Knowledge Center

PROTO

X-RAY DIFFRACTION

Indexing strategies

LS-refinement and autoindexing methods

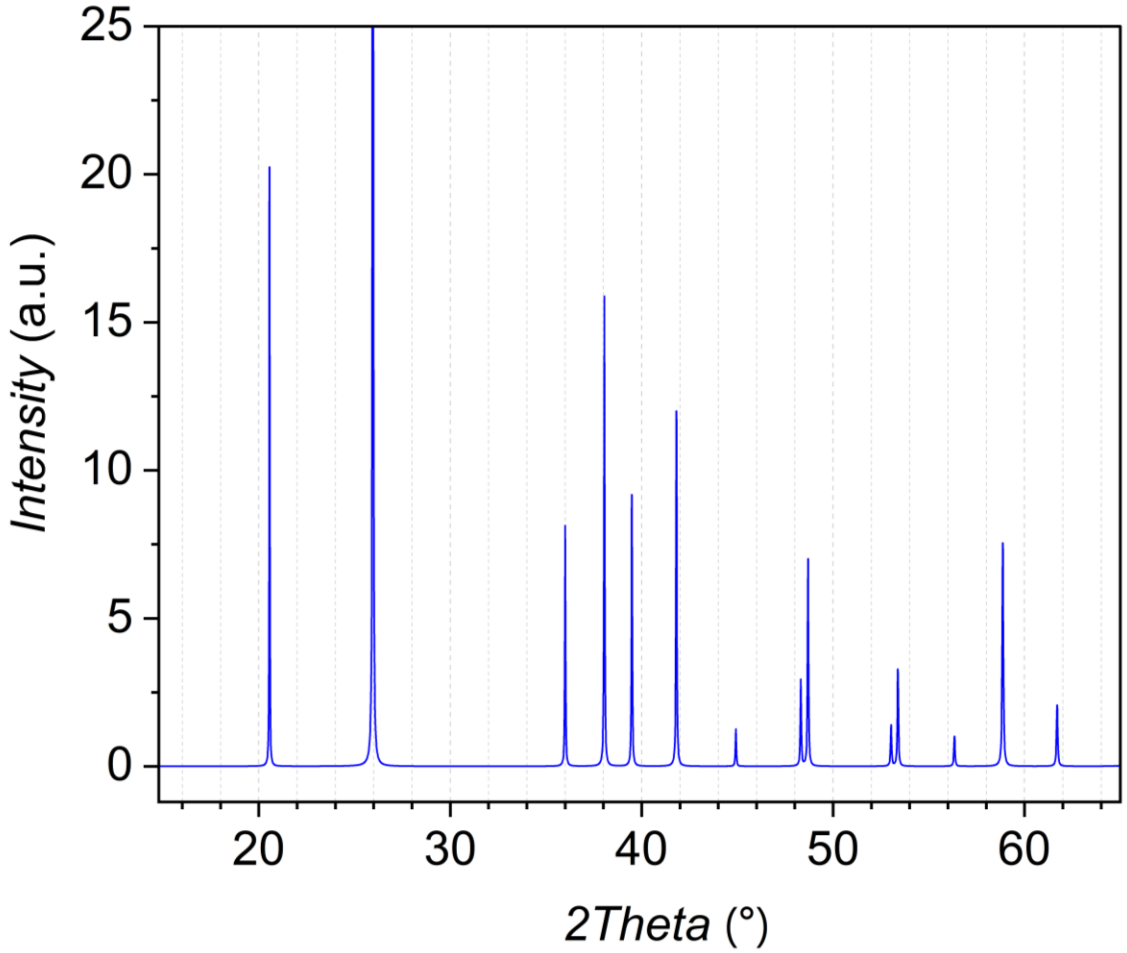
Anton Dmitrienko

Chemical crystallographer

Indexing

Indexing – assignment of crystallographic indices (Miller indices, *hkl*) to the peaks on the diffractogram.

Indexing is a basic procedure for sample characterization with PXRD.



Experimental diffractogram of GeO_2

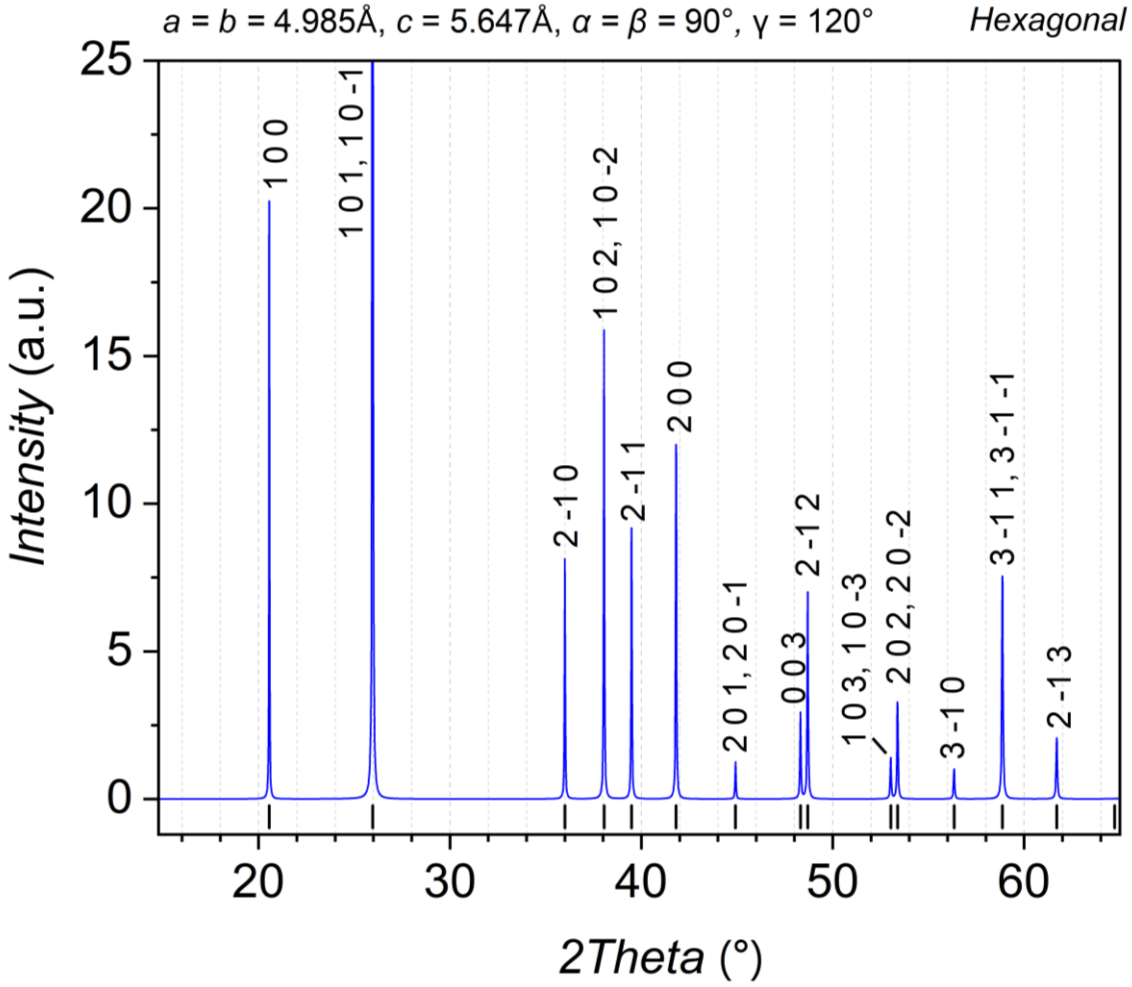
Indexing

Indexing – assignment of crystallographic indices (Miller indices, *hkl*) to the peaks on the diffractogram.

Indexing is a basic procedure for sample characterization with PXRD which provides information on:

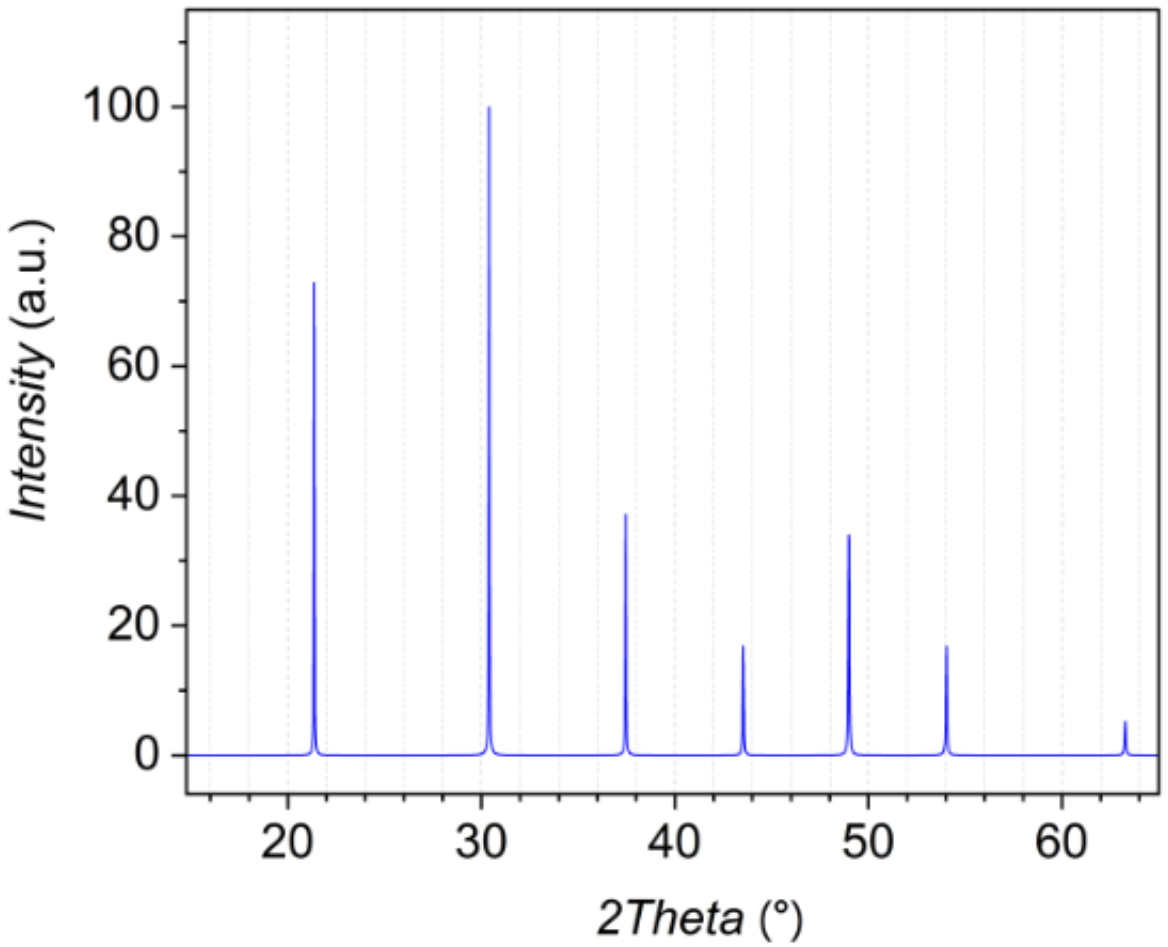
- Unit cell dimensions
- Crystal class
- Positions of all possible reflections in the reciprocal lattice
- Phase purity

Indexing refers to the peak positions only and does not require estimation of the area under the diffraction peak (intensity).

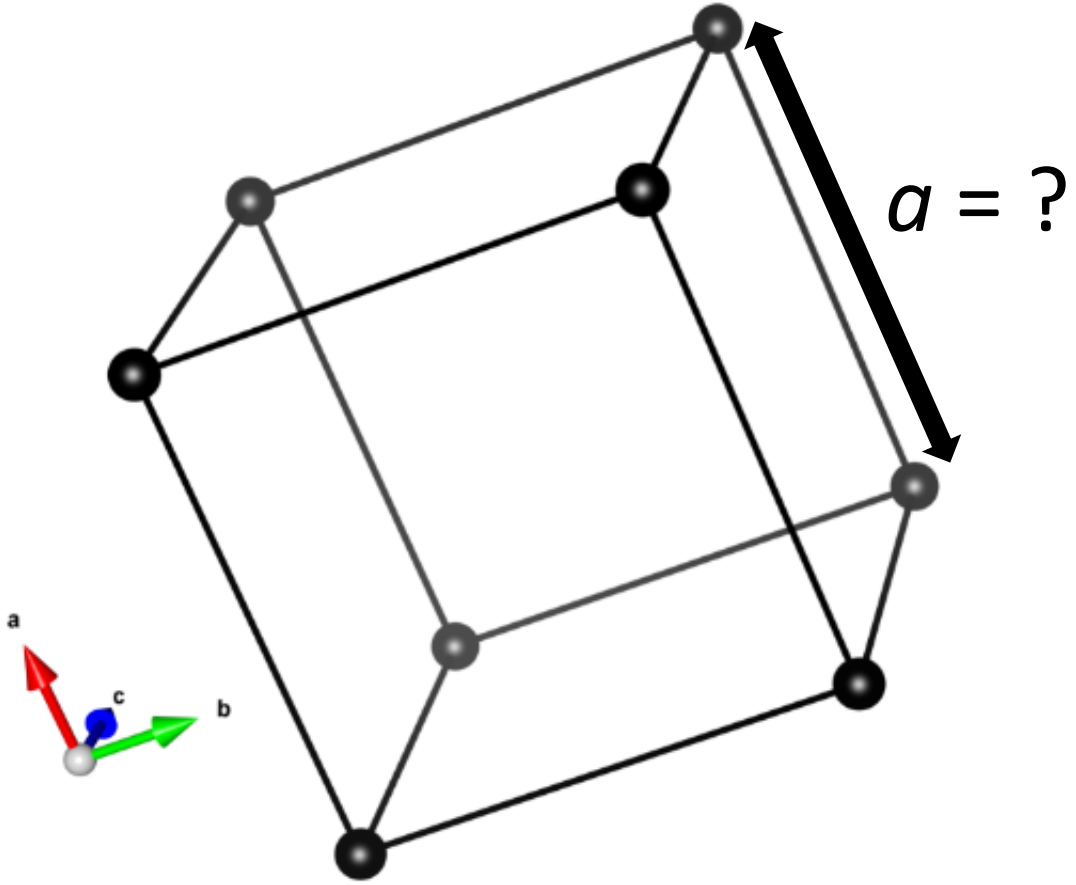


Indexed diffractogram of hexagonal GeO_2

Unit cell parameters from PXRD (cubic system)



