Symmetry of Molecules and Crystals

What does symmetry mean?

Symmetry (Greek = harmony, regularity) means the repetition of a motif and thus the agreement of parts of an ensemble (Fig. 1).



Precession pattern of LiAlSiO₄ (a*b* plane, symmetry 6mm)

-				r –
cosa	sina	x_1	_	<i>x</i> ₂
_sinα	cosa	_y1_		Y2

Matrix for a vector rotation



Radiolarian shell (Circogonia icodaedra) with icosaeder symmetry



Ice crystal (symmetry ~6mm)

B,6 .	-	-	-			•
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J.S. Bach, "Die Kunst der Fuge"



Normal modes of XeF_4 (symmetry group D_{4h})

 $V(\varphi)$ (φ) (φ)

 $\begin{array}{l} \text{Rotation of } ClH_2C\text{-}CH_2Cl\\ (\text{symmetry } C_2, \, C_{2v} \, \text{or} \, C_{2h}) \end{array}$



Anti-symmetry



3D object (csi.chemie.tu-darmstadt.de/ak/immel/)

Fig.1 Examples of symmetric objects

Symmetry can also mean harmony of proportions, or stability, order, and beauty.

Definition:

An object is symmetric if it is left invariant by a transformation, i.e., cannot be distinguished before and after transformation.

Symmetry transformations, operations, elements are:

Sym	nbol*	Symmetry operation
Sch	HM	* Notation of symmetry elements after Schönflies (Sch for moleculs) and International Notation after Hermann/Mauguin (HM for crystals)
Ε	(1)	identity (E from "Einheit" = unity, an object is left unchanged)
C _n	(n)	properrotation through an angle of $2\pi/n$ rad.
S _n		improperrotation through an angle of $2\pi/n$ rad. followed by a reflection in a plane perpendicular to the axis (rotation-reflection axis)
	n	improperrotation through an angle of $2\pi/n$ rad. followed by a reflection through a point on the axis (rotation- inversion axis)
i	1	inversion (point reflection) $(\overline{1} \equiv S_2) \rightarrow$ (x, y, z \rightarrow -x, -y, -z in Cartesian coordinates)
σ	m	mirror plane (from "Spiegel")
$\sigma_{\rm h}$		horizontal reflection in a plane passing through the origin and perpendicular to the axis with highest symmetry
σ_{v}		vertical reflection in a plane passing through the origin and the axis with highest symmetry
σ_d		diagonal reflection in a plane as σ_v and bisecting the angle between the two-fold axis perpendicular to the axis of highest symmetry
	ť	translation $\vec{t} = n_1 \cdot \vec{a} + n_2 \cdot \vec{b} + n_3 \cdot \vec{c}$
		1. column: notation after Schönflies (molecules)
		2. column: notation after Hermann/Mauguin (crystals)

Symmetry classes and combinations \Rightarrow point groups (see Table 1) (in a point group at least one point in space is left invariant by the operation)

Point gr.	Sym elements*	h***	Point gr.	Sym elements*	h***
C ₁	E	1	Ci	i	2
Cs	σ	2	C _n	C_n	n
S _n	S _n	n	C _{nv}	C_n , $n\sigma_v$	2n
C _{nh}	C_n, σ_h	2n	D _n	$C_n, nC_2 \perp C_n$	
D _{nd}	C_n , $nC_2 \perp C_n$, $n\sigma_d$	4n	D_{nh}	C_n , $nC_2 \perp C_n$, σ_h , $n\sigma_v$	4n
$C_{\infty v}$	linear no i	∞	$D_{\infty h}$	linear with i	∞
Т	tetrahedral	12	0	oktahedral	24
T_d		24	O_h	(cubic)	48
T_{h}		24			
Ι	ikosahedral	60	K _h	spherical	∞
I _h		120			

Table 1 Point groups of molecules and polyhedra*

* Schoenflies notation, ** Important symmetry elements, *** Order h (number of repetitions)

The point groups of some inorganic and organic compounds and the schematic representation of the symmetries of some important objects and polyhedra with their orders (repetitions) n = 2, 3, 4, 5, 6 and ∞ are shown in Figs. 2a und 2b.



