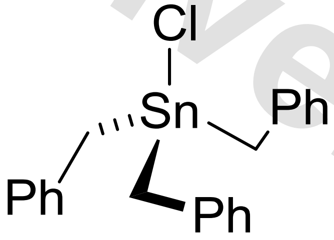
Data reduction

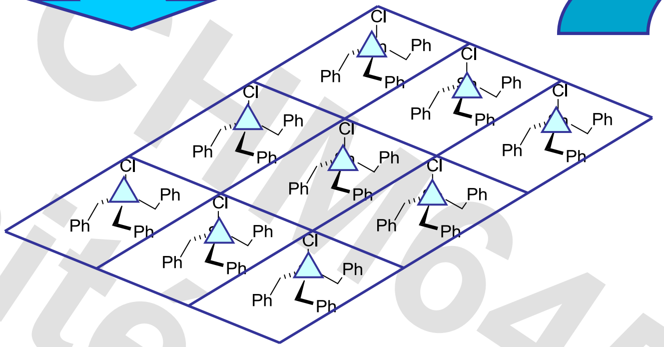
Structure determination

Crystallisation

Single crystal selection



_Molecular structure__:_
Atomic positions

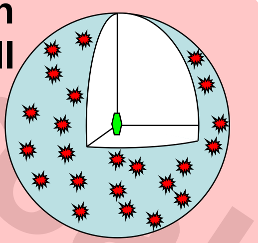


_Crystalline structure__:_
Unit cell and space group

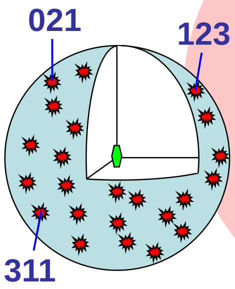
_Crystal__:_
Macroscopic dimensions

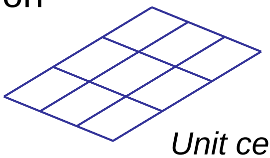
Dataset collection

Détermination of the unit cell



Raw data

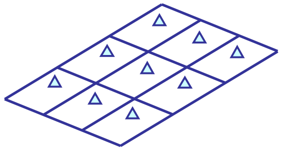




Unit cell

H	K	L	I	σ
0	0	1	134.4	12.5
0	0	2	0.2	1.2
1	1	4	52.4	2.2

Space group determination



H	K	L	I	σ
0	0	1	134.4	12.5
0	0	2	0.2	1.2
1	1	4	52.4	2.2

_Unit cell + space group__:_
Dimensions and symmetry of the crystalline structure
Intensity of the reflections:
Atomic positions

Solution and Refinement

Programs used in a single crystal diffraction study

• Grow a crystal	
• Choose and mount a single crystal	
• **Collect the dataset**	APEX2 ⇒ images
• Determine the unit cell	APEX2 ⇒ .p4p
• **Integration of the image files and data reduction**	
• **Lorentz correction**	SAINT
• **Polarisation correction**	SAINT ⇒ .raw
• **Absorption correction**	SADABS ⇒ .hkl
• **Other corrections (twinning etc.)**	
• **Space group determination**	XPREP ⇒ .ins, .hkl, .pcf, .prp
• **Structure solution**	XS (SHELXS) ⇒ .res, .lst
• **Structure refinement**	XL (SHELXL) ⇒ .res, .lst, .cif
• **Validation**	checkcif, PLATON
• Preparation of tables and figures	XP, XSHELL, PLATON etc.
• Data backup	

Data reduction

- During data reduction we transforme a dataset, which is **specific to the instrument and the crystal used** into a general, instrument independent data set for this structure.
- During the process several corrections are applied to the data.
- Ideally, each X-ray diffraction study (of the same compound) would yield the same data set, independant of crystal, instrument of radiation employed.

Images or reflection profiles (raw data, several giga bytes)

↓

Réduction des données / data reduction

- Integration of reflections (uses the unit cell determined)
- Lorentz and polarisation correction (LP-correction)
- Corrections for crystal decomposition
- Other corrections

List of reflection data (.raw file): h,k,l, intensity, standard deviation σ, orientation of the crystal on the diffractometer (direction cosines)

