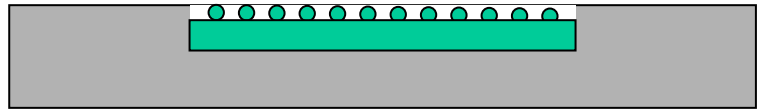
$$I_{hkl} = K \times |F_{hkl}|^2 \times P_{hkl} \times E_{hkl} \times T_{hkl} \times (LP)_\theta \times A_\theta \times DW_\theta$$

- K: scale factor
- F_{hkl}: structure factor
- P_{hkl}: multiplicity
- E_{hkl}: extinction
- T_{hkl}: preferred orientation
- $(LP)_\theta$: Lorentz-polarisation factor
- A_θ: absorption
- DW_θ: Debye-Waller factor

➢ Surface roughness:

- intensity reduced as a function of 2θ
- reduced intensity for low angle peaks
- negative atomic displacement parameters





XRPD and sample preparation “crimes” 😢

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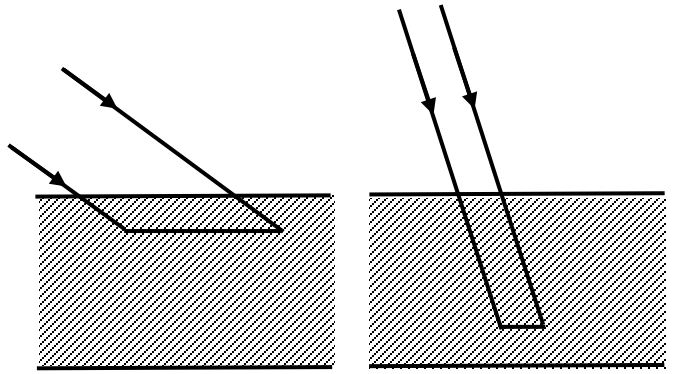
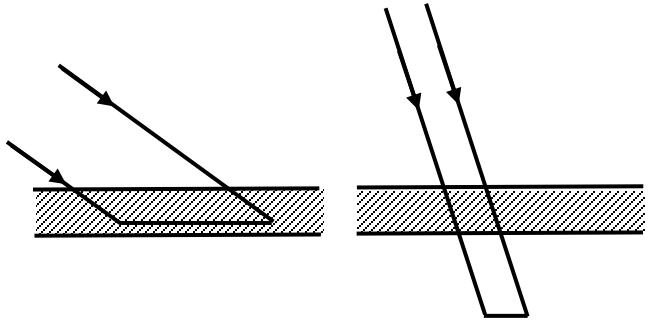


✓



✗

- Need infinitely thick sample to avoid intensities varying with 2θ
- Thick sample: constant volume probed as a function of 2θ
- Thin sample: diffraction volume varies with 2θ

XRPD and sample preparation “crimes” 😢

Factors that affect peak intensities

$$I_{hkl} = K \times |F_{hkl}|^2 \times P_{hkl} \times E_{hkl} \times T_{hkl} \times (LP)_\theta \times A_\theta \times DW_\theta$$

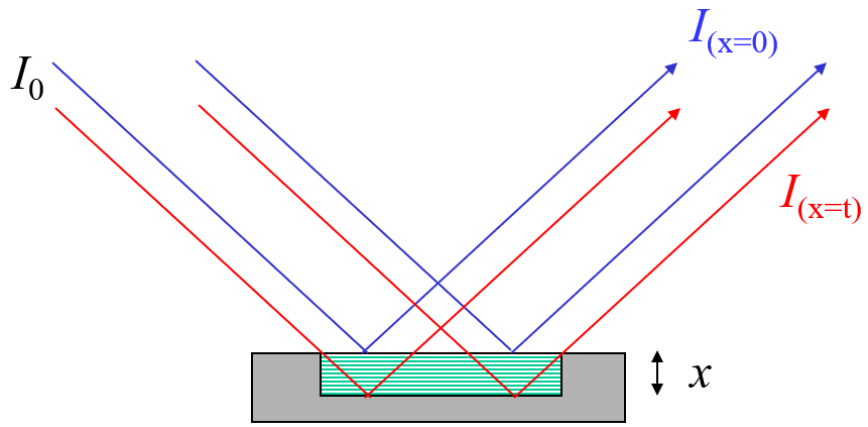
- K: scale factor
- F_{hkl}: structure factor
- P_{hkl}: multiplicity
- E_{hkl}: extinction
- T_{hkl}: preferred orientation
- $(LP)_\theta$: Lorentz-polarisation factor
- A_θ: absorption
- DW_θ: Debye-Waller factor

Intensity diffracted from depth x in sample:

$$I_x \propto \frac{I_0}{\sin\theta} \exp\left(\frac{-2\mu x}{\sin\theta}\right)$$

What is negligible diffracted intensity?

$$\frac{I_{x=0}}{I_{x=t}} = 1000$$



➢ Need infinitely thick sample to avoid intensities varying with 2θ

XRPD and sample preparation “crimes” 😱

Factors that affect peak intensities

$$I_{hkl} = K \times |F_{hkl}|^2 \times P_{hkl} \times E_{hkl} \times T_{hkl} \times (LP)_\theta \times A_\theta \times DW_\theta$$

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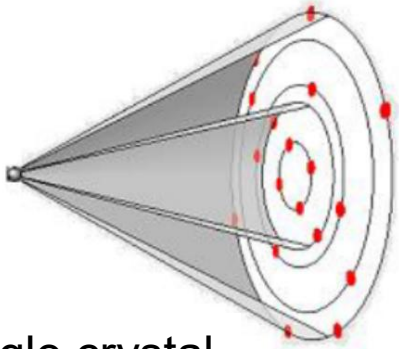
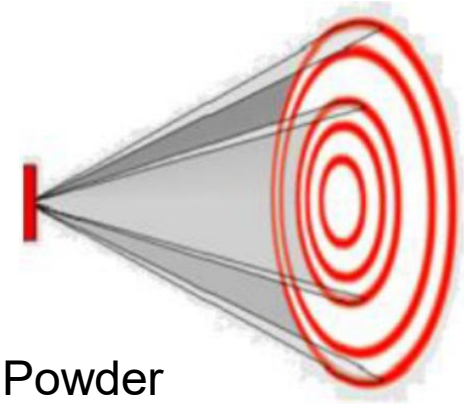
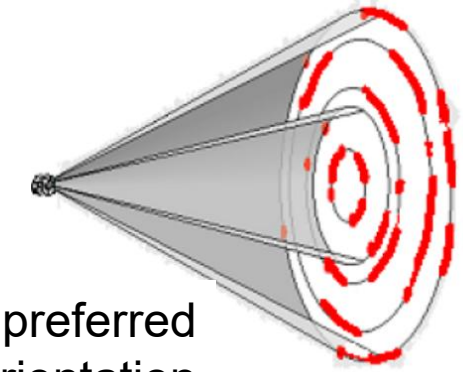


Single crystal

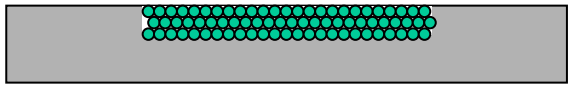


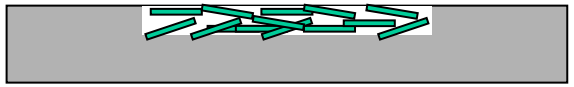
Powder



Texture / preferred orientation

➢ Loss of powder average giving systematic variation in intensities





https://www.icdd.com/assets/tutorials/HowtoAnalyzeMinerals-Fundamentals.pdf

XRPD and sample preparation “crimes” 😷

Factors that affect peak intensities

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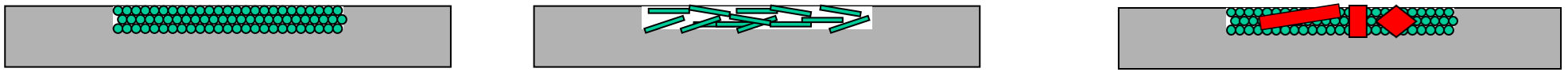
- T_{hkl}: preferred orientation
- $(LP)_\theta$: Lorentz-polarisation factor
- A_θ: absorption
- DW_θ: Debye-Waller factor

- How to avoid preferred orientation:
  - Capillary measurements
  - Sieving
  - Spray drying
  - Side/back mounting
  - Neutron diffraction
  - May be possible to correct for
- Texture:
  - Non-systematic errors in intensities
  - Harder to correct

- Loss of powder average giving systematic variation in intensities



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XRPD and sample preparation “crimes” 😢

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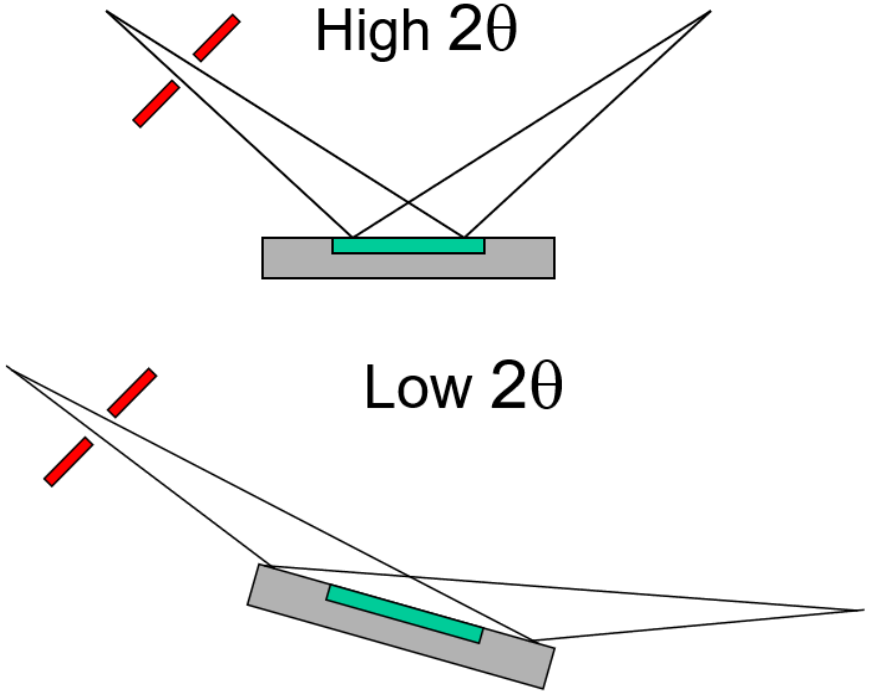
- DW_θ: Debye-Waller factor

➢ Area of beam must fall on sample for all 2θ:



➢ Intensities vary with 2θ:

- Smaller volume probed at high 2θ ∴ reduced intensities
- Scattering from sample holder at lower 2θ: extra peaks or increased background

https://www.icdd.com/assets/tutorials/HowtoAnalyzeMinerals-Fundamentals.pdf

XRPD and sample preparation ~~"crimes"~~ 😢

Factors that affect peak intensities

$$I_{hkl} = K \times |F_{hkl}|^2 \times P_{hkl} \times E_{hkl} \times T_{hkl} \times (LP)_\theta \times A_\theta \times DW_\theta$$

- K: scale factor
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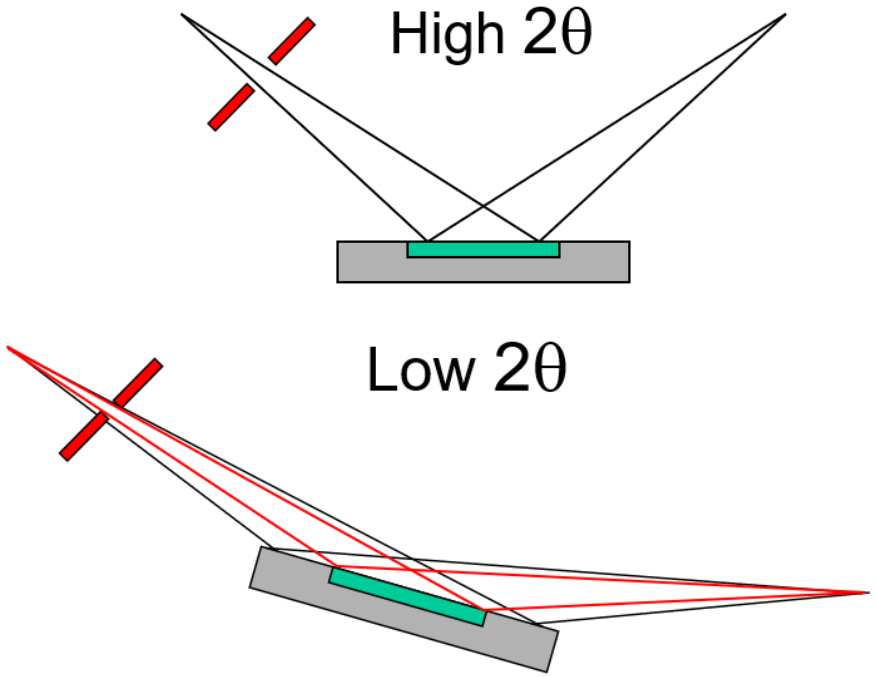
- P_{hkl}: multiplicity
- E_{hkl}: extinction
- T_{hkl}: preferred orientation
- $(LP)_\theta$: Lorentz-polarisation factor
- A_θ: absorption
- DW_θ: Debye-Waller factor

- Area of beam must fall on sample for all 2θ;
- **Variable slits** compensate for this:



- $\sin\theta$ correction
- Do not assume Poisson statistics as intensities manipulated

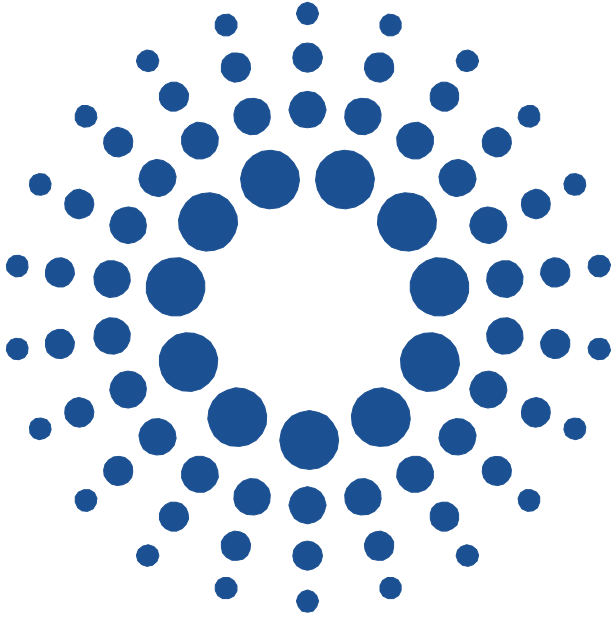
Conclusion

- Design and plan your experiment according to:
  - the aims of the experiment;
  - the sample;
  - the instrument and time available.

- Enjoy getting the most out of suitable, high-quality data.
  - (don’t waste time on inadequate quality or unsuitable data)

Lecture notes

Lecture notes

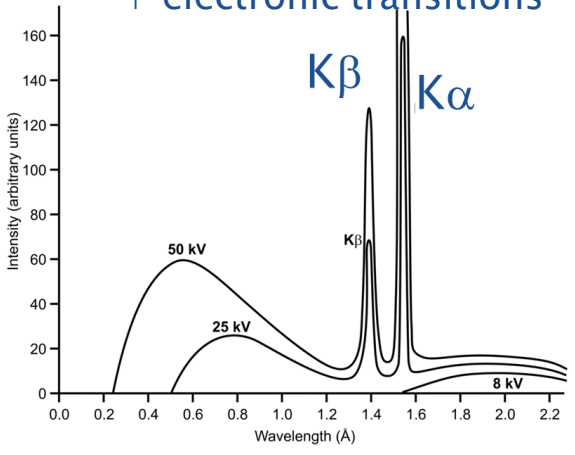


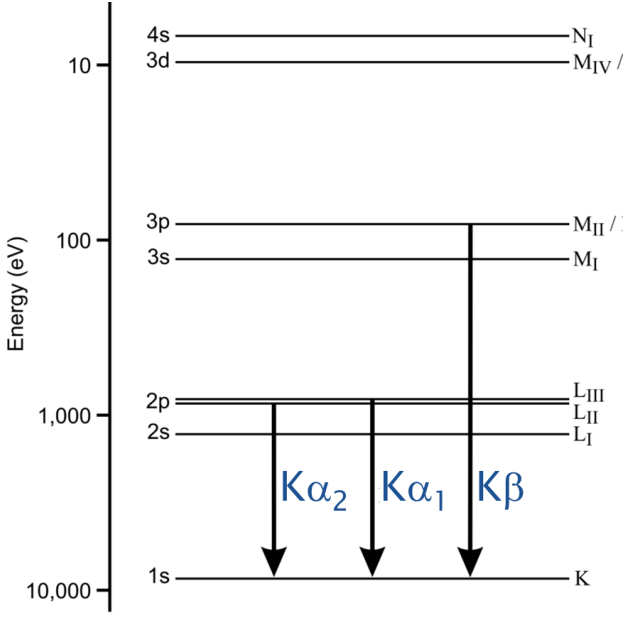
Session 11: Synchrotron Radiation and Neutrons

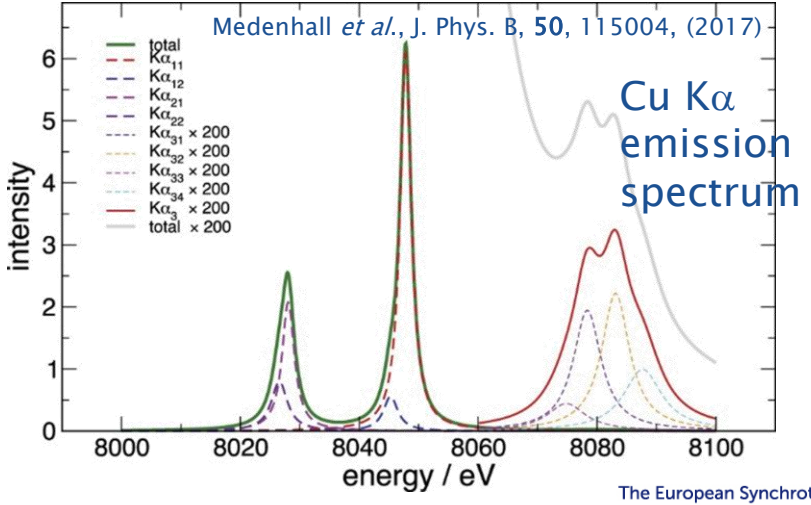
Andy Fitch
ESRF, Grenoble, France
fitch@esrf.fr

Laboratory X-ray source

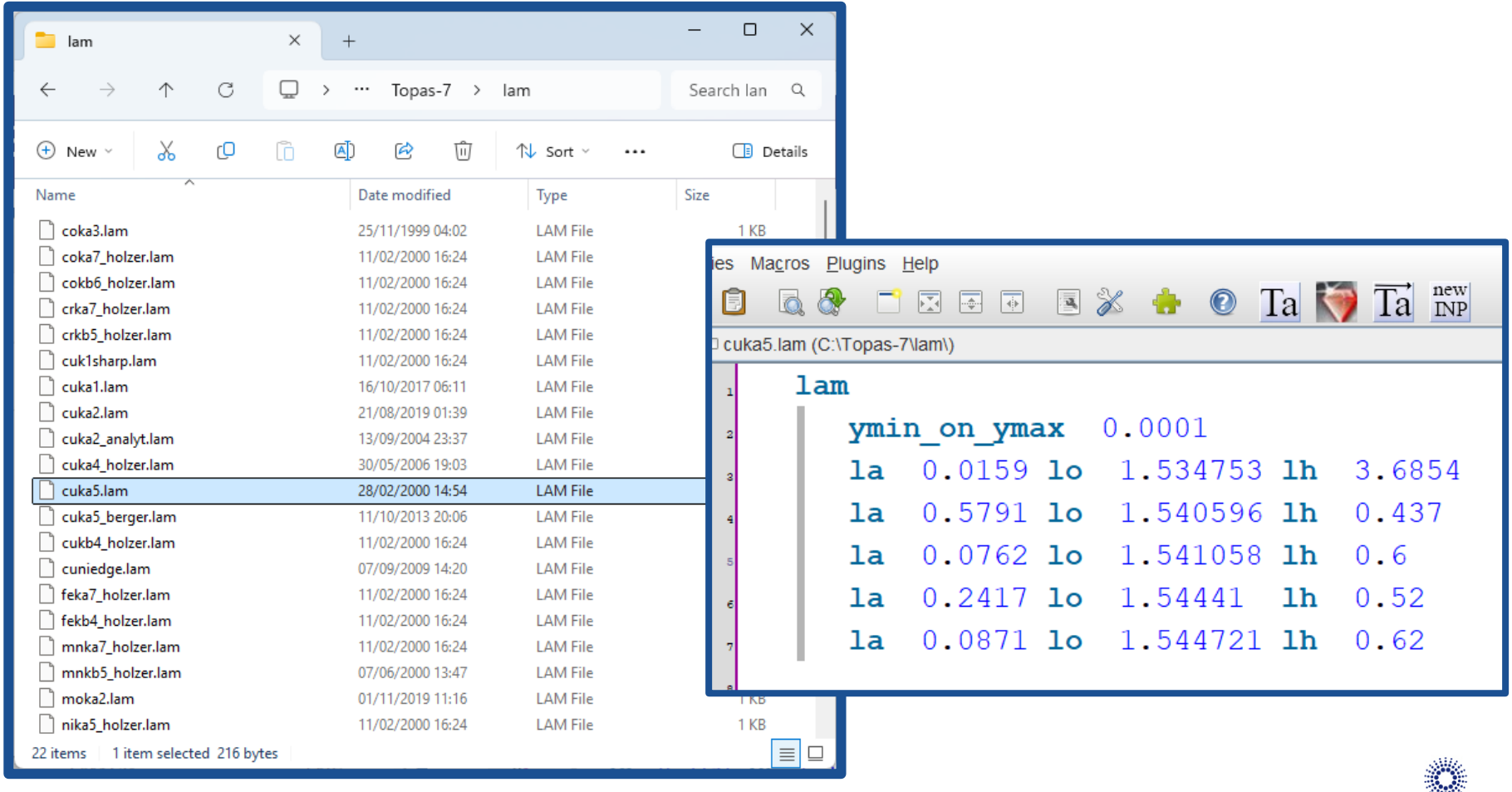
Bremsstrahlung (background)
+ electronic transitions







Laboratory X-ray source



Advantages of a laboratory instrument

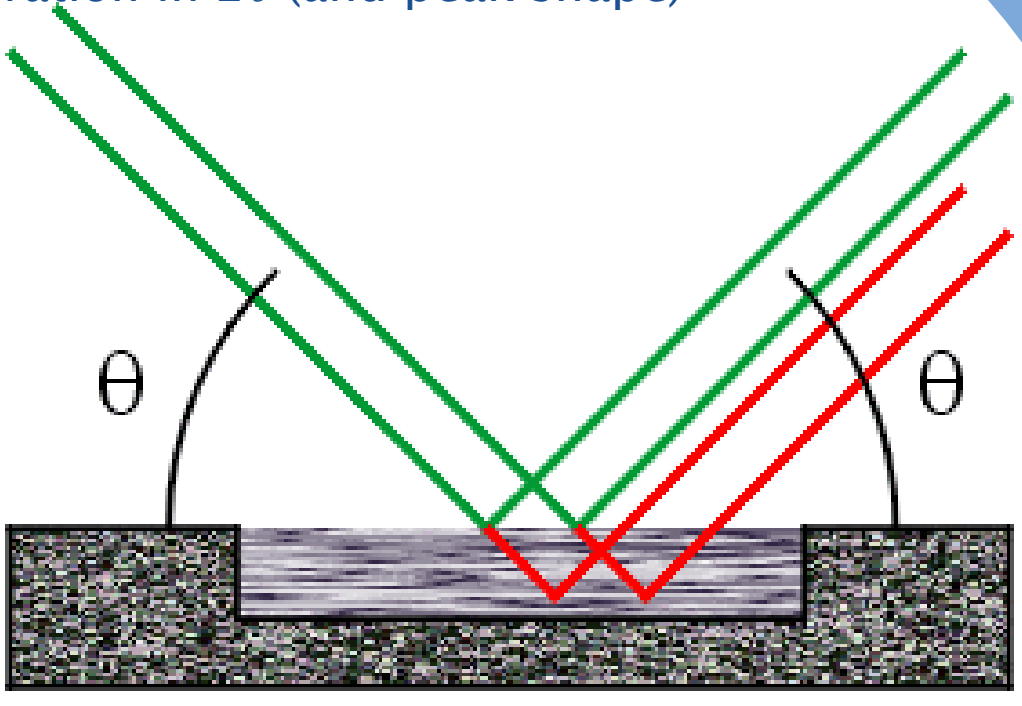
- It's yours. It's available. No long wait to use it.
- Modern instruments are adaptable and have good precision and resolution.
- Manufactured to defined specifications.
- Sample environments and ancillary equipment are commercially available.
- Delivered with useful software, e.g. search and match, phase analysis, Rietveld refinement, etc.

Limitations of a laboratory instrument

- Limited 2θ resolution, (divergent beams, low X-ray spectral purity).
- Maybe suffer from $\alpha_1\alpha_2$ doublets (unless you have a pre-sample monochromator).
- Limited to fixed wavelengths, CuKα, MoKα.
- Modest flux.
- Aberrations due to specimen transparency, surface effects, sample misalignment, etc.
- Limited adaptability.

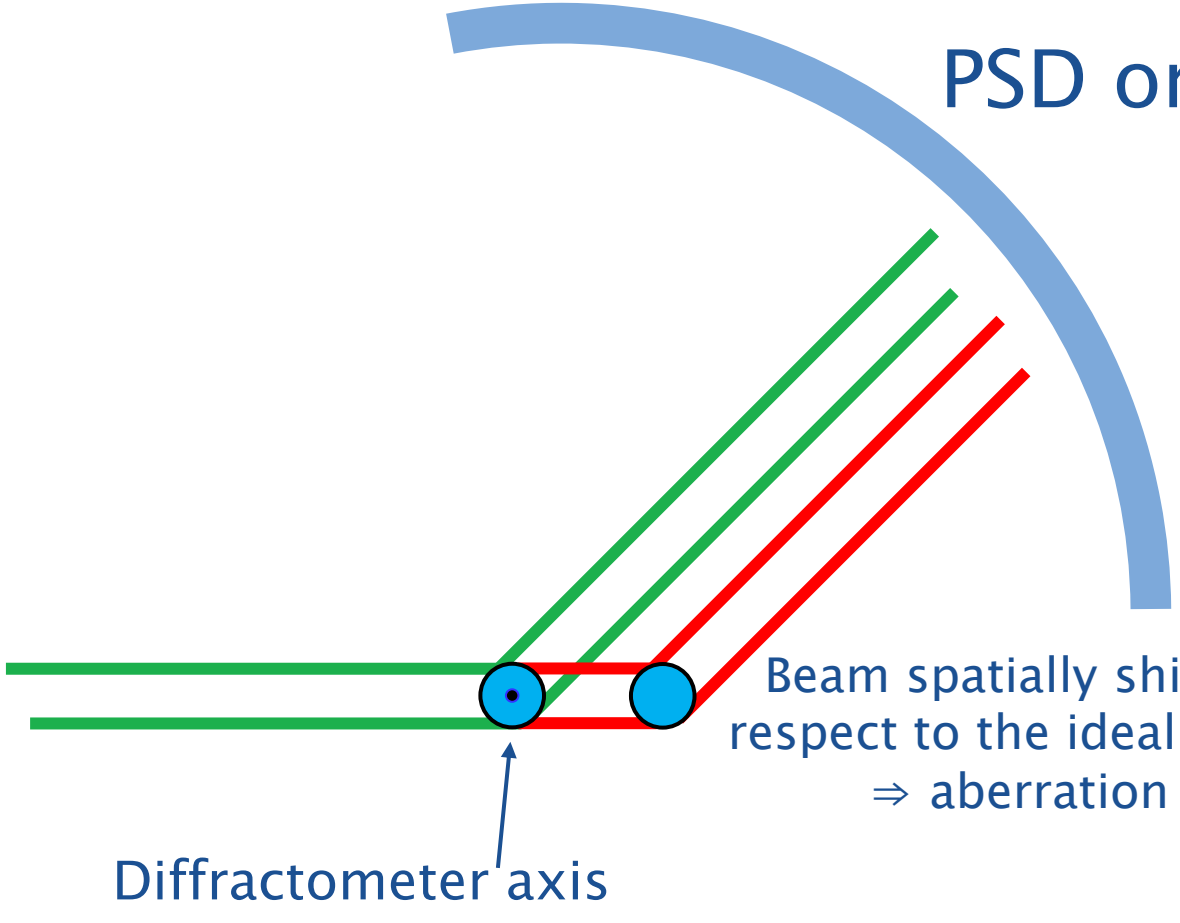
Transparency or surface aberrations

Diffracted beam spatially shifted
with respect to the ideal beam path
⇒ aberration in 2θ (and peak shape)

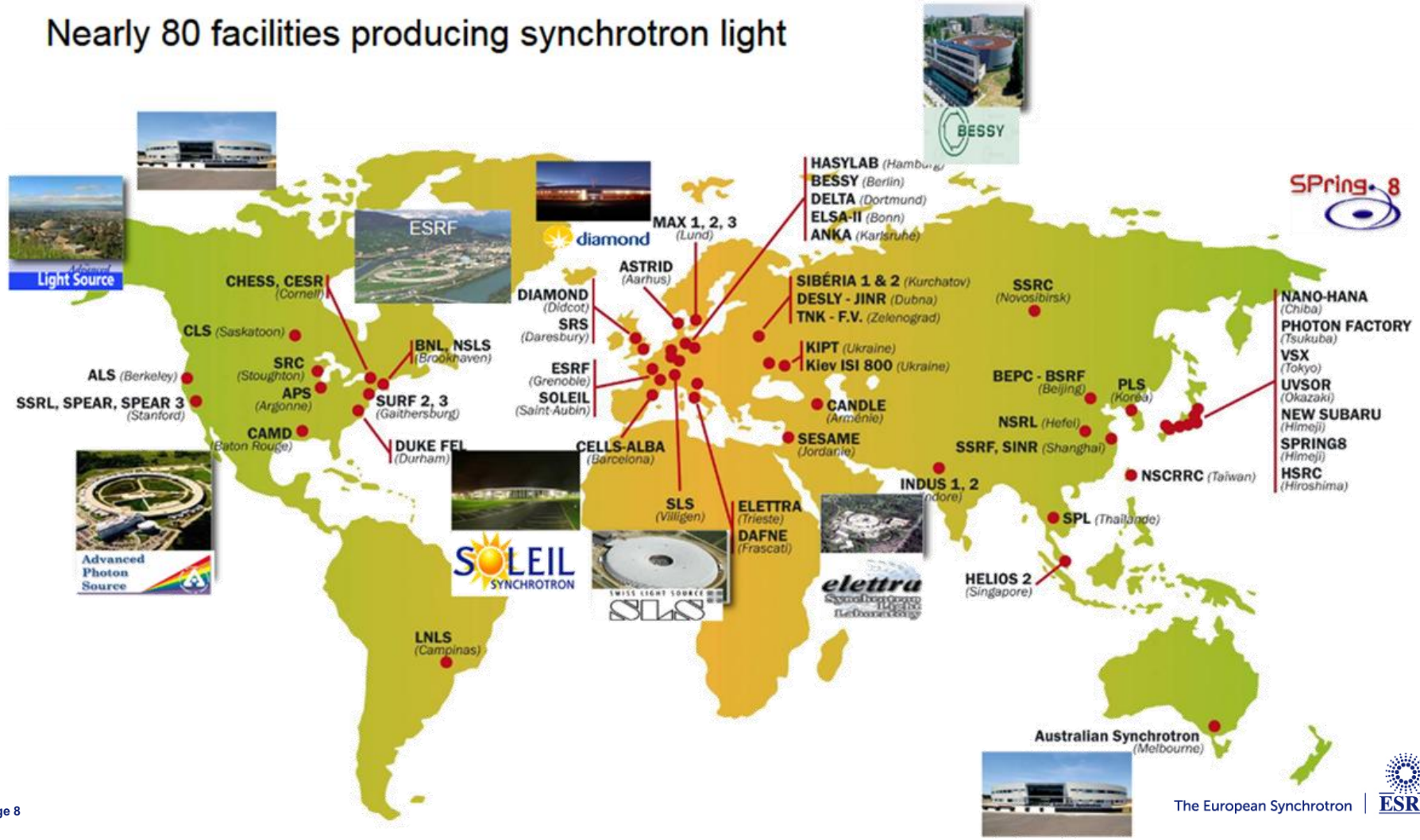


PSD or
slit

Debye-Scherrer geometry susceptible to aberrations



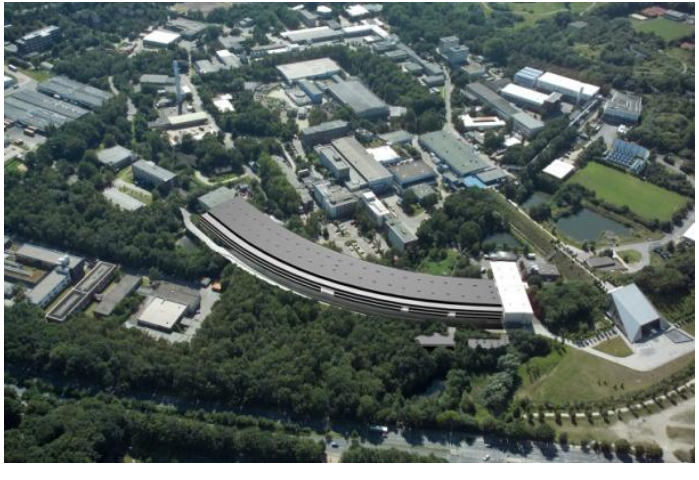
Synchrotrons



APS, Argonne, 7 GeV

Shanghai, 3 GeV

Petra, 6 GeV



Australia, 3 GeV


HZB
Helmholtz
Zentrum Berlin
MAX-lab
DESY
ANKA
diamond
SOLEIL
SYNCHROTRON
PAUL SCHERRER INSTITUT
PSI
ESRF
ALBA
elettra

SINQ+SLS, 2.7 GeV ring

ISIS+Diamond, 3 GeV ring


ESRF,
6 GeV ring
ILL, 58 MW
reactor


ESRF,
6 GeV ring

Synchrotron radiation and powder diffraction

High intensity, collimation and λ tunability

$\Downarrow$

- High angular resolution, i.e. inherently narrow peak widths
- Rapid data collection / good statistics
- Highly monochromatic X-rays so well-defined instrumental peak shape (no $\alpha_1\alpha_2$ doublets, etc)
- λ tunable: measure at absorption edges, or well away; optimise for the experiment
- High energies for increased Q range, PDF, or penetrate through absorbing samples or sample environments

Storage ring energy = an orbiting electron's total energy

Electron at rest : $E_e = m_e c^2 = 8.1871057880(26) \times 10^{-14}$ J

m_e = electron rest mass = $9.1093837139(28) \times 10^{-31}$ kg
c = speed of light = 299792458 m s^{-1}

1 eV = $1.602176634 \times 10^{-19}$ J

$$E_e = 5.1099895069(16) \times 10^5 \text{ eV}$$
$$= 5.1099895069(16) \times 10^{-4} \text{ GeV}$$

Electron with speed v : $E_e = \gamma m_e c^2$

where $$\gamma = \frac{1}{\sqrt{1-(v^2/c^2)}}$$

Storage ring energy = an orbiting electron's total energy

If $E_e = 1$ GeV

$$\Rightarrow 1 \text{ GeV} = \gamma \; 5.1099895069 \times 10^{-4} \text{ GeV}$$

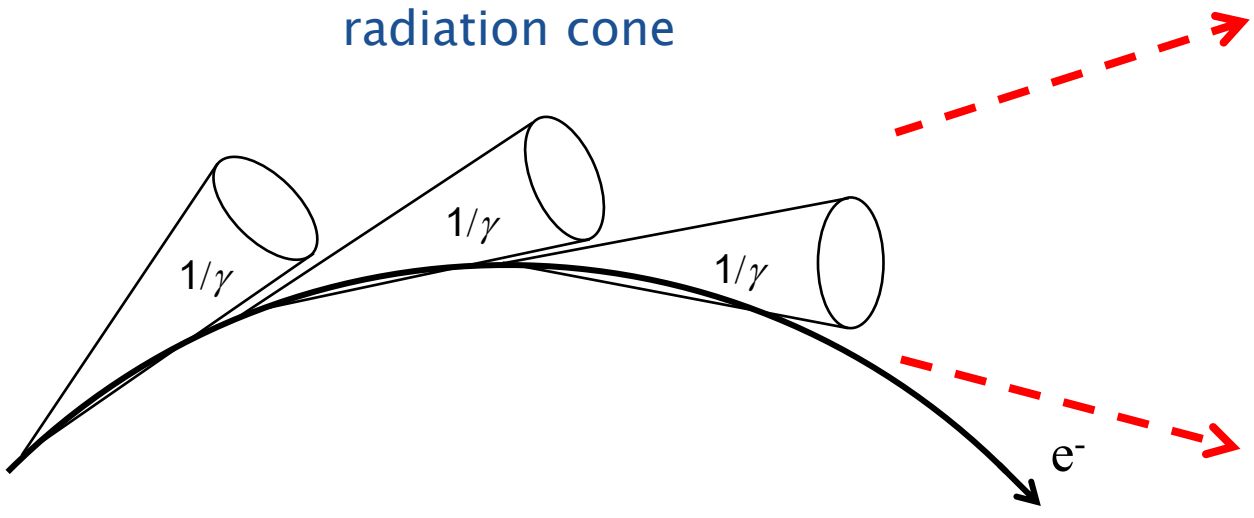
$$\Rightarrow \gamma = 1 \; / \; (5.1099895069 \times 10^{-4})$$

$$\Rightarrow \gamma \approx 1957 \; E_e \; [\text{GeV}]$$

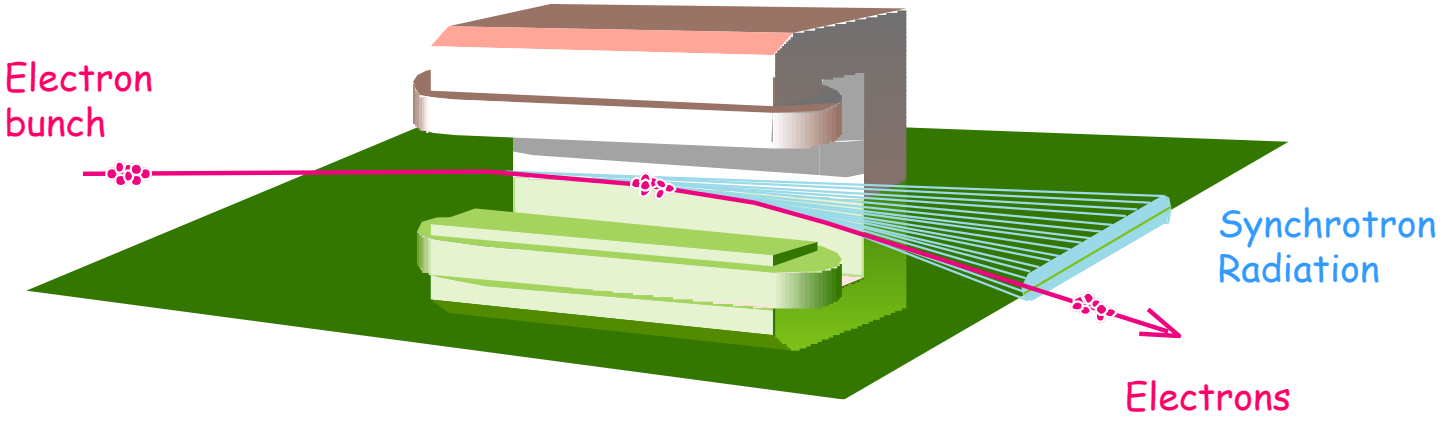
- 6 GeV $\Rightarrow \gamma = 11742 \Rightarrow v = 0.9999999964 \; c$
- ESRF circumference = 844 m
- Electron lap time = $844/c$ = 2.82 μs, so 355036 laps s^{-1}
- Ring current per electron = 355036 e $s^{-1} \approx 56.9 \times 10^{-15}$ A
- Ring current of 200 mA ≡ 3.5×10^{12} electrons.

Synchrotron radiation

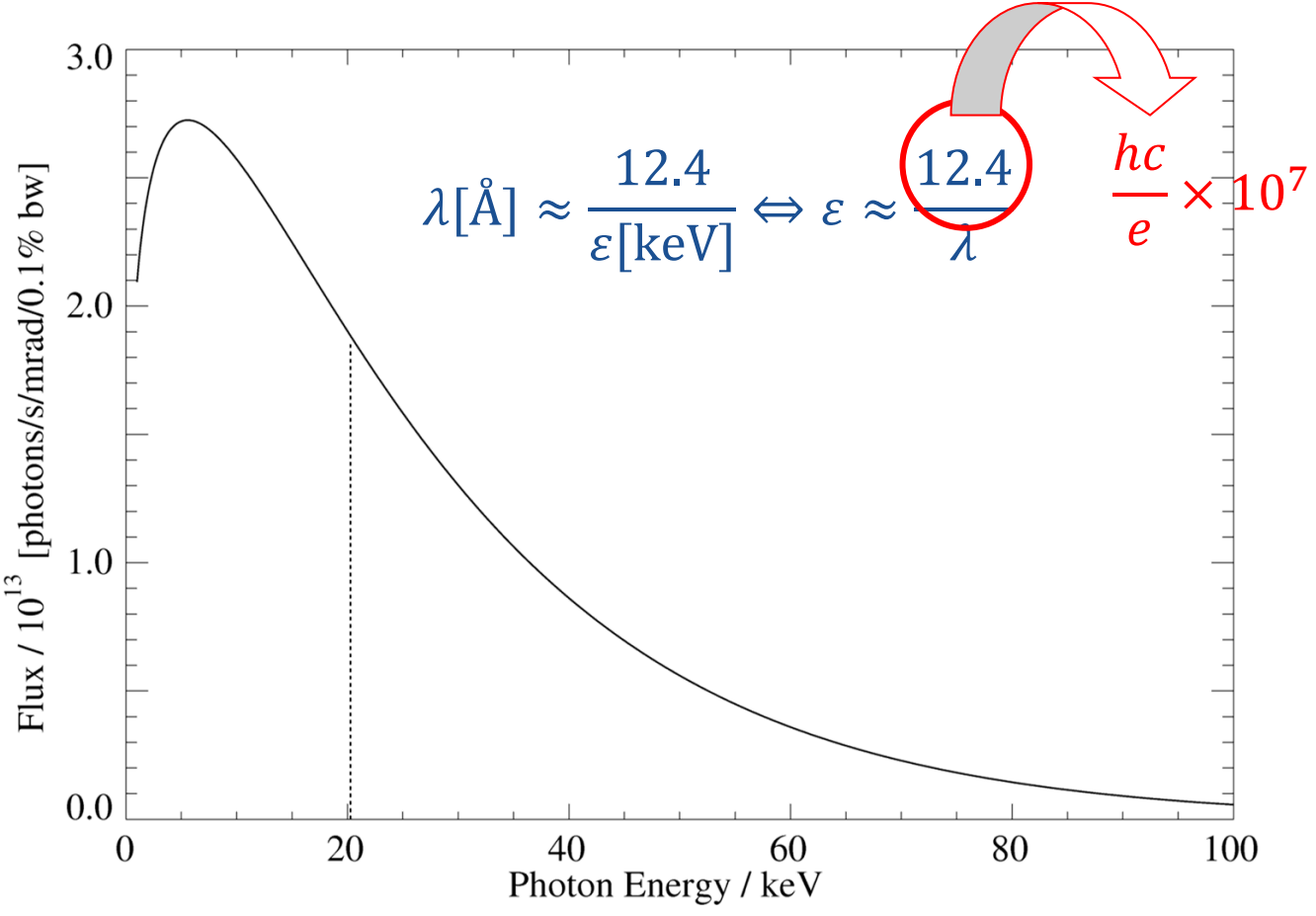
Emitted tangentially when charged particles follow a curved path at relativistic speeds



Bending magnet

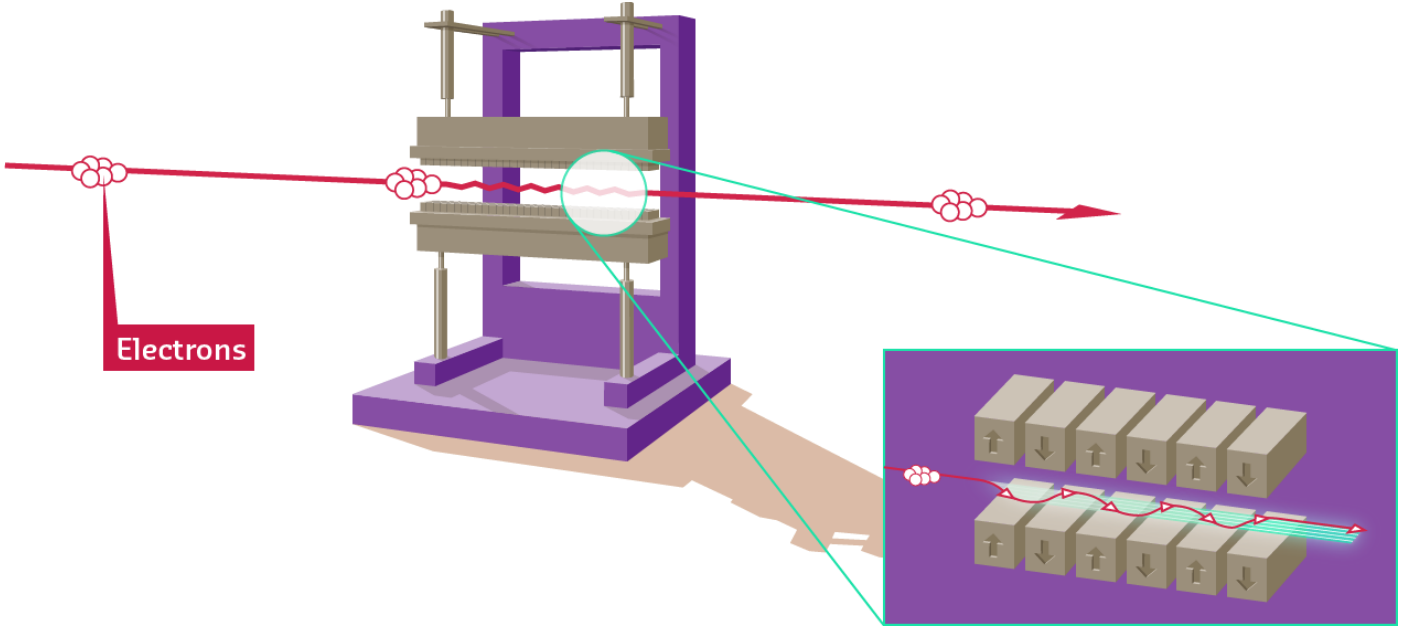


ESRF bending magnet spectrum

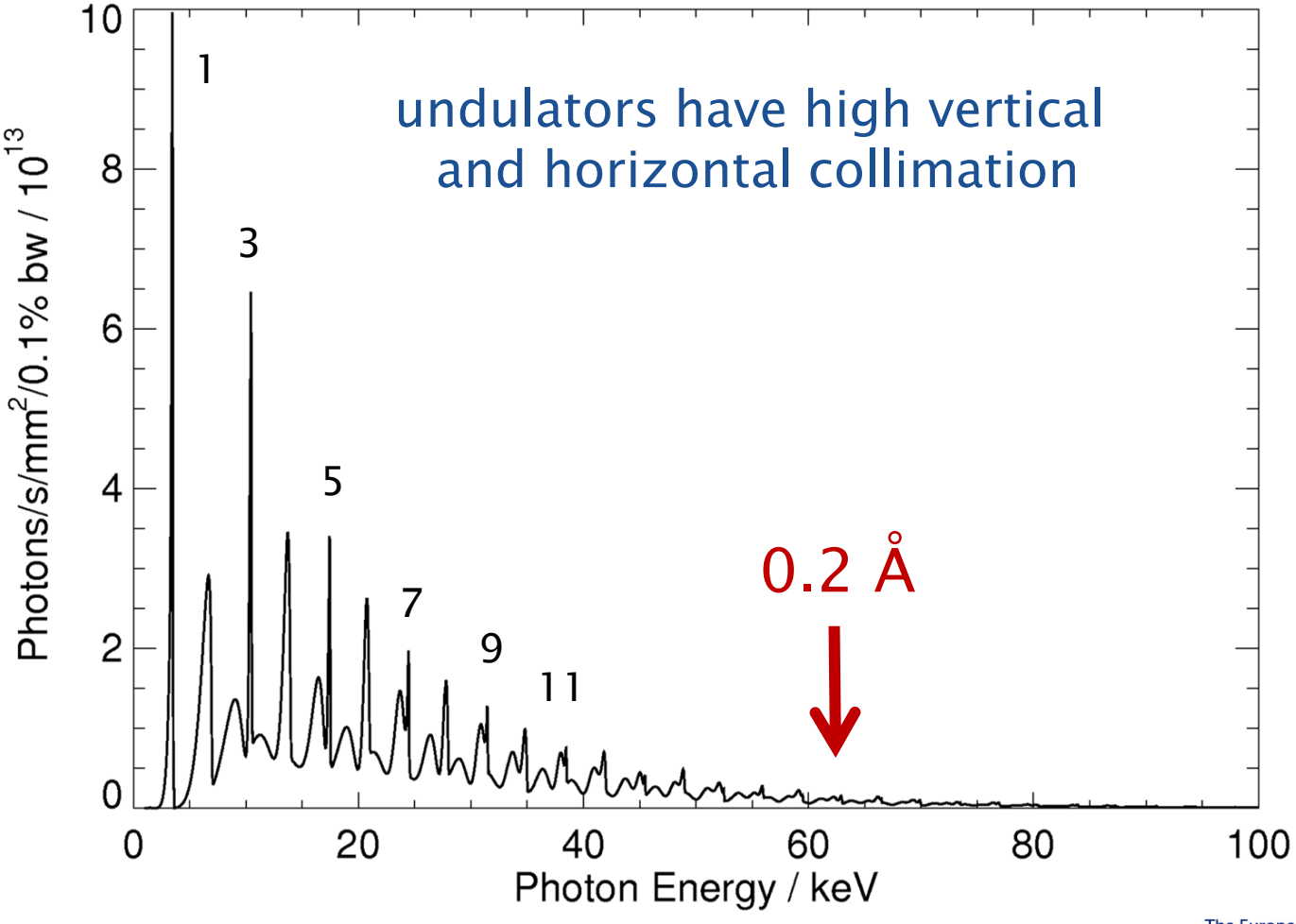


Insertion devices

Wigglers and undulators
arrays of magnets that cause the electron path to oscillate and emit radiation.

