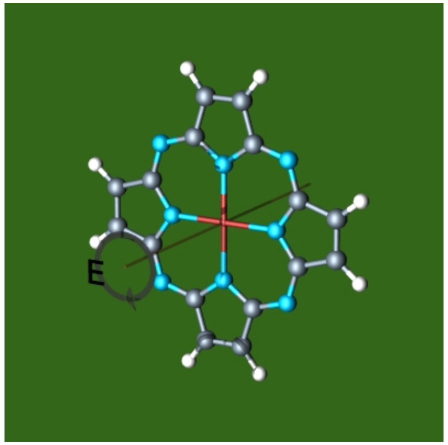
Chapter 5 Symmetry



Reading Assignment:

1. W. B-Ott, Crystallography-chapter 5, 7, 8

http://www.popularphilosophy.com/ideas/2005/3/15/symmetry-of-symmetries.html

http://www.wittandwisdom.com/photos/witt_and_wisdom_photos/symmetry.html

http://www.sculpturegallery.com/sculpture/symmetry.html

Contents

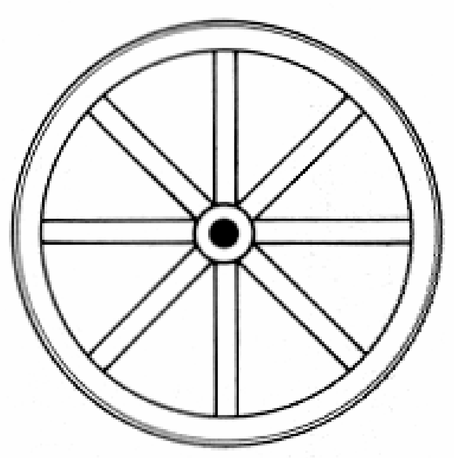
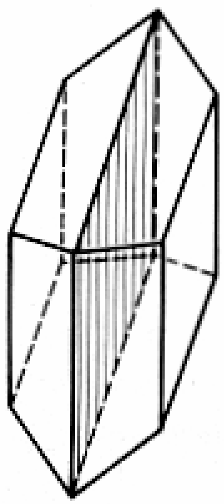
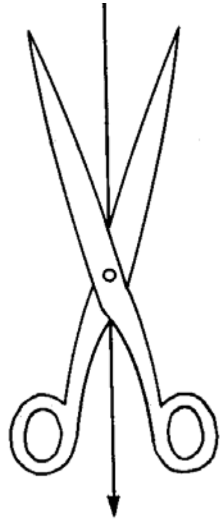
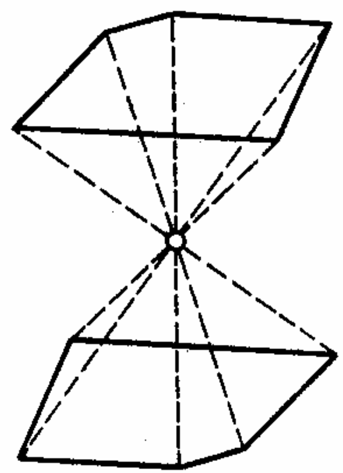
Symmetry

- Repetition

  1. Lattice translation- three non-coplanar lattice translation

     space lattice

  2. Rotation (회전)
  3. Reflection (반사)
  4. Inversion (반전)

Symmetry Aspects of M. C. Escher's Periodic Drawings

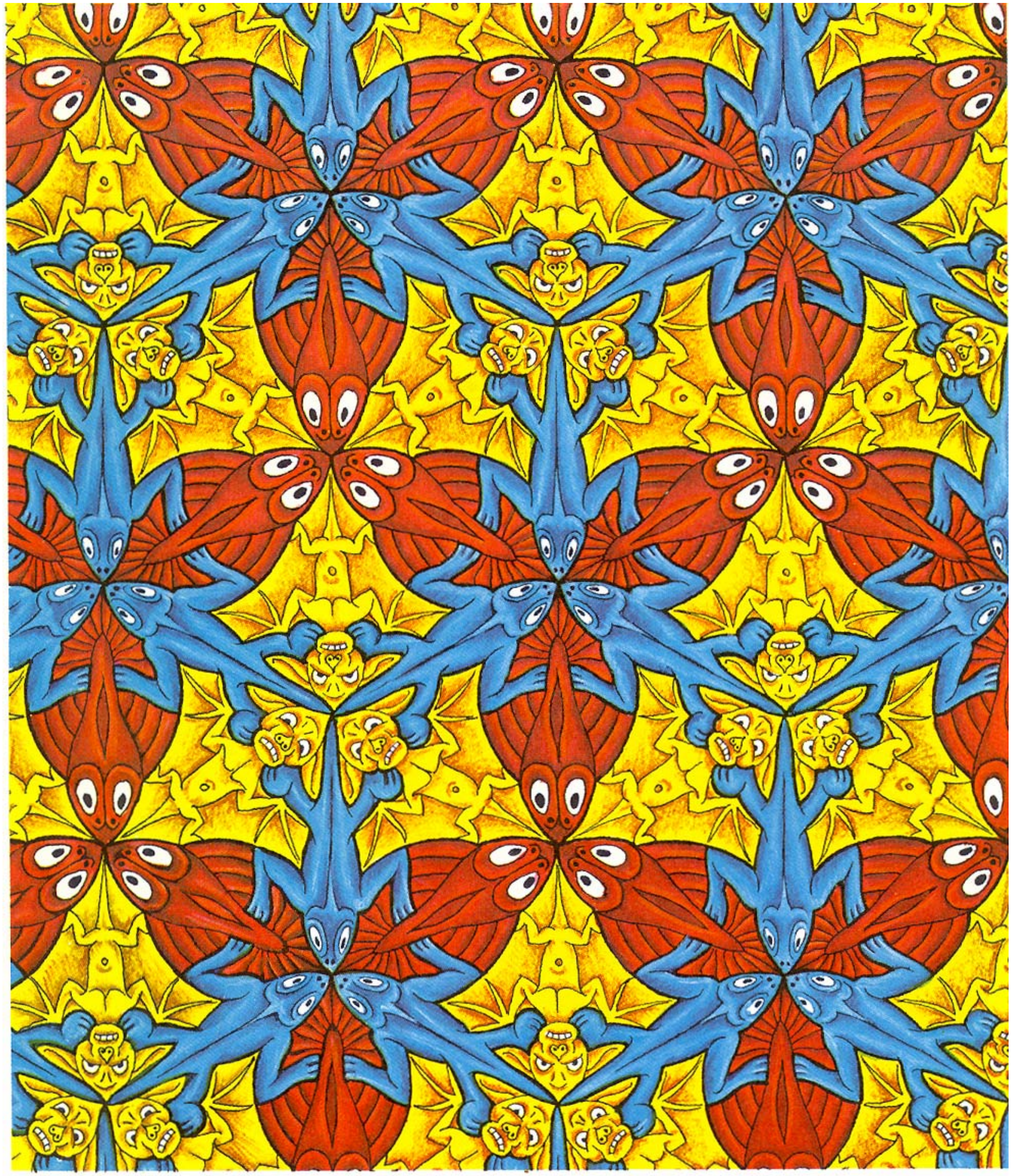


PLATE 9

Fig. 1.1. Pattern based on a fourteenth-century Persian tiling design.

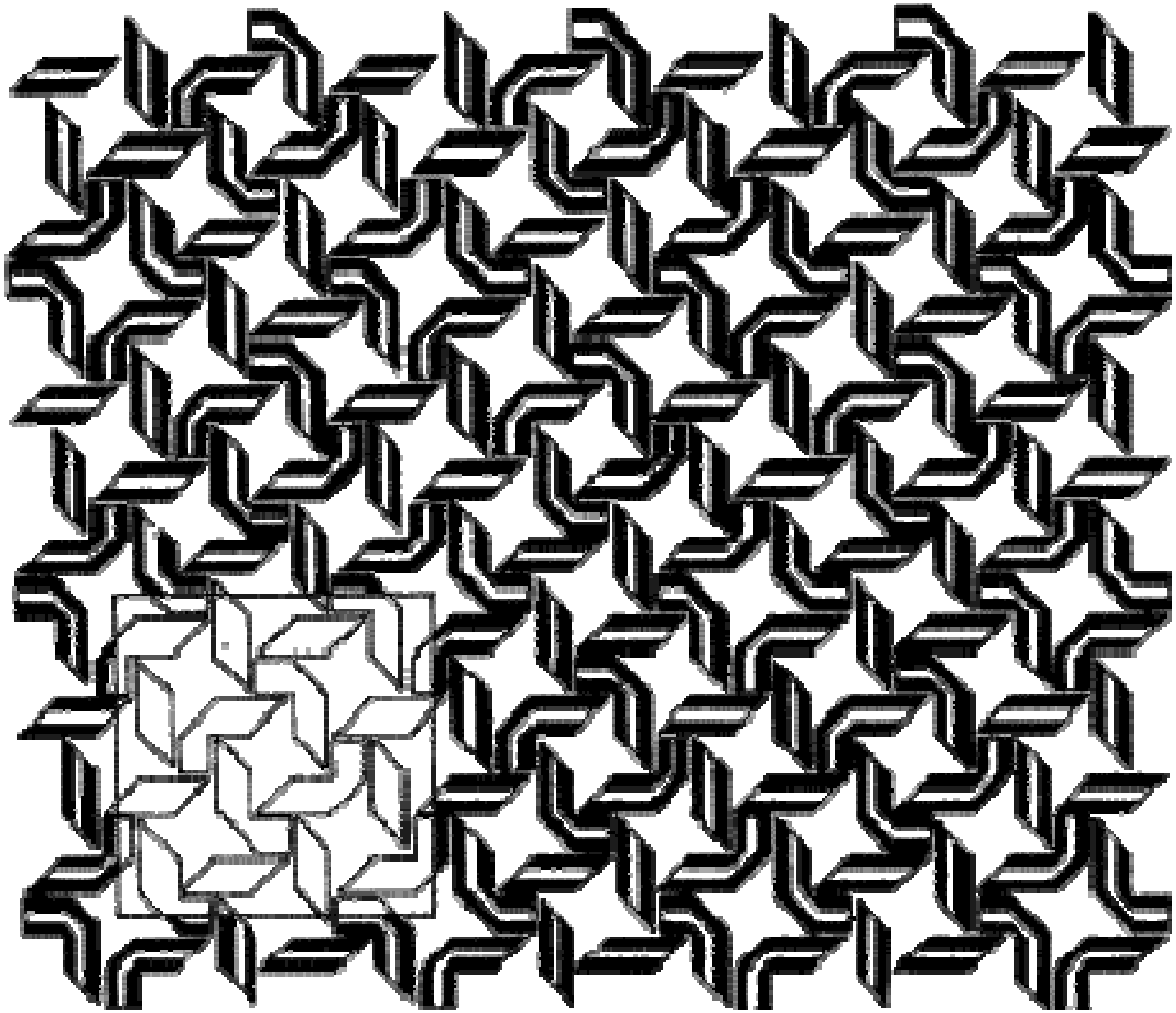


Fig. 1.2. A teacup, showing its mirror plane of symmetry. (After L. S. Dent Glasser, Crystallography & its applications: Van Nostrand Reinhold, 1977.)

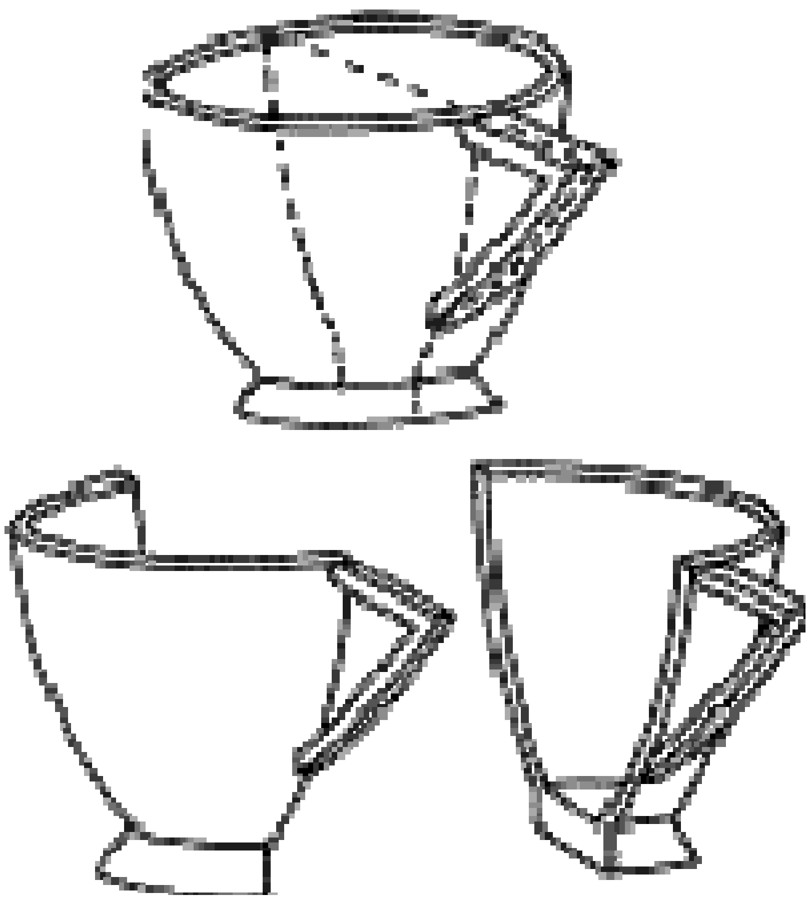
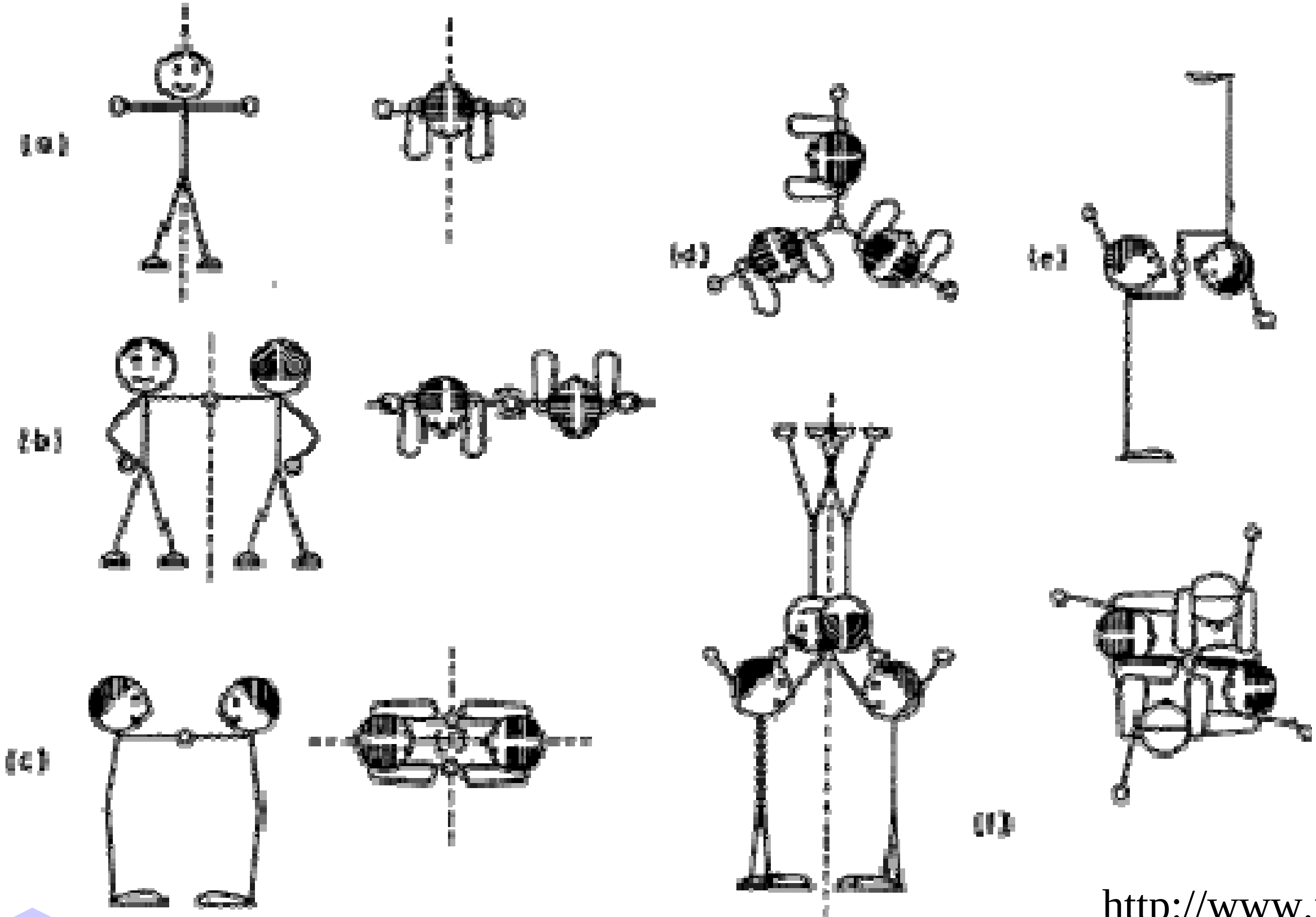


Fig. 1.3. Some symmetry elements, represented by human figures. (a) Mirror plane, shown as dashed line, in elevation and plan. (b) Twofold axis, lying along broken line in elevation, passing perpendicularly through clasped hands in plan. (c) Combination of twofold axis with mirror planes; the position of the symmetry elements given only in plan. (d) Threefold axis, shown in plan only. (e) Centre of symmetry (in centre of clasped hands). (f) Fourfold inversion axis, in elevation and plan, running along the dashed line and through the centre of the clasped hands.

