Knowledge Center
PROTO
X-RAY DIFFRACTION

Crystallography with PXRD vs. SC-XRD

Introduction to the principles of structure determination

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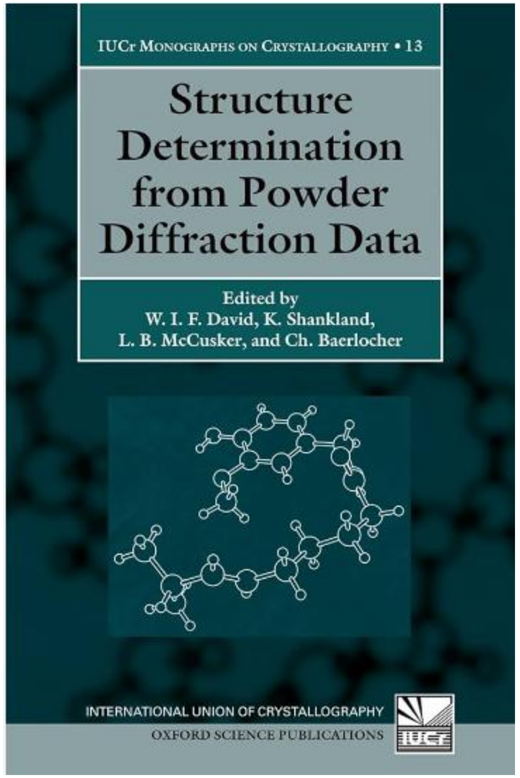
SC-XRD

The art of solving a crystal structure from powder diffraction data has developed rapidly over the last ten years. Prior to 1990, very few unknown crystal structures had been determined directly from powder diffraction data, and each structure solved could be regarded as a *tour de force* of ingenuity and perseverance. Today, the situation is quite different and numerous crystal structures, both organic and inorganic, have been solved from powder data.



PXRD

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In the chapters that follow, experts in the field discuss both the fundamental and applied aspects of structure solution from powder diffraction data. The process is sequential, with any particular stage depending crucially on the successful completion of all previous steps, and the ordering of the chapter within the book essentially reflects this flow. Although Rietveld methods of structure refinement from powder diffraction data is often loosely considered to be synonymous with

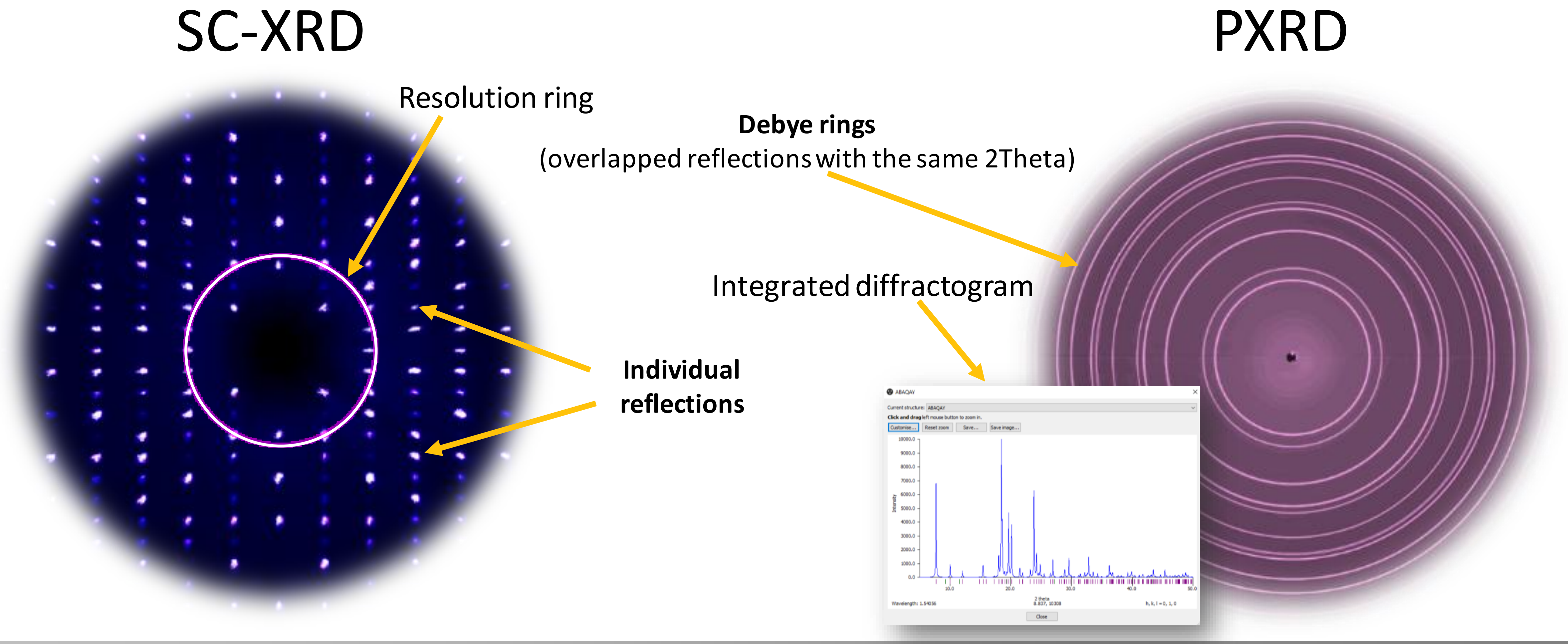
SC-XRD

- Indexing
- Crystal system
- Collection strategy
- Data acquisition
- Integration
- Scaling
- Space group determination
- Structure solution
- LS-refinement