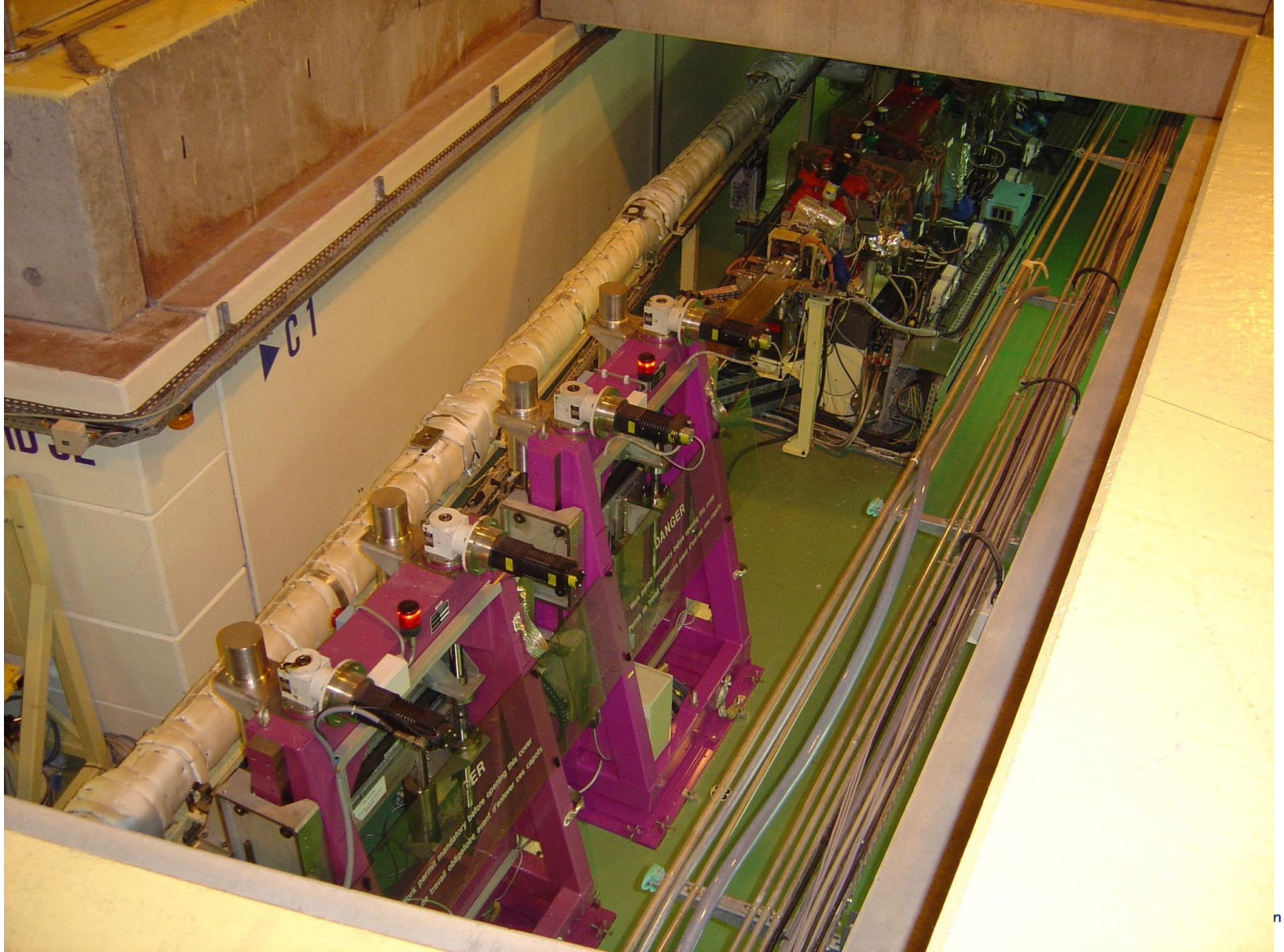


ESRF (6 Gev) u35 undulator, G =11 mm gap



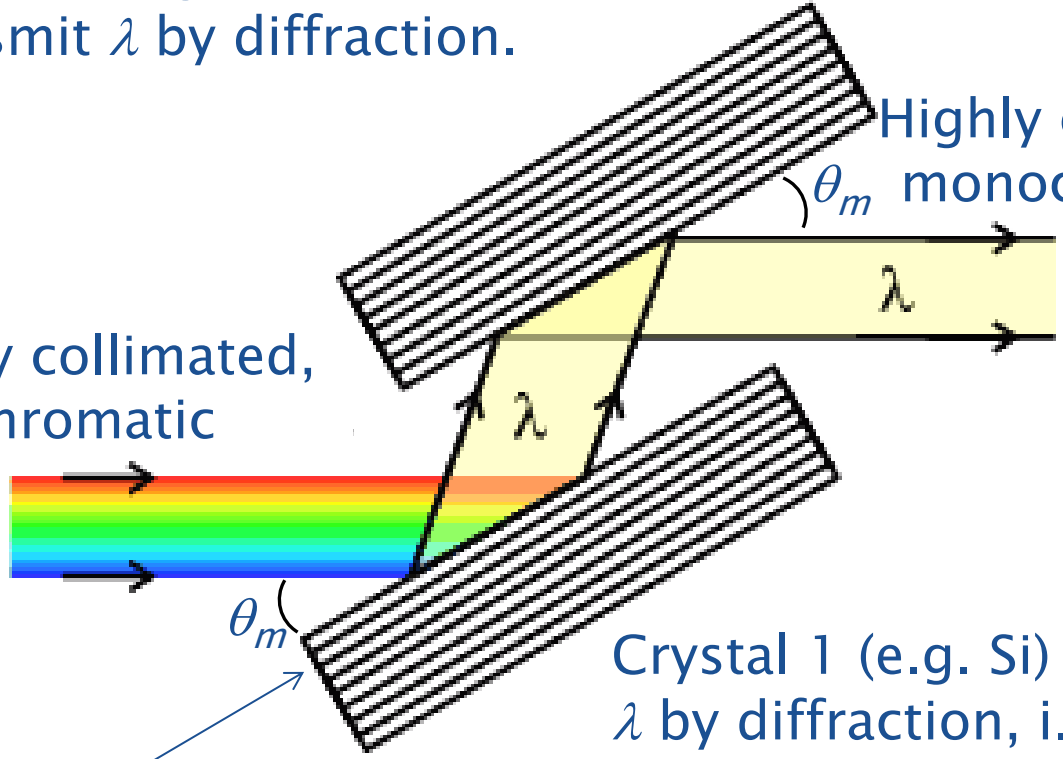
Ex-vacuum and in-vacuum undulators

G = variable gap between poles to tune magnetic field


C1
DANGER

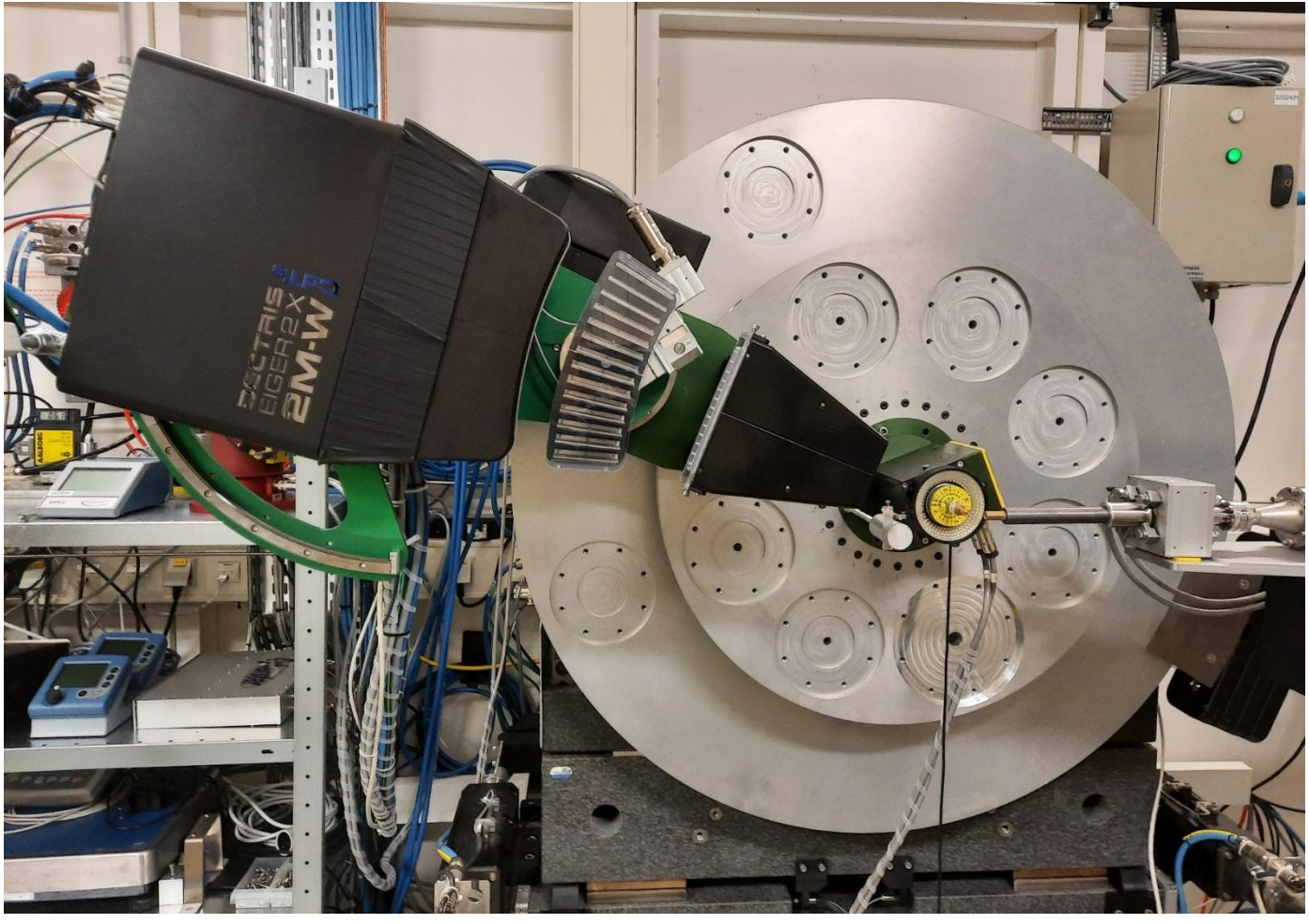
Double crystal monochromator

Crystal 2 is aligned with crystal 1
to transmit λ by diffraction.

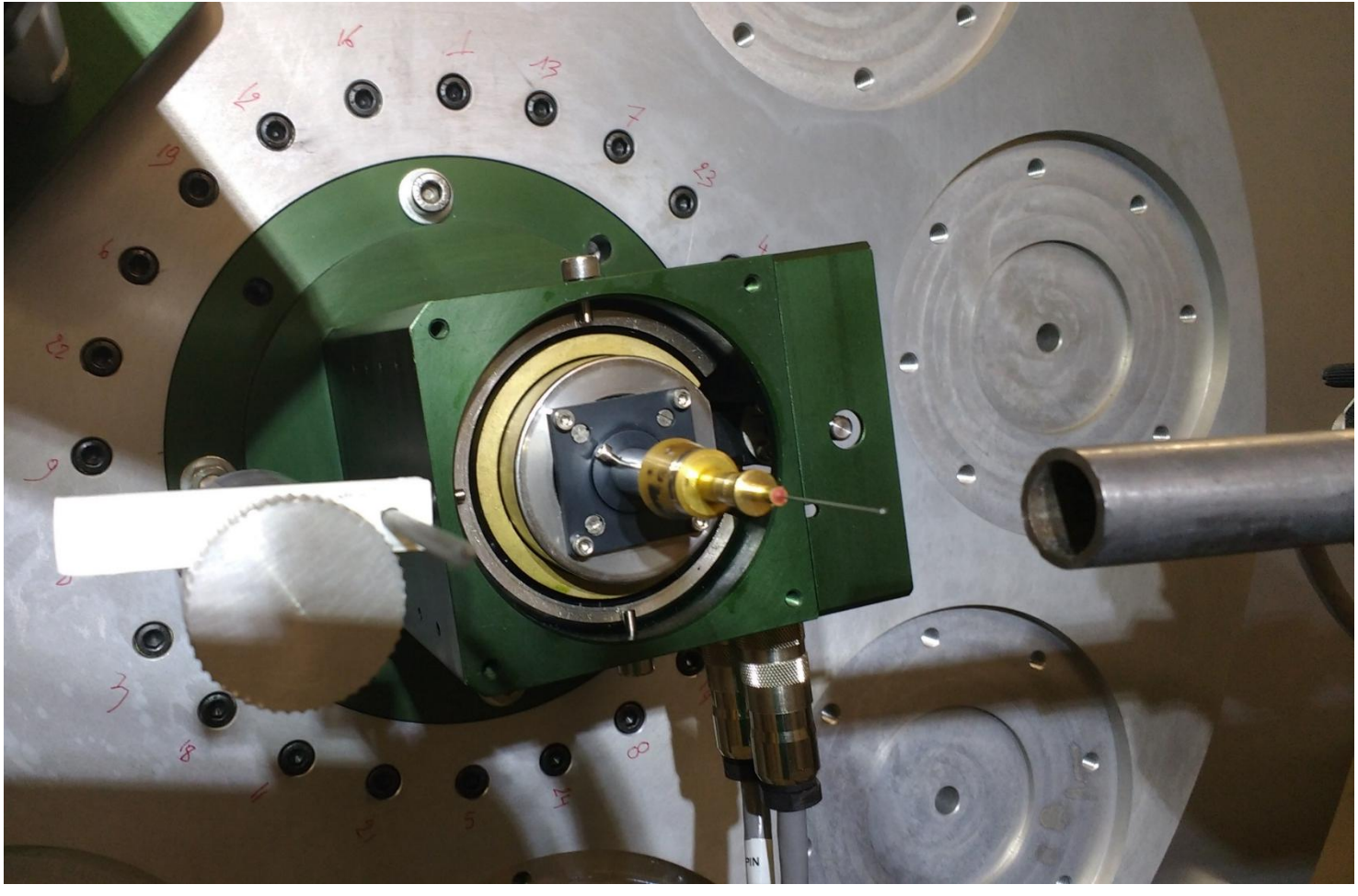


Crystal 1 (e.g. Si) selects
λ by diffraction, i.e.
$\lambda = 2 d_{hkl} \sin \theta_m$

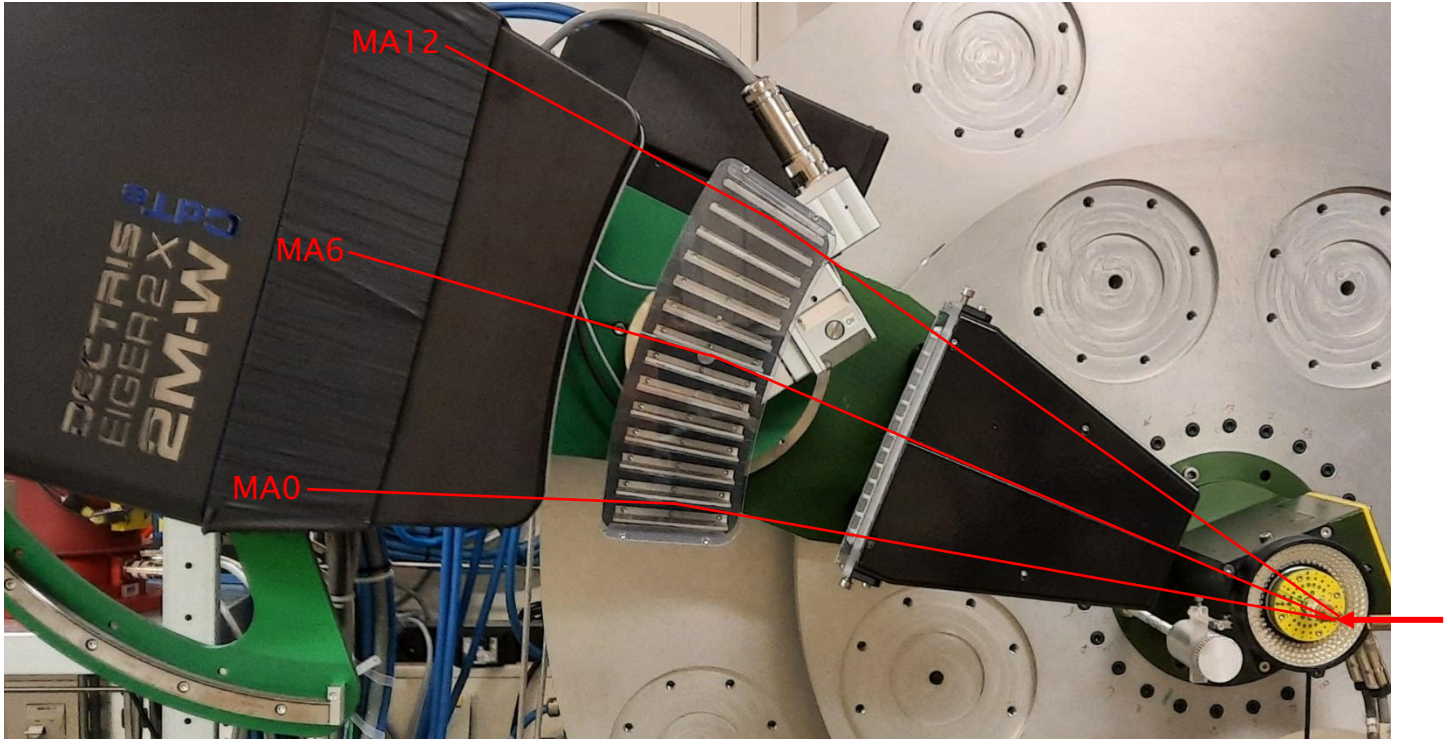
Powder diffractometer with multi-analyser stage



Capillary sample spinner

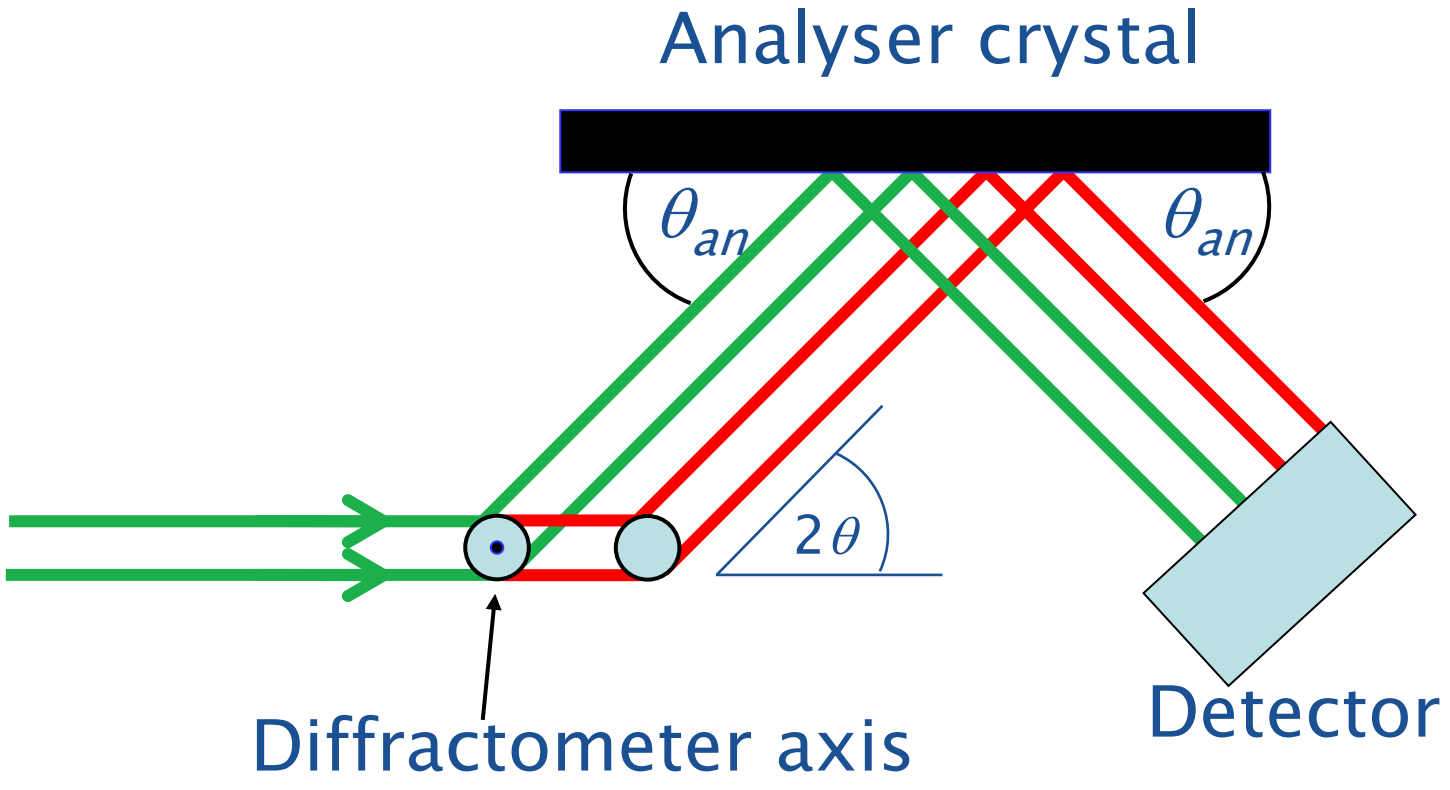


13-channel Si 111 multi-analyser stage



Original 9-channel version conceived by J.-L. Hodeau, M. Anne, P. Bordet, A. Prat, Institut Néel, Grenoble. Hodeau *et al*. *Proceedings SPIE*, **3448,** 353-361, (1998)

High resolution + minimises aberrations

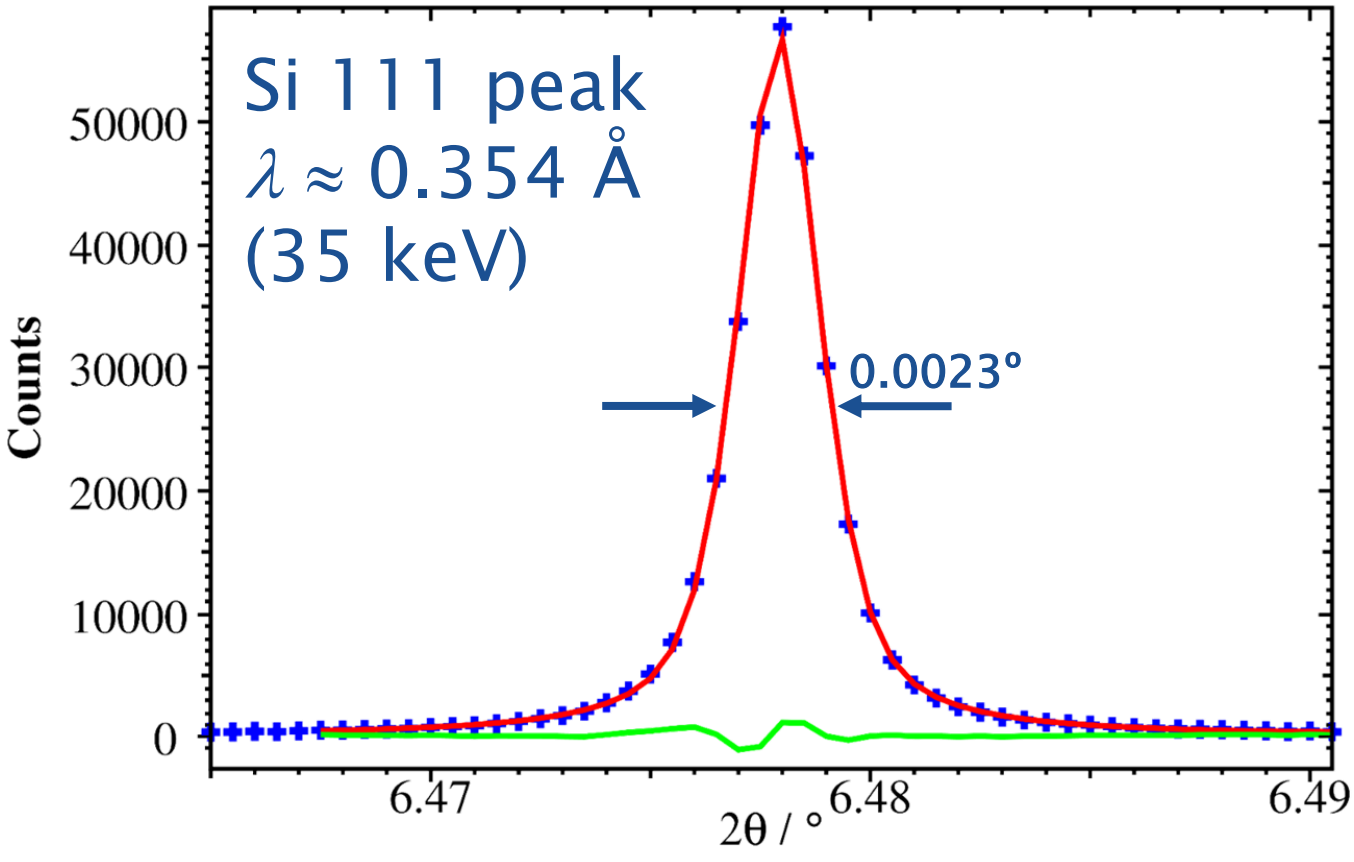


Analyser crystal

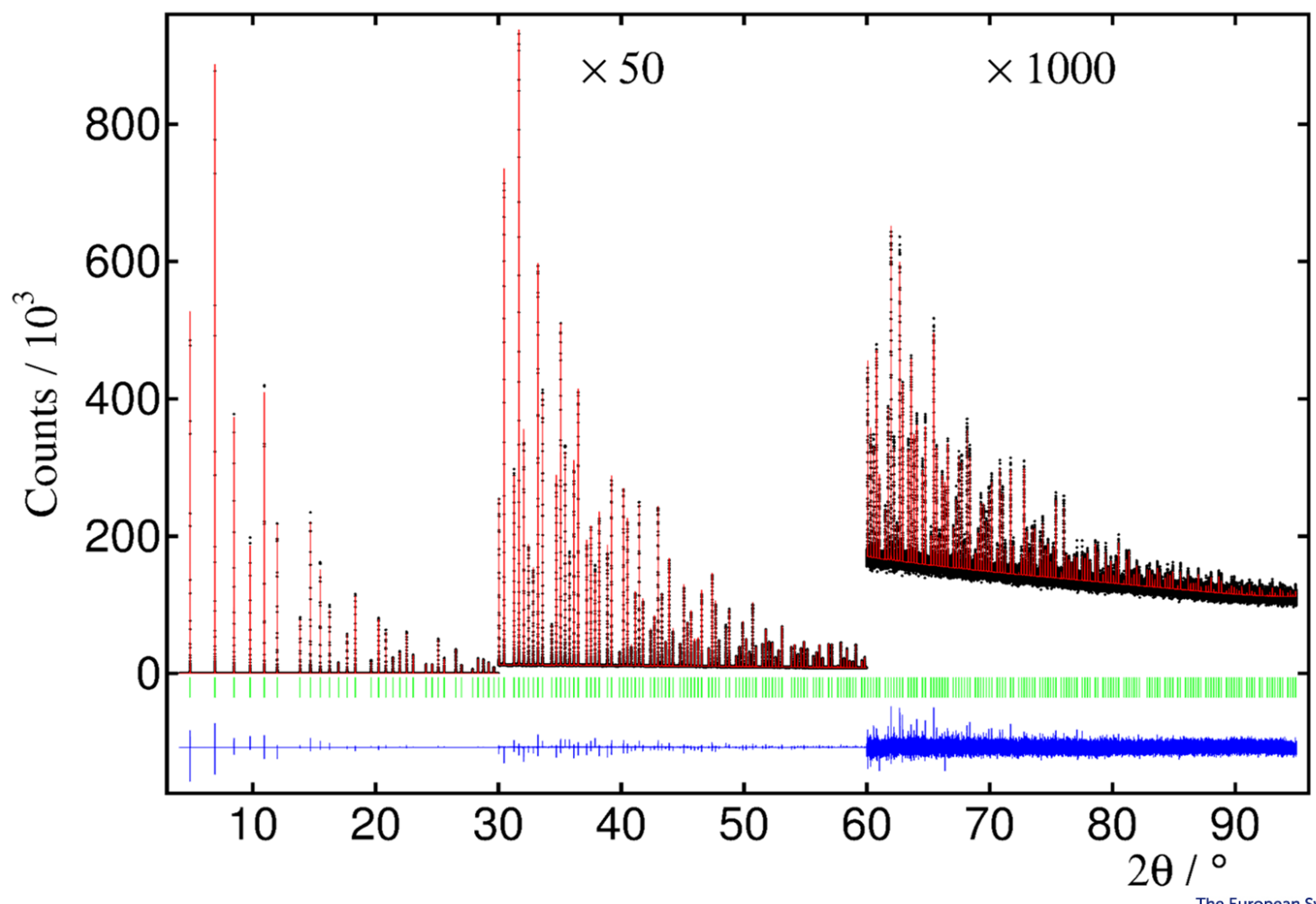
Stringently defines a true 2θ *angle* rather than infers 2θ from the *position* of a slit or pixel of a PSD.

- Narrow (sample-limited) peaks with accurate positions
- Peak positions are insensitive to displacement-type aberrations, sample misalignment, specimen transparency, size / shape / surface effects, etc.
- Peak widths are independent of any $\theta/2\theta$ parafocusing condition
- Supresses fluorescence, Compton, parasitic scatter.
- But it needs to be scanned, so is not as fast as a PSD.

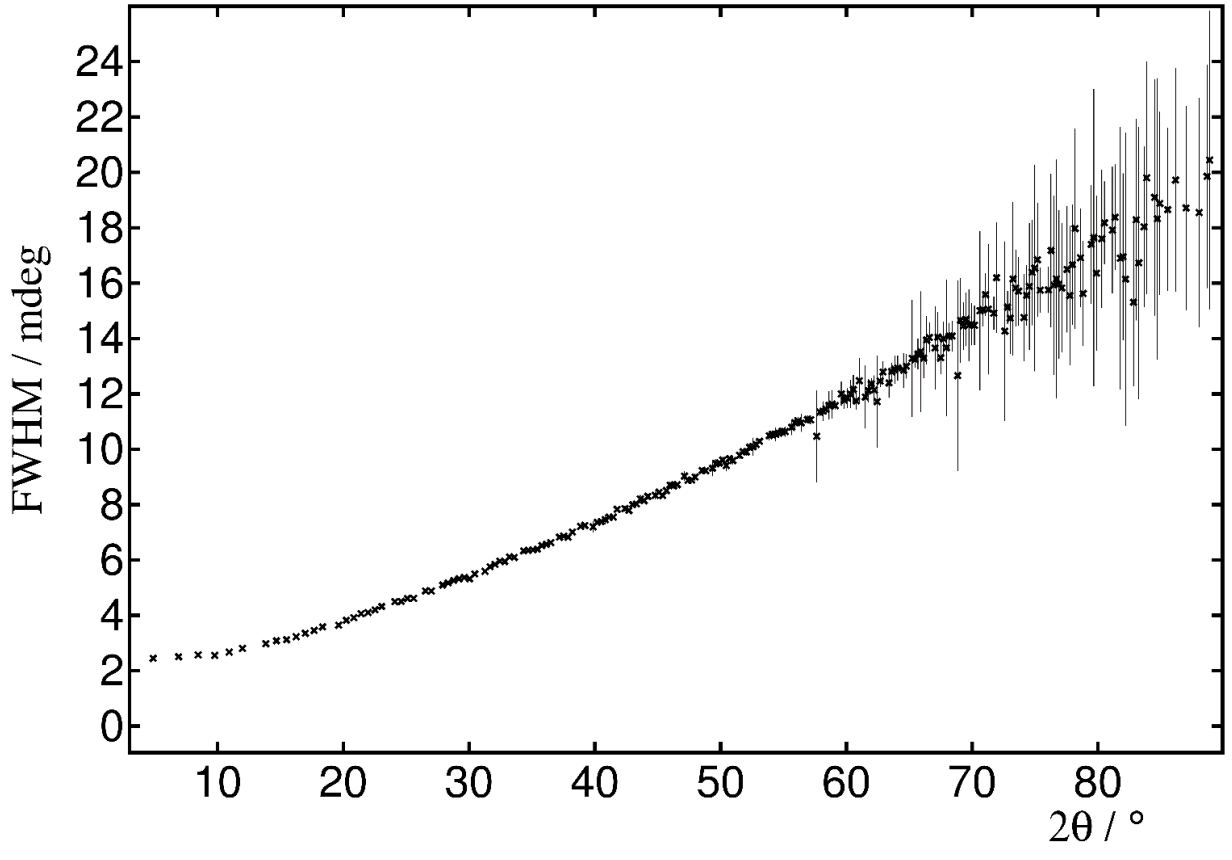
High angular resolution



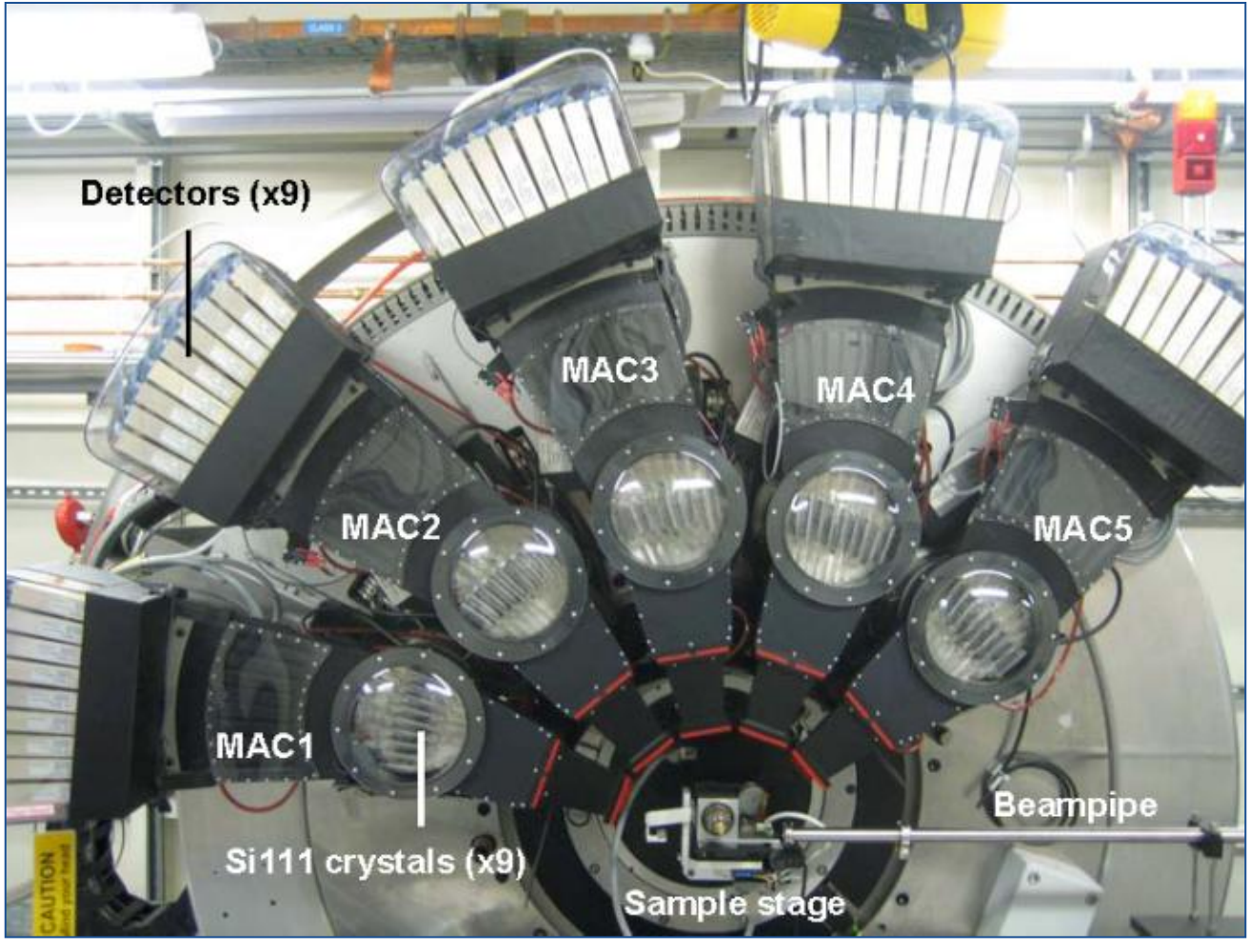
Rietveld fit to LaB_6 at 35 keV (0.354 Å)



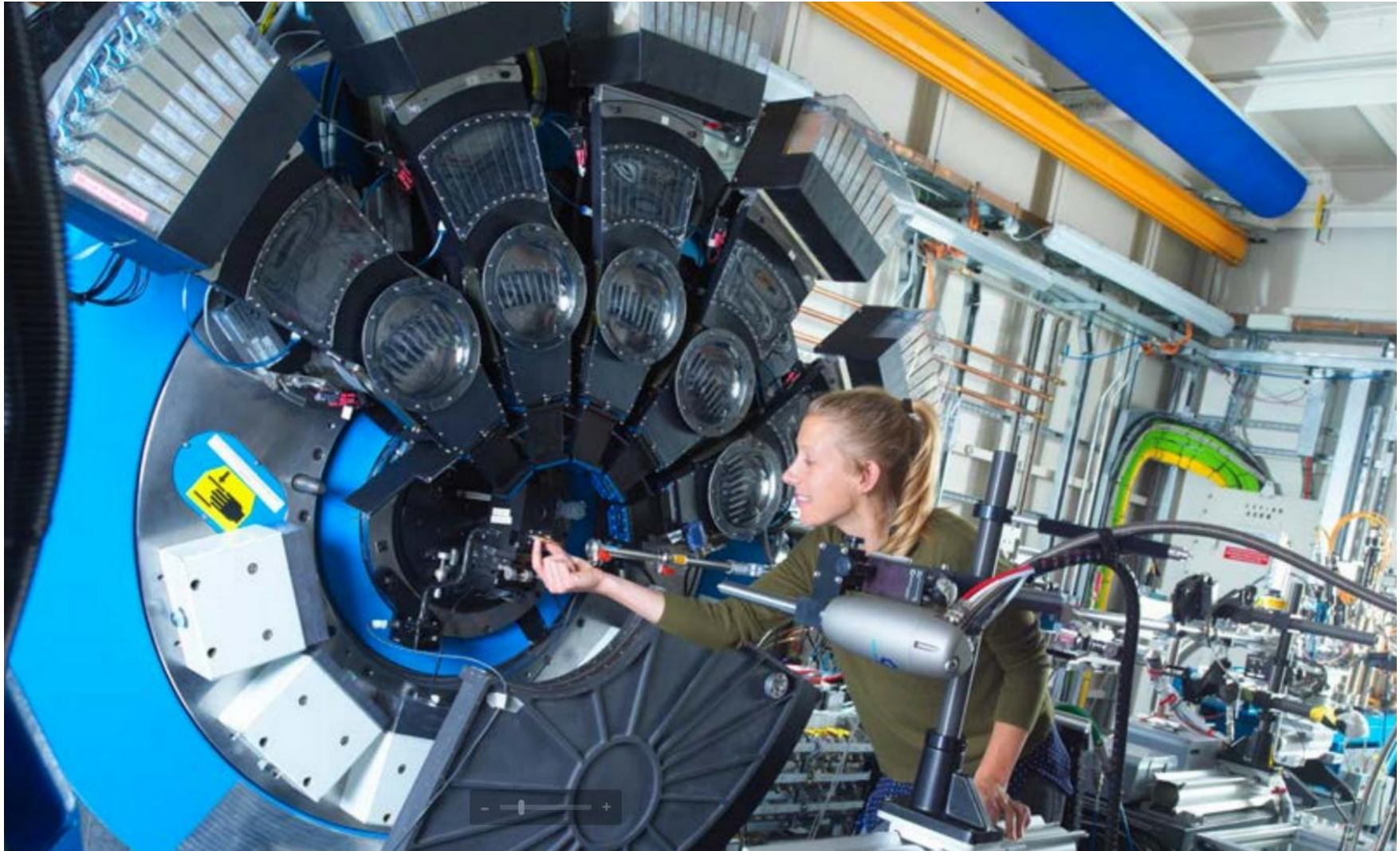
FWHM of LaB_6 at 35 keV (0.354 Å)



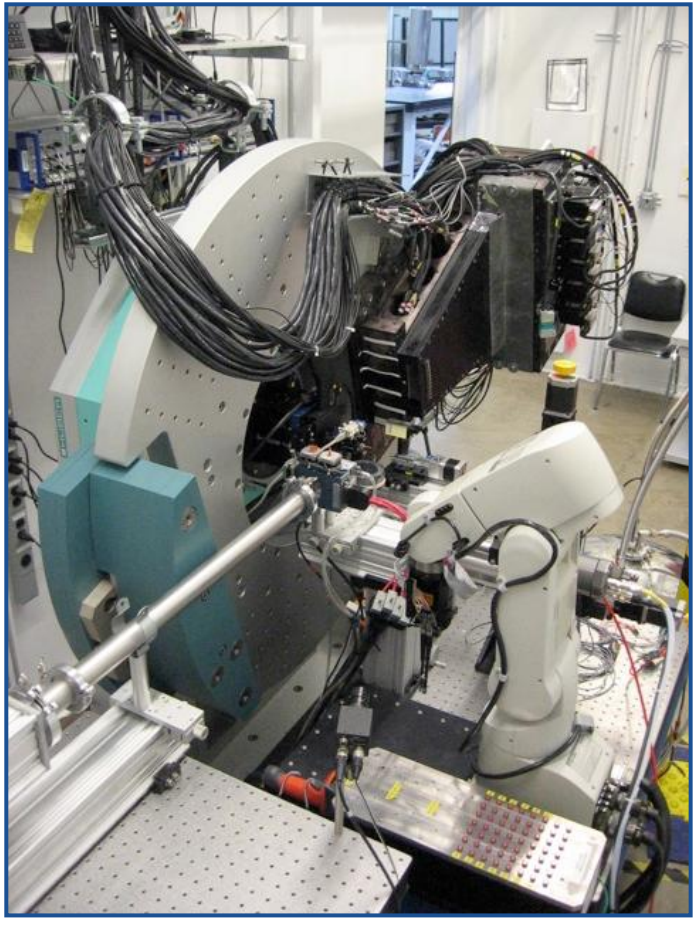
Beamline I11at Diamond, 45 analyser crystals

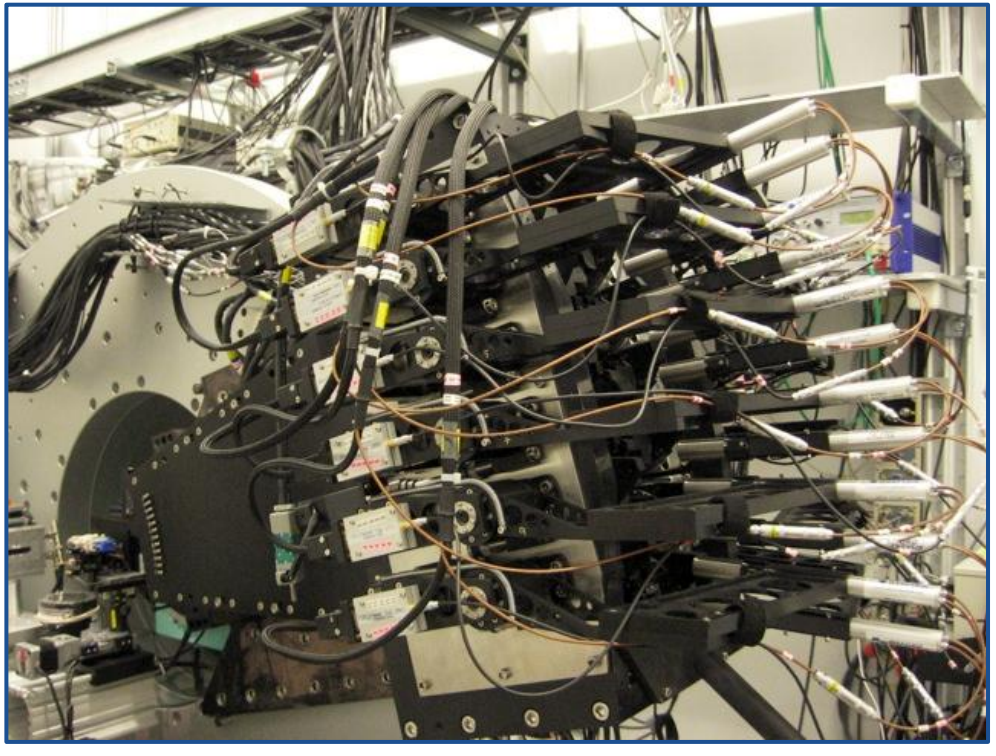


Beamline I11at Diamond, 45 analyser crystals



Beamline 11-BM at APS, 12 analyser crystals

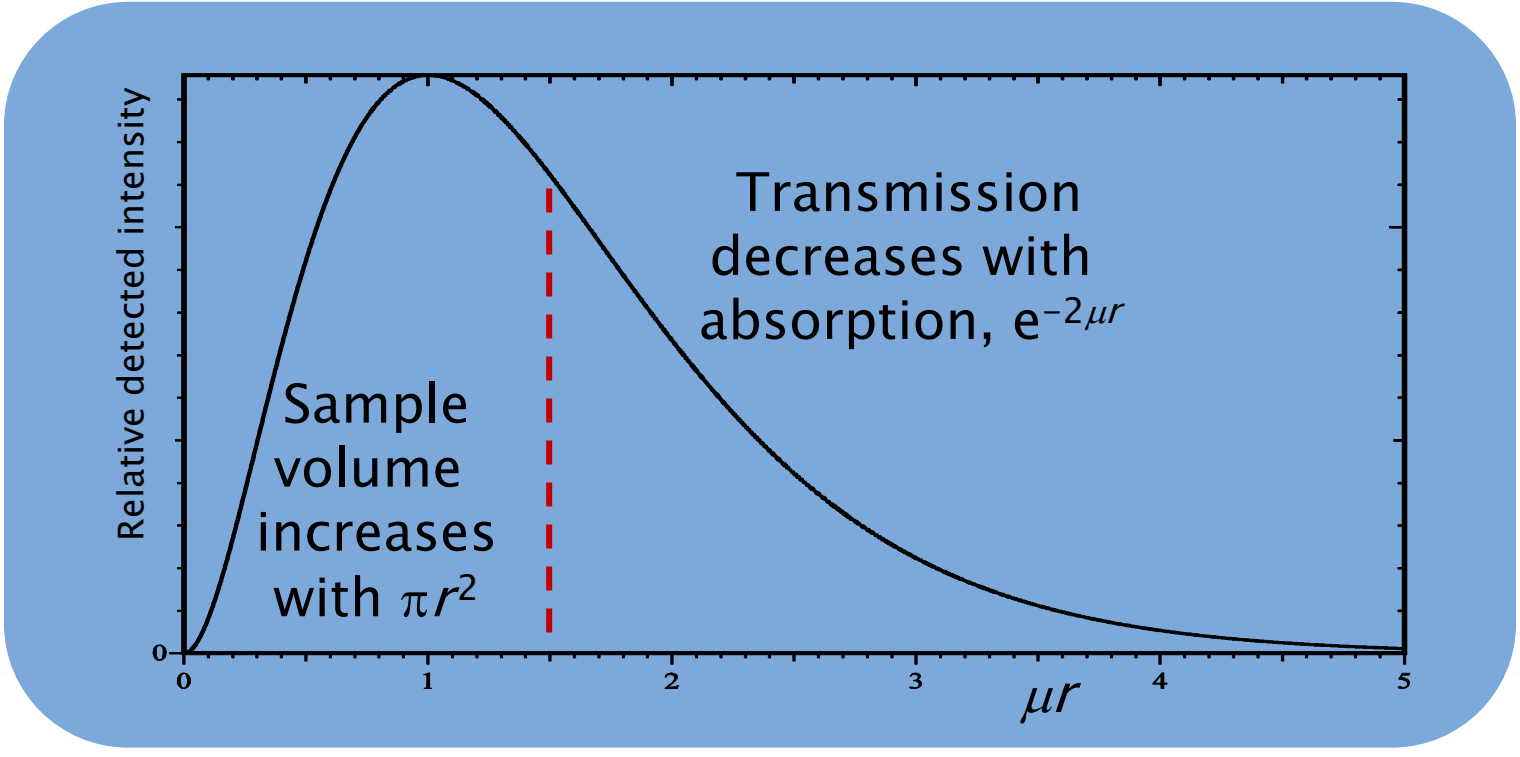




Accurate data

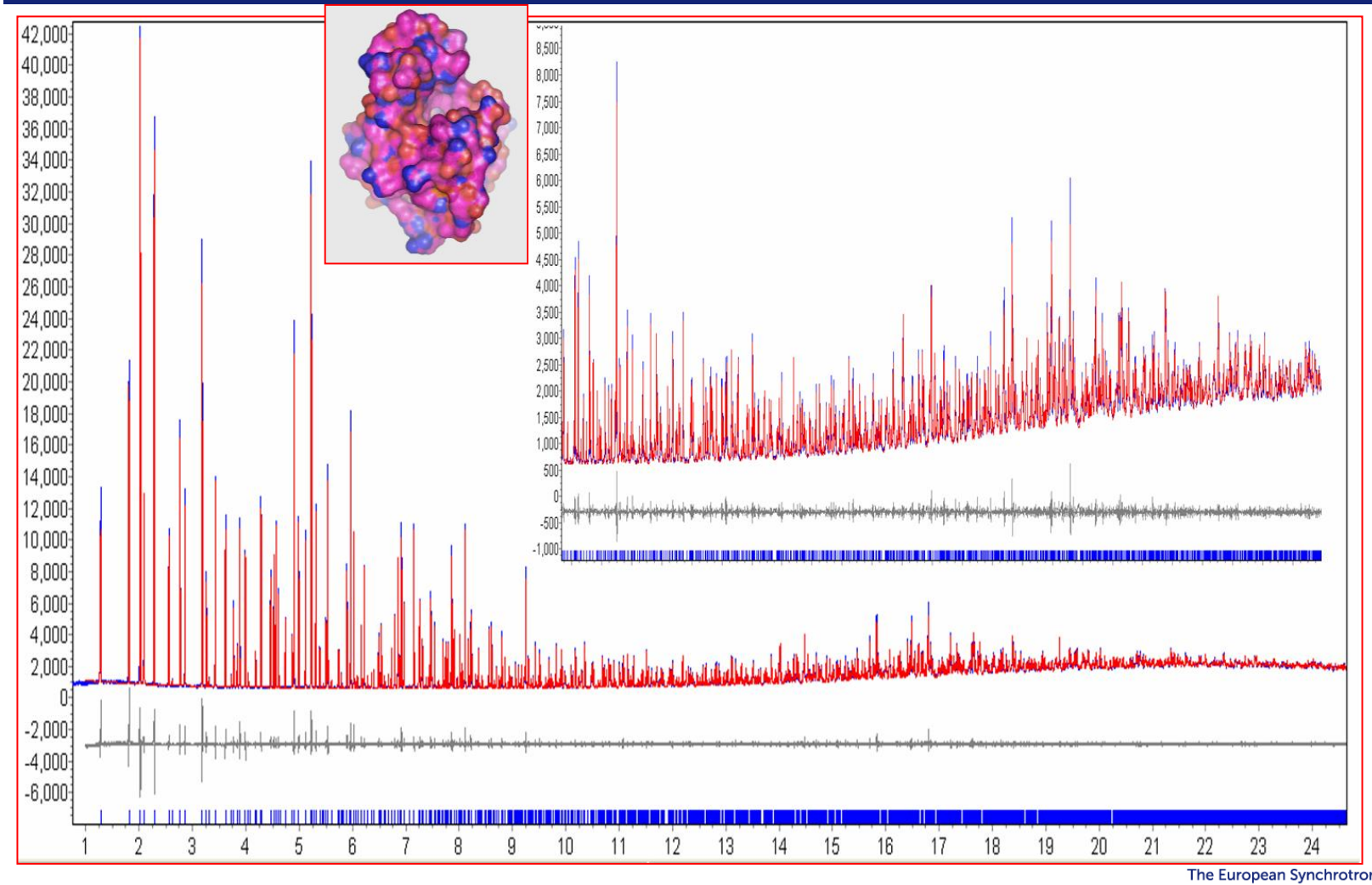
- Peak positions $\Rightarrow$ indexing, strain, etc.
- Spinning capillaries $\Rightarrow$ more-accurate intensities (less preferred orientation).
- Can choose λ and capillary size so $\mu \times r < 1.5$
- Usually choose $\lambda < 1$ Å
- At ESRF we routinely work with $\lambda \approx 0.354$ Å.