↓

- Absorption correction

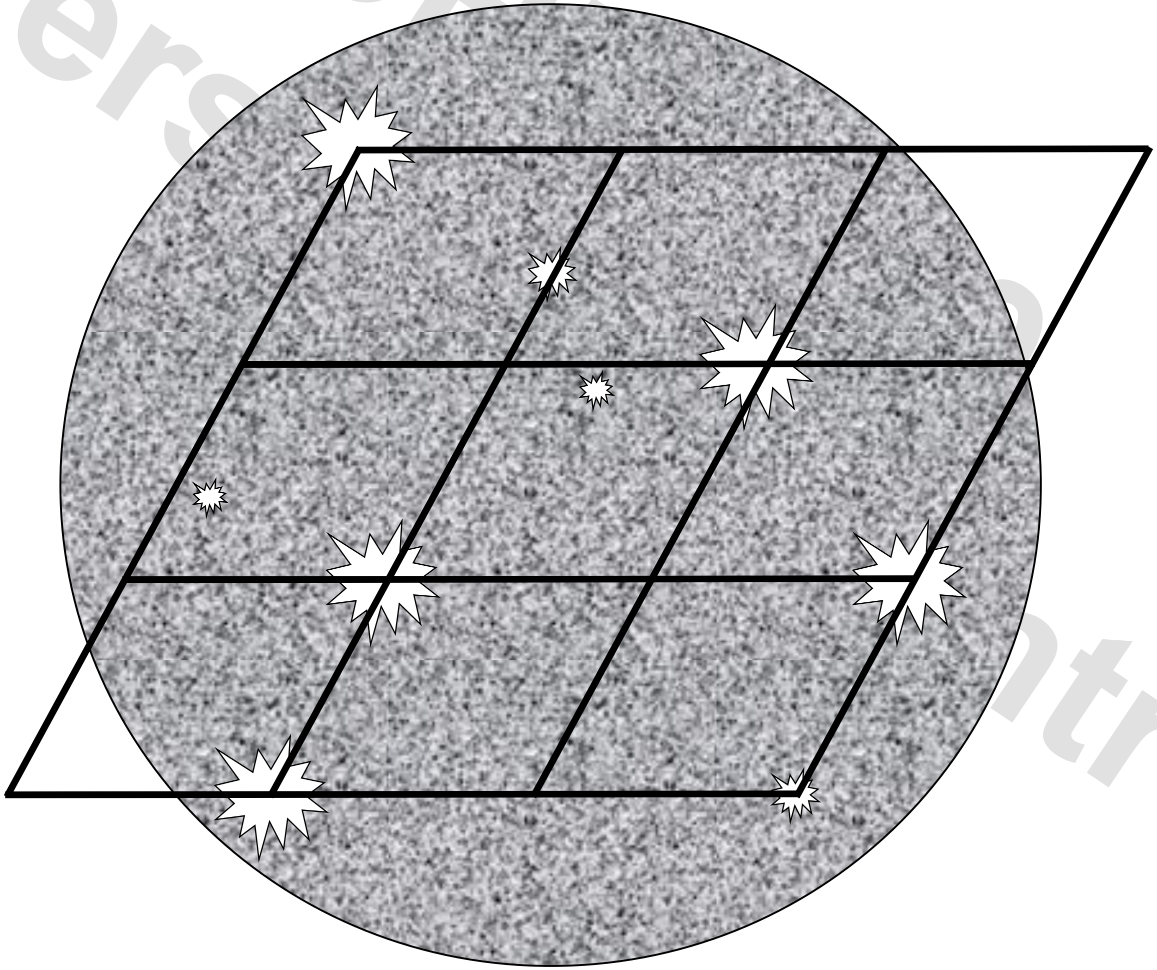
List of reflection data (.hkl file): h,k,l, intensity, standard deviation s

Integration

1. **Unit cell determination**
2. **Integration**

Integration of reflections

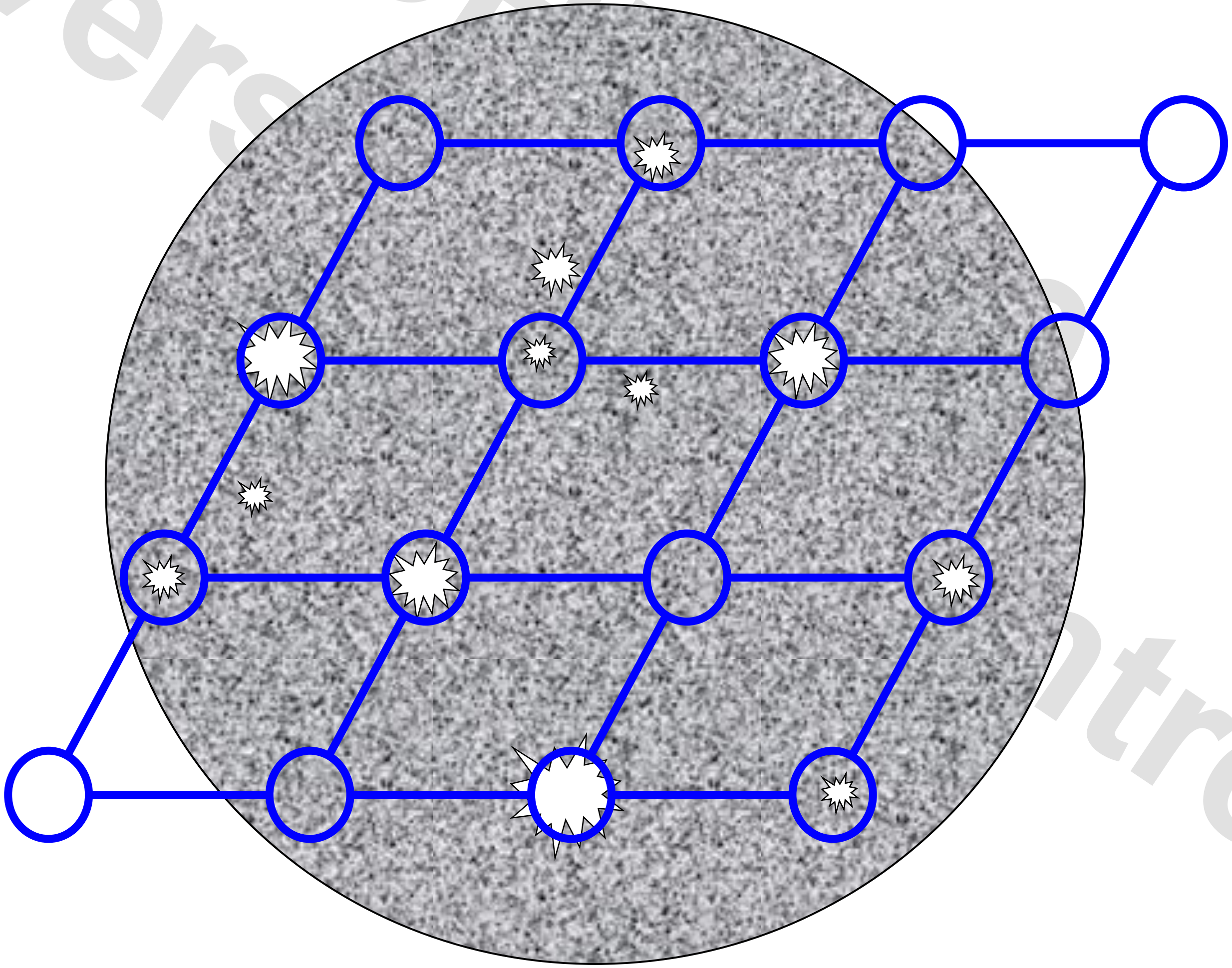
1. Harvest a number of strong reflections and determine the unit cell