(After L. S. Dent Glasser, Chapter 19, The Chemistry of Cements: Academic Press, 1964.)



http://www.iucr.ac.uk/

Symmetry

* All repetition operations are called symmetry operations.
  Symmetry consists of the repetition of a pattern by the application of specific rules.
* When a symmetry operation has a locus, that is a point, or a line, or a plane that is left unchanged by the operation, this locus is referred to as the symmetry element.

Symmetry operation	symmetry element
reflection	mirror plane
rotation	rotation axis
inversion	inversion center (center of symmetry)

Rotation Axis

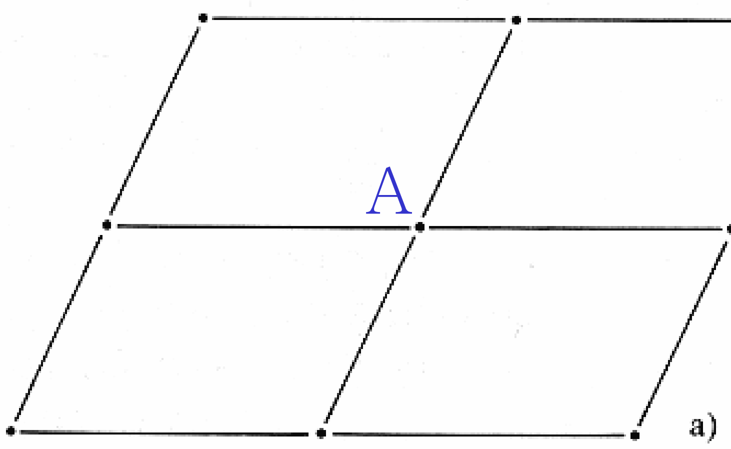
- general plane lattice

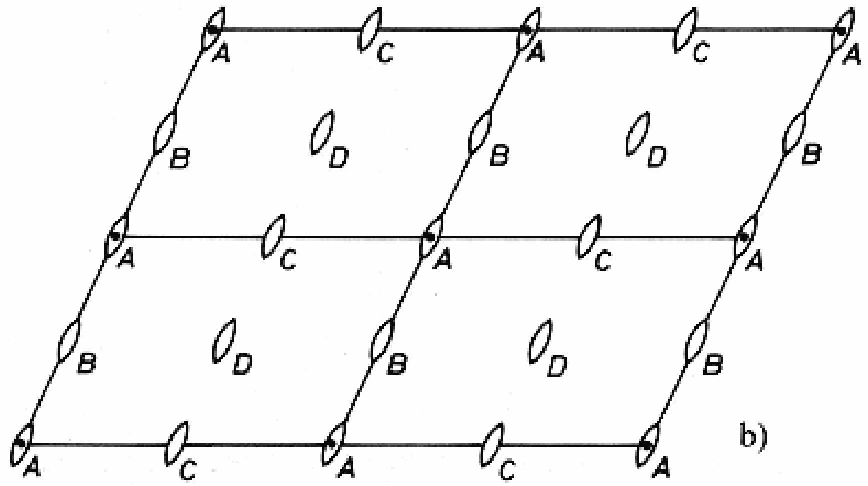
180° rotation about the central lattice point A- coincidence

- 2 fold rotation axis

symbol: 2, ⬮ → normal or parallel to plane of paper

$$n = \frac{360^o}{\phi} = \frac{2\pi}{\phi}$$



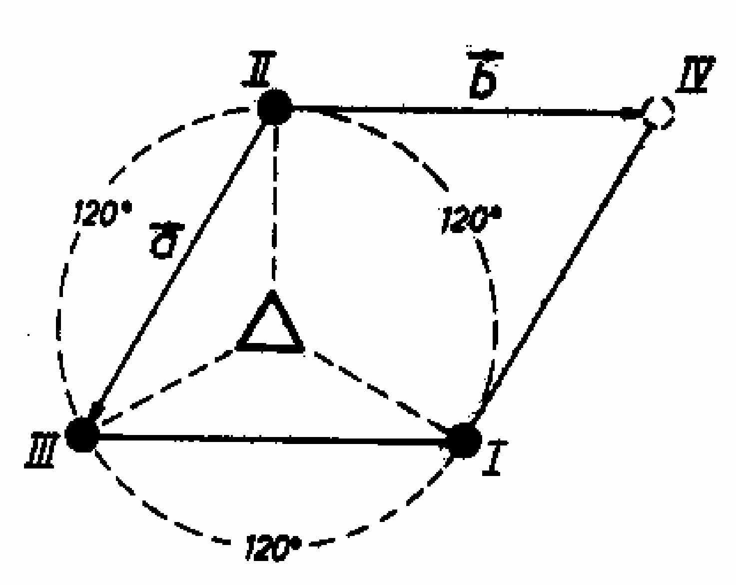


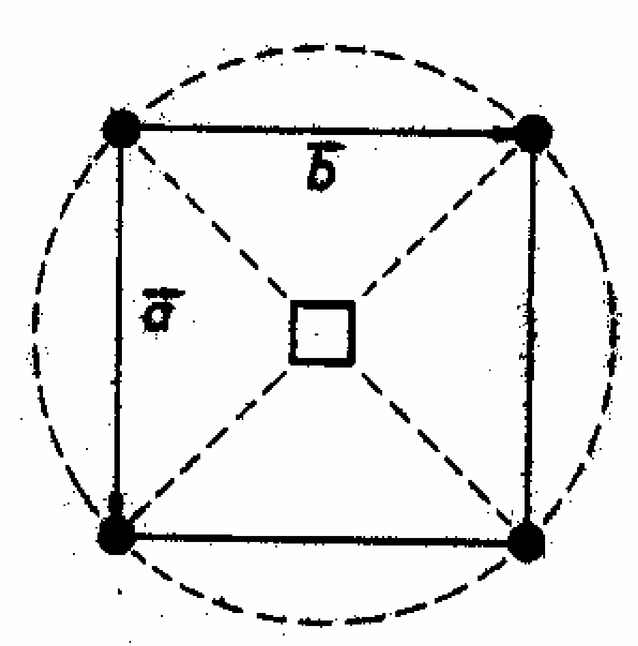
Rotation Axis

-n-fold axis $n = \frac{360^o}{\phi} = \frac{2\pi}{\phi}$ φ: minimum angle required to reach a position indistinguishable

-n > 2 produce at least two other points lying in a plane normal to it
  - three non-colinear points define a lattice plane
  - fulfill the conditions for being a lattice plane (translational periodicity)

- 3 fold axis: ϕ= 120°, n=3, ▲ - 4 fold axis: ϕ=90°, n=4, ■

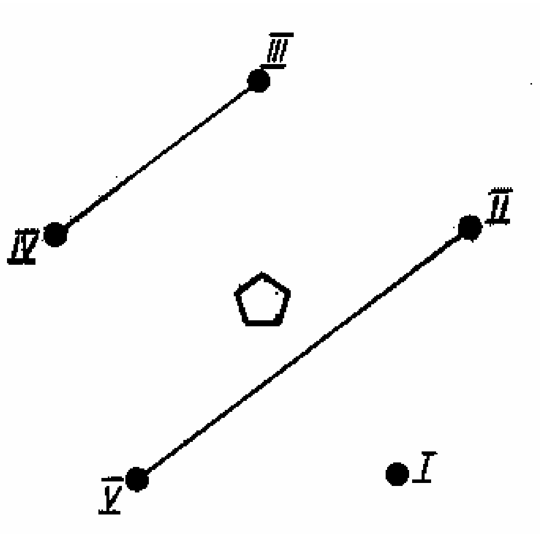


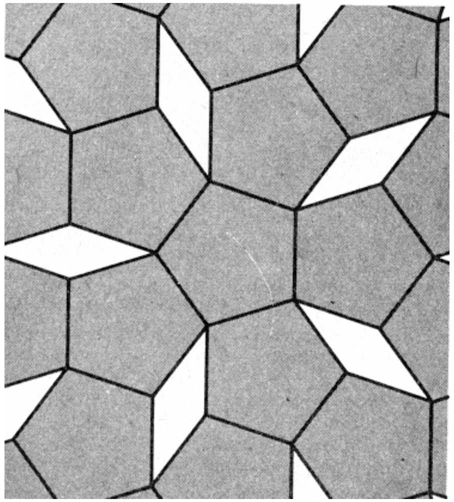


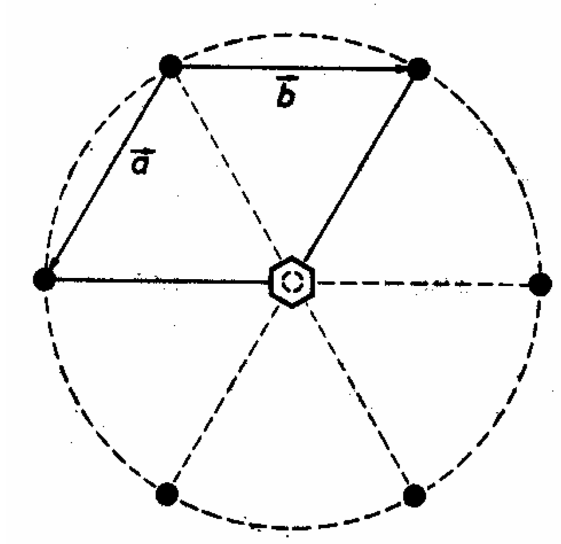
Rotation Axis

–5 fold axis: ϕ= 72°, n=5,

– 6 fold axis: ϕ=60°, n=6, ⬢

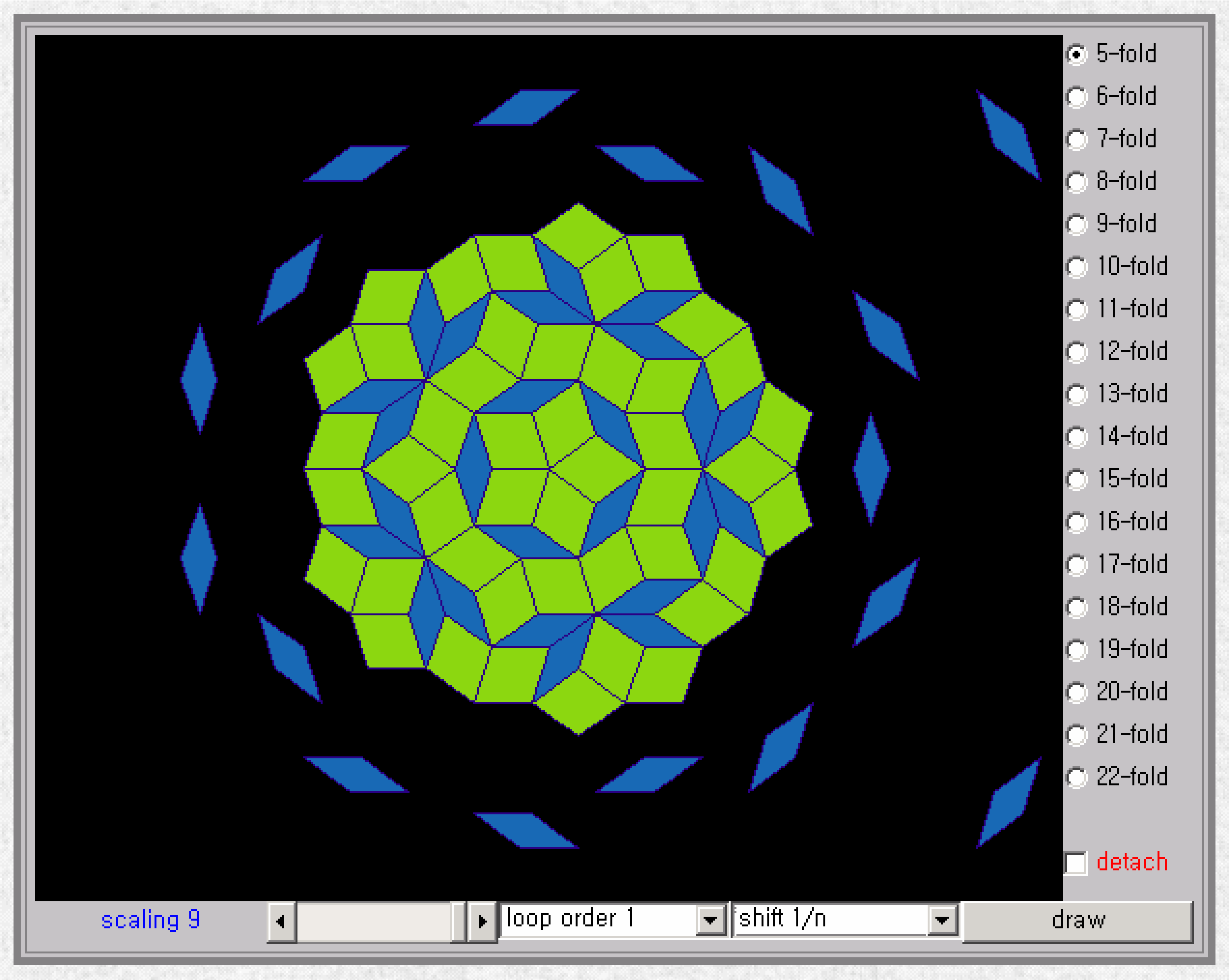






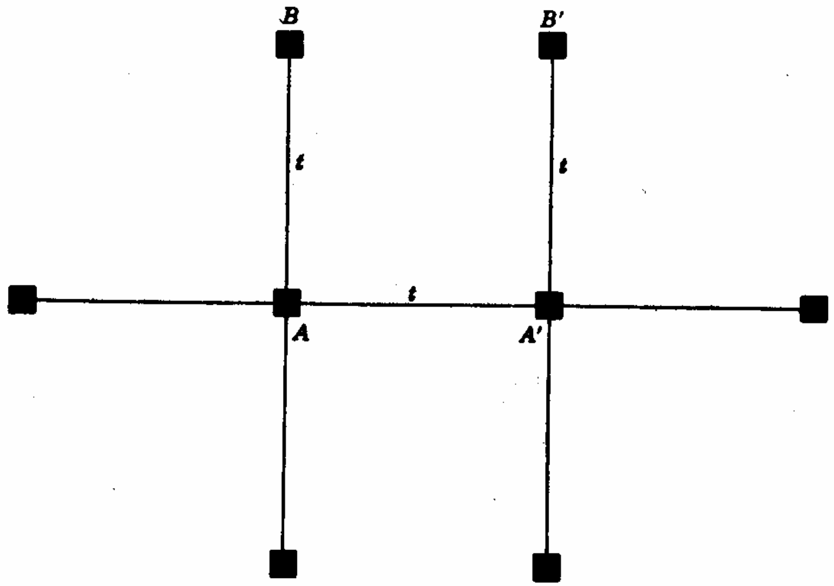
II–V and III–IV parallel but
not equal or integral ratio

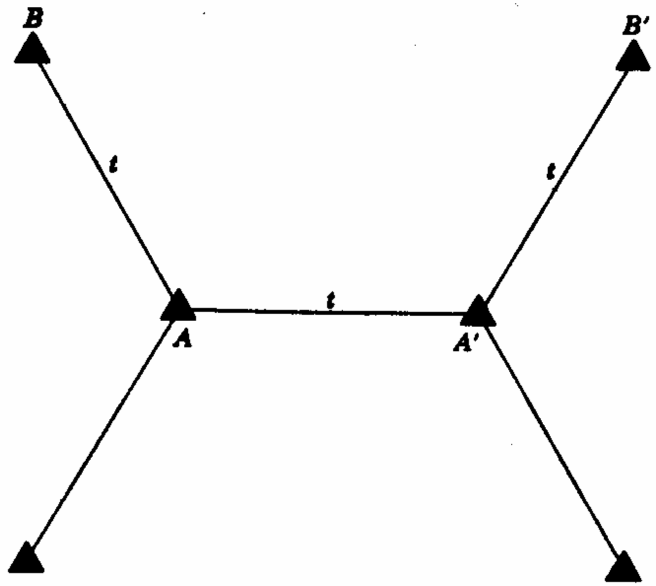
* In space lattices and consequently in crystals, only 1–, 2–, 3–, 4–, and 6–fold rotation axes can occur.