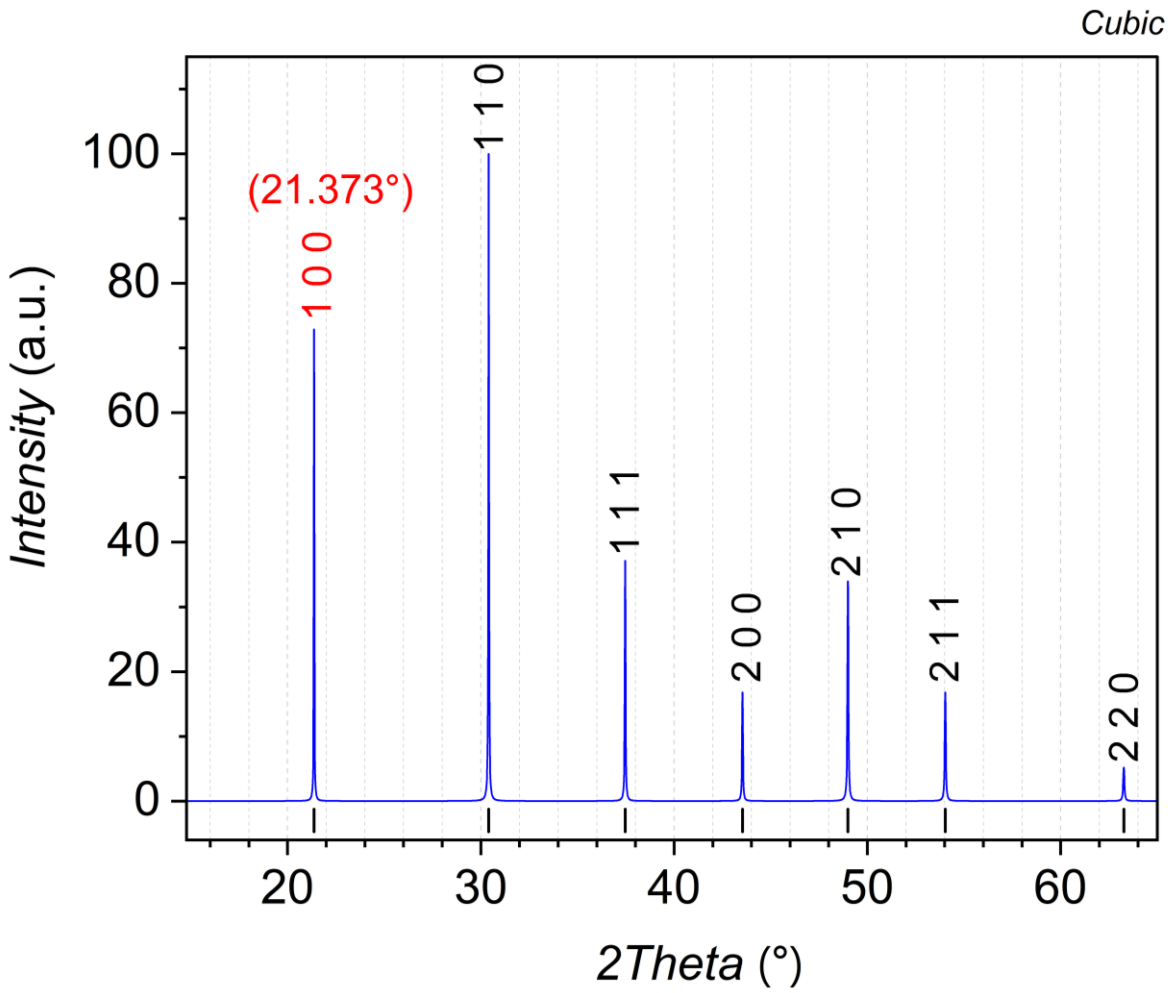
Experimental diffractogram of cubic LaB_6



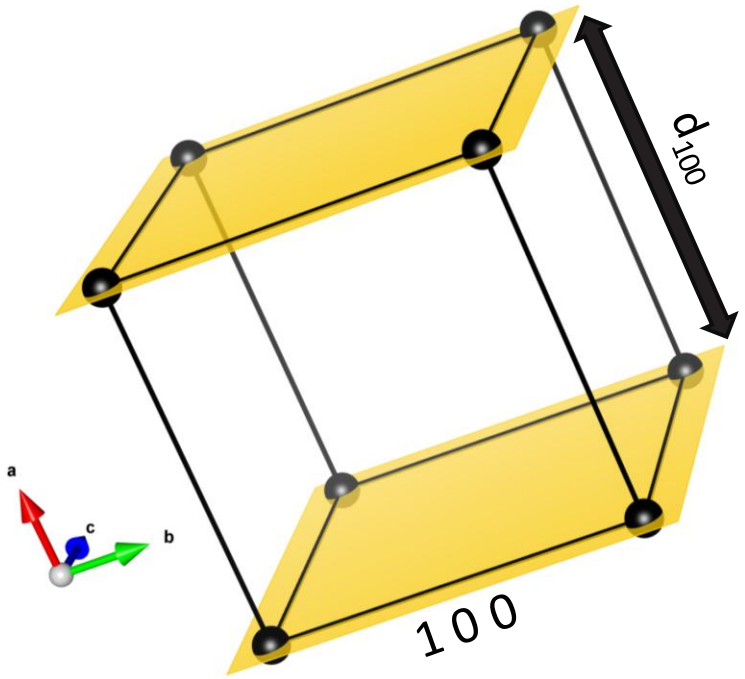
$a = b = c$; $\alpha = \beta = \gamma = 90°$

Primitive cubic unit cell of LaB_6

Unit cell parameters from PXRD (cubic system)

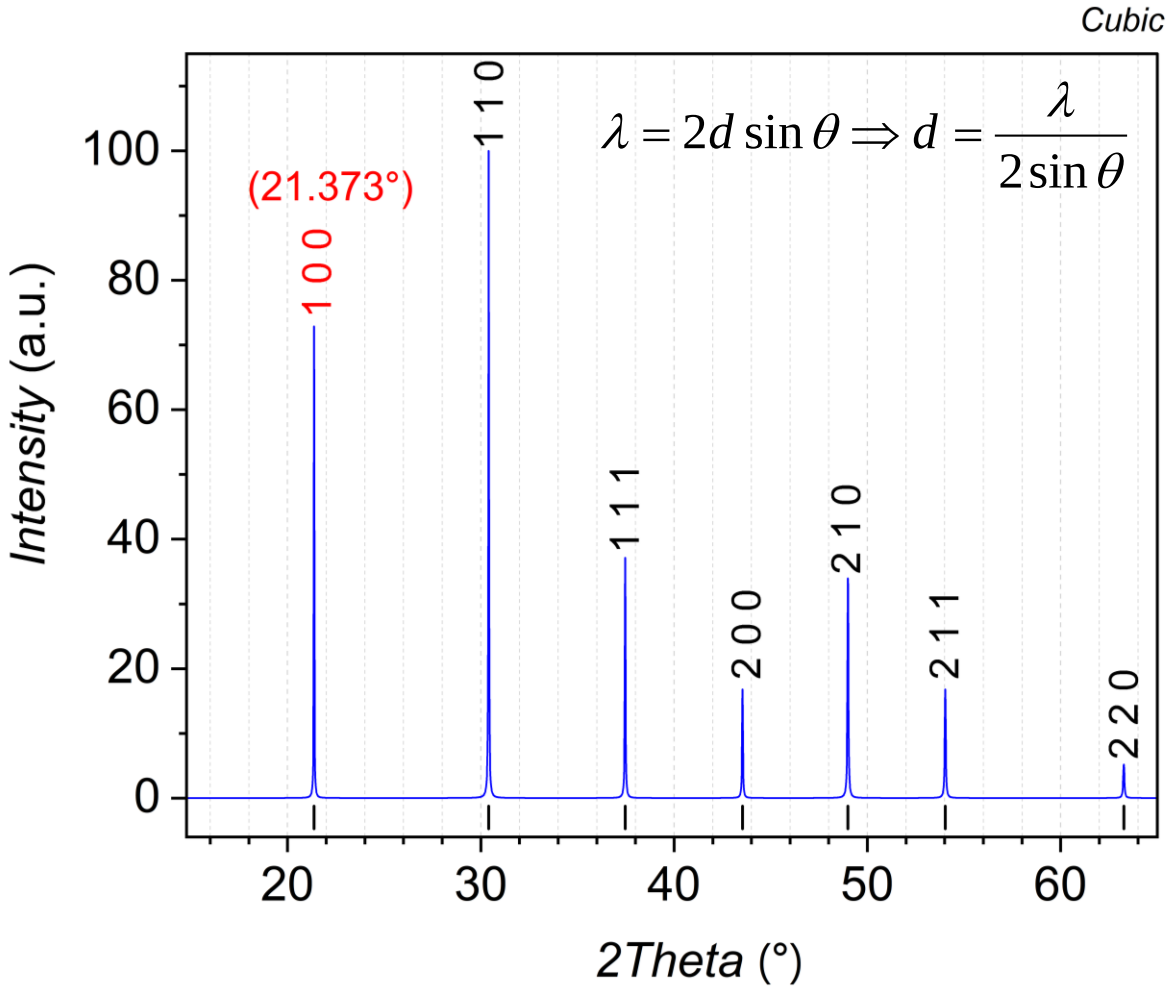


Indexed diffractogram of cubic LaB_6



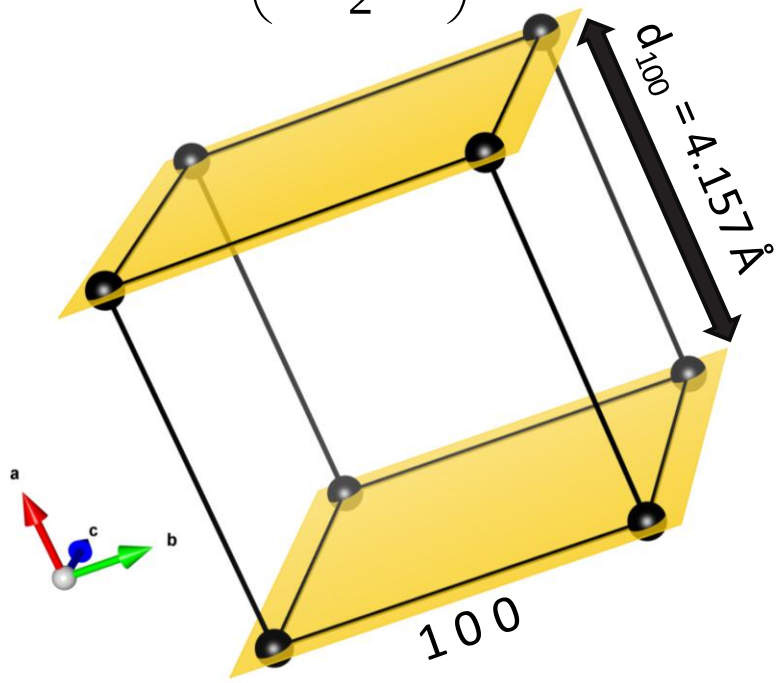
Primitive cubic unit cell of LaB_6

Unit cell parameters from PXRD (cubic system)



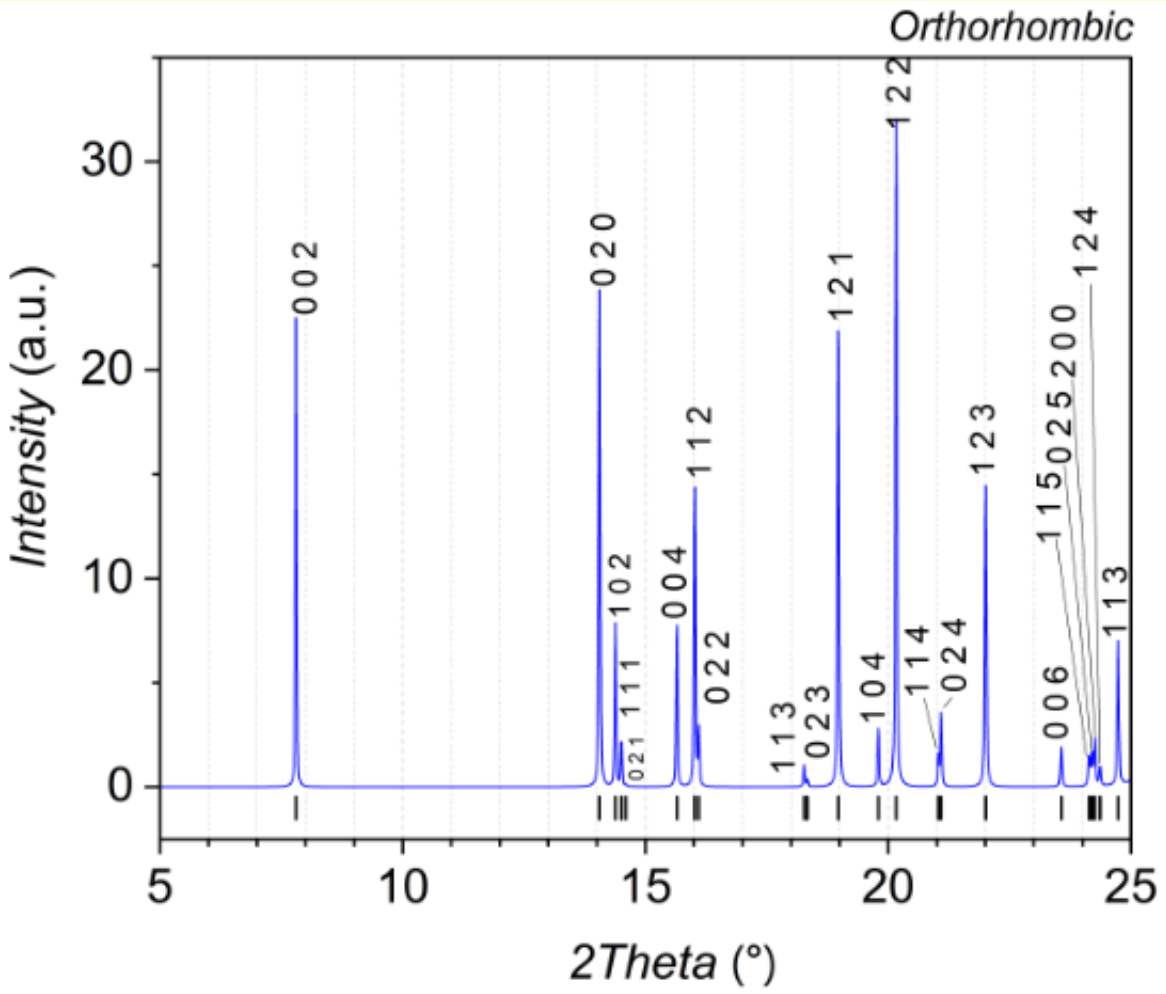
Indexed diffractogram of cubic LaB_6

$$a = d_{100} = \frac{1.5418 \text{ angstrom}}{2\sin\left(\frac{21.373°}{2}\right)} = 4.157 \text{ angstrom}$$