Integration of reflections

1. Harvest a number of strong reflections and determine the unit cell
2. Integrate a certain given area at the possible positions in all other image files

This means that – even if all the space is recorded – the program integrates **only** at positions defined by the unit cell



Integration

1. **Unit cell determination**
2. **Integration**

Probable errors:

- **Unindexed reflections:**

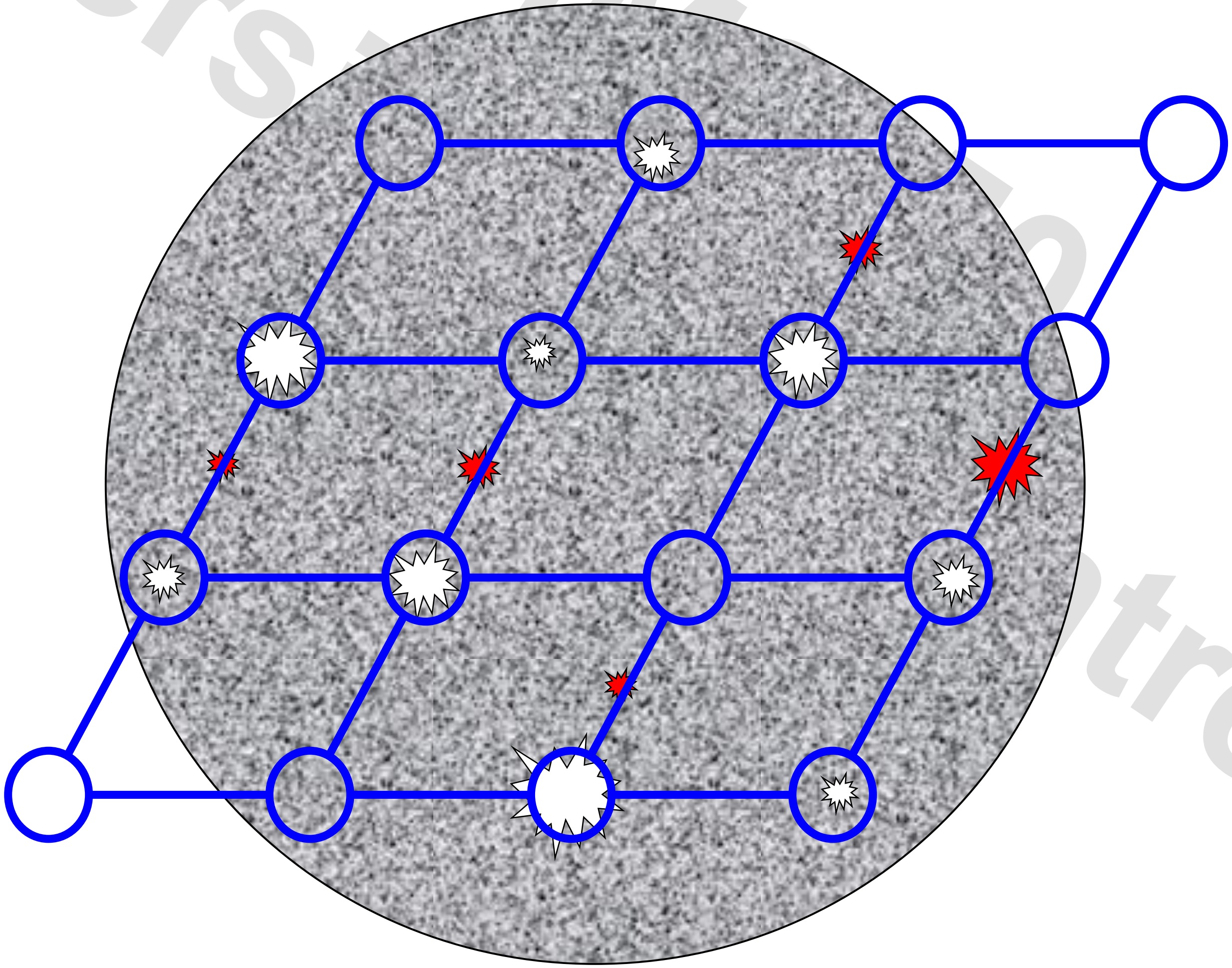
  If the unit cell determined is incorrect (e. g. a superstructure, which yielded an apparently smaller unit cell), reflections which cannot be indexed with the current unit cell are ignored.

