# Chemical Crystallography and Structural Chemistry

VO 270287

Lecture № 6 — 29th April 2021

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## Reminder: Start the recording!

# Contents

# 1 Unit Cell: Axes and Reindexing

## 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)

## 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
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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
```
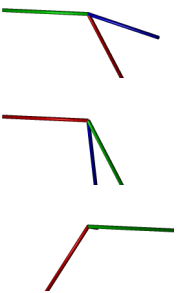



## Axis settings and Re-indexing

- Single data set: choice of axis settings is irrelevant, each one is equally good
- Several data sets: with "wrong" settings, intensities do not match
- 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

# 2 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:

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

(The last step includes 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:

$$I(\vec{h}) = I(R^T \vec{h}) = I(R^T R^T \vec{h}) = \ldots$$

- Crystal symmetry also means symmetry for the reflections
- Translational symmetry has no effect on intensities

## 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]

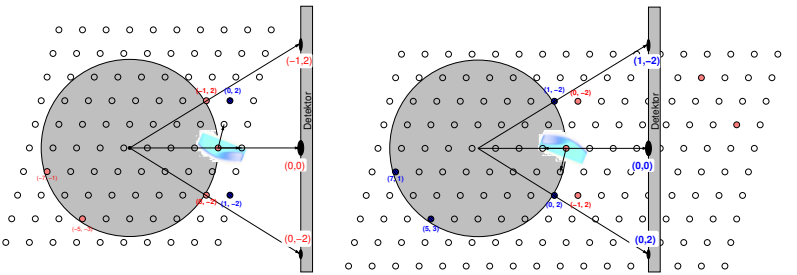
[2] Georges Friedel, 1865–1933

## Excursus: Mathematics for Friedel's Law

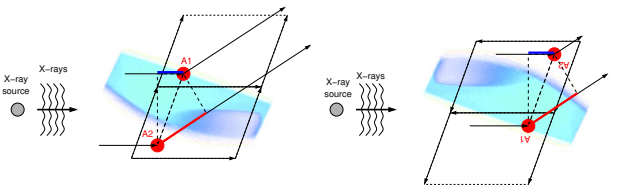
$$
\begin{aligned}
I(\bar{h}\bar{k}\bar{l}) &= \left| \int_{V(\text{E.Z.})} \rho(x,y,z) e^{2\pi i(\bar{h}x+\bar{k}y+\bar{l}z)} d^3x \right|^2 \\
&= \left| \int_{V(\text{E.Z.})} \rho(x,y,z) e^{-2\pi i(hx+ky+lz)} d^3x \right|^2 \\
&= \int_{V(\text{E.Z.})} \rho(x,y,z) e^{-2\pi i(hx+ky+lz)} d^3x * \left(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

## 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

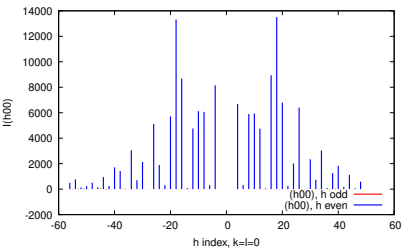
- Extinctions are reflections with systematically zero intensity.
- Extinctions occur in non-primitive Bravais lattices or in the presence of symmetry elements with translational part, *i.e.* glide planes and screw axes.
- Extinctions are important for space group determination, *e.g.* to differentiate 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 $(hkl) = \ldots(00-6)$, $(00-3)$, $(003)$, ...: 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
- 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         5     3  3490  2365  2359  2358    89  1549
N I>3s    0     0  2188  1256  1361  1275     0   931
<I>     0.9   0.9  97.0  64.6  80.7  65.4   0.8  85.0
<I/s>   0.2   0.2   8.2   6.7   7.3   6.6   0.4   7.5
Option  Space Group  No.  Type  Axes  CSD  R(sym) N(eq)  Syst. Abs.   CFOM
[A] P4(1)2(1)2     # 92  chiral   1   245  0.067 140065  0.4 /  6.6   1.99
[B] P4(3)2(1)2     # 96  chiral   1   245  0.067 140065  0.4 /  6.6   1.99
```

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.