Abb. 2a Point groups of some inorganic and organic molecules



Fig. 2b Schematic representation of some figures and polyhedra with their symmetry properties, orders n and point groups

The point group notation after Hermann-Mauguin is given in the part Crystal symmetry.

As exercise (find, note and systematize), the symmetry elements and point groups of some molecules (without electron pairs) are listed in Fig. 3. A symmetry flow chart is given in Fig. 4.

Point- group	Symmetry elements	Structure/shape	Example(s)
		9	
C_1	E	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	SiBrCIFI
<i>C</i> ₂	E,C_2		$H_{2}O_{2}$
C _s	E,σ		NHF ₂
<i>C</i> _{2v}	$E, C_2, \sigma_{\mathrm{v}}, \sigma_{\mathrm{v}}$		H_2O , SO_2CI_2
C_{3v}	$E, 2C_3, 3\sigma_v$	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	$NH_3,\ PCI_3,\ POCI_3$
$C_{\infty \mathbf{v}}$	$E, C_2, 2C_{\phi}, \ldots \infty \sigma_{\mathbf{v}}$	•0	CO, HCI, OCS
$D_{2\mathrm{h}}$	$E, C_2(x, y, z), \sigma(xy, yz, zx), i$		N_2O_4, B_2H_6
		d b	
D _{3h}	$E, C_3, 3C_2, 3\sigma_v, \sigma_h, S_3$		BF ₃ , PCI ₅
		9	
$D_{ m 4h}$	$E, C_4, C_2, 2C'_2, 2C'', i, S_4, \sigma_h, 2\sigma_v, 2\sigma_d$	00	XeF_4 , trans- MA_4B_2
$D_{\infty h}$	$E, C_{\infty}, \ldots, \infty \sigma_{v}, i, S_{\infty}, \ldots, \infty C_{2}$		$H_2,\ CO_2,\ C_2H_2$
T _d	$E, 3C_2, 4C_3, 6\sigma_d, 4S_4$		CH ₄ , SiCl ₄
$O_{ m h}$	$E, 6C_2, 4C_3, 3C_4, 4S_6, 3S_4, i, 3\sigma_h, 6\sigma_d$		SF ₆

Fig. 3 Point groups and symmetry elements of some molecules





Representation/demonstration of symmetry properties

To demonstrate the symmetry properties of three-dimensional (spatial) objects (e.g. molecules, optional figures or frames, polyhedra, crystals) in a plane, projections like e.g. the stereographic projection are used (Fig. 5).



Fig. 5 Principle of a stereographic projection

The treated object, polyhedron, crystal etc. is positioned at the center of a sphere so that his main symmetry axis (axis of highest symmetry) is oriented perpendicularly to the equatorial plane. Its surface normals or center beams will meet the surface of the sphere at the so called point or plane pole P. The connecting line of the point or plane pole P with the opposite sphere pole (north or south pole) will meet the equatorial (projection) plane at the projection point P' of the point or plane pole P.

The angle between two point or plane poles corresponds to the angle between two center beams or the normal angles of two of the figure or crystal faces (normal angle = 180° - plane angel), respectively, and gives the equatorial angle (azimuth β) and the vertical angle (90° - pole altitude α). I.e., the stereographic projection is isogonal (s. Fig. 6 und 7).



Fig. 6 Stereographic projection of a tetragonal prism (a) and tetragonal pyramid (b). The angle coordinates $\varphi = \beta$ and $\delta = \alpha$ of the planes of the pyramid are also given.



Fig. 7 Plane poles and stereographic projection of a galenite crystal

The plane poles of a crystal mostly are positioned on few great circles. The corresponding planes belong to so called crystal zones. The zone axis is oriented perpendicularly to the plane of the respective great circle. With the help of stereographic projections one can show/demonstrate, point or plane poles, plane angles, and thus the symmetry properties of molecules, polyhedra, or crystals.