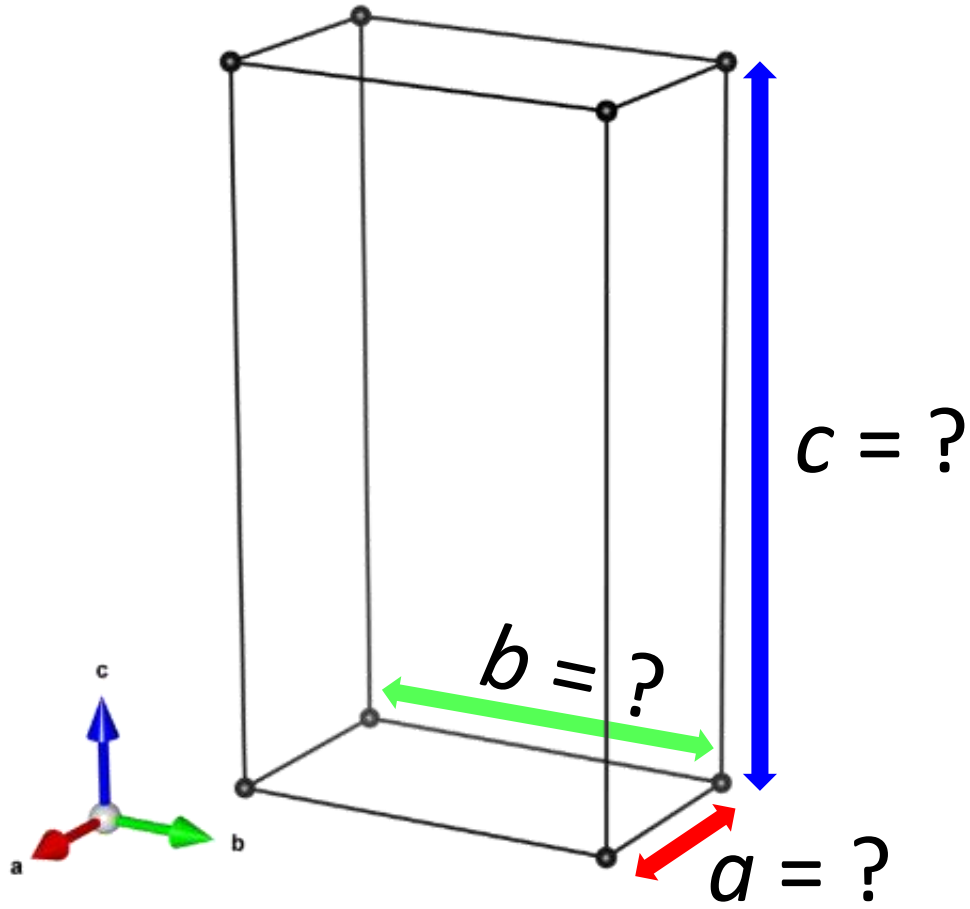


Primitive cubic unit cell of LaB_6

Unit cell parameters from PXRD (orthorhombic system)



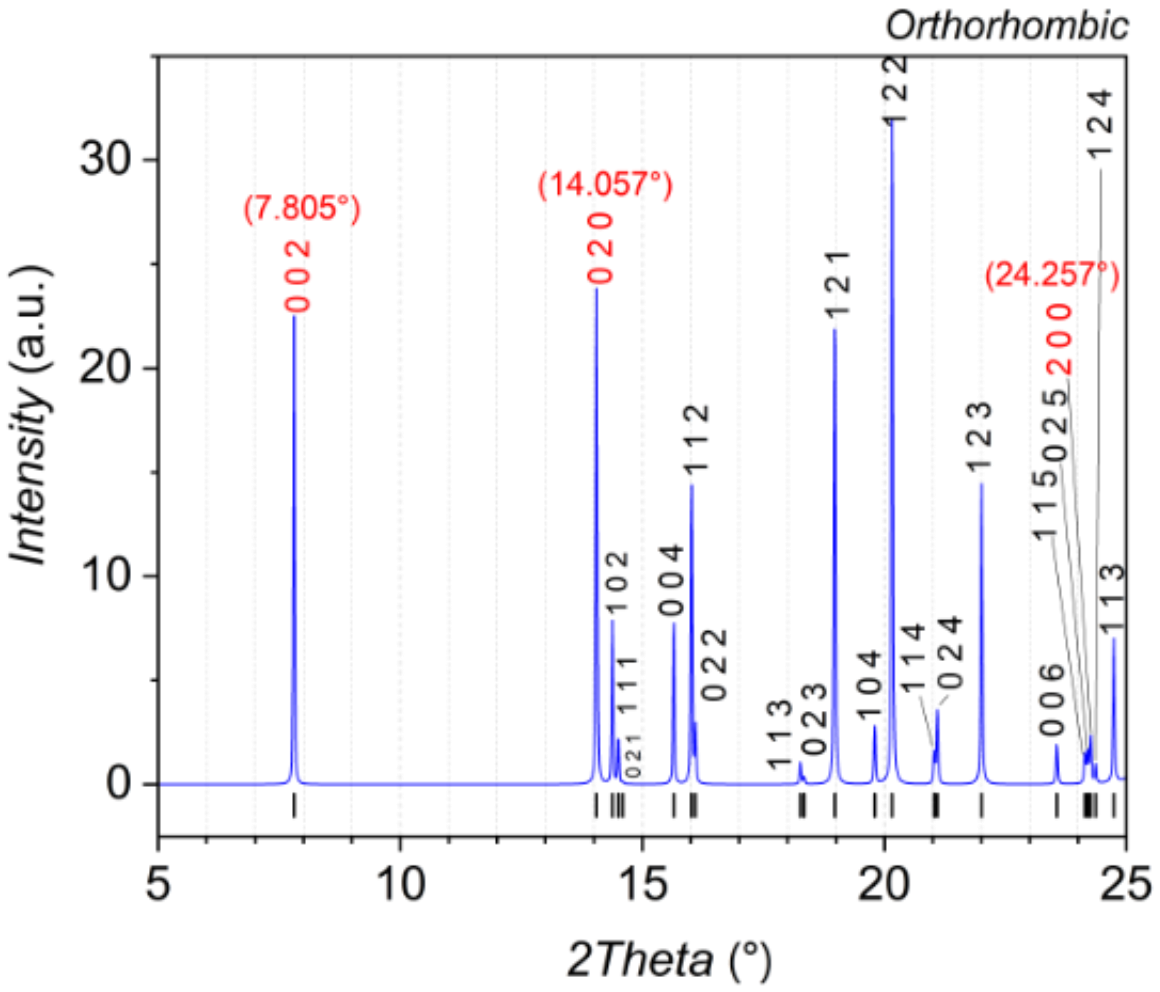
Experimental diffractogram of paracetamol trihydrate



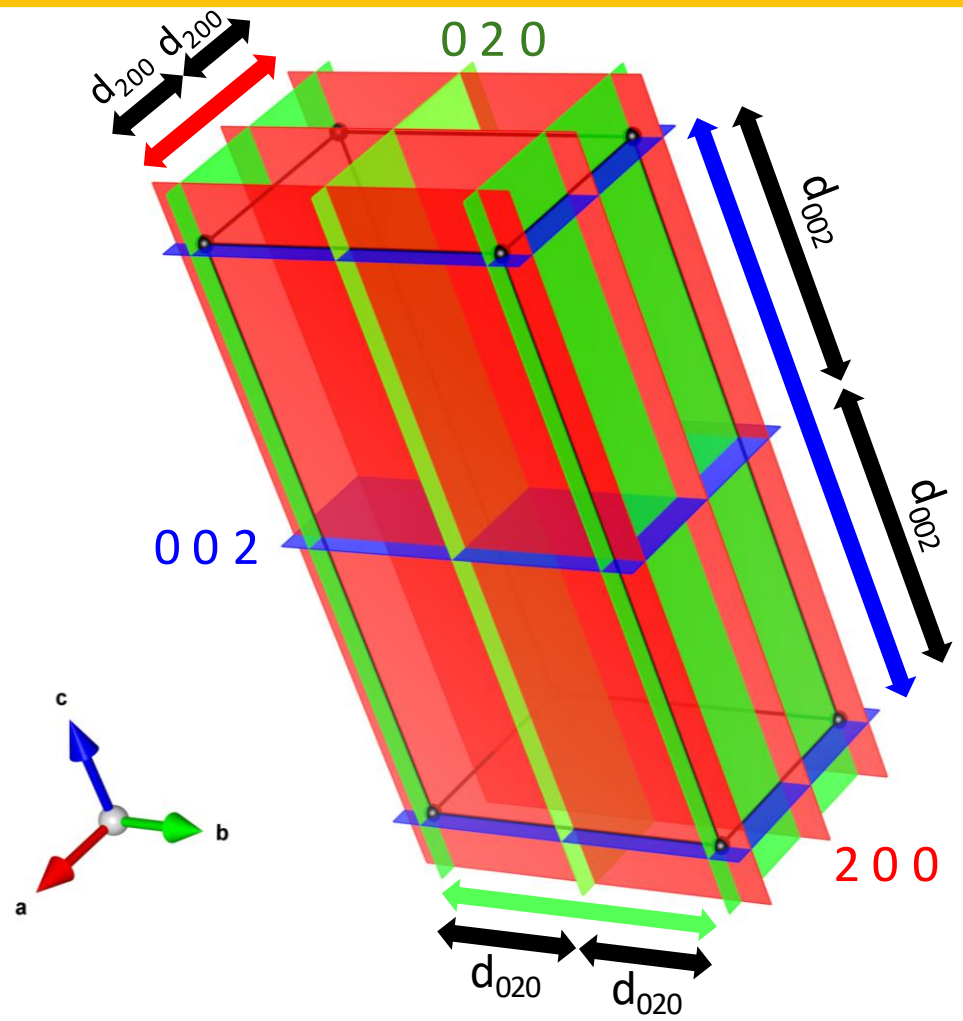
$a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$

Primitive orthorhombic unit cell of Paracetamol trihydrate

Unit cell parameters from PXRD (orthorhombic system)



Experimental diffractogram of paracetamol trihydrate



Primitive orthorhombic unit cell of paracetamol trihydrate

Unit cell parameters from PXRD (orthorhombic system)

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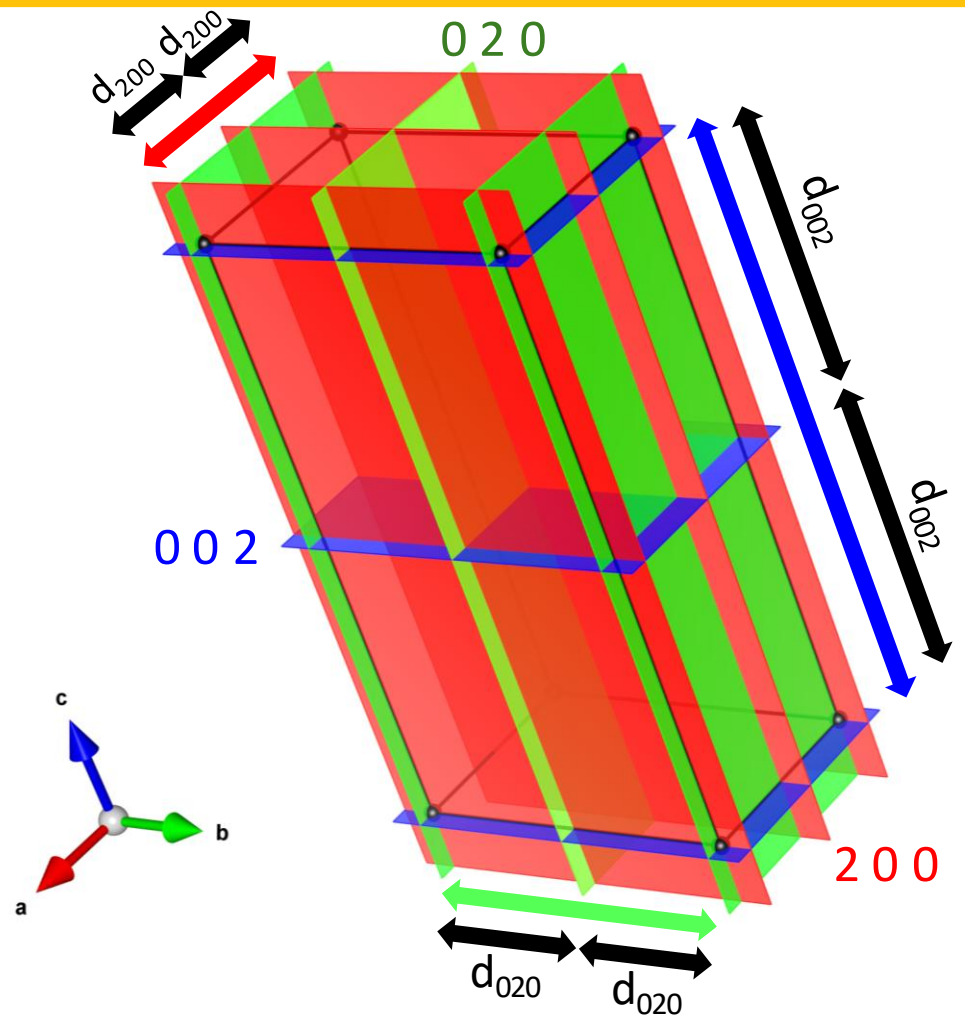
$$\lambda = 2d\sin\theta \Rightarrow d = \frac{\lambda}{2\sin\theta}$$

$$a = 2\times d_{200} = 2\times\frac{1.5418\ \text{angstrom}}{2\sin\left(\frac{24.257°}{2}\right)} = 7.338\ \text{angstrom}$$

$$b = 2\times d_{020} = 2\times\frac{1.5418\ \text{angstrom}}{2\sin\left(\frac{14.057°}{2}\right)} = 12.600\ \text{angstrom}$$

$$c = 2\times d_{002} = 2\times\frac{1.5418\ \text{angstrom}}{2\sin\left(\frac{7.805°}{2}\right)} = 22.654\ \text{angstrom}$$