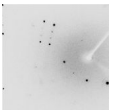
## Summary: Space group determination

- 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

# 3 Experimental procedure: from data collection to structure

## From Data Collection to Structure

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



several GB

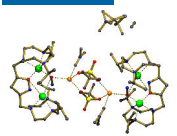
```
0  0 -1      2.7   0.9
0  0  1      4.0   1.0
0  0 -2 1'257.0  35.5
0  0 -2 1'600.0  42.7
```

several files, 100's MB

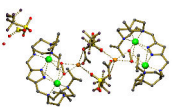
```
0  0 -1      2.8   0.55
0  0  1      3.8   0.63
0  0 -2 1'432.0  95.7
0  0 -2 1'282.0  85.9
```

1 "hkl"-file, 50MB

→ **Phasing** → **Refinement**



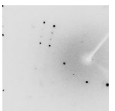
Starting model



Chemically sensible model

## Data Collection

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



several GB

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0 0 -1      2.7   0.9
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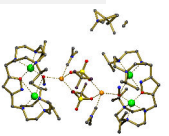
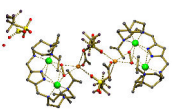
1 "hkl"-file, 50MB

→ Phasing → Refinement



Starting model

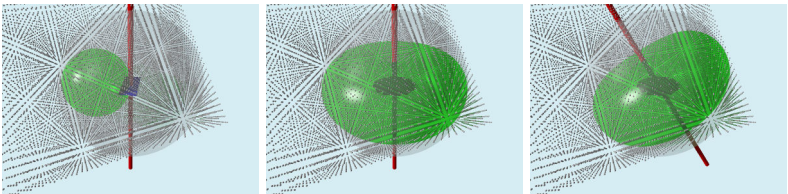


Chemically sensible model

## 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

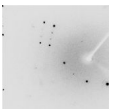


- grey dots: reciprocal lattice
- grey sphere: resolution limit, radius $2/\lambda$
- green sphere: Ewald sphere, radius $1/\lambda$
- red bar: rotation axis of crystal

Rotation about a single axis by $360^\circ$ 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

```
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

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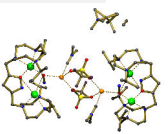
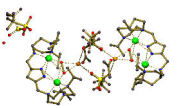
→ **Phasing** → **Refinement**



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/`)

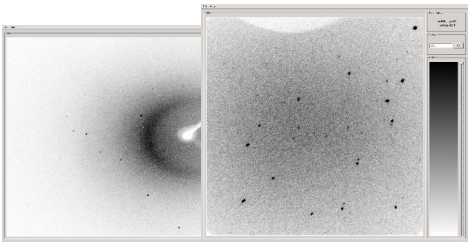
**EVAL Suite** Free for non-commercial users (`http://www.crystal.chem.uu.nl/distr/eval`). Can integrate *e.g.* incommensurate crystals

**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/`)

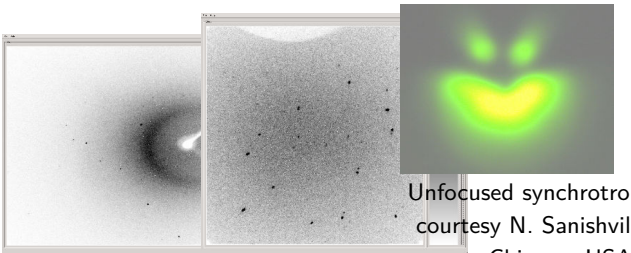
## Indexing



"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

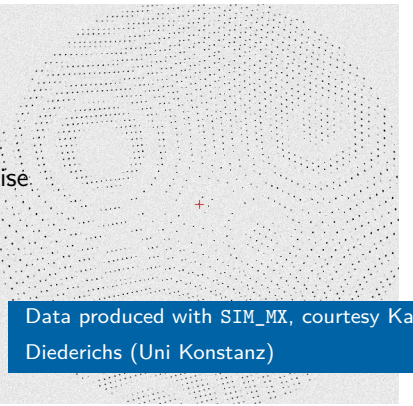
Possible reasons for indexing problems:

- 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*

# 4 Spot Intensity

## Ideal diffraction image

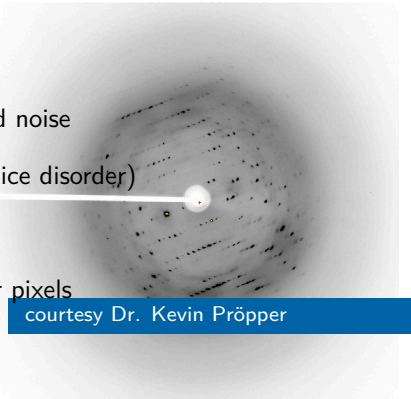
- no lattice disorder
- no background noise
- perfect beam



Data produced with `SIM_MX`, courtesy Kay Diederichs (Uni Konstanz)

## Realistic diffraction image

- strong background noise
- smeary spots (lattice disorder)
- spot overlap
- saturated detector pixels
- finite resolution



courtesy Dr. Kevin Pröpper