Chemical Crystallography and Structural Chemistry

VO 270287

Lecture № 5 — 28th April 2022

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Course Details

3rd	March	Lecture № 1	10th	March	Lecture № 2
17th	March	**no lecture**	24th	March	Exercise № 1
31st	March	Lecture № 3			
7th	April	Discussion Ex. 1	14th	April	**Easter break**
21st	April	**Easter break**	28th	April	Lecture № 4
5th	May	Lecture № 5	12th	May	**no lecture**
19th	May	Lecture № 6	26th	May	Exercise № 3
2nd	June	Lecture № 7	8th	June	Lecture № 8
16th	June	Exercise № 4	23rd	June	Lecture № 9
30th	June	**no lecture**			

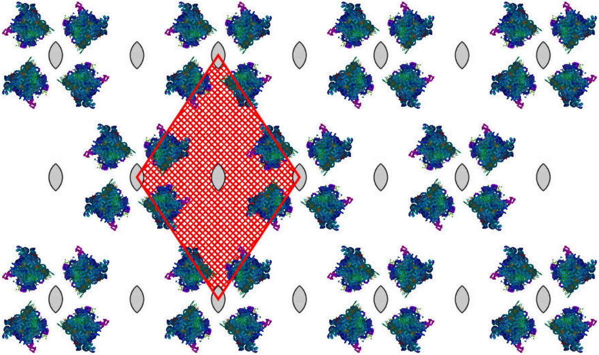
Previous Lecture

- Symmetry operations without and with translation
- 32 crystallographic point groups
- 230 crystallographic space group
- Matrix presentation of symmetry operations
- International Tables of crystallography
- Unit cell: definitions, conventions, choices

Contents

1 Unit Cell, Asymmetric Unit, Relation with Symmetry

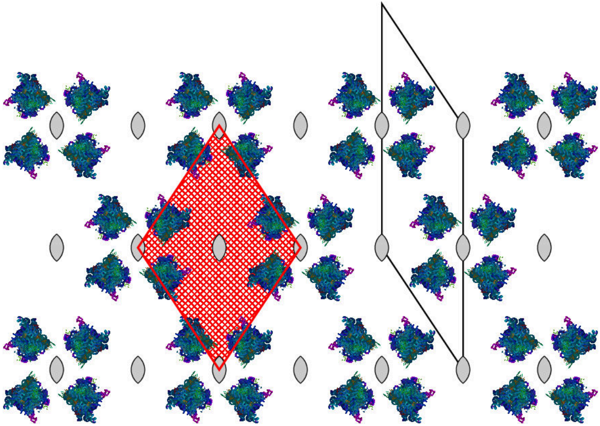
Choice of Unit Cell



- Place origin of unit cell with position of one of the symmetry elements: simplifies matrix description:

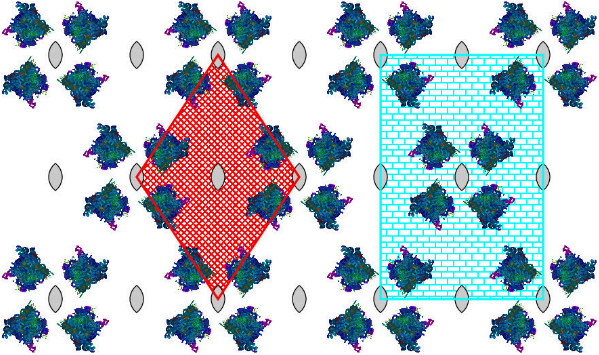
$$(x'y'z') = R(xyz)$$

Choice of Unit Cell



Every crystal possesses a unit cell with no symmetry element *inside* the cell. This unit cell is named the **primitive cell**.