PXRD

- Data acquisition
- Indexing
- LeBail integration
- Space group determination
- Building the initial model
- Structure solution
- Rietveld refinement

Crystallography with PXRD vs. SC-XRD



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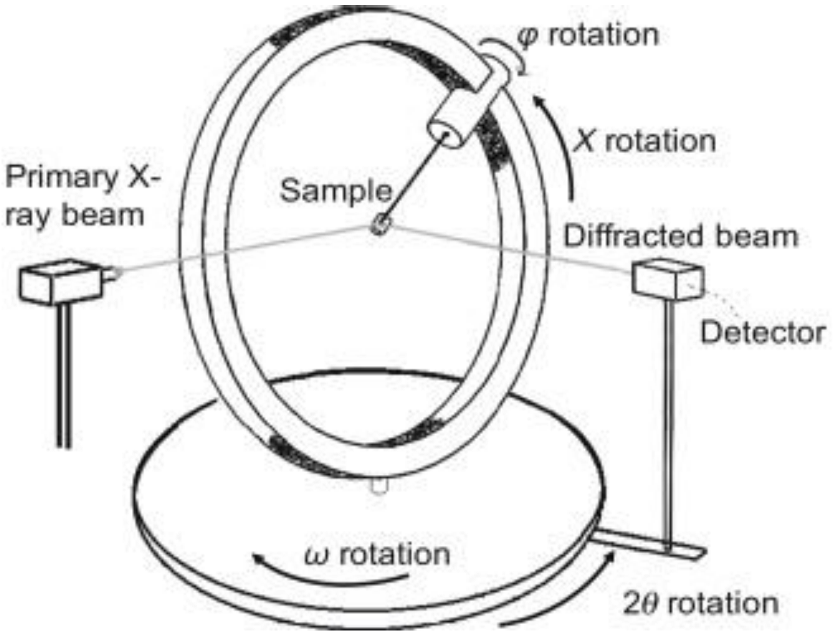
SC-XRD



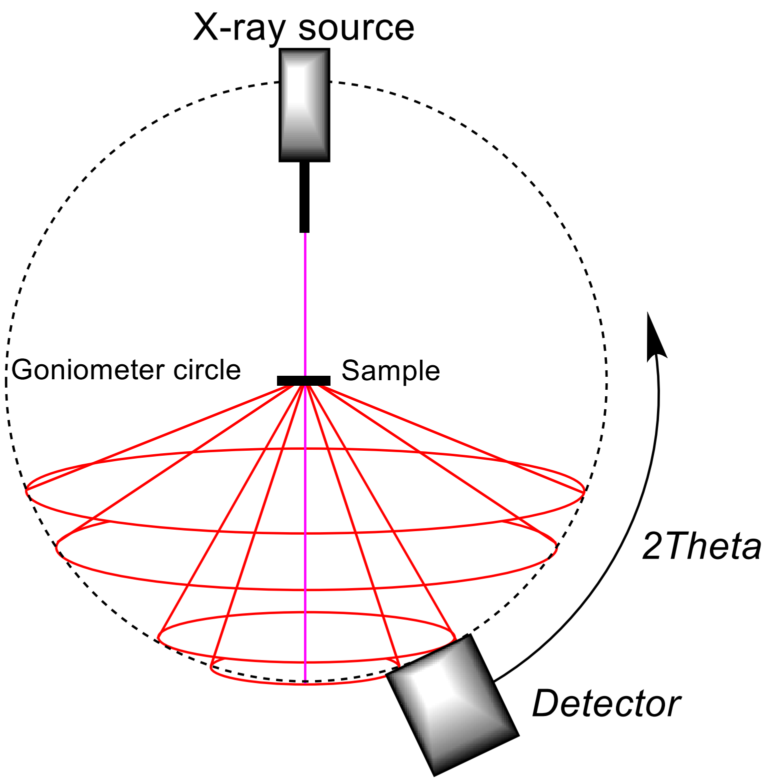
SC-XRD

- 4-circle goniometer
- Sample orientation regarding instrumental geometry is important
- Data is collected as ϕ/ω-scans

PXRD

- 2-circle goniometer
- Sample orientation is not important
- Data is collected as 2θ-scan
- Data collection strategy is not required