Symmetry and geometry of crystals

The basic feature of the crystalline state is (idealized) the high degree of order, i.e., the components of crystals (atoms, molecules, ions) are repeated in a regular way, i.e., are 3D periodic (Kepler, 1611; Hooke, 1665; Bergmann, 1773; Haüy, 1782)



Fig. 8 Representation of a (2D) crystal structure

Crystals can be described as consisting of a structural motif (one or more atoms, molecules, ions) belonging to one lattice point and being repeated by a 3D lattice translation (Fig. 8).

Structural motiv (basis) + 3D translation (crystal lattice) \rightarrow Crystal structure Unit cell: Parallelepiped representing crystal lattice+crystal structure (Fig. 9)



Fig. 9 Unit cells with unit cell vectors (lattice translations) $\vec{a}, \vec{b}, \vec{c}$.

Motif (basis), unit cell, crystal lattice and crystal structure have a definite, combined symmetry (Fig. 9).



Fig. 9 Translational repetitions of symmetric motifs.

The asymmetric unit is repeated by symmetry m (a) and 4 (b), resulting in 2D lattice arrangements of symmetry m (a) and 4 (b), respectively.

Crystallographic symmetry elements/operations

Since crystals are 3D translational subjects, only space filling symmetry elements are allowed. Besides a mirror plane (m) and an inversion center $(\overline{1})$, those space filling symmetry elements are the rotation axes 1, 2, 3, 4, and 6 only (Figs. 10, 11, 12).



Fig. 10 Space filling symmetry elements (n = 5, 7, 8, ... not allowed)



able 1-1 Convention	al designation	of	improper axes	
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Rotoinversion axis	Rotoreflection axis	Conventional designation	on
$ \frac{\overline{1}}{\overline{2}} \\ \overline{3} \\ \overline{4} \\ \overline{6} $	2 1 6 4 3	Center of symmetry Mirror plane 3-fold rotoinversion 4-fold rotoinversion 6-fold rotoinversion	1 m3 4 6



Fig. 11 Demonstration, designation, and stereographic projections of proper and improper crystallographic (space filling) axes





Crystal classes (crystallographic point groups)

Omitting translations, there are exactly 32 combinations possible for crystals, resulting inexactly 32 crystallographic point groups or crystal classes. They are used for the description of the morphology of crystals and represented e.g. in form of stereographic projections (Fig 13).



Fig. 13 Stereographic representation of the 32 crystal classes

Lattice symmetry (holoedric classes, crystal systems)

Also crystal lattices and the related parallelepipeds (unit cells) have a special symmetry (exactly 7 possibilities) \rightarrow holoedric classes and crystal systems with different orientations/relations of the crystal axes (Figs. 14, 15).



Fig. 14 Crystal systems and lattice constants

System	Number of lattices in system	Lattice symbols	Nature of unit- cell axes and angles ⁽¹⁾	Lengths and angles to be specified	Symmetry of lattice ⁽²⁾
Triclinic	1	Р	a≠b≠c a≠β≠γ	a, b, c a, β, γ	Ι.
Monoclinic ⁽³⁾	2	1st setting $\begin{bmatrix} P \\ B \end{bmatrix}$	$a \neq b \neq c \\ a = \beta = 90^{\circ} \neq \gamma$	а, b, c ү	2/m
•		2nd setting $\begin{pmatrix} P \\ C \end{pmatrix}$	$a \neq b \neq c \\ a = \gamma = 90^{\circ} \neq \beta$	a, b, c β	
Orthorhombic	4	P C ⁽⁴⁾ I F	$a\neq b\neq c a=\beta=\gamma=90^{\circ}$	a, b, c	mmm
Tetragonal	2	P ⁽⁵⁾ I	$a=b\neq c$ $a=\beta=\gamma=90^{\circ}$	<i>a</i> , c	4/mmm
Cubic	3	P I F	$a=b=c \\ a=\beta=\gamma=90^{\circ}$	a	m3m
Trigonal	1	R ⁽⁶⁾	$a=b=c$ $a=\beta=\gamma$ <120°, \neq 90°	a a	3 <i>m</i>
Hexagonal	11	P(7)	$a=b\neq c$ $a=\beta=90^{\circ}$ $\gamma=120^{\circ}$	a. c	6/mmm