$*\lambda(CuK\alpha) = 1.5418\ \text{angstrom}$

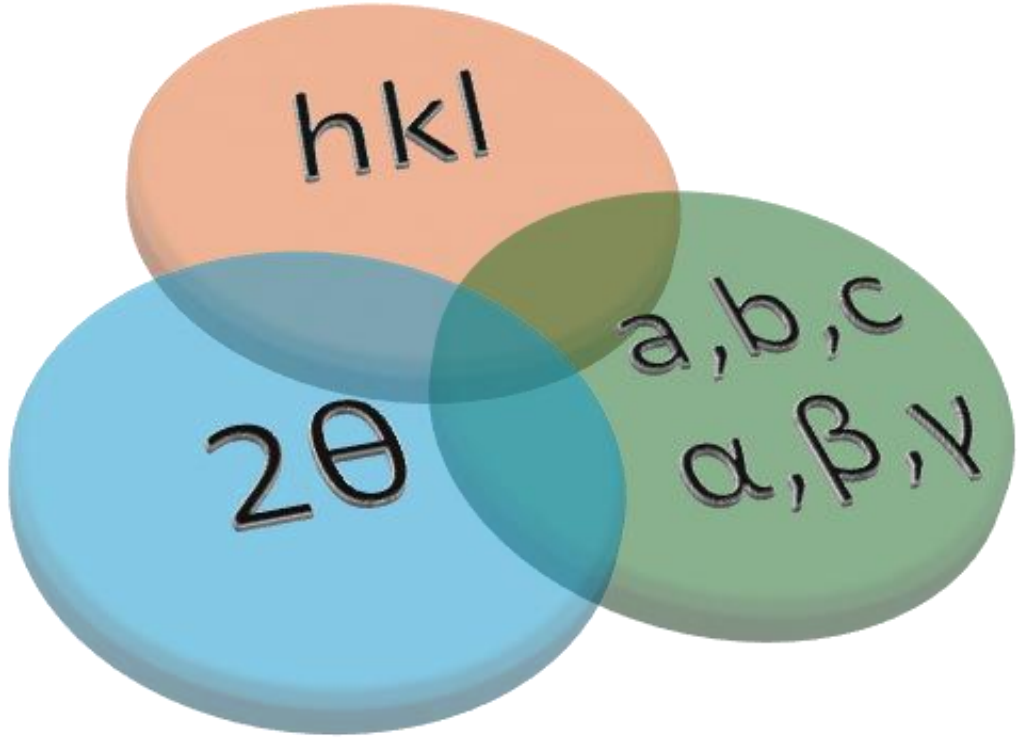


Primitive orthorhombic unit cell of Paracetamol trihydrate

Indexing principle

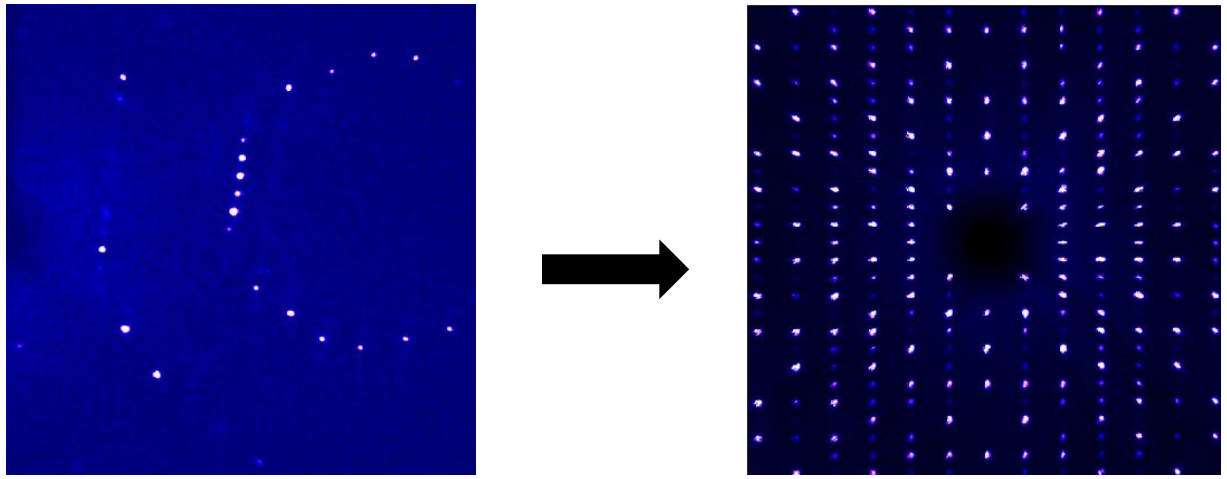
Indexing procedure requires a general equation that would bind together *hkl* indices, positions of reflections (2θ or *d*) and unit cell metrics.

This equation can be derived by considering reciprocal lattice.



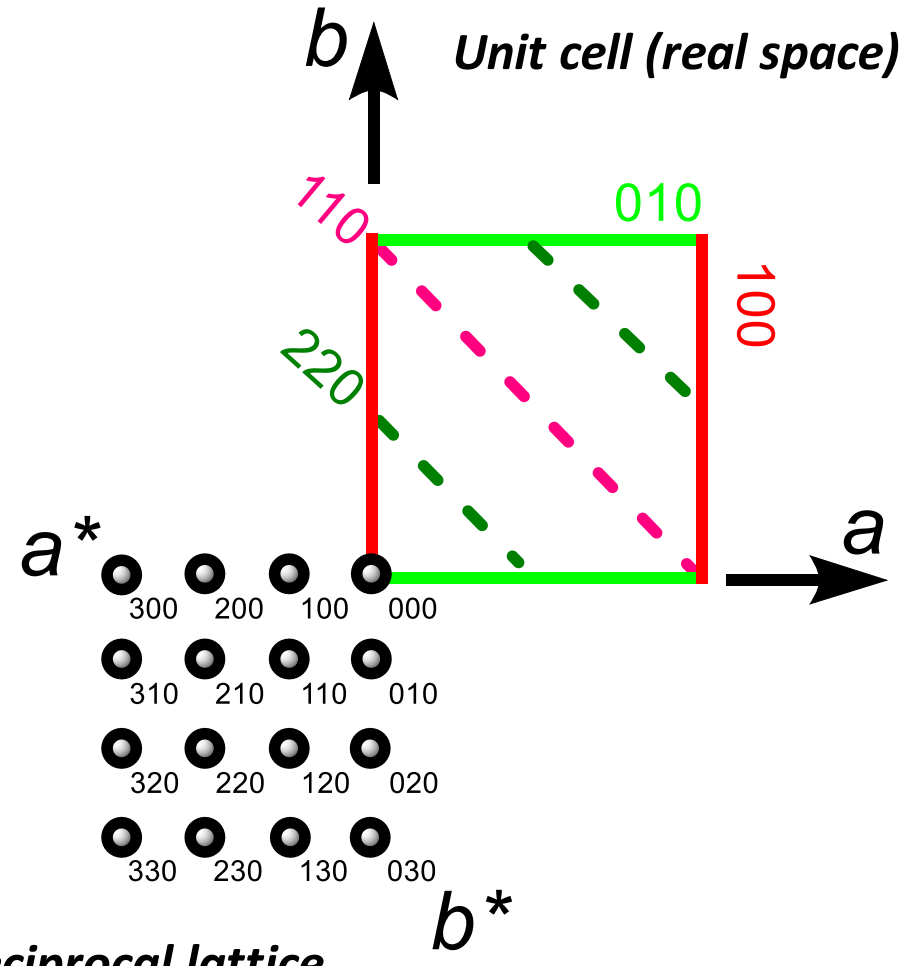
Reciprocal lattice – a 3-dimensional map describing positions of diffraction reflections.

Reciprocal lattice can be reconstructed from SC-XRD experiment once all collected frames are summed up.



SC-XRD frame illustrating a slice of reciprocal space

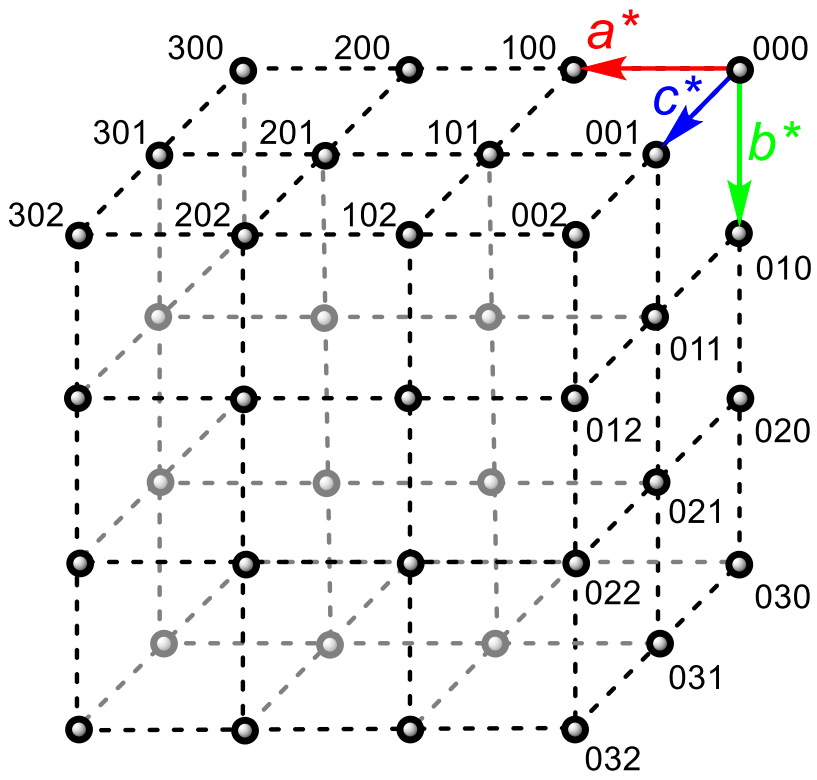
Reciprocal lattice synthesized from multiple SC-XRD frames



Reciprocal lattice

Any point of the reciprocal lattice can be described with a ***vector equation***:

$$\vec{d}^{*} = h\vec{a}^{*} + k\vec{b}^{*} + l\vec{c}^{*}$$



Magnitude of d* can be expressed as a dot product of d* with itself:

$$\left(d^{*}\right)^{2} = \vec{d}^{*} \cdot \vec{d}^{*} = \left(h\vec{a}^{*} + k\vec{b}^{*} + l\vec{c}^{*}\right) \cdot \left(h\vec{a}^{*} + k\vec{b}^{*} + l\vec{c}^{*}\right)$$

$$\left(d^*\right)^2 = h^2\left(a^*\right)^2 + k^2\left(b^*\right)^2 + l^2\left(c^*\right)^2 + 2hka^*b^*\cos\gamma^* + 2klb^*c^*\cos\alpha^* + 2hla^*c^*\cos\beta^*$$

Hiding cell metrics and coefficients under A-F terms the indexing equation can be obtained:

$$\frac{1}{d^2} = \left(d^*\right)^2 = Ah^2 + Bk^2 + Cl^2 + Dhk + Ekl + Fhl$$

Indexing equation for different crystal classes

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$$\frac{1}{d^2} = \left(d^*\right)^2 = Ah^2 + Bk^2 + Cl^2 + Dhk + Ekl + Fhl$$

Various crystal systems apply geometrical constraints that would modify the equation:

Crystal class	Geometrical constraints	Indexing equation in real space
Cubic	$a = b = c$; $\alpha = \beta = \gamma = 90°$	$1/d^2 = (h^2 + k^2 + l^2) / a^2$
Tetragonal	$a = b \neq c$; $\alpha = \beta = \gamma = 90°$	$1/d^2 = (h^2 + k^2) / a^2 + l^2/c^2$
Orthorhombic	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$	$1/d^2 = h^2 / a^2 + k^2 / b^2 + l^2 / c^2$
Hexagonal	$a = b \neq c$; $\alpha = \beta = 90°$; $\gamma = 120°$	$1/d^2 = 4(h^2 + hk + k^2) / 3a^2 + l^2 / c^2$
Trigonal	$a = b = c$; $\alpha = \beta = \gamma \neq 90$	Very complicated
Monoclinic	$a \neq b \neq c$; $\alpha = \gamma = 90°$; $\beta \neq 90°$	Very complicated
Triclinic	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma$	Very complicated

Manual and Auto- indexing

***Indexing* –**procedure for generation of *hkl* triplets and their assignment to the diffraction peaks resulting in a determination of a unit cell.

Manual indexing – manual assignment of hkl triples to diffraction reflections.

- **Refinement of analogue**
- **Pattern matching**

Autoindexing – indexes are assigned and swapped by the software automatically to solve the indexing equation.

