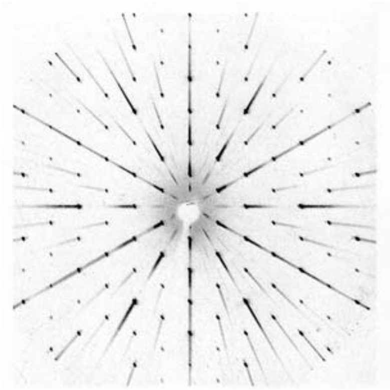
Symmetry of Molecules and Point Groups

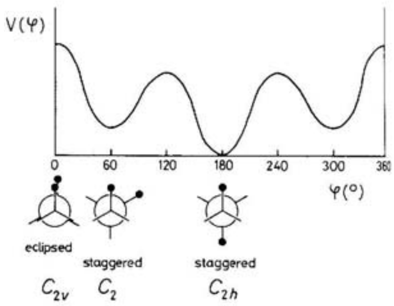
What does symmetry mean?

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



Precession pattern of $LiAlSiO_4$
(a*b* plane, symmetry 6mm)

Ice crystal
(symmetry ~6mm)

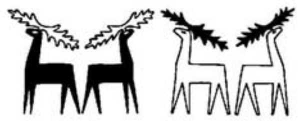


Rotation of $ClH_2C\text{-}CH_2Cl$
(symmetry C_2, C_{2v} or C_{2h})

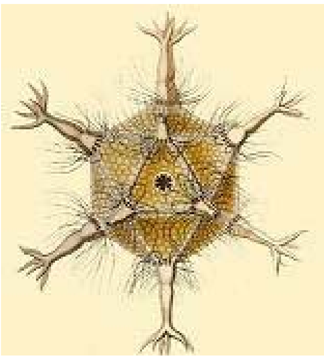
$$\begin{bmatrix} \cos\alpha & \sin\alpha \\ -\sin\alpha & \cos\alpha \end{bmatrix} \cdot \begin{bmatrix} x_1 \\ y_1 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \end{bmatrix}$$

Matrix for a vector rotation

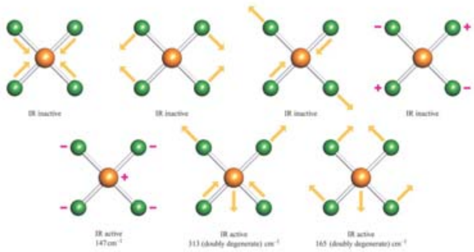
J.S. Bach, „Die Kunst der Fuge“



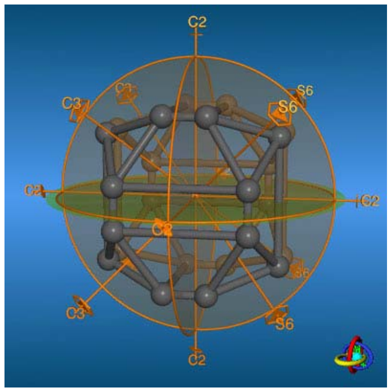
Anti-symmetry



Radiolarian shell (Circogonia icodaedra) with icosaeder symmetry



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



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:

Symbol*		Symmetry operation
Sch	HM	* Notation of symmetry elements after Schönflies (Sch for moleculs) and International Notation after Hermann/Mauguin (HM for crystals)
E	(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)
	$\bar{n}$	improperrotation through an angle of $2\pi/n$ rad. followed by a reflection through a point on the axis (rotation-inversion axis)
i	$\bar{1}$	inversion (point reflection) ($\bar{1} \equiv S_2$) $\rightarrow$ (x, y, z $\rightarrow$ -x, -y, -z in Cartesian coordinates)
σ	m	mirror plane (from “Spiegel”)
σ_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
	t	translation $\mathbf{t} = n_1 \cdot \mathbf{a} + n_2 \cdot \mathbf{b} + n_3 \cdot \mathbf{c}$
		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)

Table 1 Point groups of molecules and polyhedra*

Point gr.	**Sym elements***	**h*****	**Point gr.**	**Sym elements***	**h*****
C_1	E	1	C_i	i	2
C_s	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	∞
T	tetrahedral	12	O	oktahedral	24
T_d		24	O_h	(cubic)	48
T_h		24			
I	ikosahedral	60	K_h	spherical	∞
I_h		120			

* 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.