Fig. 15 Crystal systems, unit cell axes and angles of the 7 holoedric classes

Bravais lattices (centered cells/lattices)

Normally there is only 1 lattice point per unit cell (P), but for special axis relations $(\vec{t}_1 \cdot (\vec{t}_2 \cdot \vec{t}_1))$ a higher symmetry (with orthogonal axes) is possible under increase of the lattice point number per unit cell to 2 or 4 \rightarrow centered cells C (2), I (2), R (2), F (4) \rightarrow 14 Bravais lattices.



Fig. 16 The 14 Bravais lattices with their coordinate systems, lattice constants, and space group symbols

Space groups (3D symmetry groups)

Inclusion of translation \vec{t} results in further symmetry elements, the so-called translation symmetry elements, the screw axis and glide planes (Fig. 17)



Fig. 17 Effect of an inversion center, a screw axis, and a glide plane

Translation symmetry elements are:

a) screw axis: n_m

Rotation by $2\pi/n$ and translation II to the screw axis by $m/n \cdot |\vec{t}|$ (2₁, 3₁, 3₂, 4₁, 4₃, 4₂, 6₁, 6₅, 6₂, 6₄, 6₃ are possible, see Fig. 18).



Fig. 18 Crystallographic screw axes n_m

b) glide planes: *a*, *b*, *c*, *n*, *d* Reflection and translation parallel to the mirror plane by *a*/2 II *a* for *a*; *b*/2 II *b* for *b*; *c*/2 II c for *c* by |*a*+*b*|/2, |*b*+*c*|/2, |*a*+*c*|/2 parallel *a*+*b*, *b*+*c*, *a*+*c* for *n* by |*a*+*b*|/4, |*b*+*c*|/4, |*a*+*c*|/4 parallel *a*+*b*, *b*+*c*, *a*+*c* for *d* (for I and F cells only)

Combination of axes/planes and translations are restricted by the 3D periodicity of the crystal lattices.

Combination of the 14 Bravais lattices with the "space filling" point groups/ symmetry elements results in the 230 (3D) space groups (e.g. Fig. 19).

Point groups:	describe the symmetry of crystal faces.
Space groups:	describe the symmetry of crystal bulks.

A summary of all symmetry elements of the 230 space groups are given in the International Tables for Crystallography, Vol. A (see e.g. Fig. 19).



Fig. 19 Example of space group information

Atomic coordinates, equivalent positions

There are 3 possibilities for the description of crystal structures:

- 1. Every (translatorial) independent type of atom has its own crystal lattice and the total crystal structure is given as the sum of all the (shifted) "atomic translation lattices" all with the same basic translations $\vec{a}, \vec{b}, \vec{c}$.
- 2. The crystal structure is given as the sum of the motiv or basis and the translation or Bravais lattice.
- 3. Basis and lattice translations are represented/extracted by/from the parallel epiped (unit cell: P, C, I, F, R) built by the basic lattice translations \vec{a} , \vec{b} , \vec{c} .

The best and simplest description/representation of a crystal structure is the unit cell with its basic translations $(\vec{a}, \vec{b}, \vec{c})$ or the lattice constants (a, b, c, α , β , γ) and its content (atoms, ions, molecules etc.).

The atomic positions in the unit cell are given by the position vectors

$$\vec{r}_{j} = \mathbf{x} \cdot \vec{a}, + \mathbf{y} \cdot \vec{b} + \mathbf{z} \cdot \vec{c}$$

or (abbreviated) by their (contravariant) vector components x, y, z.

If the space group is known, the non-symmetric part of the unit cell, i.e. the asymmetric unit, is sufficient for describing the complete (ideal) crystal structure by using the equivalent positions listed in the International Tables.