  Example: The unit cell has an *a* axis which is only ½ of the correct value. Reflections with *h* (in the correct unit cell) would have non-integer values in the too small cell (3 -> 1.5) and are not integrated.

Integration of reflections

1. Harvest a number of strong reflections and determine the unit cell
2. Integrate a certain given area at the possible positions in all other image files

Possible errors/problems: Reflections not part of the unit cell (twin, too small unit cell, superstructure) are not integrated



Integration

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  Example: The unit cell has an *a* axis which is only ½ of the correct value. Reflections with *h* (in the correct unit cell) would have non-integer values in the too small cell (3 -> 1.5) and are not integrated.

  Indications: The programs used for integration often allow to show the images and indicate the integrated reflections. Should there be remaining reflections which are not integrated this might indicate a problem.

  Sometimes we notice from the later refinement that our unit cell might be too small (impossible disorder or packing diagrams).

  Solution: Redo the unit cell determination using more reflections including eventually those of smaller intensity.

Integration

1. **Unit cell determination**
2. **Integration**

Probable errors:

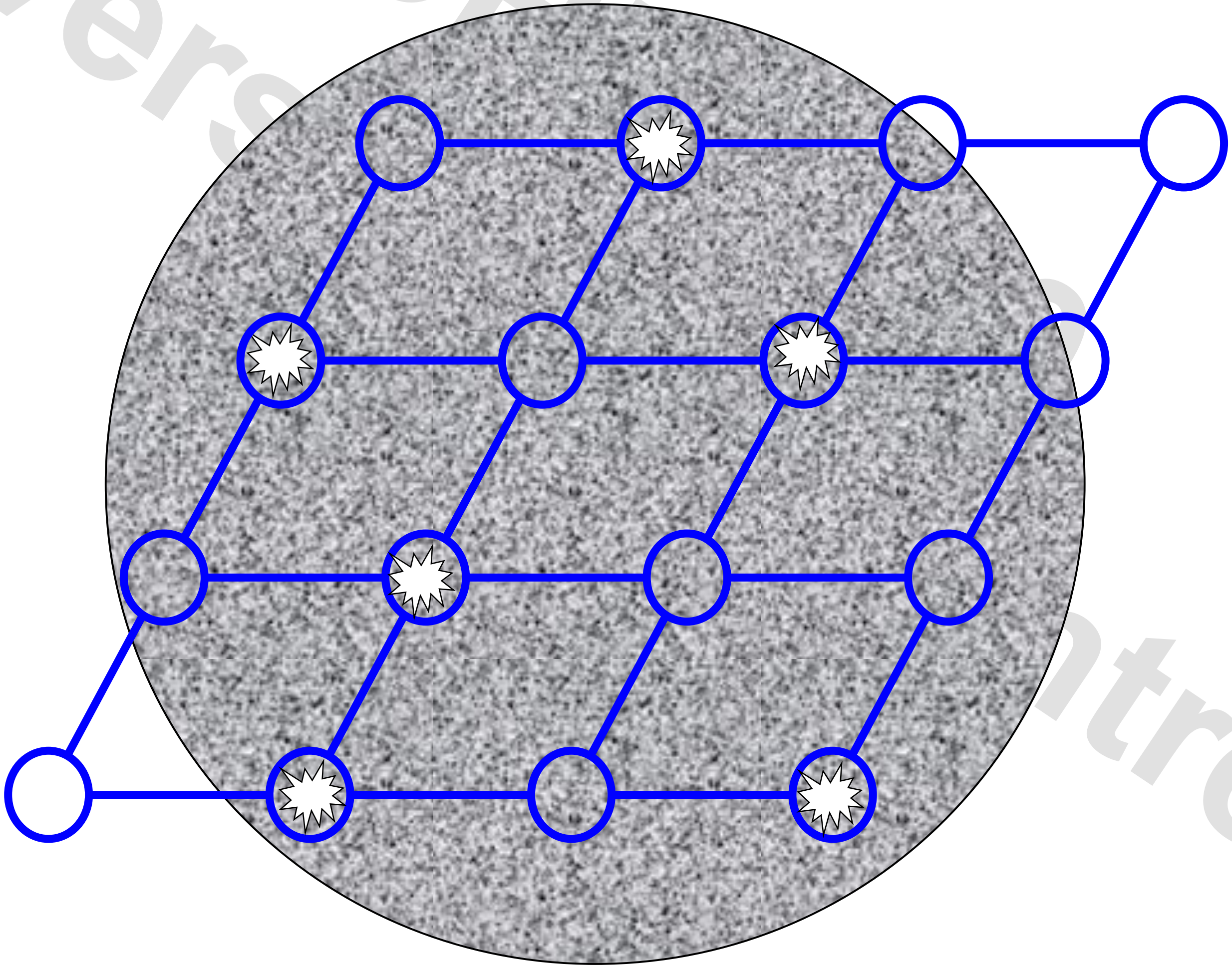
- **Unindexed reflections**
- **Bad intensities:**