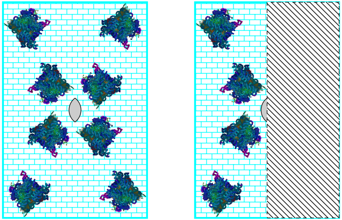
Choice of Unit Cell



- The **primitive cell** does not necessarily reflect the crystal symmetry
- here: 2-fold axes, but angles $\neq 90^\circ$
- By convention: choose as unit cell the smallest cell which reflects the symmetry, *e.g.* trigonal (3-fold rotation axis) or hexagonal (6-fold rotation axis) system : $\gamma = 120^\circ$

Asymmetric unit

The unit cell is the smallest box that creates the entire crystal solely by integer translations.



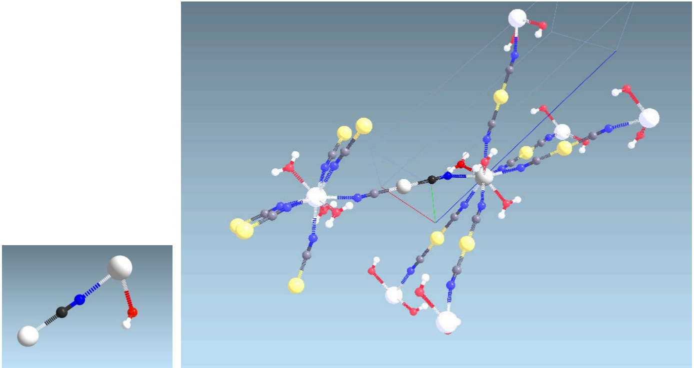
The **asymmetric unit** is the smallest box that creates the entire crystal from integer translations and all symmetry operations of the space group.

All atoms and molecules inside the asymmetric unit are independent from each other and never symmetry related

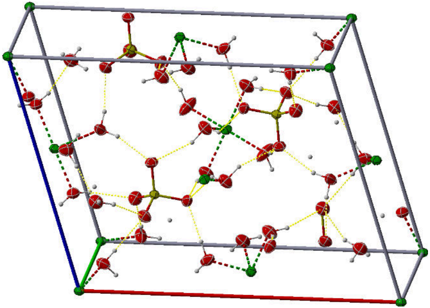
Crystallography determines the atom positions only inside the unit cell. Everything else is derived.

Example: $La[Au(CN)_2]_3 \cdot 3H_2O$, **Space group:** $P6_3/mcm$ **[1]**

The asymmetric unit does not always make chemical sense:

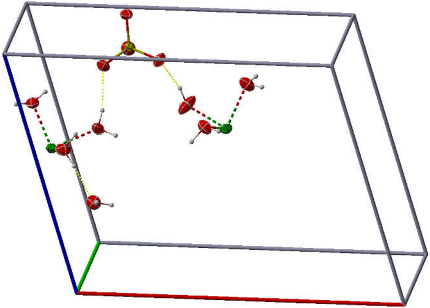


Example: $Fe^{II}SO_4 \cdot 6H_2O$



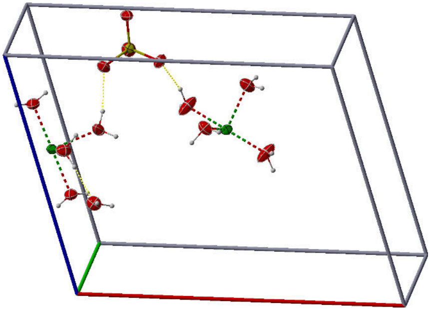
- full unit cell
- hydrogen bonds
- can be overwhelming
- “single H-atoms”: rest of H_2O outside unit cell

Example: $Fe^{II}SO_4 \cdot 6H_2O$



- asymmetric unit
- crystallographically complete
- chemically incomplete

Example: $Fe^{II}SO_4 \cdot 6H_2O$



- "GROW" command of many graphical programs
- chemically sensible structure
- computer guessed, may not be perfect: incomplete coordination of Fe

