

Chemical Crystallography and Structural Chemistry

VO 270287

Lecture N° 5 — 22nd April 2021

Dr. Tim Grüne
Centre for X-ray Structure Analysis
Faculty of Chemistry
University of Vienna
tim.gruene@univie.ac.at

Reminder: Start the recording!

Contents

- | | | |
|----------|--|----------|
| 1 | Symmetry and Space Groups (continued) | 4 |
| 2 | Choice of Unit Cell | 9 |

1 Symmetry and Space Groups (continued)

Presentation of Symmetry in the *International Tables*

The *International Tables for Crystallography* contain a description for each of the 230 space groups.

Each description contains the sections

- **Symmetry Operations**
- **Positions**

Example Space group $R\bar{3}c$ (No. 167) [1]

CONTINUED

No. 167

 $R\bar{3}c$ **Symmetry operations**For $(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$ + set

- | | | |
|--|--|--|
| (1) $t(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$ | (2) $3^+(0, 0, \frac{1}{3}) \quad \frac{1}{3}, \frac{1}{3}, z$ | (3) $3^-(0, 0, \frac{1}{3}) \quad \frac{1}{3}, 0, z$ |
| (4) $2(\frac{1}{2}, \frac{1}{2}, 0) \quad x, x - \frac{1}{6}, \frac{z}{12}$ | (5) $2(\frac{1}{2}, 0, 0) \quad x, \frac{1}{3}, \frac{z}{12}$ | (6) $2 \quad \frac{1}{3}, y, \frac{z}{12}$ |
| (7) $\bar{1} \quad \frac{1}{3}, \frac{1}{3}, \frac{z}{6}$ | (8) $3^+ \quad \frac{1}{3}, -\frac{1}{3}, z; \quad \frac{1}{3}, -\frac{1}{3}, \frac{z}{6}$ | (9) $3^- \quad \frac{1}{3}, \frac{1}{3}, z; \quad \frac{1}{3}, \frac{1}{3}, \frac{z}{6}$ |
| (10) $g(\frac{1}{6}, -\frac{1}{6}, \frac{z}{6}) \quad x + \frac{1}{3}, \bar{x}, z$ | (11) $g(\frac{1}{6}, \frac{1}{6}, \frac{z}{6}) \quad x + \frac{1}{3}, 2x, z$ | (12) $g(\frac{2}{3}, \frac{1}{3}, \frac{z}{6}) \quad 2x, x, z$ |

Generators selected (1); $t(1, 0, 0)$; $t(0, 1, 0)$; $t(0, 0, 1)$; $t(\frac{2}{3}, \frac{1}{3}, \frac{1}{3})$; (2); (4); (7)**Positions**

Multiplicity,
Wyckoff letter,
Site symmetry

Coordinates

 $(0, 0, 0) + (\frac{2}{3}, \frac{1}{3}, \frac{1}{3}) + (\frac{1}{3}, \frac{2}{3}, \frac{2}{3}) +$

36	<i>f</i>	1	(1) x, y, z	(2) $\bar{y}, x - y, z$	(3) $\bar{x} + y, \bar{x}, z$
			(4) $y, x, \bar{z} + \frac{1}{2}$	(5) $x - y, \bar{y}, \bar{z} + \frac{1}{2}$	(6) $\bar{x}, \bar{x} + y, \bar{z} + \frac{1}{2}$
			(7) $\bar{x}, \bar{y}, \bar{z}$	(8) $y, \bar{x} + y, \bar{z}$	(9) $x - y, x, \bar{z}$
			(10) $\bar{y}, \bar{x}, z + \frac{1}{2}$	(11) $\bar{x} + y, y, z + \frac{1}{2}$	(12) $x, x - y, z + \frac{1}{2}$

18	<i>e</i>	.2	$x, 0, \frac{1}{4}$	$0, x, \frac{1}{4}$	$\bar{x}, \bar{x}, \frac{1}{4}$	$\bar{x}, 0, \frac{1}{4}$	$0, \bar{x}, \frac{1}{4}$	$x, x, \frac{1}{4}$
----	----------	----	---------------------	---------------------	---------------------------------	---------------------------	---------------------------	---------------------