- **Trial methods**
- **Dichotomy methods**
- **Zone indexing**
- **Monte-Carlo indexing**

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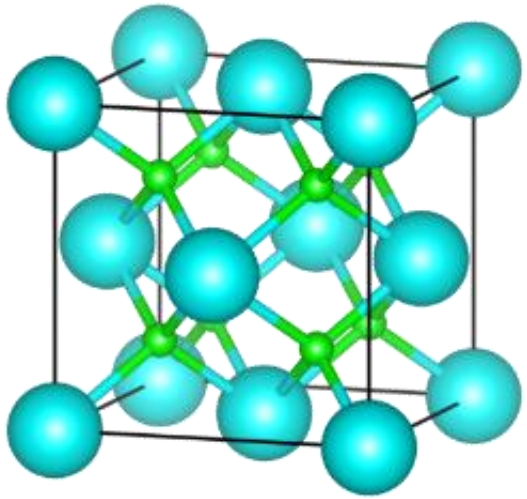
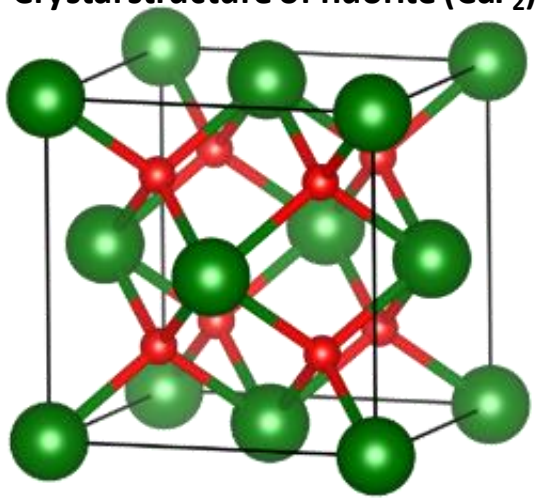
Inorganic lattices (alloys, salts, oxides) have very distinctive crystal structure with only few crystallographic positions.

Crystal structure of the sample can be described through an ***isostructural analogue***

Calcium fluoride (fluorite) *Fm*-3*m*				**Uranium oxide *Fm*-3*m***			
Atom	**x**	**y**	**z**	**Atom**	**x**	**y**	**z**
Ca	0	0	0	U	0	0	0
F	0.25	0.25	0.25	O	0.25	0.25	0.25



Crystal structure of fluorite (CaF_2)



Crystal structure of uranium oxide (UO_2)

Manual indexing: LS-refinement of the analogue

Approach

1. Identify the analogue
2. Make *hkl* – 2ϑ list for individual reflections starting from low angle (10-20 reflections based on symmetry)
3. Use LS-cell refinement to adjust unit cell parameters of the analogue to the diffractogram from your sample

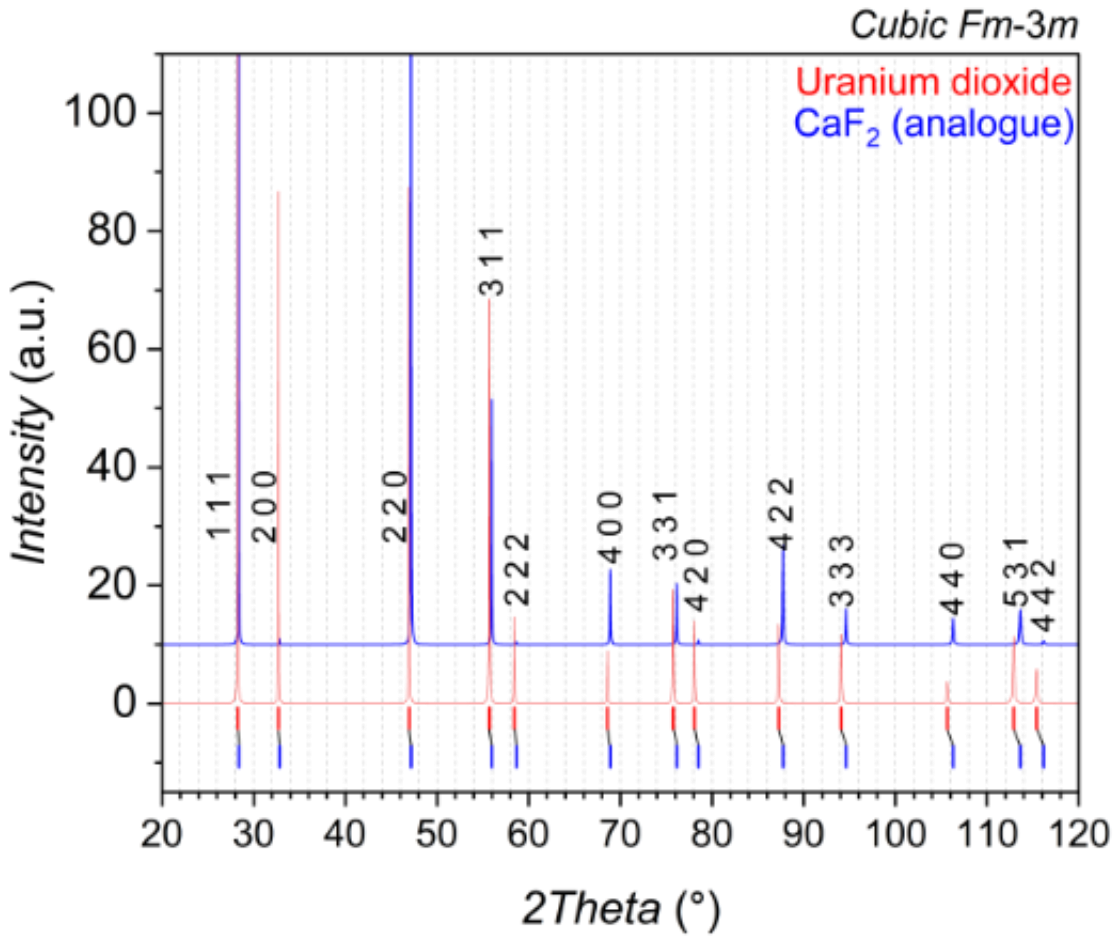
Least-squares method:

$$S = \left(\sum_{n=1}^{N} w_n \left(2\theta_{obs} - 2\theta_{calc} \right)^2 \right) \rightarrow \min$$

$$\lambda = 2d \sin\theta \Rightarrow 2\theta_{calc} = 2 \arcsin\left(\frac{\lambda}{2} \cdot \frac{1}{d} \right)$$

$$\frac{1}{d} = \sqrt{Ah^2 + Bk^2 + Cl^2 + Dhk + Ekl + Fhl}$$

n – reflection number
$\boldsymbol{w_n}$ – weight ($1/\sigma^2$)
$\boldsymbol{2\vartheta_{obs}}$ – peak position from experiment
$\boldsymbol{2\vartheta_{calc}}$ – peak position calculated from cell parameters



Diffractograms of UO_2 and its analogue - fluorite

Manual indexing: LS-refinement of the analogue

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Advantages

+ Crystal class is known
+ Indices are already provided
+ Fast and reliable
+ LS-refinement generates *esd*

Disadvantages

– Structural analogue is required
– Misassignment of indices due to large deviations in cell dimensions
– Manual peak picking limits accuracy of cell parameters

Bottom line

- LS-refinement is commonly used in solid state inorganic chemistry when the structural type is known;
- Unique shape of small organic molecules and low packing symmetry prevent identification of structural analogue

Manual indexing: Pattern matching (cubic symmetry)

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Indexing equation

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

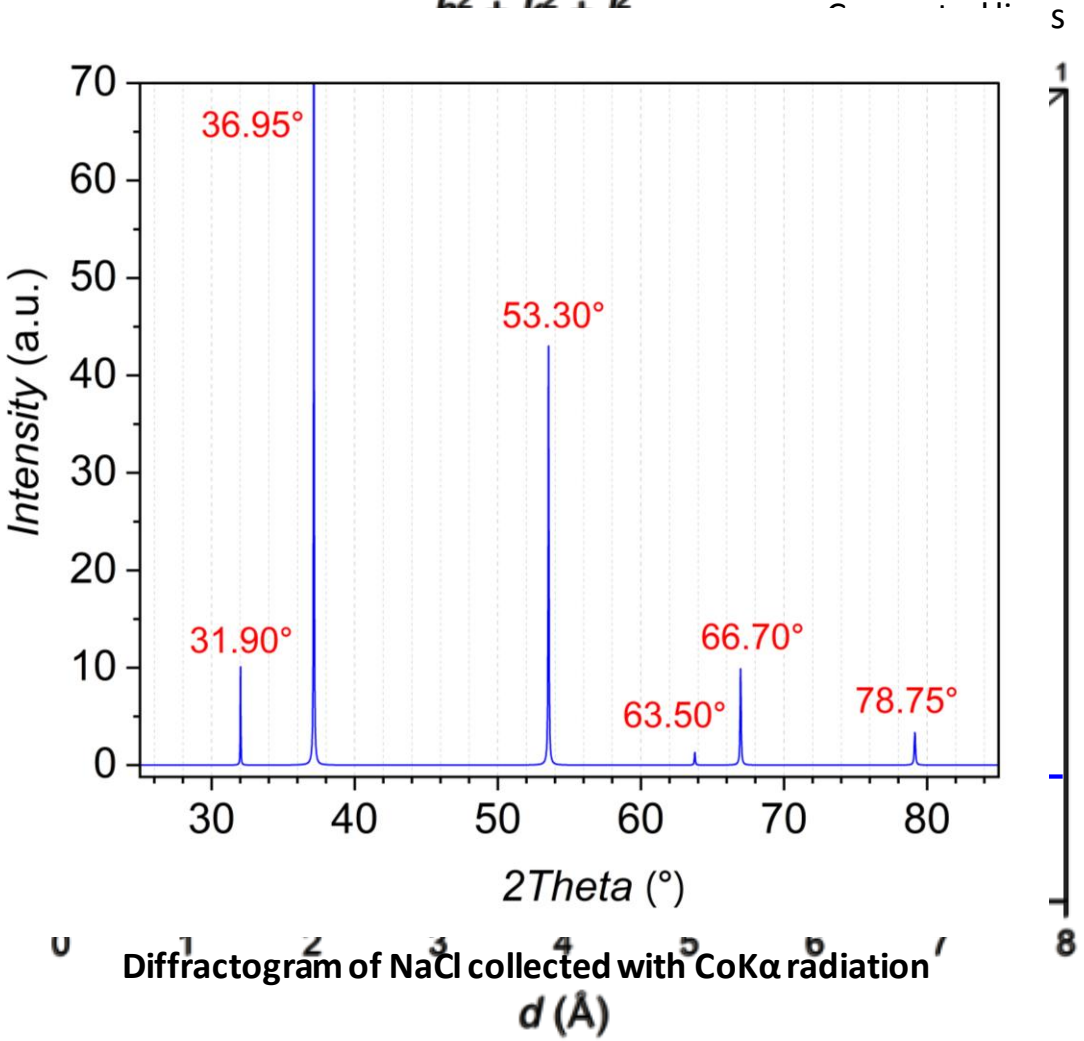
$$a = d \cdot \sqrt{h^2 + k^2 + l^2}$$

2ϑ (°)	d (Å)
31.90	3.258
36.95	2.826
53.30	1.996
63.50	1.702
66.70	1.629
78.75	1.411

hkl	$h^2+k^2+l^2$
100	1
110	2
111	3
200	4
210	5
211	6
220	8
300	9
310	10
311	11
222	12
320	13
321	14
400	16

Approach

1. Generate a list of unique *hkl* in the ascending order of the sum ($h^2+k^2+l^2$);
2. Plot $a = f(d)$ for every ($h^2+k^2+l^2$);
3. Calculate d-spacing from peak positions;
4. Add reflection positions to the graph;
5. Move along *a* axis until all reflections are found on one line.



Diffractogram of NaCl collected with CoKα radiation

Manual indexing: Pattern matching (cubic symmetry)

PROTO X-RAY DIFFRACTION

Indexing equation

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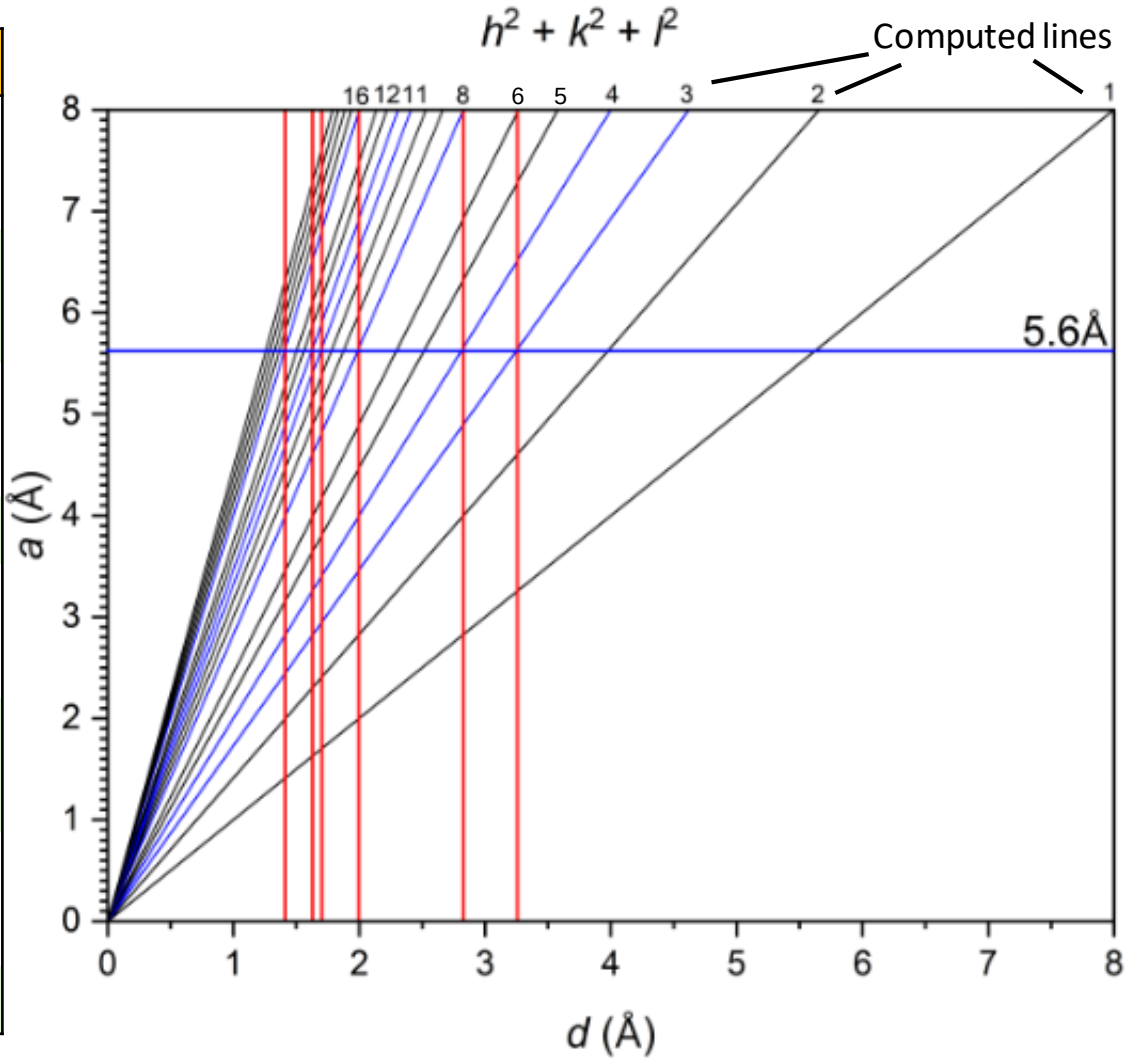

