Chemical Crystallography and Structural Chemistry

VO 270287

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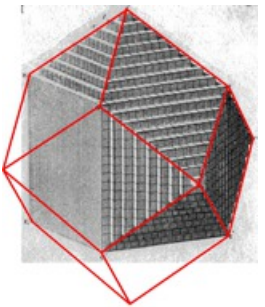
Reminder: Start the recording!

Contents

1 Symmetry and Space Groups

Shape and Appearance of Crystals



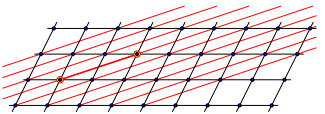
Steve Lower [1]

Historically, the science of crystallography describes the appearance and (visual) regularity of crystals.

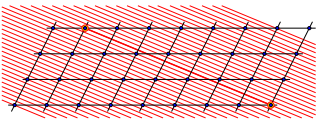
Nicolaus Steno (1638–1686) states the "law of constant angles" or the "first law of crystallography" (1669)

> Angles between corresponding faces on crystals are the same for all specimens of the same mineral

Steno: Law of Constant Angles



lattice plane (120)
low order Miller index
$\hat{=}$ large lattice distance d
(low resolution reflection)
high atom density along plane: stable

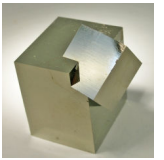


lattice plane $(3\bar{1}0)$
high order Miller index
$\hat{=}$ smalle lattice distance d
(high resolution reflection)
low atom density along plane: unstable

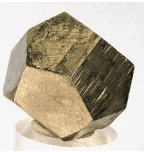
Crystal breaks between stable planes with low Miller indices

Example Crystals

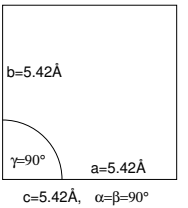
Ruby [2]
$(Al_2O_3 + Cr)$



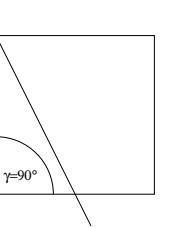
Pyrite [3] (FeS_2)

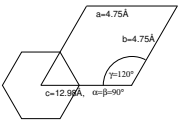


(100)-direction



(210)-direction





hexagonal cell

cubic cell

History of Symmetry of Crystals

1801 René-Just Haüy describes crystal symmetries using group theory.

1850 Auguste Bravais describes the 14 Bravais lattices.

1890/1891 Arthur Moritz Schönflies und Jewgraf Stepanowitsch Fjodorow derive all 230 *space groups*.

1912 Max von Laue, Walter Friedrich und Paul Knipping carry out the first X-ray diffraction experiment. They prove:

- X-rays are waves
- crystals consists of a lattice

Meaning of Symmetry for Structure Determination

The symmetry of a crystal is important because it affects

- data acquisition and scaling
- structure solution
- refinement

2 Symmetry in molecules

Symmetry in molecules

1. What is symmetry?
2. elementary symmetry operations: rotation, mirror plan, inversion centre
3. Combination of symmetry operations: point groups

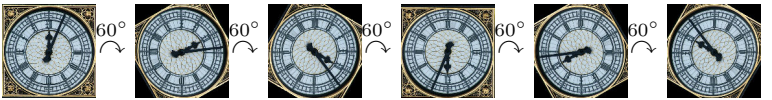
The Term “Symmetry”

Symmetry is part of our daily lives:

Butterfly with a mirror plane

Flower with 5-fold rotational symmetry

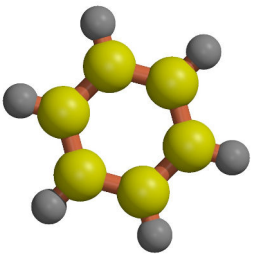
Example: 12-fold Rotational Symmetry

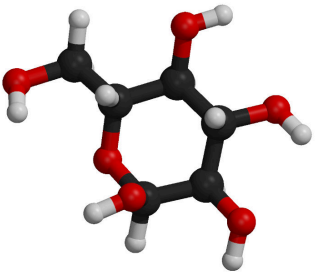


Wikipedia, [4]

Symmetry (in real life) is never ideal.
Ideally, all six images would be identical.
The symmetry of crystals and of individual molecules is much closer to the mathematical meaning of symmetry than macroscopic symmetry.