Reflection conditions

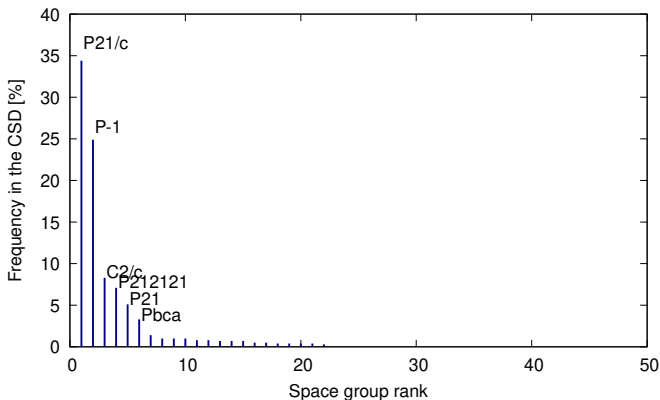
General:

$hkil : -h + k + l = 3n$
 $hki0 : -h + k = 3n$
 $hh\bar{2}hl : l = 3n$
 $h\bar{h}0l : h + l = 3n, l = 2n$
 $000l : l = 6n$
 $h\bar{h}00 : h = 3n$

Special: as above, plus

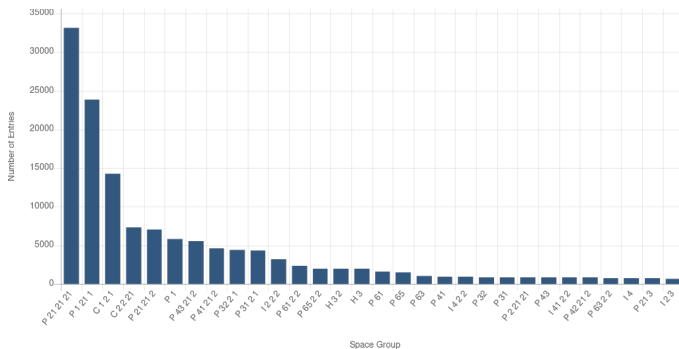
no extra conditions

Frequency of space groups for chemical compounds (CSD, April 2020)



<http://www.ccdc.cam.ac.uk/>

Frequency of space groups for Macromolecules (PDB, April 2020)



<http://www.rcsb.org>

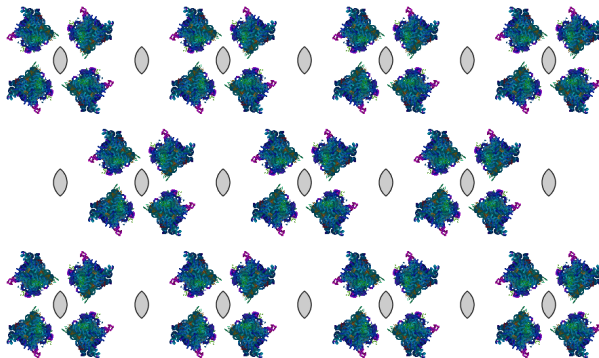
2 Choice of Unit Cell

Choice of Unit Cell

Overview:

- primitive cell
- asymmetric unit
- 7 crystal classes
- 14 Bravais lattices

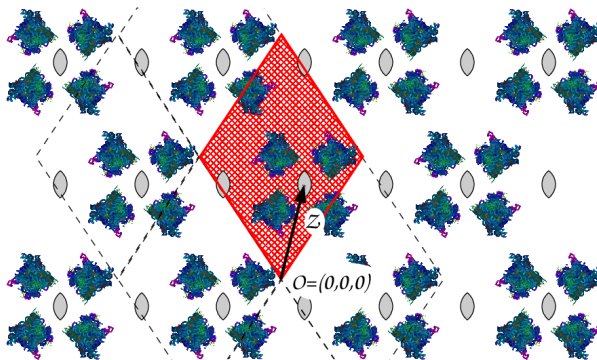
Choice of Unit Cell



Nature determines symmetry, not *vice versa*

- The position of the molecules determines the position of the symmetry operators
- Here: **2-fold** rotation axes (not 4-fold!)