Autoindexing: Trial methods (*N-TREOR90*)

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Trial methods is an automated approach for indexing via pattern matching.

$$Q = \frac{10^4}{d^2} = Ah^2 + Bk^2 + Cl^2 + Dhk + Ekl + Fhl$$

Select crystal class (*n* metric tensors)	Assign first ***n*** peaks with generated *hkl*	Solve with respect to *A, B, C*	Calculate Q_{hkl} for all *hkl* permutations
Orthorhombic *a ≠ b ≠ c; α = β = γ = 90°* ***n* = 3**	$Ah_1^2 + Bk_1^2 + Cl_1^2 = Q_1$ $Ah_2^2 + Bk_2^2 + Cl_2^2 = Q_2$ $Ah_3^2 + Bk_3^2 + Cl_3^2 = Q_3$	*Is solution physical A, B, C > 0?*	*Do the computed peaks match with experimental?*

*$Q = \frac{10^4}{d^2} = \frac{4 \cdot 10^4 \sin^2\theta}{\lambda^2}$ - from Bragg's law

Autoindexing: Trial methods (*N-TREOR90*)

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Advantages

+ Trial methods are exhaustive

Disadvantages

– Sample must be pure (no spurious lines)

– Time-consuming for low symmetry

Bottom line

- Trial method is efficient for high symmetry cases
- Suspicious peaks (odd peak width, shape, low intensity) should be examined carefully

$$Permutations = \frac{N!}{(N-n)!}$$

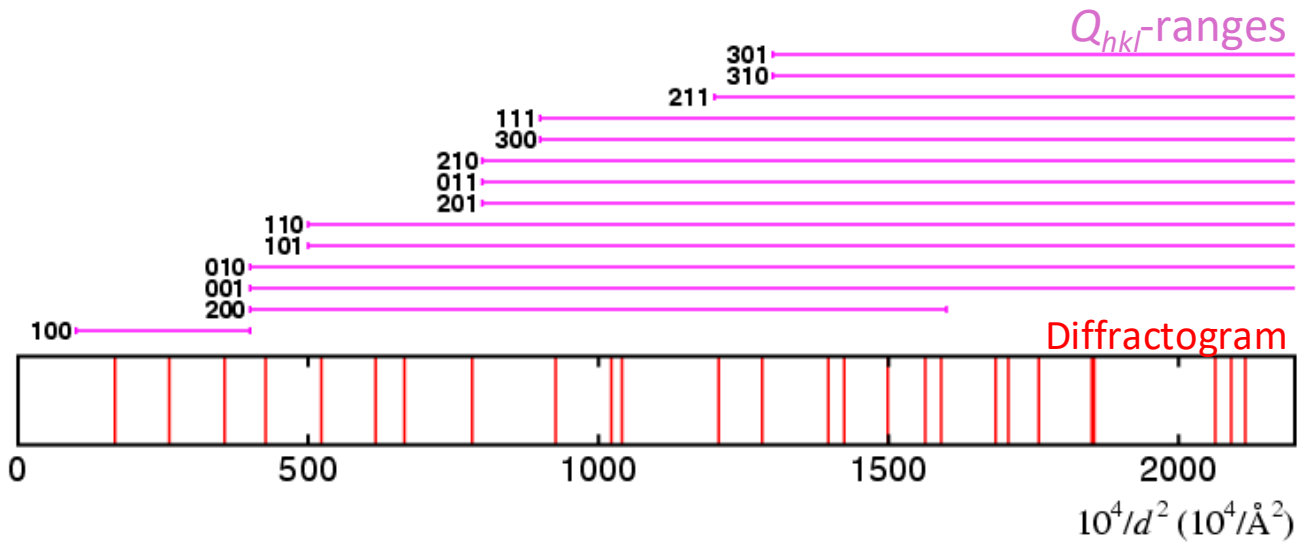
N – number of computer generated *hkl*
n – number of unknown cell metrics

Number of permutations for 20 generated *hkl triplets*

Symmetry	Permutations
Cubic	20
Trigonal	380
Tetragonal	380
Orthorhombic	6,840
Monoclinic	116,280
Triclinic	2,790,720

Dichotomy methods are based on the variation of cell parameters within finite ranges, which are progressively reduced via dichotomy algorithm until the solution is found.

$$\Delta Q_{hkl} = \left| Q_{\min} - Q_{\max} \right| = \left(A_{\max} - A_{\min} \right) h^2 + \left(B_{\max} - B_{\min} \right) k^2 + \left(C_{\max} - C_{\min} \right) l^2 + \ldots$$



Q_{hkl} ranges calculated for orthorhombic unit cell with dimensions 5.0 < *a* <10.0 Å, 1.0 < *b* < 5.0 Å, 1.0 < *c* < 5.0 Å

http://pd.chem.ucl.ac.uk/pdnn/unit2/dichot.htm

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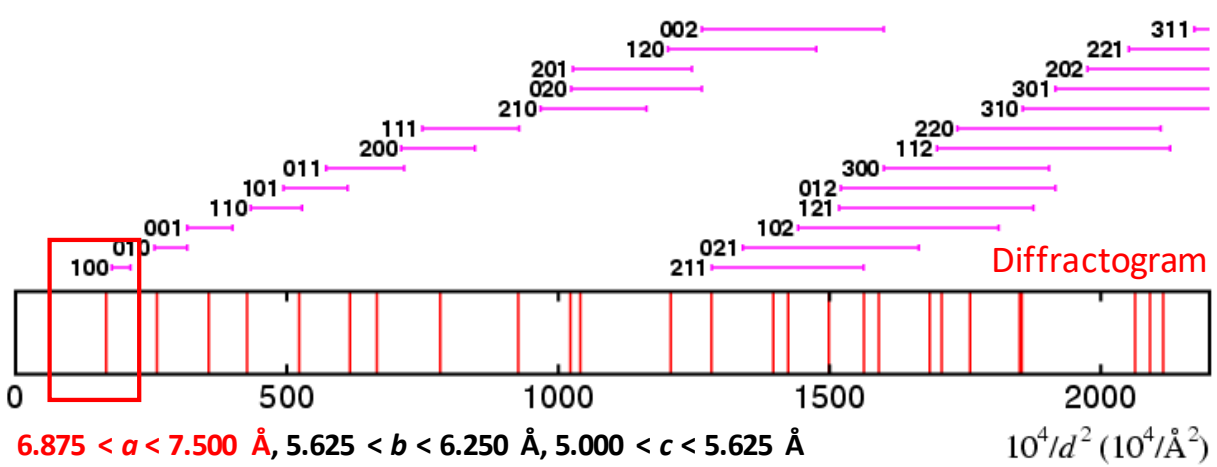
6.875 < *a* < 8.125 Å

Left part

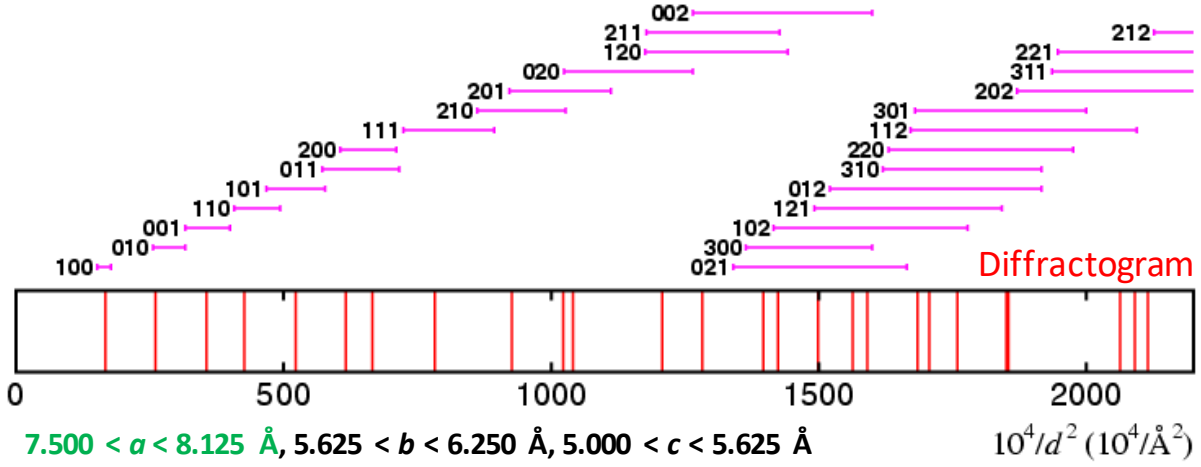
6.875 < *a* < 7.500 Å



- First diffraction peak is not indexed by a single Q_{hkl} range!
- Left part is therefore **discarded!**

Right part

7.500 < *a* < 8.125 Å



- Every diffraction peak is still covered by at least one Q_{hkl} range. Right part is **accepted!**
- Use for another round of dichotomy until every peak is covered by only one Q range

http://pd.chem.ucl.ac.uk/pdnn/unit2/dichot.htm

Advantages

+ Works well for cubic, trigonal, tetragonal and orthorhombic systems
+ Not as dependent on accurate low angle data as *TREOR* (trial methods) or *ITO* (zone indexing)

Disadvantages

– Very slow for monoclinic class

– Requires restrictions to index triclinic unit cells

Bottom line

- Processing time can be reduced if cell metric ranges are chosen carefully
- Do not use more than 25 lines, as it may prevent finding any solution at all

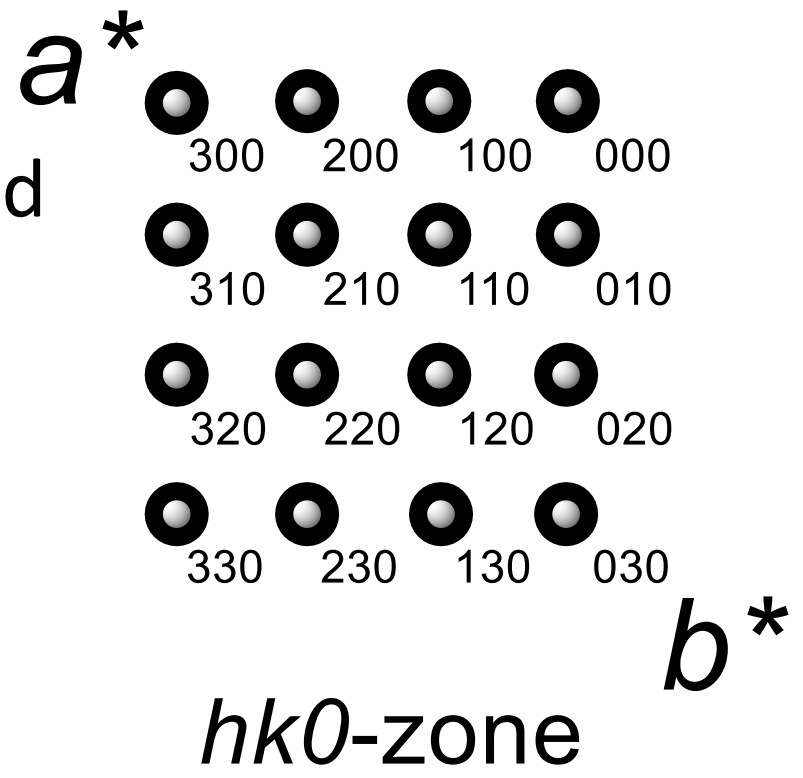
Central zone **–** plane in reciprocal space passing through the origin (*hk0*, *h0l*, *0kl*)

Peaks lying in the central zones can be described with the following *Q*s:

$$Q_{hk0} = Ah^2 + Bk^2 + Dhk$$

$$Q_{h0l} = Ah^2 + Cl^2 + Fhl$$

$$Q_{0kl} = Bk^2 + Cl^2 + Ekl$$



hk0-zone

For ***hk0*** zone the following equations are valid:

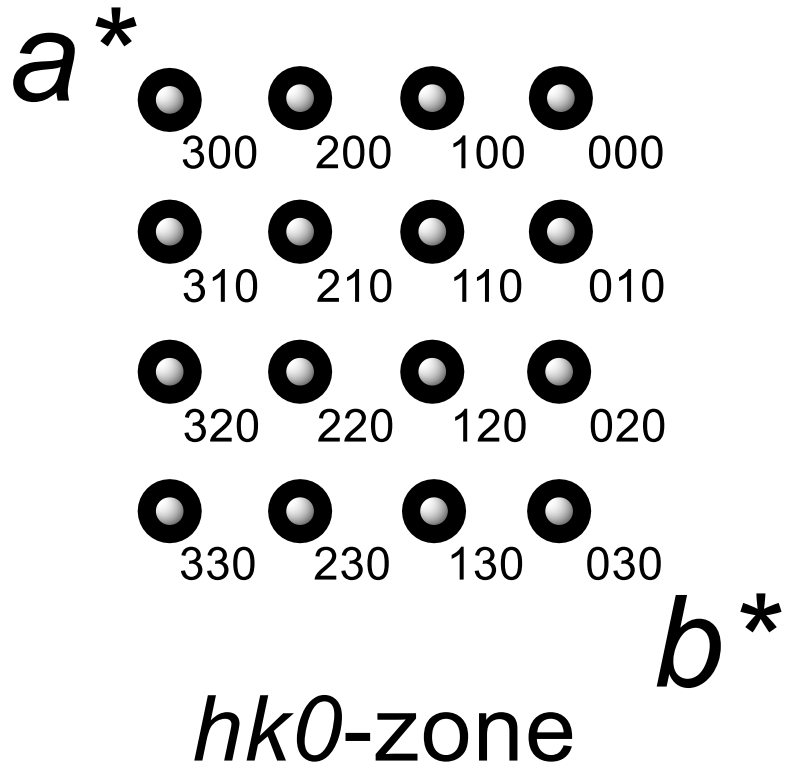
$$Q_{hk0} = Ah^2 + Bk^2 + Dhk$$

$$Q_{h00} = Ah^2; Q_{0k0} = Bl^2$$

Therefore:

$$Q_{hk0} = Q_{h00} + Q_{0k0} + Dhk$$

$$D = \frac{Q_{hk0} - Q_{h00} - Q_{0k0}}{hk}$$



hk0-zone

Figures of Merit

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Figure of Merit – a criterion for the physical plausibility of indexing