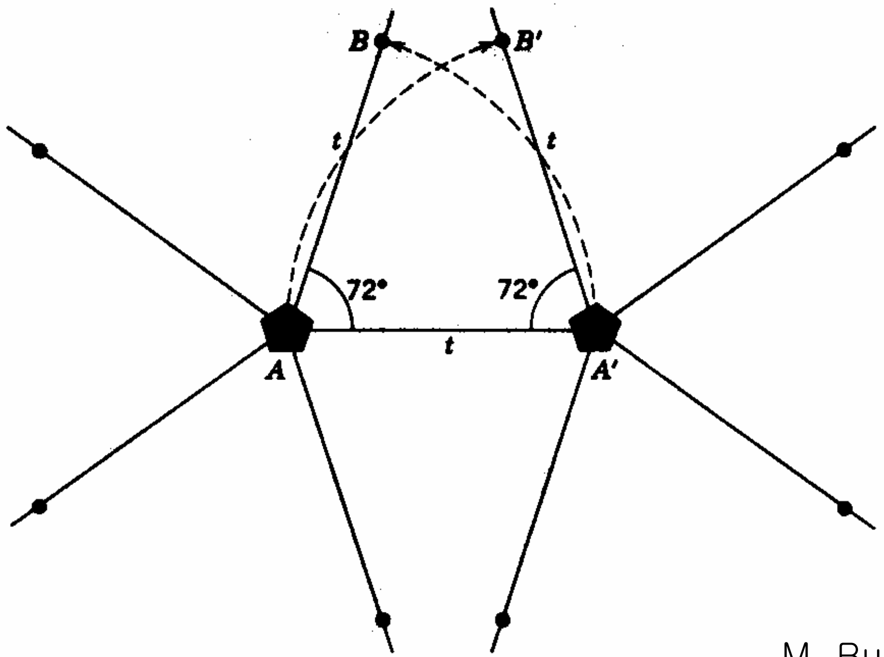


http://jcrystal.com/steffenweber/JAVA/jtiling/jtiling.html

Rotation Axis



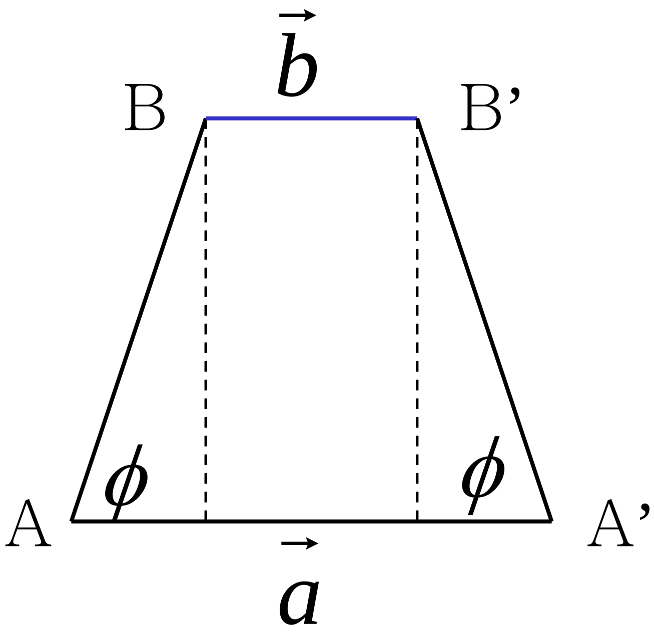




M. Buerger, Elementary Crystallography

Rotation Axis

- limitation of ϕ set by translation periodicity



$$\vec{b} = m\vec{a}$$ where m is an integer

$$ma = a - 2a\cos\phi$$

$$m = 1 - 2\cos\phi$$

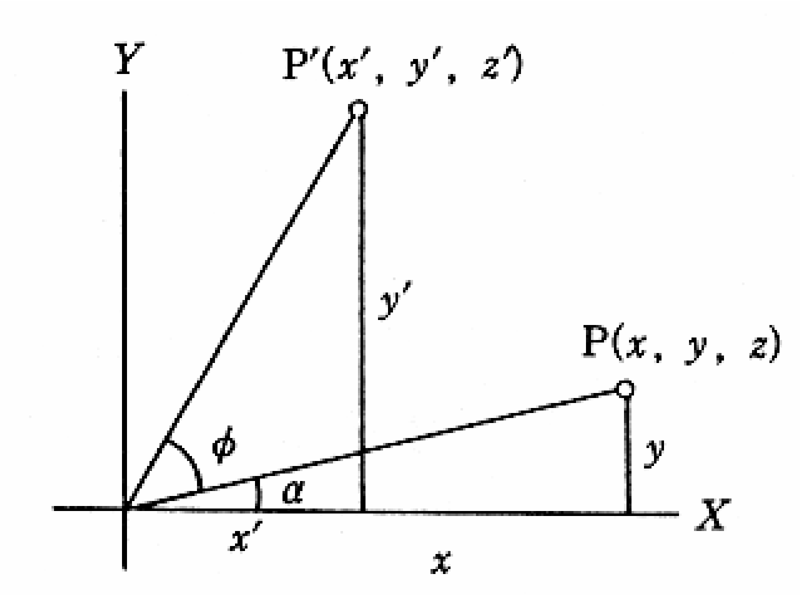
$$\cos\phi = \frac{1-m}{2}$$

m	cosϕ	ϕ	n
−1	1	2π	1
0	½	$\pi/3$	6
1	0	$\pi/2$	4
2	−½	$2\pi/3$	3
3	−1	π	2

1. 2, 3, 4, 6

Rotation Axis

– Matrix representation of rotation in Cartesian coordinate



직교축계에서 z축을 회전축으로 하고
ϕ각만큼 회전시킨 회전조작

$$R(n_z^1) = \begin{pmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$R(2_z^1) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$R(3_z^1) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$R(3_z^2) = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Rotation Axis

$$R(4_z^1)=\begin{pmatrix}0 & -1 & 0\\ 1 & 0 & 0\\ 0 & 0 & 1\end{pmatrix}\quad R(4_z^2)=R(2_z^1)=\begin{pmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{pmatrix}\quad R(4_z^3)=\begin{pmatrix}0 & 1 & 0\\ -1 & 0 & 0\\ 0 & 0 & 1\end{pmatrix}$$

$$R(4_z^1)\bullet R(4_z^2)=\begin{pmatrix}0 & -1 & 0\\ 1 & 0 & 0\\ 0 & 0 & 1\end{pmatrix}\begin{pmatrix}-1 & 0 & 0\\ 0 & -1 & 0\\ 0 & 0 & 1\end{pmatrix}=\begin{pmatrix}0 & 1 & 0\\ -1 & 0 & 0\\ 0 & 0 & 1\end{pmatrix}=R(4_z^3)$$

$$R(6_z^1)=\begin{pmatrix}\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0\\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0\\ 0 & 0 & 1\end{pmatrix}$$

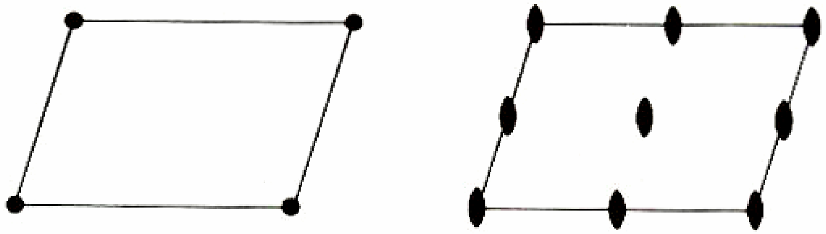
$$R(6_z^2)=R(3_z^1)$$

$$R(6_z^3)=R(2_z^1)$$

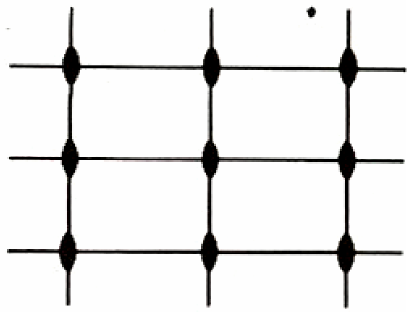
$$R(6_z^4)=R(3_z^2)$$

$$R(6_z^5)=\begin{pmatrix}\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0\\ 0 & 0 & 1\end{pmatrix}$$

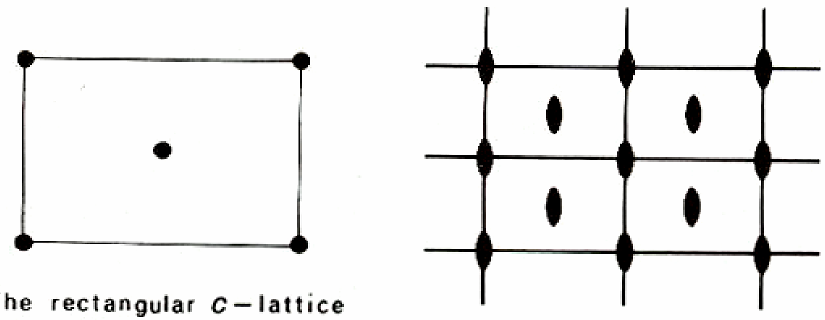
Five Plane Lattices



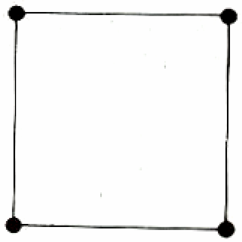
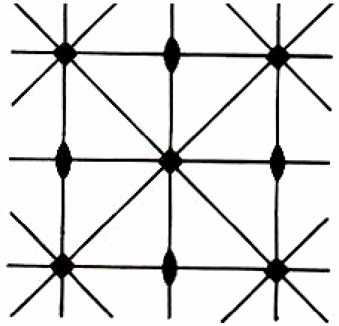
The oblique *p*− lattice



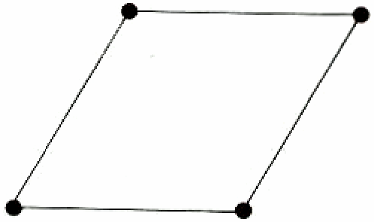
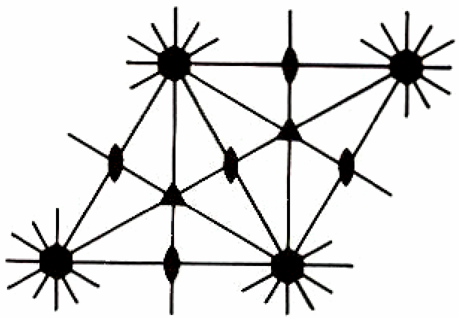
The rectangular *p*− lattice



The rectangular *c*−lattice

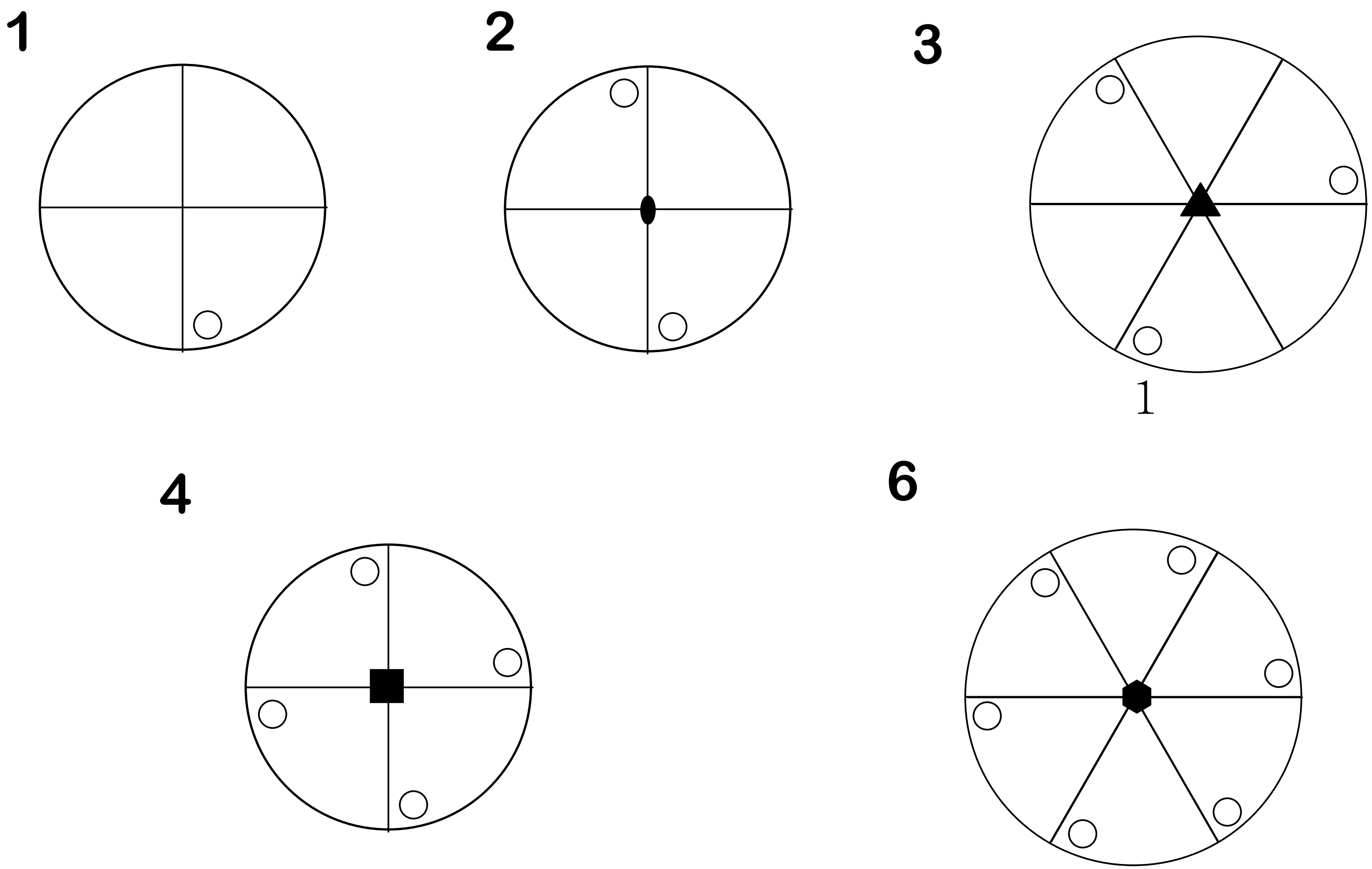



The square *p*−lattice

The hexagonal *p*−lattice

Rotation Axis

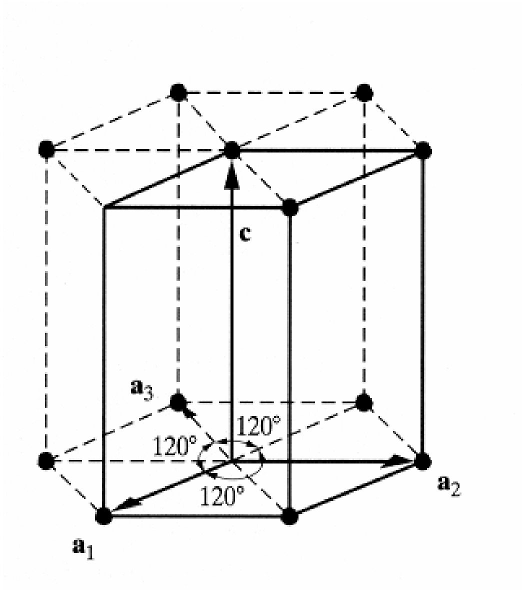


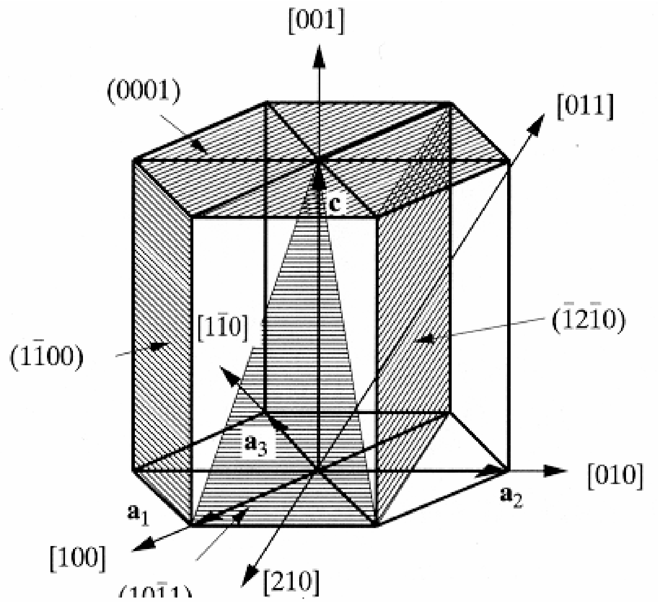
Rotation Axis

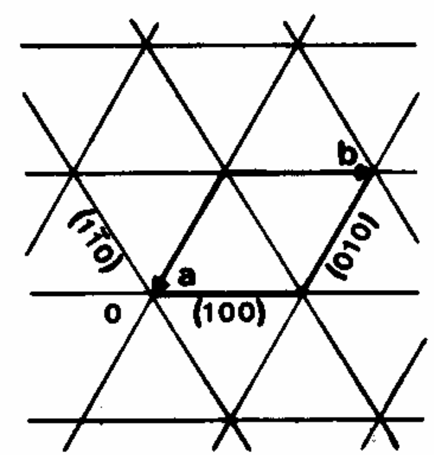
- hexagonal coordinate

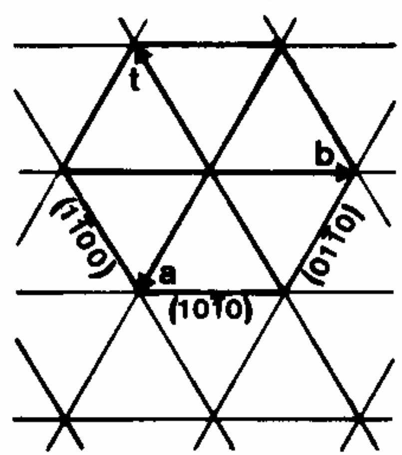
  a_1, a_2, a_3, c

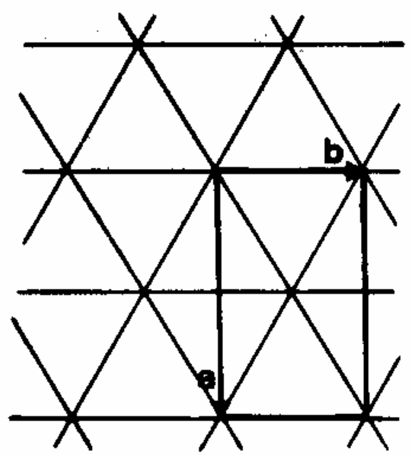
  Miller-Bravais indices (h k i l) i=-(h+k)