PXRD



Indexing: SC-XRD

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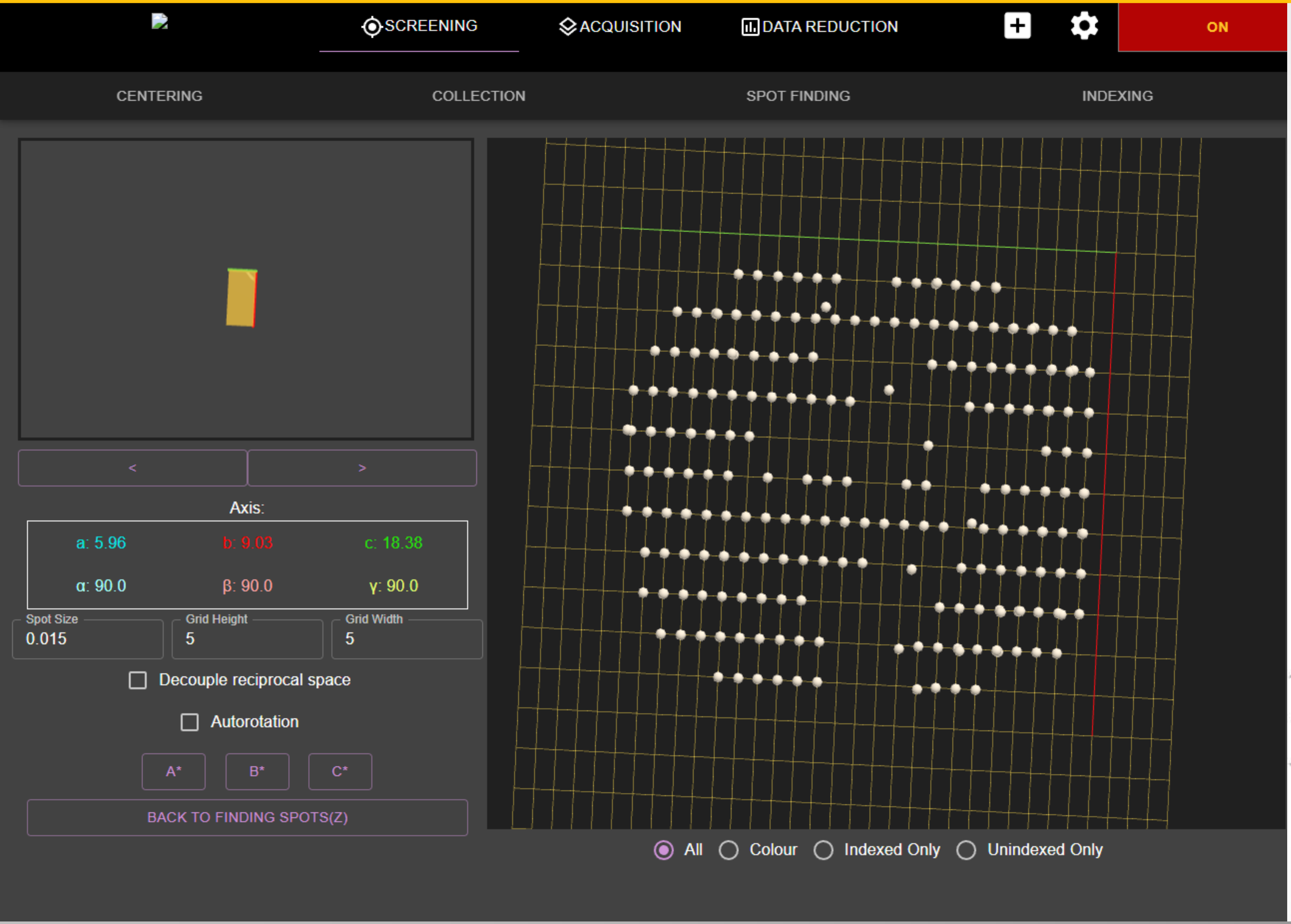
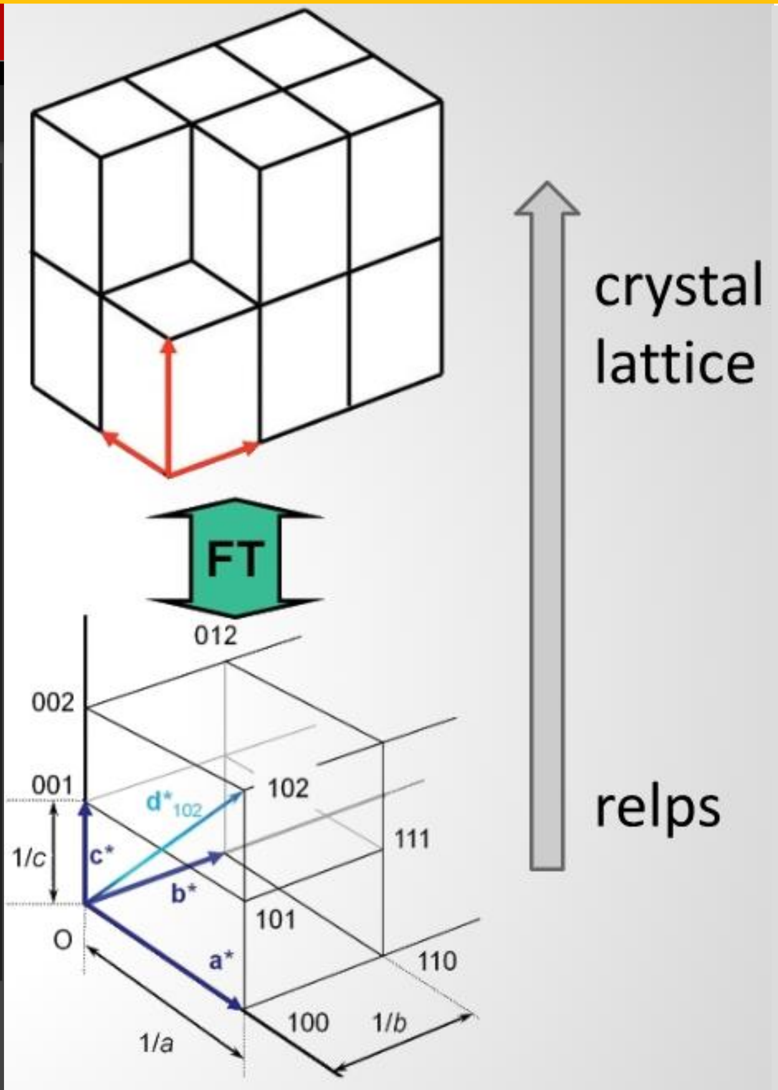
X-RAY DIFFRACTION