7 Crystal Systems [2]

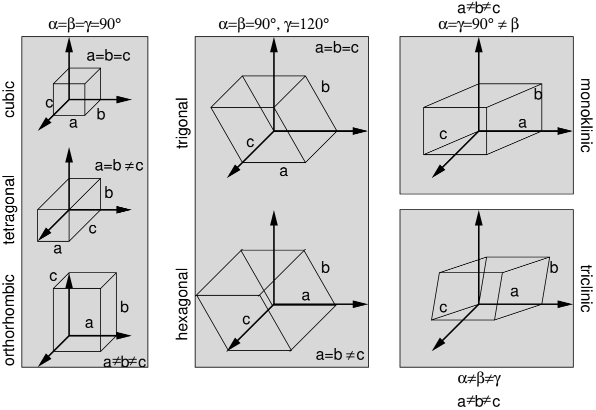
The 7 crystal systems [2]

Indepently from the content of the unit cell, the unit cell parameters $a, b, c, \alpha, \beta, \gamma$, can be classified according to regularity. These classifications result in the **seven crystal systems**

System		Conditions lengths	Conditions angles
triclinic	a	none	none
monoclinic	m	none	$\alpha = \gamma = 90°$
trigonal	h	$a = b = c$	$\alpha = \beta = 90°$ $\gamma = 120°$
hexagonal	h	$a = b$	$\alpha = \beta = 90°$ $\gamma = 120°$
orthorhombic	o	none	$\alpha = \beta = \gamma = 90°$
tetragonal	t	$a = b$	$\alpha = \beta = \gamma = 90°$
cubic	c	$a = b = c$	$\alpha = \beta = \gamma = 90°$

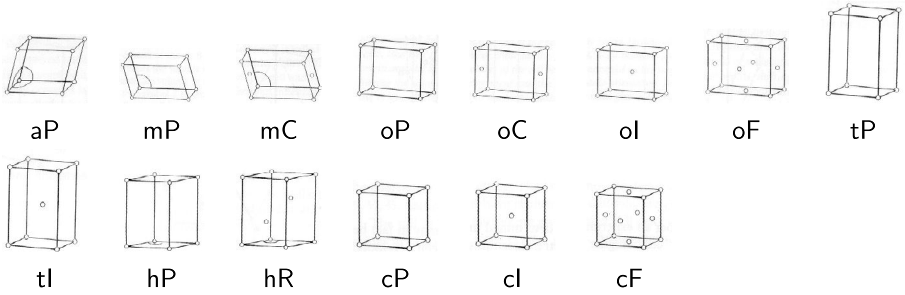
The 7 crystal systems [2]

Indepently from the content of the unit cell, the unit cell parameters $a, b, c, \alpha, \beta, \gamma$, can be classified according to regularity. These classifications result in the **seven crystal systems**



14 Bravais lattices [2]

7 crystal systems plus the requirement that the unit cell reflects the symmetry results in **14 Bravais lattices**:



Dots: Positions of symmetry elements

14 Bravais lattice — naming conventions

- lower case letters (a, m, h, o, t, c): crystal system (shape of cell).
- upper case letters (P, C, F, I, R): Symmetry. They present positions of symmetry elements within the unit cell in addition to the unit cell corners.

  P **p**rimitiv, symmetry elements only at corners

  C **C**-centred: Symmetry element at centre of C-faces (spanned by $\vec{a}$ and $\vec{b}$); (correspondingly: A- and B)

  F **f**ace centred (centred at each face)

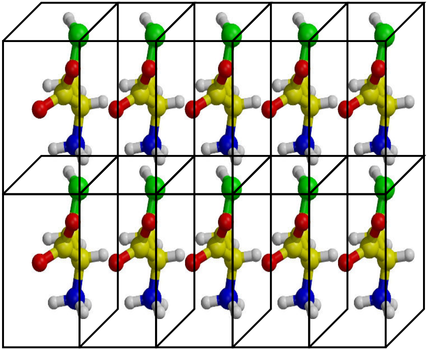
  I body centred: at the centre of the cell (German: **i**nnenzentriert)

  R **r**hombohedral

- the (P, C, F, I, R) are the same as in the Hermann-Mauguin names for space groups ($P2_12_12$, $C2/c$, ...)