Symmetric molecules





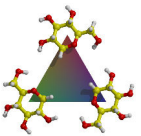
Benzene: 6-fold rotational symmetry + mirror planes

α-D-Glucose: no proper symmetry

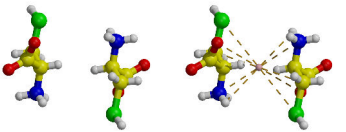
non-symmetric molecules can still crystallise

Symmetry by arrangement: towards a crystal

Crystals without proper symmetry can still be arranged symmetrically.



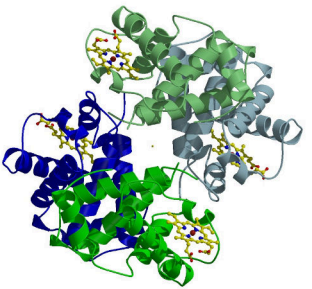
α-D-Glucose about 3-fold rotation axis



L-Cys und D-Cys with centre of inversion

Symmetric arrangement

Sometimes, the arrangement in a crystal may have a chemical meaning.



Hemoglobin in blood cells forms a dimer (dark/light) of two hetero dimers (α/β-globin green and blue) with a 2-fold rotation axis.
Hemoglobin crystallises with the same arrangement (PDB-ID 3ONZ)

3 Elementary Symmetry Operations

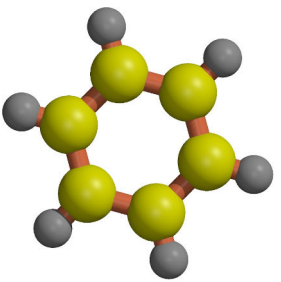
Symmetry Operations

"Definition": A Symmetry operation is a "movement" that does not change what an image looks like.
Any (finite) object as three elementary symmetry operations:

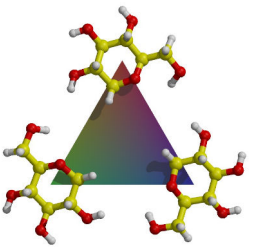
1. (n-fold) **rotation**
2. **mirror plane**
3. **inversion** (=point of reflection)

Symmetry operations: Rotation

An object with an n-fold axis of rotation can be rotated about this axis by $\frac{360^\circ}{n}$ without changing its apparition.
With n such rotations, the object is back to where it was at the beginning.



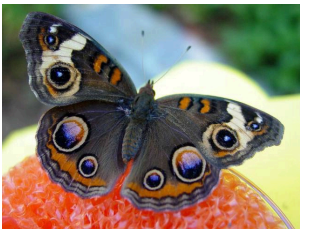
Benzene: 6-fold axis of rotation *perpendicularly* to plane of this slide



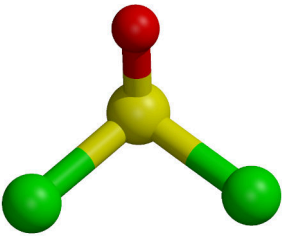
Three glucose molecules with a 3-fold axis of rotation.

Clock face with 12-fold axis of rotation

Symmetry operations: Mirror plane

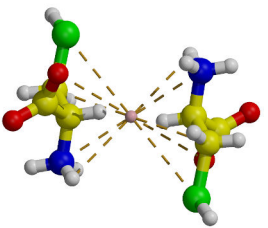


Butterfly with mirror plane

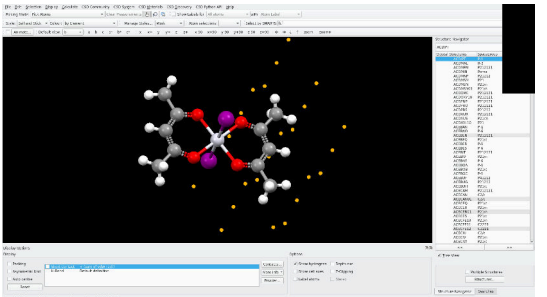


Thionyl chloride ($SOCl_2$) with mirror plane.

Symmetry operations: Inversion



L- and D-Cysteine

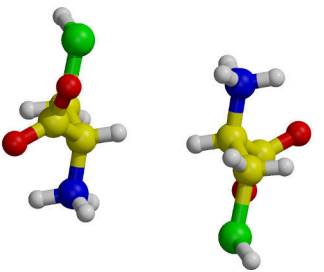


$C_{10}H_{14}I_2O_4Pt$, CSD entry № ACDIPT displayed with MERCURY

All connections of corresponding atoms run through one single point, the *inversion centre* of the object.