❖ **De Wolff M_{20} (1968)**

$$M_{20} = \frac{Q_{20}}{2 \cdot \langle Q \rangle \cdot N_{20}}$$

Q of 20th observed line

Mean discrepancy between Q_{obs} and Q_{calc}

Number of generated hkl with different $Q \leq Q_{20}$

Synchrotron data:
$M_{20} \approx 500 – 700$
Laboratory data:
$M_{20} \approx 20 – 60$

- ***M_{20}* < 4.0** – solution is "worthless" and should be discarded;
- ***M_{20}* > 10.0** – solution is physically reliable if the number of unindexed lines is no more than two
- ***M_{20}*** increases systematically with symmetry

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Figure of Merit – a criterion for the physical plausibility of indexing

❖ **Smyth and Snyder *F* index (1979)**

Number of observed lines

$$F_N = \frac{1}{\langle \Delta 2\theta \rangle} \cdot \frac{N}{N(\theta_g)}$$

Mean discrepancy between $2\vartheta_{obs}$ *and* $2\vartheta_{calc}$

Number of calculated Q up to ϑ_g

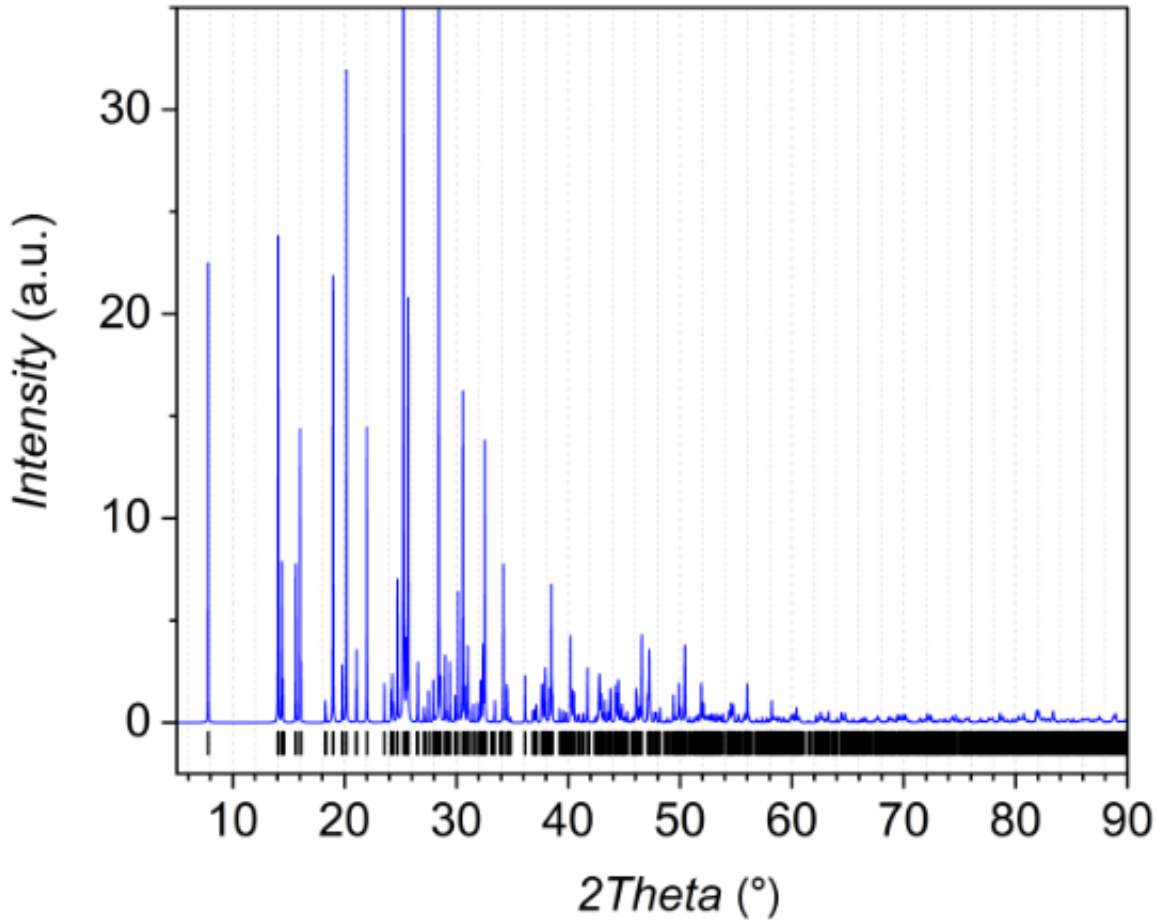
- F_N index is superior for ranking solutions than M_{20}
- F_N index does not estimate physical plausibility of the cell very well

Experimental Consideration

PROTO X-RAY DIFFRACTION

- Greater number of diffraction lines increases the chance of successful indexing
- Low angle peaks are well separated and more important for indexing

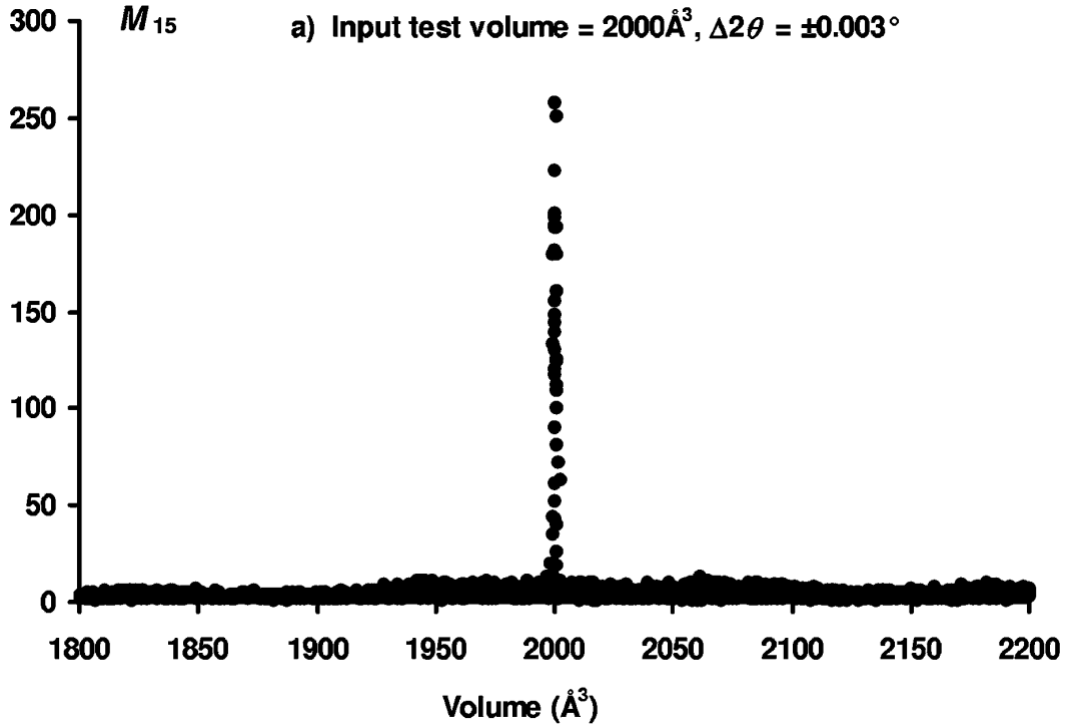
Crystal class	Success rate (%)	
	10 diffraction peaks	20 diffraction peaks
Orthorhombic	75	98.5
Monoclinic	60	91
Triclinic	30	88

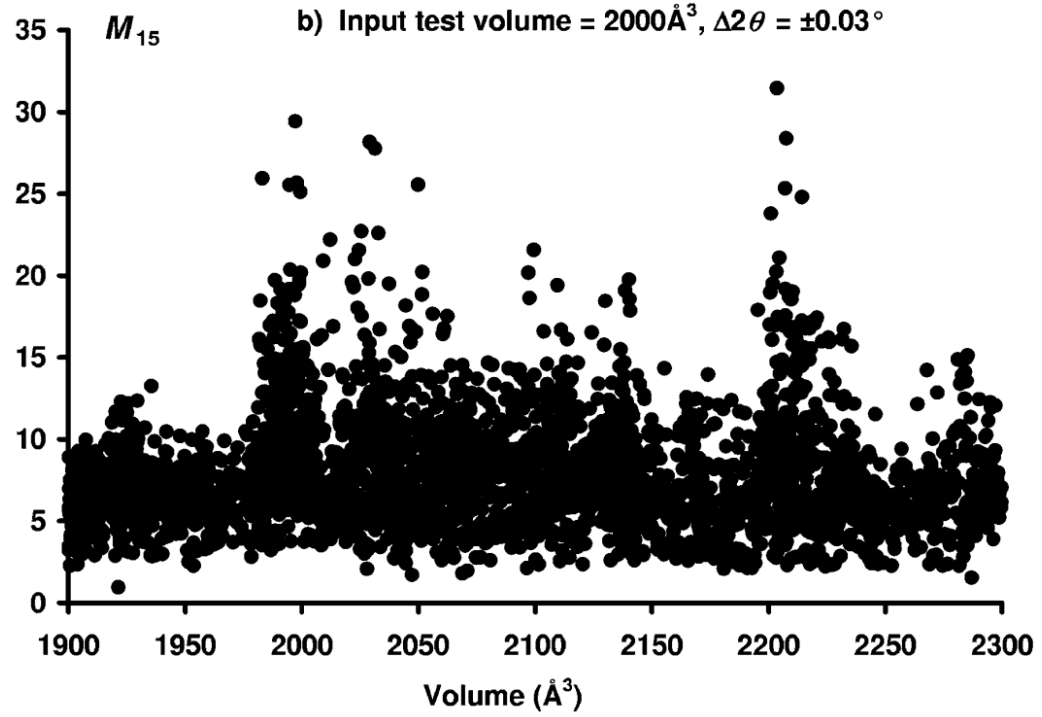


Diffractogram of paracetamol trihydrate

Coehlo A. A. *J. Appl. Cryst.* **2003**, 36, 89-95.

- Random error is mainly caused by manual peak peaking
- Peak picking via profile modelling minimizes random errors associated with peak positions





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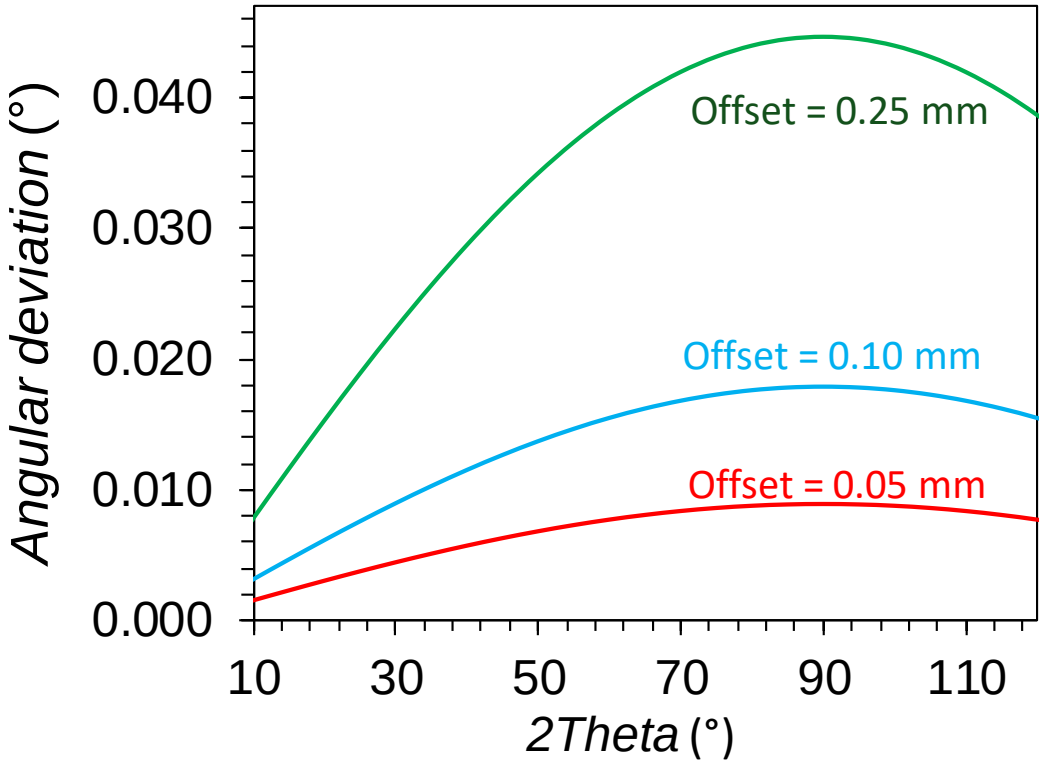
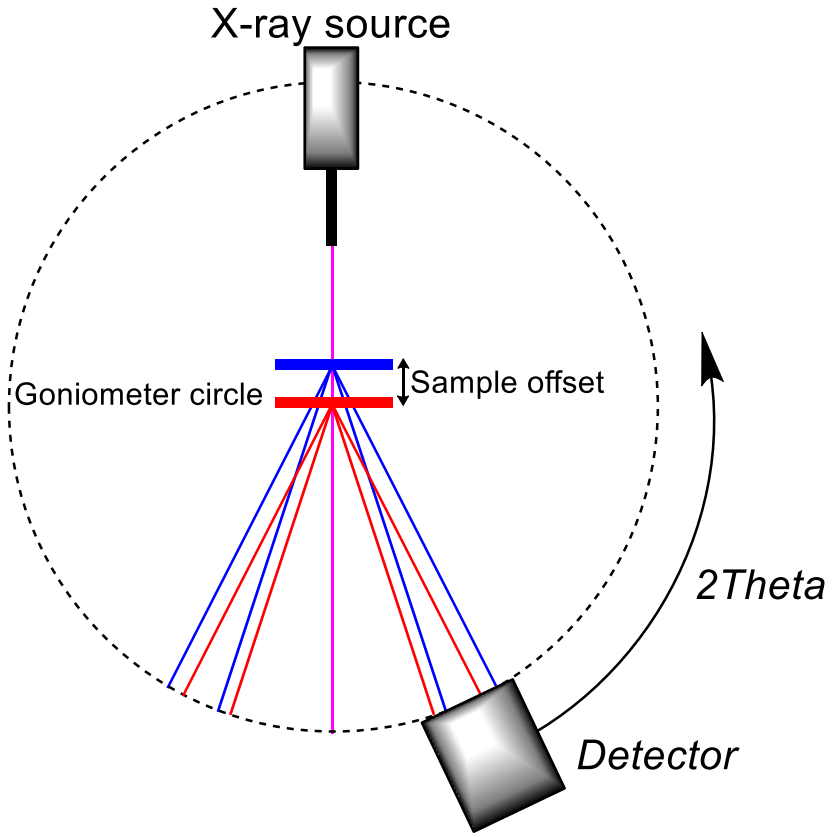
- Sample height displacement results in systematic errors associated with peak positions
- Systematic error of 0.02° can be “disastrous” for determination of unit cell from powder diffraction



