

Structural Chemistry Methods Workshop

Crystallography III:

Point Groups (Crystal Classes),
Bravais Lattice, and
Space Groups

Crystallographic Point Groups

So far ...

- * Symmetry-related objects gather around the various symmetry operators
- * Symmetry elements remain fixed in space (if crystal lattice translation is ignored)
- * Symmetry elements are points, lines, or planes

When looking at all symmetry-derived points ...

- * after X-fold application of symmetry operators, one obtains the original point
 - * the entity of all points is thus something 'closed', 'cyclic'
 - * this is called a mathematical group
-
- * each set of points arising from crystallographic rotation and rota-inversion forms a group
 - * these groups are called **crystal classes**
 - * Hermann-Mauguin: crystal classes are named by denomination of their axis

Crystal Classes

- * In most cases, crystal classes contain not only one, but many symmetry elements
- * How can the different elements be combined to yield a congruent pattern (i.e. to form a group)?
- * The combination will require restrictions as to the angles between axes added to an existing point group
- * This leads to 32 different possibilities

The 32 Crystal Classes

	Triclinic	Monoclinic (1st setting)	Tetragonal	Trigonal	Hexagonal	Cubic	
X	 1	 2	 4	 3	 6	 23	X
\bar{X} (even)	—	 $m(-\bar{2})$	 4	—	 6	—	\bar{X} (even)
X (even) plus centre and \bar{X} (odd)	 1	 $2/m$	 $4/m$	 3	 $6/m$	 $m3$	X (even) plus centre and \bar{X} (odd)
	Monoclinic (2nd setting)		Orthorhombic				
$X2$	 2	 222	 422	 32	 622	 432	$X2$
Xm	 m	 $mm2$	 $4mm$	 $3m$	 $6mm$	—	Xm
$\bar{X}2$ (even) or $\bar{X}m$ (even)	—	—	 $42m$	—	 $6m2$	 $43m$	$\bar{X}2$ (even) or $\bar{X}m$ (even)
$X2$ or Xm plus centre and $\bar{X}m$ (odd)	 $2/m$	 mmm	 $4/mmm$	 $\bar{3}m$	 $6/mmm$	 $m3m$	$X2$ or Xm plus centre and $\bar{X}m$ (odd)