  Intensities at high θ angle are strongly broadened

  Example: Strong disorder or twinning by reticular merohedry

Integration of reflections

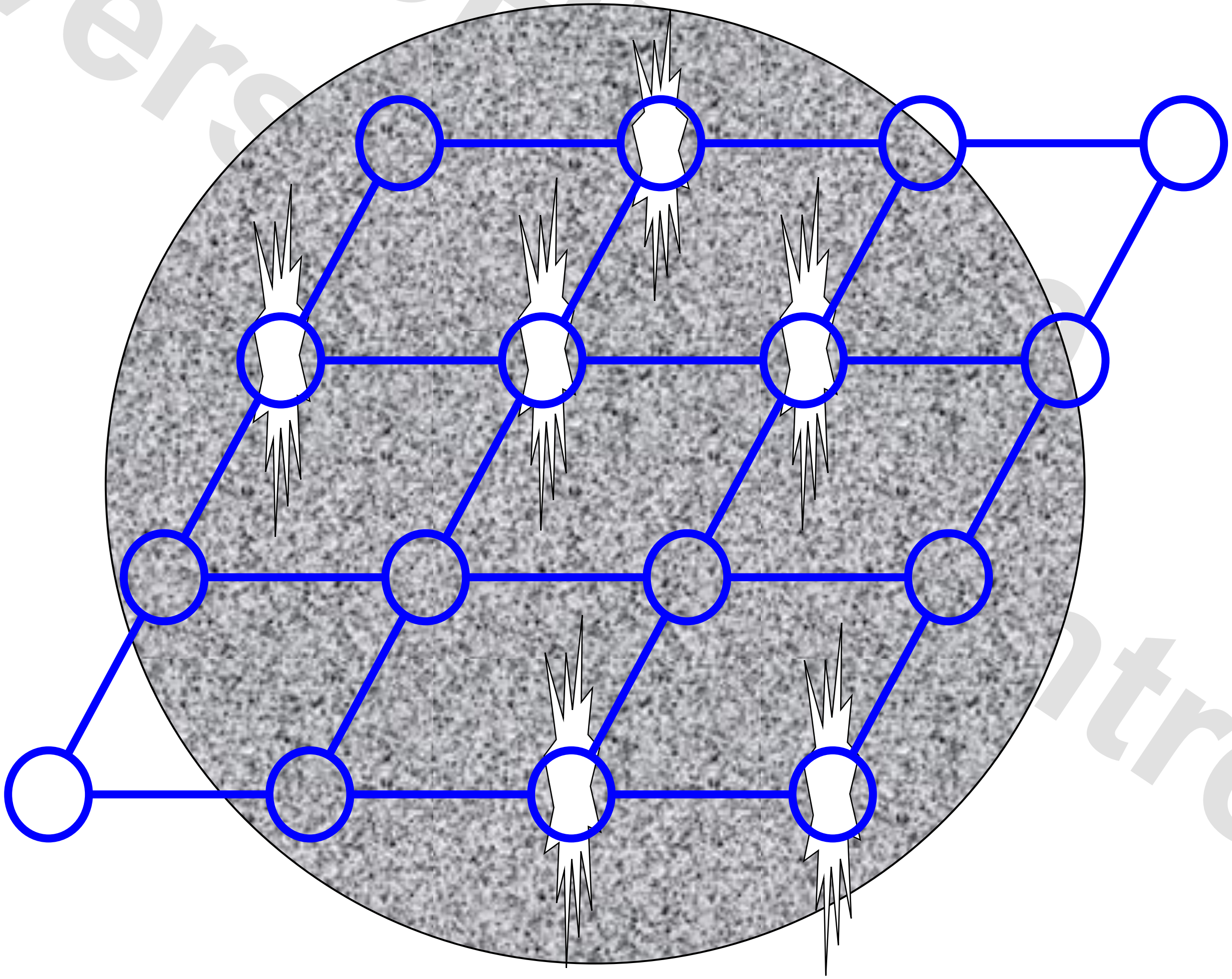
The integration window is determined from reflections at low theta angle.



Integration of reflections

The integration window is determined from reflections at low theta angle.

If angles broaden unproportionally at high theta angles the determined integration window is ill-suited for the task.



Integration

1. **Unit cell determination**
2. **Integration**

Probable errors:

- **Unindexed reflections**
- **Bad intensities:**

Intensities at high θ angle are strongly broadened

Example: Strong disorder or twinning by reticular merohedry

Indication: The most disagreeable reflections are at high θ and have $F_c > F_o$ or they are at small θ with $F_c < F_o$.

Solution: Adapt the parameters governing the integration in the appropriate program (APEX, SAINT etc.) to choose a bigger integration window.