Space group determination: SC-XRD

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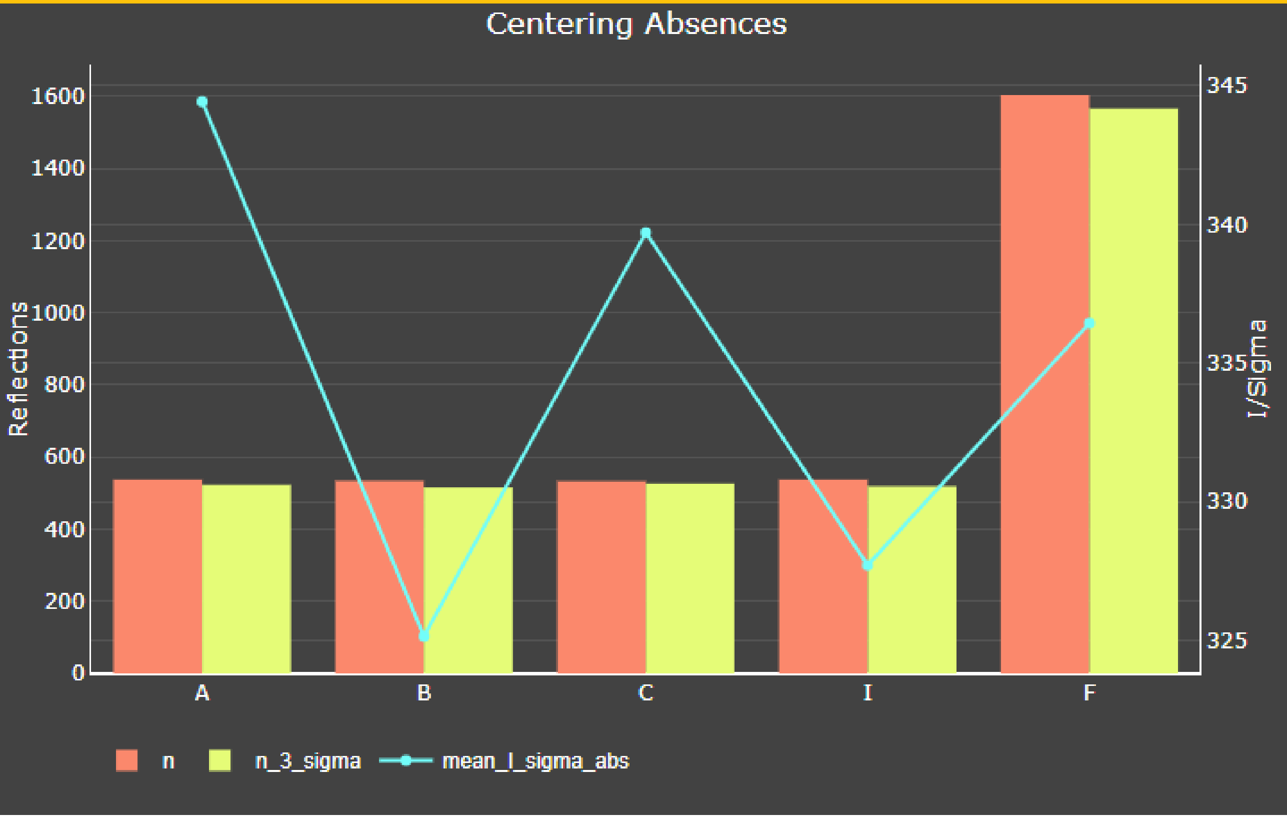
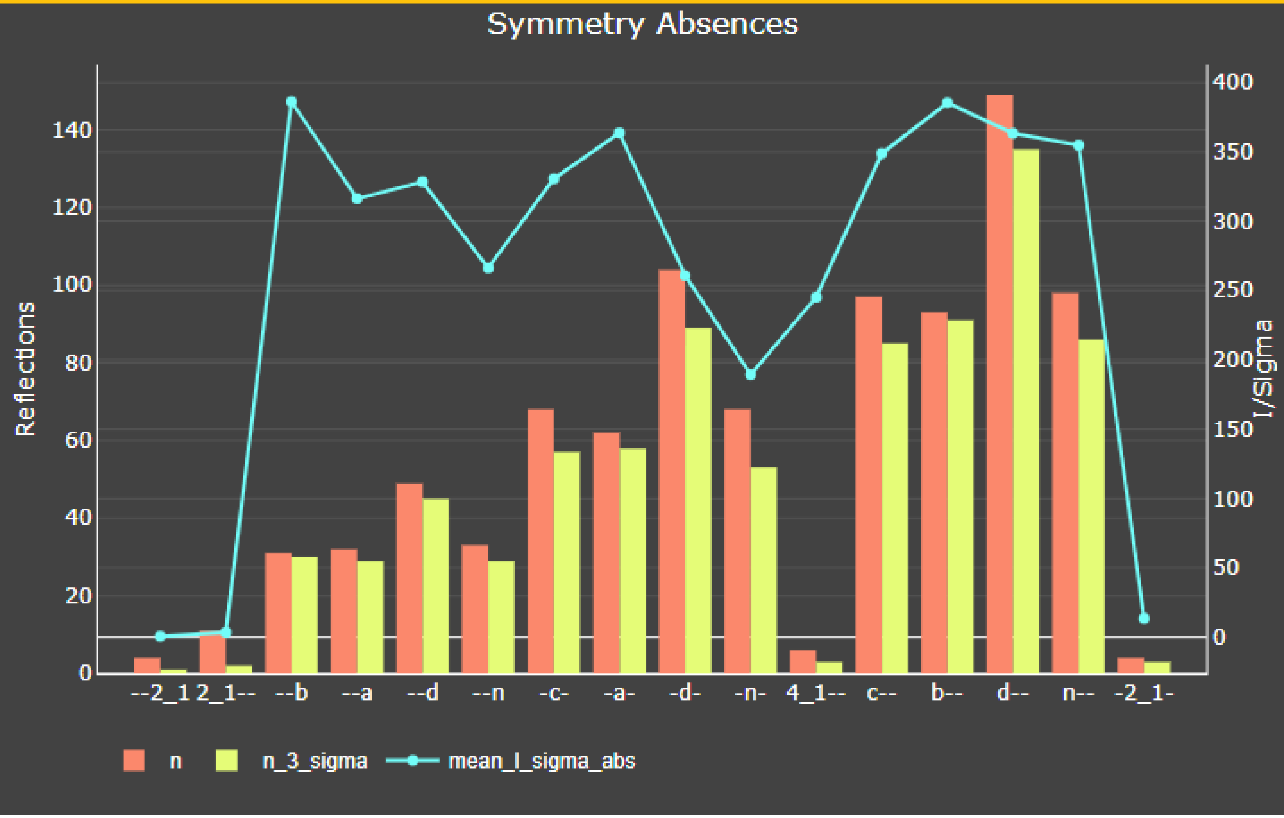
X-RAY DIFFRACTION





