Chemical Crystallography and Structural Chemistry

VO 270287

Lecture № 4 — 31st March 2022

Dr. Tim Grüne
Centre for X-ray Structure Analysis
Faculty of Chemistry
University of Vienna

tim.gruene@univie.ac.at

Course Details

3rd	March	Lecture № 1	10th	March	Lecture № 2
17th	March	**no lecture**	24th	March	Exercise № 1
31st	March	Lecture № 3			
7th	April	Lecture № 4	14th	April	**Easter break**
21st	April	**Easter break**	28th	April	Exercise № 2
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	23th	June	Lecture № 9
30th	June	**no lecture**			

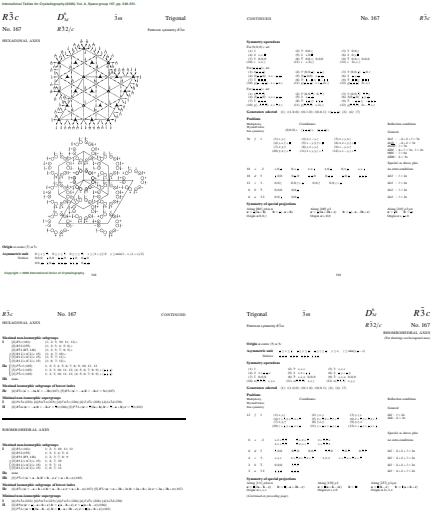
Previous Lecture

- Symmetry operations without and with translation
- 32 crystallographic point groups
- 230 crystallographic space group
- Matrix presentation of symmetry operations
- International Tables of crystallography

Contents

1 Presentation of Symmetry in the International Tables

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



Example Space group $R\bar{3}c$ (No. 167) (Int. Tables, [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) $3^+(0,0,\frac{1}{3})$ $\frac{1}{3},\frac{1}{3},z$	(3) $3^-(0,0,\frac{1}{3})$ $\frac{1}{3},0,z$
(4) $2(\frac{1}{3},\frac{1}{3},0)$ $x,x-\frac{1}{6},\frac{5}{12}$	(5) $2(\frac{1}{3},0,0)$ $x,\frac{1}{6},\frac{5}{12}$	(6) 2 $\frac{1}{3},y,\frac{5}{12}$
(7) $\bar{1}$ $\frac{1}{3},\frac{1}{6},\frac{1}{2}$	(8) $\bar{3}^+$ $\frac{1}{3},-\frac{1}{3},z;$ $\frac{1}{3},-\frac{1}{3},\frac{1}{6}$	(9) $\bar{3}^-$ $\frac{1}{3},\frac{2}{3},z;$ $\frac{1}{3},\frac{2}{3},\frac{1}{6}$
(10) $g(\frac{1}{6},-\frac{1}{6},\frac{5}{6})$ $x+\frac{1}{2},\bar{x},z$	(11) $g(\frac{1}{6},\frac{1}{3},\frac{5}{6})$ $x+\frac{1}{2},2x,z$	(12) $g(\frac{2}{3},\frac{1}{3},\frac{5}{6})$ $2x,x,z$

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 $(0,0,0)+$ $(\frac{2}{3},\frac{1}{3},\frac{1}{3})+$ $(\frac{1}{3},\frac{2}{3},\frac{2}{3})+$			Reflection conditions
36 f 1	(1) x,y,z	(2) $\bar{y},x-y,z$	(3) $\bar{x}+y,\bar{x},z$	General:
	(4) $y,x,\bar{z}+\frac{1}{2}$	(5) $x-y,\bar{y},\bar{z}+\frac{1}{2}$	(6) $\bar{x},\bar{x}+y,\bar{z}+\frac{1}{2}$	$hkil$: $-h+k+l=3n$
	(7) $\bar{x},\bar{y},\bar{z}$	(8) $y,\bar{x}+y,\bar{z}$	(9) $x-y,x,\bar{z}$	$hki0$: $-h+k=3n$
	(10) $\bar{y},\bar{x},z+\frac{1}{2}$	(11) $\bar{x}+y,y,z+\frac{1}{2}$	(12) $x,x-y,z+\frac{1}{2}$	$hh\bar{2}hl$: $l=3n$
				$h\bar{h}0l$: $h+l=3n,\ l=2n$
				$000l$: $l=6n$
				$hh\bar{h}00$: $h=3n$
				Special: as above, plus
18 e .2	$x,0,\frac{1}{4}$	$0,x,\frac{1}{4}$ $\bar{x},\bar{x},\frac{1}{4}$	$\bar{x},0,\frac{3}{4}$ $0,\bar{x},\frac{3}{4}$ $x,x,\frac{1}{4}$	no extra conditions