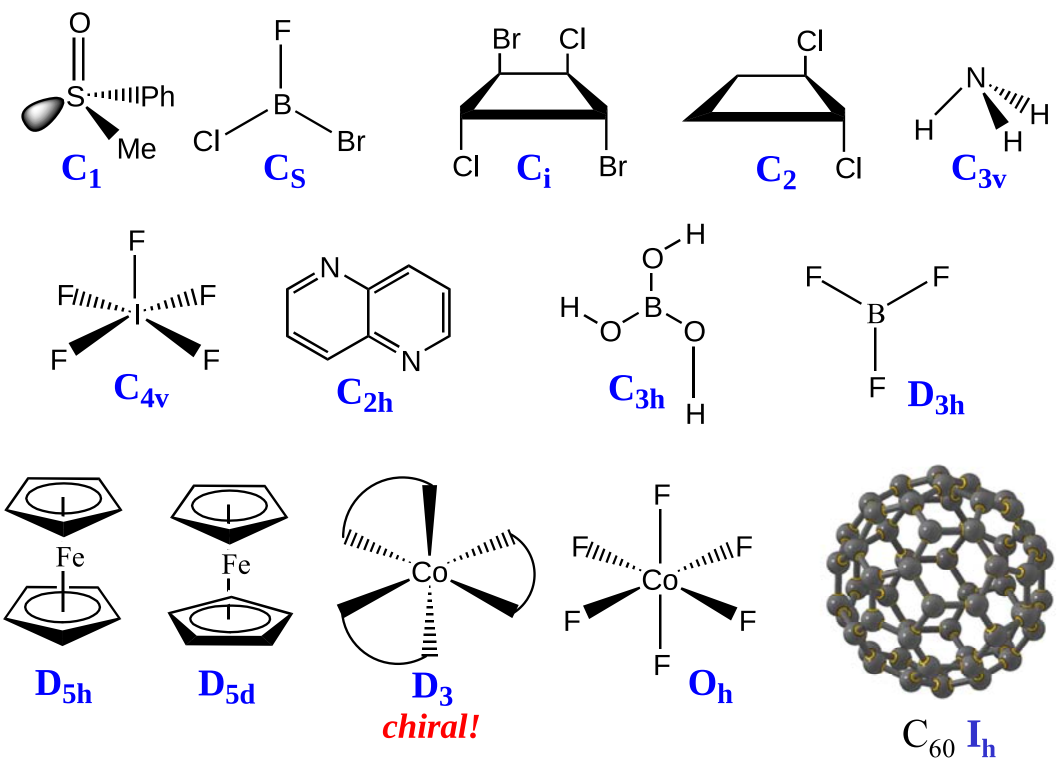


Abb. 2a Point groups of some inorganic and organic molecules

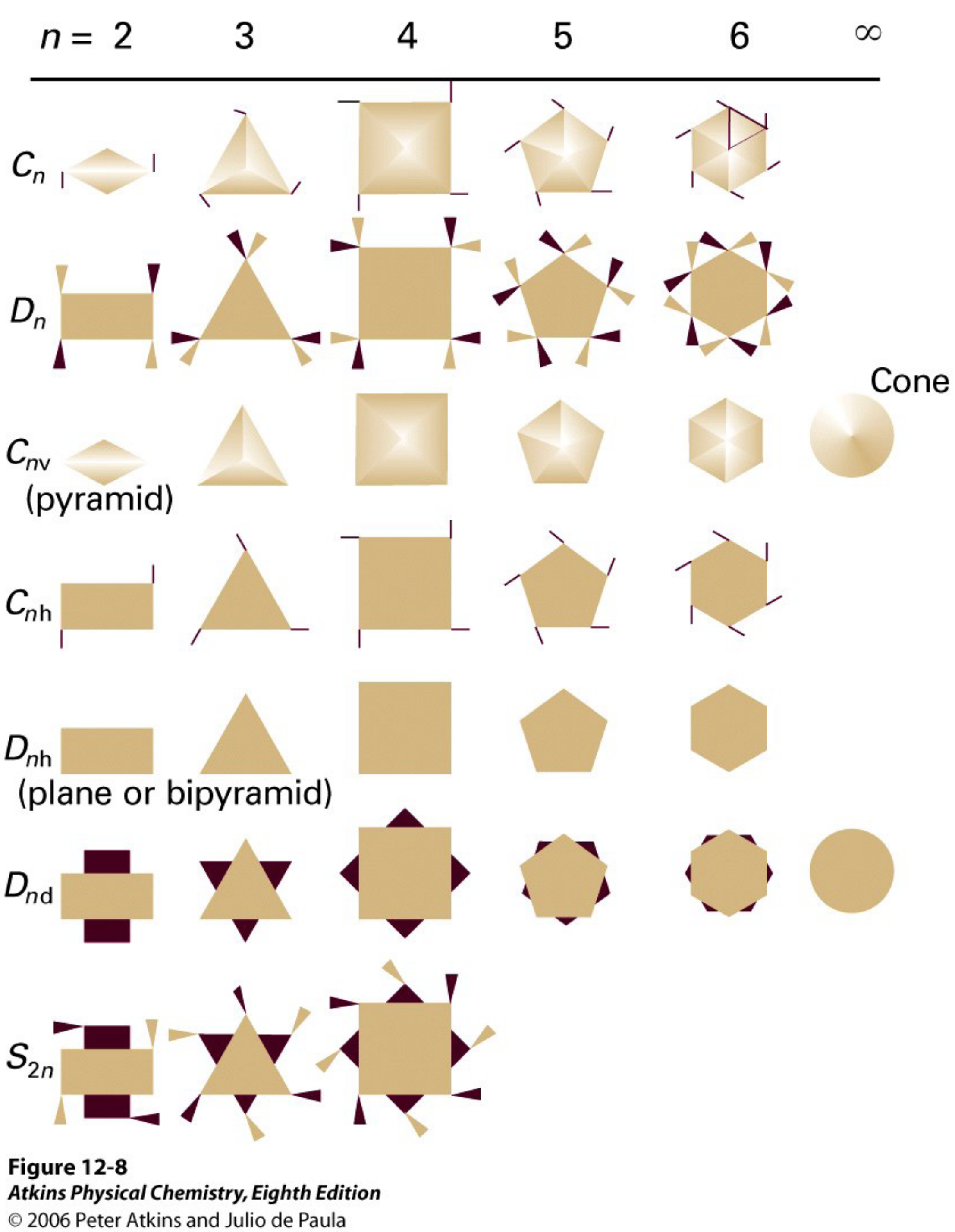


Fig. 2b Schematic representation of some figures and polyhedra with their symmetry properties, orders n and point groups

The point group notation after Hermann-Mauguin is given in the part Crystal Symmetry and Space Groups.

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.

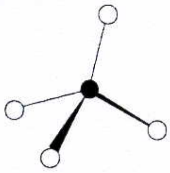
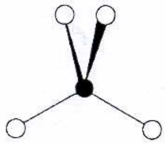
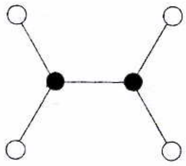
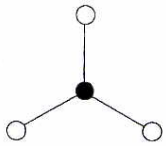
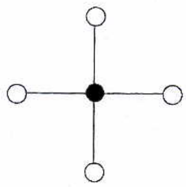
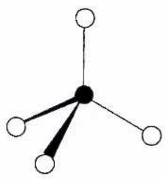
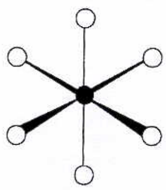
Point-group	Symmetry elements	Structure	Example
C_1	E		SiBrClFI
C_2	E, C_2		H_2O_2
C_s	E, σ		NHF_2
C_{2v}	$E, C_2, \sigma_v, \sigma_v$		H_2O, SO_2Cl_2
C_{3v}	$E, 2C_3, 3\sigma_v$		NH_3, PCl_3, $POCl_3$
$C_{\infty v}$	$E, C_2, 2C_\phi, \ldots \infty\sigma_v$		CO, HCl, OCS
D_{2h}	$E, C_2(x,y,z), \sigma(xy,yz,zx), i$		N_2O_4, B_2H_6
D_{3h}	$E, C_3, 3C_2, 3\sigma_v, \sigma_h, S_3$		BF_3, PCl_5
D_{4h}	$E, C_4, C_2, 2C_2', 2C_2'', i, S_4, \sigma_h, 2\sigma_v, 2\sigma_d$		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_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