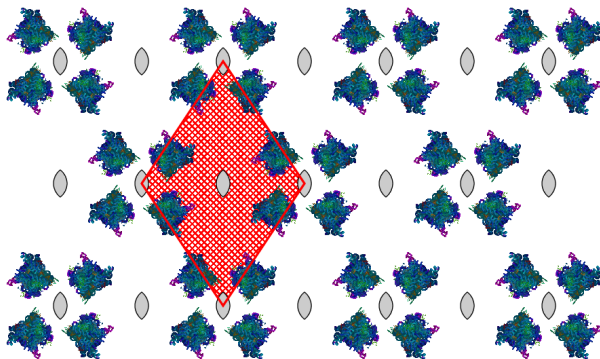
Choice of Unit Cell



- Uni cell: Helper construction, molecules are “ignorant” of the unit cell
- Condition for unit cell: integer translations cover the entire crystal
- If placed arbitrarily: matrix description becomes awkward:

$$(x'y'z') = R((xyz) - Z) + Z$$

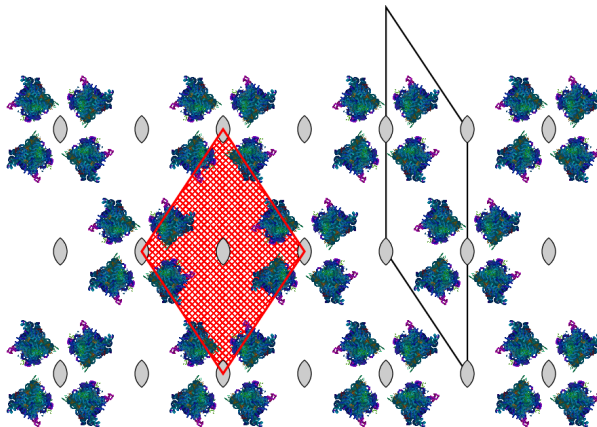
Choice of Unit Cell



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

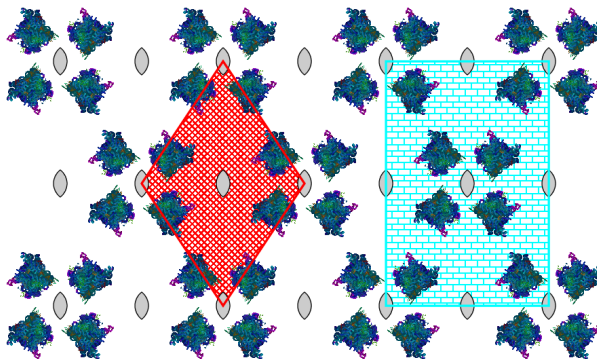
$$(x'y'z') = R(xyz)$$

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**.

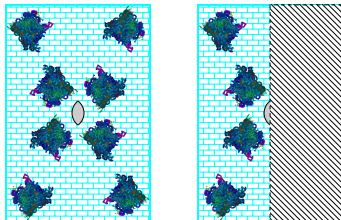
Choice of Unit Cell



- 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.



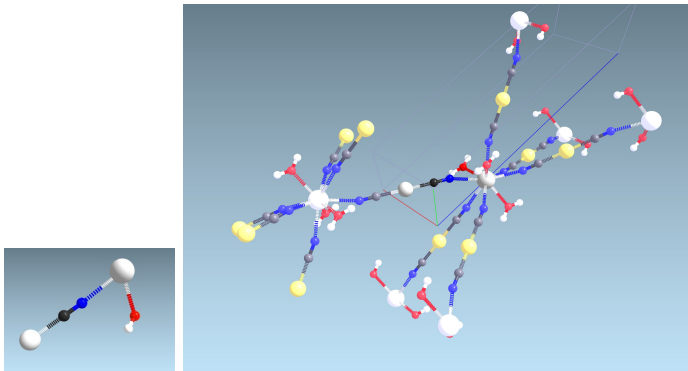
The **asymmetric unit** is the smallest box that creates the entire crystal from integer translations and all symmetry operations of the space group.

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:** $P6_3/mcm$
[2]

The asymmetric unit does not always make chemical sense:



7 Crystal Systems [3]

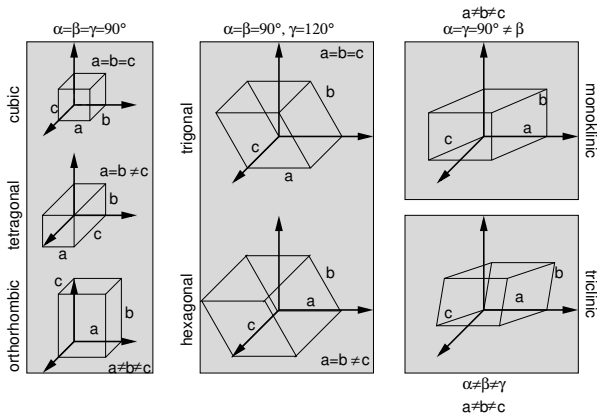
The 7 crystal systems [3]