Integration

1. **Unit cell determination**
2. **Integration**

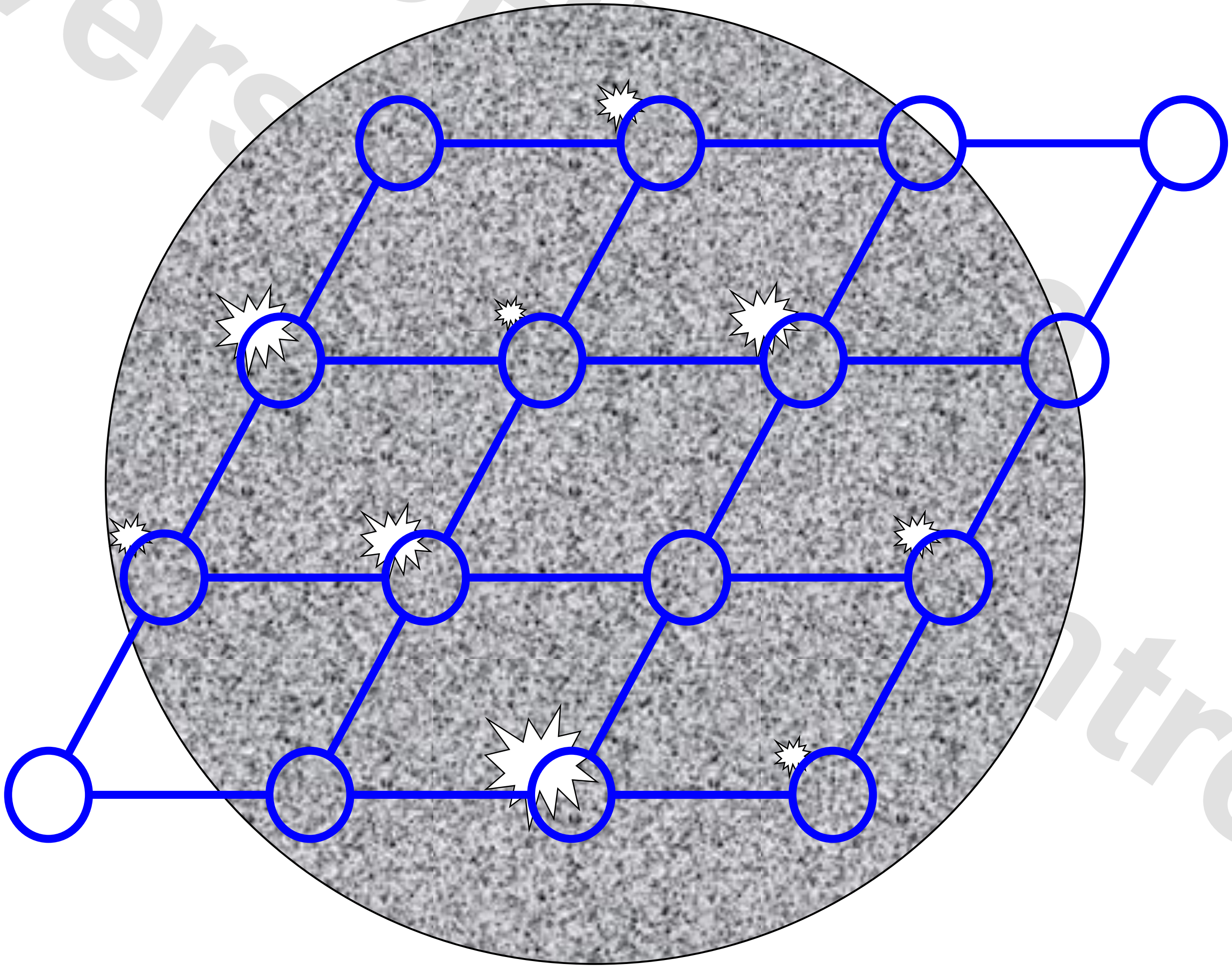
Probable errors:

- **Unindexed reflections**
- **Bad intensities**
- **Bad Laue group**

  If a wrong Laue group was chosen, this imposes geometric constraints which prevent the unit cell to describe correctly the location reflections. This is more noticeable at high theta angles.

Integration of reflections

Assumed unit cell : monoclinic. Reality: triclinic with $\alpha = 91°$ and $\gamma = 92°$. At high θ, integration positions and reflection positions do not agree anymore.



LP correction

1. Polarisation factor

Reminder: The Thomson diffusion is described by:

$$I_{Th} = I_i \frac{e^4}{m^2 r^2 c^4} \frac{1+\cos^2 2\theta}{2}$$

The intensities have to be corrected by a **polarisation factor *p***:

$$p = \frac{1}{2}\left(1+\cos^2 2\theta\right)$$

If we use a graphite monochromator, the reflections of the monochromator are influenced in the same manner and we have to introduce another factor *K*.

$$p = \frac{1}{1+K}\left(1+K\cos^2 2\theta\right)$$

For Mo radiation the difference is often small (<1%) and ignored.

Correction LP

2. Lorentz factor

Reflections at high θ angle remain longer in the reflection condition during detector movement than reflections at low θ (provided we use a constant angular speed ω).

This effect, which depends on the θ angle, is corrected by the Lorentz factor:

$$L = 1 / \sin 2\theta$$

The two corrections are often applied at the same time.

$$Lp = \frac{1}{2\sin 2\theta}\left(1 + \cos^2 2\theta\right)$$

$$I_{corr} = I / Lp$$

Correction of crystal decomposition

During the collection of the data set, the crystal might decompose or suffer radiation damage. This introduces a systematic change in intensity, which we have to correct.

With old-style linear detectors (collection over several days), several (e.g. threes) check reflections were measured in constant intervals (time or number of reflections measured).