Chiral Molecule

A molecule without *centre of inversion* and without *mirror plane* is called *chiral*.
Inversions or mirroring the molecule creates a *different* molecule.
The two forms are called right handed (R(ectus)) and left handed (S(inister)).

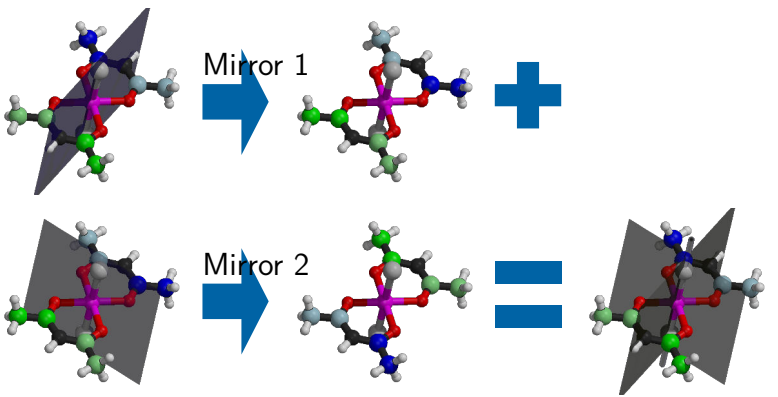


Important example: amino acids (and therefore all proteins), and nucleic acds (and therefore DNA and RNA)

4 Combination of symmetry operations

Combination of symmetry operations

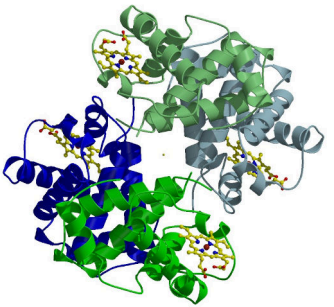
Symmetry operations can be combined arbitrarily: any object with two different symmetry operators is also symmetry with respect to the third symmetry operators, the combination of the two.



two perpendicular mirrors = 180° rotation axis

"De-"combination of Symmetry operations

N. B.: The inverse statement is not necessarily correct: not every molecule with a 2-fold rotation axis contains two mirror planes:



natural proteins are composed of S-amino acids and are always chiral. They never contain a centre of inversion, or a mirror plane.

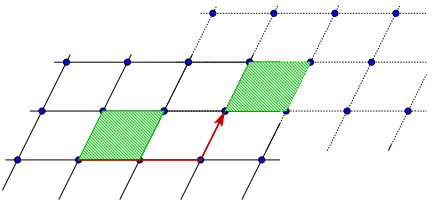
Symmetry of crystals

1. Additional symmetry operations due to translational symmetry
2. Restrictions for the total number of symmetry

Symmetry of crystals: Translation

ideal crystal: infinitely large

Therefore: Additional symmetry due to translation by integer shifts of the unit cell.

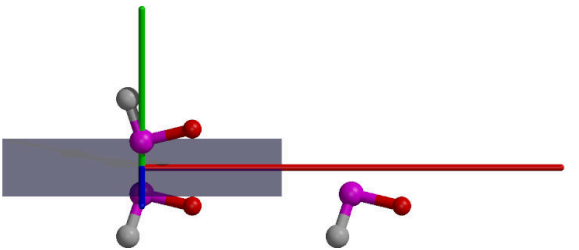


Additional symmetry operations:

1. **glide plane**
2. **screw axis**

Glide Plane

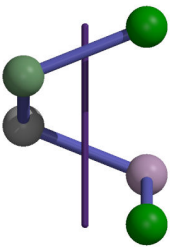
1. mirror plane
2. translation along one unit cell axis by 1/2 of its length L"ange



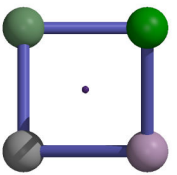
racemates (*i.e.* equimolar mixtures of R- and S-form) often crystallise with glide mirror planes: efficient packing.

Screw Axis

A combination of an n-fold rotation axis by $\frac{360^\circ}{n}$ with a shift along one of the unit cell axes by $1/n$ of its length is called a *scree axis*. Screw axis always run parallel to one it the unit cell axes.