Capilliary: scattered intensity *vs* μr

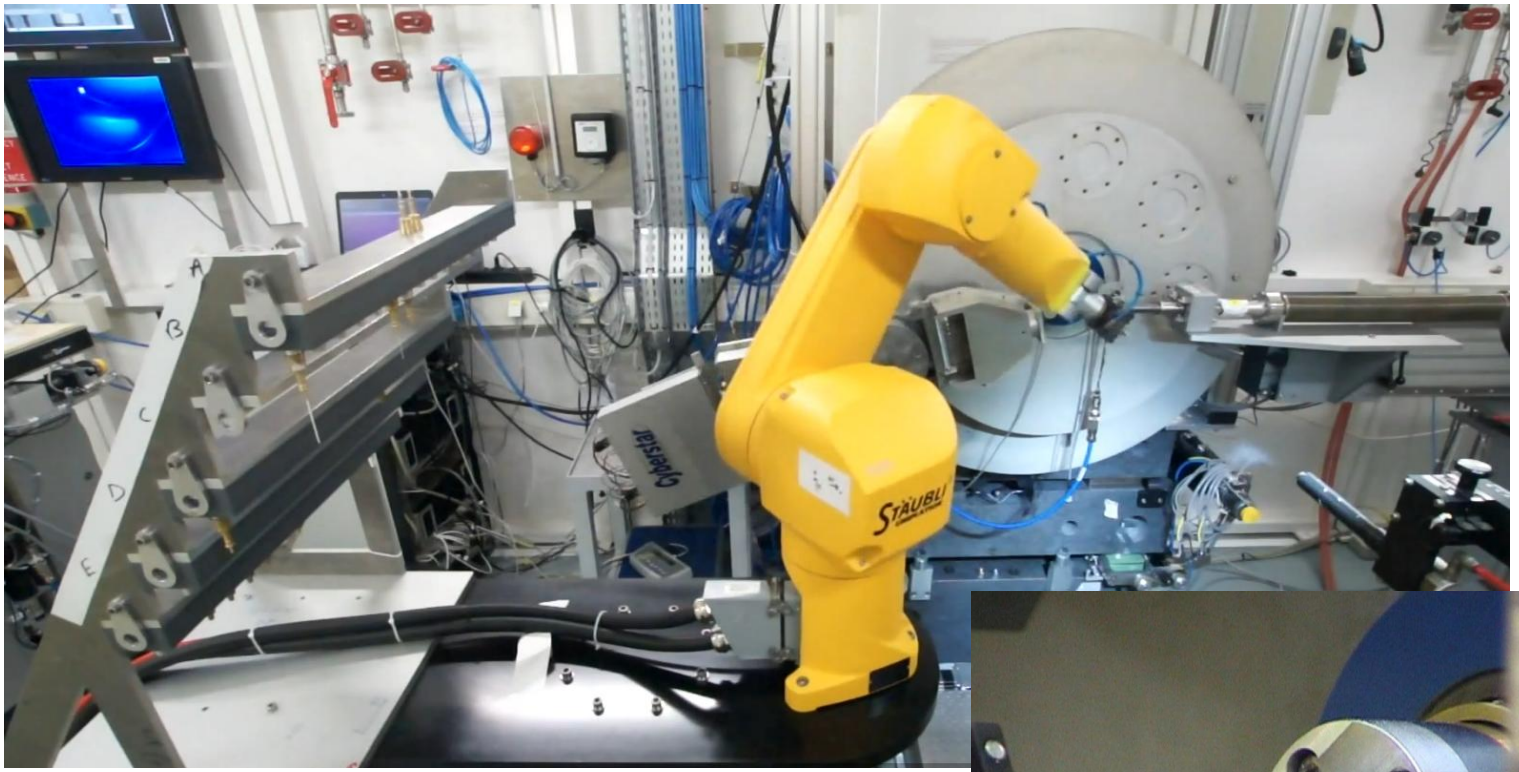


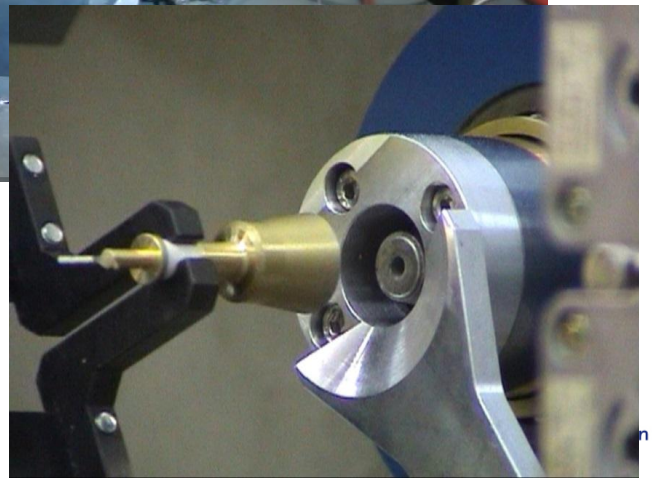
μ= linear absorption coefficient
r = capillary radius

Lysozyme


42,000
40,000
38,000
36,000
34,000
32,000
30,000
28,000
26,000
24,000
22,000
20,000
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
-2,000
-4,000
-6,000
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24
8,500
8,000
7,500
7,000
6,500
6,000
5,500
5,000
4,500
4,000
3,500
3,000
2,500
2,000
1,500
1,000
500
0
-500
-1,000

Robotic sample changer

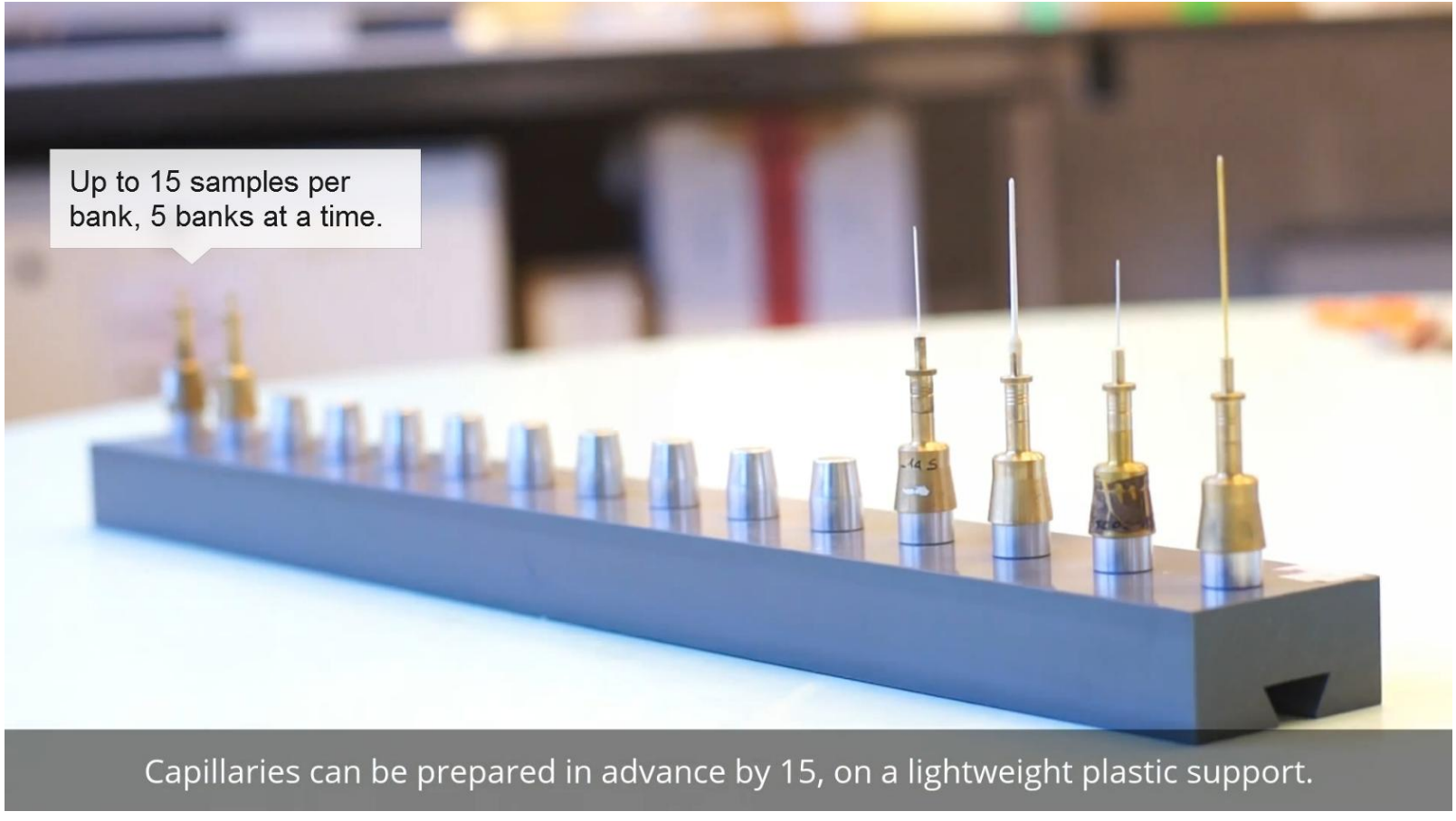




See our YouTube video!!

https://www.youtube.com/watch?v=OEhf8Logz44

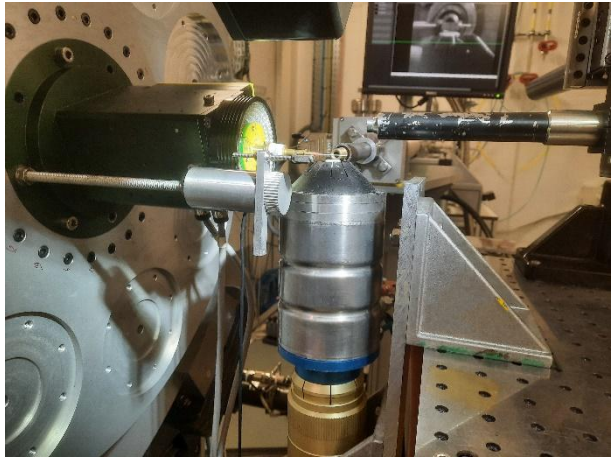
Up to 75 samples, in 5 banks of 15



Powder Diffraction = Sample Environments

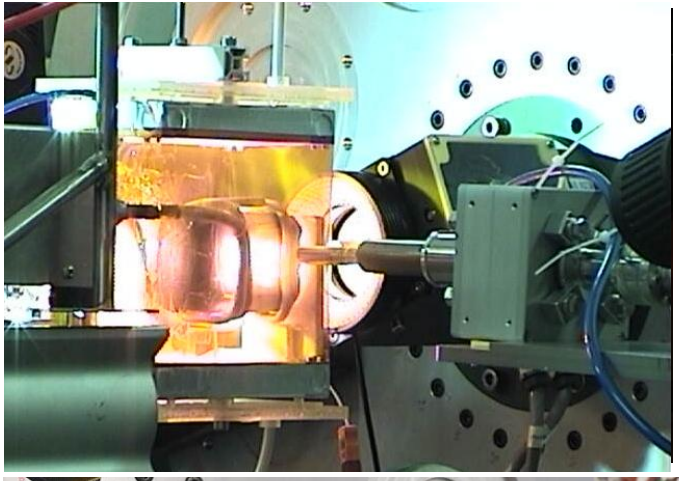
- Low temperature: Cryostream N_2 blower, 80–500 K
  Cryostat, ≥ 4 K ?
- High temperature: Air blowers, electrical heaters, mirror and induction furnaces, etc.
- Gas adsorption: Adsorption cells
- High pressure: Specialised beamlines with diamond anvil cells
- Electrochemistry: Electrochemical cells
- Strain: Strain rigs
- Chemistry: Reaction cells
- Etc.

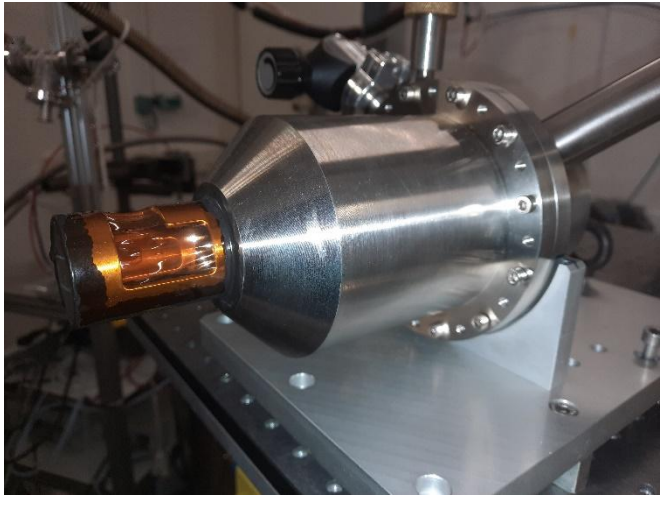
Sample environments

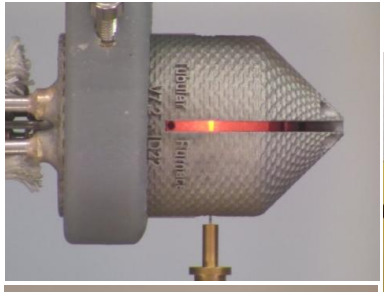


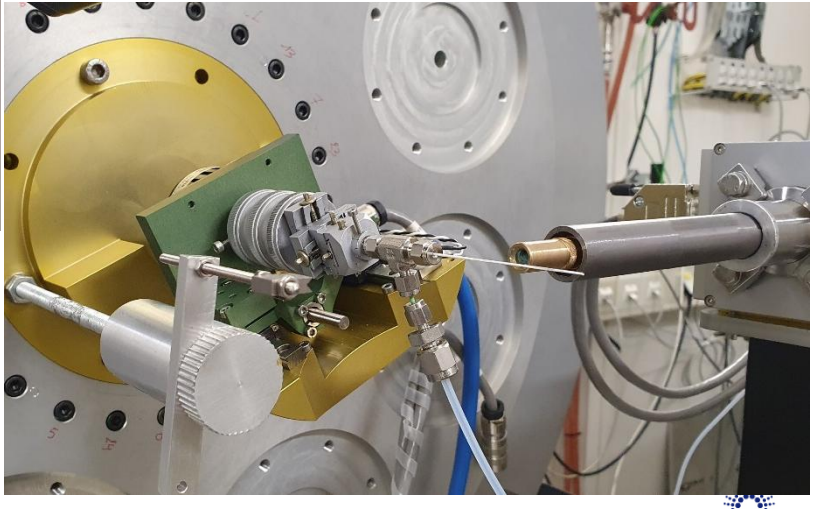
Cryostream & blower ⇐

Induction furnace ⇒







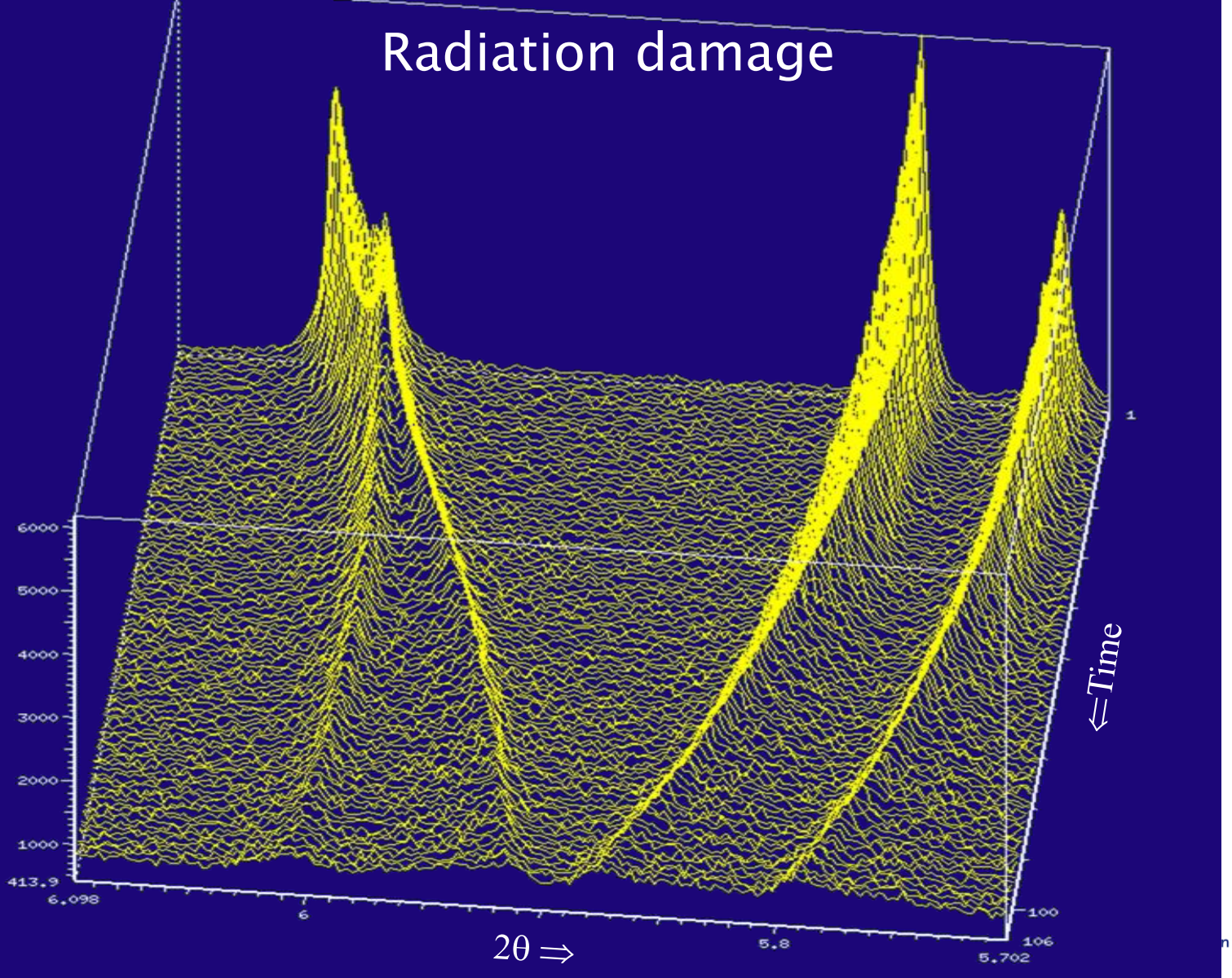


Liquid-He cryostat

Apollo 22

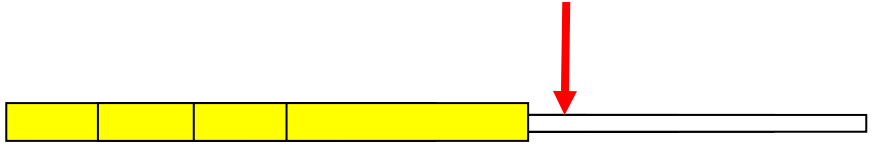
Gas cell

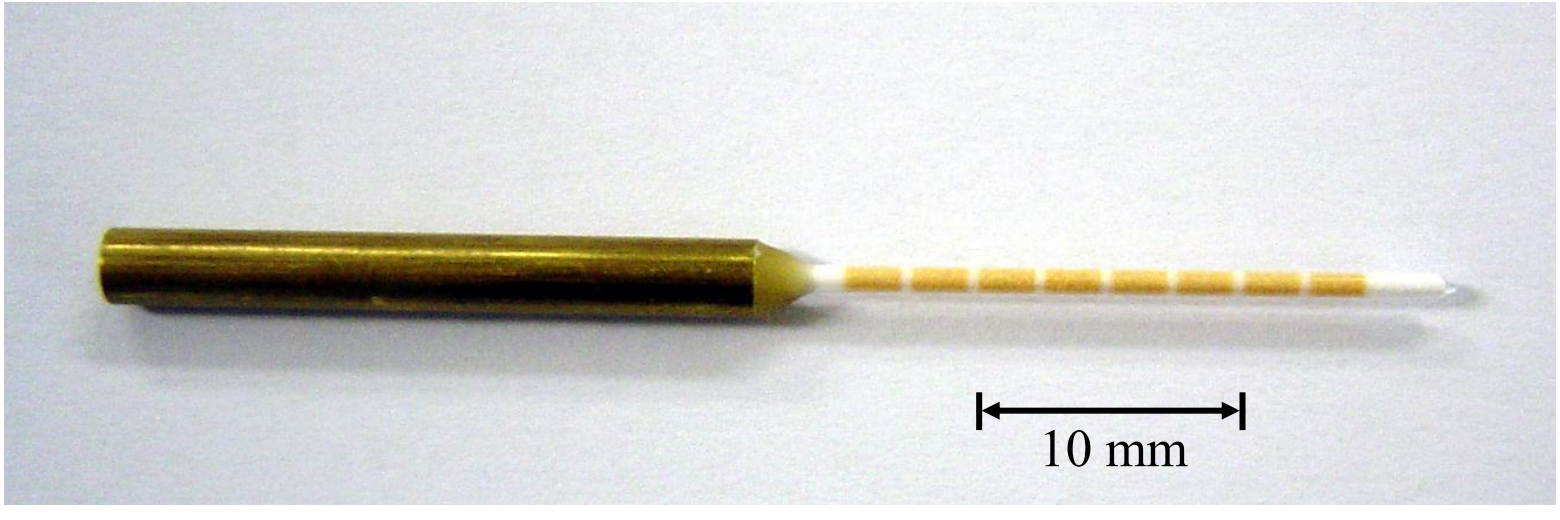
Radiation damage



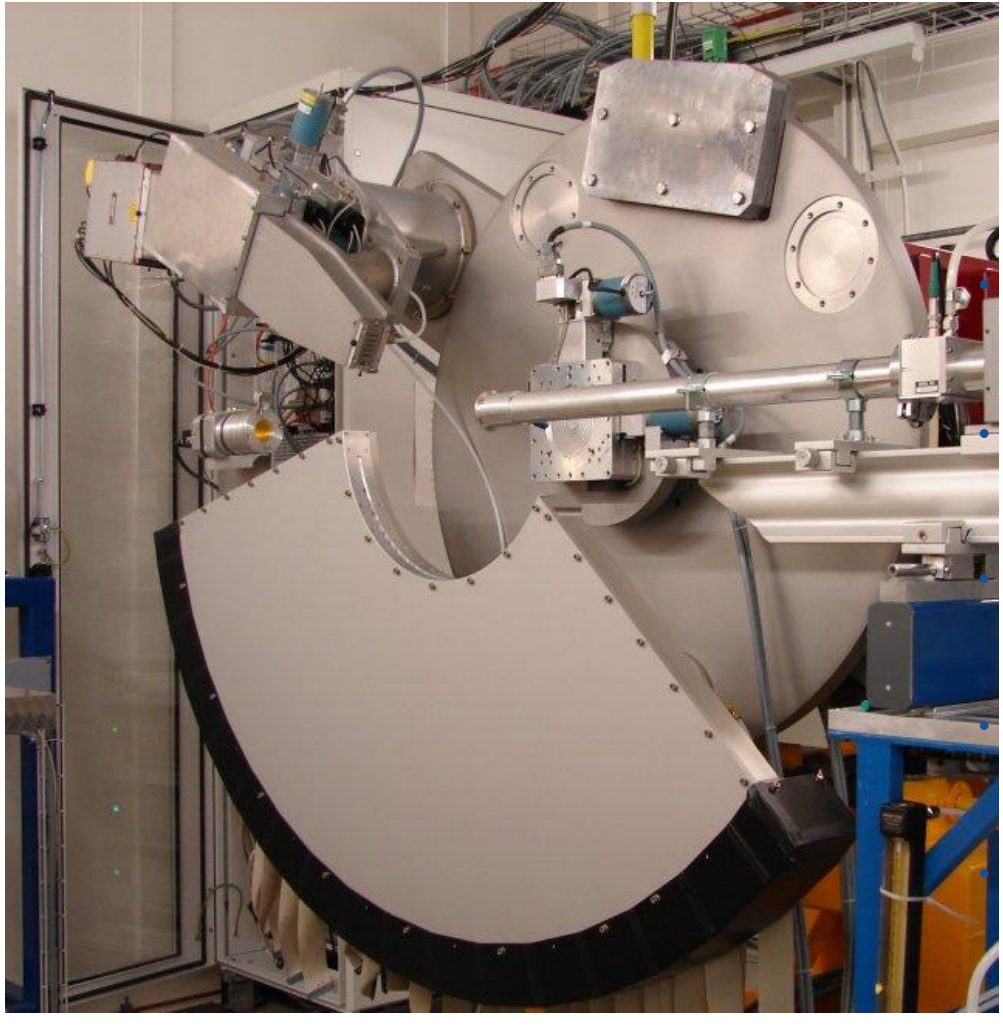
Radiation damage

Axial translation to expose fresh sample to the beam.





Mythen strip detector



Modular Si-strip photon-counting detector

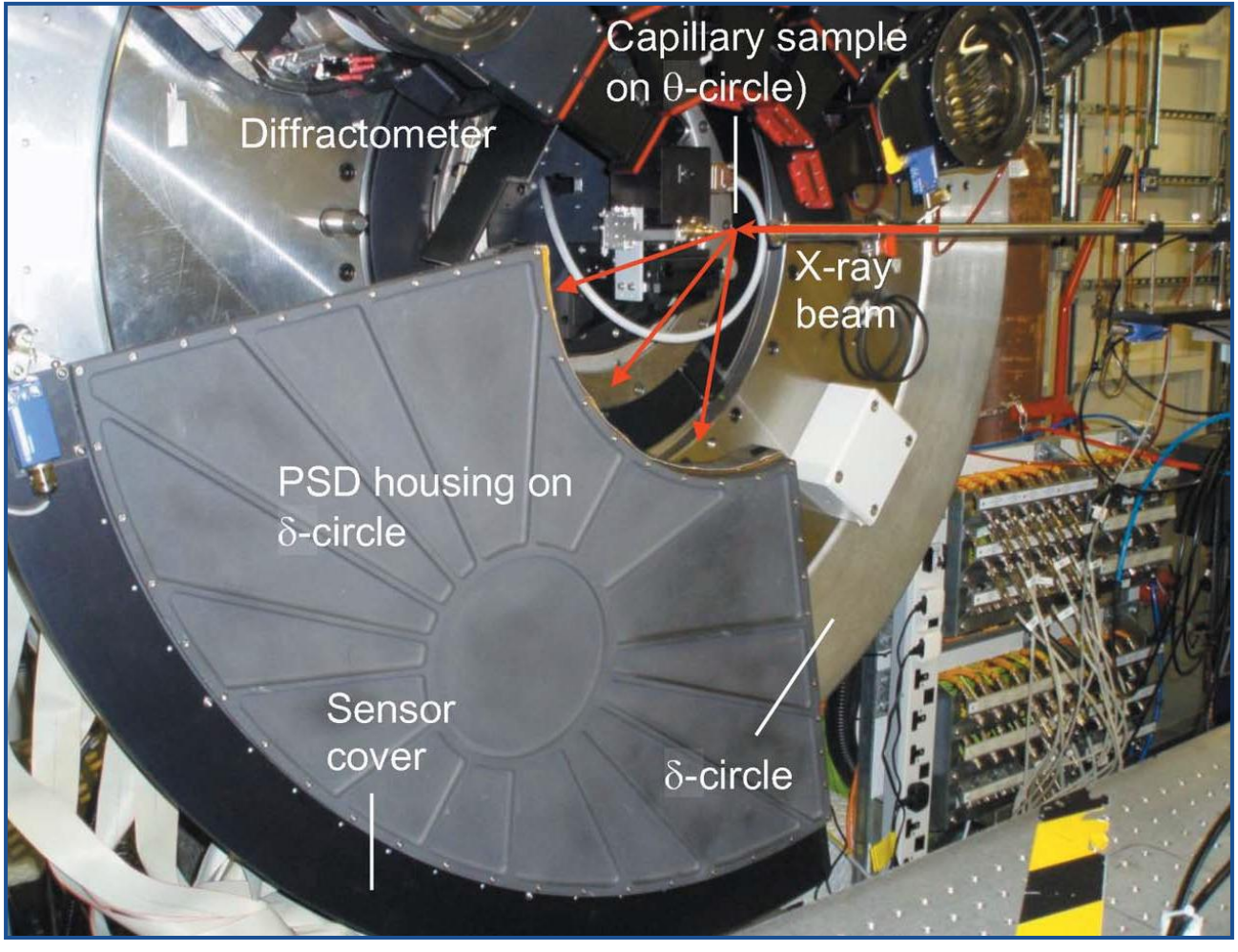
Unit =1280 channels, 50μm step, ≈ 4.83°, (step ≈ 0.004°)

The best 1d PSD for soft and intermediate energies ≤ 30 keV

Excellent statistical quality in seconds

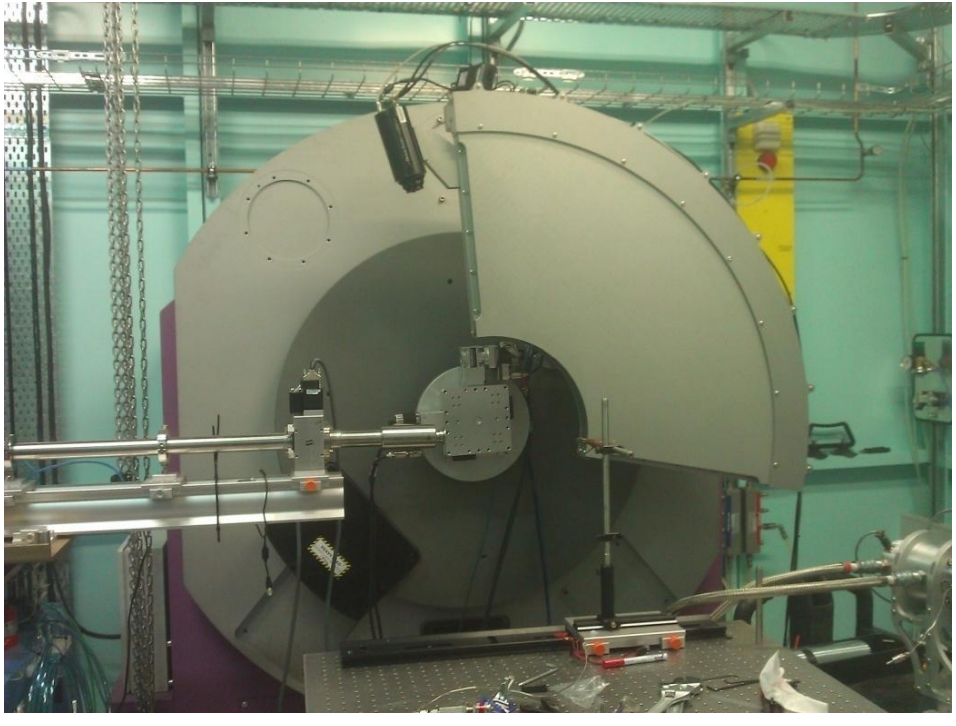
Much faster than analysers

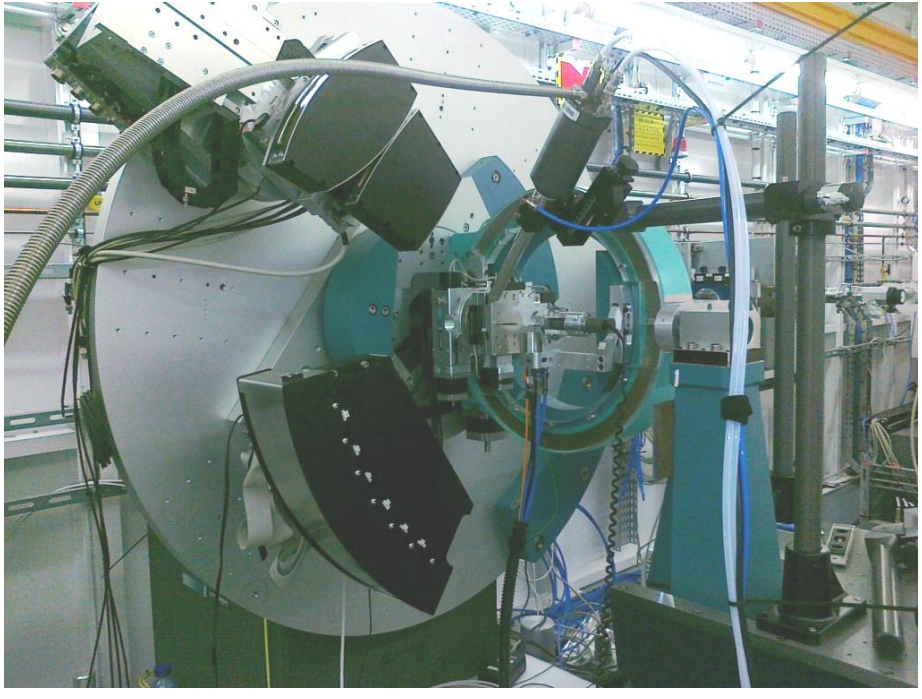
I11 Diamond


Capillary sample
on θ-circle)
Diffractometer
X-ray
beam
PSD housing on
δ-circle
Sensor
cover
δ-circle

Mythen strip detector

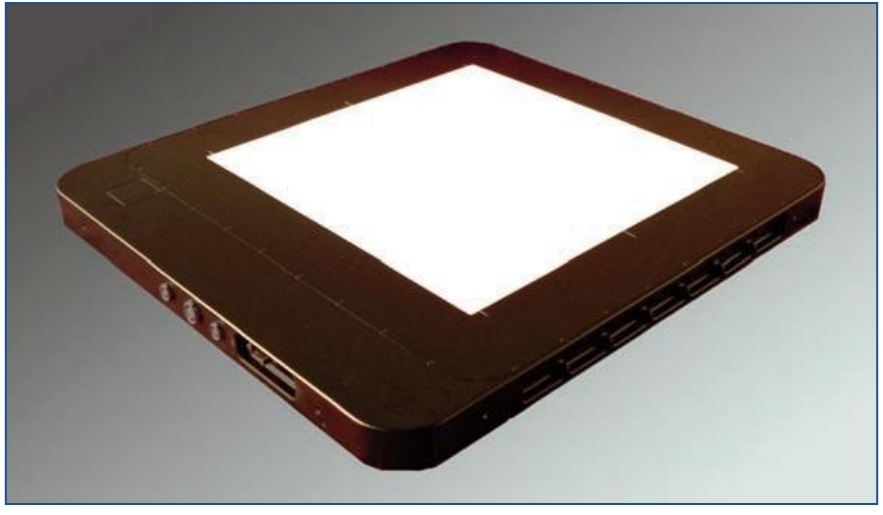
Australia





ALBA (Spain)
Mythen and multianalyser detectors

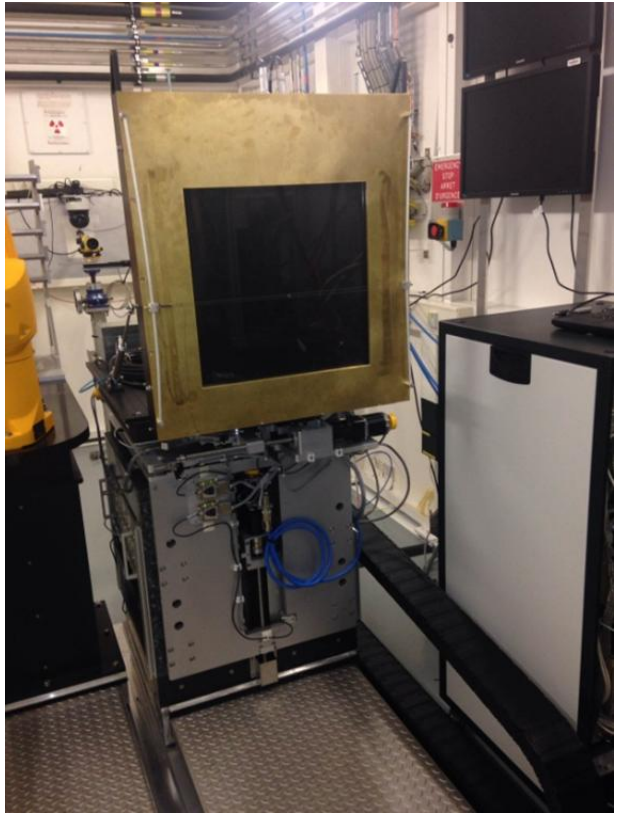
2d detectors



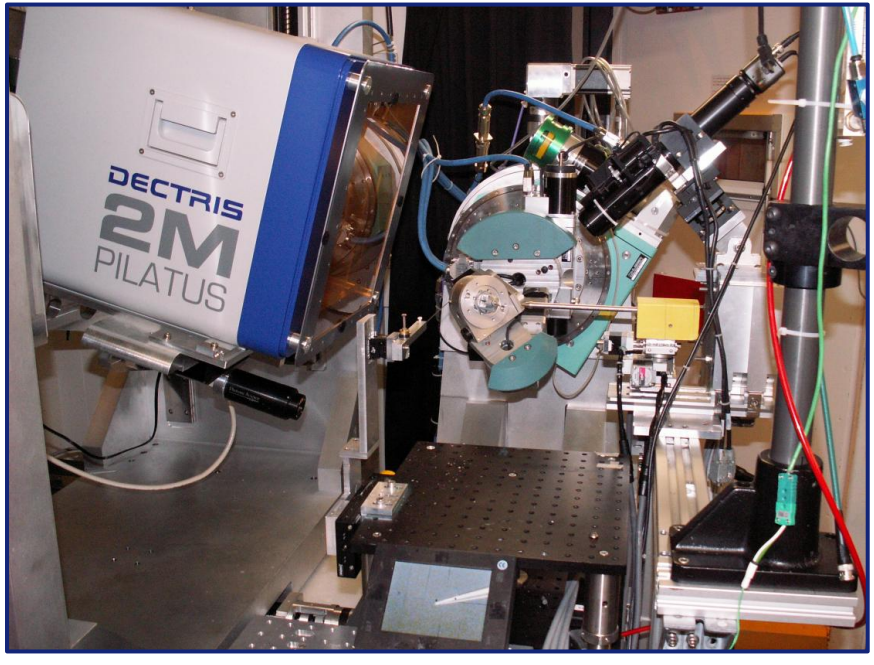
Perkin-Elmer/Varex medical imaging amorphous Si + scintillator 41× 41 cm^2 (100 or 200 μm pixel) (ID22, PETRA-III, APS, NSLS-II, etc.)

Dectris pixel detectors. Photon counting with Si or CdTe semiconductor sensor.

2d detectors

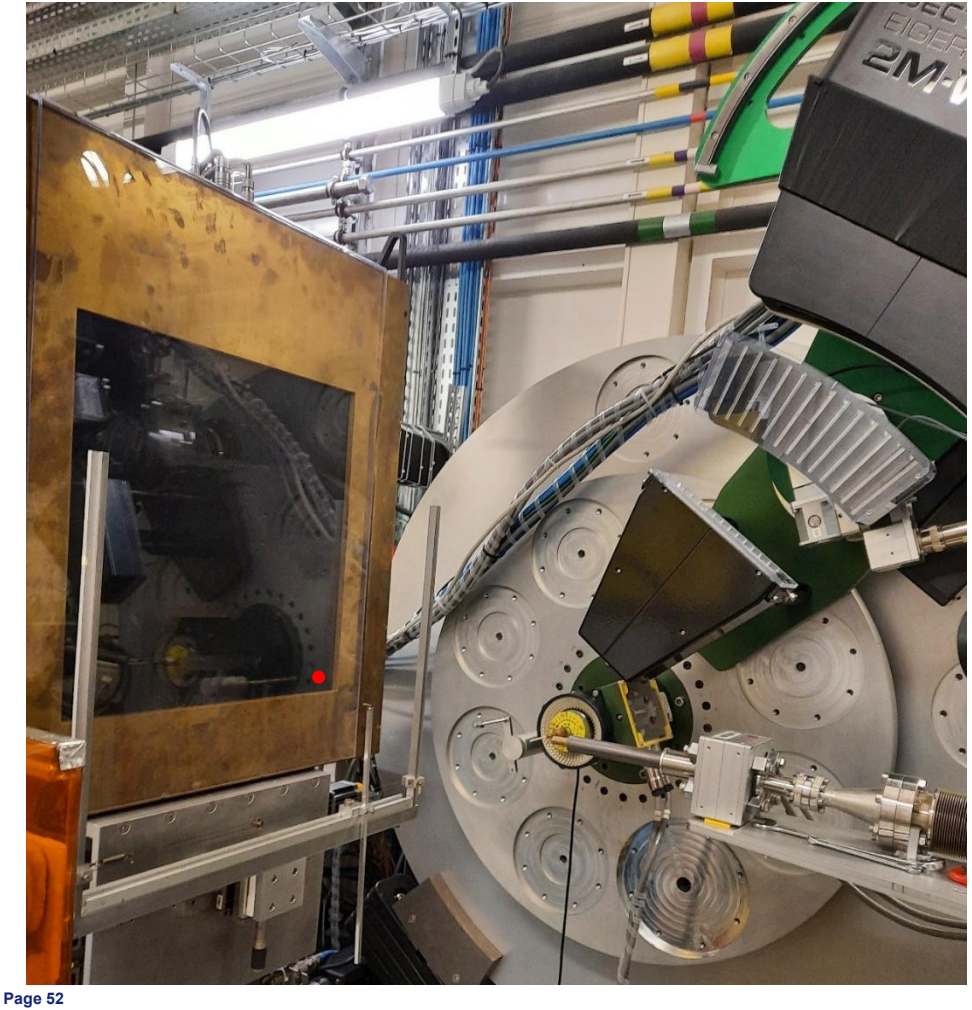


Perkin-Elmer medical imaging detectors (ID22, PETRA-III, APS, SLS-II, etc.), for fast PDF measurements.

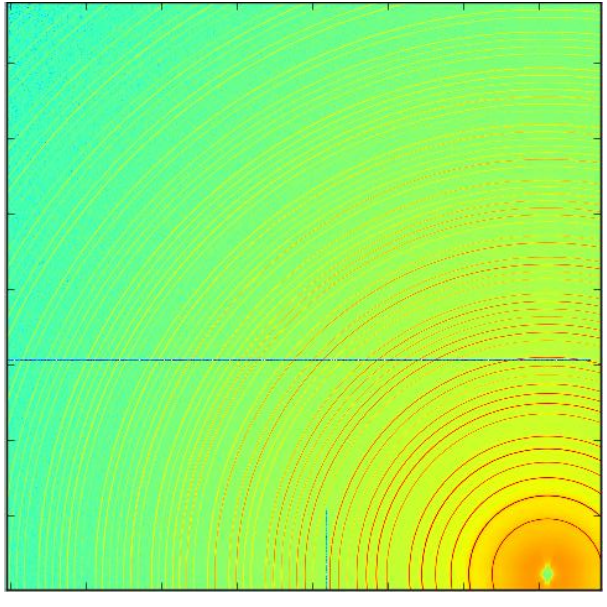


Dectris pixel detectors. Photon counting with Si or CdTe semiconductor sensor; Pilatus 2M on BM01A)

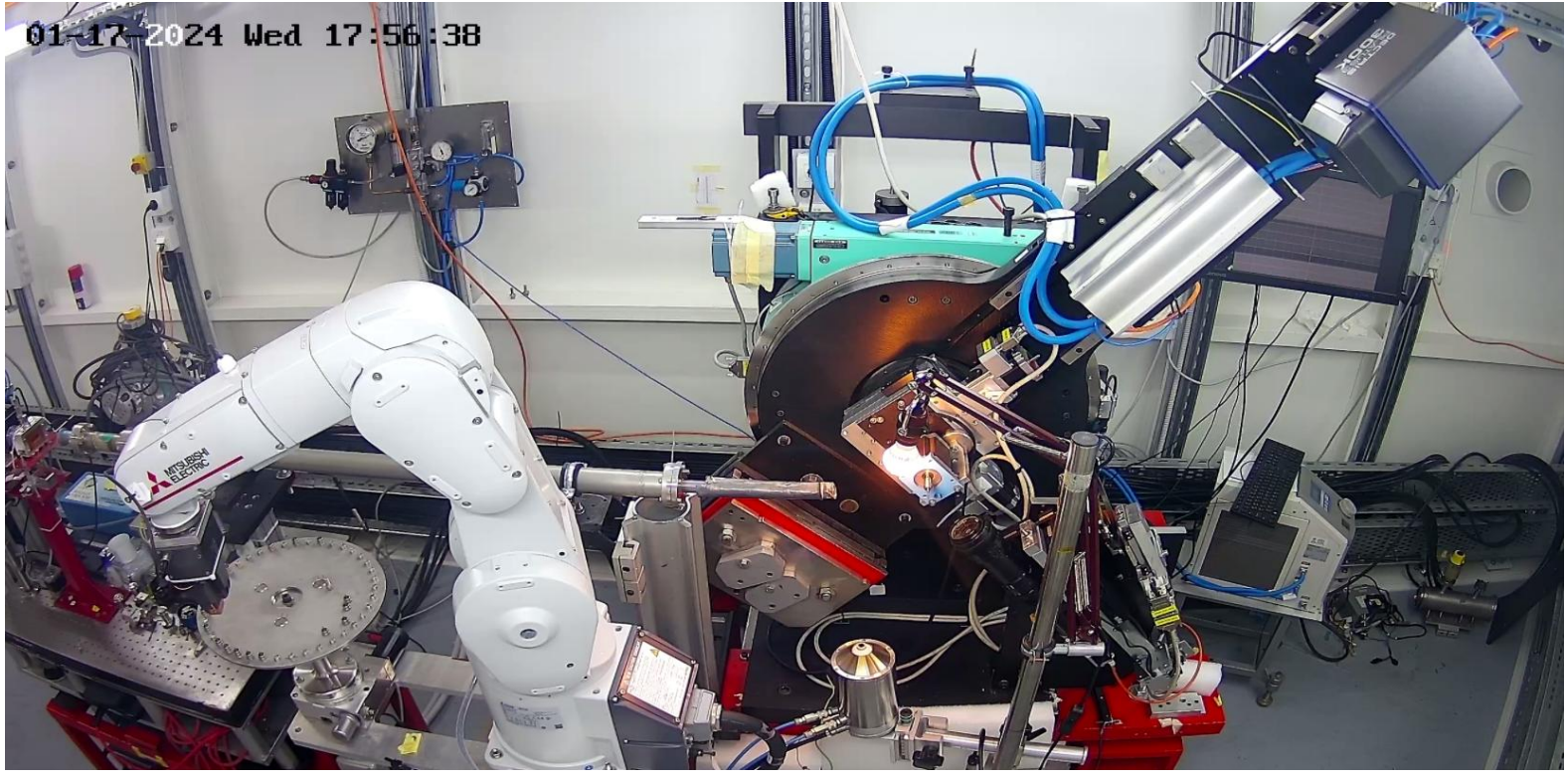
2d medical-imaging detector



41 × 41 cm² Perkin Elmer XRD 1611 medical-imaging detector for measurements up to 75 keV.



Scanned pixel detector



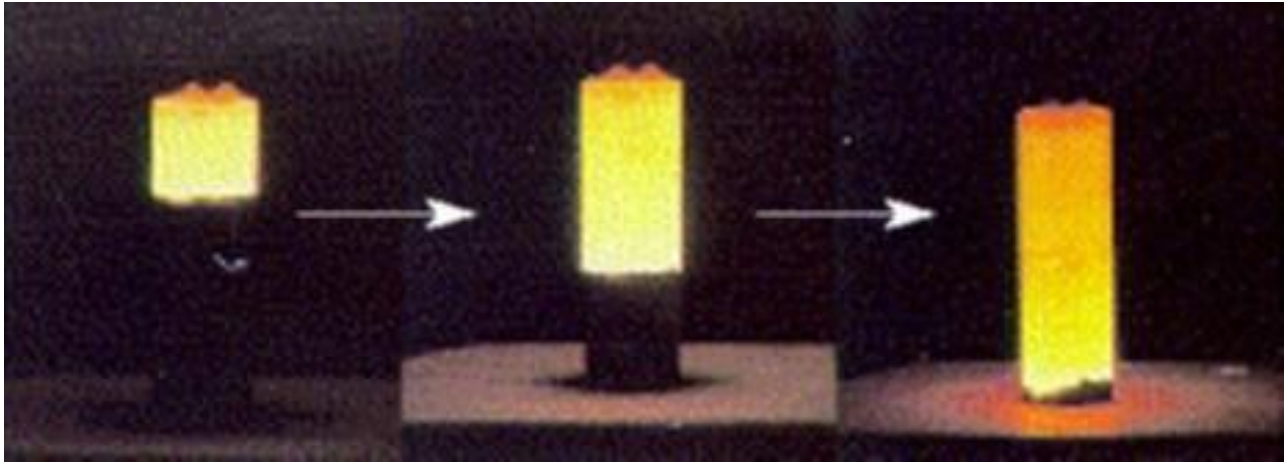
SESAME MS beamline

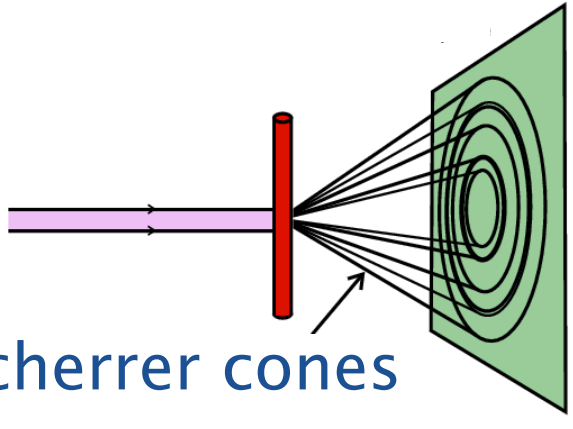
What sorts of experiments?

- Structural studies – crystal structures, atomic PDF analysis, etc.
- *In-situ* studies – evolution with temperature, time, atmosphere, voltage, etc., phase changes, solid-state chemistry, gas adsorption, electrochemistry.
- Anomalous scattering – distinguish neighbouring elements in the Periodic Table.
- High throughput – many samples, varied compositions or preparation conditions, etc.
- Quantitative analysis – many phases, trace phases.
- Microstructure – detailed analysis of peak shapes.
- Residual strain – mapping peak positions in components.
- Anything you can fit on. Very flexible instruments!