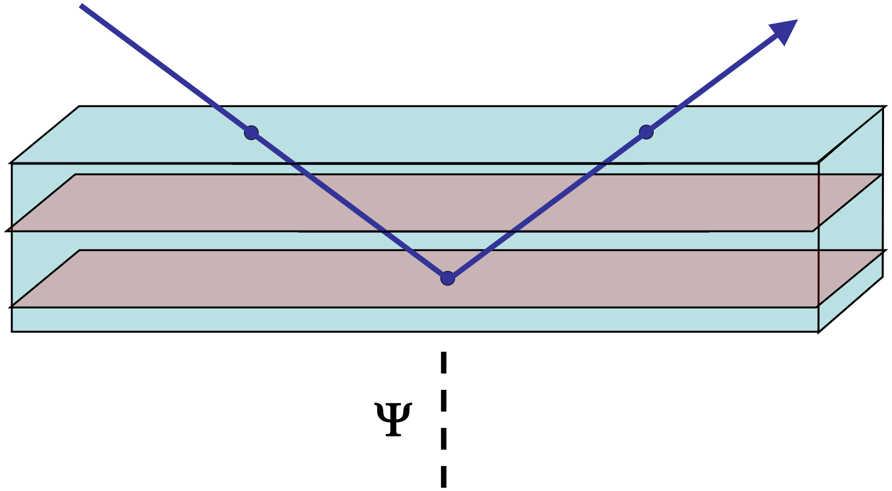
With area detectors, decomposition correction became less important and is normally ignored. At UdeM we nevertheless collect the same data (ca. 300 - 600 reflections) at the beginning and the end of the measurement. Make sure that your standard conditions include these repeated reflections and if you doubt crystal stability, you can still apply decomposition correction measures.

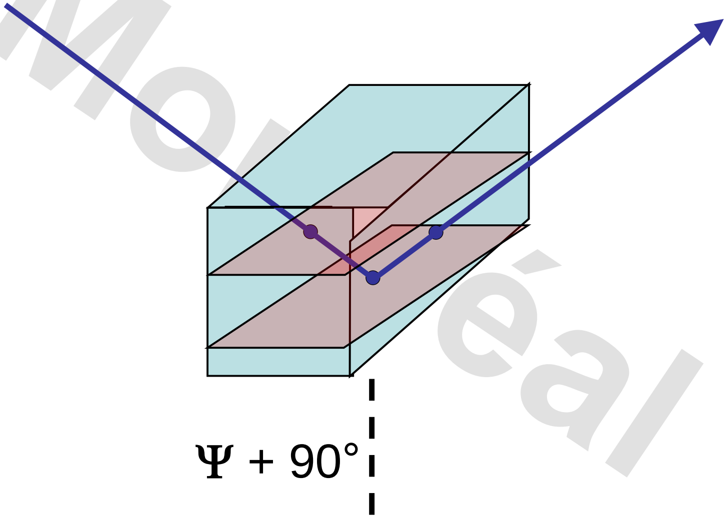
Absorption correction

A crystal can be rotated around the Ψ axis, the axis perpendicular to the lattice plan, without taking the crystal out of the reflection condition. For an anisotropic (non-spherical) crystal there are thus a multitude of orientation possible, in which a reflection can be measured. Since the crystal is completely immersed in the X-ray beam, the same amount of X-rays are reflected, independent of its orientation.

Depending on its orientation, however, the beams have to travel more or less through the crystal and absorption effects depend thus on the form of the crystal and the orientation in which it was measured.

An absorption correction takes care of these effects.





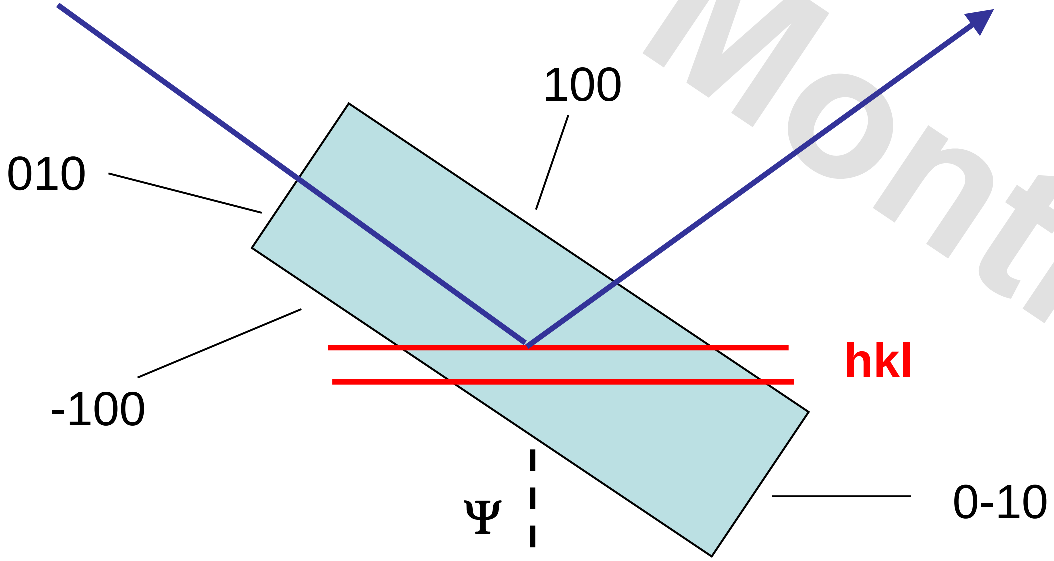
Absorption correction

1. Face indexing (Numerical absorption correction)

In principle the best method.