Side view

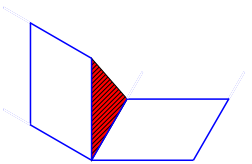


top view

Example for a 4_1 screw axis: Rotation about $1/4 \cdot 360^\circ = 90^\circ$ plus shift by $1/4$ along the rotation axis

Symmetry of crystals: Limitations

The lattice of crystals creates additional symmetry operations in comparison with single molecules (glide mirror plancs and scew axes). However, since every symmetry operation must map the lattice into itself, the number of combinations is finite.

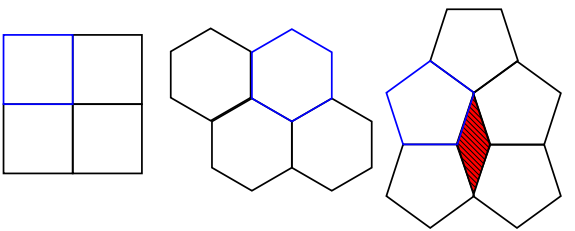


This cell as angles $\neq 90°$. This prohibits a 4-fold rotation: a rotation by $90°$ creates gaps in the crystal lattice.

We cannot combine any symmetry operation with any cell.

Symmetry of crystals: Limitations

- A mirror plane, or a centre of inversions, or a rotation axis imposes restrictions onto the crystal lattice.
- Therefore, not every combination of lattice and symmetry operation is possible.
- Only 2-fold, 3-fold, 4-fold, or 6-fold rotations are possible



(gap-free tiling of the plane with regular squares or hexagons. Impossible with regular pentagons.)

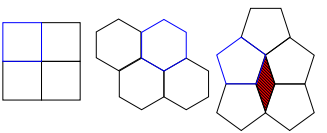
5 Point groups and Space groups

Point Groups and Space Groups

1. Classification and nomenclature
2. Symbols for symmetry elements

Point Groups

- Point groups consider symmetry without translation
- Symmetry operations:
  1. mirror plane
  2. inversion centre
  3. n-fold rotation
- In crystallography: only 2-fold, 3-fold, 4-fold,6-fold rotations



Point Groups

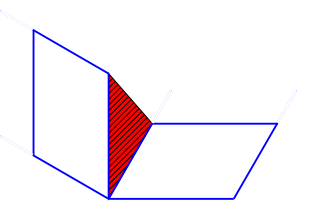
The combination of all symmetry operations that are compatible with unit cells leads to 32 different groups, the

32 crystallographic point groups

N.B. There are many more point groups for molecules, only 32 are compatible with the requirements from the unit cell.
cf. Crystallographic point group on Wikipedia.

Space Groups

- Point groups combined with translation of the infinite lattice
- Symmetry operations:
  1. mirror plane
  2. inversion centre
  3. n-fold rotation
  4. glide plane
  5. screw axis
- Not every unit cell type is compatible with every symmetry operation



Space Groups

The combination of 32 point groups with translation of the infinite crystal lattice creates

230 space groups

- Every crystal belongs to one out of 230 different space groups.
- Chiral compounds belong to a subset, 65 different Sohncke groups [1]. The Sohncke groups do not violate the chirality of the compound.
- All point groups and space groups are listed in the in *"International Tables of Crystallography"*, Volume A (International Union of Crystallography, IUCr)

[1] Leonhard Sohncke, 1842–1897, German mathematician and physicist

Nomenclature

There are mainly two different types of nomenclatures for point groups and for space groups:

- Hermann-Mauguin System (primarily used in crystallography)
- Schönflies System (primarily used for symmetry of molecules, spectroscopy)

Nomenclature: Hermann-Mauguin System [5, Ch. 6]

- Space groups have names like $P2_1/c$ or $I\bar{4}3m$.
- subscripts can be replaced with brackets: $P2(1)/c$
- bars can be replaced with a minus sign: I-43m
- first,capital letter: lattice type (see below)
- next: three positions for a, b, c axes
- by conventions, axes with '1' are dropped: $P2_1/c = P\ 1\ 2_1/c\ 1$

Nomenclature: Hermann-Mauguin System [5, Ch. 6]

- n-fold rotation axis: n
- centre of inversion: $\bar{1}$ or $\bar{N}$
- mirror plane: m
- glide mirror plane: a, b, c, n, d, g

Nomenclature: Hermann-Mauguin System [5, Ch. 6] ct'd.