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

- Symmetry operation number (10): glide mirror plane $g(1/6, -1/6, 5/6)\ x+1/2, \bar{x}.z$:
  1. mirror all points of the unit cell at the plane $x + 1/2, \bar{x}, z$
  2. translate the points by the fractional vector $(1/6, -1/6, 5/6)$
- The "General position" number (10), $\bar{y}, \bar{x}, z + 1/3$:

$$x' = R_{11}x + R_{12}y + R_{13}z + t_1$$
$$y' = R_{21}x + R_{22}y + R_{23}z + t_2$$
$$z' = R_{31}x + R_{32}y + R_{33}z + t_3$$

$$\begin{pmatrix} \bar{y} \\ \bar{x} \\ z + 1/3 \end{pmatrix} = \begin{pmatrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ 1/3 \end{pmatrix}$$

2 Choosing the Unit Cell

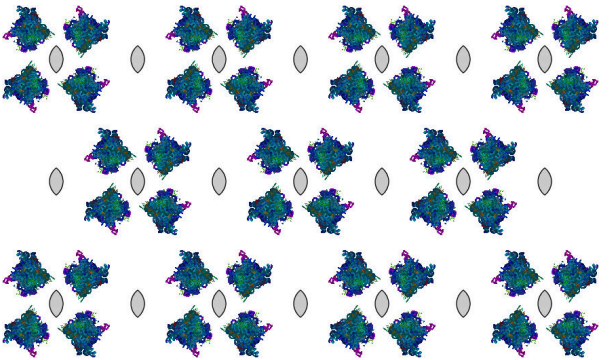
Unit Cell

- the entire crystal can be created by translations of the unit cell
- the unit cell is described by the three unit cell lengths a, b, c and the respective angles α, β, and γ.
- the unit cell is not unique

Unit Cell — Overview

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

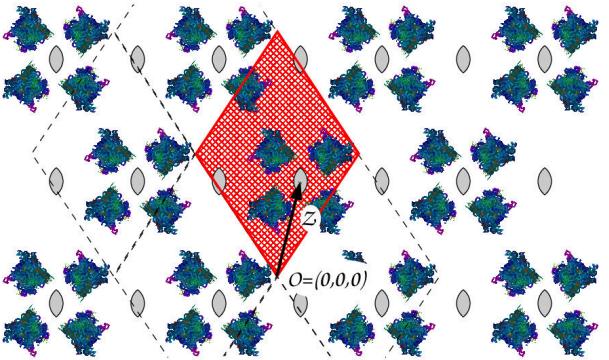
Choice of Unit Cell



The space group and the symmetry of the crystal is given by the crystal.

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

Choice of Unit Cell

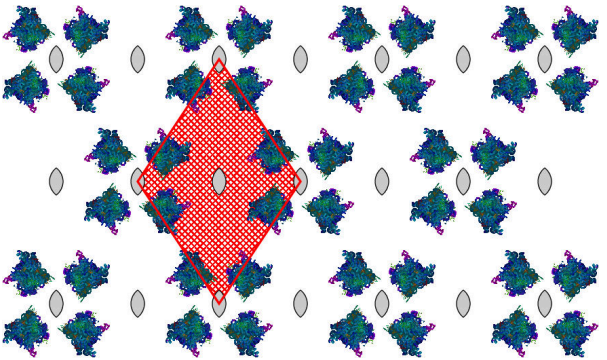


- Uni cell: Mathematical construct, molecules are “ignorant” of the unit cell
- Condition for unit cell: integer translations cover the entire crystal

- If placed arbitrarily: matrix description becomes awkward:

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

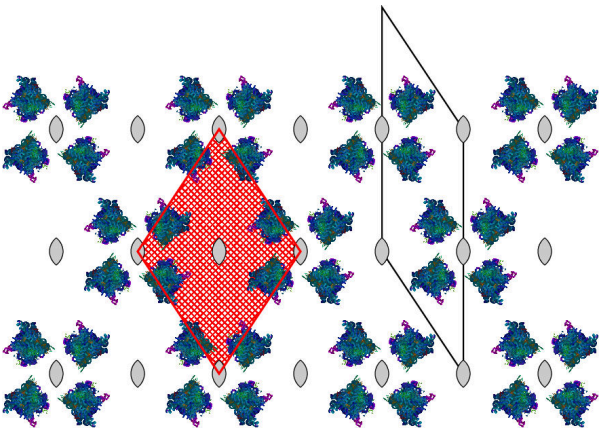
Choice of Unit Cell



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

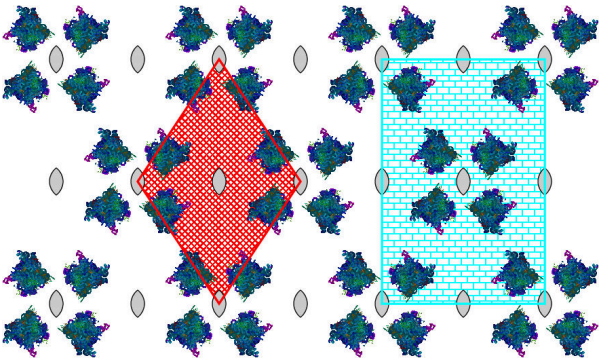
$$(x'y'z') = R(xyz)$$

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 $\neq 90°$
- 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 : $\gamma = 120°$

References

[1] Th Hahn, ed. *International Tables of Crystallography*. Vol. A. Wiley, 2006.