- 3-dimensional diffraction data allows for estimation of systematic absences based on the intensity
- Software calculates the number of absent reflections based on centering and systematic absences and compares it to the number of reflections violating these conditions

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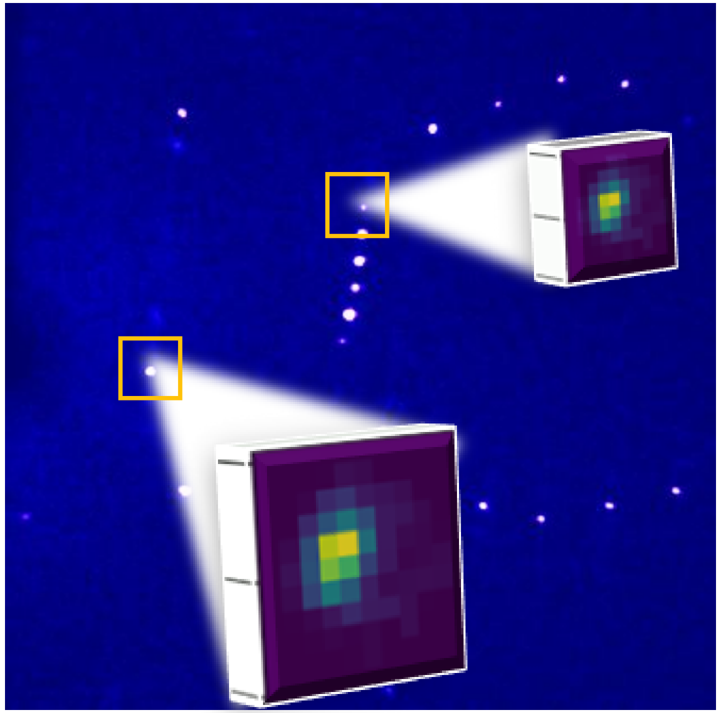
SC-XRD