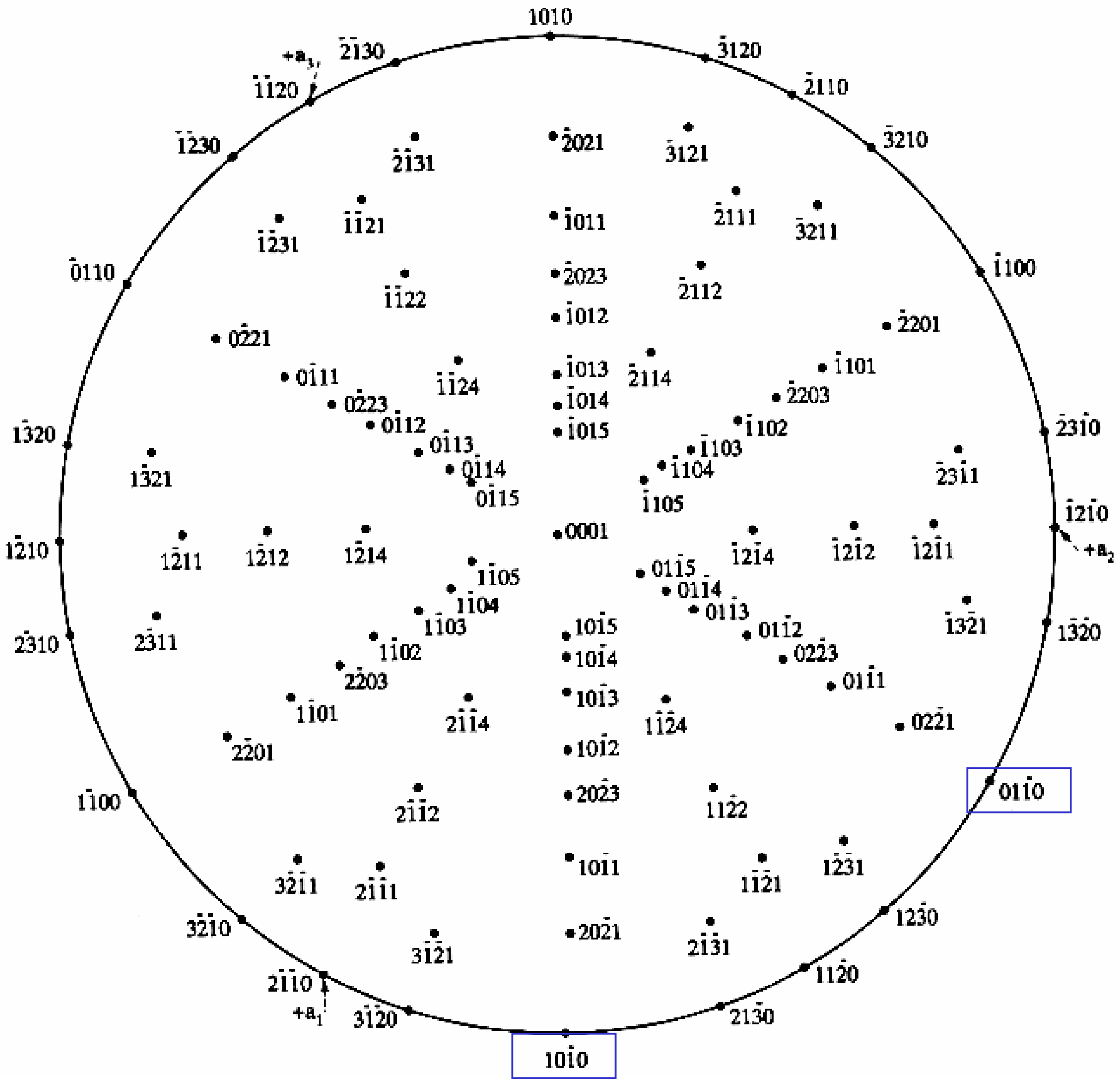






B. D. Cullity, Elements of X-ray Diffraction

Rotation Axis



Standard (0001) projection (hexagonal, c/a=1.86)

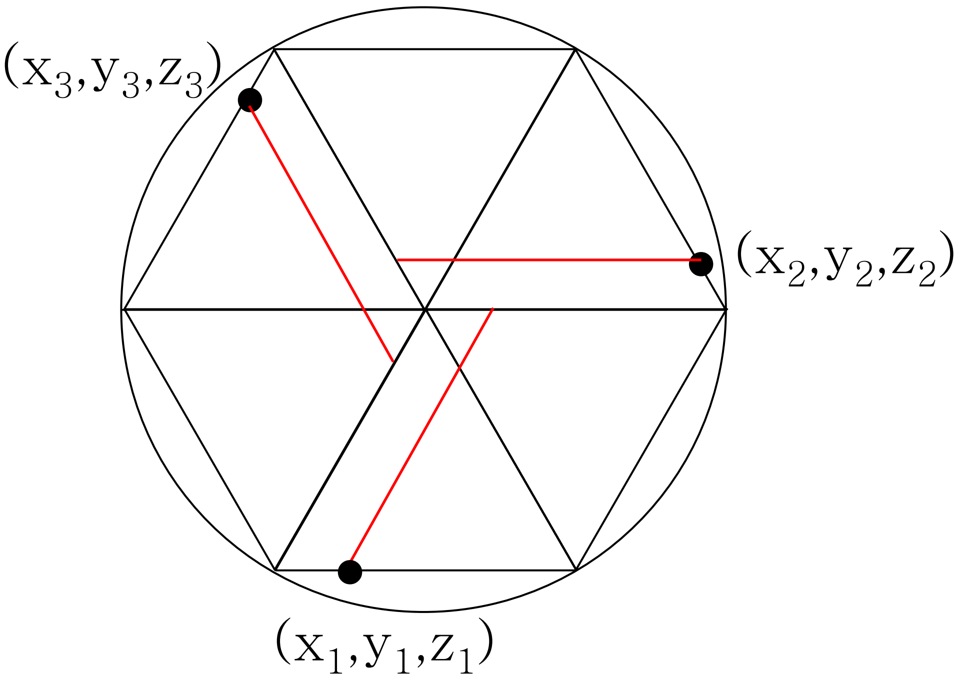
B. D. Cullity, Elements of X-ray Diffraction

Rotation Axis

$$x_2 = -y_1 \qquad y_2 = x_1 - y_1 \qquad z_2 = z_1$$

$$x_3 = -x_1 + y_1 \qquad y_3 = -x_1 \qquad x_3 = z_1$$

$$R(3_z^1) = \begin{pmatrix} 0 & -1 & 0 \\ 1 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad R(3_z^2) = \begin{pmatrix} -1 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

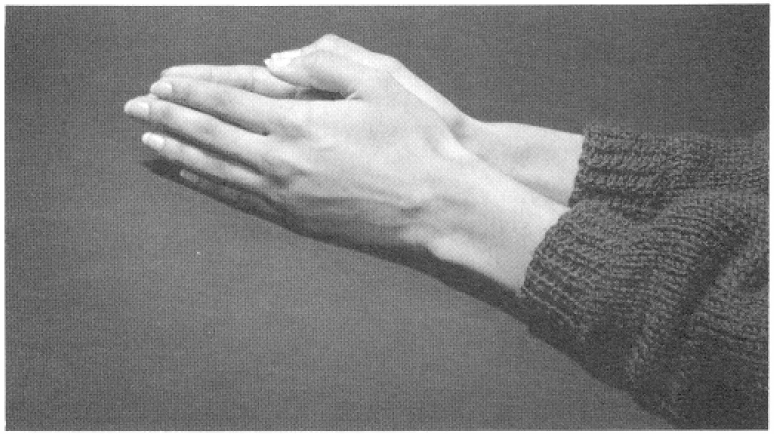


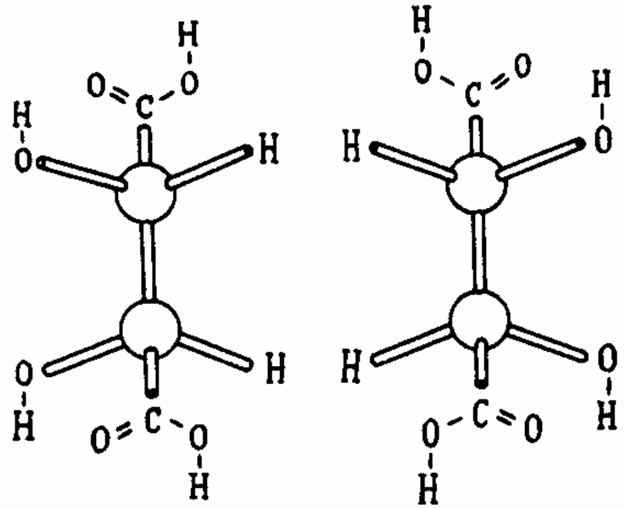
* Cartesian coordinate

$$R(3_z^1) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

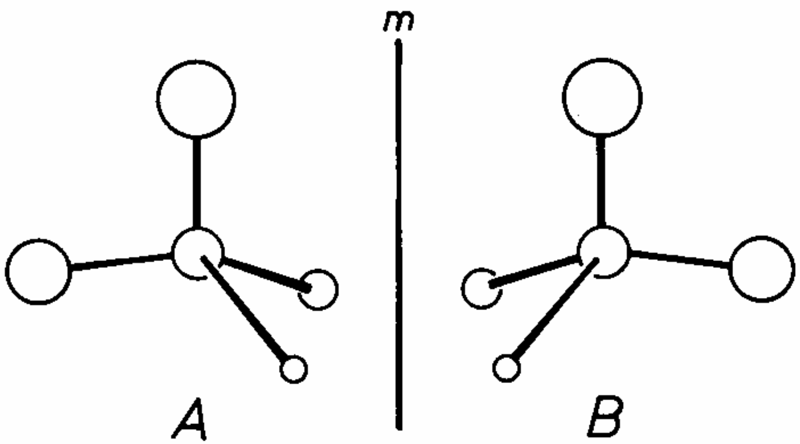
Reflection

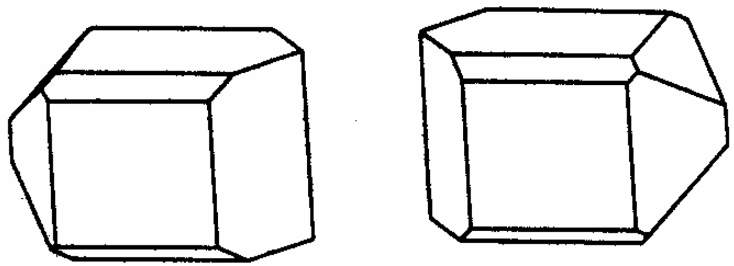
– reflection, a plane of symmetry or a mirror plane, m, |, ┌





(a)

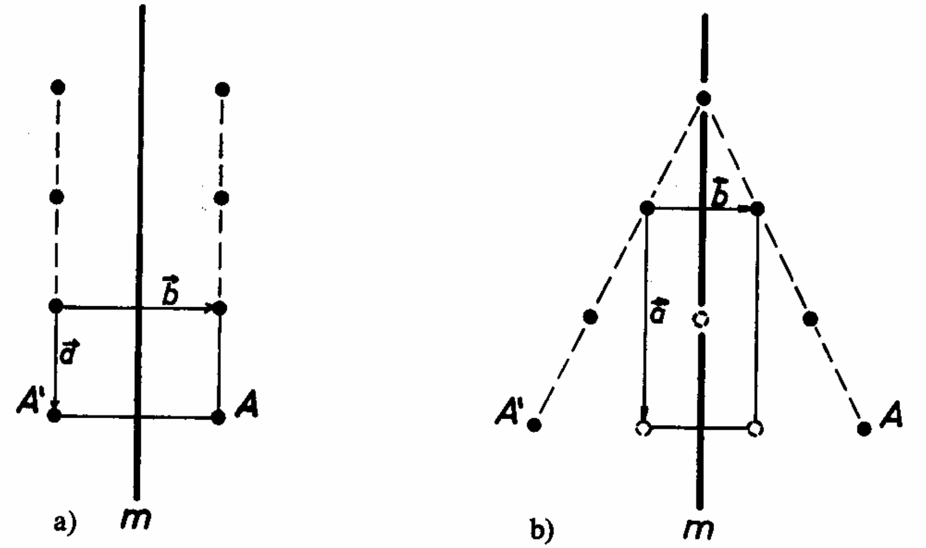




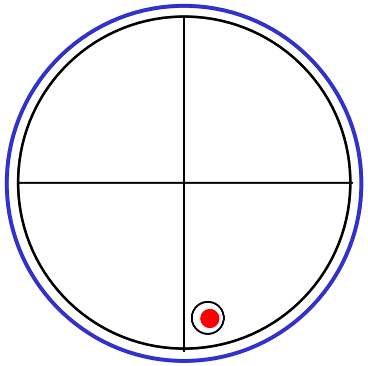
(b)

Tartaric acid

Reflection



rectangular   centered rectangular



m_{xy} (m_z)

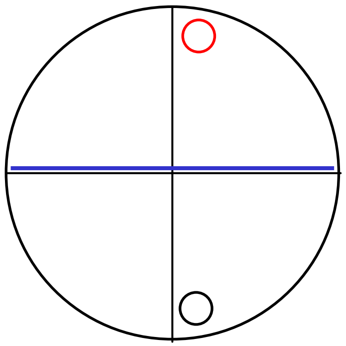
$$x_2 = x_1$$
$$y_2 = y_1$$
$$z_2 = -z_1$$

$$R(m_z) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

$$|R(m_z)| = -1$$

enantiomorph

대장상



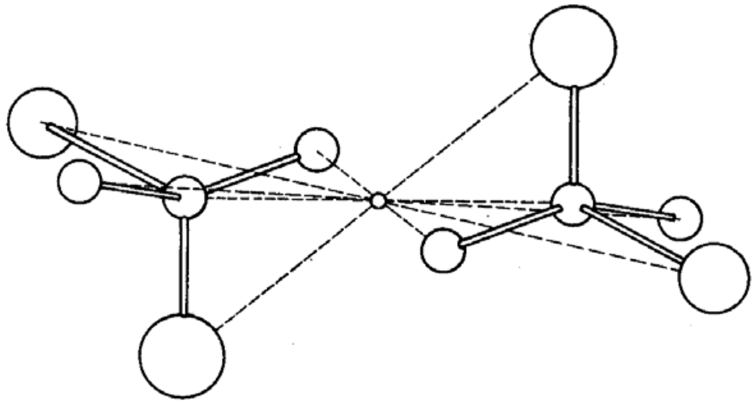
m_{yz} (m_x)

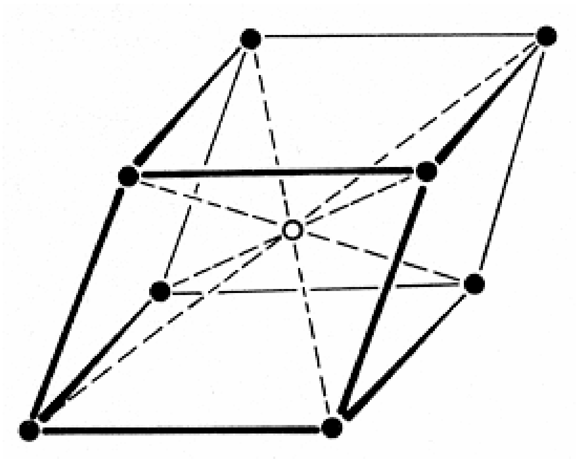
$$x_2 = -x_1$$
$$y_2 = y_1$$
$$z_2 = z_1$$

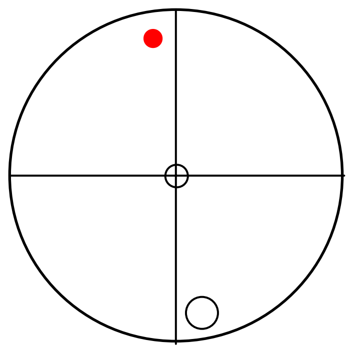
$$R(m_x) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Inversion

- inversion, center of symmetry or inversion center, $\bar{1}$ ○







$$x_2 = -x_1$$
$$y_2 = -y_1$$
$$z_2 = -z_1$$

$$R(\bar{1}) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

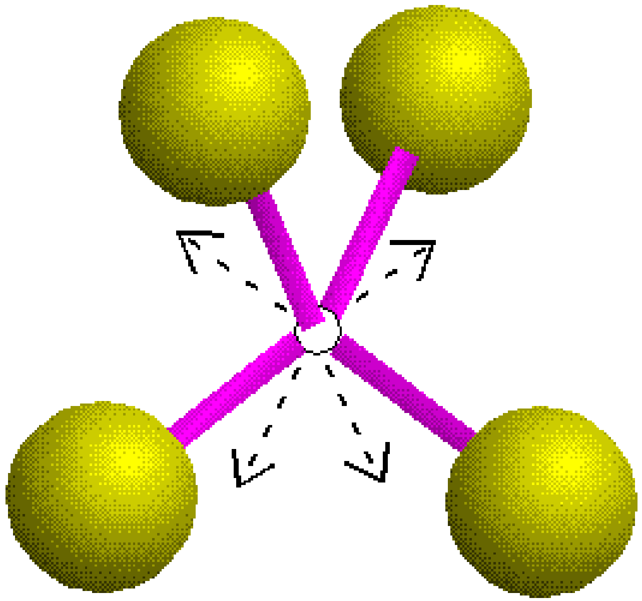
All lattices are centrosymmteric.