Very fast measurements

Self propagating combustion synthesis





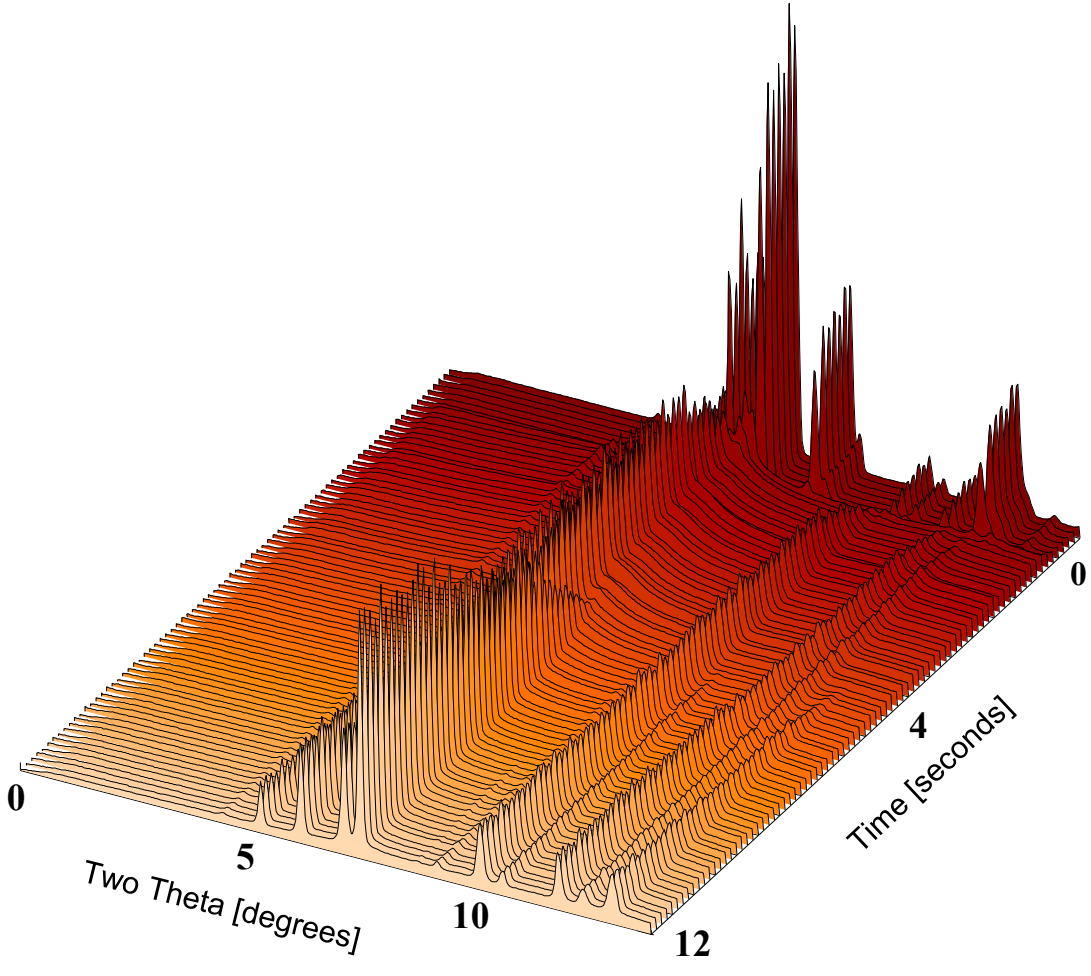
Fast, 2D detector

Debye-Scherrer cones

We have ignition

We have ignition

Powder pattern *vs* time



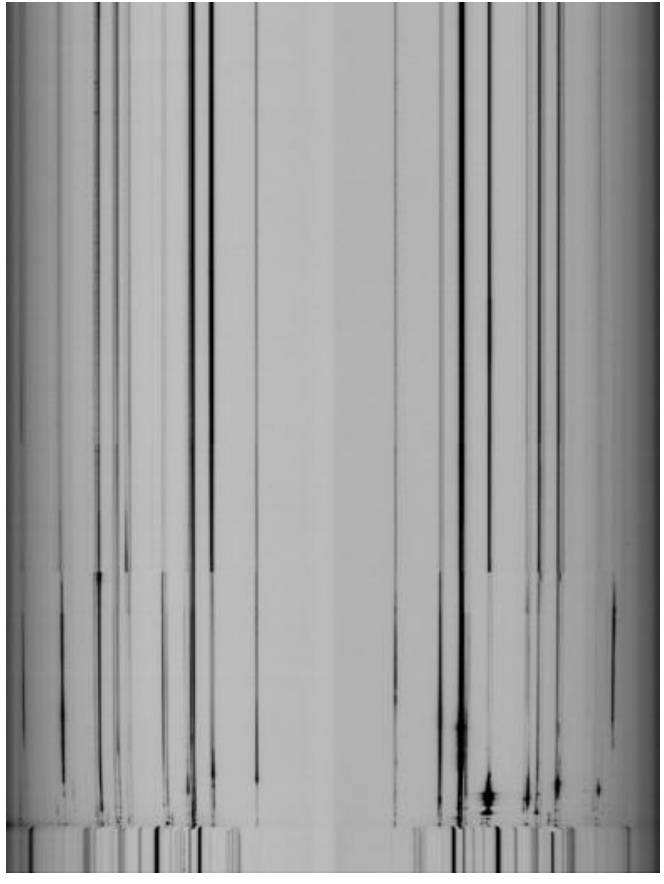
Synthesis of Jacobsite Fe_2MnO_4

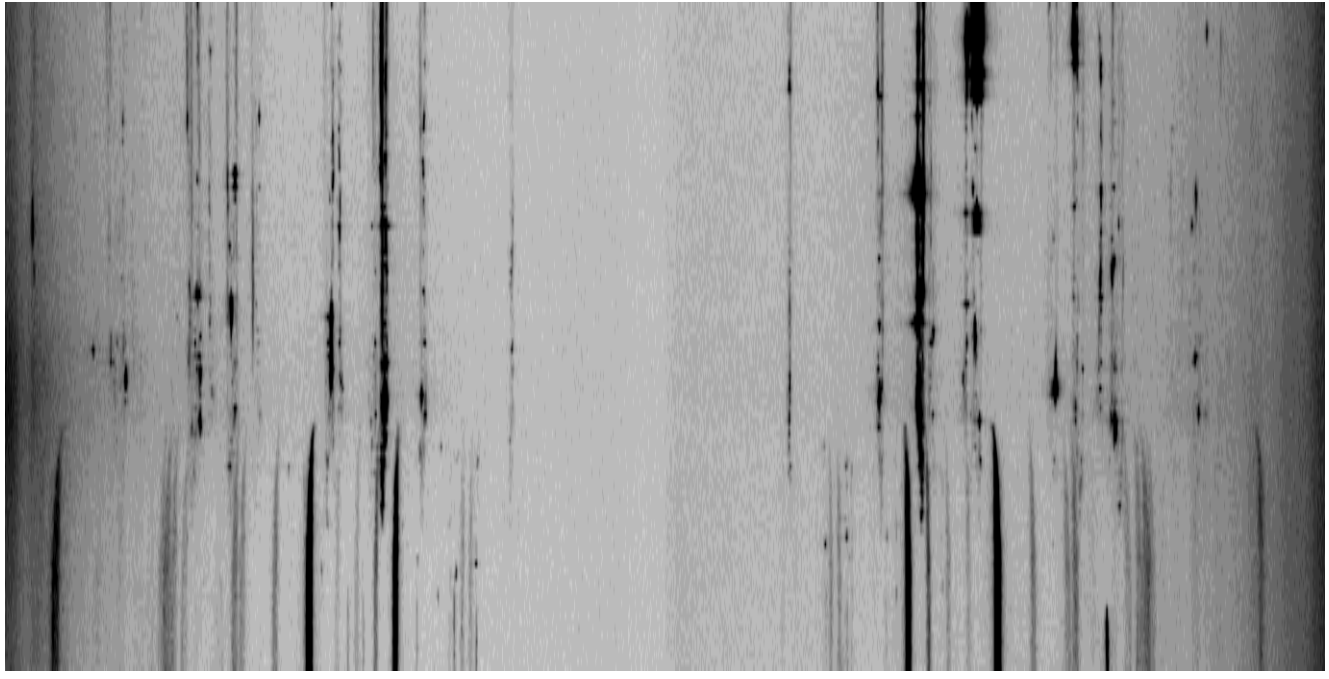
$12Mn_2O_3 + 8\ Fe_2O_3 + 32\ Fe + 9NaClO_4$

$\Rightarrow 24\ Fe_2MnO_4 + 9\ NaCl$

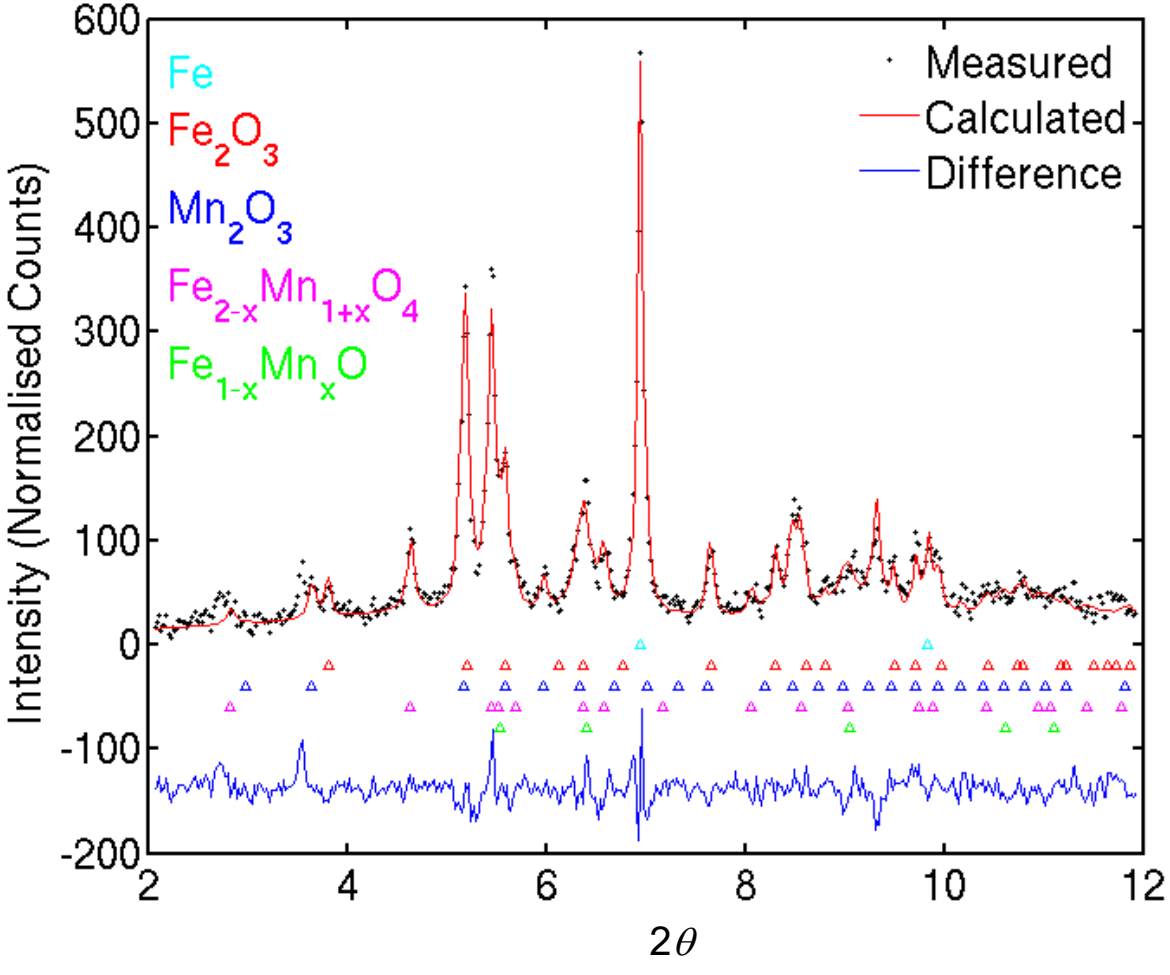
8192 diffraction patterns

5 ms acquisition each

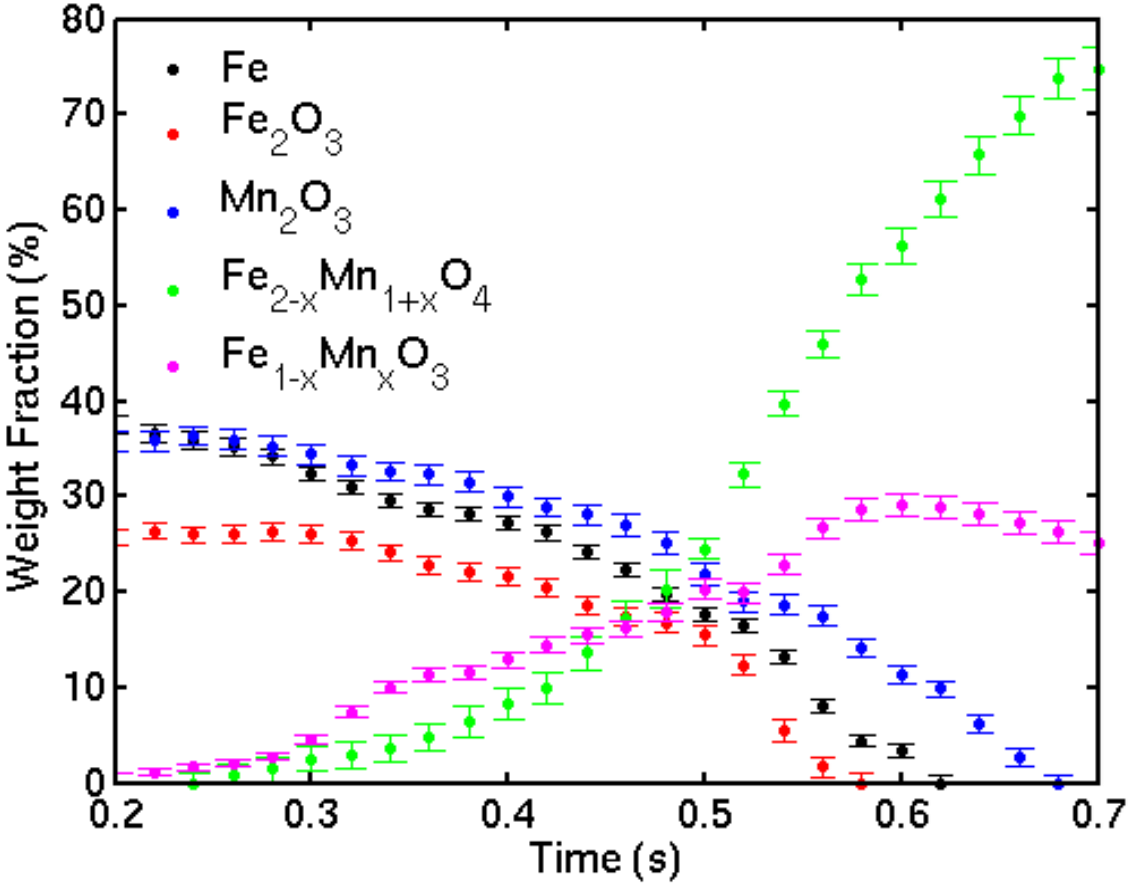



50 ms

Five-phase Rietveld refinement from 5 ms data



Evolution of phases



Anomalous scattering

$$F_{hkl} = \sum_n f_n \exp(2\pi i (hx_n + ky_n + lz_n))$$

where $f_n = f^0{}_n + f'_n + i f''_n$

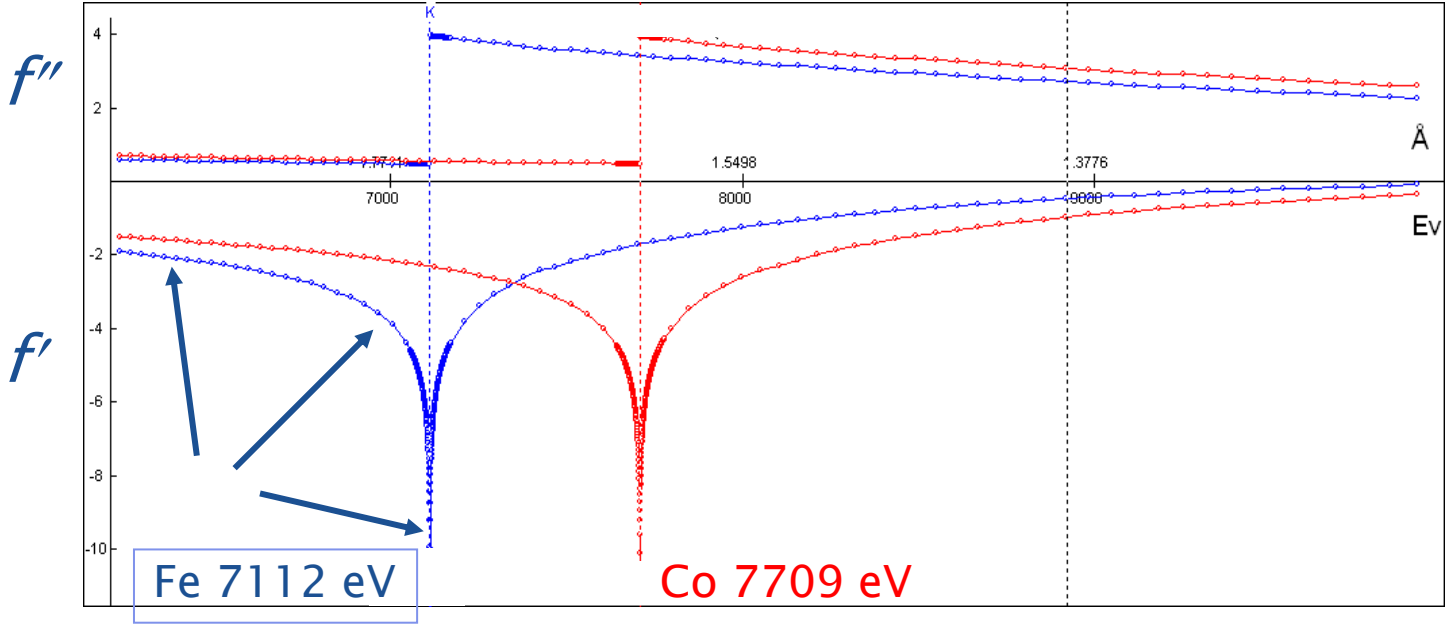
$f^0{}_n$ = normal scattering form factor

f'_n = real anomalous scattering term

if''_n = imaginary anomalous scattering term

Anomalous scattering

e.g. enhance sensitivity between Co and Fe



Luminescent mixed rare-earth pyrosilicates

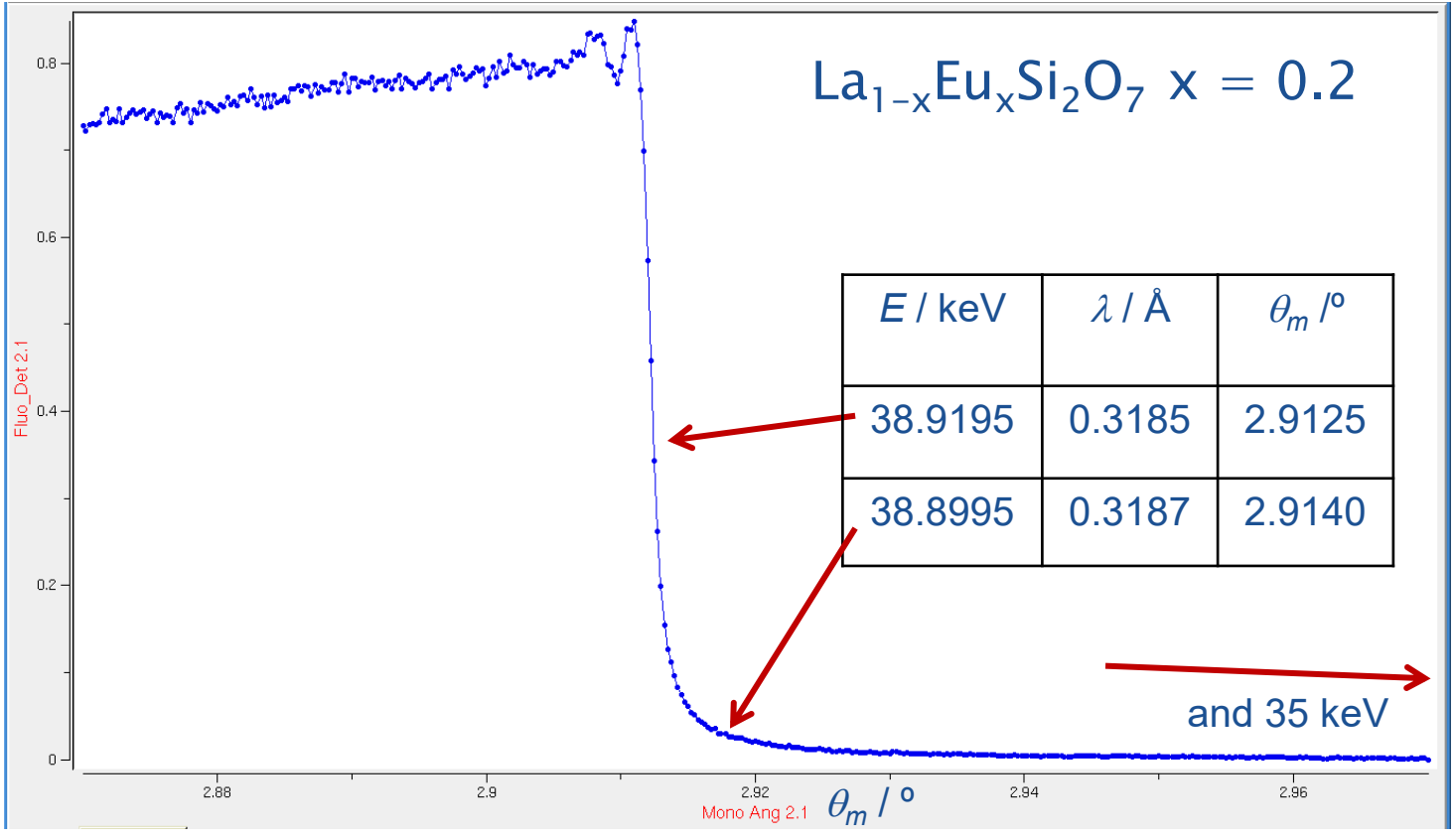
- $La_{1-x}Ho_xSi_2O_7$ and $La_{1-x}Eu_xSi_2O_7$
- Rare-earth pyrosilicates adopt various structures

  Ho-doped material = monoclinic with 2 RE sites

  Eu-doped material = tetragonal with 4 RE sites
- How are the RE metal ions distributed?
- Difficult (even with neutrons because of absorption)
- Tune to La K edge (38.9246 keV $\Leftrightarrow \lambda = 0.3185$ Å) to enhance contrast between RE elements via anomalous scattering
- $f = f_0 + f' + if''$

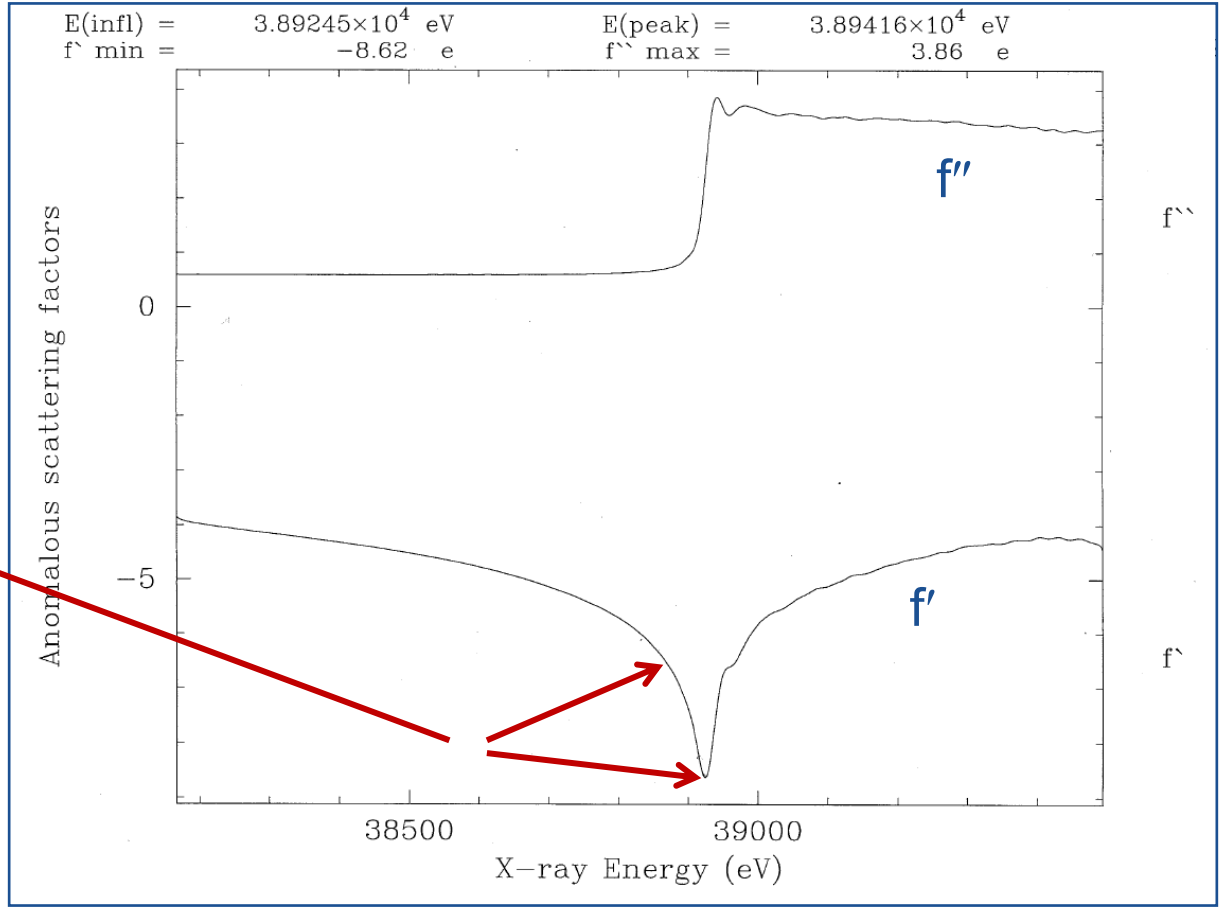
J. Phys. Chem. **C 117**, 20876, (2013); Inorg. Chem. **52**, 13469, (2013)

Fluorescence spectrum at La K edge



E / keV	λ / Å	θ_m /°
38.9195	0.3185	2.9125
38.8995	0.3187	2.9140

Kramers-Kronig inversion using CHOOCH



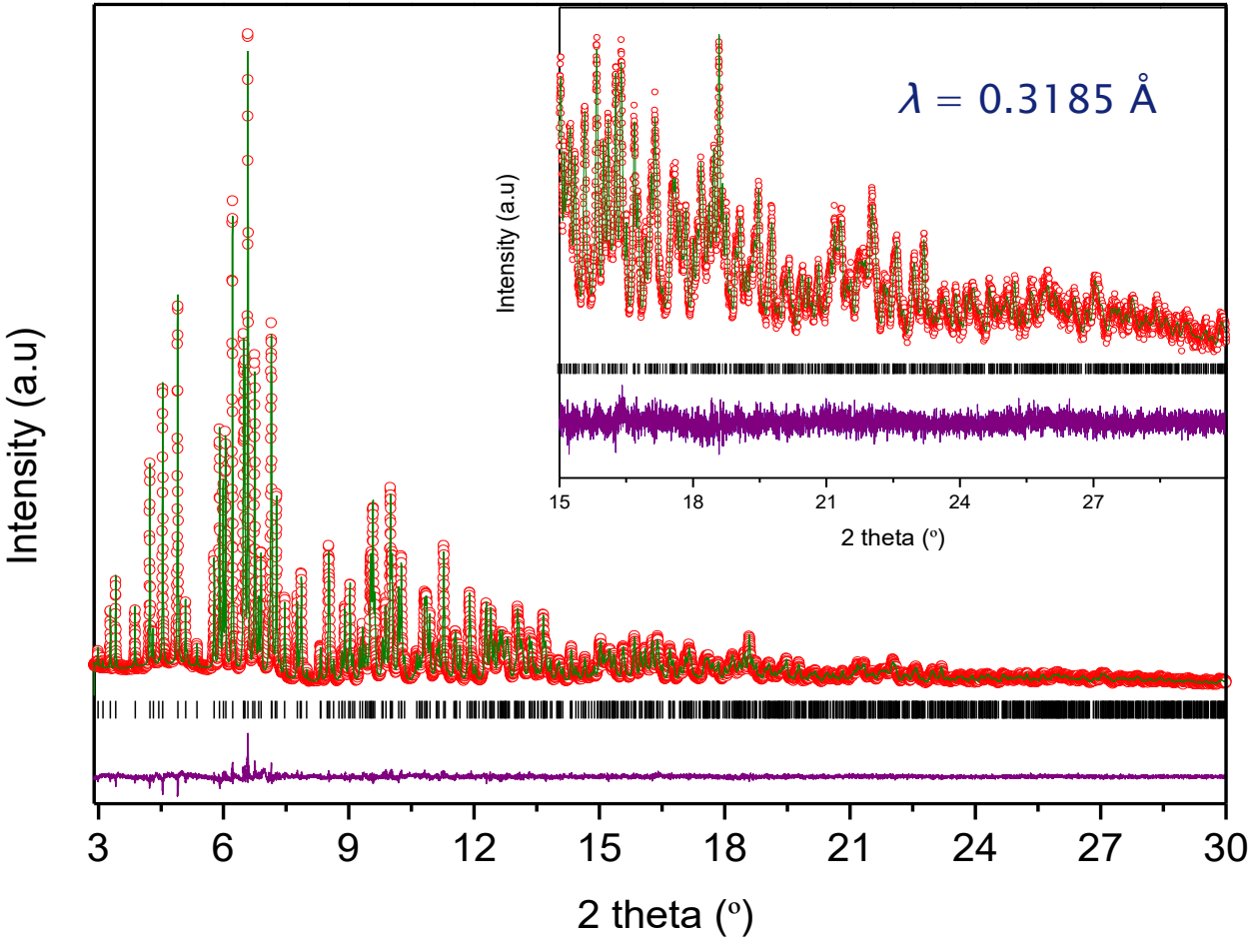
Refine with Topas

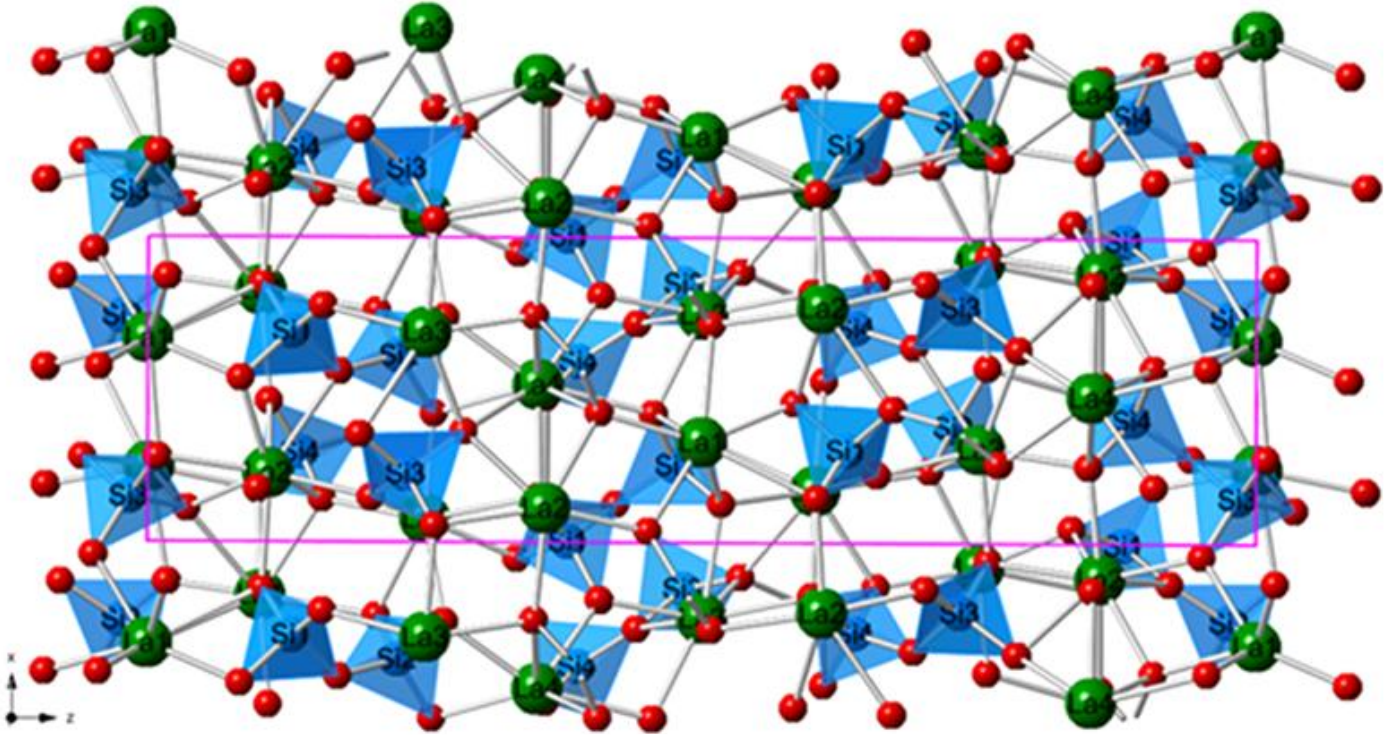
```
space_group "P41"
prm !o1 0.80
prm o2 -0.02711`_0.00942
prm o3  0.09960`_0.00837
prm o4  0.05321`_0.00512

prm slo = o1+o2+o3+o4 ; :  0.92570`_0.01360
prm s2o = o1-o2+o3-o4 ; :  0.87350`_0.01360
prm s3o = o1+o2-o3-o4 ; :  0.62007`_0.01360
prm s4o = o1-o2-o3+o4 ; :  0.78072`_0.01360
site La1    x x1  0.75932`_0.00012 y y1  0.30413`_0.00011 z 0                    occ La+3 = slo  ;
                                                                                 occ Eu+3 = 1 - slo ;
site La2    x x2  0.52106`_0.00012 y y2  0.17115`_0.00012 z z2  0.14854`_0.00005 occ La+3 = s2o ;
                                                                                 occ Eu+3 = 1 - s2o ;
site La3    x x3  0.33678`_0.00011 y y3  0.92222`_0.00011 z z3  0.00079`_0.00006 occ La+3 = s3o ;
                                                                                 occ Eu+3 = 1 - s3o ;
site La4    x x4  0.12002`_0.00012 y y4  0.76699`_0.00012 z z4  0.14043`_0.00004 occ La+3 = s4o ;
                                                                                 occ Eu+3 = 1 - s4o ;
```

- Fit to three data sets simultaneously
- Partially flexible rigid body for Si_2O_7 units
- Constrain overall RE occupancies to known values

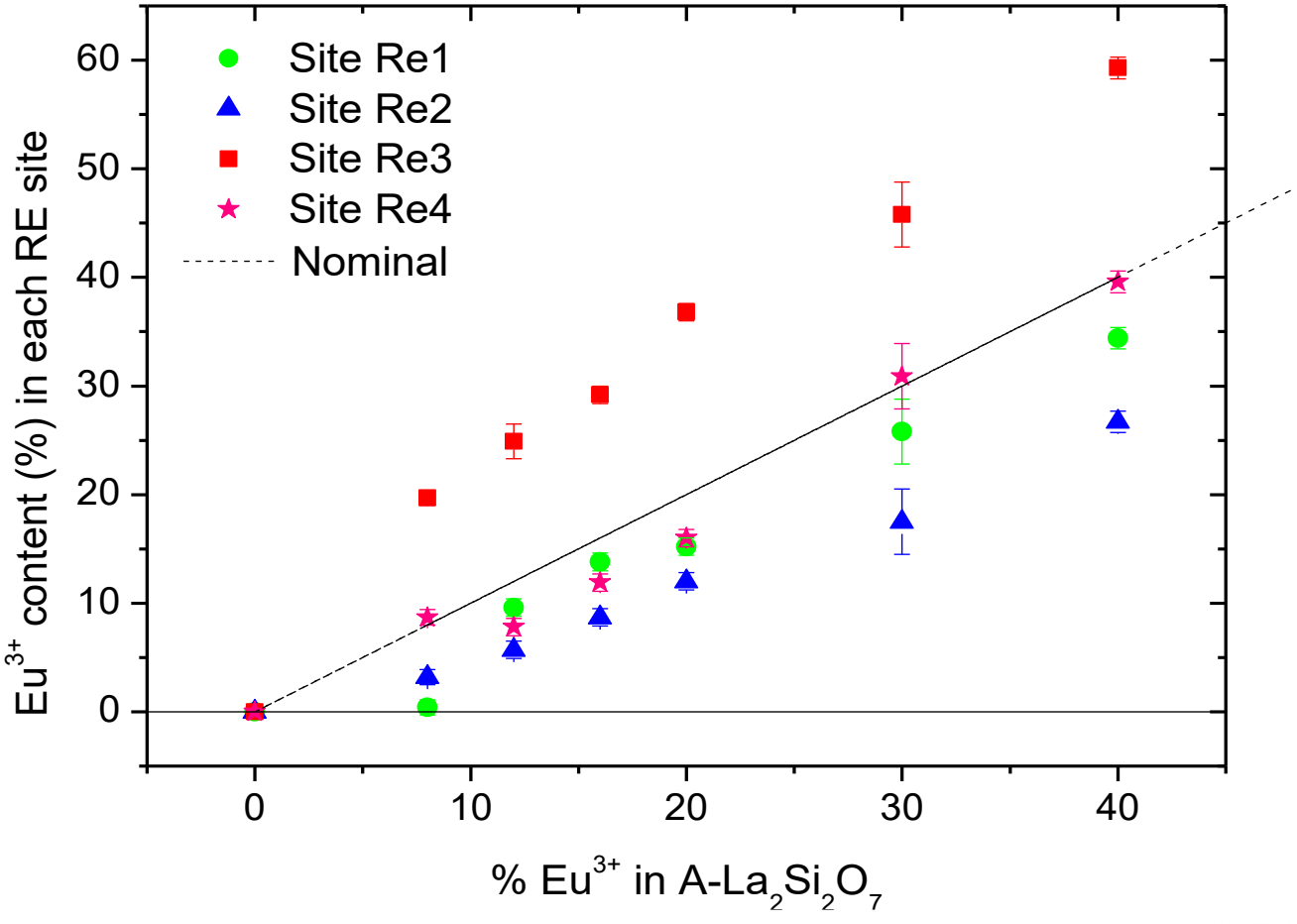
Rietveld fit simultaneously to the 3 data sets

Space group $P4_1$, a = 6.77798(4) Å, c = 24.6762(1) Å




La1
La2
La3
La4
Si1
Si2
Si3
Si4
Si5
x
z

Preference for Eu in site 3



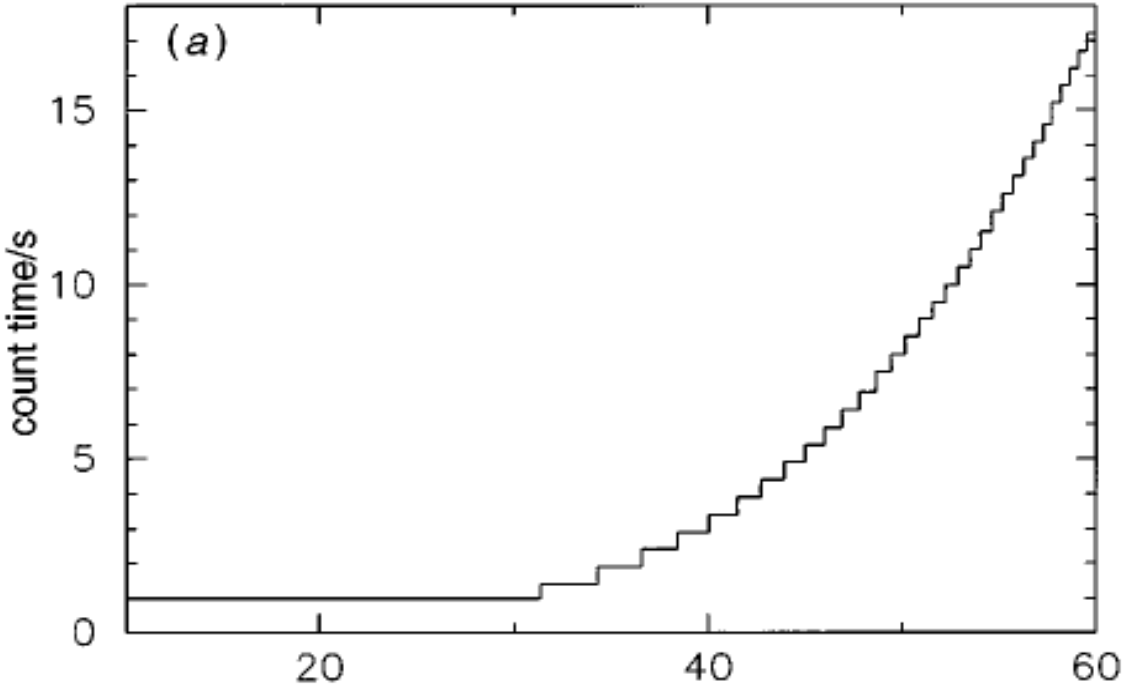
PDF analysis

Pair Distribution Function analysis allows structural information to be obtained despite a lack of translational periodicity in crystallographically-challenged materials, e.g.

- glasses,
- quasicrystals,
- nanoparticles, nanocrystals,
- disordered and heavily defective materials,
- aperiodic materials, etc.

How long to count?

Variable count time to compensate for decrease in scattering power with θ (form factors, B factors)



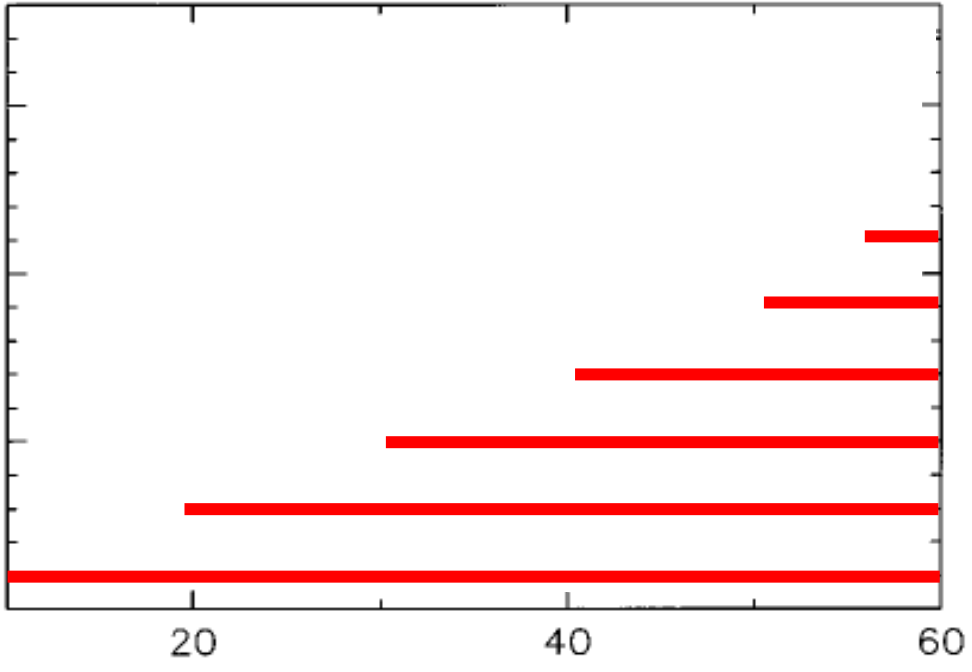
Shankland *et al.* J. Mat. Chem. **7**, 569, (1997)

How long to count?

Know what you want to use the data for

e.g. for crystallography count until
$R_{exp} = [N / \sum_i w_i y_i(\text{obs})^2]^{1/2} < 0.02$

#	2θ range
6	55–60
5	50–60
4	40–60
3	30–60
2	20–60
1	0–60



See McCusker *et al.* J. Appl. Cryst. **32**, 36–50, (1999) for general sound advice

Page 76

Limitations of synchrotron diffraction

- Access – proposal, waiting, travelling, sample shipping, limited beam time.
- Not yours – lack of control of facilities, conditions, options.
- Radiation damage for sensitive samples.
- Reproducibility of beamline setup?

Neutrons

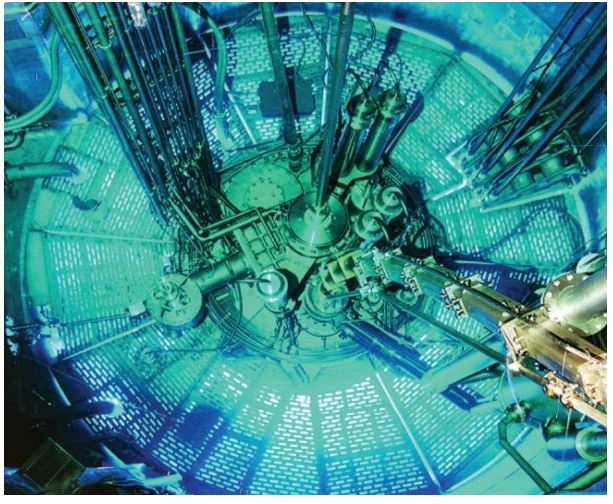
Mass m_n	$1.67492750056(85) \times 10^{-27}$ kg
Charge	0
Spin	½
Magnetic moment	$-9.6623653(23) \times 10^{-27}$ J T^{-1}
	$-1.041\ 875\ 65(25) \times 10^{-3}\ \mu_B$

- Interacts with atomic nuclei via strong nuclear force and electromagnetically with unpaired spins.
- De Broglie relationship, $\lambda = h/m_n v$

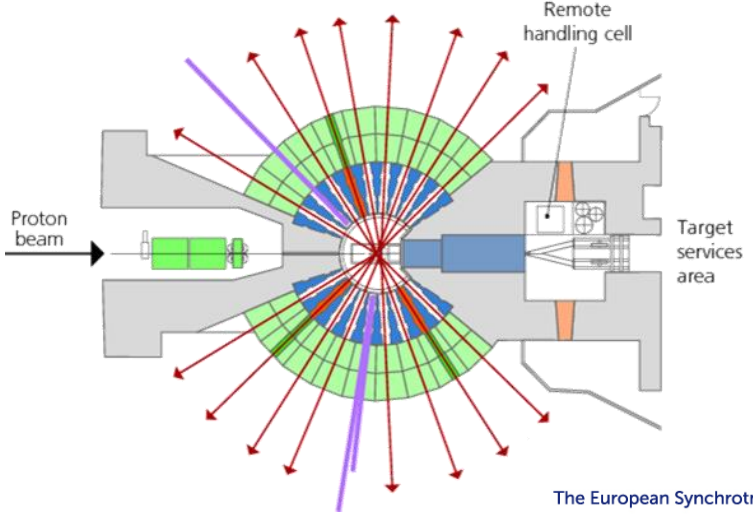
  $\Rightarrow$ a neutron moving at 2200 m s^{-1} has $\lambda \approx 1.8$ Å.
- Very weakly absorbed, except by certain nuclei, ^{6}Li, ^{10}B, ^{113}Cd, ^{155}Gd, ^{157}Gd, etc.

Production of neutrons

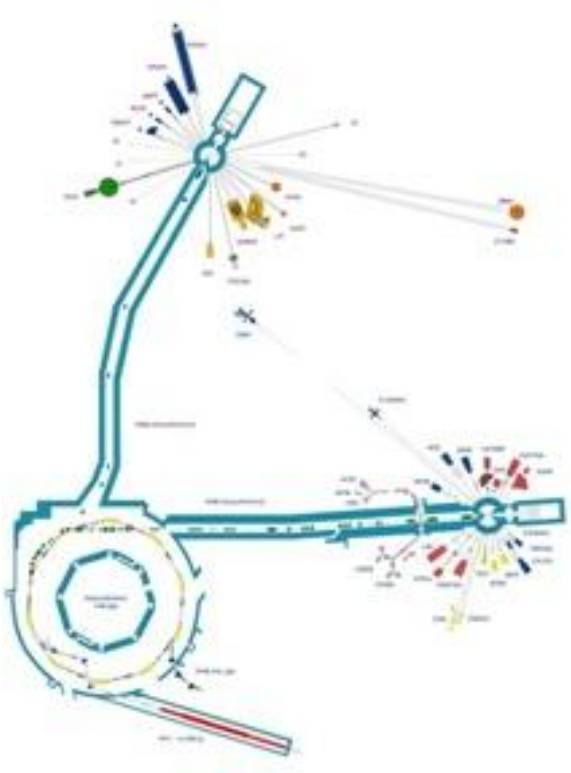
Nuclear reactor, via fission of ^{235}U.



Spallation source, energetic particles, usually protons with kinetic energy of up to 1 GeV, bombard a heavy-element target such as Pb, Ta, Hg.



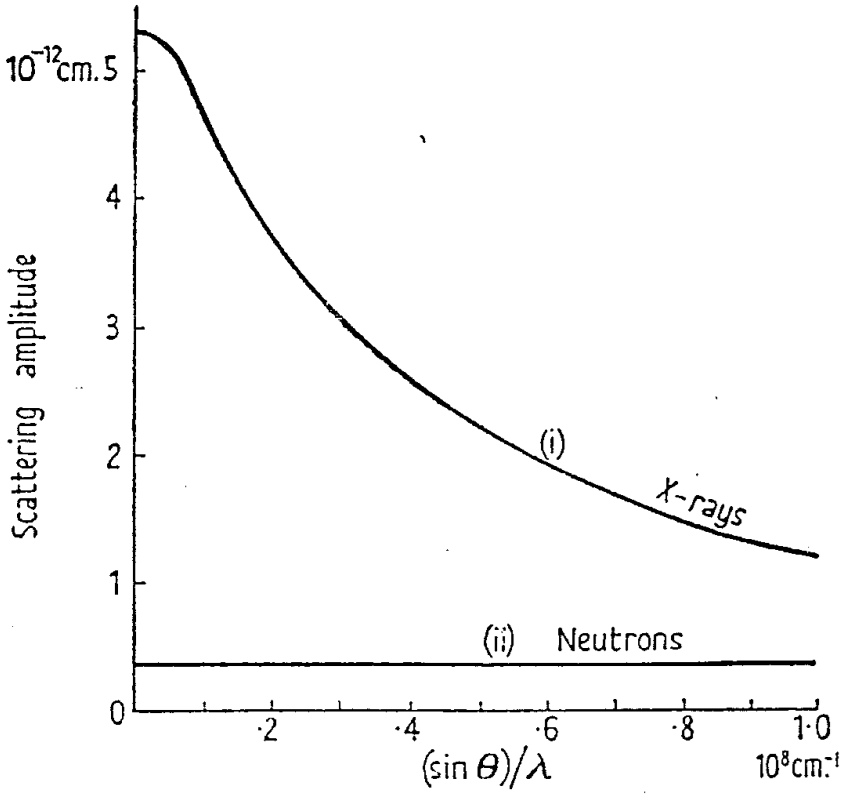
Rutherford Appleton Laboratory spallation neutron source ISIS



European Spallation Source (Lund)

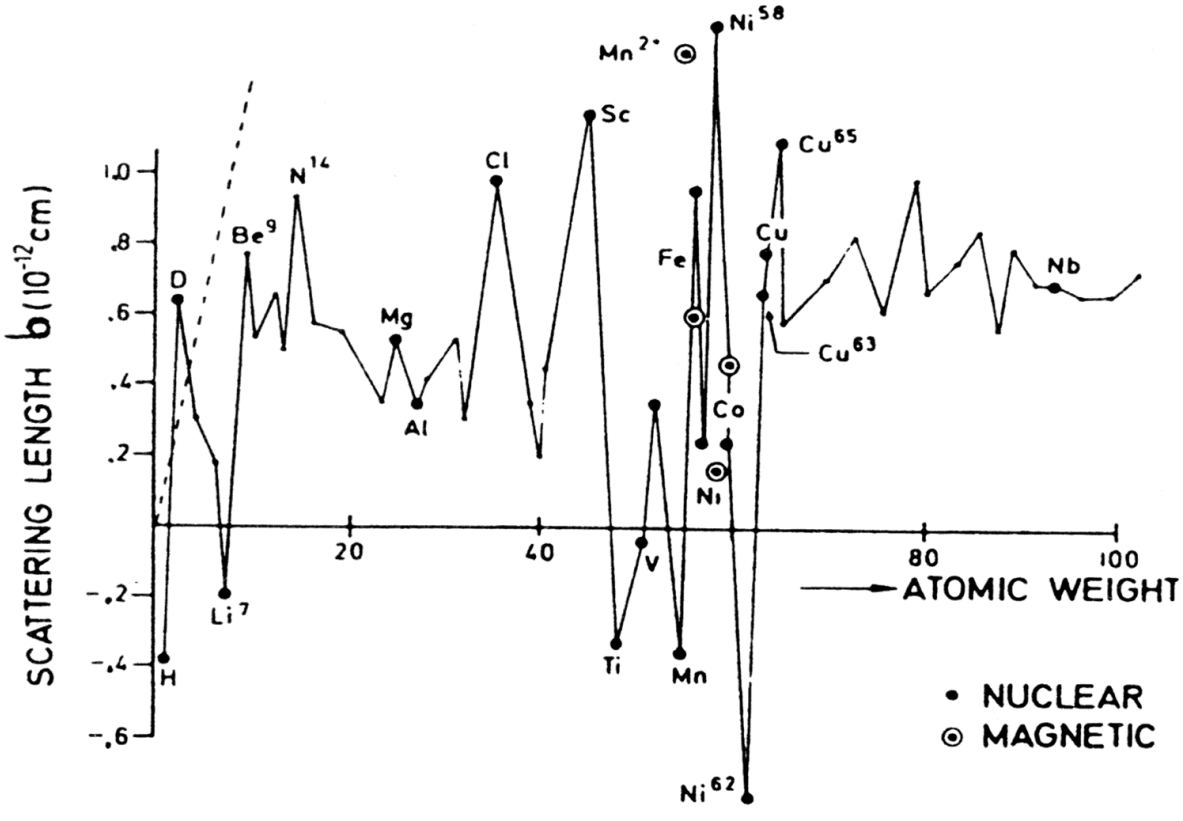
Neutron nuclear scattering lengths

No fall off in scattering power with 2θ, e.g. for potassium



Neutron nuclear scattering lengths

Vary with atomic nucleus, from isotope to isotope



Sample holders for neutrons

Vanadium cans

Silica glass

Uses of neutron diffraction

- Magnetic structures.
- Refinement of light atoms, especially when heavy ones are also present in the sample.
- Hydrogen bonding (often via deuterated sample).
- Refinement of systems with disorder, non-stoichiometry, etc. because "high-2θ" (low-d-spacing) data quality.
- In-situ studies, complex sample set ups (because of penetration).