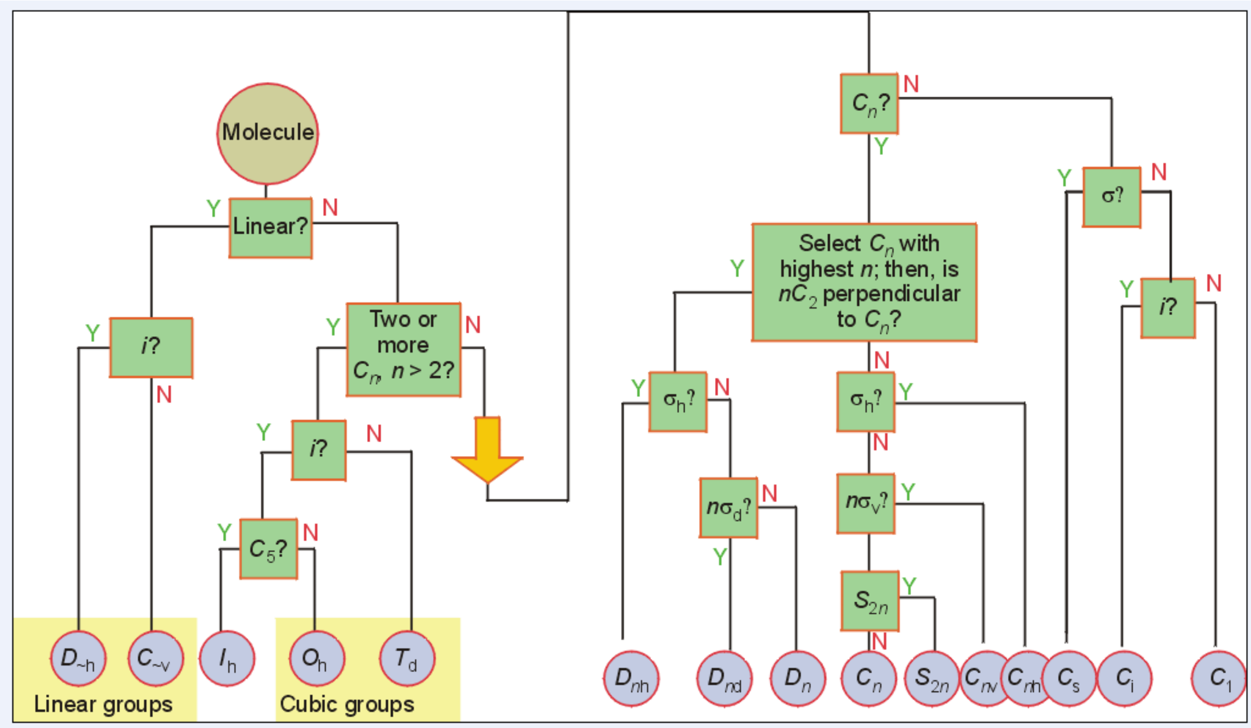


Fig. 4 Symmetry flow chart for the determination of point groups

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).