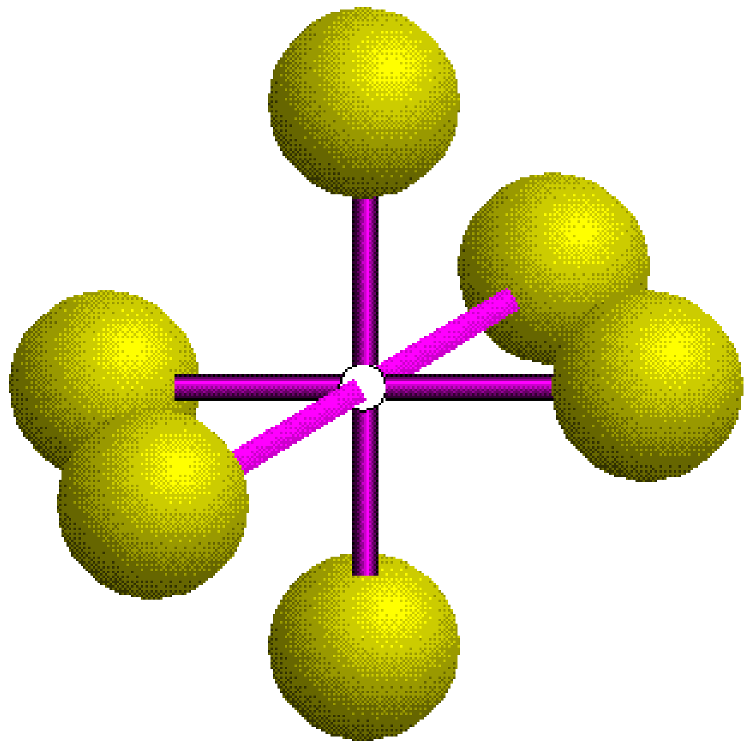
$$\left| R(\bar{1}) \right| = -1$$

C. Hammond, The Basic Crystallography and Diffraction

Inversion

Inversion centre





No inversion centre

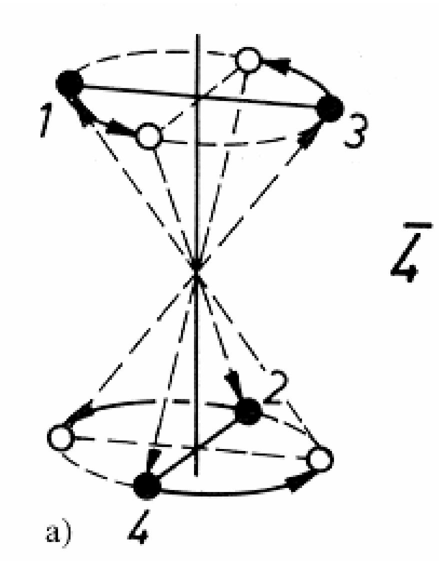
http://www.gh.wits.ac.za/craig/diagrams/

Compound Symmetry Operation

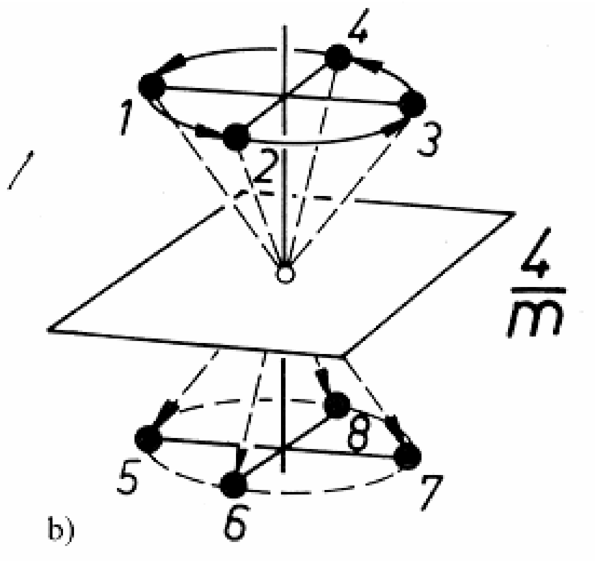
- link of translation, rotation, reflection, and inversion operation

-compound symmetry operation
two symmetry operation in sequence as a single event

- combination of symmetry operations
two or more individual symmetry operations are combined
which are themselves symmetry operations



compound



combination

Compound Symmetry Operation

Table 5.1. Compound symmetry operations of simple operations. The corresponding symmetry elements are given in round brackets

	Rotation	Reflection	Inversion	Translation
Rotation	×	Roto-reflection	Roto-inversion	Screw rotation
Reflection	(Roto-reflection axis)	×	2-fold rotation	Glide reflection
Inversion	(Roto-inversion axis)	(2-fold rotation axis)	×	Inversion
Translation	(Screw axis)	(Glide plane)	(Inversion centre)	×

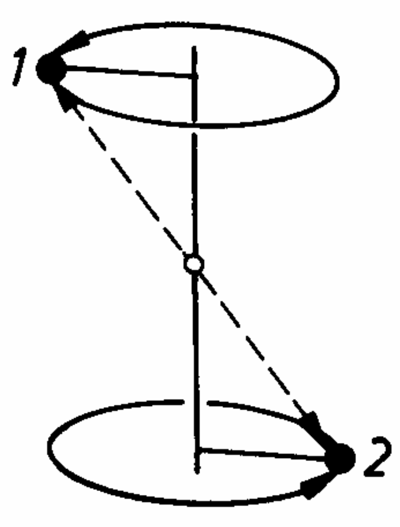
Rotoinversion

-compound symmetry operation of rotation and inversion

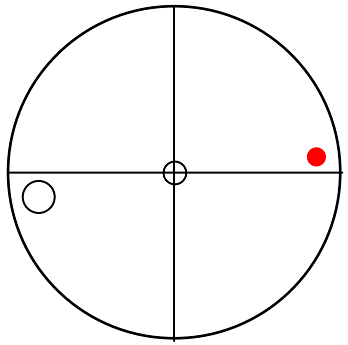
-rotoinversion axis $\bar{n}$

- 1, 2, 3, 4, 6 –> $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$, $\bar{6}$

- $\bar{1}$



$\bar{1}$ ≡ inversion centre

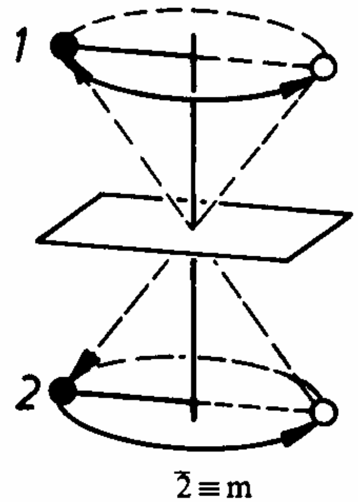


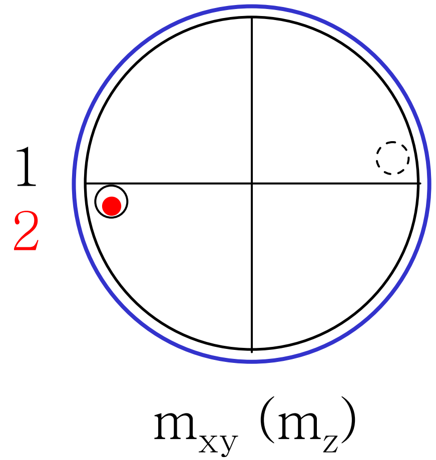
● down, left

○ up, right

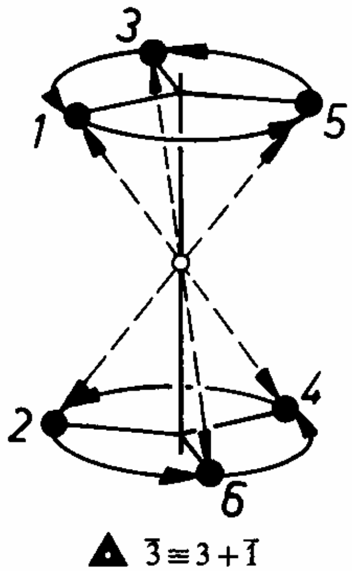
Rotoinversion

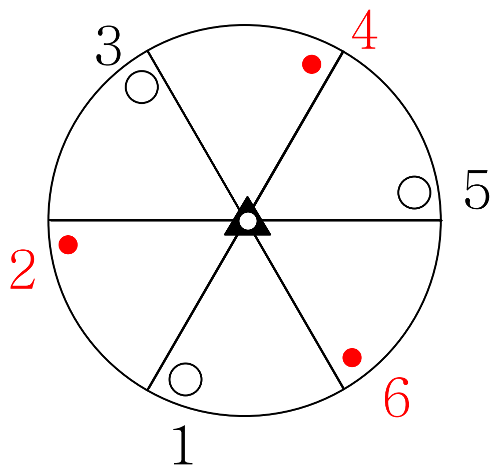
$-\bar{2}(\equiv m)$





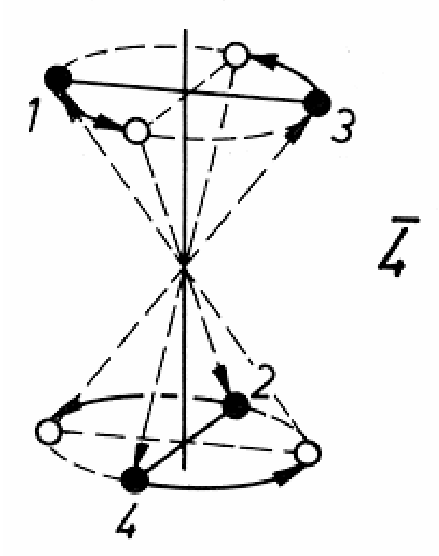
$-\bar{3} \equiv 3 + \bar{1}$ ▲

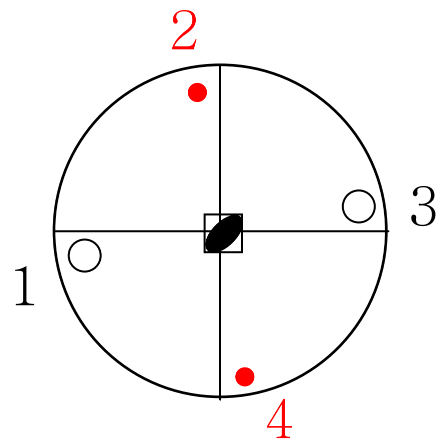




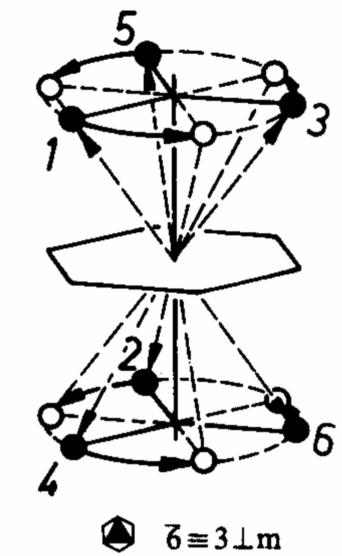
Rotoinversion

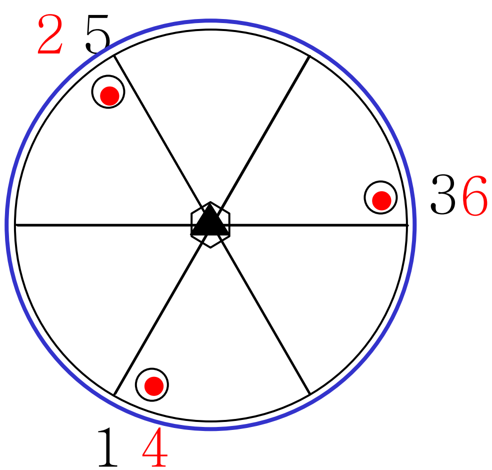
− $\bar{4}$





− $\bar{6}$





Rotoinversion

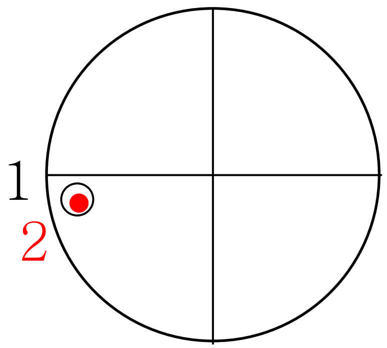
- $\bar{1} \equiv$ inversion center, $\bar{2} \equiv m$, $\bar{3} \equiv 3 + \bar{1}$, $\bar{4}$ implies 2, $\bar{6} \equiv 3 \perp m$,

- only rotoinversion axes of odd order imply the presence of an inversion center

Rotoreflection

$S_1 = m \quad S_2 = \bar{1} \quad S_3 = \bar{6} \quad S_4 = \bar{4} \quad S_6 = \bar{3}$

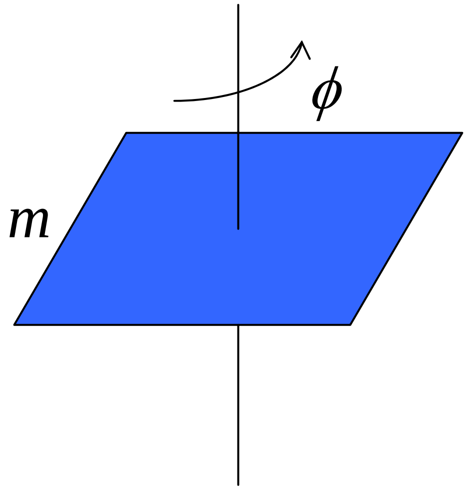
$S_1 = m$



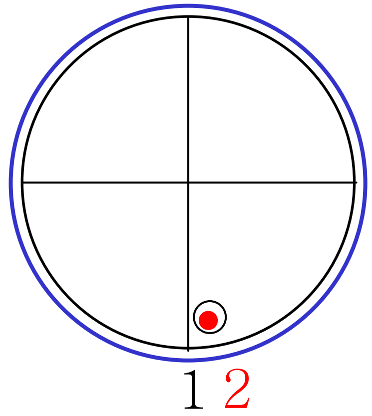
- The axes n and $\bar{n}$, including $\bar{1}$ and m, are called point-symmetry element, since their operations always leave at least one point unmoved

Combination

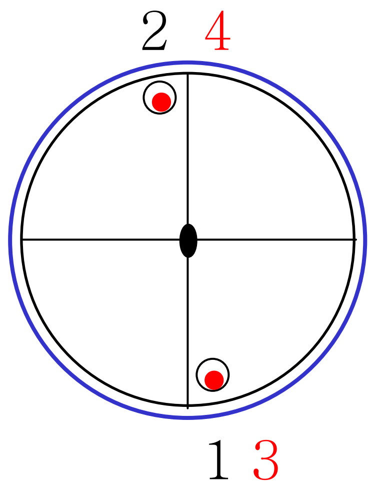
– a mirror plane is added normal to the rotation axis, $\frac{X}{m}$