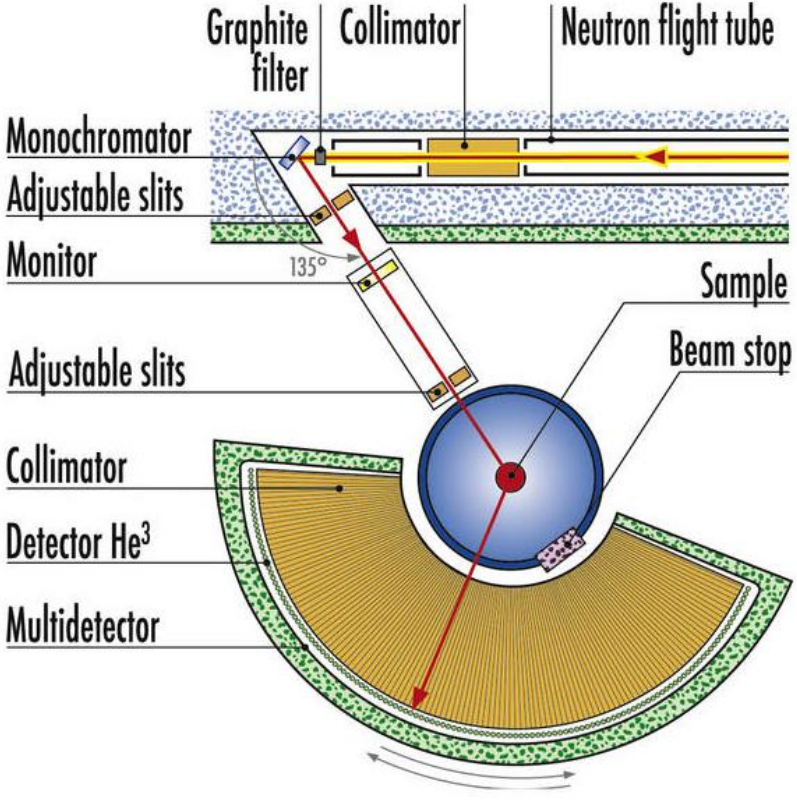
Monochromatic angle dispersive

Steady-state source, e.g. reactor or continuous spallation source.

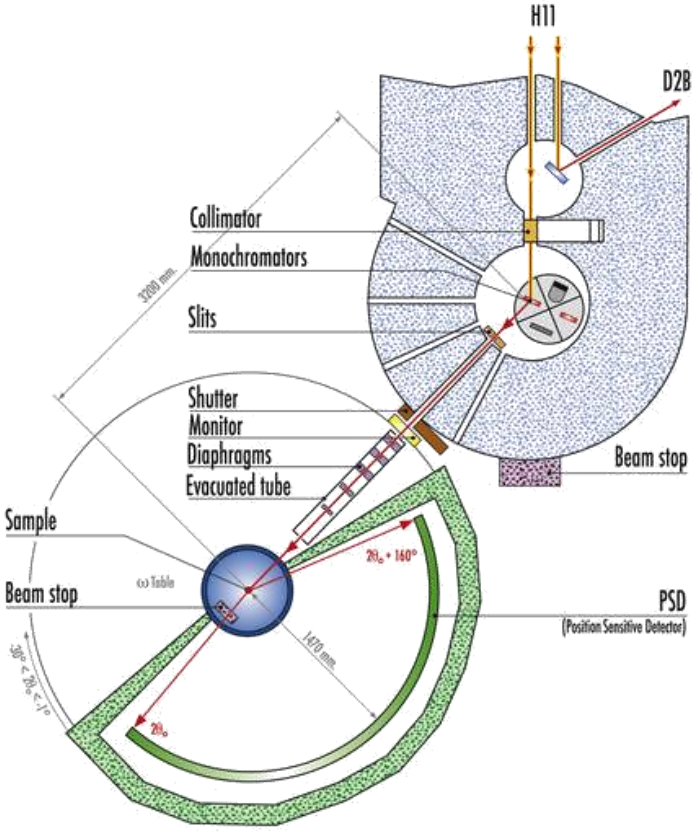
λ selected by a single-bounce monochromator.

Multiple detectors scanned, or PSD.

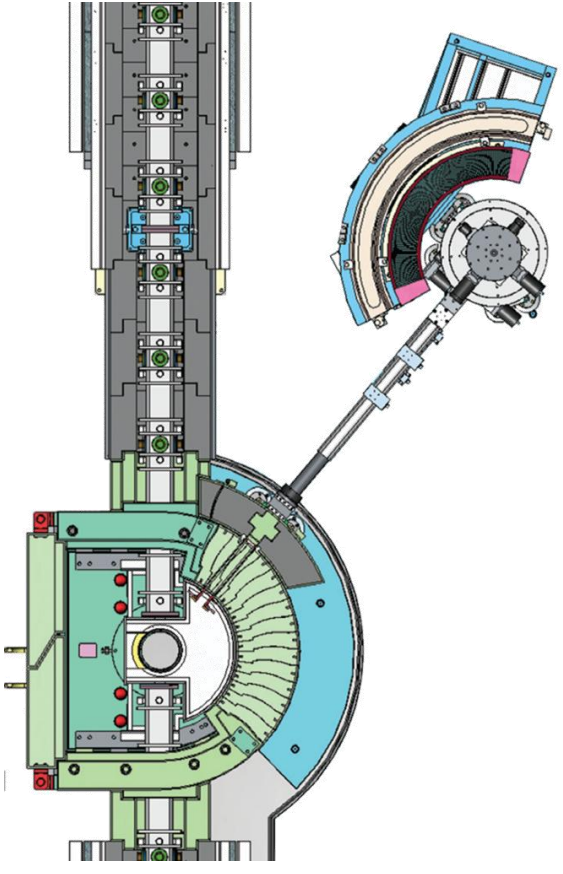
e.g. D2B at ILL



Monochromatic angle dispersive

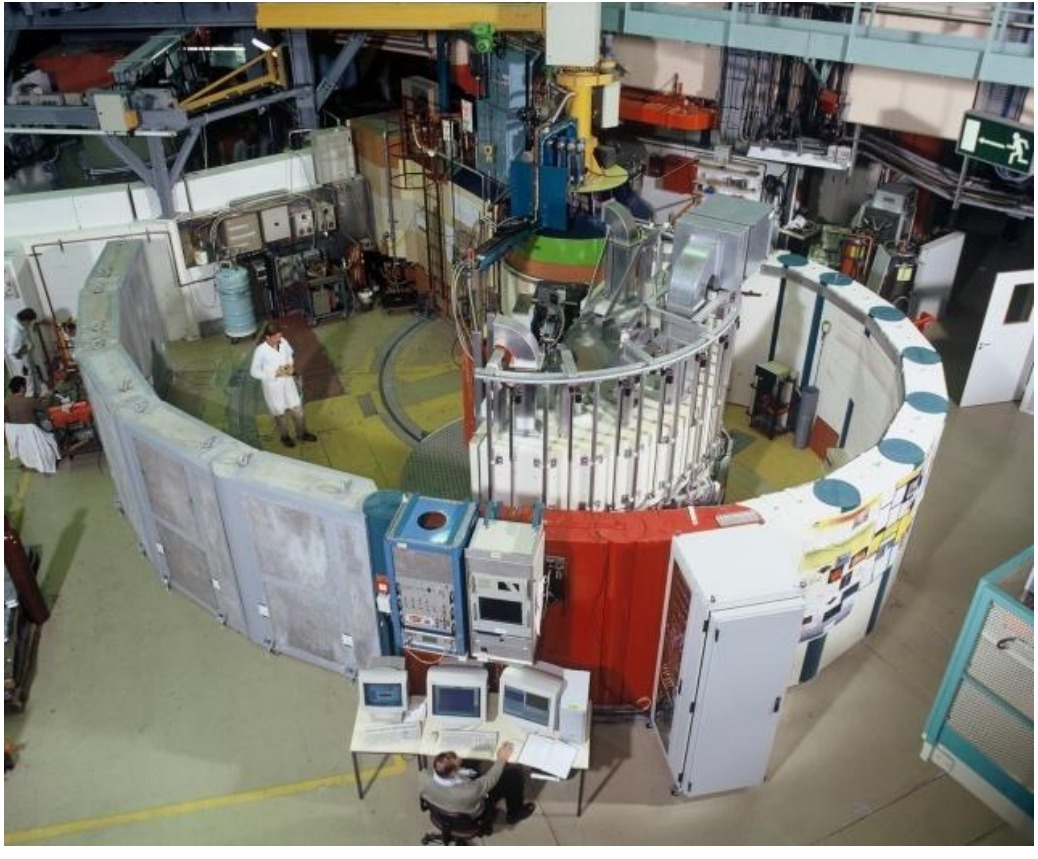


D20 ILL



Wombat ANSTO

Monochromatic angle dispersive



D20

Time of flight technique

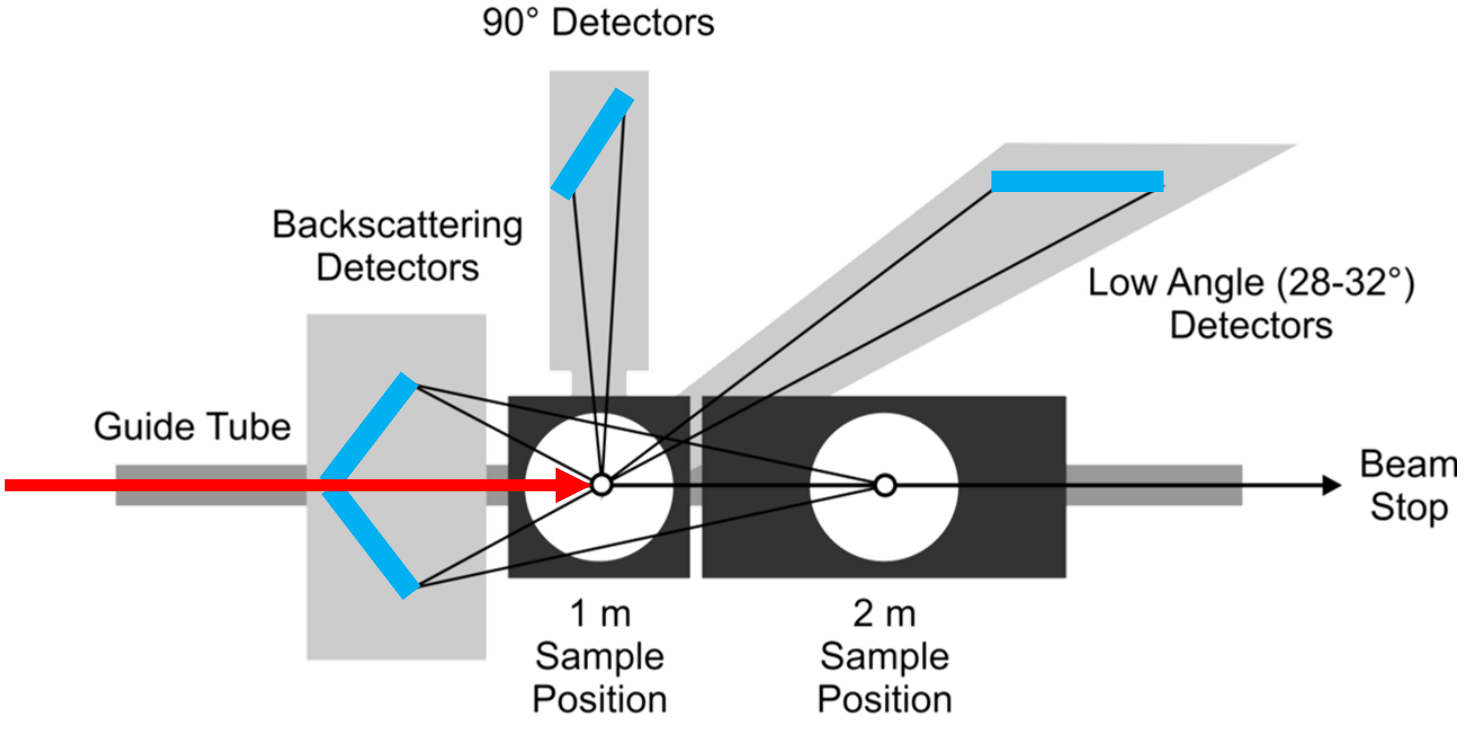
- Uses a pulsed source (usually via spallation).
- Polychromatic beam.
- Fixed-angle detectors.
- Wavelength of each detected neutron is calculated from its time of flight t from source to detector at distance L.
- De Broglie $\Rightarrow \lambda = h/m_n v = h/m_n \; t/L$

- Thus $\lambda = h/m_n \; t/L = 2d \sin\theta$

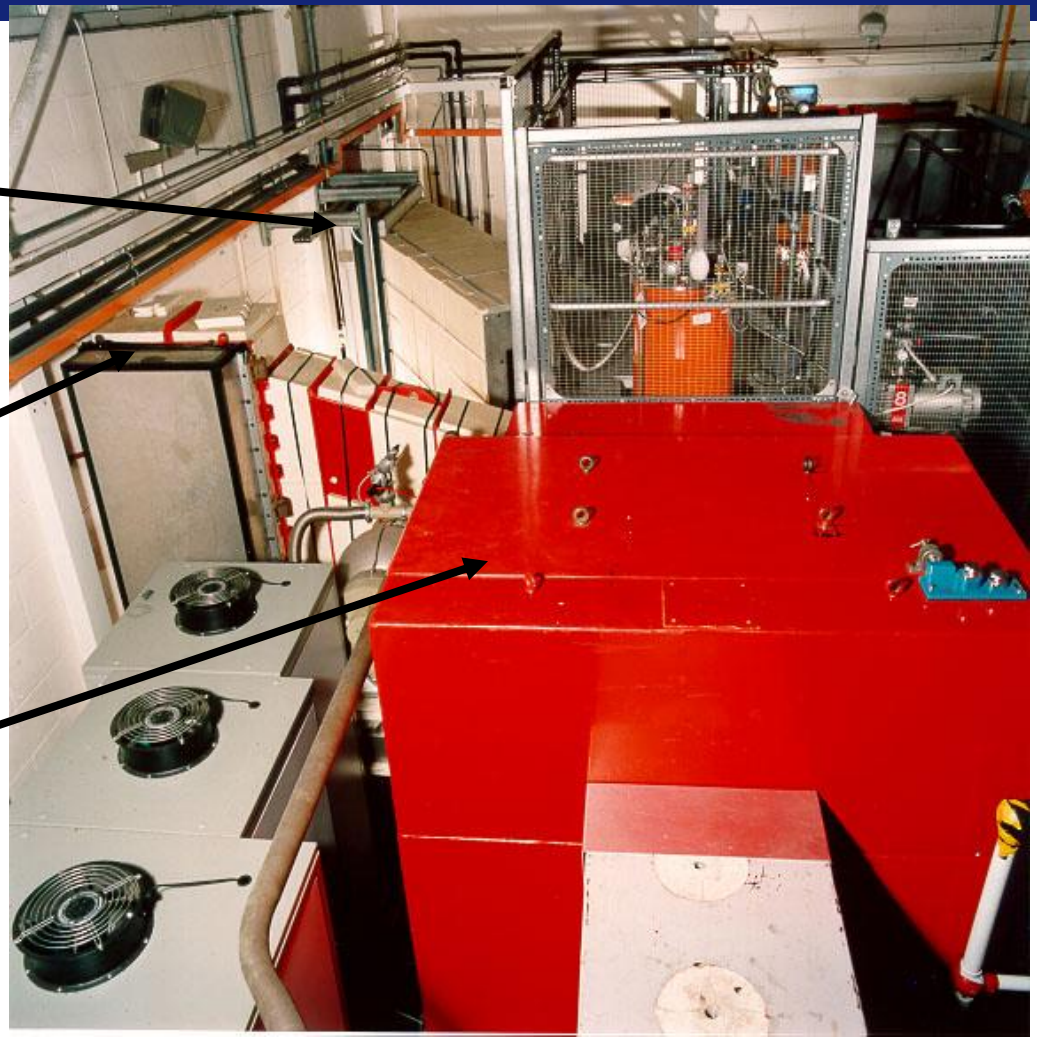
$$d = ht/(2m_n L \sin\theta)$$

HRPD at ISIS

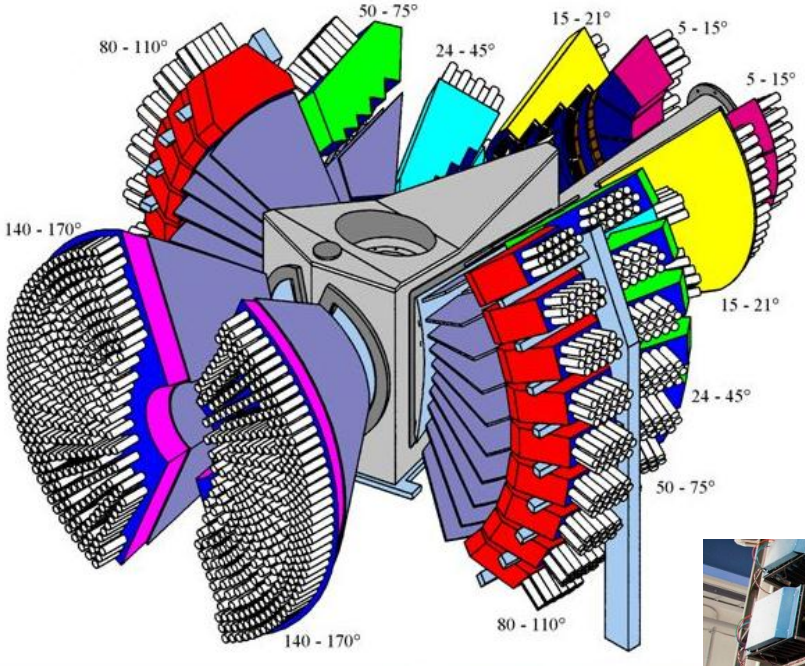
TOF diffractometers usually have multiple detector banks



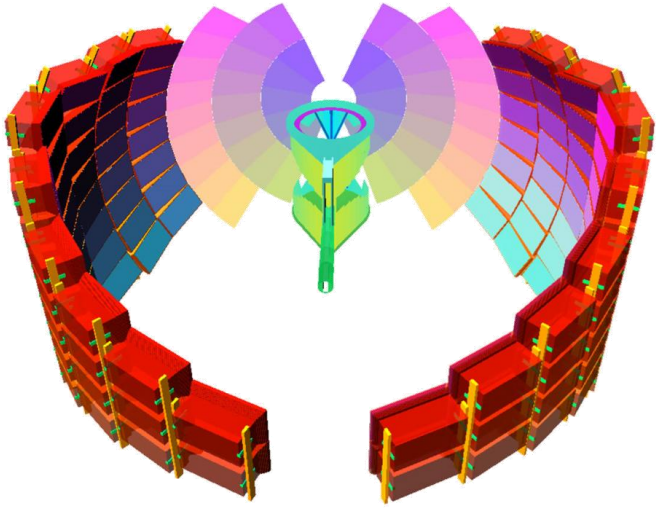
HRPD at ISIS

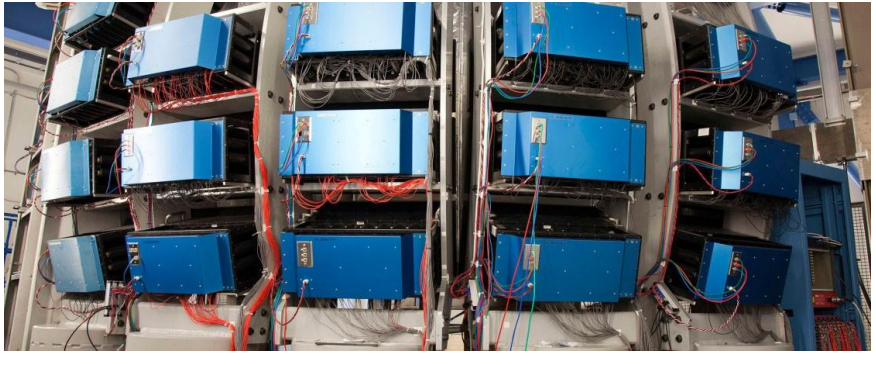


Other time of flight diffractometers

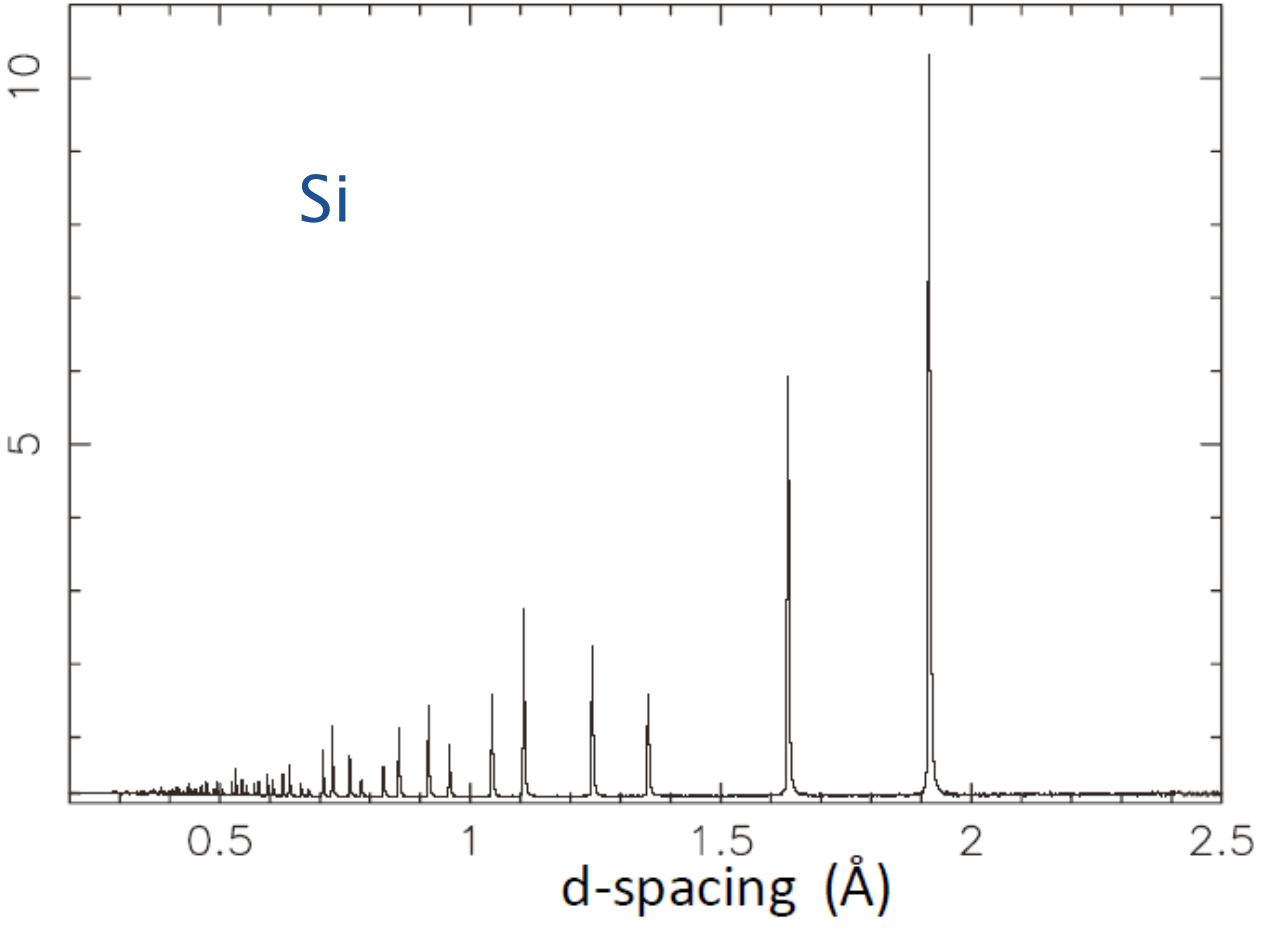


GEM ISIS





POWGEN ORNL


Si
10
5
0.5
1
1.5
2
2.5
d-spacing (Å)

Lecture Notes

Session 13: Introduction to Software/Problems and Interactive Rietveld Refinement

Prof. John S.O. Evans

Durham University, Department of Chemistry

TOPAS and TOPAS Academic

- Useful for teaching as can input equations, see everything in file very quickly

- Powerful and flexible
  - Powder, single crystal, PDF and other data (NMR, spectroscopy)
  - X-ray, neutron
  - Constant λ, time of flight, energy dispersive
  - Structural models, Pawley fitting, peak fitting, fit_obj user fitting
  - Restraints, constraints, only_penalty fitting
  - Multi phase, multi histogram
  - Non crystallographic applications
  - Simulated Annealing for structure solution
  - Distortion Mode refinements
  - Magnetism
  - Parametric refinements, stacking mode refinements, etc, etc

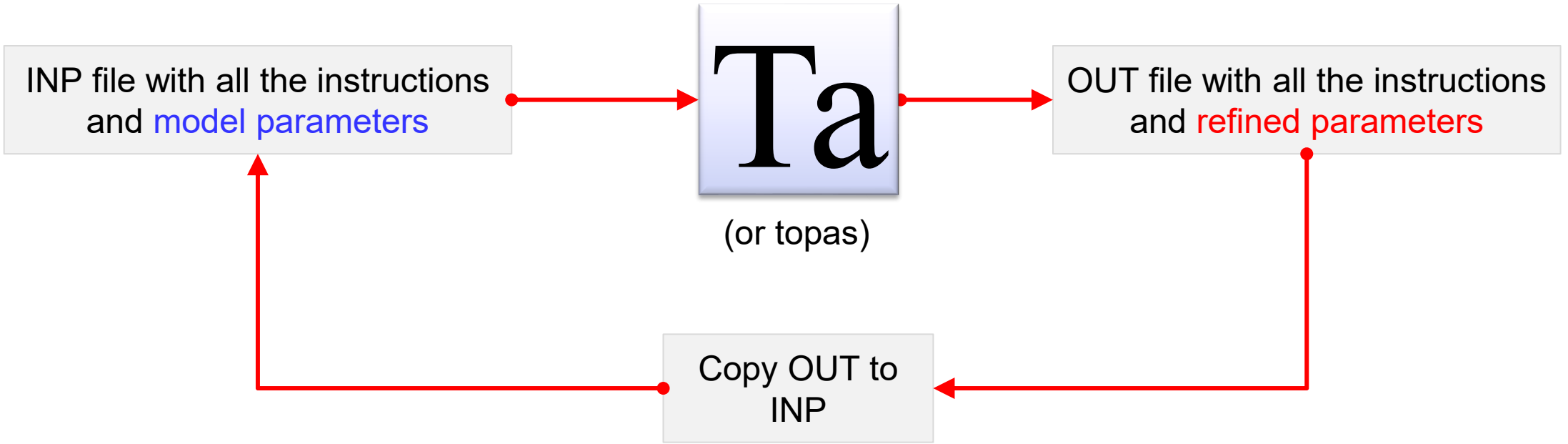
- Quick and stable – fight the science not the data

Acknowledgement

- Alan Coelho (TOPAS/TOPAS Academic author)
- http://www.topas-academic.net/
- Bruker for licenses, Michael Evans for software support for school

Ta ‘s

TOPAS Academic INP/OUT files



TOPAS graphics and windows

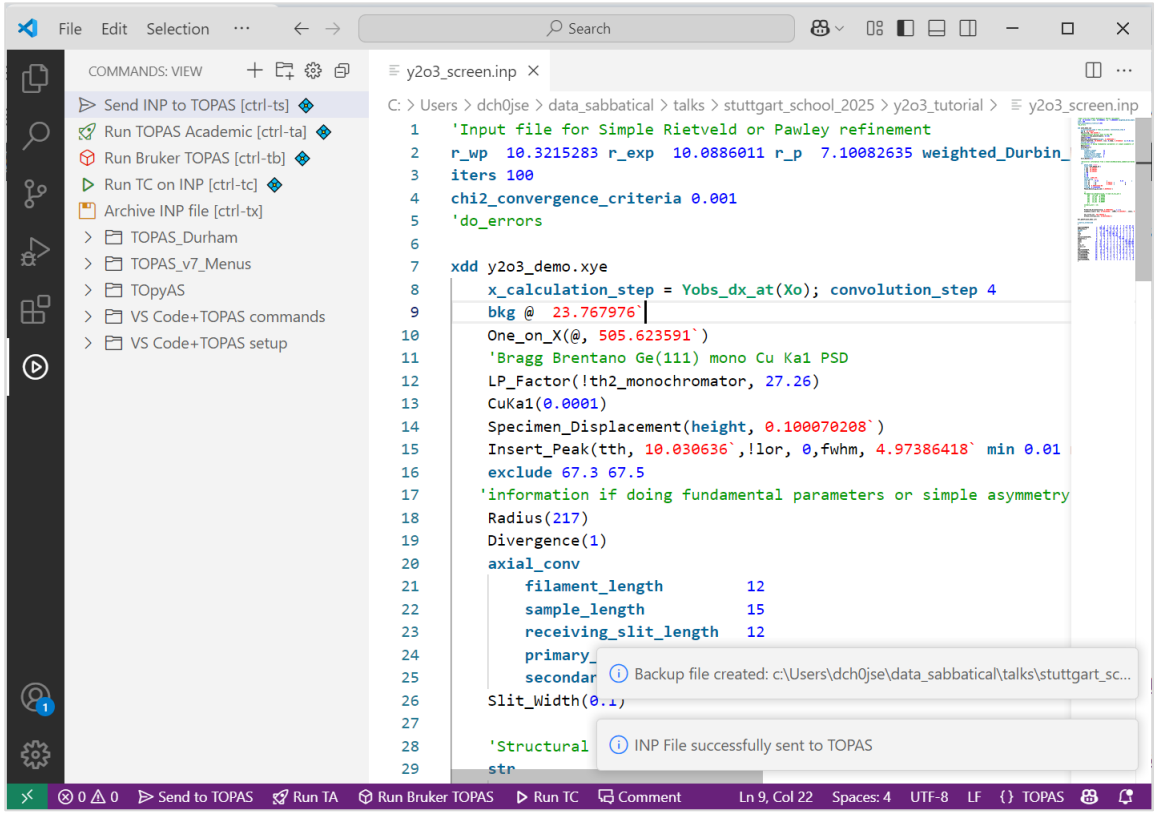
TOPAS simplest launch mode INP file

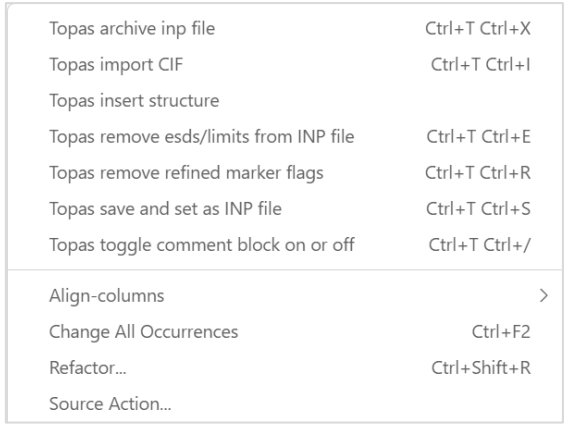
```
'Minimum INP file for Simple Rietveld
‘Overall information, dataset (xdd) information, structural (str) information
r_wp  10.3215283 r_exp  10.0886011 r_p  7.10082635 gof  1.02308815
iters 100
chi2_convergence_criteria 0.001

xdd y2o3_demo.xye
    x_calculation_step = Yobs_dx_at(Xo);
    bkg @  0 0 0
    LP_Factor(!th2_monochromator, 27.26)
    CuKa1(0.0001)
    str
        space_group "Ia-3"
        site Y1     x 0.25  y 0.25  z 0.25  occ Y+3  1  beq 0.25
        site Y2     x 0.97  y 0.00  z 0.25  occ Y+3  1  beq 0.25
        site O1     x 0.39  y 0.15  z 0.38  occ O-2  1  beq 0.25
        TCHZ_Peak_Type(pku, 0.039,pkv, -0.02,pkw, -0.001,!pkz, 0.00,pkx, 0.009, pky, 0.001)
```

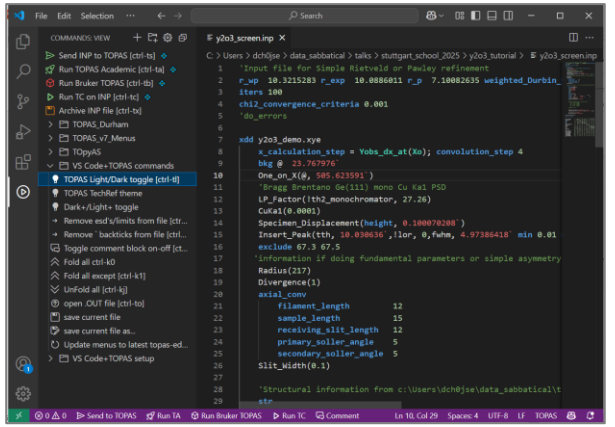
Software interface – topas-editor

- Menus to do the most common things
- TOPAS academic and commercial
- Light and dark schemes
- Easy to install, customise and auto-update

- New commands/ways of working
- Ctrl-t keys: ta, tc, ts, etc
- Pop up help
- Integrates well with python







TOPAS INP file layout: keywords and scope

```
'Refinement controls and overall instructions
r_wp 0 gof 0
iters 100

xdd filename.xye ' First data set to fit
    bkg @ 0 0 0
    LP_Factor(!th2_monochromator, 27.26)
    CuKa1(0.0001)
    Specimen_Displacement(height,0)
    str     ' Information about structure 1
          space_group Ia-3
          site Y1 x 0 y 0 z 0 occ Y 1 beq @ 0.2
    str     ' Information about structure 2
          space_group Fm-3m
          site Cu1 x 0 y 0 z 0 occ Cu 1 beq @ 0.1

xdd filename2.xye ' Second data set to fit
    str     ' Information about structure 1
    str     ' Information about structure 2
    hkl_Is  ' Information about a Pawley phase for sample holder
    xo_Is   ' Information about a peaks phase for impurity
    fit_obj ' Information about user object for e.g. background

    ...     ' Whatever is needed

' Overall information for each xdd
for xdds { ...
    for strs { ... } ' information for each str in each xdd
}
```

Flexible

- Multiple data sets, multiple structures
- Mix fitting of structures, intensities, peaks, etc

Syntax

- **Keywords** colour coded for clarity
- Fixed numbers blue, refined red
- Comments in green

Scope

- `height` could belong to an individual `str`
- `height` could belong to all `str`'s in an `xdd`
- `for {...}` feeds into multiple places

TOPAS/topas-editor demo

- Demonstration of jEdit to refine TiO_2 from laboratory X-ray data
- This is one of this afternoon's tutorials

- Either use menus or use templates

Fixed/refined unit-cell parameters

```
str 'fixed cell parameters for orthorhombic structure
    a    7.31192
    b    7.53699
    c    7.69967
```

```
str 'refined cell parameters with @ symbol
    a  @  7.31192`
    b  @  7.53699`
    c  @  7.69967`
```

```
str 'refined cell parameters with parameter names
    a  lpa  7.31192`
    b  lpb  7.53699`
    c  lpc  7.69967`
```

Refining parameters – using names, macros or equations

```
str 'cell parameters for cubic structure with names
    a lpa  10.60992
    b lpa  10.60992
    c lpa  10.60992
```

```
str 'cell parameters for cubic structure in a macro
    Cubic(@ 10.60992)
```

```
str 'cell parameters for cubic structure with equations
    a lpa  10.60992
    b = lpa;
    c = Get(a);
```

Fixing parameters with ! outside and inside macros

```
str 'fixed cell params for a cubic structure
    a !lpa  10.60992
    b !lpa  10.60992
    c !lpa  10.60992
```

- N.B. topas-editor column editing – hold down ctrl-alt and type all !'s at once

```
'a TOPAS macro for zero point
Zero_Error(   , 0.000 )   'fixed zero point
Zero_Error( @ , 0.013`)   'refined zero point


Zero_Error( !zero, 0.000 ) 'fixed zero point with name
Zero_Error(  zero, 0.013`) 'refined zero point
```

User-defined equations

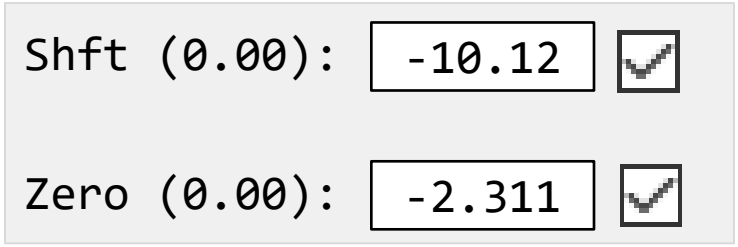
```
'Zero_Error(zero, 0.01) macro expands to (topas.inc):
prm zero    0.01
th2_offset = zero;
```

```
'more complex 2-theta correction in input file:
prm zero    0.01
prm corr1   0.003
prm corr2   0.001
th2_offset = corr2 * X^2 + corr1 * X + zero;
```

```
'silly(?) example of TOPAS equation:
prm zero    0.01
prm corr1   0.003
prm !date   21 'st April
th2_offset = zero + corr1 * date;
```

User-defined equations

- TOPAS has flexible system for defining your own equations
- A “programmable program”
- e.g. GSAS might have something like:



$$corr = 3600*shft/p*radius$$

$$2q_{obs} = 2q_{calc} + zero - 2*corr*Cos(q)$$

- TOPAS has this pre-written or anything you want:

```
'TOPAS height/zero point correction in input file
prm zero    0.01
prm height  0.15
th2_offset = zero - 2*height*Cos(Th)/radius;
```

Simulated annealing

- Flexible simulated annealing approach for complex problems with multiple minima:

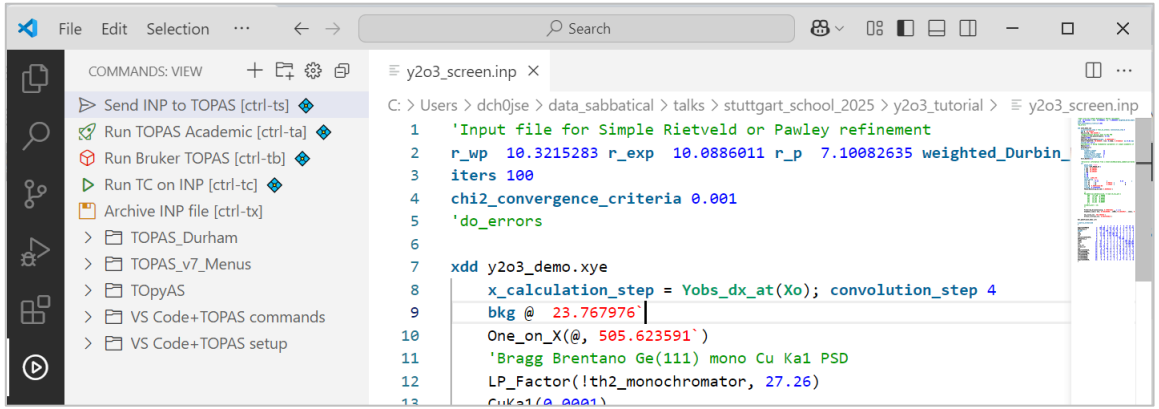
```
'flag for simulated annealing:
continue_after_convergence

'explicit expression in input file
val_on_continue = Val + Val * Rand(-0.1,0.1);
val_on_continue = ideal_coor + Rand(-0.1,0.1);

'or to perturb proportional to errors:
randomize_on_errors

'or something built-in optimised for structure solution:
Auto_T(5)
```

TOPAS interactive session

- Group therapy refinement on Y_2O_3

Running tutorial problems – session 14

- Rest of afternoon is hands-on practical Rietveld refinement
- Use topas-editor to set up input files
- You only need to launch TOPAS once
- Initial problems have very detailed instructions, later ones much more vague
- Later problems on different data types, restrained refinement, etc, etc



Rietveld/Pawley problems

- Tutorial 3.2 – TiO_2 Rietveld and Pawley
- Tutorial 3.6 – the Y_2O_3 example with some twists from the demo
- Tutorial 3.7 – ZrW_2O_8 X-ray/neutron/neutron time of flight
- Tutorial 3.8 – Multiphase Rietveld refinement
- Tutorial 3.9 – $LaMnO_3$ with no instructions (Q6 from Symmetry problems)
- Tutorial 4.4 – Jeremy's $PbSO_4$ example
- Tutorial 4.5 – Combined X-ray and neutron refinement (also gsas3/gsas4)
- GSAS (later) – Jeremy's $PbSO_4$ data
- Tutorial 8.1 - Quantitative Rietveld refinement

Lecture notes

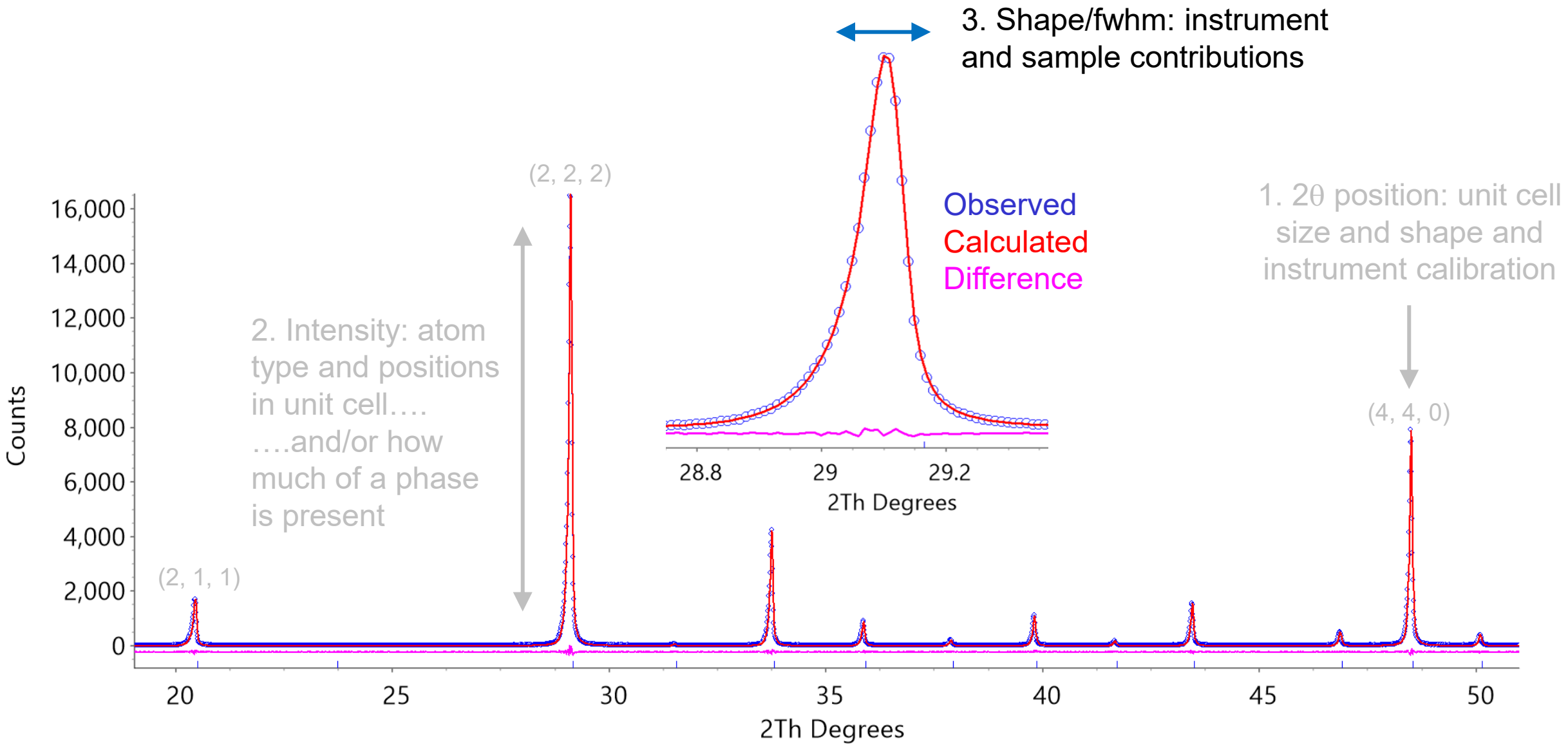
Lecture notes

Session 16: Peak Shapes

Prof. John S.O. Evans

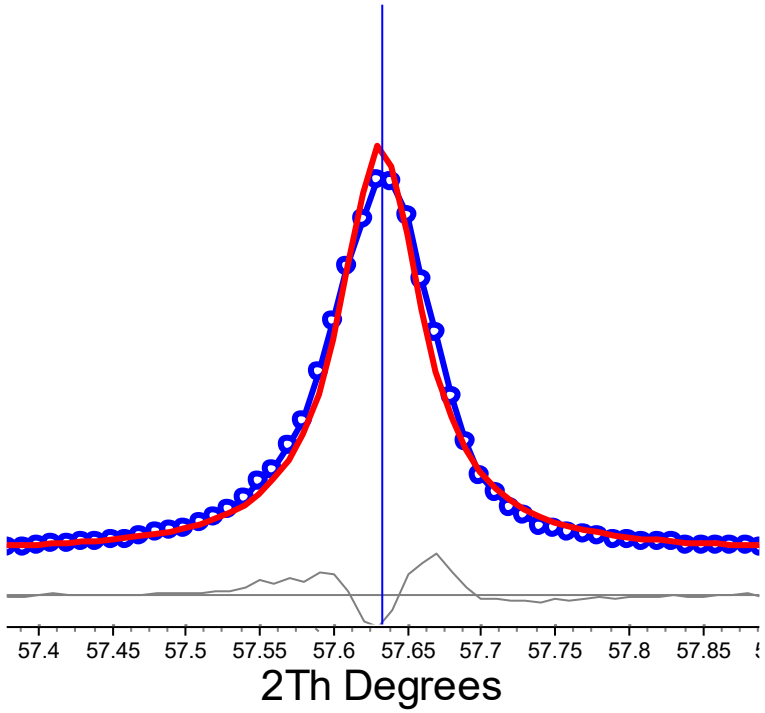
Durham University, Department of Chemistry

What do we have to think about in the Rietveld model?



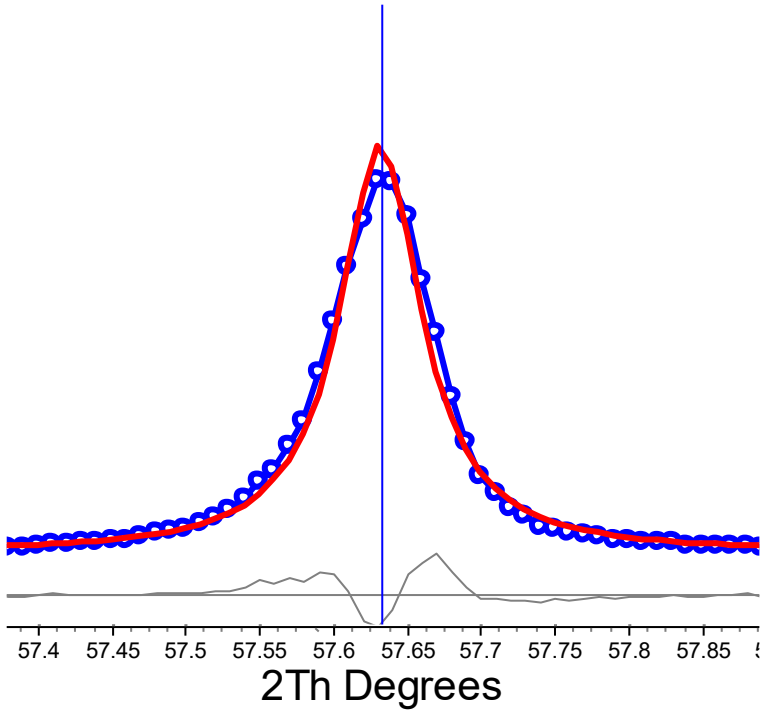
Peak shapes – opinion 1

- Peak shapes are a nuisance. For Rietveld refinement we only fit peaks to get a sufficient agreement between y_{obs} and y_{calc} to give us an accurate intensities for a structural model
- We're therefore not interested in the mathematical details of the peak shape model
- Failure to fit the finest details of the peak shape (e.g. tails of the peaks) isn't very important, minor wiggles will probably cancel each other out



Peak shapes – opinion 2

- Peak shapes in a powder diffraction pattern result from a combination of instrumental effects and sample effects (size/microstrain/stacking faults)
- There is a wealth of fascinating information contained in experimental peak shapes and we should worry about every last detail of the peakshape



Peak shapes – 3 approaches

- Empirical peak shapes
  - Available in most Rietveld packages
  - Whatever function fits the data is good

- Fundamental parameters
  - Instrumental contributions to peak shape
  - Sample contributions to peak shape
  - Excellent fits with very few parameters

- Semi empirical
  - Define instrument with an empirical function (IRF for Instrument Resolution Function)
  - Convolute IRF with sample contribution

Empirical peak shapes in powder diffraction

Gaussian: $$G = \frac{C_0^{1/2}}{fwhm \cdot \pi^{1/2}} \exp\left(\frac{-C_0(2\theta - 2\theta_{hkl})^2}{fwhm^2}\right)$$

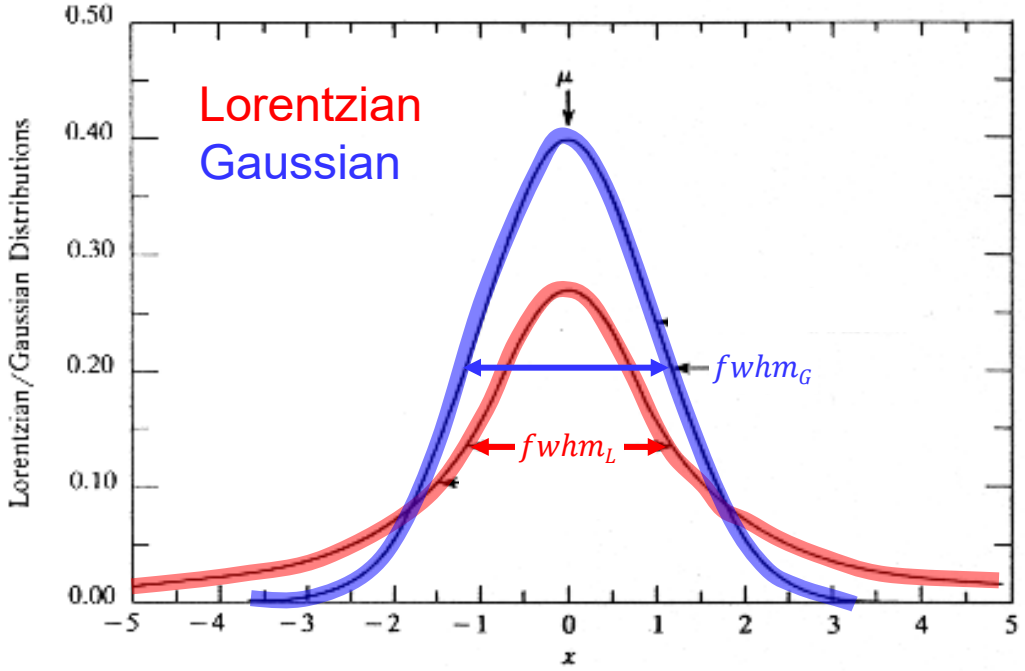
Lorentzian: $$L = \frac{C_1^{1/2}}{fwhm \cdot \pi} 1 \Big/ \left[1 + C_1 \frac{(2\theta - 2\theta_{hkl})^2}{fwhm^2}\right]$$

Pseudo Voigt: $$pV = \eta L + (1 - \eta)G$$

$C_0 = 4 \ln 2$, $C_1 = 4$, 2θ = diffraction angle in question, $2\theta_{hkl}$ the peak position, η = mixing parameter.