Lattice planes, sets (families) of lattice planes, Miller indices

Parallel planes through all the points of a crystal lattice form sets of planes with equidistant atoms and spacings (distances d of the planes of such a set of planes), where the atomic distances and spacings depend on the orientation of those planes with respect to the lattice/unit cell vectors \vec{a} , \vec{b} , and \vec{c} (Fig. 20).



Lattice or unit cell vectors \vec{a} , \vec{b} , \vec{c} Miller indices (hkl) Spacings d_(hkl)

Fig. 20 Sets of lattice planes (hkl) with different orientation and spacings d_n (or $d_{(hkl)}$) for a monoclinic 3D point lattice projected parallel $-\vec{c}$

Each set of planes divide the lattice axes \vec{a} , \vec{b} , and \vec{c} into an integral number of equal parts (see Fig. 20). These fractional intercepts h (for \vec{a}), k (for \vec{b}), and l (for \vec{c}) are the so-called Miller index triples or Miller indices (hkl).

A specific set of planes is characterized by the Miller indices (hkl) and also by its normal vector \vec{n} (length 1) and the respective spacing d_n or d_(hkl) (Fig. 21).

 $\vec{R}_{1}, d_{1} \rightarrow (0\bar{1}0)$ $\vec{R}_{2}, d_{2} \rightarrow (3\bar{1}0)$ $\vec{R}_{3}, d_{3} \rightarrow (\bar{1}20)$ dat Raumgitter n,

Fig. 21 Three different sets of lattice planes of a monoclinic 3D point lattice (lattice vectors \vec{a} , \vec{b} , and \vec{c} , projected parallel $-\vec{c}$) with their normal vectors \vec{n}_i , spacings d_i , and Miller indices (hkl)

Sets of planes, crystal faces, sets of symmetry equivalent planes or faces, and directions in a crystal or point lattice are described as follows:

- (hkl) define sets of lattice planes and crystal faces e.g. $(100) \equiv$ yz or bc plane, $(010) \equiv$ xz or ac plane, $(001) \equiv$ xy or ab plane
- {hkl} define symmetry equivalent sets of planes and crystal faces e.g. $\{100\}_{cubic} \equiv (100), (010), (001), (-100), (0-10), (00-1)$
- [uvw] define directions in a crystal lattice and a crystal corresponding to the components of the translation vector $\vec{t} = u \cdot \vec{a} + v \cdot \vec{b} + w \cdot \vec{c}$ e.g. [100] $\equiv x$ or a axis, [010] $\equiv y$ or b axis, [001] $\equiv z$ or c axis

Some examples of sets of lattice planes with their spacings $d_{(hkl)}$ and of origin nearest lattice planes representing specific sets of lattice planes and the corresponding Miller indices are given in Fig. 22. For the definition of directions see Fig. 23.





Fig. 22 Examples of lattice planes and plane sets with their Miller indices

To construct the origin nearest lattice plane of a lattice plane set (hkl) please:

- 1. select the origin 000,
- 2. mark intercepts 1/h, 1/k, 1/l of the plane (hkl) on \vec{a} , \vec{b} , and \vec{c} ,
- 3. draw the plane.

For negative indices, first shift the origin accordingly.



Fig. 23 Directions [hkl] in crystal lattices and crystals

Reciprocal lattice (labelling of lattice planes and lattice plane sets)

Lattice plane sets of a crystal or crystal lattice with basis vectors \vec{a} , \vec{b} , and \vec{c} , are characterized by their plane normals $\vec{n}_{(hkl)}$ and spacings $d_{(hkl)}$. The endpoints of vectors $(1/d_n) \cdot \vec{n}_n$ or $(1/d_{(hkl)}) \cdot \vec{n}_{(hkl)}$, respectively, form a point lattice named reciprocal lattice (Fig. 24)



Fig.24 Relation between crystal lattice (left) and reciprocal lattice (right)

The relation between the basis vectors \vec{a}^* , \vec{b}^* , \vec{c}^* of the reciprocal lattice and the basis vectors \vec{a} , \vec{b} , and \vec{c} , of the crystal lattice is demonstrated in Fig. 25.