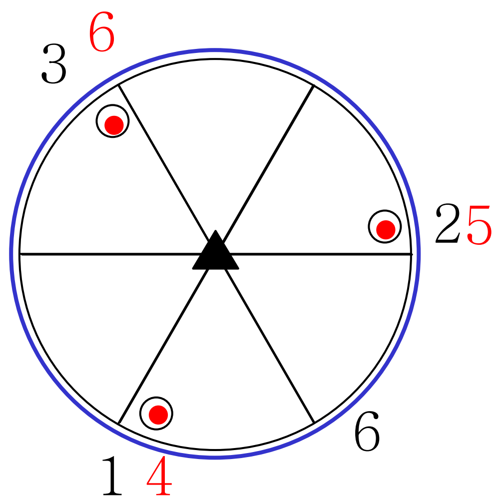
– $\frac{1}{m}$ $(\equiv m)$



– $\frac{2}{m}$



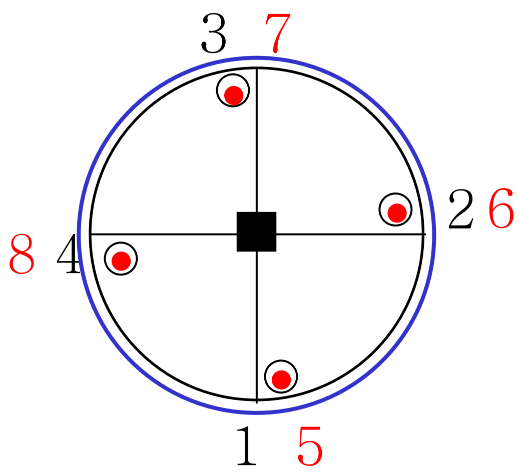
– $\frac{3}{m}$ $(\equiv \bar{6})$



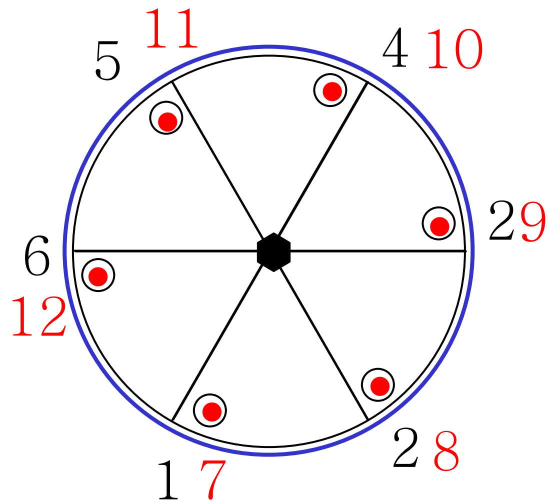
Combination

– a mirror plane is added normal to the rotation axis, $\frac{X}{m}$

$\frac{4}{m}$

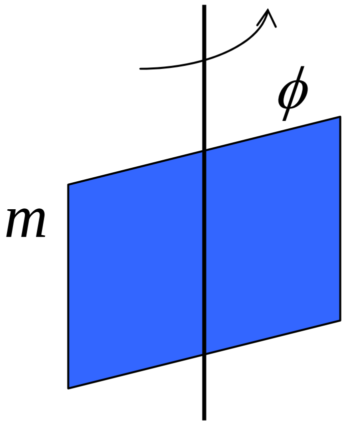


$\frac{6}{m}$

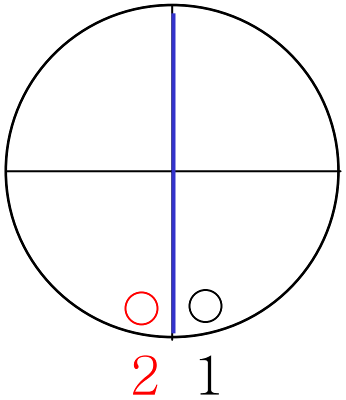


Combination

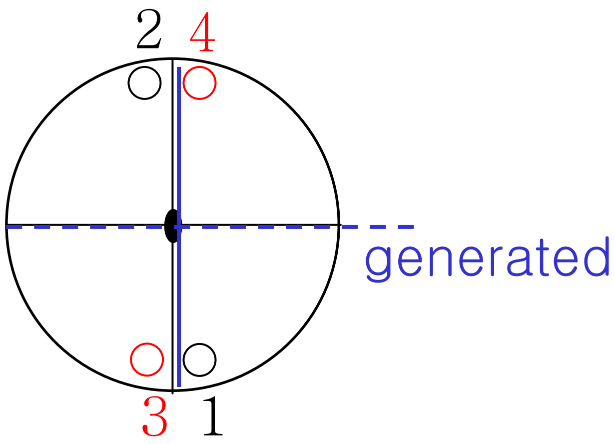
- a mirror plane is added normal to the rotation axis, Xm



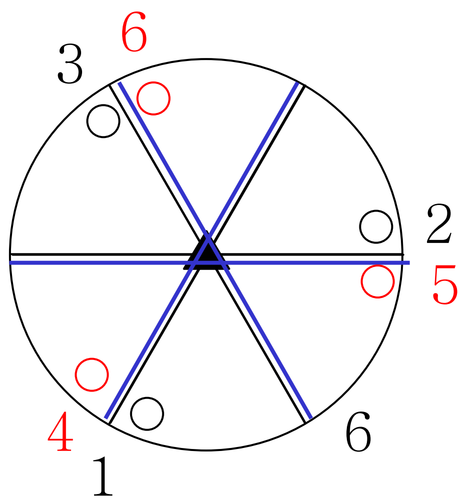
$-1m(\equiv m)$



$-2m(\equiv 2mm, mm2)$



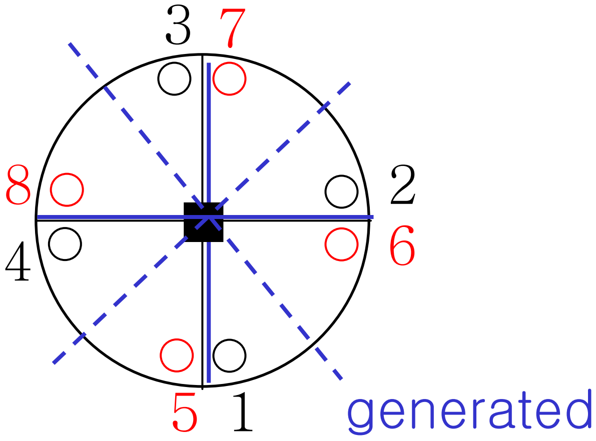
$-3m$



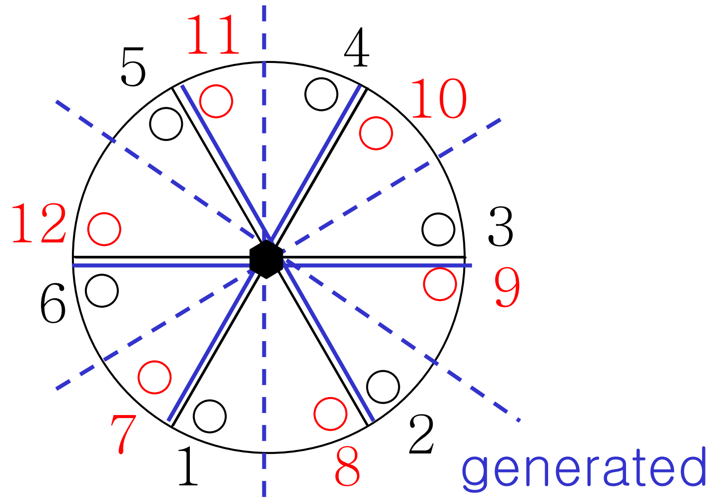
Combination

- a mirror plane is added normal to the rotation axis, Xm

$-4m(\equiv 4mm)$

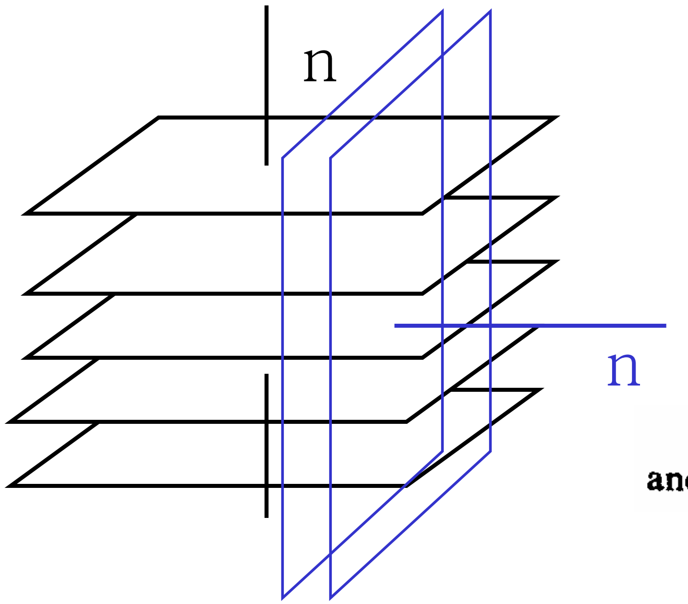


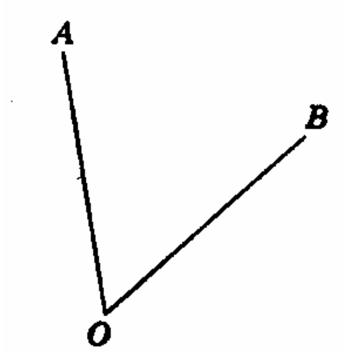
$-6m(\equiv 6mm)$



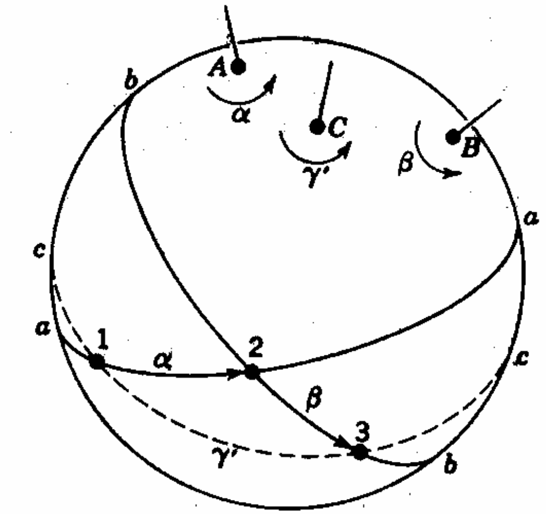
Combination of rotation axes

- space lattice
  - regarded as a stack of plane lattices
  - only have symmetry axes with n=1,2,3,4,or 6, normal to a net
  - many possible planes
  - each such plane conform to the symmetry of a particular n-fold axis
  - restriction to the angular relationships between intersecting n-fold axes





Rotation axes *A* and *B* intersecting at *O*.



The result of combining a rotation through angle α about *A* with a rotation through angle β about *B*.

Combination of rotation axes

– Euler construction

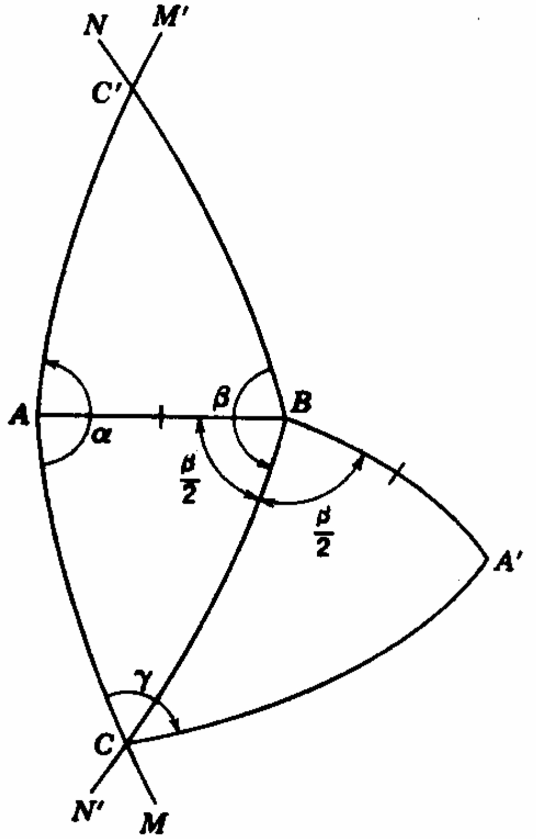
- select for attention line AM

$$\angle MAB = \angle M'AM = \alpha/2$$

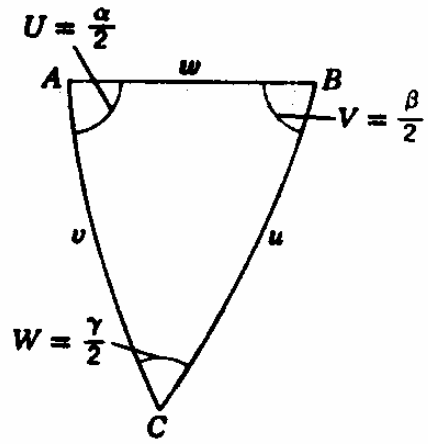
- select for attention line BN

$$\angle NAB = \angle N'AM = \beta/2$$

- intersection of AM' and BN is C'
  intersection of BN' and AM is C
- 1: A_α brings C to C'
  2: B_β brings C' to C



Euler's construction for the combination of a rotation through angle α about *A* with a rotation through angle *β* about *B*.



Spherical triangle *ABC* for use in computations based upon Euler's construction.

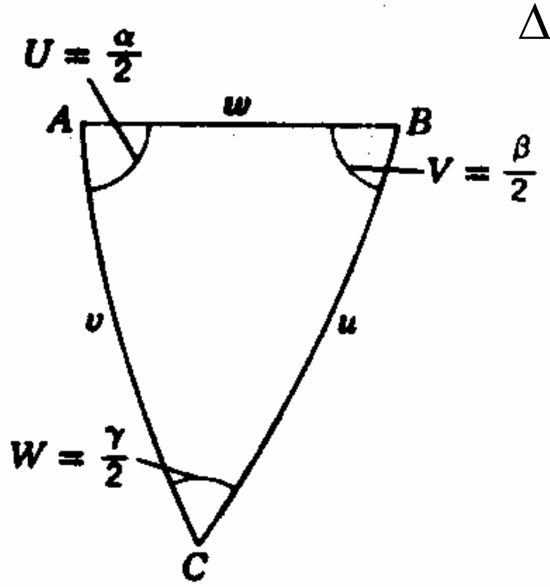
M. Buerger, Elementary Crystallography

Combination of rotation axes

- euler construction
  - A_α and B_β leaves C unchanged
  - if there is a motion of points on the sphere due to A_α and B_β, it must be a rotation about an axis OC
  - 1: A_α leaves A unmoved
    2: B_β moves A to A'
  - consider the spherical triangle BA'C

$$\angle ABC = \angle A'BC = \phi / 2 \qquad AB = A'B$$

$$\Delta ABC = \Delta A'BC \qquad \angle ACB = \angle A'CB = \gamma / 2$$



- rotation about C carries A to A' through twice $\angle ACB$ or through angle γ
- $U = \alpha / 2, V = \beta / 2, W = \gamma / 2$

$u, v, w : arcs$

$$\cos w = \frac{\cos W + \cos U \cos V}{\sin U \sin V}$$

Combination of rotation axes

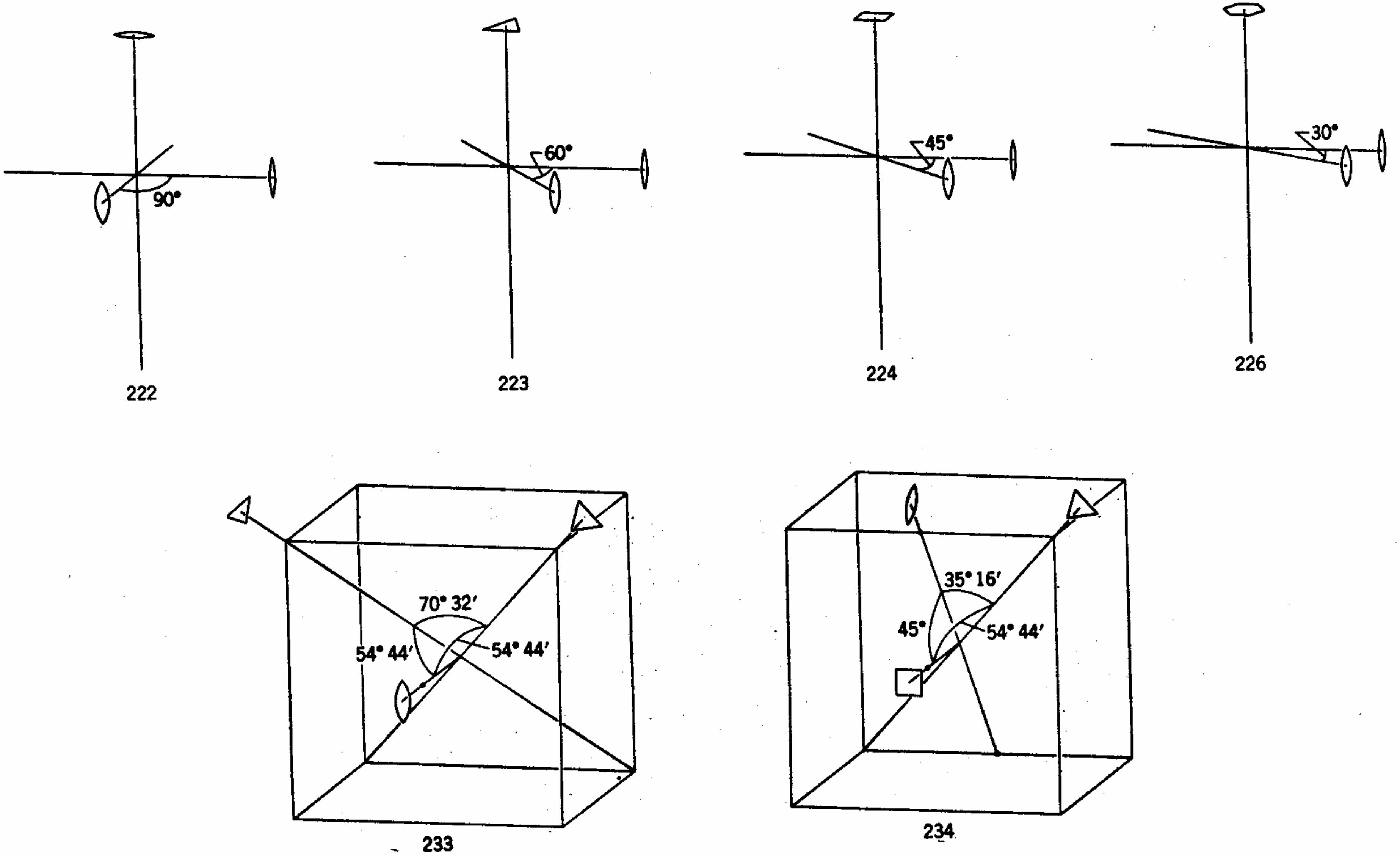


FIG. 13. The six permissible nontrivial crystallographic combinations of rotations.