Crystal system $\neq$ Space group

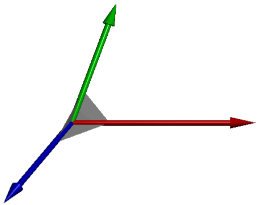
Do not draw conclusions on the space group from the shape of the unit cell: the unit cell **also** depends on the cell content.



orthorhombic box, non-symmetric space group $P1$

Positions and naming of unit cell axes: Conventions

- The origin $(0, 0, 0)$ is placed at a position of high symmetry. If present, it is placed at a centre of inversion
- There are $6 \times 4 \times 2 = 48$ possibilities to name the axes as $\vec{a}$, $\vec{b}$, und $\vec{c}$
- Conventions:
  1. right-handed coordinate system
  2. highest possible symmetry
  3. small as possible volume of unit cell
  4. $a \leq b \leq c$



(see *e.g.* http://xrayweb.chem.ou.edu/notes/symmetry.html)

2 Axis settings and Re-indexing

Axis settings and Re-indexing

- Despite these conventions, *some* space groups still have several possible axis settings
- For a single data set, the choice is arbitrary
- when two data sets or more are collected, care must be taken to index both consistently
- Modern programs automatically take care of consistent indexing.

Axis settings and Re-indexing

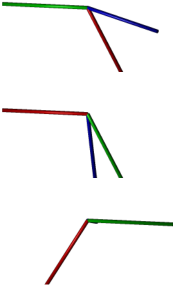
Example: trigonal space group P3

```
!!! WARNING !!! SOLUTION MAY NOT BE UNIQUE.

UNIT_CELL_A-AXIS=  -140.027  -180.486   -28.163
UNIT_CELL_B-AXIS=   188.097    21.258  -130.933
UNIT_CELL_C-AXIS=   123.664  -120.609   158.073

UNIT_CELL_A-AXIS=   188.097    21.258  -130.933
UNIT_CELL_B-AXIS=  -140.027  -180.486   -28.163
UNIT_CELL_C-AXIS=  -123.664   120.609  -158.073

UNIT_CELL_A-AXIS=    48.070  -159.228  -159.096
UNIT_CELL_B-AXIS=  -188.097   -21.258   130.933
UNIT_CELL_C-AXIS=  -123.664   120.609  -158.073
```



Axis settings and Re-indexing

- Single data set: choice of axis settings is irrelevant, each one is equally good
- Several data sets: with “wrong” settings, intensities do not match weil unterschiedlich indiziert
- either from the same crystal or different crystal
- re-indexing of second data set required in order to match intensities of the first one → **Reindexing of the coordinate system required**
- Worst case: testing of all possibilities
- Already mentioned: automated in modern software

3 Symmetry and X-ray data

Symmetry and X-ray data

Overview

- Effect of symmetry on X-ray data
- Friedel's law
- Laue groups: point groups in reciprocal space

Note: Calculation of reflex intensities

Once the chemical composition *i.e. atom types and their positions*, of the asymmetric unit is know, one can calculate the electron density $\rho(x,y,z)$. The intensity of every reflection can be calculated from the electron density $\rho(x,y,z)$[1]

$$I(hkl) = \left| \int_{V(\text{u.c.})} \rho(x,y,z) e^{2\pi i(hx+ky+lz)} d^3x \right|^2$$

---

[1] *International Tables* Volume B, Ch. 1.2

Symmetry in reciprocal space

Reminder: A symmetry operation $(R, \vec{t})$ leaves the entire crystal, and in particular the unit cell, unchanged, *i.e.* for every point in the unit cell:

$$\rho(R\vec{x} + \vec{t}) = \rho(\vec{x}) \text{“u.c.”} = R \cdot \text{“u.c.”} + \vec{t}$$

This translates towards the intensities:

$$\begin{aligned}
\Rightarrow I(hkl) &= \left| \int_{V(\text{u.c.})} \rho(x, y, z) e^{2\pi i (hx + ky + lz)} d^3 x \right|^2 \\
&= \left| \int_{V(\text{u.c.})} \rho(R\vec{x} + \vec{t}) e^{2\pi i (\vec{h}^T (R\vec{x} + \vec{t}))} d^3 (R\vec{x} + \vec{t}) \right|^2 \\
&= I(R^T \vec{h})
\end{aligned}$$

(The last step include quite some calculations)

This means: The intensities of the two reflections (h, k, l) and $R(h, k, l)$ are identical.