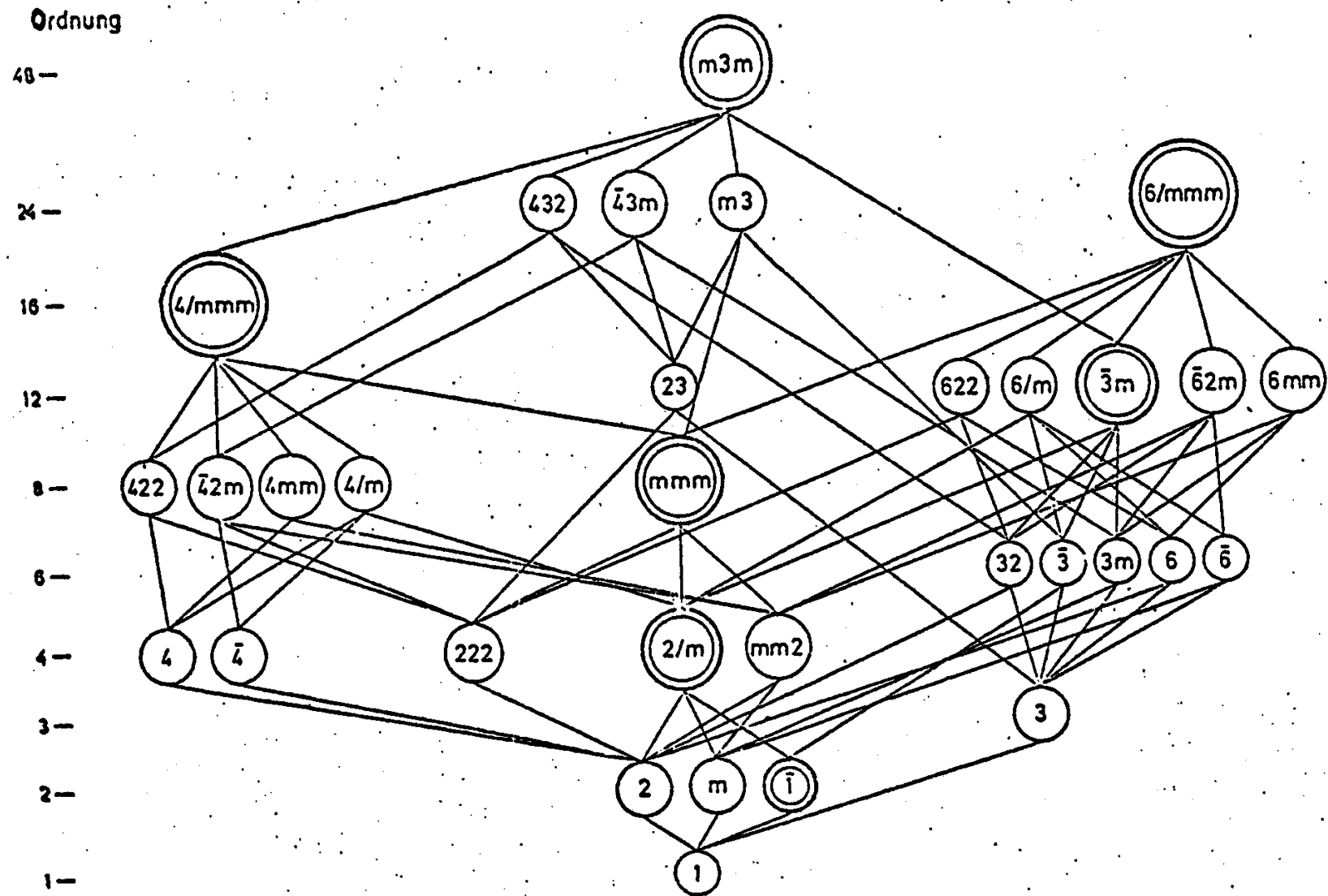
Fixing the directions

- * The symmetry scaffold of the crystallographic point groups is indefinitely repeated in the crystal lattice
- * The scaffold can be used to define a basis system:
 - basis vectors are oriented alongside of symmetry elements
 - per convention, basis vector **c** is parallel to symmetry element X
 - **a** and **b** are then perpendicular to **c** (exception: triclinic crystal system)
- * Monoclinic crystal system: the standard setting is **b** parallel to X

The 7 Crystal Systems

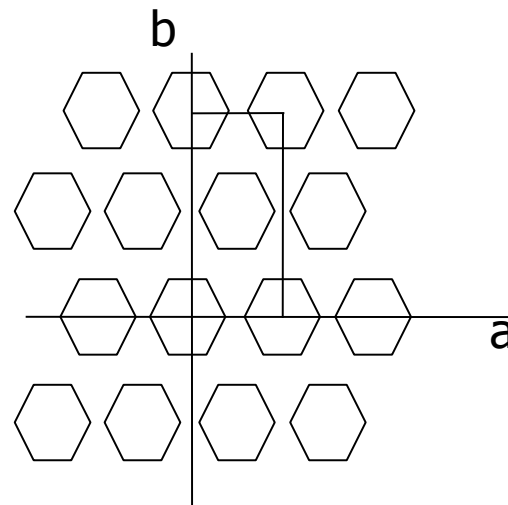
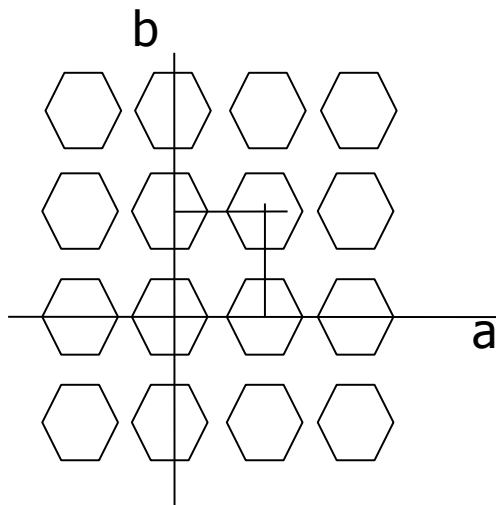
crystal system	1. direction	2. direction	3. direction	metric
triclinic	---	---	---	free
monoclinic	---	[010]	---	$a \neq b \neq c; \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$
orthorhombic	[100]	[010]	[001]	$a \neq b \neq c; \alpha = \beta = \gamma = 90^\circ$
tetragonal	[001]	[100],[010]	[110], etc.	$a = b; \alpha = \beta = \gamma = 90^\circ$
trigonal hexagonal	[001]	[100],[010]	[210], etc.	$a = b; \alpha = \beta = 90^\circ, \gamma = 120^\circ$
cubic	[100],[010],[001]	[111], etc.	[110],[101],[011], etc.	$a = b = c; \alpha = \beta = \gamma = 90^\circ$