PXRD

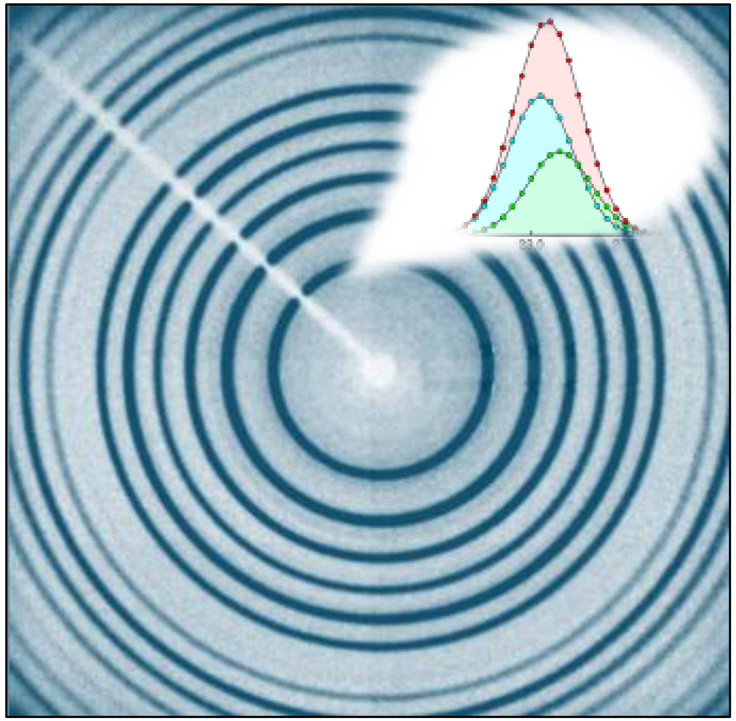


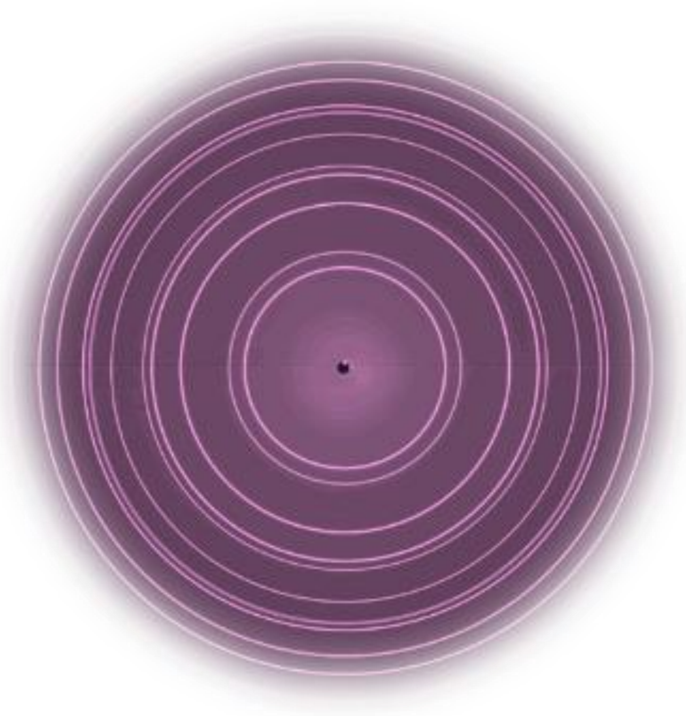
SC-XRD

- Peaks are well separated in 3D space
- Integration is performed with "shoeboxes"

PXRD

- Spatial resolution is lost
- All peaks with the same 2θ contribute to intensity of the Debye ring
- Peak deconvolution is used to apportion intensities to individual reflections





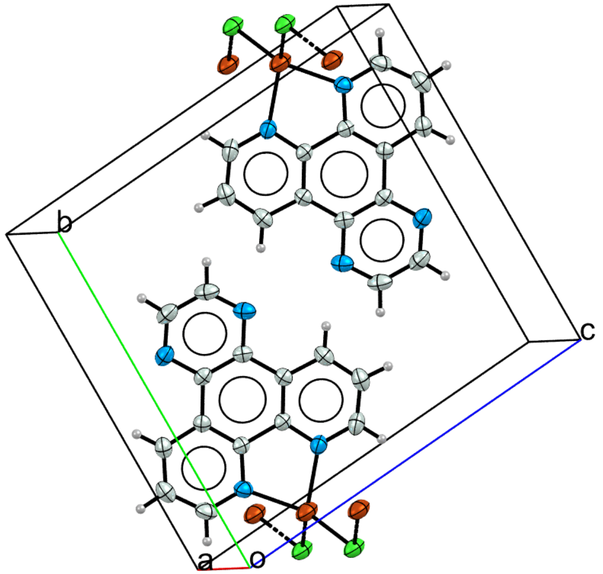
$$\rho_{xyz} = \frac{1}{V}\sum_{hkl}\left|F_{hkl}\right| \cdot e^{i\phi_{hkl}} \cdot e^{-2\pi i\left(hx+ky+lz\right)}$$