Face indexing requires indexing of the faces, determining their distance to each other and their orientation on the diffractometer. With this information, the pathlength of each initial and diffused X-ray beam can be calculated and correted for every given orientation of the crystal.

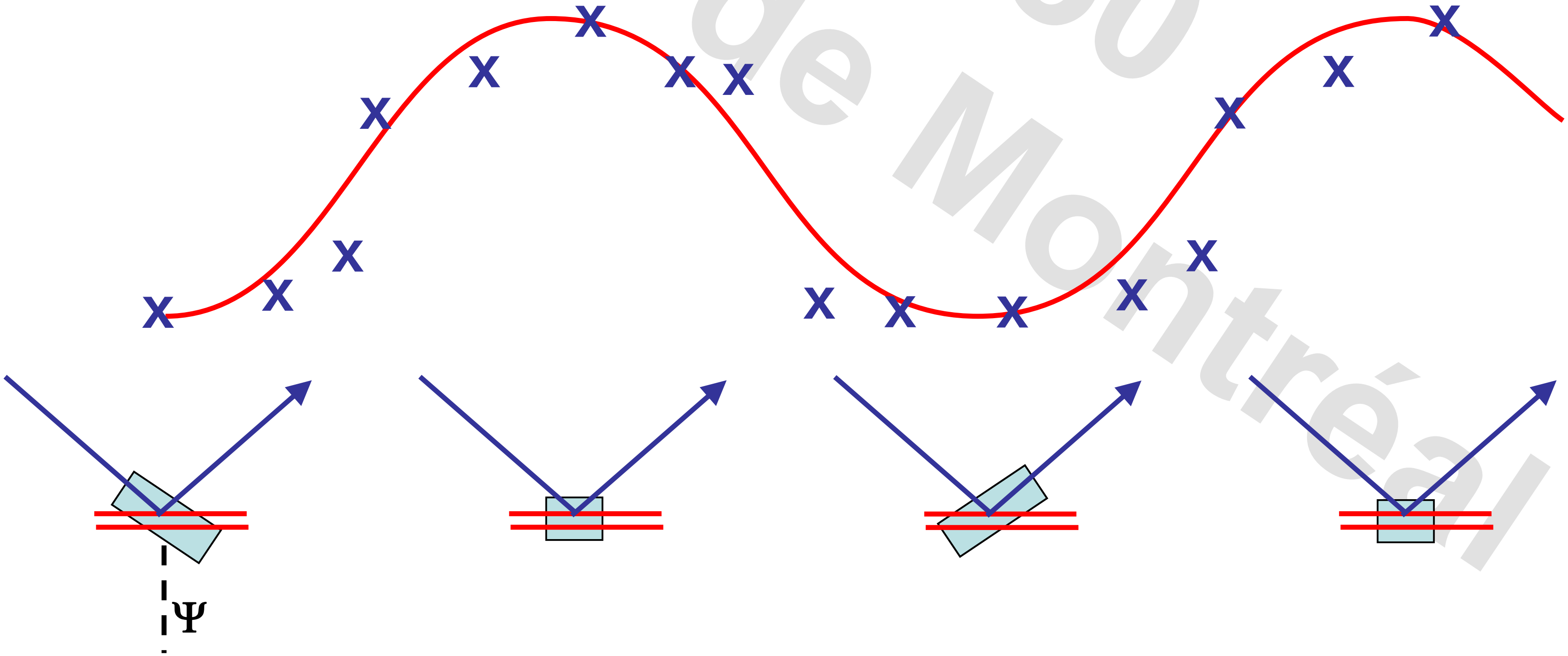
Face indexing can be a very time-consuming process or very straight-forward, depending on the instrument and software used (and the visibility of the crystal).



Absorption correction

2. An old method: Ψ-scan (semi-empirical)

A limited number of reflections are measured by turning the crystal around the Ψ axis (perpendicular to the reflection plane). The obtained intensities of all reflections are fitted with an approximate crystal shape in form of an ellipsoid.



Absorption correction

3. Multiscan (SADABS)

- To determine which reflections should be identical, SADABS uses the Laue group supplied by you. Thus if you decide later on that the Laue group was incorrect, you **have to redo the integration and SADABS**.

- In theory, Friedel-equivalents should not be considered equivalent by SADABS in non-centrosymmetric crystals. Funnily, better Flack-parameters are obtained if the absorption correction is done assuming centrosymmetry, i. e. attempting to equalize the Friedel equivalents.

  Since absorption and other effects corrected by SADABS are normally bigger than anomalous dispersion, the better correction due to the additional statistical redundancy due to the inclusion of Friedel equivalents yields better data than correction using a non-centrosymmetry.

  Note: Recent results on the liquid Ga anode instrument seems to put this in doubt. In particular with highly absorbing crystals in non-centrosymmetric space groups or for high errors in Flack-*x*, you might want to try SADABS with the non-centrosymmetric setting.

Empirical correction (DIFFABS)

A theorectical crystal shape is refined which minimizes R-values. **I. e. the data is made to best fit the model.** While there were justifications for the use of this method in linear-detector times, these do not exist anymore.

Do not use!