Hierarchy of crystal classes



The smallest unit

- * What is the smallest unit that contains all information about the structure of the crystal (and the crystal structure ...)?
- * Symmetry of crystallographic point groups needs to be combined with translations of the crystal lattice
- * This seems trivial: There are 7 different types of crystal systems, so we should have 7 different smallest units
- * However:



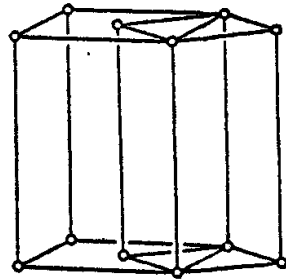
Holohedry

- * When considering translations of the crystallographic unit cell, different centering operations can be found
- * The translational lattices are distinguished by a system proposed by Bravais
- * Each lattice describes the entity of all point group -related objects within one unit cell: Holohedry

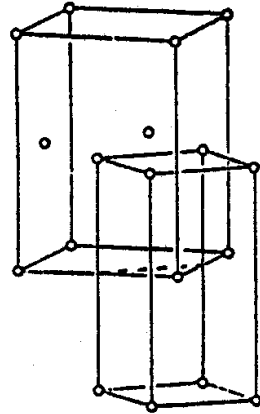
P	primitive		000
A	one side face-centred	(100)	000; $0\frac{1}{2}\frac{1}{2}$
B		(010)	000; $\frac{1}{2}0\frac{1}{2}$
C		(010)	000; $\frac{1}{2}\frac{1}{2}0$
F	all sides face-centred		000; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$
I	room-centred		000; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
R	rhomboedric		000; $\frac{2}{3}\frac{1}{3}\frac{1}{3}$; $\frac{1}{3}\frac{2}{3}\frac{2}{3}$

Determining the Bravais lattice: The **smallest** unit...

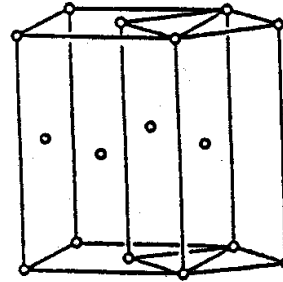
b ↑



a



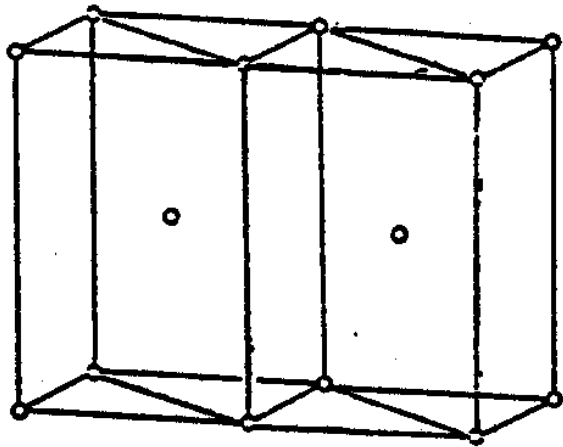
b



c

Two times face-centred and all side face-centred can be transformed to room-centred

b ↑



Sometimes, there are equivalent solutions: e.g. I and C.
Conventionally, C is preferred.

The 14 Holohedries

Crystal system

Bravais lattice with conventional choosing

triclinic

P

monoclinic

P C

orthorhombic

P C I F

tetragonal

P I

trigonal

P R

hexagonal

P

cubic

P I F

Space groups

- * The combination of crystal classes with the Bravais lattices of their systems yields the space group
- * The space group is thus a combination of all symmetry operations (point group elements and translational elements) in 3D that forms a mathematical group
- * There are 230 space groups

1 P1

2 $\bar{P}1$

3 P2

4 $P2_1$

5 C2

6 Pm

...

- Proteins are chiral.
- They crystallise in non-centrosymmetric space groups.
- Non-centrosymmetric space groups comprise polar and chiral space groups.
- Chiral space groups have no roto-inversion elements.

Impressum

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