Symmetry in reciprocal space

For every symmetry operation $(R, \vec{t})$ of the space group of a crystal:

$$I(\vec{h}_1) = I(\vec{h}_2 = R^T \vec{h}_1) = I(\vec{h}_3 = R^T R^T \vec{h}_1) = \dots$$

- Crystal symmetry also means symmetry for the reflections
- Translational symmetry is “dropped” in reciprocal space
- Translational symmetry results in a phase shift, that cannot be measured.

Friedel's Law

Even without any symmetry, *i.e.* in all space groups including $P1$:

$$I(h,k,l) = I(\bar{h},\bar{k},\bar{l})$$

- Reciprocal space **always** has a centre of inversion. This is called Friedel's law[2]
- Later we will see that Friedel's law is only an approximation. Deviations are used to determine the absolute configuration.

---

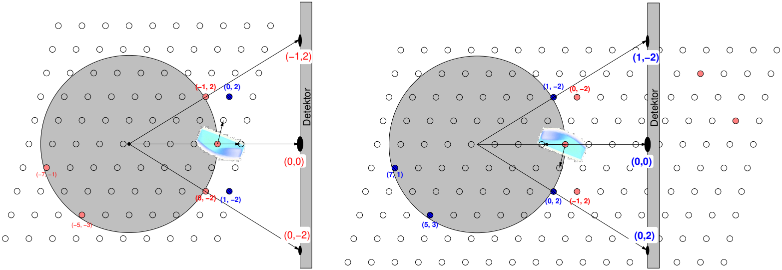
[2] Georges Friedel, 1865–1933

Excursus: Mathematics for Friedel's Law

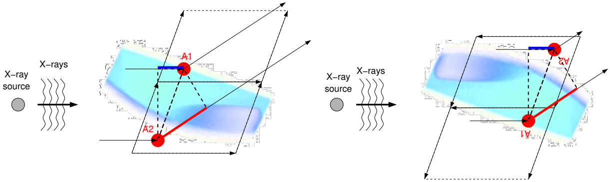
$$
\begin{aligned}
I(\bar{h}\bar{k}\bar{l}) &= \left|\int_{V(\text{E.Z.})} \rho(x,y,z) e^{2\pi i(\bar{h}x+\bar{k}y+\bar{l}z)} d^3x\right|^2 \\
&= \left|\int_{V(\text{E.Z.})} \rho(x,y,z) e^{-2\pi i(hx+ky+lz)} d^3x\right|^2 \\
&= \int_{V(\text{E.Z.})} \rho(x,y,z) e^{-2\pi i(hx+ky+lz)} d^3x \times \left(\int_{V(\text{E.Z.})} \rho(x,y,z) e^{-2\pi i(hx+ky+lz)} d^3x\right)^* \\
&= \int_{V(\text{E.Z.})} \rho(x,y,z) e^{-2\pi i(hx+ky+lz)} d^3x \times \int_{V(\text{E.Z.})} \rho(x,y,z) e^{2\pi i(hx+ky+lz)} d^3x \\
&= \left(\int_{V(\text{E.Z.})} \rho(x,y,z) e^{2\pi i(hx+ky+lz)} d^3x\right)^* \times \int_{V(\text{E.Z.})} \rho(x,y,z) e^{2\pi i(hx+ky+lz)} d^3x \\
&= \left|\int_{V(\text{E.Z.})} \rho(x,y,z) e^{2\pi i(hx+ky+lz)} d^3x\right|^2 \\
&= I(hkl)
\end{aligned}
$$

Measurement of Friedel pairs

Two reflections $I(hkl)$ and $I(\bar{h}\bar{k}\bar{l})$ form a **Friedel pair**. They can be measured *e.g.* by rotation the crystal by $180°$