"Rietveld refinement in Excel", Evans and Evans, *J. Chem. Educ.*, 2021, **98**, 495−505

Empirical peak shapes in powder diffraction



www.phys.unsw.edu.au/~mgb/pics/gausscauchy.gif

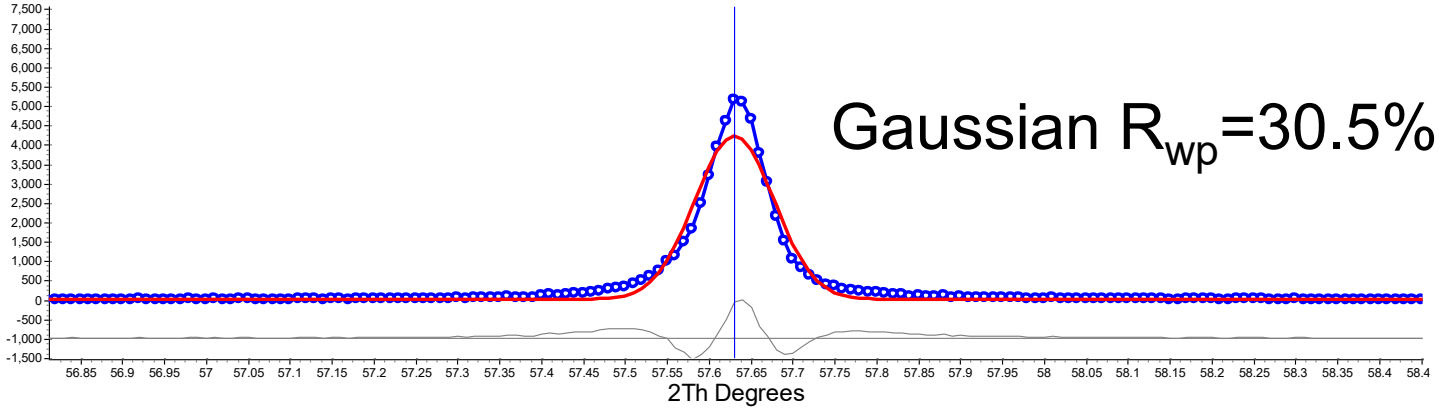
- Gaussian has rounded maximum and small tails
- Lorentzian sharper near maximum but has long tails away from peak
- *fwhm* broader for Gaussian

- Pseudo Voigt mixes the two functions

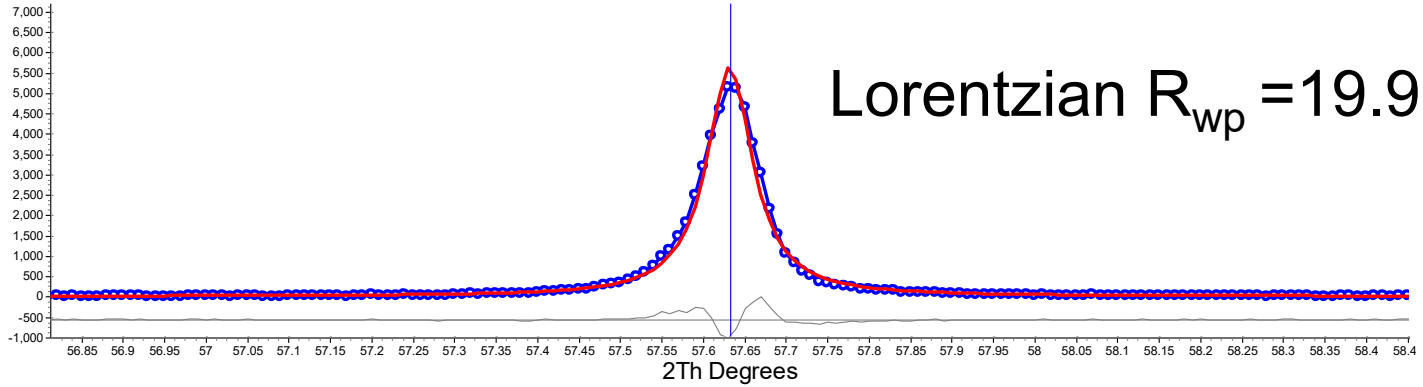
$$pV = \eta L + (1 - \eta)G$$

- Mixing η 0 to 1

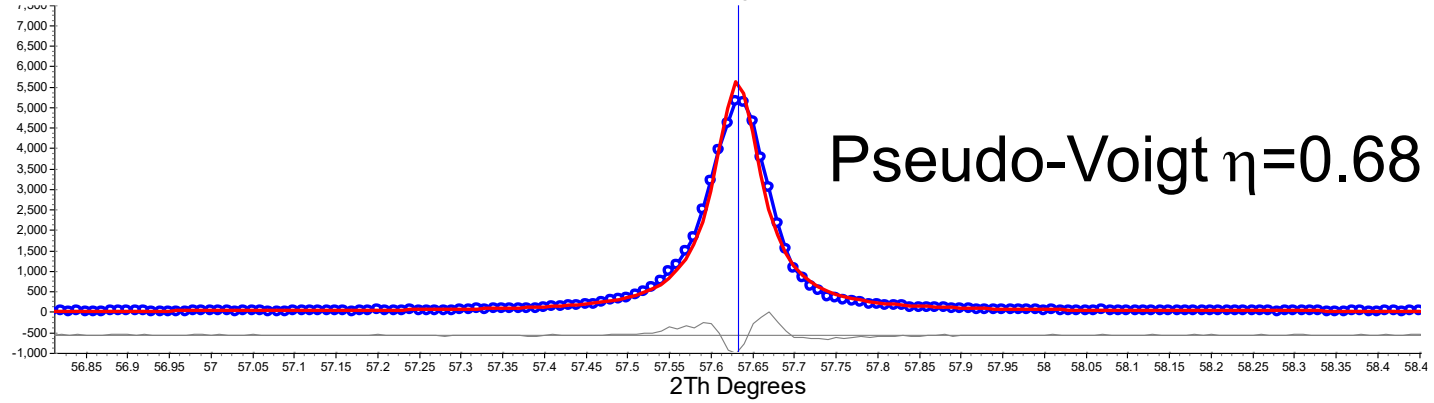
Empirical peak shapes in powder diffraction



Gaussian R_{wp}=30.5%



Lorentzian R_{wp} =19.9%



Pseudo-Voigt η=0.68 R_{wp} =17.6%

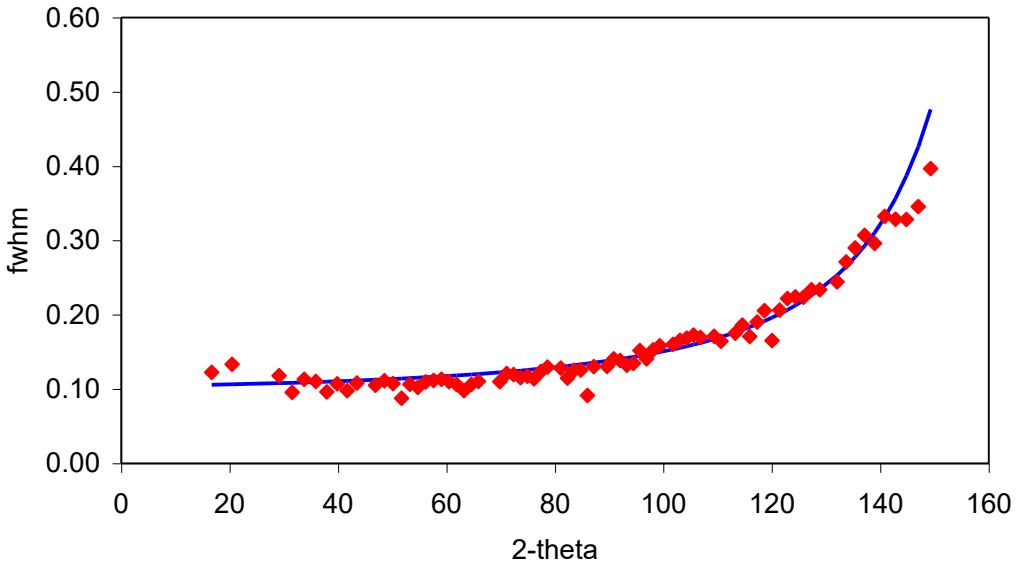
Empirical peak shapes in powder diffraction

Gaussian: $fwhm = \left(U \tan^2 \theta + V \tan \theta + W + \frac{Z}{\cos^2 \theta} \right)^{1/2}$

Lorentzian: $fwhm = X \tan \theta + \frac{Y}{\cos \theta}$

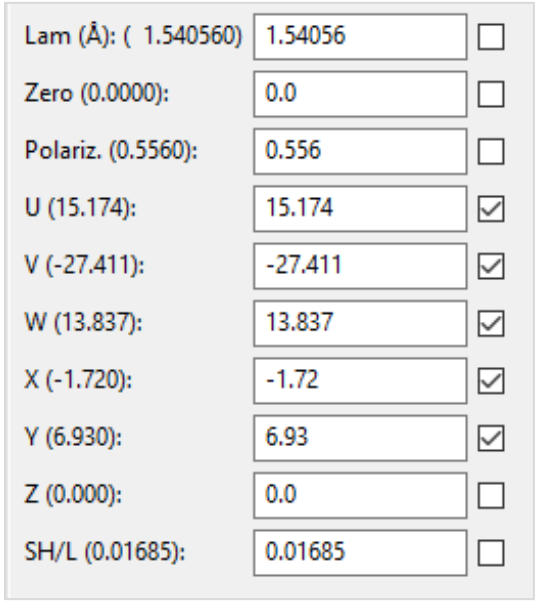
U, V, W, X, Y (and Z) refinable parameters

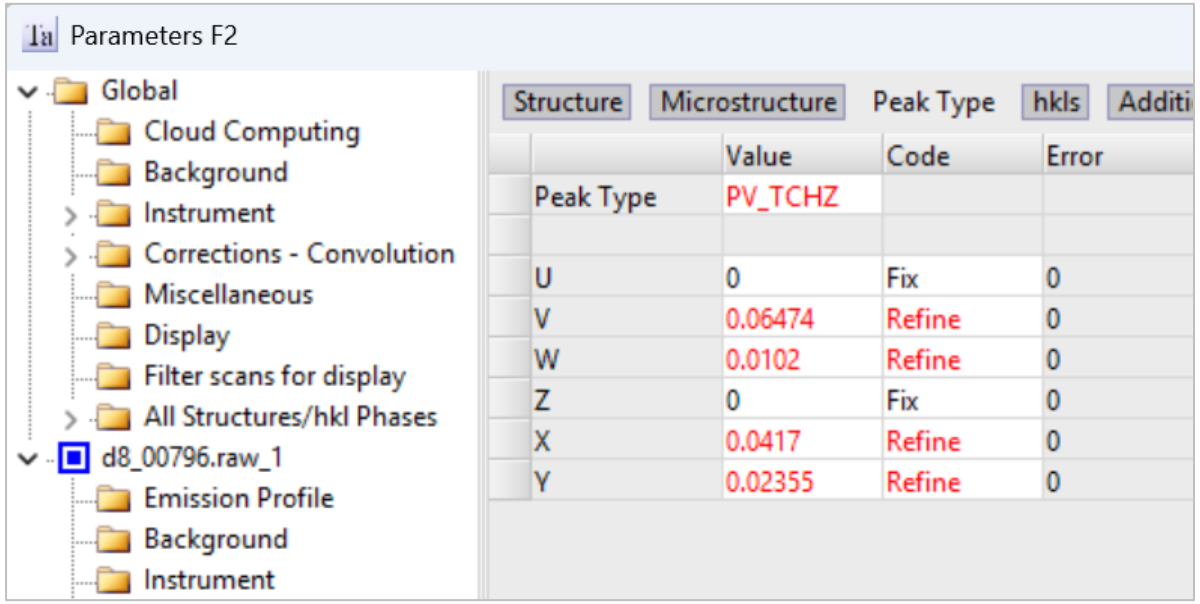
Peaks can be anisotropic - shape depends on *hkl*



Tutorial 5.1

GSAS/TOPAS interfaces






```
'TOPAS TCHZ peak shape function
TCHZ_Peak_Type(!pku, 0.00000, pkv, 0.06474`, pkw,0.01020`, !pkz, 0.0000, pkx, 0.0417`, pky, 0.02355`)
```

GSAS/TOPAS TCHz function

- Modified Thompson-Cox-Hastings pseudo-Voigt

$\Gamma_G = (U \tan^2\theta + V \tan\theta + W + Z / \cos^2\theta)^{0.5}$

$\Gamma_L = X \tan\theta + Y / \cos\theta$

with U, V, W, X, Y, Z as refineable parameters.

$\eta = 1.36603\ q - 0.47719\ q^2 + 0.1116\ q^3$

where

$q = \Gamma_L / \Gamma$

$\Gamma = (\Gamma_G^5 + A\Gamma_G^4\Gamma_L + B\Gamma_G^3\Gamma_L^2 + C\Gamma_G^2\Gamma_L^3 + D\Gamma_G\Gamma_L^4 + \Gamma_L^5)^{0.2} = \text{fwhm}$

$A = 2.69269,\ B = 2.42843,\ C = 4.47163,\ D = 0.07842$

Look in topas.log or topas.inc to see what's happening

```
'TOPAS TCHZ peak shape function

TCHZ_Peak_Type(!pku, 0.00000, pkv, 0.06474`, pkw,0.01020`, !pkz, 0.0000, pkx, 0.0417`, pky, 0.02355`)
```

```
macro TCHZ_Peak_Type(u, v, w, z, x, y)
   {
      local #m_unique tch_p_l = x Tan(Th) + y / Cos(Th);
      local #m_unique tch_p_g = Sqrt( Abs( u Tan(Th)^2 + v Tan(Th) + w + z / Cos(Th)^2) );
      local #m_unique tch_p =
         (
                   tch_p_g^5 +
            2.69269 tch_p_g^4 tch_p_l +
            2.42843 tch_p_g^3 tch_p_l^2 +
            4.47163 tch_p_g^2 tch_p_l^3 +
            0.07842 tch_p_g   tch_p_l^4 +
                              tch_p_l^5
         )^0.2;
      local #m_unique tch_q = tch_p_l / tch_p;
      peak_type pv
         pv_lor = 1.36603 tch_q - 0.47719 tch_q^2 + 0.1116 tch_q^3;
         pv_fwhm = tch_p;
   }
```

Fundamental parameters convolution approach

- Peak widths depend on
  - X-ray source contributions
  - Instrumental contributions
  - Sample contributions
- Convolution or folding “blends” these functions together

$$(Source \otimes Instrument) \otimes Sample = Y(2\theta)$$

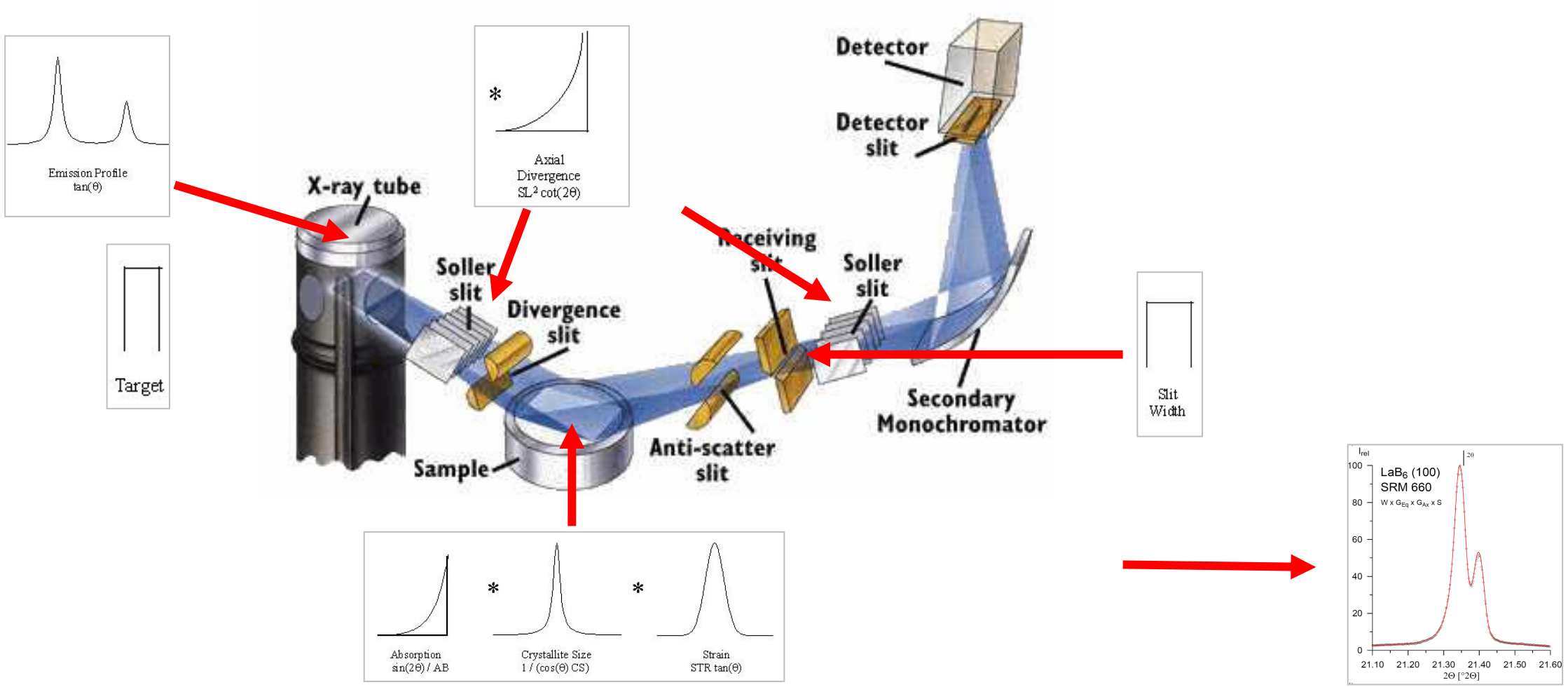
(or empirical instrumental resolution function IRF)

Overall peak shape

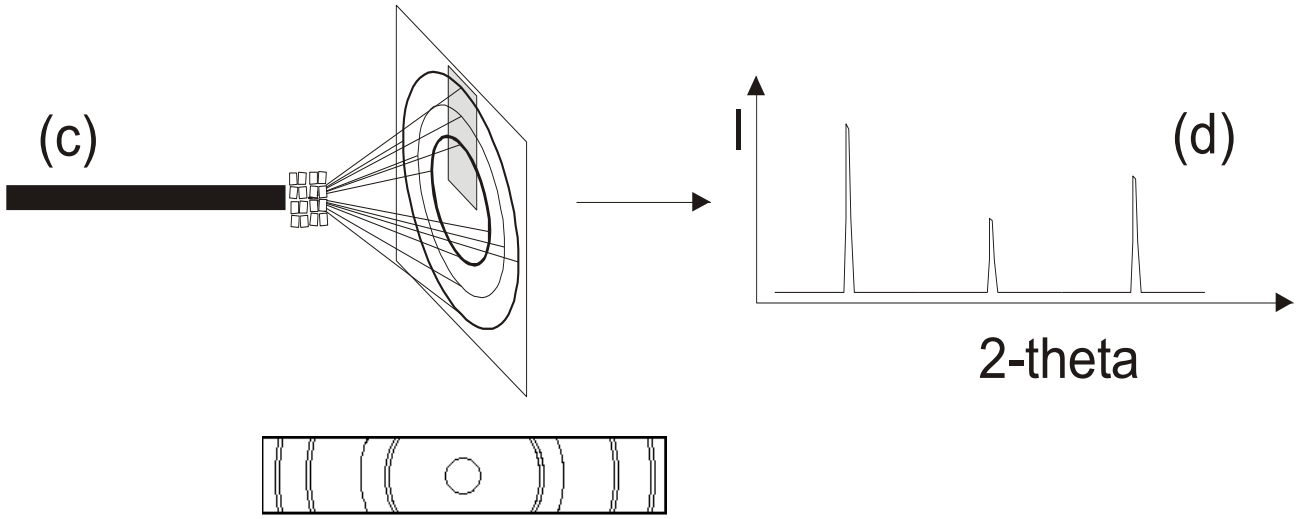
$$f(2\theta) \otimes g(2\theta) = \int_{-\infty}^{\infty} f(2\theta')\, g(2\theta - 2\theta') d(2\theta') = \int_{-\infty}^{\infty} g(2\theta')\, f(2\theta - 2\theta') d(2\theta')$$

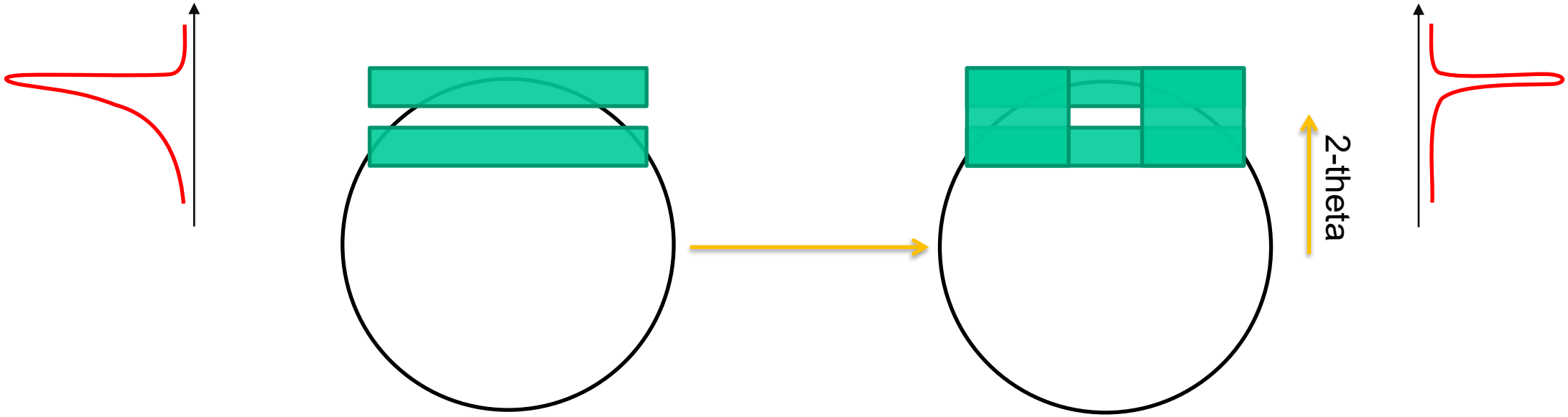
Contributions to peak shape

$$(Source \otimes Instrument) \otimes Sample = Y(2\theta)$$



An instrumental contribution





Definition of convolution

- The process of convolution is one in which the product of two functions $f(2\theta)$ and $g(2\theta)$ is integrated over all space

$$f(2\theta) \otimes g(2\theta) = \int_{-\infty}^{\infty} f(2\theta')\, g(2\theta - 2\theta') d(2\theta') = \int_{-\infty}^{\infty} g(2\theta')\, f(2\theta - 2\theta') d(2\theta')$$

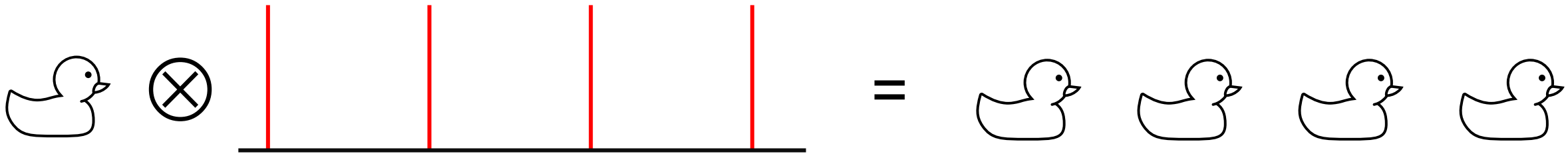
- In simple terms, convolution can be understood as "blending" one function with another, producing a kind of very general "moving average". The convoluted function is obtained by setting down the origin of the first function in every possible position of the second, multiplying the values of both functions in each position, and taking the sum of all operations.
- See e.g. https://lpsa.swarthmore.edu/Convolution/CI.html

- If you have an old java-compatible browser: https://pages.jh.edu/signals/index.html

Convolution in crystallography

atoms $\otimes$ lattice = structure

Reference: J.K. Cockcroft, *Powder Diffraction and Rietveld School*, Yesterday.



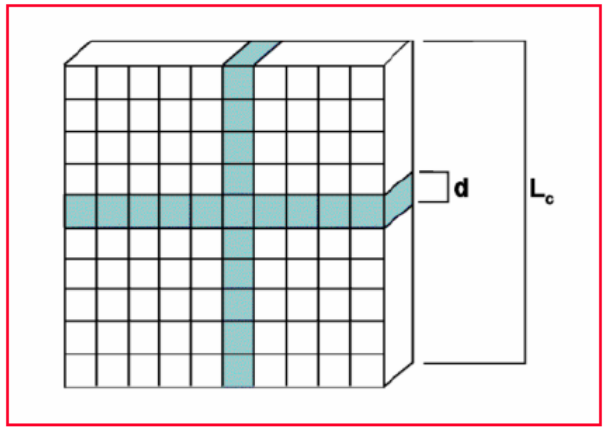
regularly-spaced delta functions

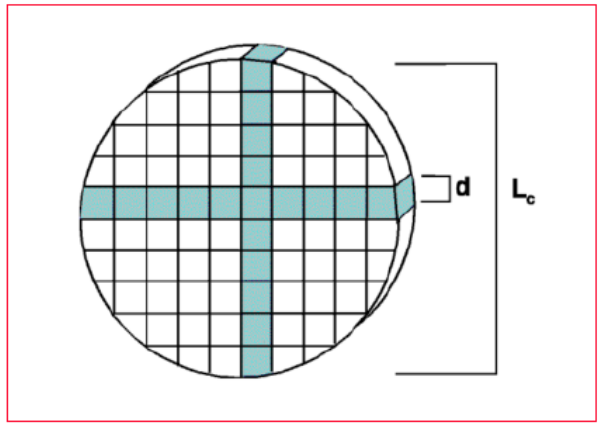
Sample contributions – domain size

- Scherrer formula
- *k* a constant
- L_{Vol} is volume weighted mean column height
- For cubic crystals and *h*00 reflections only it is equal to L_0 in figures below
- Derivation in “Rietveld Refinement” book P8

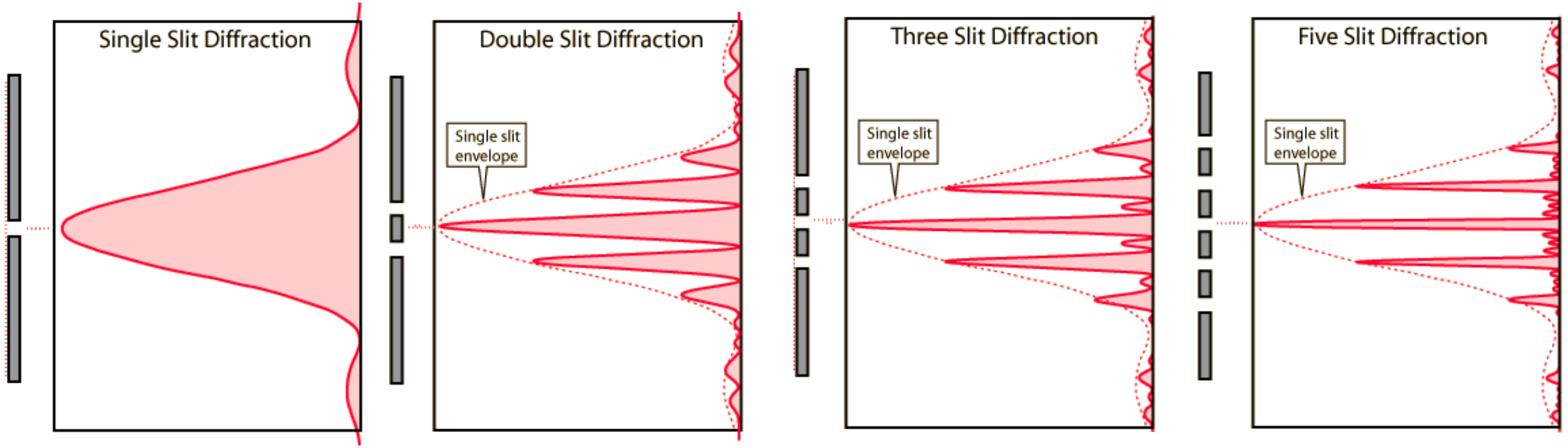
$$fwhm = \frac{k\lambda}{L_{Vol}\cos\theta}$$

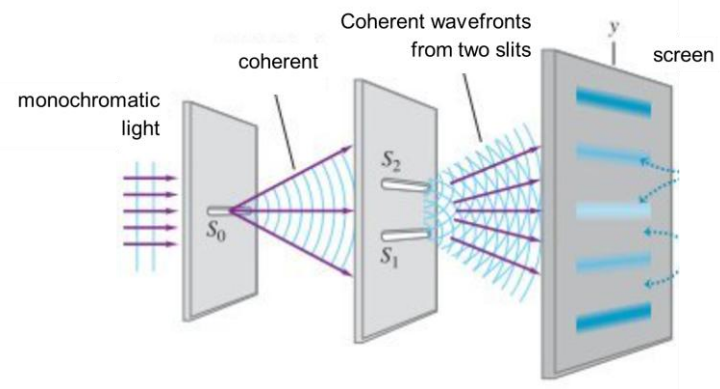
a axis
*h*00 refl’s



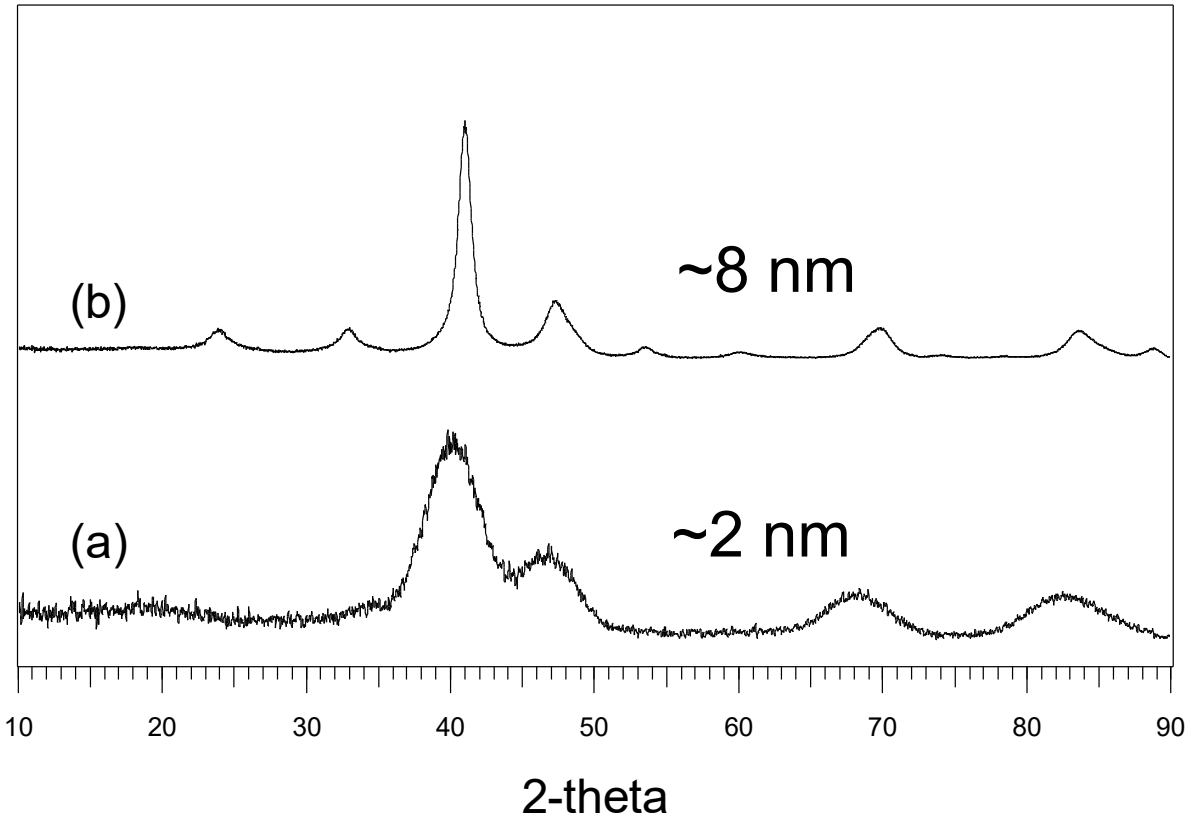


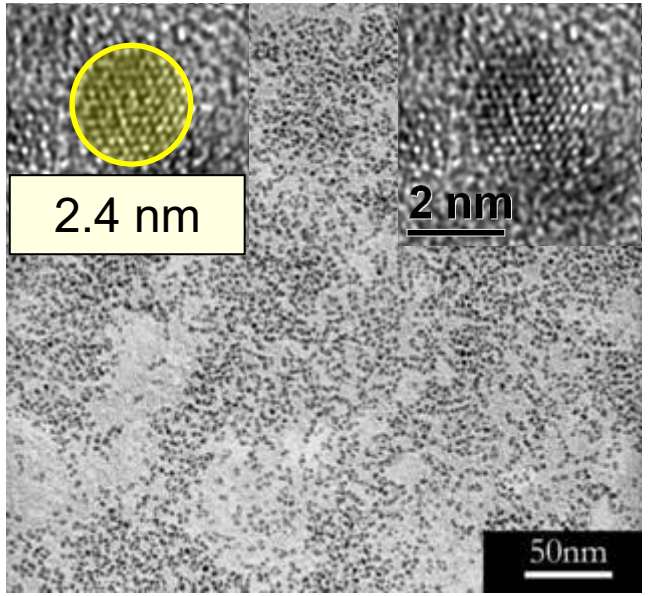
Emma's slide: multiple slits

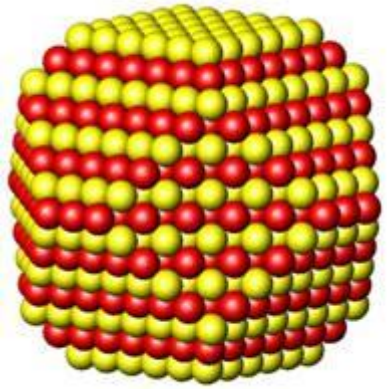




Domain size broadening







3 nm, 1100 atoms

Size distribution

- Make sure you're measuring the same thing with different techniques

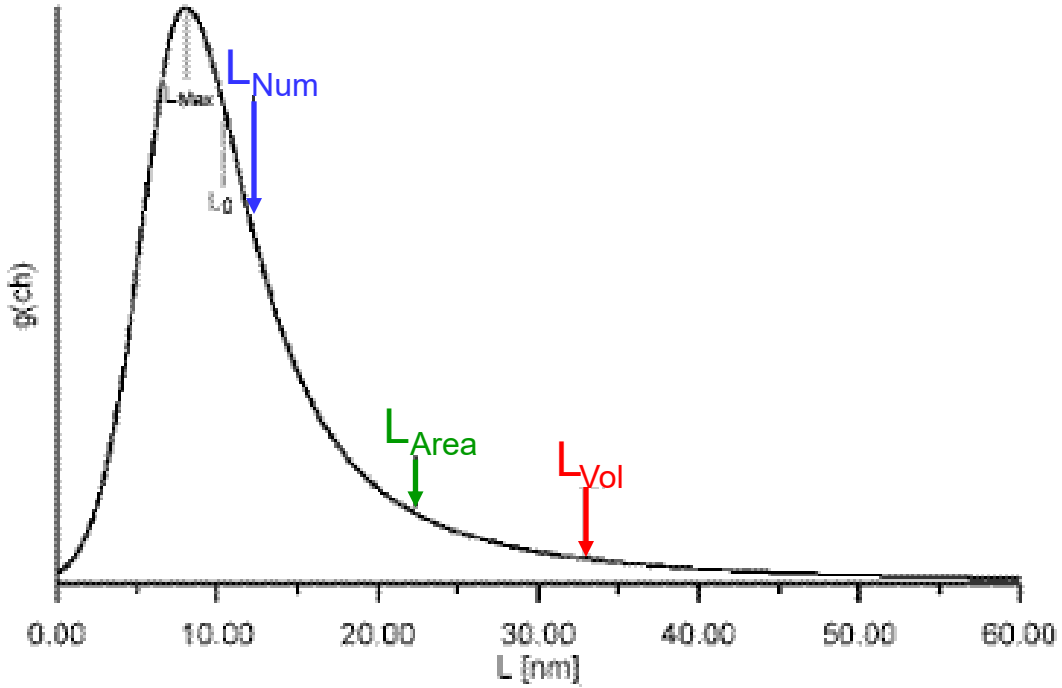


Fig. 3-18: Schematic representation of a column height distribution g(ch) showing the following characteristic points:

L_{Max} : most probable value

L_0 : median

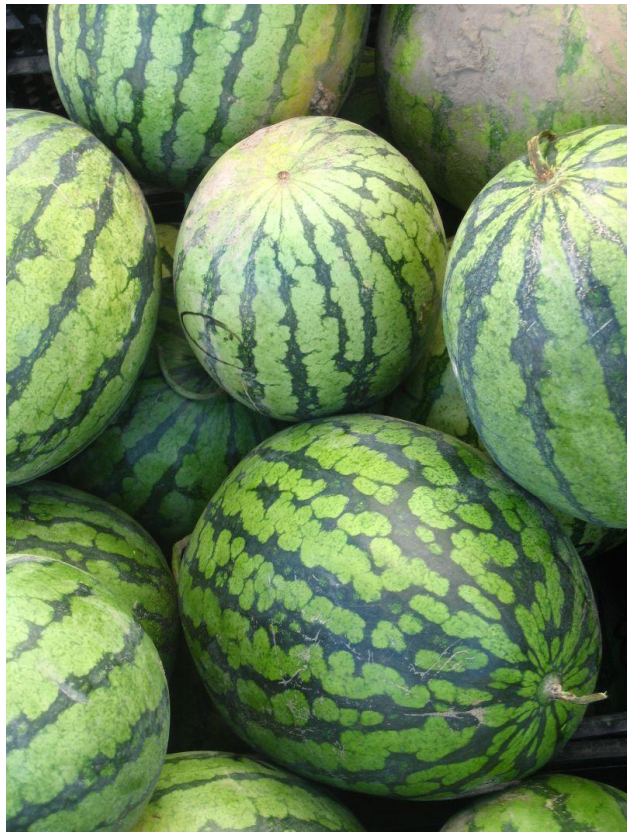
L_{Num} : number weighted mean

L_{Area} : area weighted mean

L_{Vol} : volume weighted mean

For monodispersed spheres: L_{Vol}= 1.5 * radius

Average size of 20 pieces of fruit - beware



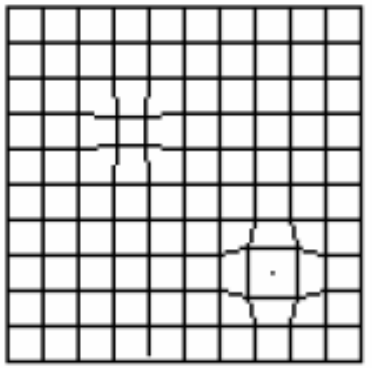
5 melons @ 30 cm
5 grapes @ 2 cm
} 16 cm average

10 oranges @ 16 cm

Sample contributions - microstrain

- *d*-spacings of $d+\Delta d$ and $d-\Delta d$
- $\varepsilon_0=\Delta d/d$
- Assume Bragg's law gives different 2θ for different *d*-spacings

$$fwhm = 4\varepsilon_0 \tan\theta$$



Sample contributions - microstrain

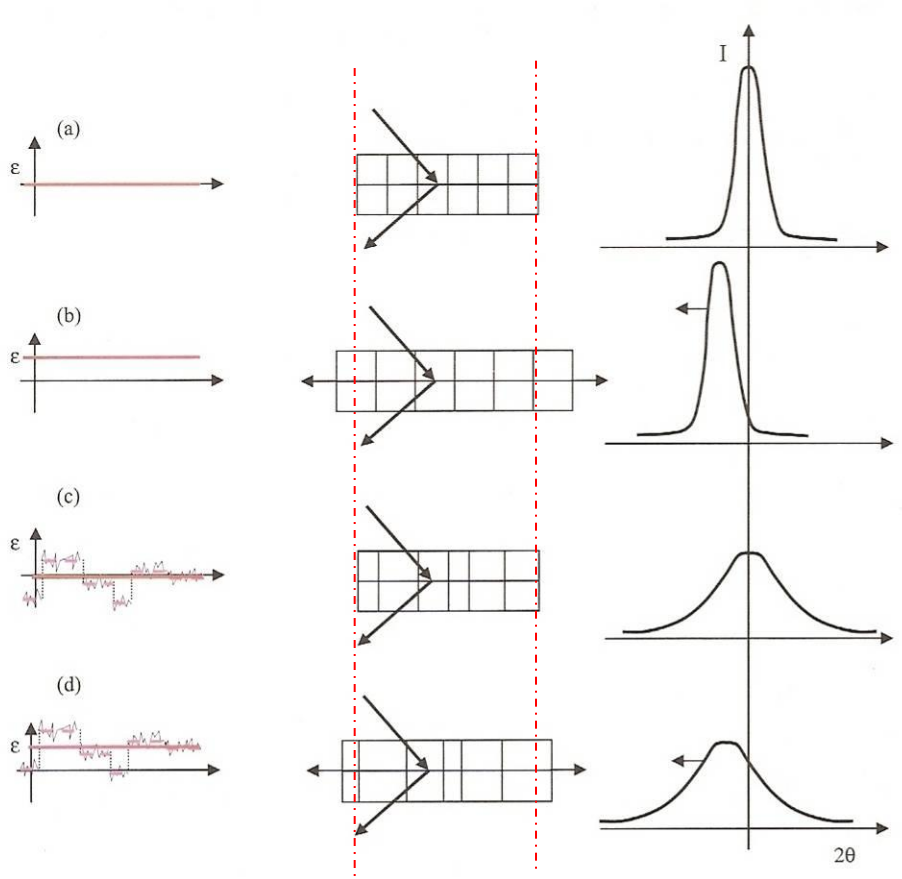


Figure 13.4 PD peak profile for zero strain (no macrostrain and no microstrain) (a), (tensile) macrostrain (b), microstrain (c) and combined effect of microstrain and macrostrain (d). Strain (ε) is plotted on the left as a function of the position within a material microstructure sketched in the middle drawing.

Paolo Scardi, Powder Diffraction, Theory and Practice

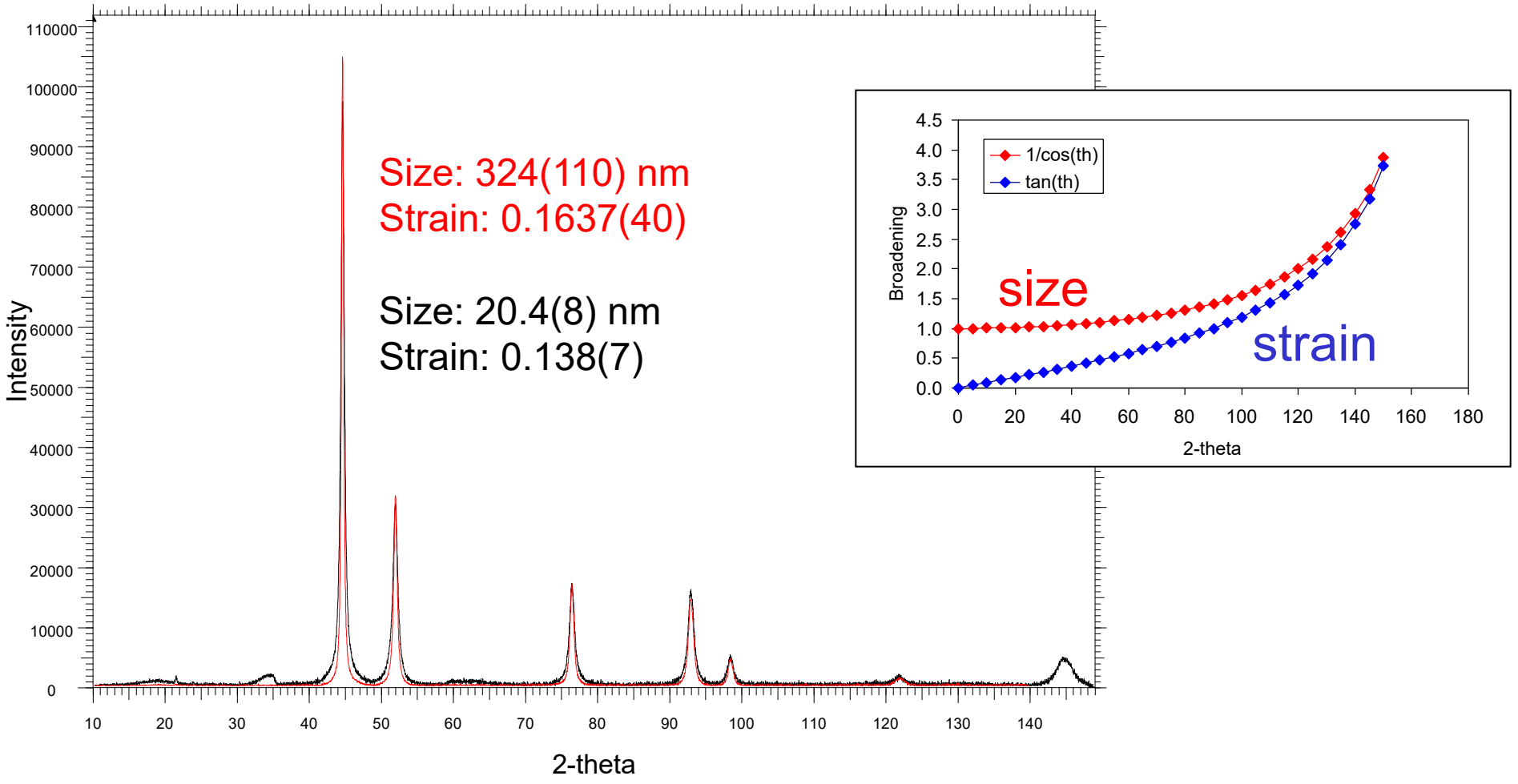
No strain

Macrostrain – homogeneous strain

Microstrain – inhomogeneous strain

Microstrain and macrostrain

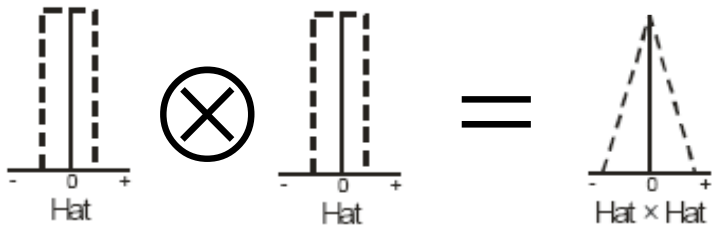
X-ray size/strain from peak shape



- Size broadening – “broad over whole 2-theta range”
- Strain broadening – “narrow at low 2-theta”

TOPAS: joy of convolution

- Topas demo (inspired by Arnt)
- File: **conv_joy_01.inp**

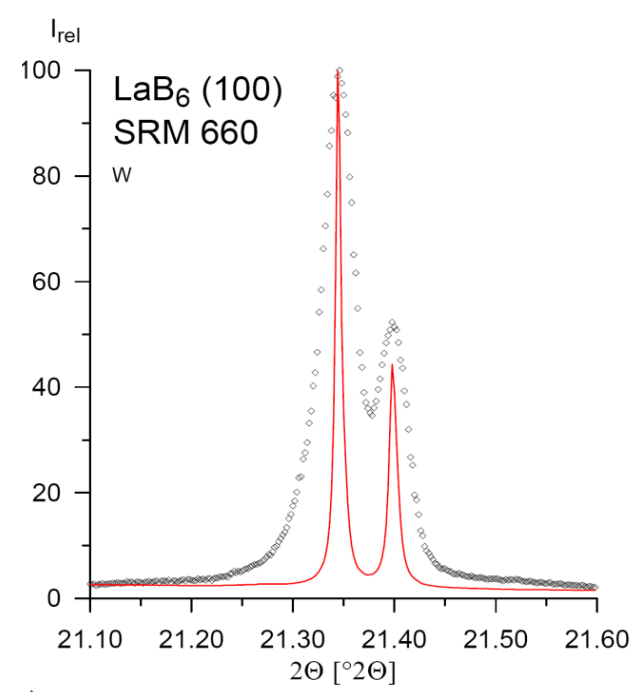


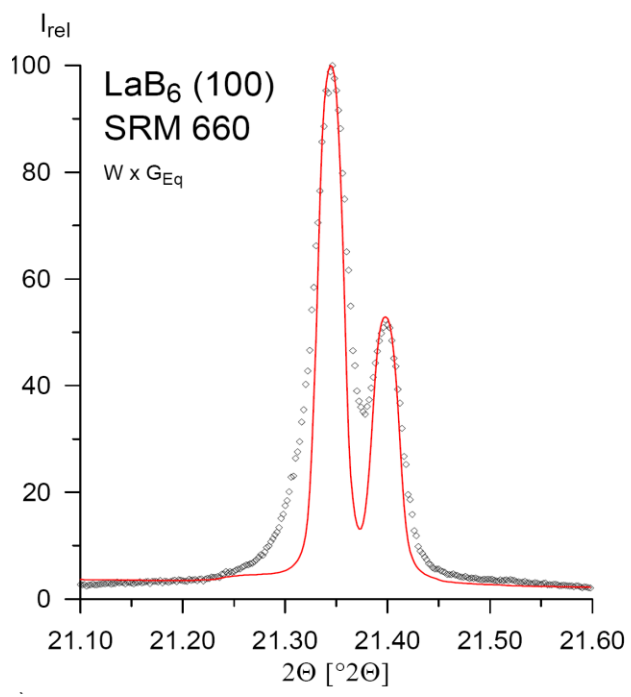
TOPAS language

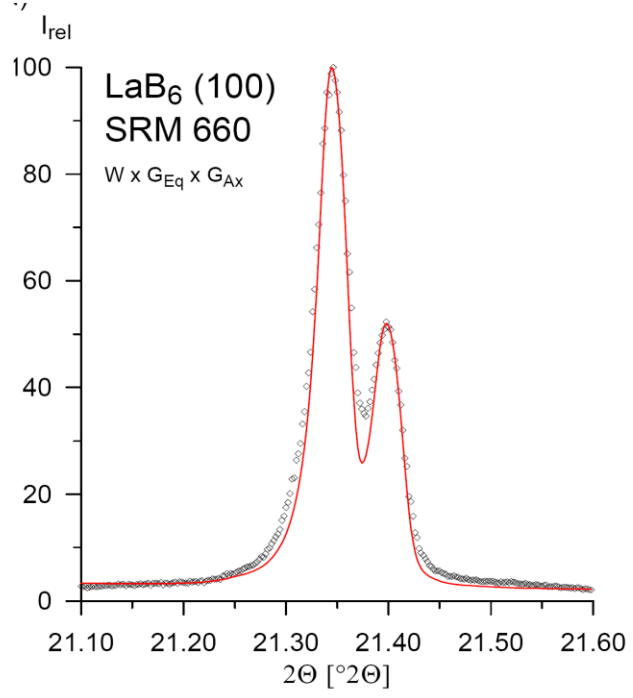
```
'instrumental contributions here
xdd data.xye
  Radius(217) 'diffractometer radius
  Divergence(1) 'divergence slit deg
  Slit_Width(0.1) 'receiving slit
  axial_conv
      filament_length          12
      sample_length            15
      receiving_slit_length    12
      primary_soller_angle     5.1
      secondary_soller_angle   5.1

'sample contributions
str
  CS_L(size_lor, 329.49186) 'size term nm
  Strain_G(strain_g, 0.04939) 'microstrain term
```