Combination of rotation axes

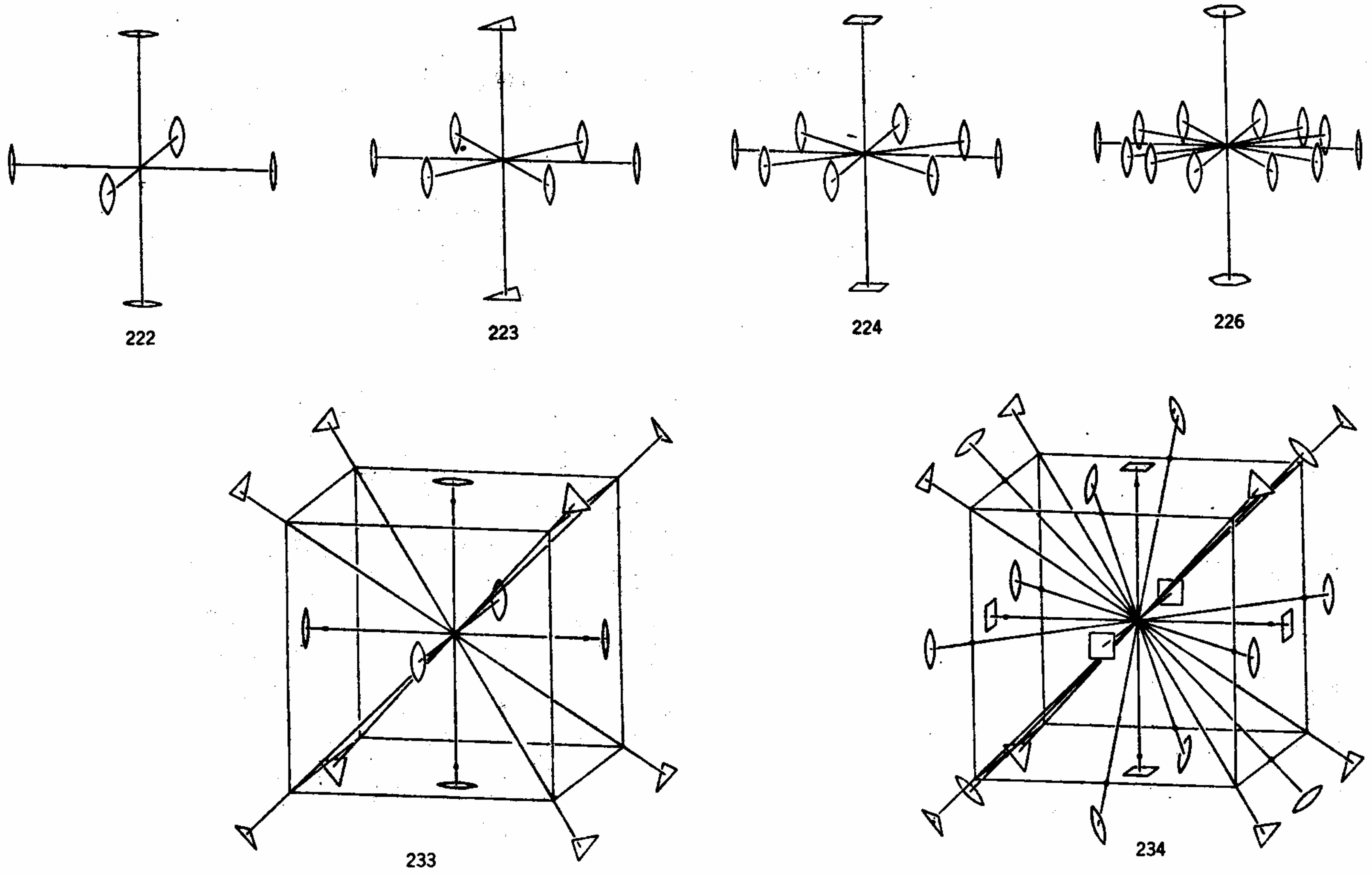
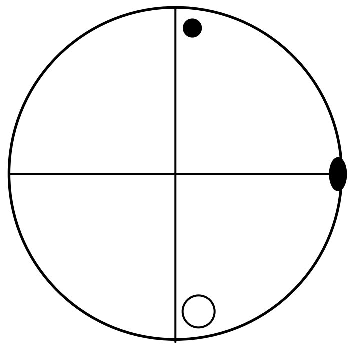


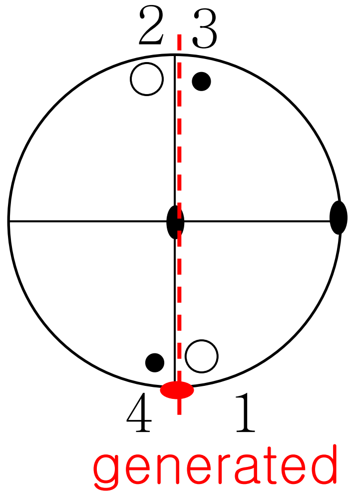
FIG. 14. The six crystallographic axial symmetries based upon the combinations in Fig. 13.

Combination of rotation axes, n2

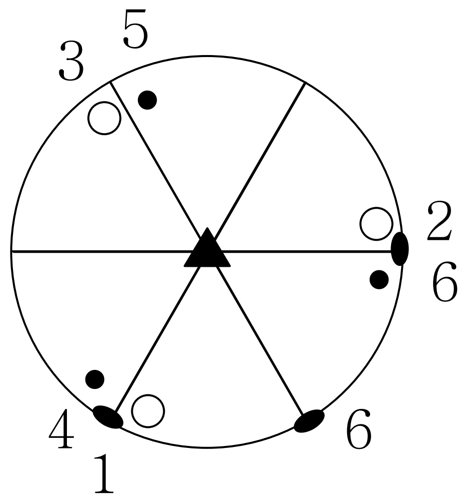
- 12(≡2)