Independently 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	$\alpha = \gamma = 90^\circ$
trigonal	h	$a = b = c$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$
hexagonal	h	$a = b$	$\alpha = \beta = 90^\circ$ $\gamma = 120^\circ$
orthorhombic	o	none	$\alpha = \beta = \gamma = 90^\circ$
tetragonal	t	$a = b$	$\alpha = \beta = \gamma = 90^\circ$
cubic	c	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$

The 7 crystal systems [3]

Independently 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 [3]

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



aP



mP



mC



oP



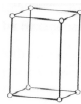
oC



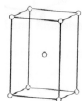
oI



oF



tP



tI



hP



hR



cP



cI



cF

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 primitiv, 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)

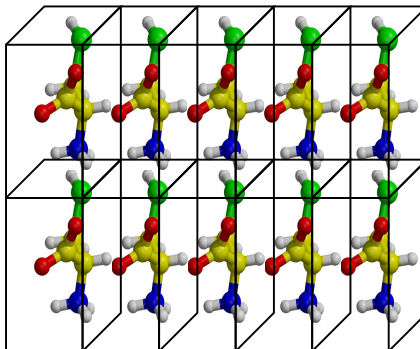
F face centred (centred at each face)

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

R rhomboedral

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

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
- when two data sets or more are collected, care must be taken to index both consistently
- 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
```

- Modern programs automatically take care of consistent indexing.

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 → **Umstellung der Achsen notwendig.**
- Worst case: testing of all possibilities
- Already mentioned: automated in modern software

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 known, 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 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:

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

- Crystal symmetry also means symmetry for the reflections
- Translational symmetry is “dropped” in reciprocal space

Friedel's Law

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

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

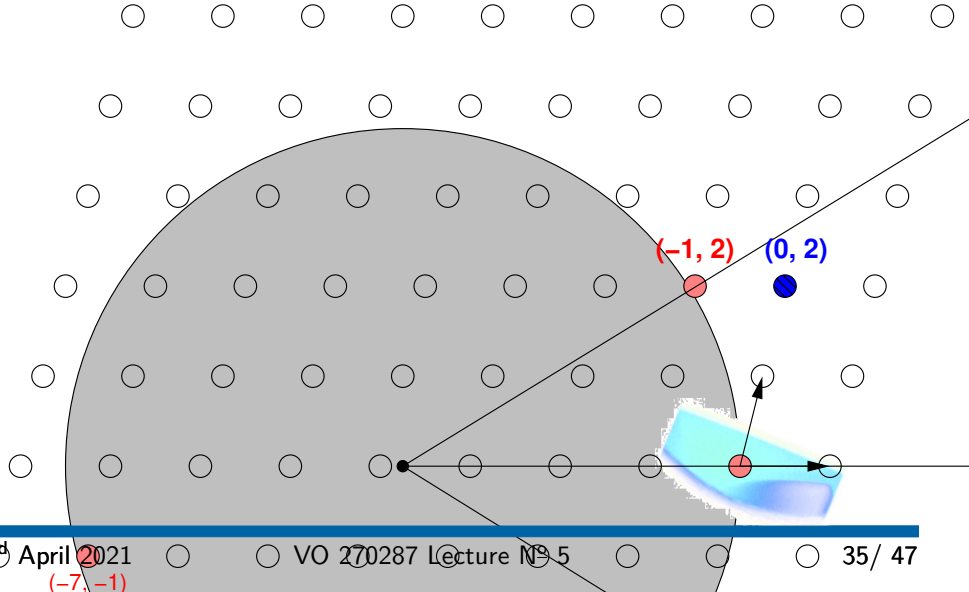
Reciprocal space **always** has a centre of inversion. This is called Friedel's law²

²Georges Friedel, 1865–1933