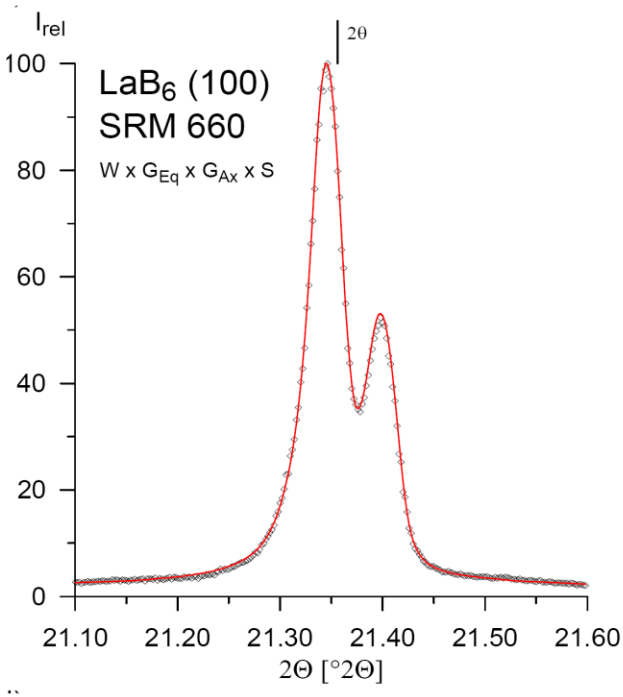
Different contributions to peak shape: LaB_6

source profile → source ⊗ equatorial → source ⊗ equatorial ⊗ axial → source ⊗ equatorial ⊗ axial ⊗ sample









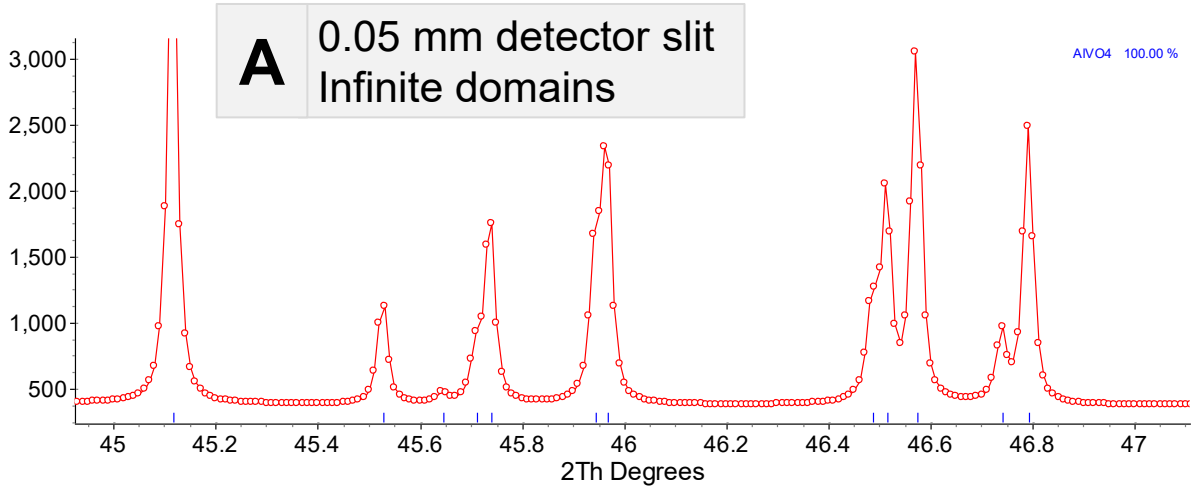
Source profile much sharper then observed peak

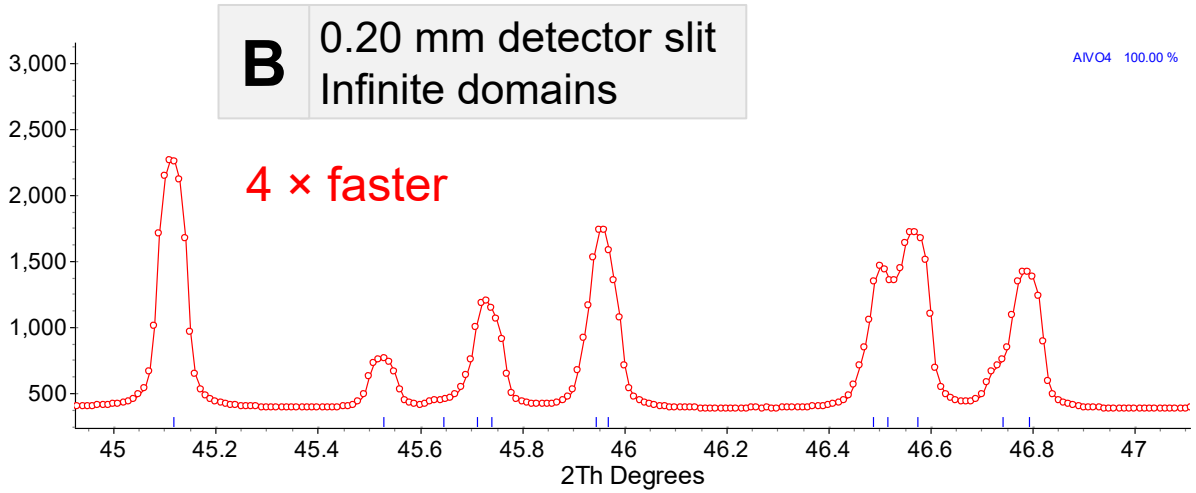
Peak broadened by instrument

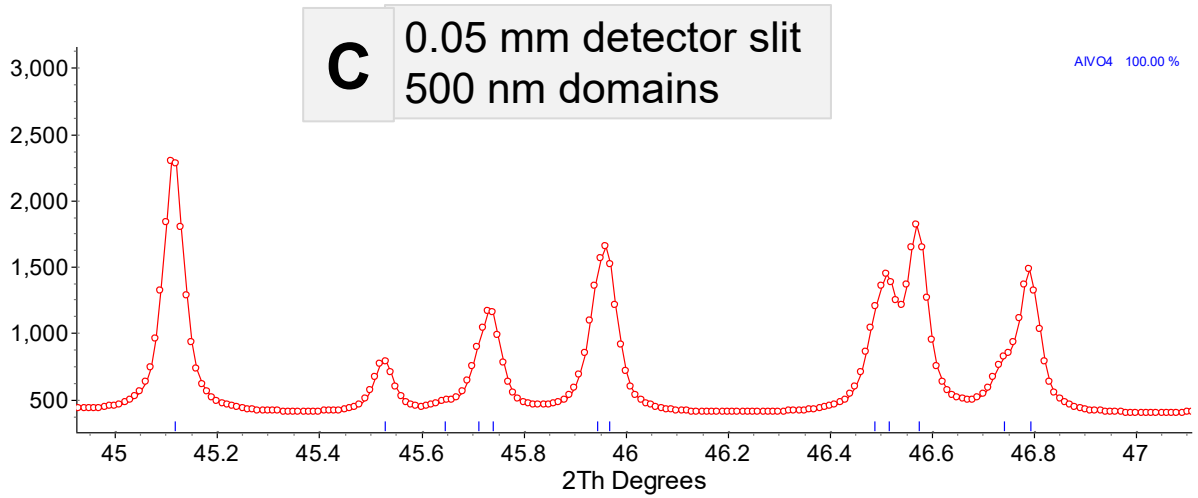
Peak now has asymmetry

Peak maximum not at calculated 2θ

Matching the instrument/measurement to the sample/science





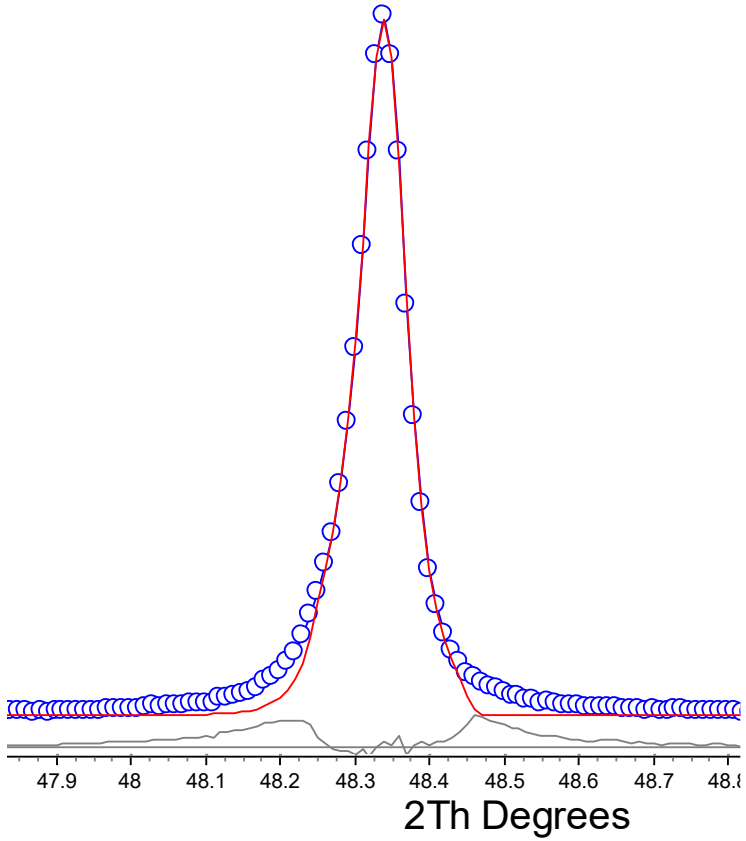


A to **B**: lower resolution means poorer information but allows significantly faster data collection

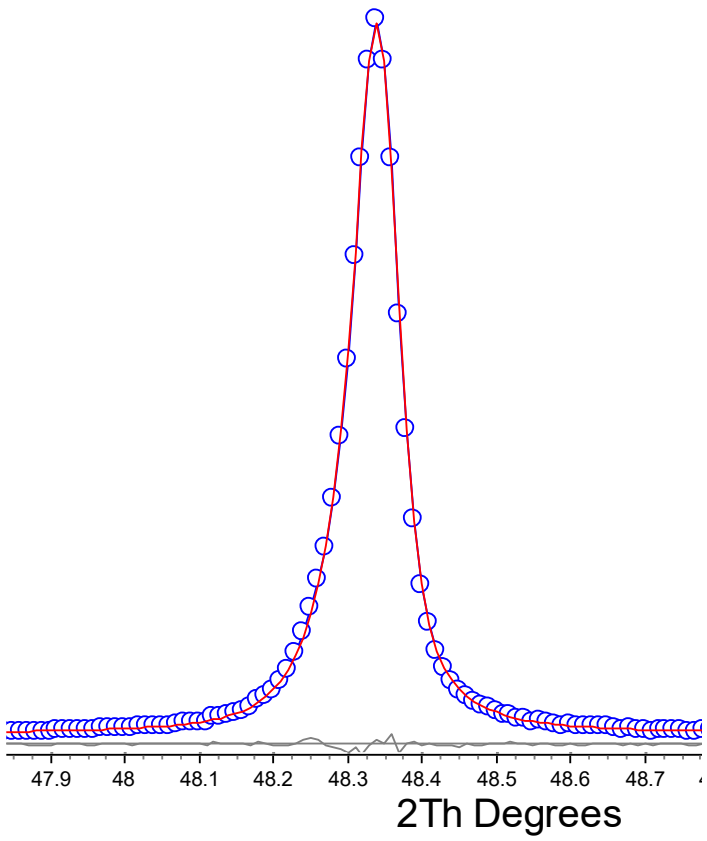
A to **C**: smaller domains broaden peaks and hkl-resolution lost – could just use lower resolution faster measurement

A/B to **C**: if you want to determine particle size instrumental broadening contribution in setup **B** may dominate sample contribution

Peak cut off



`CuKa2(0.1)`

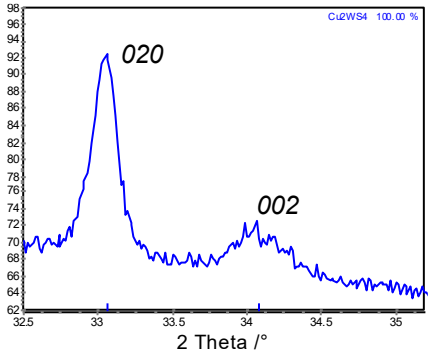


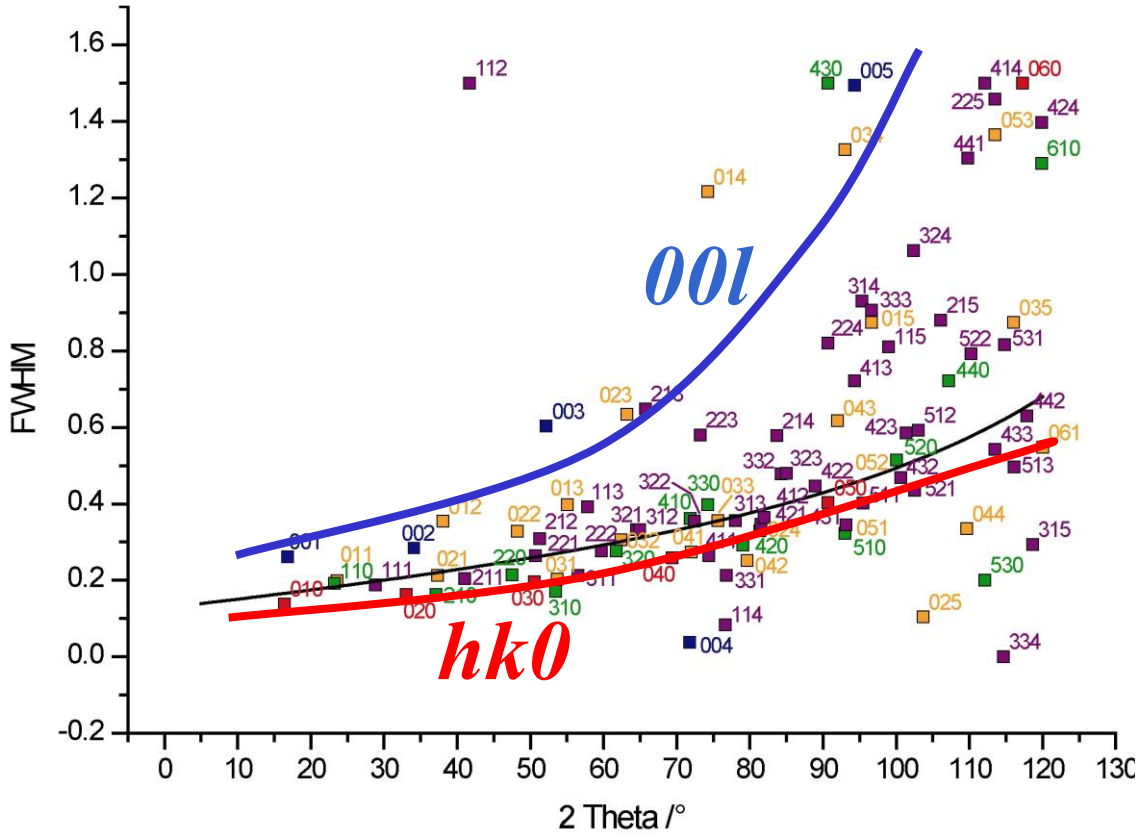
`CuKa2(0.0001)`

GSAS: W 0.1

Clare's Cu_2WS_4 – hkl dependent fwhm

- fwhm vs 2θ may reveal odd things
- 2 phases? Anisotropic peak broadening?





hkl-dependent peak shapes

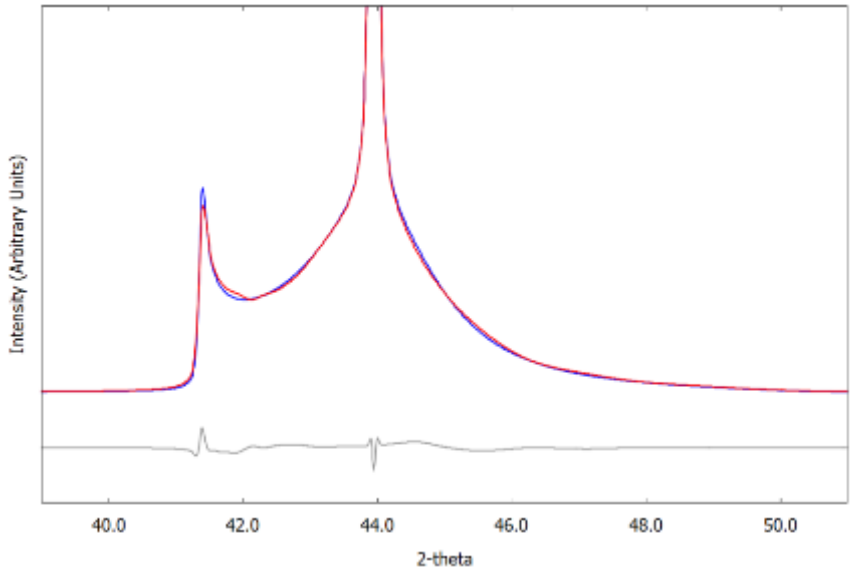
- Relatively common to find peaks have width (or asymmetry) that is hkl-dependent
- Consider using the Stephens/Popa approach (e.g. J. Appl. Cryst. (1999). 32, 281-289)

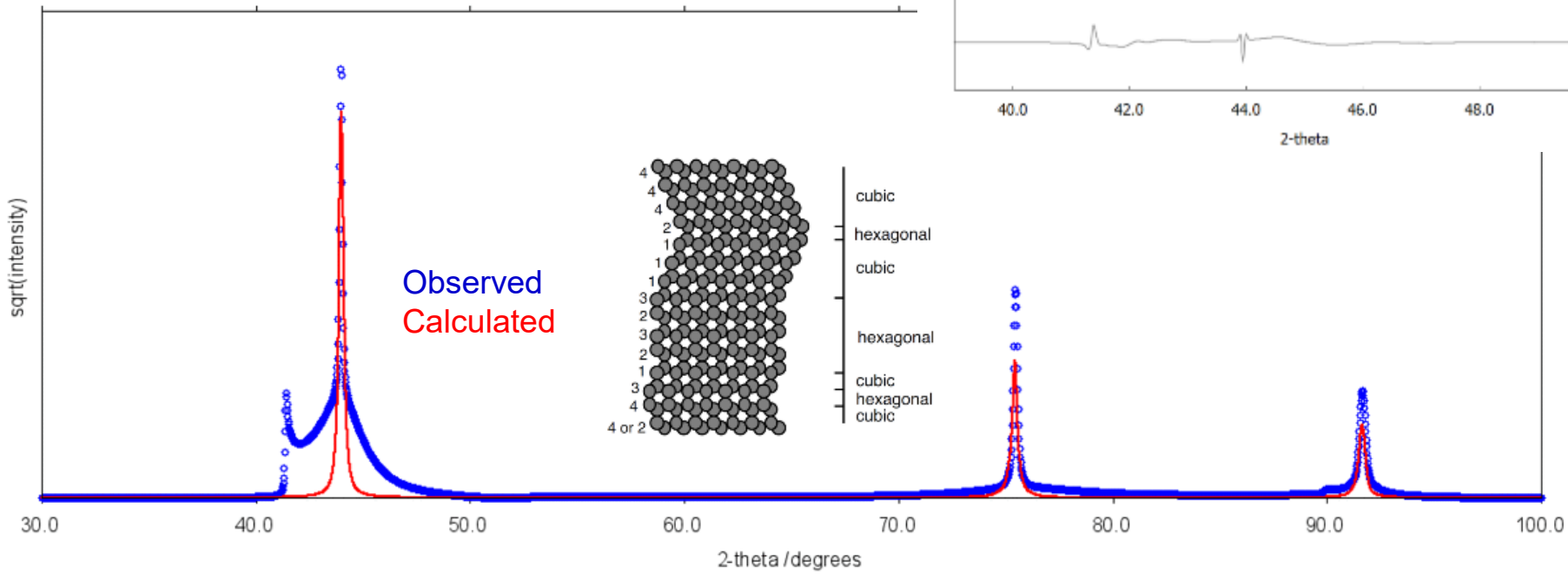
$$fwhm = d^2\sqrt{s400 \times h^4 + s040 \times k^4 + s004 \times l^4 + \ldots + s112 \times h \times k \times l^2}Tan\theta$$

- Refine $s400$, $s040$, etc
- Consider convoluting an additional *hkl*-dependent function onto peak shape (e.g. a spherical harmonic function) - [see “Rietveld Refinement” Chapter 4]
- Consider more exotic empirical convolutions (e.g. for clays)
- Consider a “stacking fault” or “diffax like” Rietveld refinement

Stacking fault refinements

- hcp/ccp diamond intergrowth
- 100 ×100 layers
- Magic smoothing
- Mimics ~50000 layers
- “Cell” ~100000 Å
- 1 parameter peak shape





Lewis, Evans, Coelho, *J. Appl. Cryst.*, 2016

Sample contributions - caveat

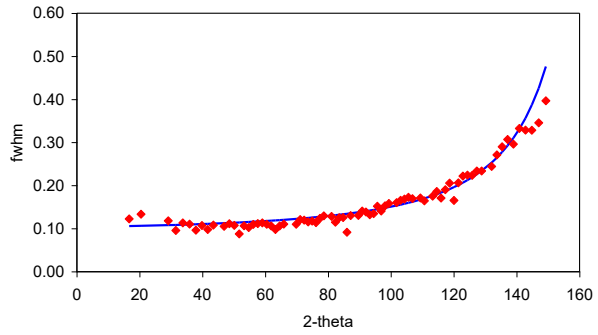
- Be careful!
- Easy to make bad mistakes with size, strain, anisotropic peak shapes etc

- Read the literature carefully

- e.g. for size/strain https://topas.webspace.durham.ac.uk/tutorial-wppm/ and links therein

Tutorial 5.1 (a bit involved!)

- Take an experimental data set
- Determine *fwhm* for all peaks and plot in excel
- Use excel to fit *fwhm*=*f*(2θ) functions
  - $fwhm = (U \tan^2\theta + V \tan\theta + W)^{0.5}$
  - $fwhm = U\,2\theta^2 + V\,2\theta + W$
- Try these same functions in a Rietveld refinement in TOPAS
- Try a fundamental parameters approach in TOPAS and get a better fit with fewer parameters.



Peak-shape related tutorials

- You could try:
  - Tutorial 5.2 – playing with convolutions
  - Tutorial 5.3 – fundamental parameters fitting
  - Tutorial 5.4 – Size/Strain analysis on the CeO_2 round robin data with an empirical instrumental function
  - Tutorial 5.5 – approximating the size of nanoparticles
  - Tutorial 5.6 – Whole Powder Pattern Modelling (WPPM) tutorial by Paolo Scardi
  - Tutorial 5.7 – stacking fault refinements

Problems for this session

1. Session 16 Q1
2. Session 10 Q3 – make sure you've done one composition at two different wavelengths to see the difference
3. If you can grab a tutor for discussion, Session 11 Q5

Lecture notes

Lecture notes

Lecture notes

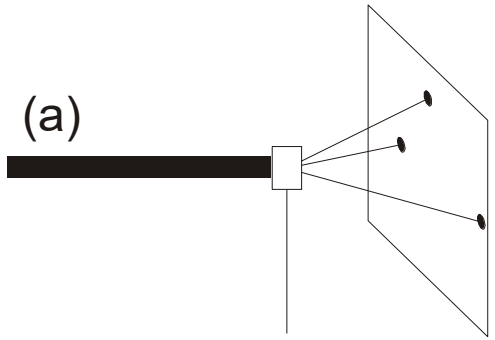
Session 17: Restraints, Constraints, Rigid Bodies and Information Content

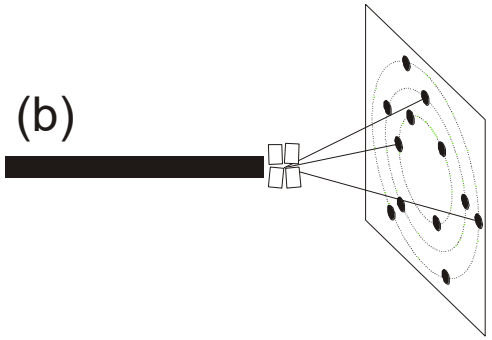
Prof. John S.O. Evans

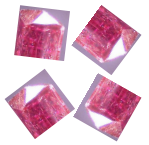
Durham University, Department of Chemistry

Data compression

Single crystal

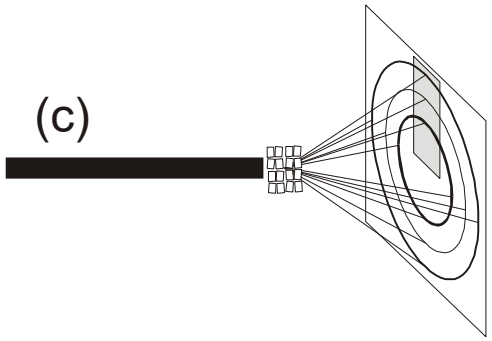


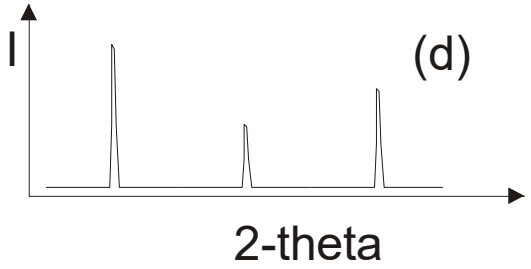




Differently oriented single crystals

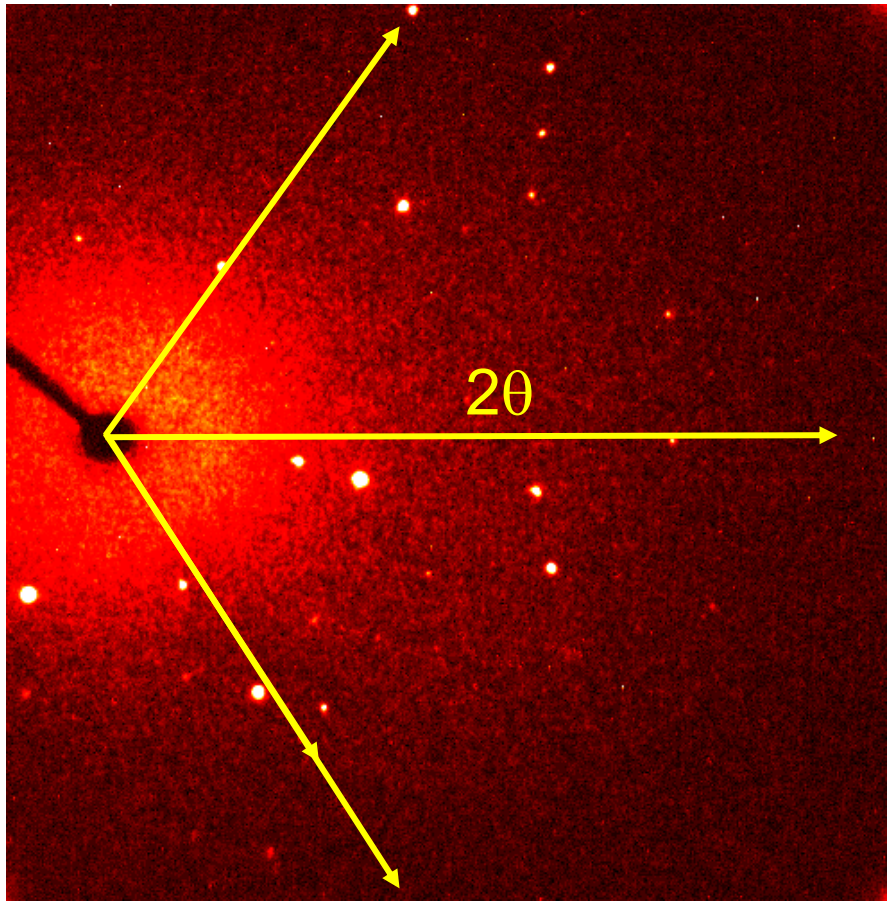
Polycrystalline material

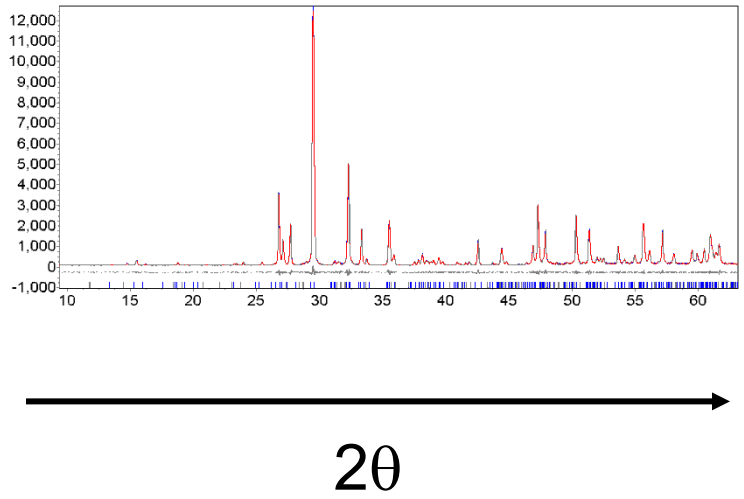




3D information compressed onto 1D

‘…data compressed into one dimension…’





Insufficient information

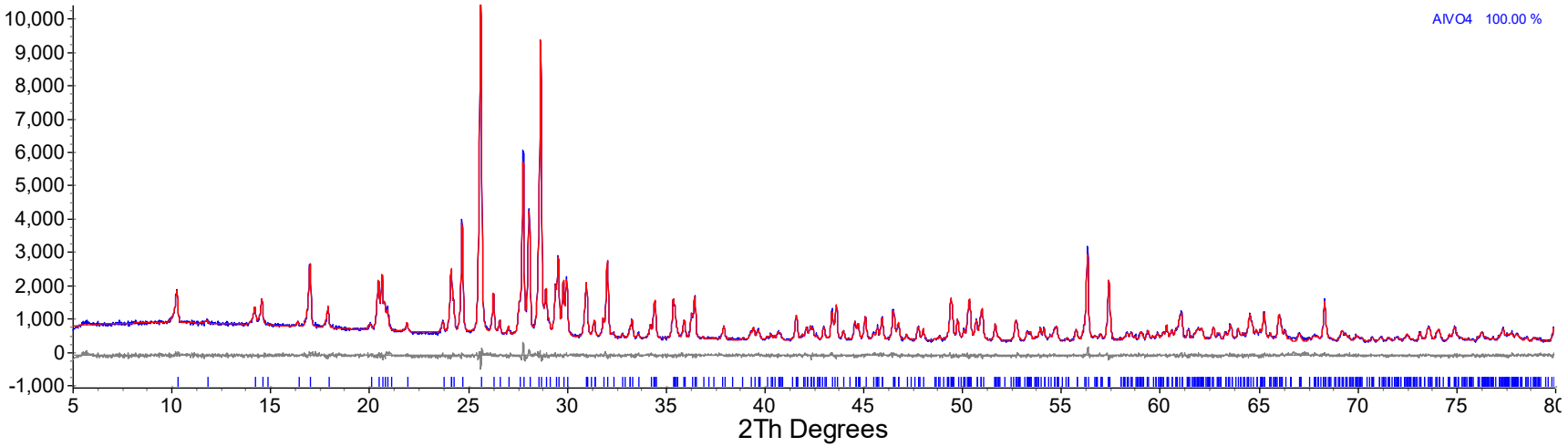
- Powder pattern 3D diffraction data compressed onto 1D
- Loss of “information” relative to a single crystal experiment
- Single crystal people like 10 observations (10 *hkl* reflections) per refined parameter
- How many “observations” do we have in a powder pattern?

Is it the number of data points?

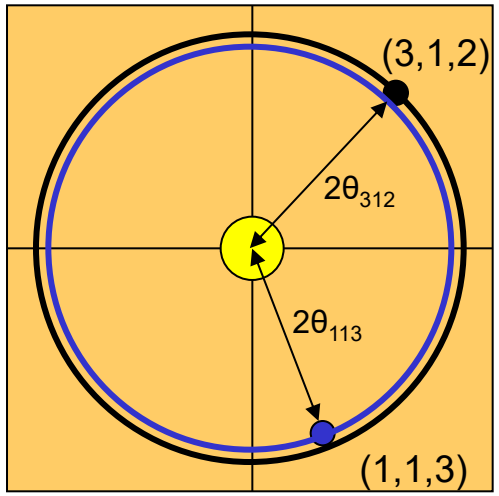
5-80° 0.02° steps = 3750 observations (hooray!)

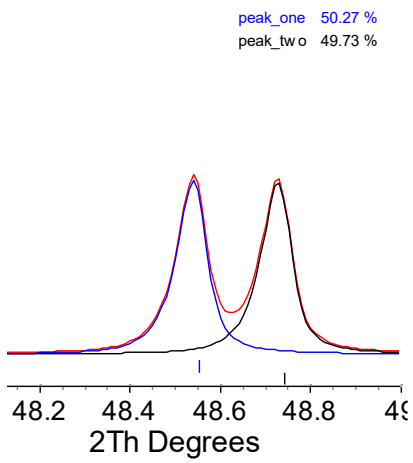
Is it the number of *hkl* tick marks?

534 predicted reflections (hooray-ish!)

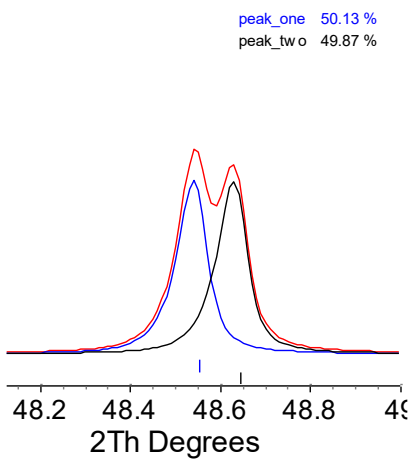


Peak overlap/resolution $\Delta d/d$ (%)

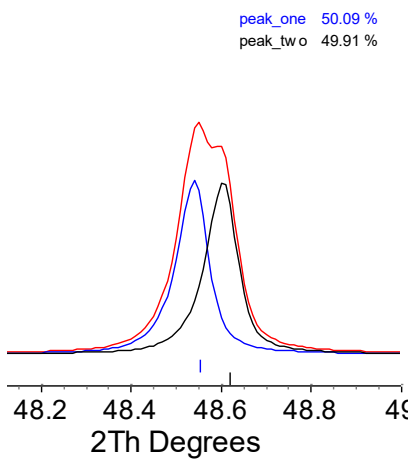




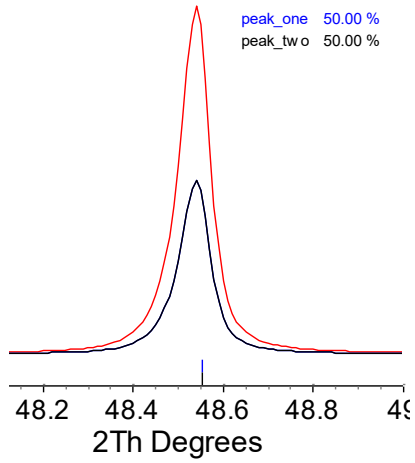
0.36 %



0.12 %



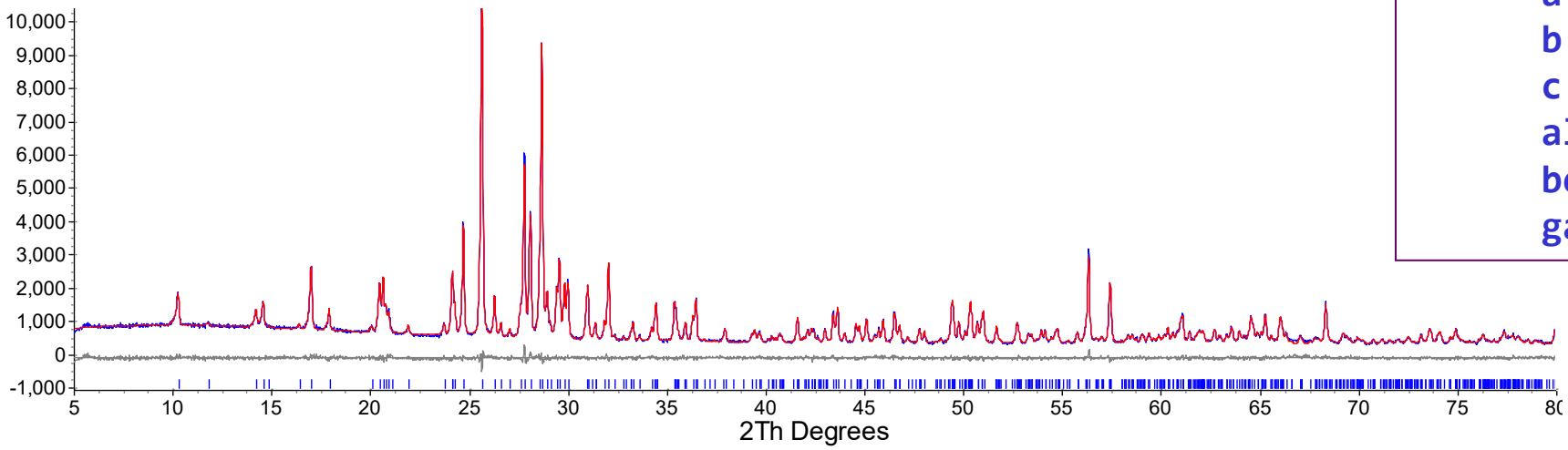
0.04 %



0.0 %

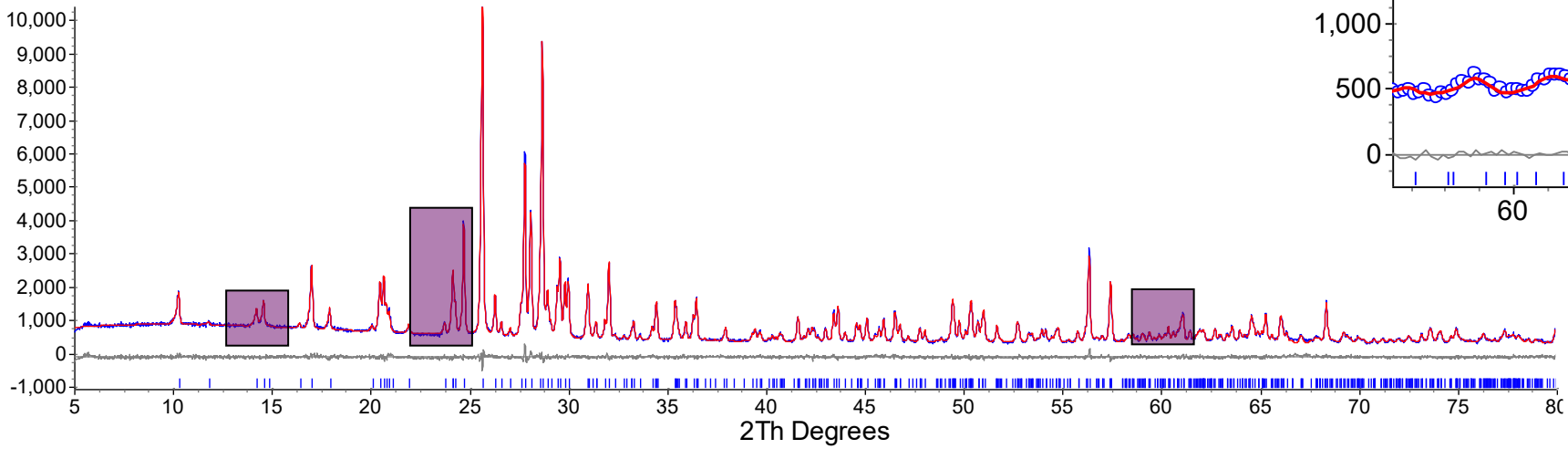
alvo4_tch.inp

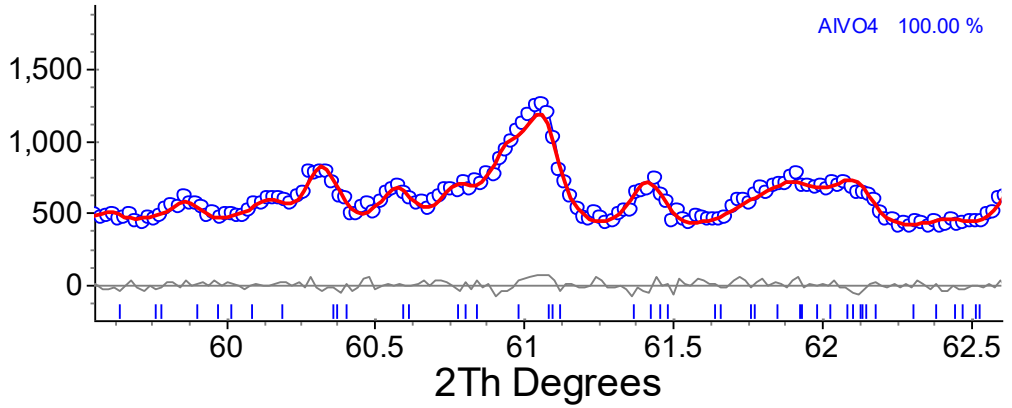
- 5−80 0.02 step 3750 observations
- 530 *hkl* reflections in 2θ range

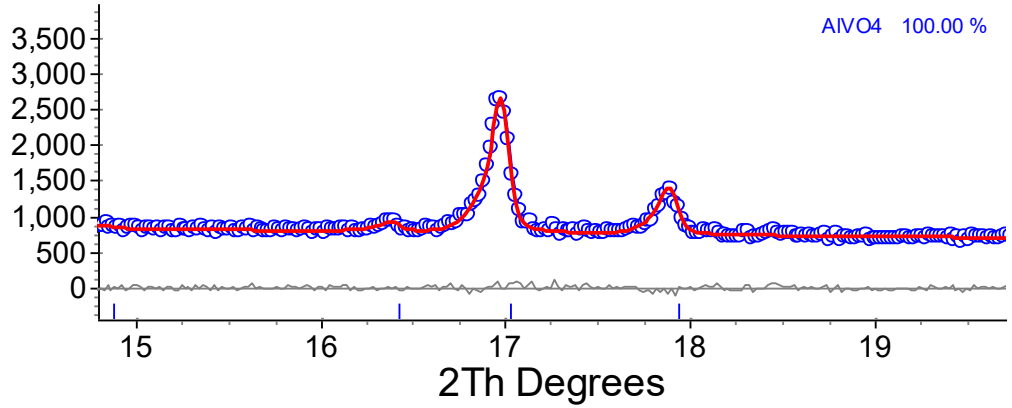


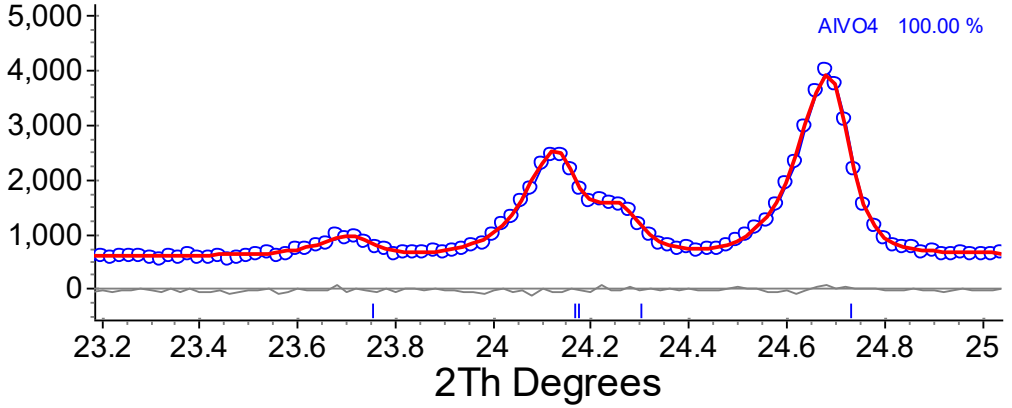

```
STR(P_-1, AlVO4)
      a    @  6.54138`
      b    @  7.75971`
      c    @  9.13591`
      al   @  96.18561`
      be   @  107.23757`
      ga   @  101.40086`
```

How many reflections/observations?

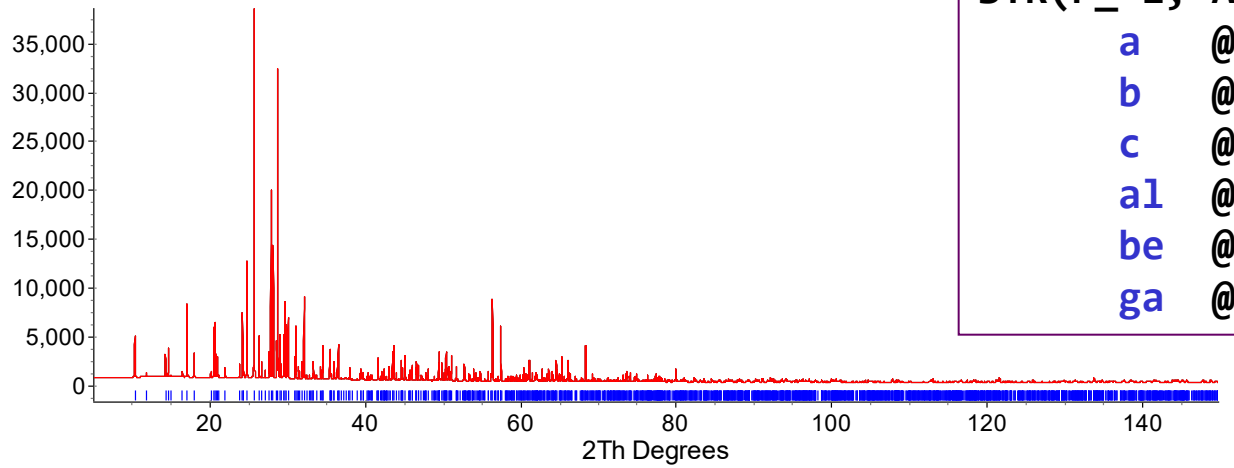




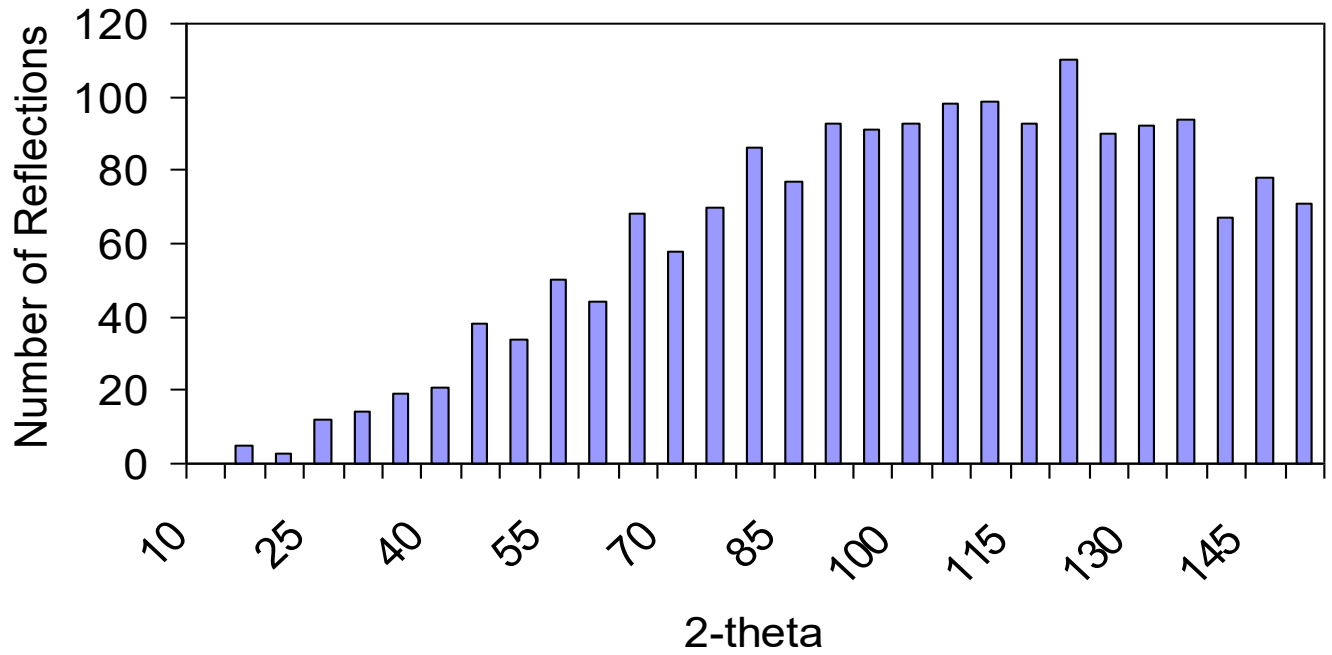




Reflection density and peak overlap




```
STR(P_-1, AlVO4)
      a    @  6.54138`
      b    @  7.75971`
      c    @  9.13591`
      al   @  96.18561`
      be   @  107.23757`
      ga   @  101.40086`
```



5 degree bins
1772 reflections

How much information in a powder pattern?

- See literature by e.g. Giacovazzo/David/Di Sivia

$$\mathbf{M} = \begin{pmatrix} & I1 & I2 & I3 & I4 & I5 & I6 & I7 \\ I1 & 100 & 3 & & & & & \\ I2 & 3 & 100 & & & & & \\ I3 & & & 100 & 98 & & & \\ I4 & & & 98 & 100 & & & \\ I5 & & & & & 100 & 90 & 60 \\ I6 & & & & & 90 & 100 & 80 \\ I7 & & & & & 60 & 80 & 100 \end{pmatrix}$$

- Rarely enough!