The respective vector equations are

$$\overrightarrow{a^*} = \frac{\overrightarrow{b} \times \overrightarrow{c}}{\overrightarrow{a} \cdot \overrightarrow{b} \times \overrightarrow{c}}; \quad \overrightarrow{b^*} = \frac{\overrightarrow{c} \times \overrightarrow{a}}{\overrightarrow{a} \cdot \overrightarrow{b} \times \overrightarrow{c}}; \quad \overrightarrow{c^*} = \frac{\overrightarrow{a} \times \overrightarrow{b}}{\overrightarrow{a} \cdot \overrightarrow{b} \times \overrightarrow{c}}$$

with the reciprocal lattice vectors vectors

$$\overrightarrow{\delta_{hkl}} = h\overrightarrow{a^*} + k\overrightarrow{b^*} + l\overrightarrow{c^*} \text{ or } \overrightarrow{H_{hkl}} = h\overrightarrow{a^*} + k\overrightarrow{b^*} + l\overrightarrow{c^*}$$

The following relations are valid

$$\overrightarrow{a^*} \cdot \overrightarrow{b^*} \times \overrightarrow{c^*} = V^*, \quad \overrightarrow{a} \cdot \overrightarrow{b} \times \overrightarrow{c} = V = 1/V^*, \quad \overrightarrow{a} \cdot \overrightarrow{a^*} = \overrightarrow{b} \cdot \overrightarrow{b^*} = \overrightarrow{c} \cdot \overrightarrow{c^*} = 1,$$
$$\overrightarrow{a} \cdot \overrightarrow{b^*} = \overrightarrow{a} \cdot \overrightarrow{c^*} = \overrightarrow{b} \cdot \overrightarrow{c^*} = \overrightarrow{a^*} \cdot \overrightarrow{b} = \overrightarrow{a^*} \cdot \overrightarrow{c} = \overrightarrow{b^*} \cdot \overrightarrow{c} = 0.$$

In orthogonal lattice systems (all angles are 90°) one has

$$a = 1/a^*, b = 1/b^*, c = 1/c^*.$$

Relations between the spacings d(hkl), reciprocal spacings 1/d(hkl) and the lattice constants a, b, and c of the 7 crystal systems are given in Table 2.

System	$1/d_{hkl}^2$
Cubic	$(h^2 + k^2 + l^2)/a^2$
Tetragonal	$\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$
Orthorhombic	$\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$
Hexagonal and trigonal (P)	$\frac{4}{3a^2}(h^2+k^2+hk)+\frac{l^2}{c^2}$
Trigonal (R)	$\frac{1}{a^2} \left(\frac{(h^2 + k^2 + l^2)\sin^2 \alpha + 2(hk + hl + kl)(\cos^2 \alpha - \cos \alpha)}{1 + 2\cos^3 \alpha - 3\cos^2 \alpha} \right)$
Monoclinic	$\frac{h^2}{a^2\sin^2\beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2\sin^2\beta} - \frac{2hl\cos\beta}{ac\sin^2\beta}$
Triclinic	$(1-\cos^2\alpha-\cos^2\beta-\cos^2\gamma+2\cos\alpha\cos\beta\cos\gamma)^{-1}\Big(\frac{h^2}{a^2}\sin^2\alpha$
	$+\frac{k^2}{b^2}\sin^2\beta+\frac{l^2}{c^2}\sin^2\gamma+\frac{2kl}{bc}(\cos\beta\cos\gamma-\cos\alpha)$
	$+\frac{2lh}{ca}(\cos\gamma\cos\alpha-\cos\beta)+\frac{2hk}{ab}(\cos\alpha\cos\beta-\cos\gamma)\Big)$

Table 2 Reciprocal spacings 1/d((hkl)) and lattice vectors a, b, and c