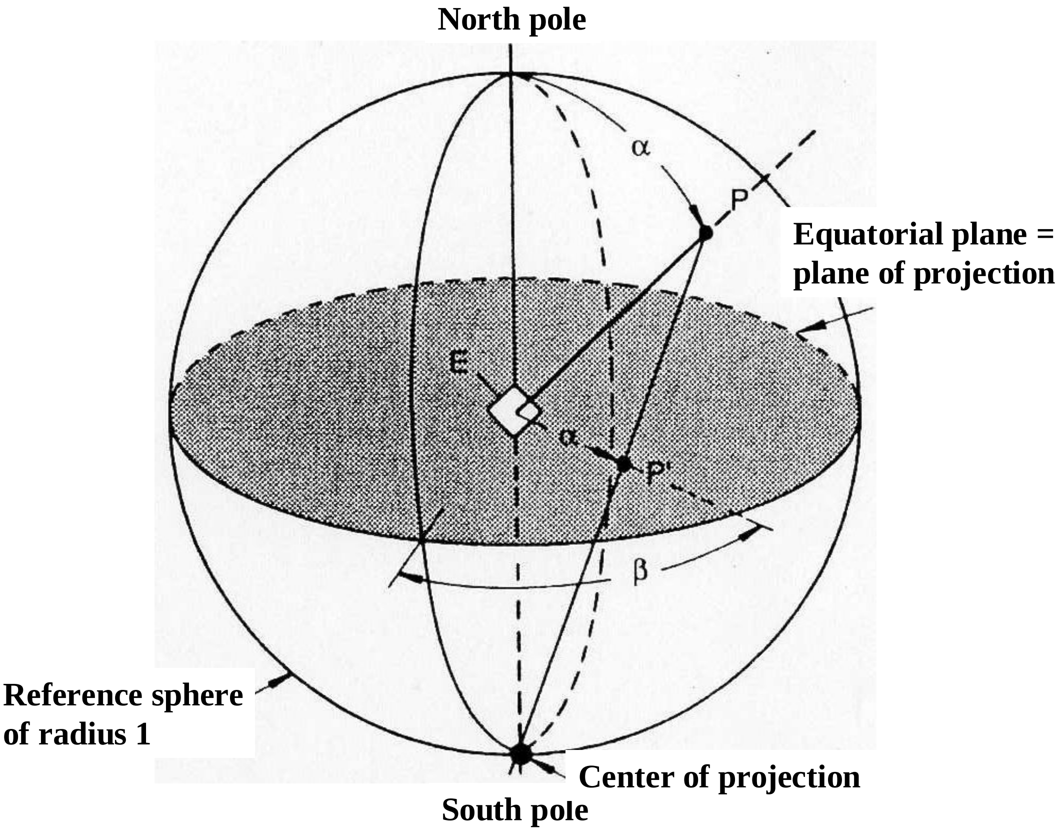


Fig. 5 Principle of a stereographic projection

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).

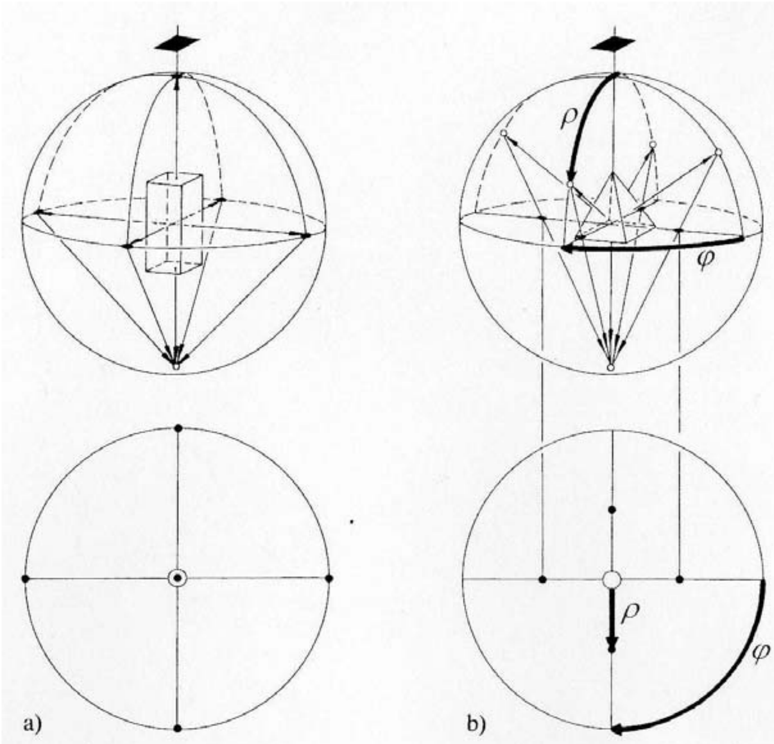


Fig. 6 Stereographic projection of a tetragonal prism (a) and tetragonal pyramid (b). The angle coordinates φ = β and δ = α of the planes of the pyramid are also given.

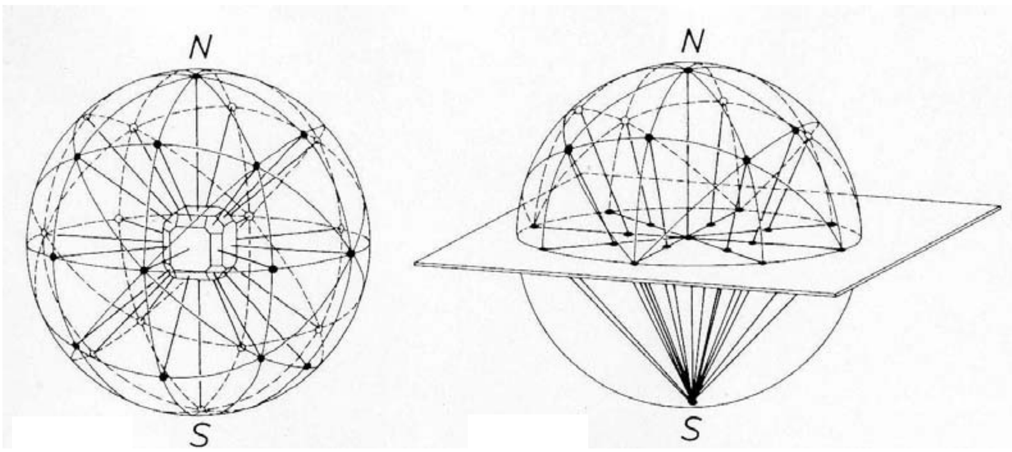


Fig. 7 Plane poles and stereographic projection of a galenite crystal

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.