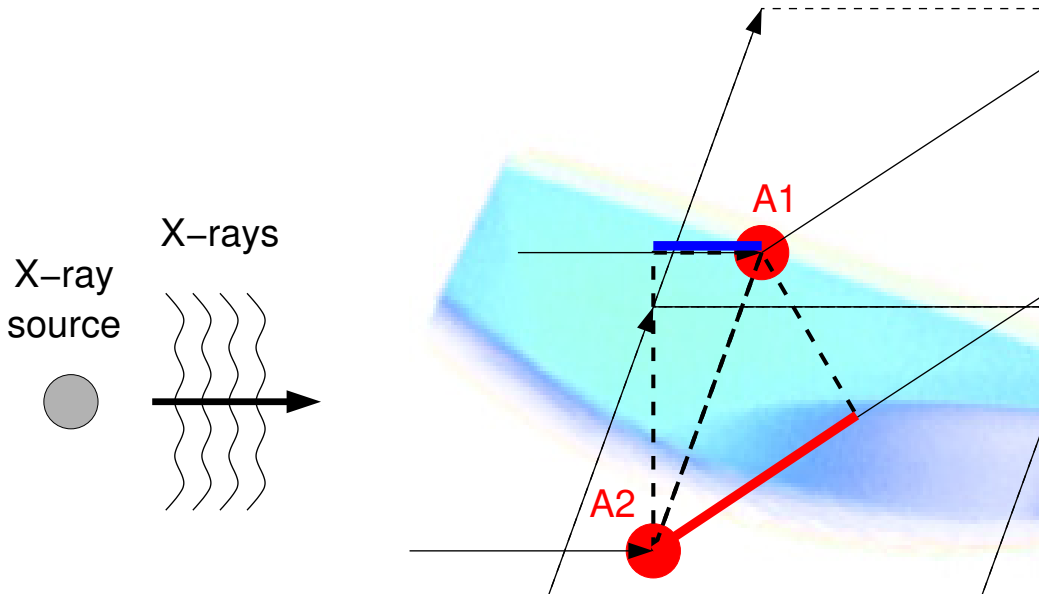
$$\begin{aligned} I(\bar{h}\bar{k}\bar{l}) &= \left| \int_{V(\text{E.Z.})} \rho(x, y, z) e^{2\pi i(\bar{h}x + \bar{k}y + \bar{l}z)} d^3x \right|^2 \\ &= \left| \int_{V(\text{E.Z.})} \rho(x, y, z) e^{-2\pi i(hx + ky + lz)} d^3x \right|^2 \\ &= \int_{V(\text{E.Z.})} \rho(x, y, z) e^{-2\pi i(hx + ky + lz)}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

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



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

($\delta = 2\pi\Delta/\lambda$:) negative phase, same path difference

since cos symmetric:

$$\cos(\delta_{\text{left}}) = \cos(-\delta_{\text{right}}) = \cos(\delta_{\text{right}})$$

no difference in total intensity

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

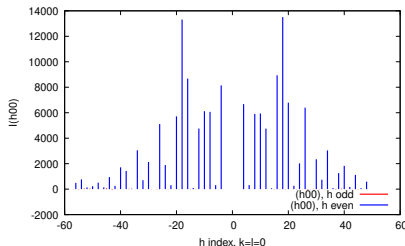
- Extinctions are reflections with systematically zero intensity.
- Extinctions occur in non-primitive Bravais lattices or in the presence of symmetry elements with translational part, *i.e.* glide planes and screw axes.
- Extinctions are important for space group determination, *e.g.* to differentiate 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 $(hkl) = \dots(00 - 6), (00 - 3), (003), \dots$: Intensities $\neq 0$;
- reflections $(001), (002), (004), (005), \dots$, 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	

Identical indices and Friedel opposites combined before calculating R

Option Space Group No. Type Axes CSD R(sym) N(eq) Syst. Abs.

[A]	$P4(1)2(1)2$	# 92	chiral	1	245	0.067	140065	0.4 /	6.6
[B]	$P4(3)2(1)2$	# 96	chiral	1	245	0.067	140065	0.4 /	6.6

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

Summary today's lecture

- Space groups and crystallographic point groups
- Choice of unit cell
- 7 Crystal systems and 14 Bravais lattices
- Symmetry in reciprocal space
- Space group determination

Next lecture: April 29th

References

- [1] Th Hahn, ed. *International Tables of Crystallography*. Vol. A. Wiley, 2006.
- [2] 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.
- [3] W. Massa. *Crystal Structure Determination*. Springer Verlag Berlin, Heidelberg, 2002.