Phase difference of Friedel pairs



$$\Delta_{\text{left}} = -\Delta_{\text{right}}$$

$$\Rightarrow \delta_{\text{left}} = -\delta_{\text{right}} \qquad (\delta = 2\pi\Delta/\lambda)$$

negative phase, same path difference:
$I(hkl) = I(\bar{h}\bar{k}\bar{l})$ and $\Phi(hkl) = -\Phi(\bar{h}\bar{k}\bar{l})$

Laue groups

- Crystals belong to one of 230 space groups
- The diffraction pattern contains the symmetry of the space group, but:
    1. no translational component
    2. always centre of inversion (Friedel's law)
- This results in a subset of groups: the 11 **Laue groups**.

11 Laue groups

Crystal system	**Laue group**	**point group**
Triclinic	$\bar{1}$	1, $\bar{1}$
Monoclinic	$2/m$	2, m, 2/m
Orthorhombic	mmm	222, mm2, mmm
Tetragonal	$4/m$	4, $\bar{4}$, 4/m
	$4/mmm$	422, 4mm, $\bar{4}2m$, 4/mmm
Trigonal	$\bar{3}$	3, $\bar{3}$
	$\bar{3}m$	32, 3m, $\bar{3}m$
Hexagonal	$6/m$	6, $\bar{6}$, 6/m
	$6/mmm$	622, 6mm, $\bar{6}m2$, 6/mmm
Cubic	$m\bar{3}$	23, $m\bar{3}$
	$m\bar{3}m$	432, $\bar{4}3m$, $m\bar{3}m$

http://de.wikipedia.org/wiki/Lauegruppe

Extinctions

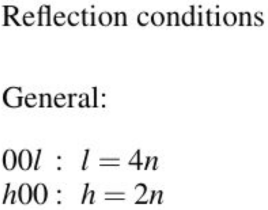
- Extinctions are reflections with systematically zero intensity.
- Extinctions occur in non-primitive Bravais lattices or in the presence of symmetry elements with translational part, *i.e.* glide planes and screw axes.
- Extinctions are important for space group determination, *e.g.* to differentiate between $P4$ and $P4_3$.
- The "Int. Tabl. Vol. A" list the "general reflection conditions", *i.e.* those reflections with non-zero intensity:

  $P3_1$ **(No. #144)** $00l : l = 3n$

  - only if $(hkl) = \dots (00-6), (00-3), (003)$, …: Intensities $\neq 0$;
  - reflections (001), (002), (004), (005), …, should have zero intensity

Example: Extinctions in $P4_32_12$

- Reflection condition: $h00 : h = 2n$ and $00l : l = 4n$
- Only reflections with $k = 0, l = 0$ and h even should have non-zero intensity
- All reflections with $k = 0, l = 0$ and h odd should have zero intensity



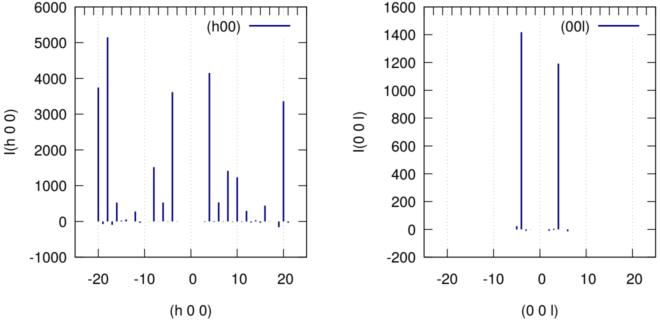
Reflection conditions

General:

$00l \; : \; l = 4n$
$h00 : \; h = 2n$

Example: Extinctions in $P4_32_12$

- Reflection condition: $h00: h = 2n$ and $00l: l = 4n$
- Only reflections with $k = 0, l = 0$ and h even should have non-zero intensity
- All reflections with $k = 0, l = 0$ and h odd should have zero intensity
- Example: Lysozyme data set