- glide mirror plane:
  - **a** translation along $\vec{a}$, i.e. $1a1$ or $11a$
  - **b** translation along $\vec{b}$, *i.e.* $b11$ or $11b$
  - **c** translation along $\vec{c}$, *i.e.* $c11$ or $1c1$
  - **n, d** translation along diagonal
  - **g** translation along arbitrary direction, needs to be followed by direction and position of mirror plane (not a standard setting).

Example: $Pnma$: n-glide plane along $\vec{b} + \vec{c}$, mirror plane perpendicular to $\vec{b}$-axis, glide mirror plane perpendicular to $\vec{c}$-axis

List of 32 crystallographic point groups

Schönflies	Hermann-Mauguin	Schönflies	Hermann-Mauguin	Schönflies	Hermann-Mauguin
C_1	1	C_4	4	$C_{3i} = S_6$	$\bar{3}$
C_i	$\bar{1}$	S_4	$\bar{4}$	D_3	32
C_2	2	D_4	422	C_{3v}	$3m$
$C_s = C_{1v}$	m	C_{4v}	$4mm$	D_{3d}	$\bar{3}m$
C_{2h}	$2/m$	C_{4h}	$4/m$	C_6	6
C_{2v}	$mm2$	D_{2d}	$\bar{4}2m$	C_{3h}	$\bar{6}$
D_2	222	D_{4h}	$4/mmm$	D_6	622
D_{2h}	mmm	C_3	3	D_{3h}	$\bar{6}m2$
C_{6h}	$6/m$	C_{6v}	$6mm$	D_{6h}	$6/mmm$
T	23	T_h	$m\bar{3}$	T_d	$\bar{4}3m$
O	432	O_h	$m\bar{3}m$		

Representation of Symmetry operators — Matrices

Each symmetry operator of the **point groups** can be expressed by a matrix:

4-fold rotation axis about $\vec{a}$ $\quad R_1 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{pmatrix}$

4-fold rotation axis about $\vec{b}$ $\quad R_2 = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}$

centre of inversion (at origin) $\quad R_3 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$

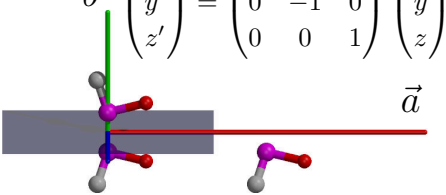
Matrices can be directly applied to atom positions with *fractional coordinates* (as *e.g.* the instruction file for SHELXL).

Symmetry with Translation

Crystal Symmetry (Space group): the translational part has to be expressed with a vector $\vec{t}$

Example: glide mirror plane perpendicular to $\vec{b}$ along $\vec{a}$:

$$\vec{b} \begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \begin{pmatrix} 1/2 \\ 0 \\ 0 \end{pmatrix} = (R, \vec{t}) \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$



A crystal with this type of glide mirror plane with a nitrogen atom at position (x,y,z) has an equivalent nitrogen atom at position (x',y',z')

"symmetric" — What does this mean?

Symmetric molecule (point groups): for every atom at position (x,y,z) of a molecule with a symmetry operator R there is an equivalent atom at position

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = R \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

.

Symmetry in crystals (space groups): for every atom at position (x,y,z) of a molecule with a symmetry operator $(R, \vec{t}$ there is an equivalent atom at position

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = (R, \vec{t}) \begin{pmatrix} x \\ y \\ z \end{pmatrix} = R \begin{pmatrix} x \\ y \\ z \end{pmatrix} + \vec{t}$$

(x, y, z) and (x', y', z') are **equivalent positions** of the crystal.

"symmetric" — What does this mean?

When anyone of the symmetry operators of the space group is applied to **all** atoms in the unit cell, the structure looks the same. Furthermore, the environment of each atom looks the same.

Think of NMR: the NMR spectrum would not change after the application of a symmetry operator to **all** atoms in the unit cell.

Meaning of Symmetry for Structure Determination

The symmetry of a crystal is important because it affects

- data acquisition and scaling — more reliable intensities with more robust standard uncertainties
- structure solution
- refinement — wrong space group can sometimes lead to unstable refinement

References

[1] S. Lower. URL: https://chem1.com/acad/webtext/states/crystals-ext.html (visited on 23/03/2021).

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