Deterministic methods →

Fourier transform

← *Stochastic methods*

$$F_{hkl} = \sum_{j} f_j \cdot e^{2\pi i\left(hx_j+ky_j+lz_j\right)}$$

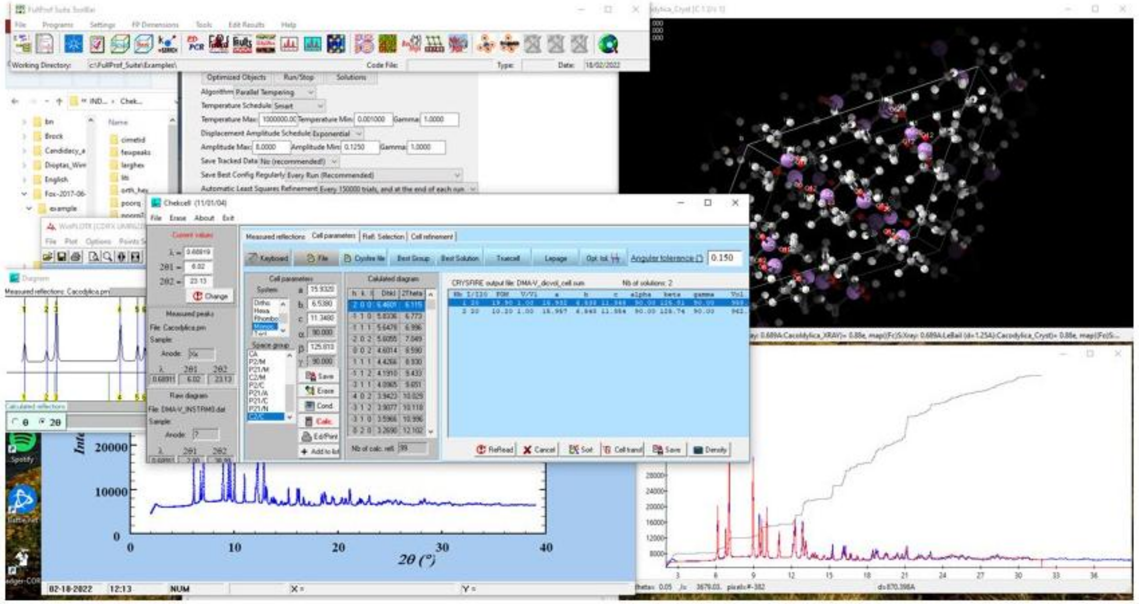


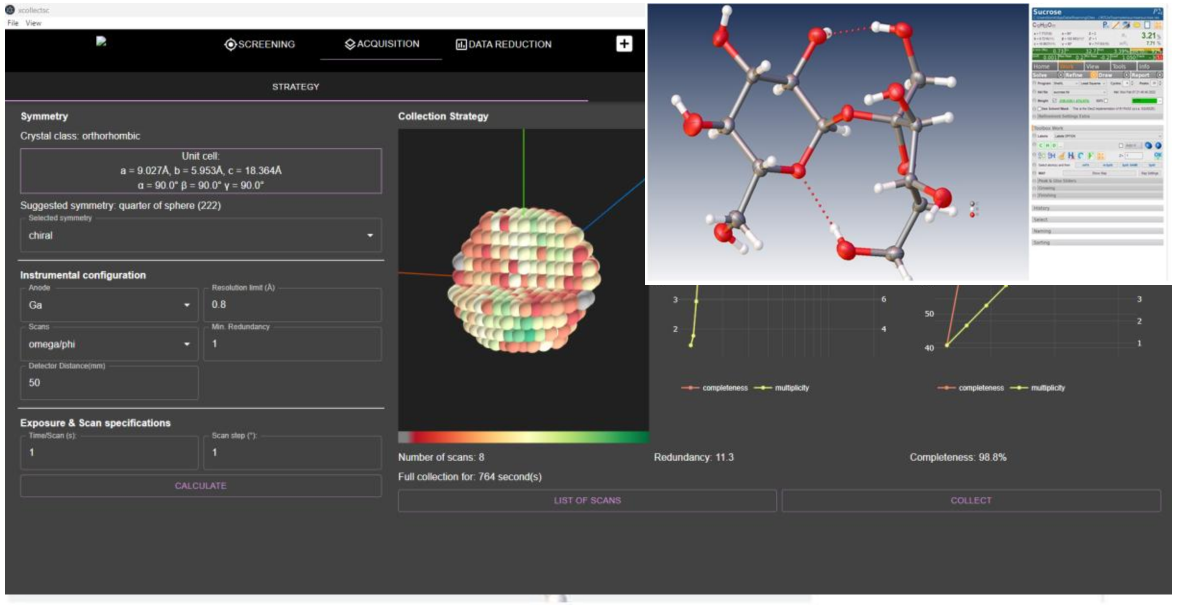
Deterministic methods

- **Concept:** To guess phases and plug them into the FT^{-1} equation
- **Requirements:**
  - Accurate intensities
- **Methods:**
  - *Direct methods*
  - *Patterson function*
  - *Charge flipping*

Stochastic methods

- **Concept:** To guess crystal structure and check how well it fits the data
- **Requirements:**
  - Time
- **Methods:**
  - *Monte-Carlo simulation*
  - *Simulated annealing*
  - *Parallel tempering*
  - *Genetic algorithm*
  - *Particle swarm*





PXRD

Data collection: AXRD
Indexing: ITO, TREOR, DICVOL, McMaille
Space group: ChekCell
Model building: AVOGADRO, OpenBabel
Structure solution: EXPO, FOX, GSAS-II
Rietveld refinement: GSAS-II
Model validation: MOGUL

SC-XRD

Data collection: XCollect
Indexing: XCollect
Space group: XCollect
Model building: SHELX
Structure solution: SHELX
LS-refinement: SHELX
Model validation: Platon
GUI: Olex2