Example: Extinctions in $P4_32_12$

Output from the program `xprep` for Lysozyme data:

```
Systematic absence exceptions:
        41/43  42    n--   -b-   -c-   -n-  -21-   --c
N           9     5   648   539   530   527    34   375
N I>3s      0     0   340   236   265   233     0   183
<I>       0.6   0.8  43.9  32.2  45.8  37.4   0.9  56.0
<I/s>     0.3   0.4   8.5   8.2   9.5   7.8   0.3  11.5

    Space Group     No.    Type    Axes   CSD  R(sym) N(eq)   Syst.
[A] P4(1)2(1)2      # 92   chiral    1    245  0.067 140065   0.4
[B] P4(3)2(1)2      # 96   chiral    1    245  0.067 140065   0.4
```

Based on the data alone, we cannot distinguish between $P4_12_12$ and $P4_32_12$ (due to Friedel's law). One has to solve the structure and see which one makes sense. For protein structures: the right space group will consist of L-amino acids, the wrong one of D-amino acids.

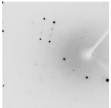
Summary: Space group determination

- Crystal symmetry is present in reflection data intensities
- No translational symmetry in reciprocal space
- Only one of the 11 Laue groups can be determined from symmetry in intensities
- Systematic absences are important to distinguish between space groups within a Laue group

4 Experimental procedure: from data collection to structure

From Data Collection to Structure

Data collection → **Data integration** → **Data Scaling**



several GB

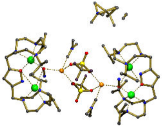
```
0 0 -1      2.7   0.9
0 0  1      4.0   1.0
0 0 -2 1'257.0  35.5
0 0 -2 1'600.0  42.7
```

several files, 100’s MB

```
0 0 -1      2.8  0.55
0 0  1      3.8  0.63
0 0 -2 1'432.0  95.7
0 0 -2 1'282.0  85.9
```

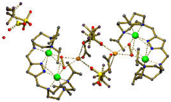
1 “hkl”-file, 50MB

→ **Phasing**



Starting model

→ **Refinement**

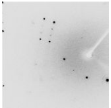


Chemically sensible model

Data Collection

Data collection → **Data integration** → **Data Scaling**

Data collection



several GB

Data integration

```
0 0 -1      2.7   0.9
0 0  1      4.0   1.0
0 0 -2 1'257.0   35.5
0 0 -2 1'600.0   42.7
```

several files, 100’s MB

Data Scaling

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0 0 -1      2.8   0.55
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0 0 -2 1'432.0   95.7
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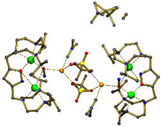
1 “hkl”-file, 50MB

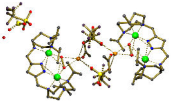
→ **Phasing** → **Refinement**

Phasing



Starting model

Refinement

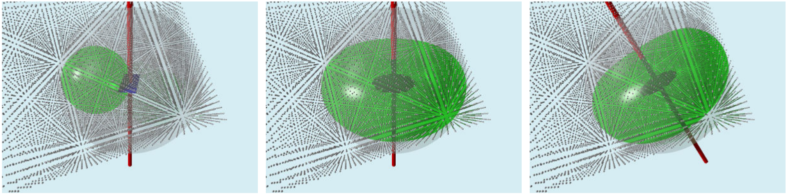


Chemically sensible model

How to collect good data

- Resolution limit $d_{\text{min}} = \lambda/2$ (or worse for poor quality crystals, *e.g.* protein crystals)
- Typical resolution limit $d_{\text{min}} = 0.84$ Å (resolution limit for publishing in Acta Crystallographica C)
- Reflections that can be measured theoretically: all Miller indices (hkl) with $\|h\vec{a^*} + k\vec{b^*} + l\vec{c^*}\| \leq 1/d_{\text{min}}$ ($\vec{a}^*, \vec{b}^*, \vec{c}^*$: reciprocal unit cell vectors)
- Multiple measurements per reflections improve data quality

Data completeness and multiplicity

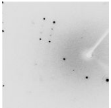


- grey dots: reciprocal lattice
- grey sphere: resolution limit, radius $2/\lambda$
- green sphere: Ewald sphere, radius $1/\lambda$
- red bar: rotation axis of crystal

Rotation about a single axis by 360° captures all reflections inside green torus. Capturing all reflections inside grey "resolution shell" requires several orientations.