Extra information: restraints

- Remember our straight line $y = mx + c$ fitting problem
- Line should pass through (0, 0) – treated as extra observation with a user-defined weight

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 0 \\ 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 2 & 1 \\ 3 & 1 \\ 4 & 1 \\ \boxed{0} & \boxed{1} \end{pmatrix} \begin{pmatrix} m \\ c \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 & 4 & 0 \\ 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 2 \\ 5 \\ 10 \\ 18 \\ \boxed{0} \end{pmatrix}$$

Extra information as an observation

$$m = 4.4$$
$$c = -1.8$$

$$\begin{pmatrix} 1 & 2 & 3 & 4 & 0 \\ 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 2 & 1 \\ 3 & 1 \\ 4 & 1 \\ \boxed{0} & \boxed{100} \end{pmatrix} \begin{pmatrix} m \\ c \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 & 4 & 0 \\ 1 & 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 2 \\ 5 \\ 10 \\ 18 \\ \boxed{0} \end{pmatrix}$$

Higher weight

$$m = 3.81$$
$$c = -0.03$$

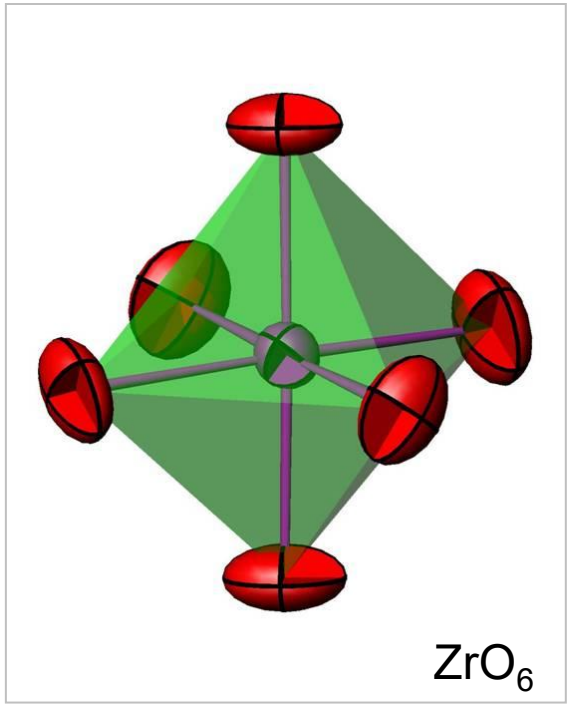
Restraints in Rietveld refinement

- You know that Zr-O bond in a ZrO_6 octahedron should be ~2.075 Å
- Use as “extra information”
- Apply a “penalty” or “restraint” if it’s not that value:

$$penalty = (model's\ ZrO_{dist} - 2.075)^2$$

$$\chi^2_{\text{restraints}} = f(all\ penalties)$$

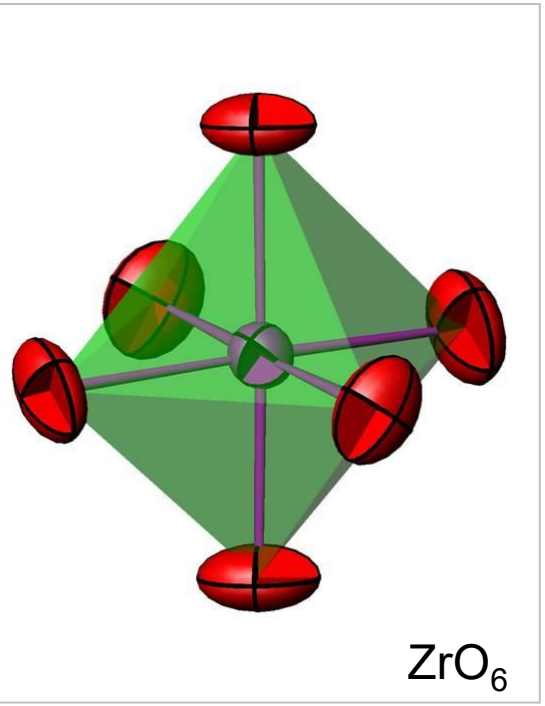
$$\chi^2_{\text{total}} = K_1 \times \chi^2_{\text{data}} + K_2 \times \chi^2_{\text{restraints}}$$

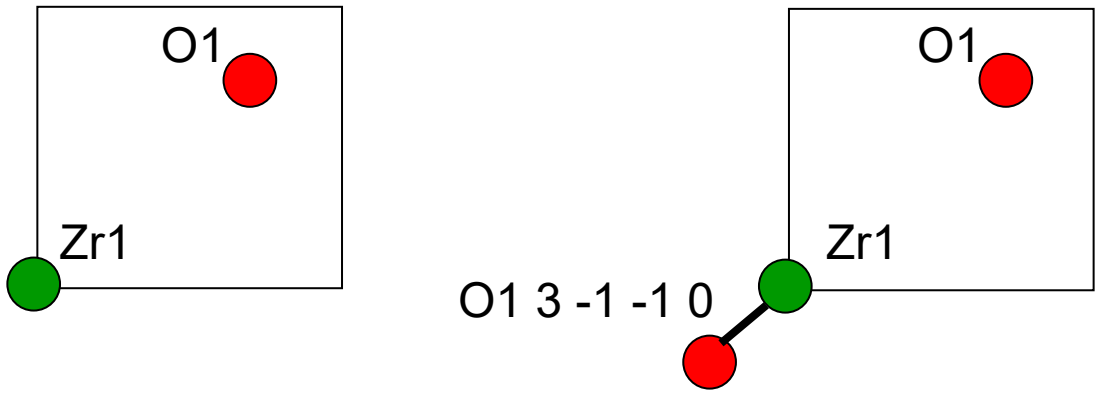


- Fit to data and restraints – restraints act like extra observations
- K_1, K_2 are weights, there could be multiple K_2‘s for different restraints

Distance restraints: TOPAS-speak

```
penalties_weighting_K1 1

Distance_Restrain(Zr1 O1, #ideal_dist, #actual_dist, #tolerance, #weight)
Distance_Restrain(Zr1 O1, 2.075, 2.037, 0.0, 1)
penalty = weight * (2.075-2.037)^2;

Angle_Restrain(O1 Zr2 02, 90, 91, 1, 1)

append_bond_lengths ' use full site name if needed

Zr1:0 O1:3 -1 -1  0 2.12510
      O1:10 0  0  0 2.12510 90.053
      O1:7 -1  0  1 2.12510 90.053 90.053
      O2:7 -1  1  1 2.12575 179.89 89.897 90.036
      O2:3  0  1 -1 2.12575 90.015 89.897 90.036 179.898
      O2:10-1  0  0 2.12575 90.015 90.015 90.036 179.898 89.897
```





Extra information: constraints

- Force sub-sections of structure to be rigid
- Force specific relationships between parameters
- Dealt with in least squares in the same way as symmetry – change the least squares equations
- “Hard Constraints”

Constraints

- Remember our $y = mx + c$ straight line that had to pass through the origin: force $c = 0$:

$mx + c = y$

$$\begin{pmatrix} 1 & 2 & 3 & 4 \\ 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 1 & 1 \\ 2 & 1 \\ 3 & 1 \\ 4 & 1 \end{pmatrix} \begin{pmatrix} m \\ c \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 & 4 \\ 1 & 1 & 1 & 1 \end{pmatrix} \begin{pmatrix} 2 \\ 5 \\ 10 \\ 18 \end{pmatrix}$$

$m = 5.3$
$c = -4.5$

$mx = y$

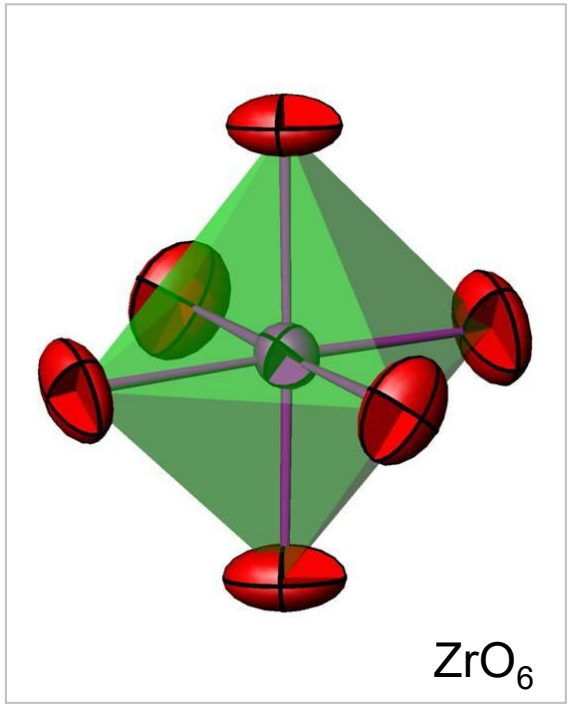
$$(1 \quad 2 \quad 3 \quad 4) \begin{pmatrix} 1 \\ 2 \\ 3 \\ 4 \end{pmatrix} (m) = (1 \quad 2 \quad 3 \quad 4) \begin{pmatrix} 2 \\ 5 \\ 10 \\ 18 \end{pmatrix}$$

$m = 3.8(5)$
$c = 0$

Constraints in Rietveld refinement – e.g. rigid bodies

- You might want to force a ZrO_6 group to be a rigid octahedron
- Constraints change the least squares equations
- 21 *xyz* parameters become 3 positions and 3 rotations?

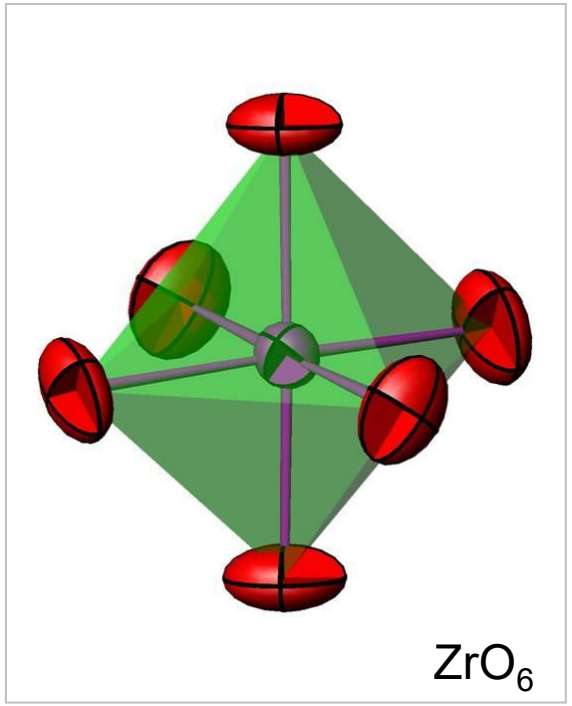
```
macro Octahedron(Zr1, o1, o2, o3, o4, o5, o6, 2.075)
{
   Point_for_site(s0,  0,  0,  0)
   Point_for_site(s1,  r,  0,  0)
   Point_for_site(s2, -r,  0,  0)
   Point_for_site(s3,  0,  r,  0)
   Point_for_site(s4,  0, -r,  0)
   Point_for_site(s5,  0,  0,  r)
   Point_for_site(s6,  0,  0, -r)
}
```



- Other common constraints are:
  - Site occupancies to maintain chemical composition
  - Atomic displacement parameters equated for multiple sites
  - (Pseudo)symmetry relationships

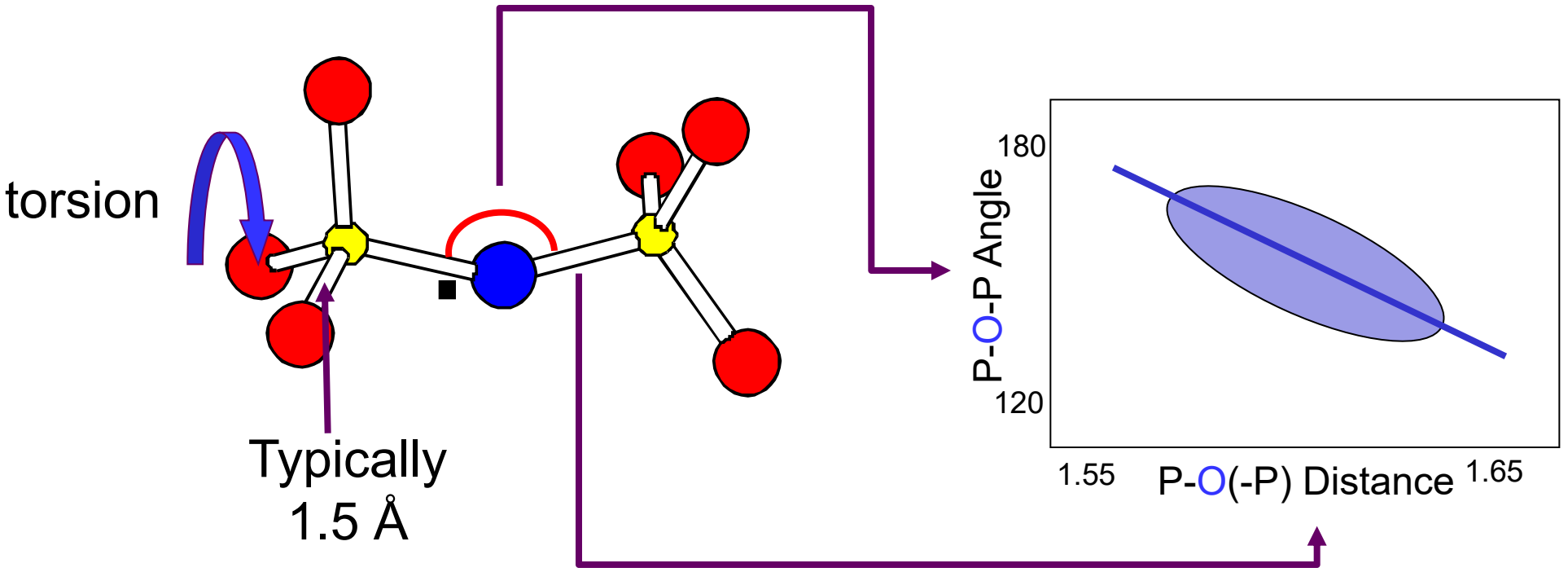
Constraints in Rietveld refinement – e.g. TLS matrices

- In a fully rigid group atoms would vibrate in related ways
- 42 u_{ij} parameters become 2 TLS parameters?
- “Rietveld Refinement” book P177



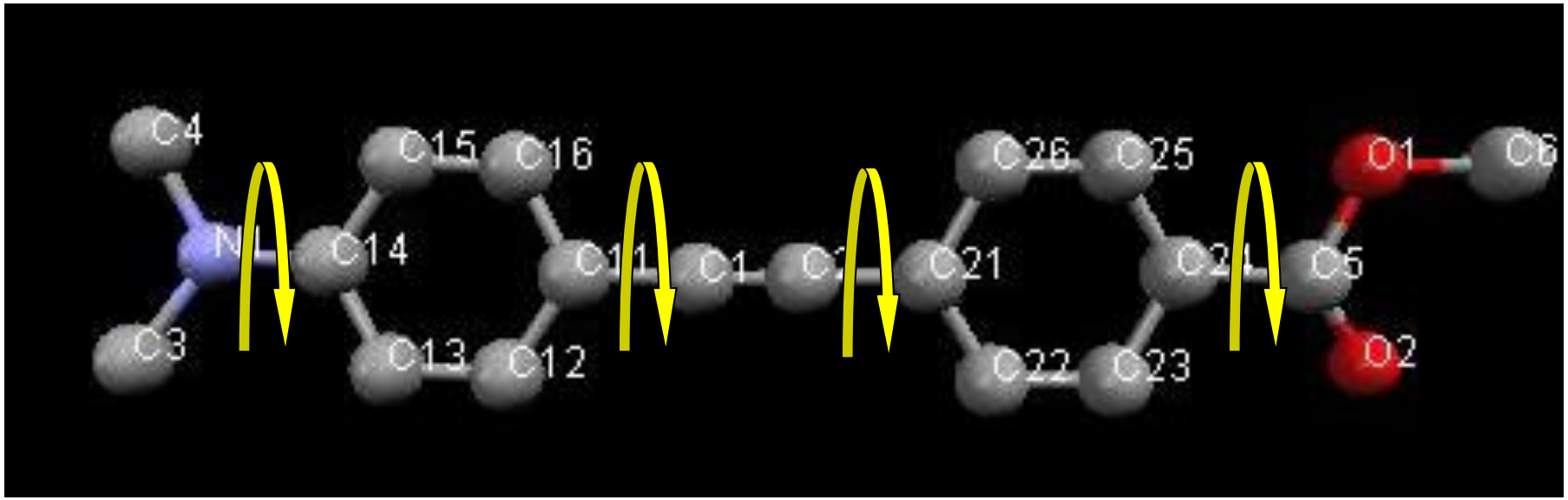
Rigid bodies with internal freedom

- P_2O_7 groups are well understood – P-$O_{terminal}$ 1.5 Å, P-O_{bridge} depends on P-O-P angle
- 0 refinable distances per P_2O_7 , an angle, a torsion and overall translations and rotations?
- 8 parameters not 27



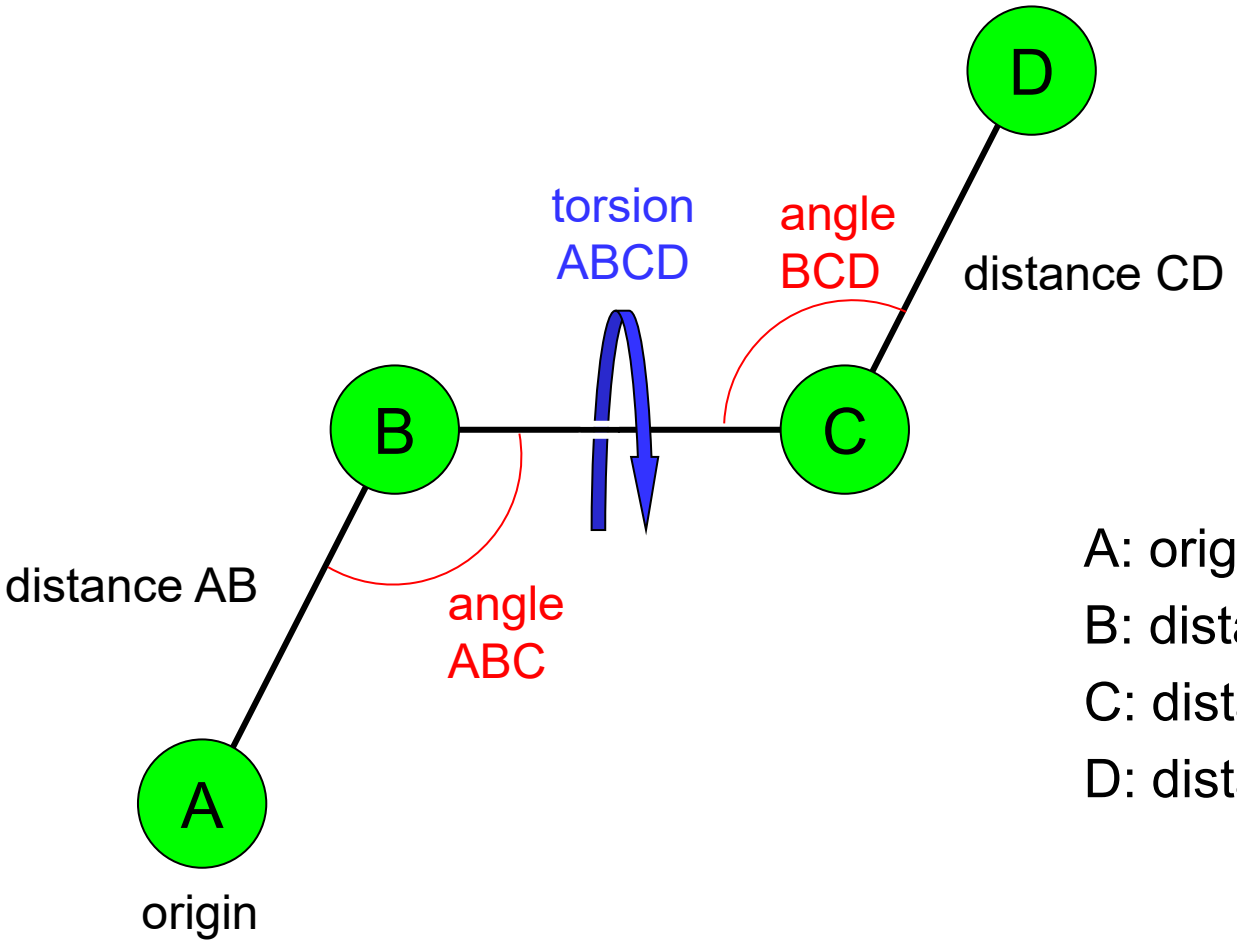
Rigid bodies – molecular species

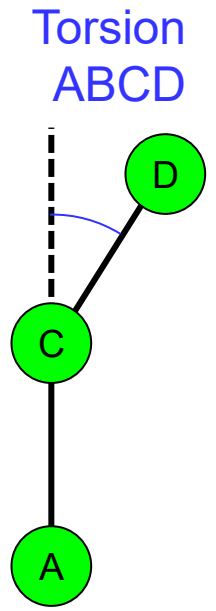
- Define in terms of rigid hexagons for benzene rings
- Allow a torsion angle between rings
- Allow a torsion angle for NMe_2 groups and CO_2H group



Z-matrix – organic molecules

- Use a distance and angle “road map” to describe coordinates
- Refine distances/angles/torsions directly





A: origin

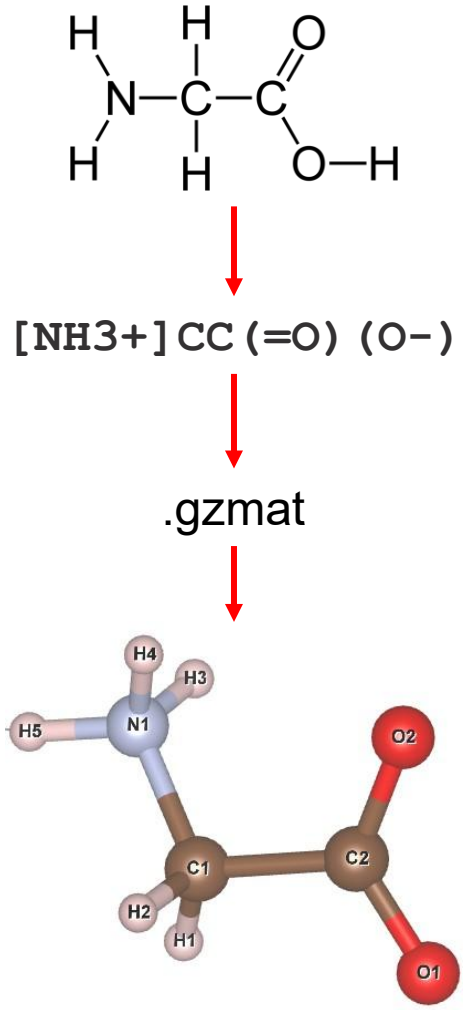
B: distance from A

C: distance from B plus angle ABC

D: distance from C plus angle BCD plus torsion ABCD

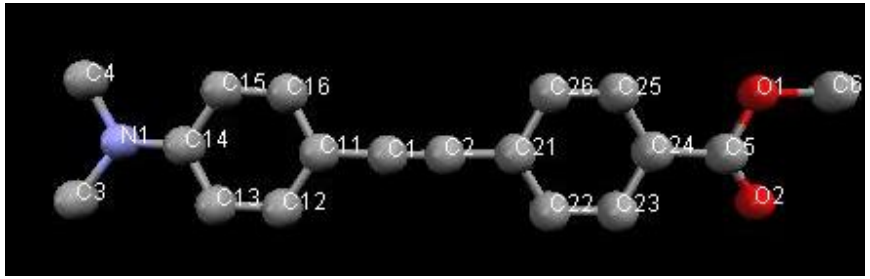
Z-matrix creation – see tutorials

```
' a rigid body defined in terms of refinable bond lengths
prm d_CN  1.47513237 min 1 max 1.6
prm d_NH  1.05996069 min 1 max 1.6
prm d_CC  1.50647087 min 1 max 1.6
prm d_CH  1.15838484 min 1 max 1.6
prm d_CO  1.27563046 min 1 max 1.6
rigid
    z_matrix N1
    z_matrix C1  N1   =d_CN;:1.47513
    z_matrix H3  N1   =d_NH;:1.05996 C1   109.4912
    z_matrix H4  N1   =d_NH;:1.05996 C1   109.4912 H3    240.0000
    z_matrix H5  N1   =d_NH;:1.05996 C1   109.4912 H3    120.0000
    z_matrix C2  C1   =d_CC;:1.50647 N1   109.4912 H3     60.0000
    z_matrix H1  C1   =d_CH;:1.15838 N1   109.4912 H4   -180.0000
    z_matrix H2  C1   =d_CH;:1.15838 N1   109.4912 H3   -180.0000
    z_matrix O1  C2   =d_CO;:1.27563 C1   120.0000 N1 @ -160.6372
    z_matrix O2  C2   =d_CO;:1.27563 C1   120.0000 O1   -180.0000
    Rotate_about_axies(xrota -61.98012, yrota -1.23756, zrota  68.83734
    Translate(xtransa  0.29638 , ytransa  0.08653 , ztransa  0.74341)
```



Tutorials – restraints/constraints

- Session 6 Q2
- Tutorial 3.7 – ZrW_2O_8
- Tutorial 6.1 – using Z-matrices
- Tutorial 6.2 – refining an organic using restraints then as a rigid group then as a Z-matrix
- Tutorial 6.3 - organic molecules from synchrotron data using z-matrix formalism
- GSAS 4 – restraints/combined refinement oxide
- GSAS 5 – rigid bodies $Sc_2(WO_4)_3$ using TLS matrices
- GSAS 7 – organic using restraints
- GSAS 9 – Ni coordination polymer using restraints



Lecture notes

Lecture notes

Lecture notes

Session 18: Introduction to GSAS/FullProf/Jana2020

Prof. John S.O. Evans

Durham University, Department of Chemistry

GSAS and GSAS-II

- General Structural Analysis System
- Bob Von Dreele/Alan Larson and Brian Toby
- Very widely used

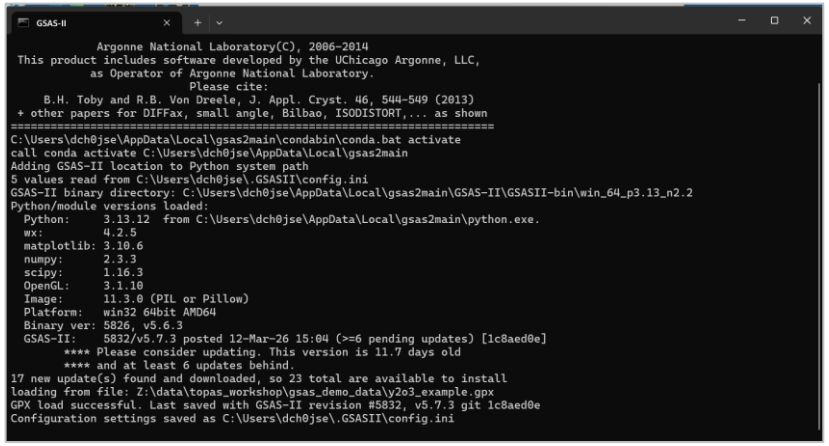
- GSAS-I ran via expedt/expgui
- Created an .exp file (like .inp file) in background

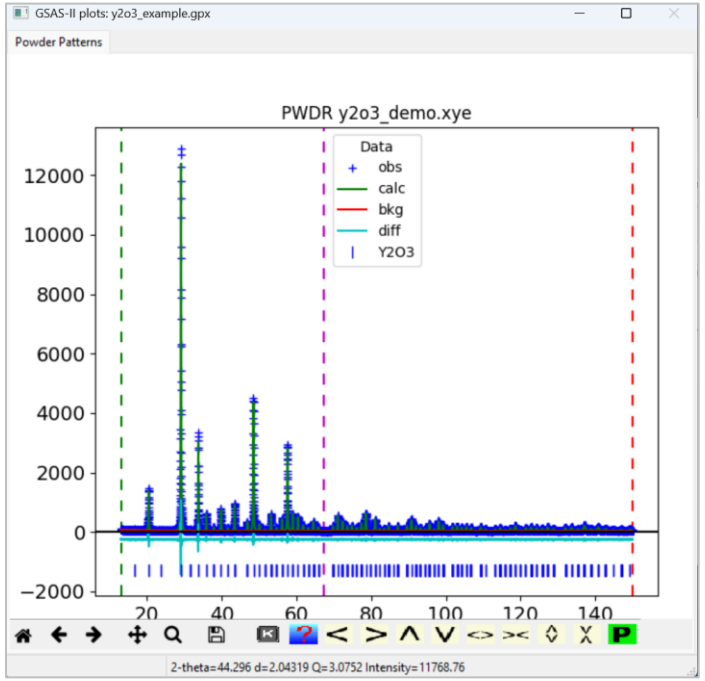
- GSAS-II new version
- Fully integrated GUI
- Open source, Python (computationally intensive parts C/Fortran)
- Python API for scripting
- Data stored in a .prj file (Python pickle, not readable)

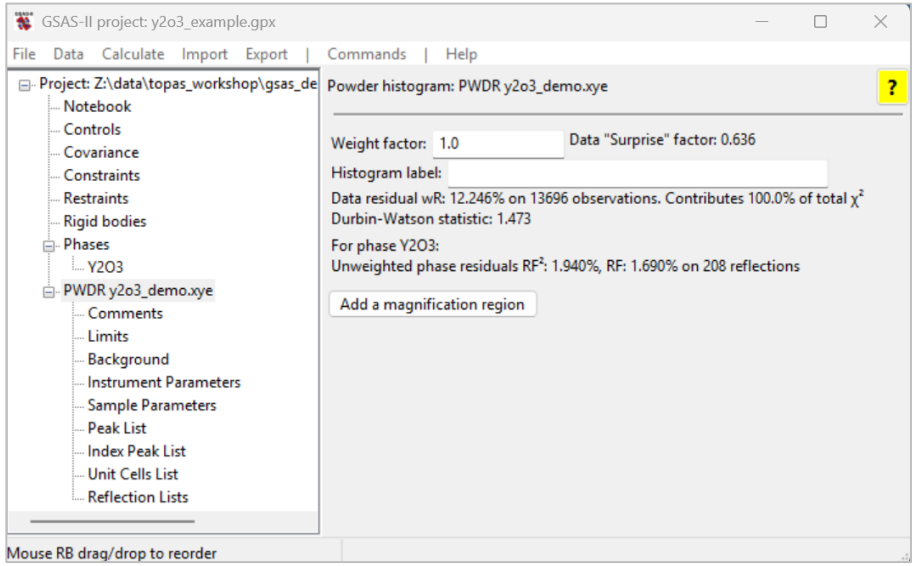
- Tutorials/videos: https://advancedphotonsource.github.io/GSAS-II-tutorials/tutorials.html

GSAS-II interface/demo

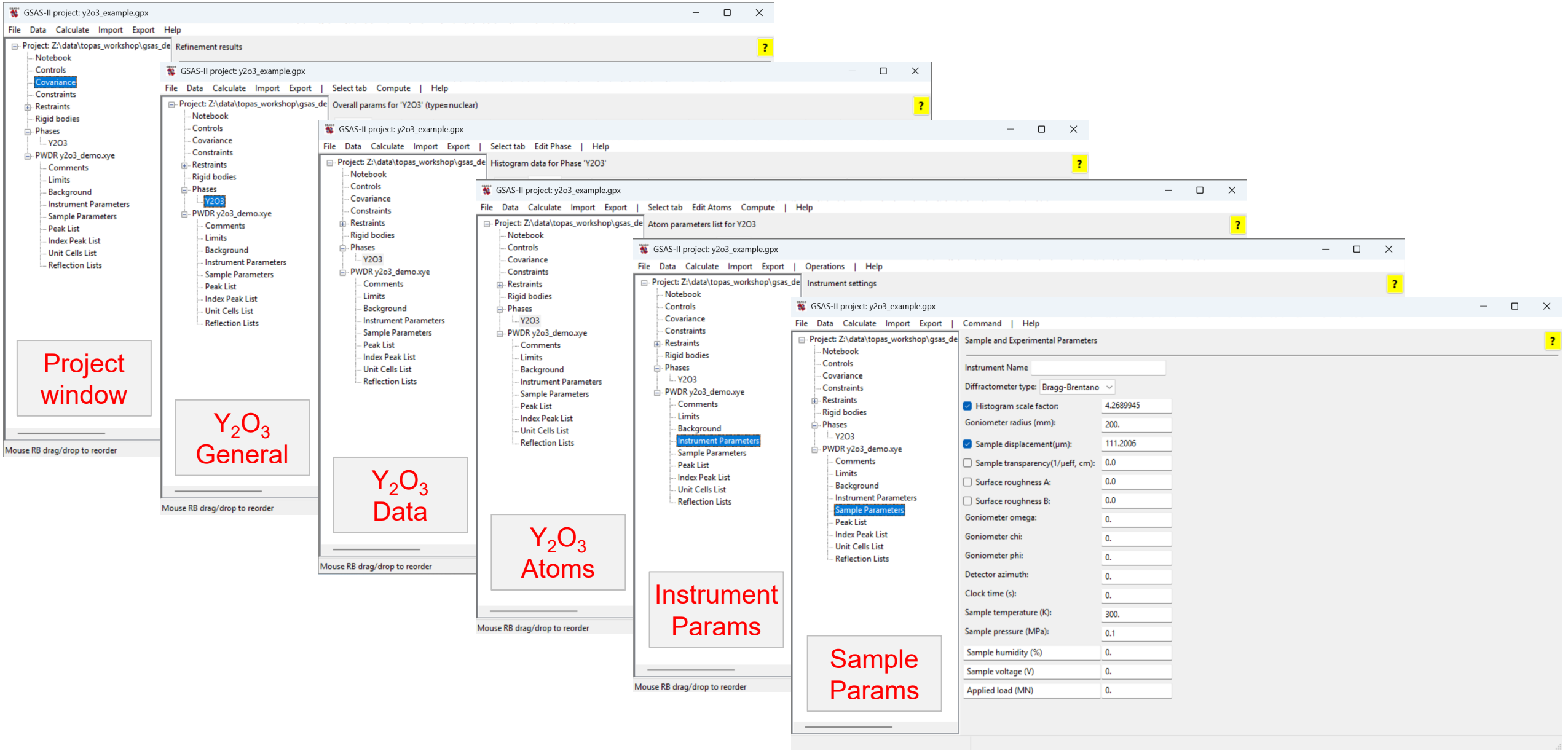
+ File/Open Project….







GSAS-II interface: tree structure and multiple tabs



GUI vs INP? ☺

```
'Minimum INP file for Simple Rietveld
‘Overall information, dataset (xdd) information, structural (str) information
r_wp  10.3215283 r_exp  10.0886011 r_p  7.10082635 gof  1.02308815
iters 100
chi2_convergence_criteria 0.001

xdd y2o3_demo.xye
    x_calculation_step = Yobs_dx_at(Xo);
    bkg @  0 0 0
    LP_Factor(!th2_monochromator, 27.26)
    CuKa1(0.0001)
    str
        space_group "Ia-3"
        site Y1     x 0.25  y 0.25  z 0.25  occ Y+3  1  beq 0.25
        site Y2     x 0.97  y 0.00  z 0.25  occ Y+3  1  beq 0.25
        site O1     x 0.39  y 0.15  z 0.38  occ O-2  1  beq 0.25
        TCHZ_Peak_Type(pku, 0.039,pkv, -0.02,pkw, -0.001,!pkz, 0.00,pkx, 0.009, pky, 0.001)
```

GSAS .instprm instrument parameter file

```
#Bank 1: GSAS-II instrument parameter file; do not add/delete items!
Type:PXC
Lam:1.54056
Zero:0.0
Polariz.:0.559
U:15.173886388495069
V:-27.411489953187225
W:13.837229494187564
X:-1.7201803482760458
Y:6.930390164249117
Z:0.0
SH/L:0.016850488708164572
Azimuth:0.0
Source:CuKa
Bank:1.0
```

- Describes the instrument you're using
- Just like parts of the .inp file

```
'TOPAS equivalent
CuKa1(0.0001)
Specimen_Displacement(height, 0.091`)
LP_Factor(!th2_monochromator, 27.26)
TCHZ_Peak_Type(pku, 0.002`,pkv,  0.003`,pkw, 0.001`,!pkz, 0.000,pkx, 0.088`, pky, 0.003`)
Simple_Axial_Model(axial, 10.7329535`)
```

GSAS/TOPAS – Beware LP Corrections

```
'TOPAS .INP
CuKa2(0.0001)
LP_Factor(!th2_monochromator, 26.6)
'GSAS-II .instprm
Lam1:1.54056
Lam2:1.54443
Polariz.:0.555
'GSAS-I .inst
INS  1  ICONS  1.5406  1.5444  0.0000  0.555  0  0.500
```

Topas:

```
LP_Factor(!th2_mono, 26.6)
```

$$LP = \frac{1 + \cos^2 2\theta \times \cos^2 2\theta_M}{\cos\theta \sin^2\theta} \qquad LP = \frac{1 + \cos^2 2\theta \times 0.8}{\cos\theta \sin^2\theta}$$

GSAS-I:

IPOL = 1, *Ph*(POLA) = 0.800

$$LP = \frac{1 + Ph \cos^2 2\theta}{\sin^2\theta \cos\theta} \qquad LP = \frac{1 + 0.8 \times \cos^2 2\theta}{\cos\theta \sin^2\theta}$$

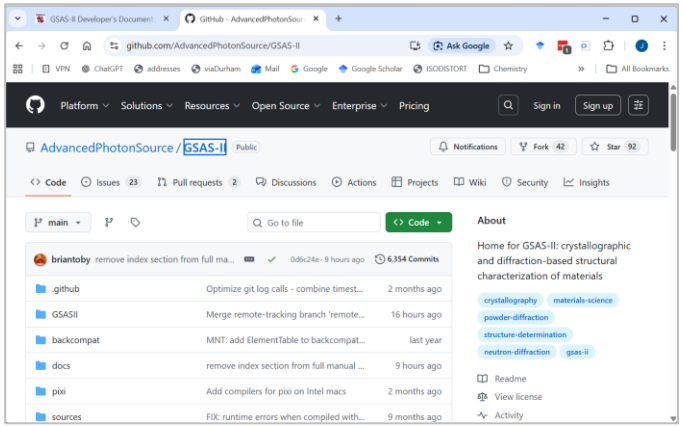
GSAS-I:

IPOL = 0, *Ph*(POLA) = 0.555

$$LP = \frac{Ph + (1 - Ph)\cos^2 2\theta}{2\sin^2\theta \cos\theta} \qquad LP = \frac{1 + \cos^2 2\theta \times 0.8}{\cos\theta \sin^2\theta} = \frac{0.5 + \cos^2 2\theta \times 0.4}{2\cos\theta \sin^2\theta} = \frac{0.9}{1}\left(\frac{0.555 + 0.444 \times \cos^2 2\theta}{2\cos\theta \sin^2\theta}\right)$$

Open source – check e.g. GSASIIpwd.py, GitHub and docs

```
'TOPAS height/zero point correction in input file
prm !zero    0.00
prm height  0.02
th2_offset = zero - 2*height*Cos(Th)/radius;
```



File Edit Selection View ··· Search

GSASIIpwd.py 6

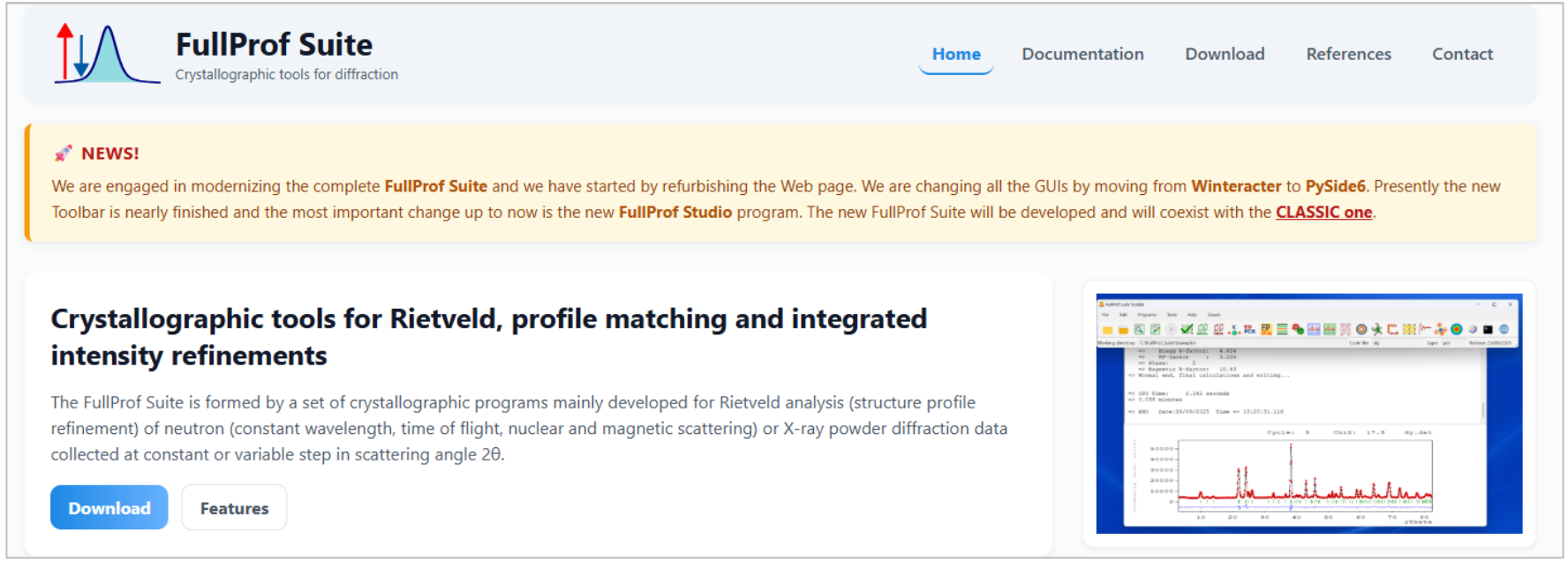
C: > Users > dch0jse > AppData > Local > gsas2main > GSAS-II > GSASII > GSASIIpwd.py > DoCalibInst > errPeakPos

```
2230  def DoCalibInst(IndexPeaks,fitPeaks,Inst,Sample):
2414          print (sigStr)
2415
2416      def errPeakPos(values,peakDsp,peakPos,peakWt,dataType,parmDict,varyList):
2417          parmDict.update(dict(zip(varyList,values)))
2418          calcPos = G2lat.getPeakPos(dataType,parmDict,peakDsp)
2419          if dataType[2] in ['A','B','C']:
2420              const = 0.18/(np.pi*parmDict['radius'])
2421              if 'Debye' in Sample['Type']:
2422                  shft = -const*(parmDict['DisplaceX']*npcosd(calcPos)+parmDict['DisplaceY']*npsind(calcPos))+par
2423              else:
2424                  shft = -2.0*const*(parmDict['Shift']*npcosd(calcPos/2.0)+parmDict['Zero'])
2425              return peakWt*(calcPos+shft-peakPos)
2426          else:
2427              return peakWt*(calcPos-peakPos)
```

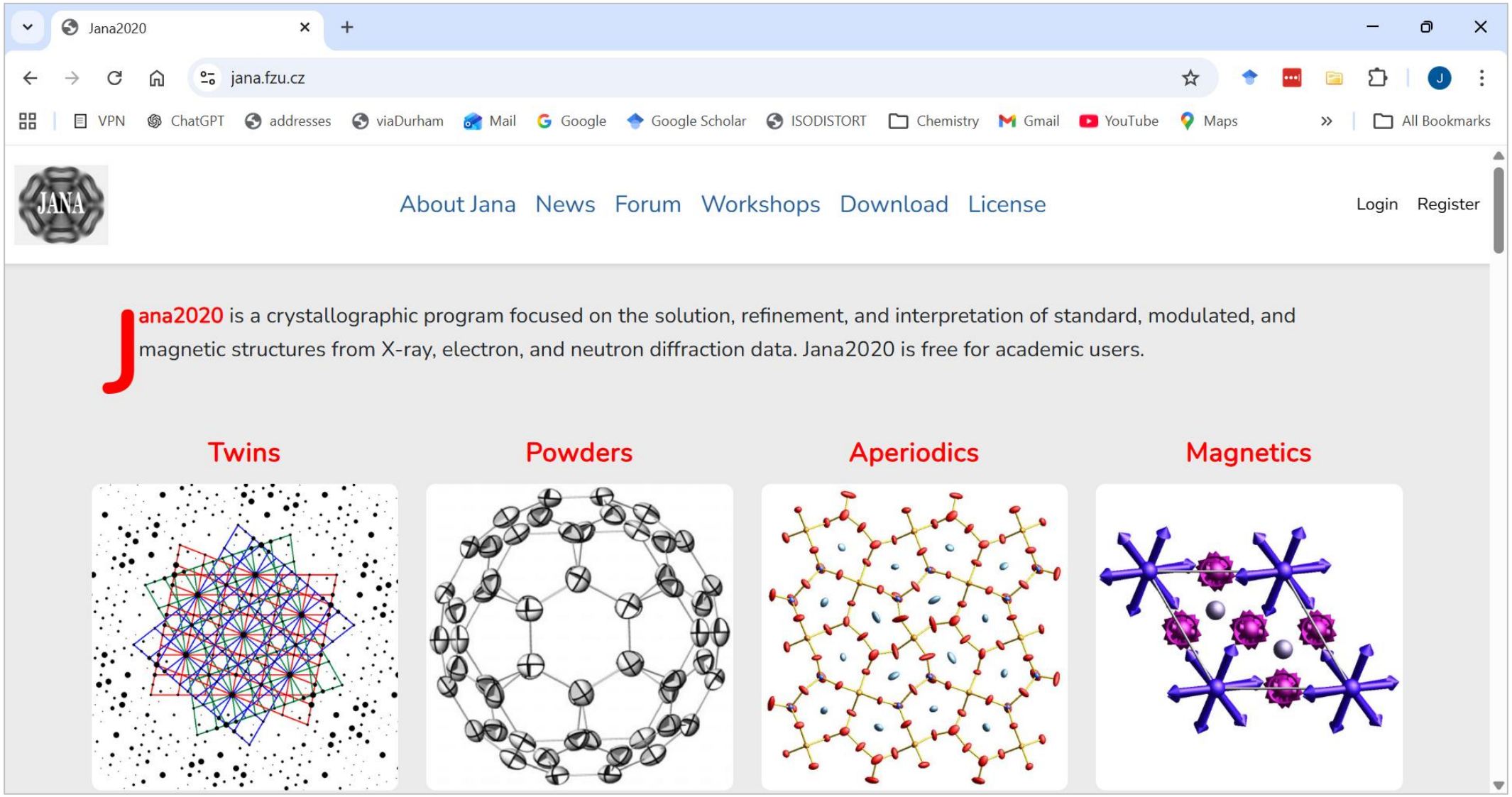
Python .py script: C:\Users\dch0jse\AppData\Local\gsas2main\GSAS-II\GSASII\GSASIIpwd.py

FullProf Suite

- Juan Rodriguez-Carvajal
- Has a .pcr file (like .inp file) in background
- Very widely used
- Magnetic refinements
- Incommensurate refinements
- Not installed by default – go to https://www.ill.eu/sites/fullprof/ or school installation page



Jana2000



Petříček, V.; Palatinus, L.; Plášil, J.; Dušek, M. *Jana2020 – a new version of the crystallographic computing system Jana*. Z. Kristallogr. (2023)

Lecture notes

Lecture notes

Session 25: Questions and Answers, Spot the Errors, Special Topics, Free Problems GSAS and FullProf

Prof. John S.O. Evans

Durham University, Department of Chemistry

Thursday: special topics, general topics, spot-the-errors

- Special topics for Thursday morning?

- Moving from exercises to real world
  - Hardest thing in practice is spotting mistakes when you don't know what the "right" answer is
  - Are there errors in model or data?
  - Emma's "Rietveld Crimes"

- Final challenge of school
  - mistake_02 to mistake_08 contain data with "errors" in them
  - Find the errors and win a prize!
  - Stick to isotropic temperature factors
  - Stick to a TCHz analytical peak shape function
  - For these instruments you can fix `pkx` and `pkz` at 0

Understanding Things

- Look in topas.log
- Look in topas.inc
- Make your own local.inc

Other Things (numbers might differ)

- Symmetry mode refinements (Tutorial 10.1-10.6)
  - using group theory to help with phase transitions
- Quantitative Rietveld (Tutorial 8.1)
  - Using Nikki Scarlett/Ian Madsen's Round Robin data
- Size strain analysis (Tutorial 5.4)
  - Using CeO_2 round robin data
- Single crystal data (Tutorial 8.3)
- Using functions to do the whole crystallographic analysis (Tutorial 8.4)
- Parametric/Surface Fitting (Tutorial 9.2-9.4)
- Multiple datasets and automatic refinements (Tutorial 9.1)

Checklist: Start to Finish

- Go through a problem or tutorials taking you through the whole process of data analysis
  - Fit peaks (Tutorial 2.1)
  - Index (manually or in topas) (Tutorial 2.2)
  - Work out space group (Session 1/2)
  - Pawley/Le Bail fit for indication of fit quality possible (Tutorial 3.2)
  - Structure solution? (Tutorial 7.1-7.3)
  - Rietveld refinement (Tutorial 3.*)

- e.g. the $PbSO_4$ data in Tutorial 4.4

Checklist: Key Skills

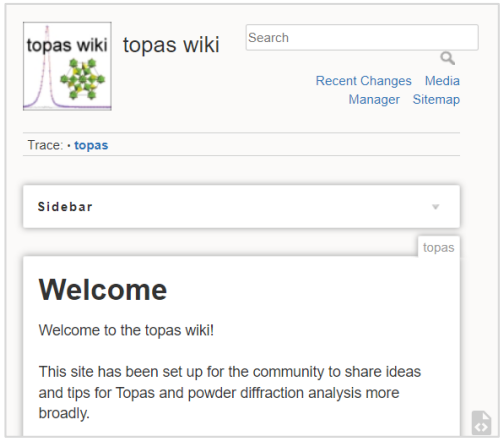
- Data types
  - Lab xrd
  - Synchrotron xrd
  - Neutron constant wavelength
  - Neutron time of flight
- Sample types
  - Inorganic extended structures
  - Small molecule structures
- Software Y_2O_3 in
  - TOPAS
  - GSAS
  - Fullprof
- Multiphase refinement
- Multiple dataset refinement

Checklist: Happy?

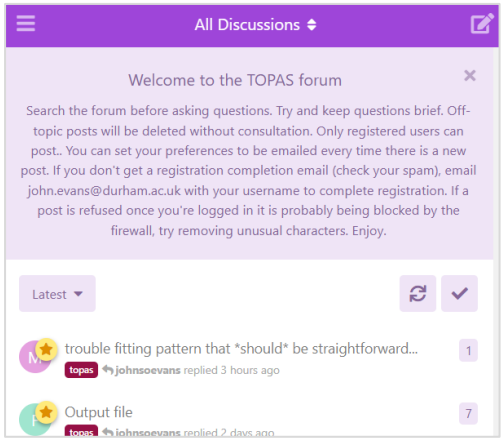
- Are you leaving knowing what you hoped you'd learn?
- If not ask!
- PLEASE COMPLETE POST-COURSE QUESTIONNAIRE

Resources during and after the school

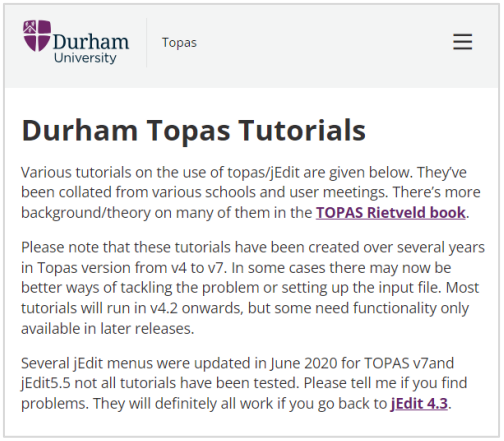
wiki site



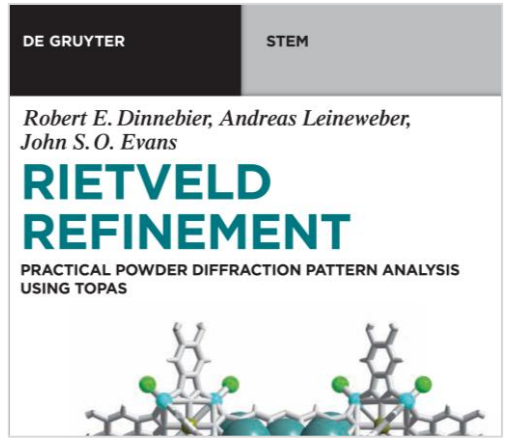
forum



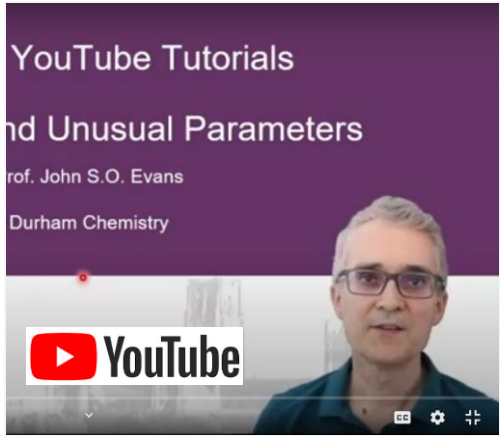
web tutorials



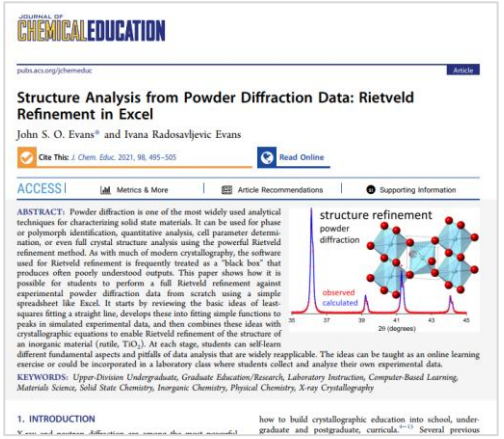
book



YouTube



Rietveld in excel



School breaks

School page