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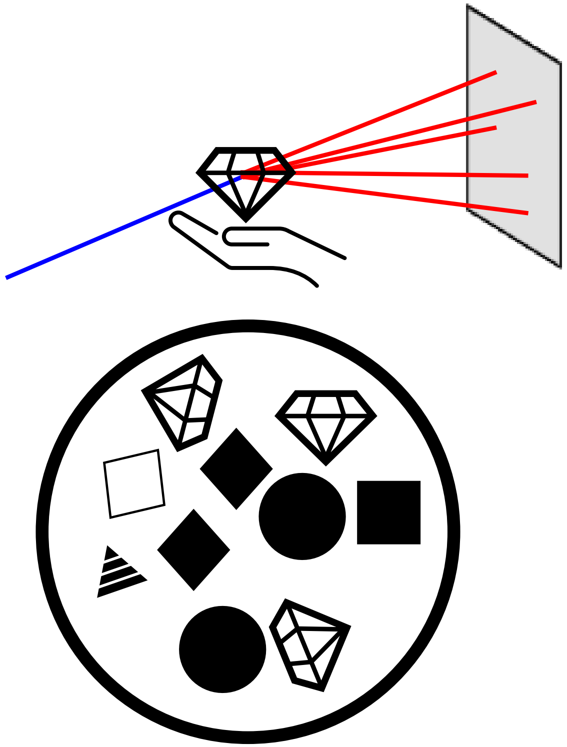
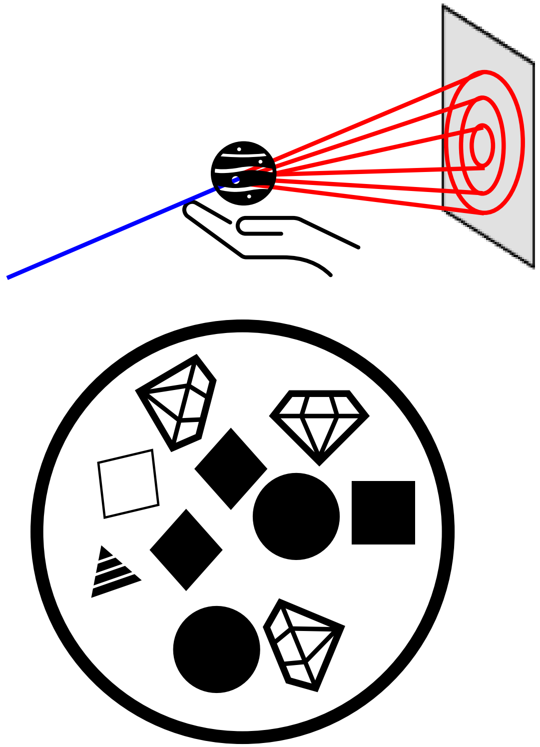
SC-XRD



PXRD



SC-XRD

- Crystal structure is specific to the mounted crystal
- SC-data is NOT representative of the sample bulk

PXRD

- Structural model is applied to the whole sample
- Complex phases can be analyzed and quantified

Limitations: Absolute configuration

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Friedel's opposites: reflections with opposite *hkl* indices (e.g. 111 and -1-1-1)

Flack parameter estimates absolute configuration of the crystal structure:

$$I_{hkl} = (1 - x)\left|F_{hkl}\right|^2 + x\left|F_{-h-k-l}\right|^2$$

Observed structural amplitude

Amplitudes for Friedel's opposites

Flack parameter
(x = 0 – correct enantiomer, x = 1 – inverted enantiomer)

- Anomalous scattering cannot be used to define handedness of the structure or racemic twinning with PXRD
- Friedel's opposites are collapsed into one peak

Crystallography with PXRD vs. SC-XRD

SC-XRD

Advantages

- Accurate estimation of diffraction intensities
- Absolute configuration
- Developed software packages (OLEX2, Apex, XCollect)

Disadvantages

- Long data acquisition (hours)
- Structural model is only applied to the studied crystal (SC-data is NOT representative of the sample bulk)
- Crystal size significantly affects quality of the data

PXRD

Advantages

- Rapid data collection (minutes)
- Structural model is applied to the bulk of the sample
- Retains information about crystallite size, percent crystallinity, presence and nature of impurities

Disadvantages

- Challenging data processing due to peak overlaps
- Absolute configuration CANNOT be determined
- Large number of different software packages to use

Structure solution *with* PXRD

Data acquisition (2Theta scan) → **Unit cell determination** → **Space group determination** → **Intensity extraction** → **Treatment of overlaps** →

Data acquisition (2Theta scan)

Parameters

- *Power settings*
- *Type of anode*
- *Dwell time (exposure)*
- *Sample spinning*
- *Temperature*
- *Pressure*

Unit cell determination

Methods of indexing

- *LS-refinement*
- *Pattern matching*
- *Trial methods*
- *Dichotomy methods*
- *Zone indexing*
- *Monte-Carlo*

Space group determination

Space group analysis

- *Systematic absences*
- *Le Bail fitting*

Intensity extraction

Integration methods

- *Iterative Le Bail*
- *The Pawley method*

Treatment of overlaps

Peak separation techniques

- *Anisotropic thermal expansion*
- *Induced texture*

→ **Building starting model** → **Structure solution** → **Rietveld refinement** → **Validation of crystal structure** → **Generation of CIF-file**

Building starting model

Methods

- *Import from databases*
- *Low-level DFT model*

Structure solution

Ab initio solution

- *Deterministic methods*
- *Stochastic methods*

Rietveld refinement

Refined parameters

- *Unit cell metrics*
- *Background*
- *Peak-shape function*
- *Strain and PO*
- *Absorption correction*
- *Atomic coordinates*
- *Temperature factors*

Validation of crystal structure

Verification methods

- *Statistical evaluation (MOGUL)*
- *DFT approach*

Generation of CIF-file

Syntax check

- *CheckCIF*