Data Integration

Data collection → **Data integration** → **Data Scaling**



several GB

```
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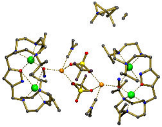
several files, 100’s MB

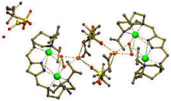
```
0 0 -1      2.8  0.55
0 0  1      3.8  0.63
0 0 -2 1'432.0  95.7
0 0 -2 1'282.0  85.9
```

1 “hkl”-file, 50MB

→ **Phasing** → **Refinement**



Starting model



Chemically sensible model

Data Integration

Data integration comprises

1. Indexing: Determination of unit cell dimensions, orientation of the crystal, point group
2. Extraction of spot intensities from detector images.
3. Optimisation of experimental parameters

Programs for data integration (incomplete)

Saint Licensed by Bruker AXS. Specific to Bruker programs. Good for data from twinned crystals. Derived from XDS.

X-Area Software suite distributed with Stoe X-ray diffractometers. Free to use. Very good interactive indexing routine, good for twinned data.

XDS Free for non-commercial users (`http://xds.mpimf-heidelberg.mpg.de`). Supports nearly all detector formats, very well documented. Very fast.

DIALS Free for non-commercial users. Very active development. (`https://dials.diamond.ac.uk/`)

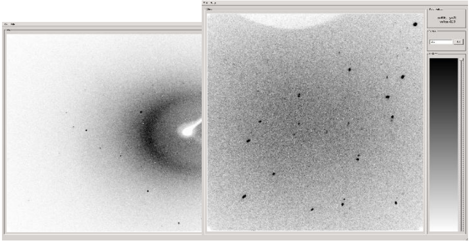
EVAL Suite Free for non-commercial users (`http://www.crystal.chem.uu.nl/distr/eval`). Can integrate *e.g.* incommensurate crystals

Crysalis Pro Licensed by Rigaku (`https://www.rigaku.com/products/smc/crysalis`)

iMosflm Free for non-commercial users, distributed with CCP4 (`http://www.ccp4.ac.uk`)

HKL3000 Very good visualisation GUI for fine-tuning of parameters. very popular in the US (`https://hkl-xray.com/`)

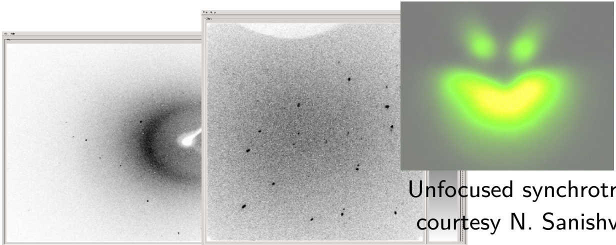
Indexing



"Ewald sphere backwards:"

- find 200–1000 **strong** spots
- backtransform into reciprocal space (Laue equations)
- find a lattice and a suitable basis
- basis for reciprocal lattice corresponds to reduced unit cell constants

Indexing



Unfocused synchrotron beam, courtesy N. Sanishvili, APS, Chicago, USA

Possible reasons for indexing problems:

- Incorrect parameters: detector distance, direction of rotation, wavelength, especially at synchrotrons
- Too few reflections
- Distorted spots (lattice defects, unfocused beam)
- Alien spots (ice, metal, contaminant)
- multiple lattices *twins*

References

[1] Julie Clarissa F. Colis et al. ‘Structural studies of lanthanide ion complexes of pure gold, pure silver and mixed metal (gold–silver) dicyanides’. In: *Dalton Trans.* (2005), pp. 675–679. DOI: `10.1039/B413967D`.

[2] W. Massa. *Crystal Structure Determination*. Springer Verlag Berlin, Heidelberg, 2002.