Angular deviations as function of diffraction angle



Space Group Determination

Space group determination: Workflow

Space group determination via powder diffraction is based on the geometrical determination of the crystal class and analysis of systematic absences to reveal translational symmetry

- Higher angular accuracy of powder diffractometers allows for a clear distinction between crystal systems, unlike in the case of single crystal diffraction
- Laue classes are indistinguishable via powder diffraction (problematic for cubic, tetragonal, hexagonal and trigonal)
- $|E^2-1|$ test is problematic due to an insufficient number of individual reflections

Space group determination: Workflow

PROTO
X-RAY DIFFRACTION

1. Determine crystal class
2. Define centring symbol
3. Check for glide planes
4. Check for screw axes
5. LeBail integration

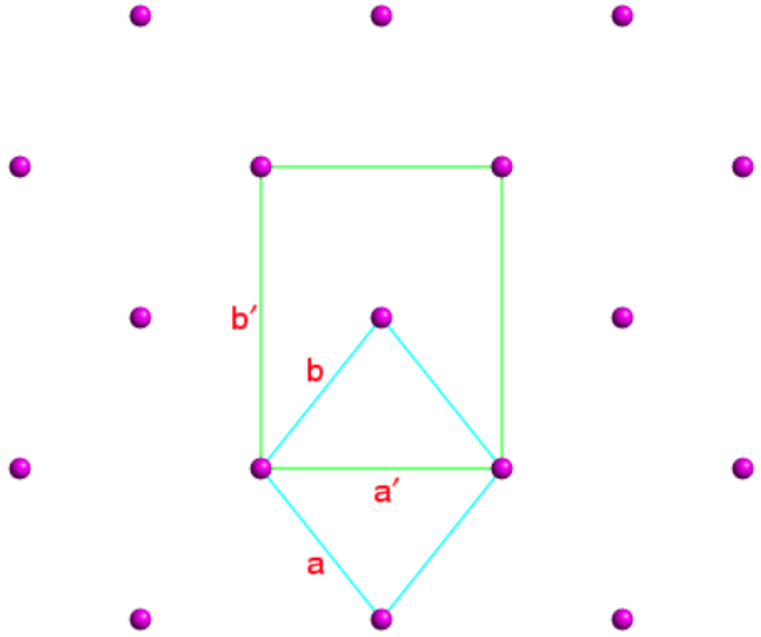
Space group determination: Workflow

PROTO X-RAY DIFFRACTION

Unit-Cell Geometry	Inferred Crystal System(s)	No. of Space Groups
$a \neq b \neq c$ and $\alpha \neq \beta \neq$ & gamma; & ne; 90°	Triclinic	2
$a \neq b \neq c$ and $\alpha = \gamma = 90°$ and $\beta \neq 90°$	Monoclinic	13
$a \neq b \neq c$ and $\alpha = \beta = \gamma = 90°$	Orthorhombic	59
$a = b \neq c$ and $\alpha = \beta = \gamma = 90°$	Tetragonal	68
$a = b = c$ and $\alpha = \beta = \gamma \neq 90°$	Trigonal (Rhombohedral)	7
$a = b \neq c$ and $\alpha = \beta = 90°$ and $\gamma = 120°$	Trigonal or Hexagonal	45
$a = b = c$ and $\alpha = \beta = \gamma = 90°$	Cubic	36

Space group determination: Centering

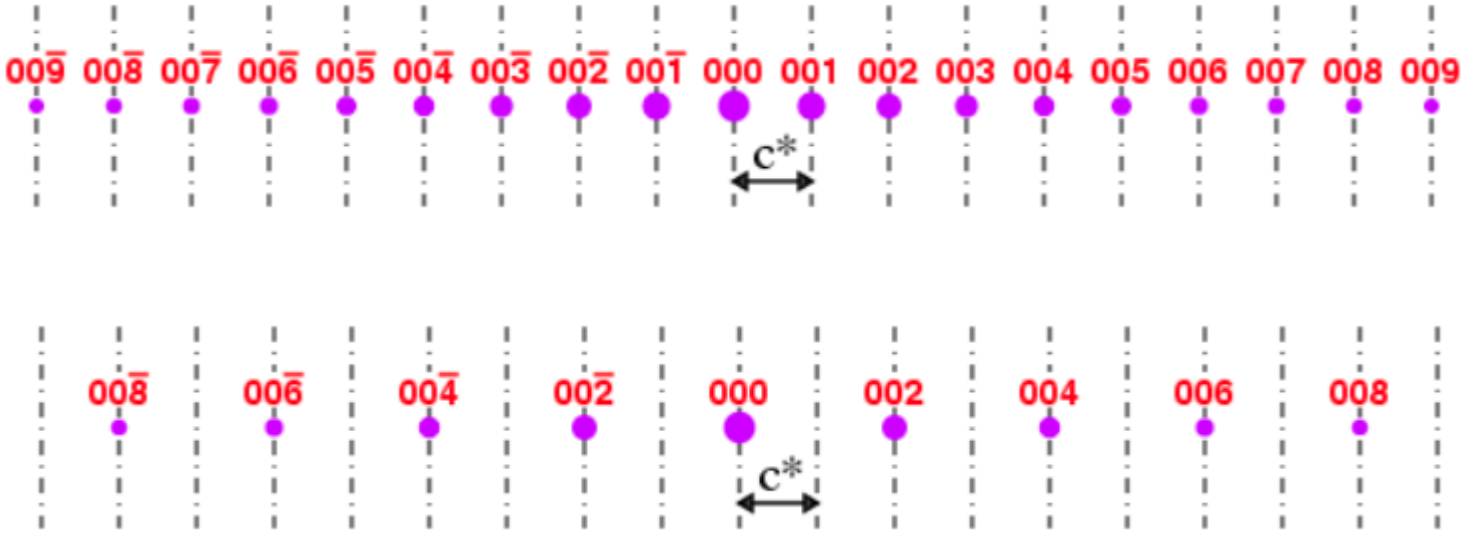
Lattice Centring	Symmetry Operator(s)	Reflection Condition
P	-	None
A	*x*,1/2+*y*,1/2+*z*	*hkl*: *k* + *l* = 2*n*
B	1/2+*x*,*y*,1/2+*z*	*hkl*: *h* + *l* = 2*n*
C	1/2+*x*,1/2+*y*,*z*	*hkl*: *h* + *k* = 2*n*
F	*x*,1/2+*y*,1/2+*z*; 1/2+*x*,*y*,1/2+*z*; 1/2+*x*,1/2+*y*,*z*	*hkl*: *k* + *l*, *h* + *l*, *h* + *k* = 2*n*
I	1/2+*x*,1/2+*y*,1/2+*z*	*hkl*: *h* + *k* + *l* = 2*n*
R	1/3+*x*,2/3+*y*,2/3+*z*; 2/3+*x*,1/3+*y*,1/3+*z*	*hkl*: -*h* + *k* + *l* = 3*n*



Space group determination: Screw axis

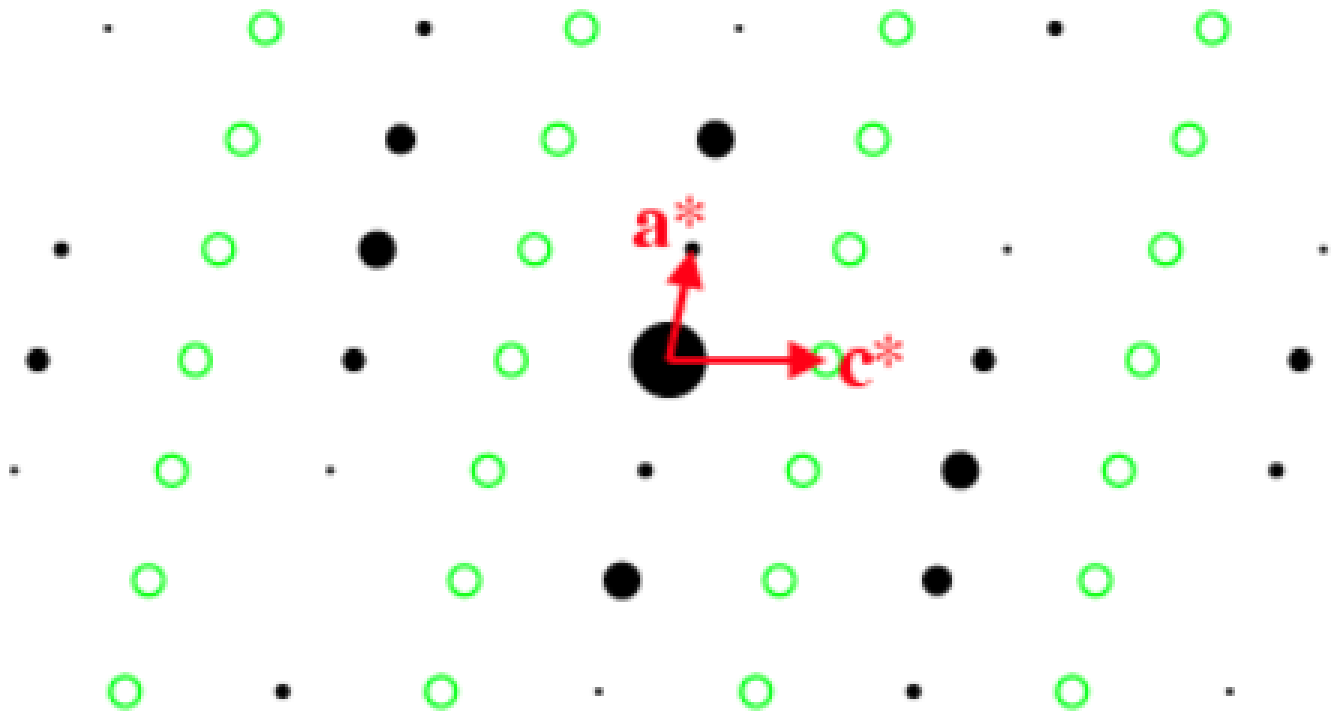
PROTO X-RAY DIFFRACTION

Screw Axis	Axis Direction	Reflection Conditions
2_1	$a \,//\, a^*$	$h00$: $h = 2n$
2_1	$b \,//\, b^*$	$0k0$: $k = 2n$
2_1	$c \,//\, c^*$	$00l$: $l = 2n$
3_1 or 3_2	$c \,//\, c^*$	$00l$: $l = 3n$
4_1 or 4_3	$c \,//\, c^*$	$00l$: $l = 4n$
4_2	$c \,//\, c^*$	$00l$: $l = 2n$
6_1 or 6_5	$c \,//\, c^*$	$00l$: $l = 6n$
6_2 or 6_4	$c \,//\, c^*$	$00l$: $l = 3n$
6_3	$c \,//\, c^*$	$00l$: $l = 2n$



Space group determination: Glide planes

Glide Plane	Symmetry Operator	Reflection Condition
$b \perp x$	$T\text{-}x,1/2+y,z$	$0kl$: $k = 2n$
$c \perp x$	$T\text{-}x,1/2+y,z$	$0kl$: $l = 2n$
$n \perp x$	$T\text{-}x,1/2+y,1/2+z$	$0kl$: $k + l = 2n$
$d \perp x$	$T\text{-}x,1/4+y,1/4+z$	$0kl$: $k + l = 4n$
$a \perp y$	$1/2+x,T\text{-}y,z$	$h0l$: $h = 2n$
$c \perp y$	$x,T\text{-}y,1/2+z$	$h0l$: $l = 2n$
$n \perp y$	$1/2+x,T\text{-}y,1/2+z$	$h0l$: $h + l = 2n$
$d \perp y$	$1/4+x,T\text{-}y,1/4+z$	$h0l$: $h + l = 4n$
$a \perp z$	$1/2+x,y,T\text{-}z$	$hk0$: $h = 2n$
$b \perp z$	$x,1/2+y,T\text{-}z$	$hk0$: $k = 2n$
$n \perp z$	$1/2+x,1/2+y,T\text{-}z$	$hk0$: $h + k = 2n$
$d \perp z$	$1/4+x,1/4+y,T\text{-}z$	$hk0$: $h + k = 4n$



Finishing remarks

PROTO X-RAY DIFFRACTION

- Finding the unit cell depends 95% on the quality of input data
- Always calibrate your instrument to eliminate angular deviations by using standards (LaB_6, silver behenate)
- If structural analogue can be identified, LS-refinement of unit cell will be enough
- Use ≈20 low angle peaks for indexing, if no solution is found, remove a few lines and repeat
- Take advantage of several methods for indexing
  (ITO is good for low symmetry, TREOR and DICVOL for symmetry higher than monoclinic)
- Cell candidates with figure of merit $M_{20} \approx 10$ should be given attention
- Perform LeBail fitting for different space groups and compare the results