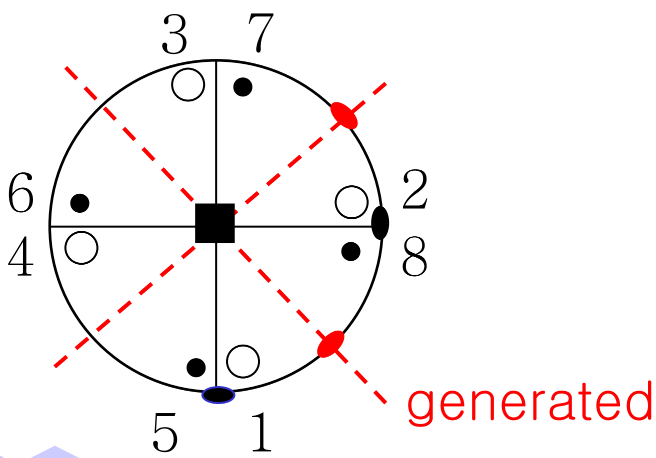
-222



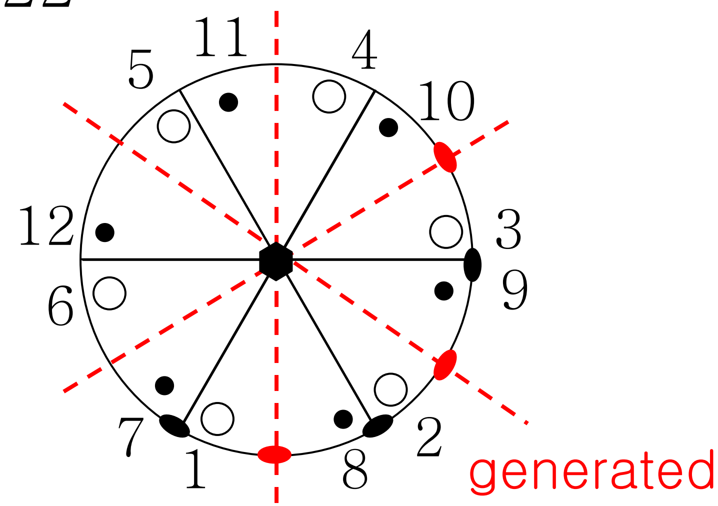
-32



- 422

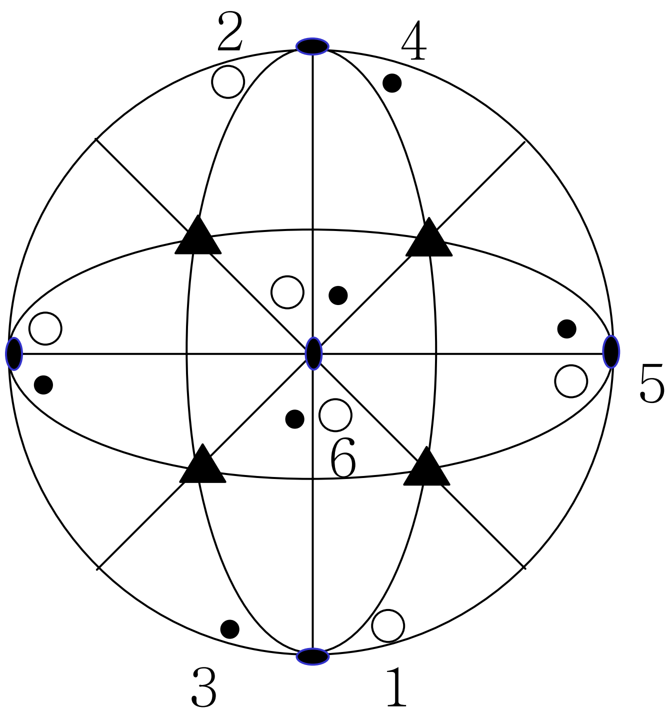


-622

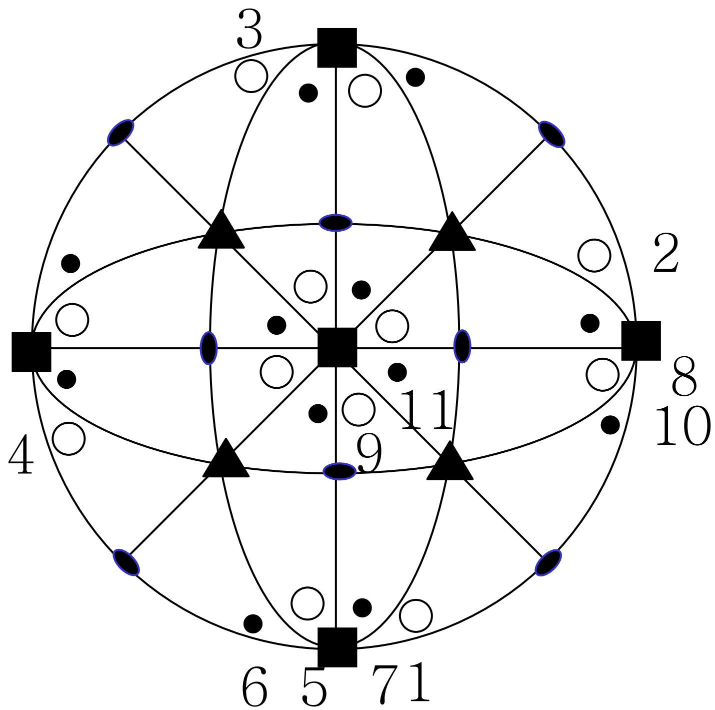


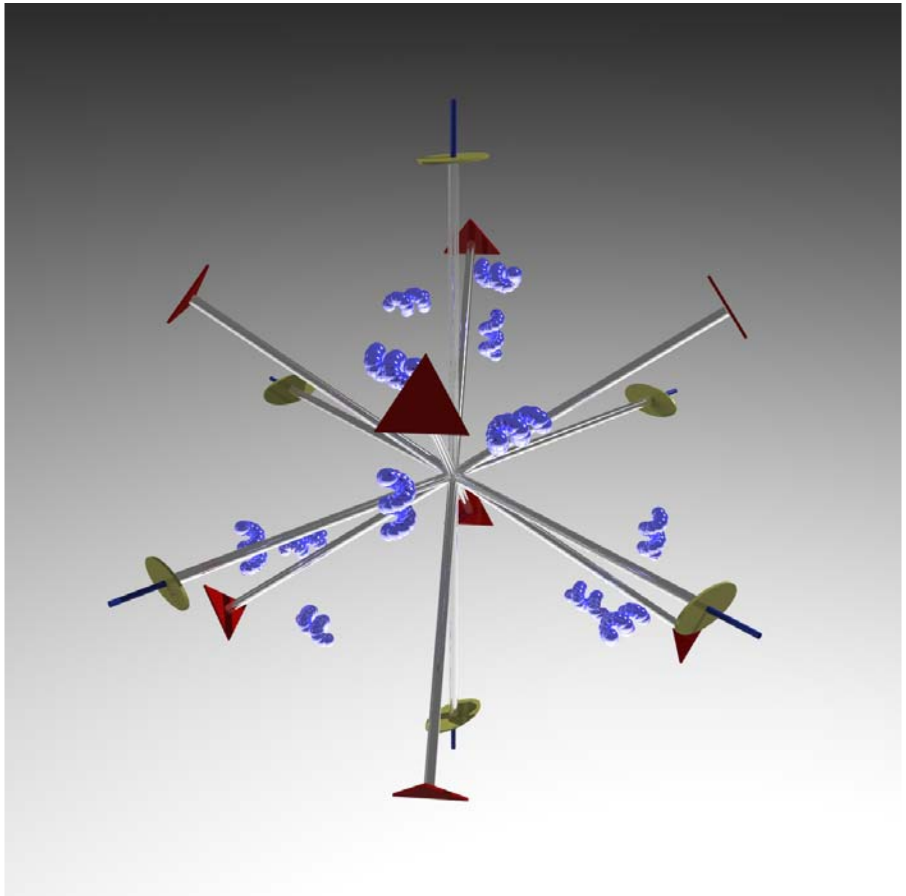
Combination of rotation axes

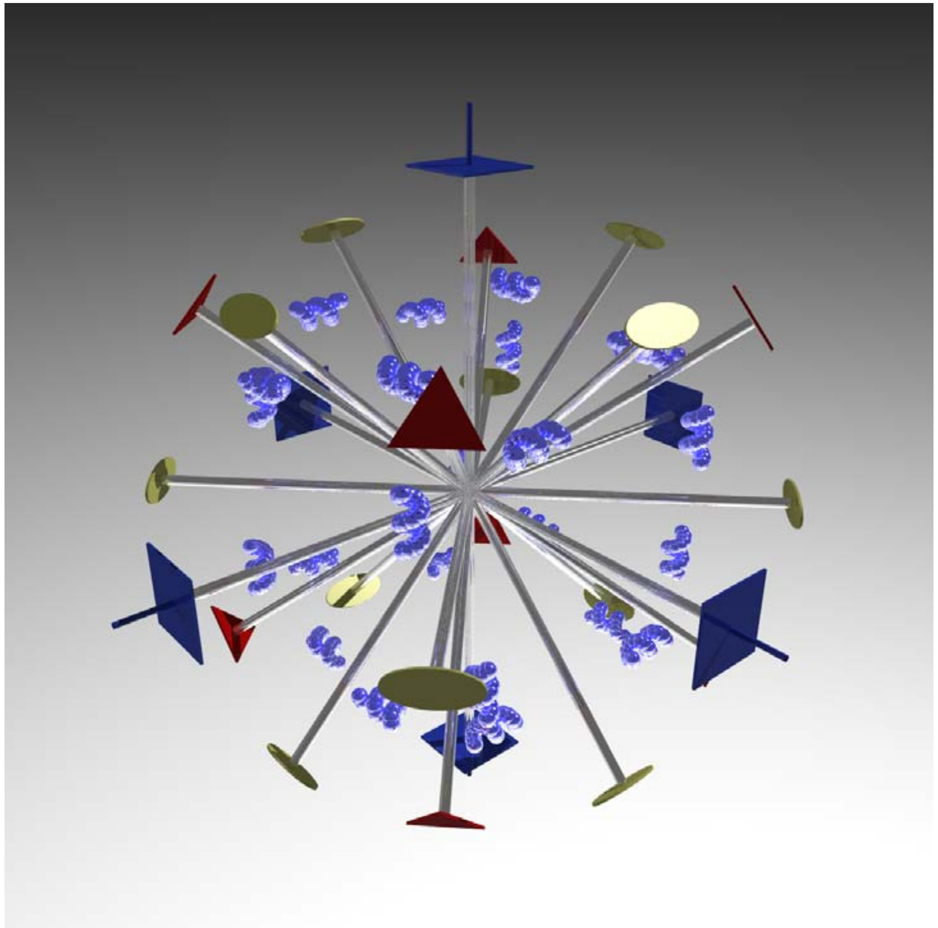
- 23



-432







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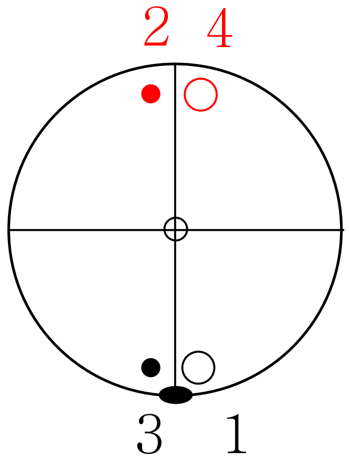
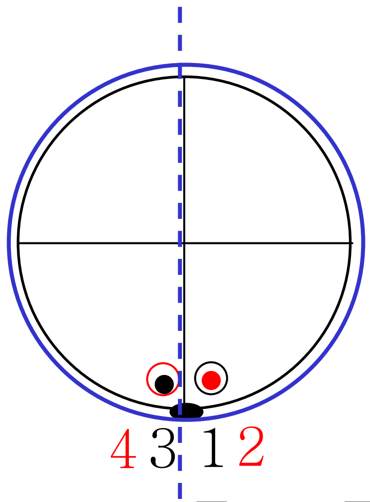
Combination of rotation axes, $\bar{n}2$

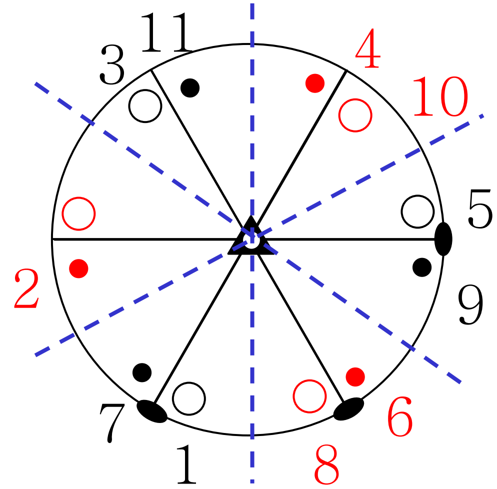
– $\bar{1}2(\equiv \frac{2}{m})$



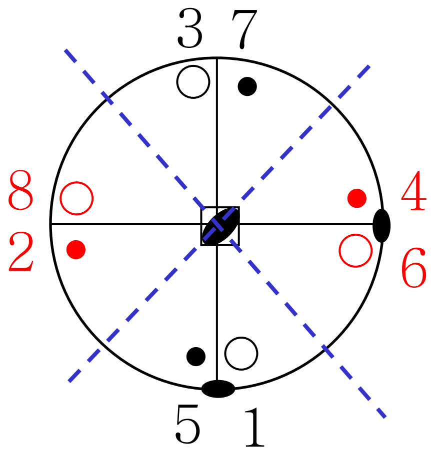
– $\bar{2}2(\equiv 2mm)$



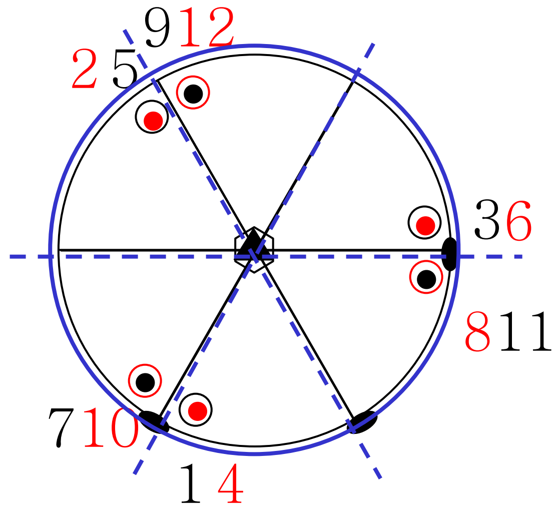
– $\bar{3}2(\equiv \bar{3}\frac{2}{m})$



– $\bar{4}2(\equiv \bar{4}2m)$

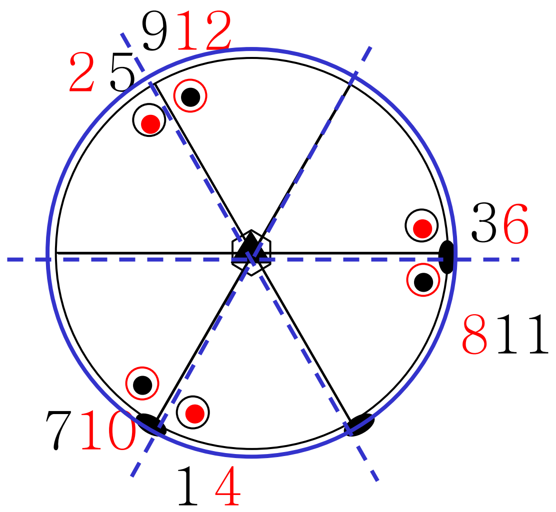


– $\bar{6}2(\equiv \bar{6}2m \equiv \bar{6}m2)$



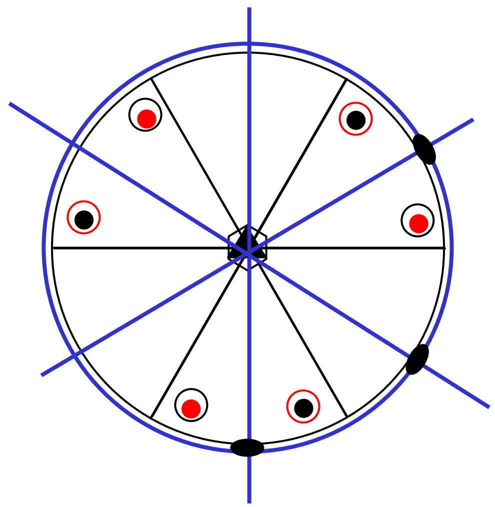
$\bar{6}2m$

<c><a><210>

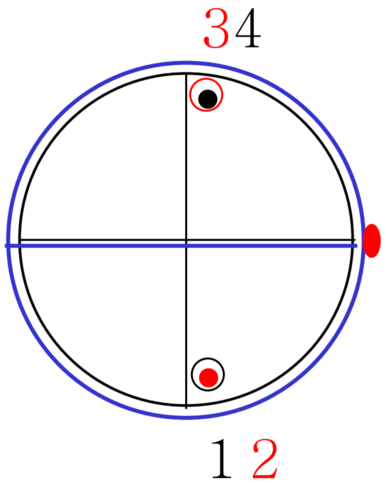


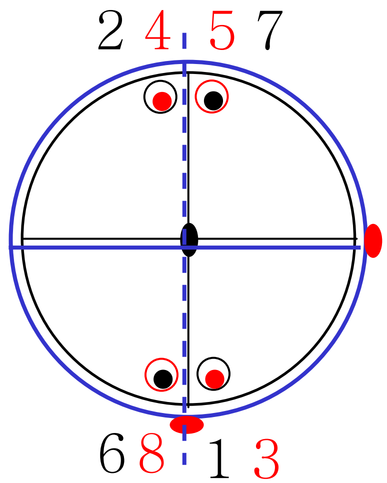
$\bar{6}m2$

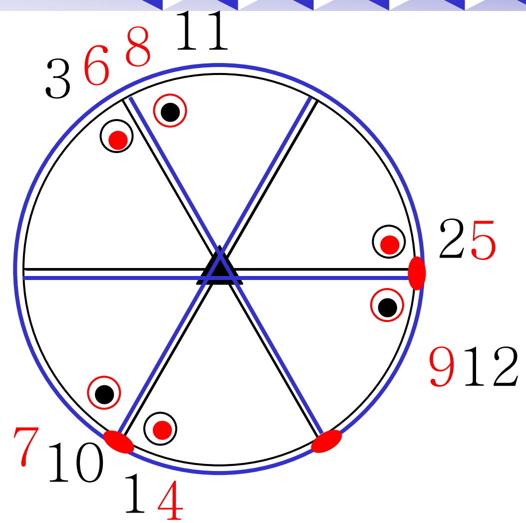
<c><a><210>



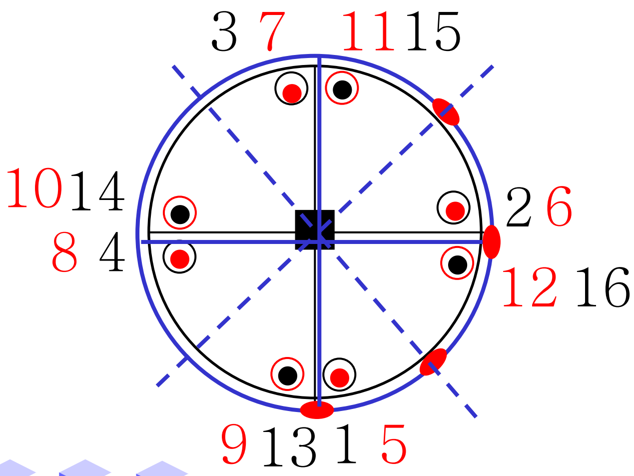
$-\frac{1}{m}m(\equiv 2mm)$ $-\frac{2}{m}m(\equiv \frac{2}{m}\frac{2}{m}\frac{2}{m})$ $-\frac{3}{m}m(\equiv \bar{6}m2)$

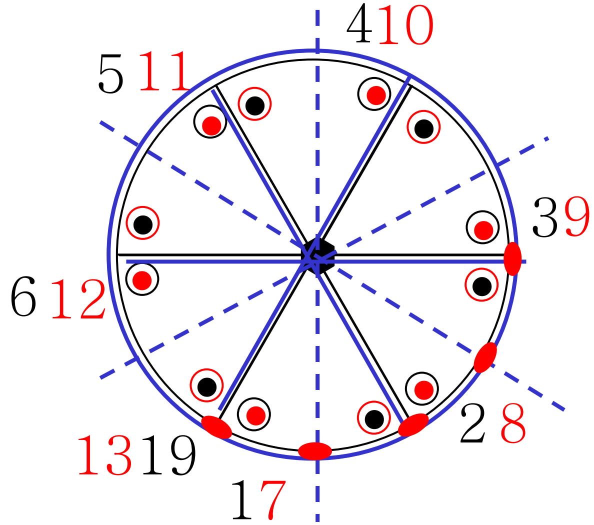




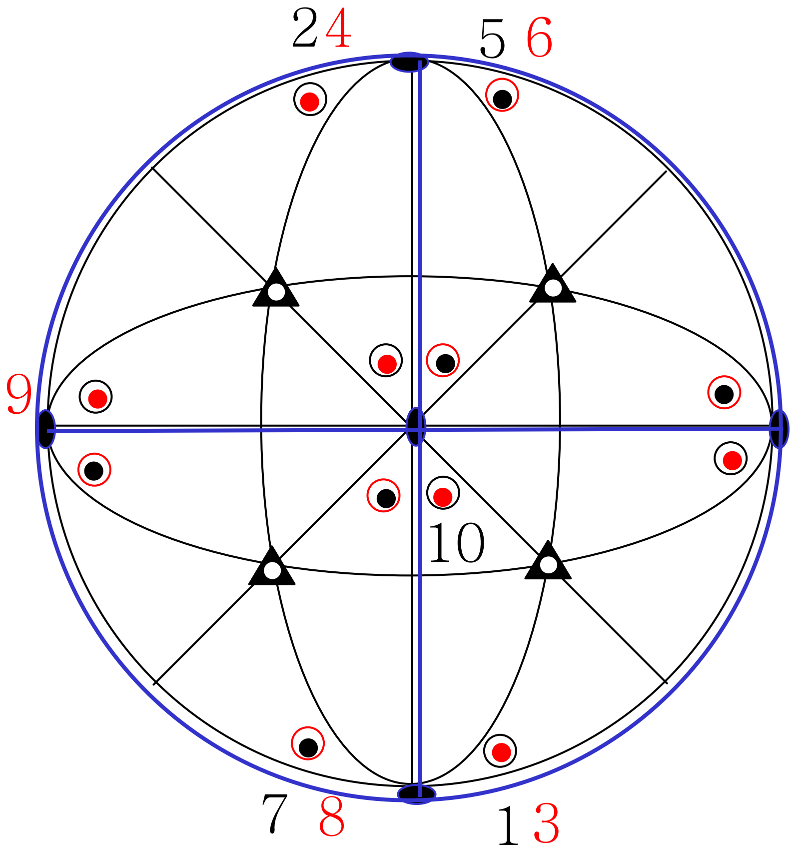


$-\frac{4}{m}m(\equiv \frac{4}{m}\frac{2}{m}\frac{2}{m})$ $-\frac{6}{m}m(\equiv \frac{6}{m}\frac{2}{m}\frac{2}{m})$

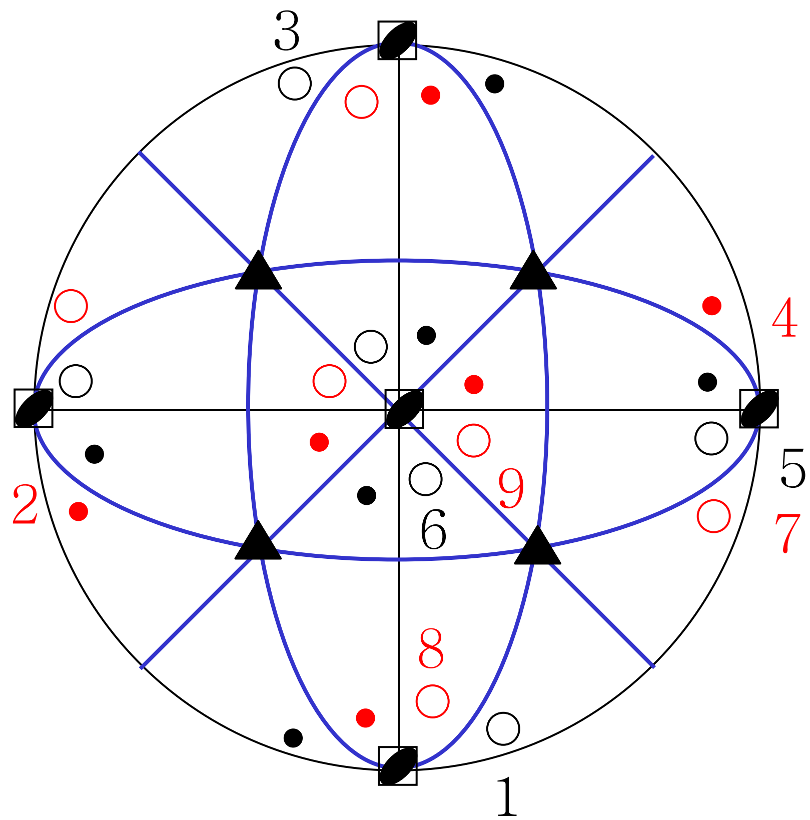




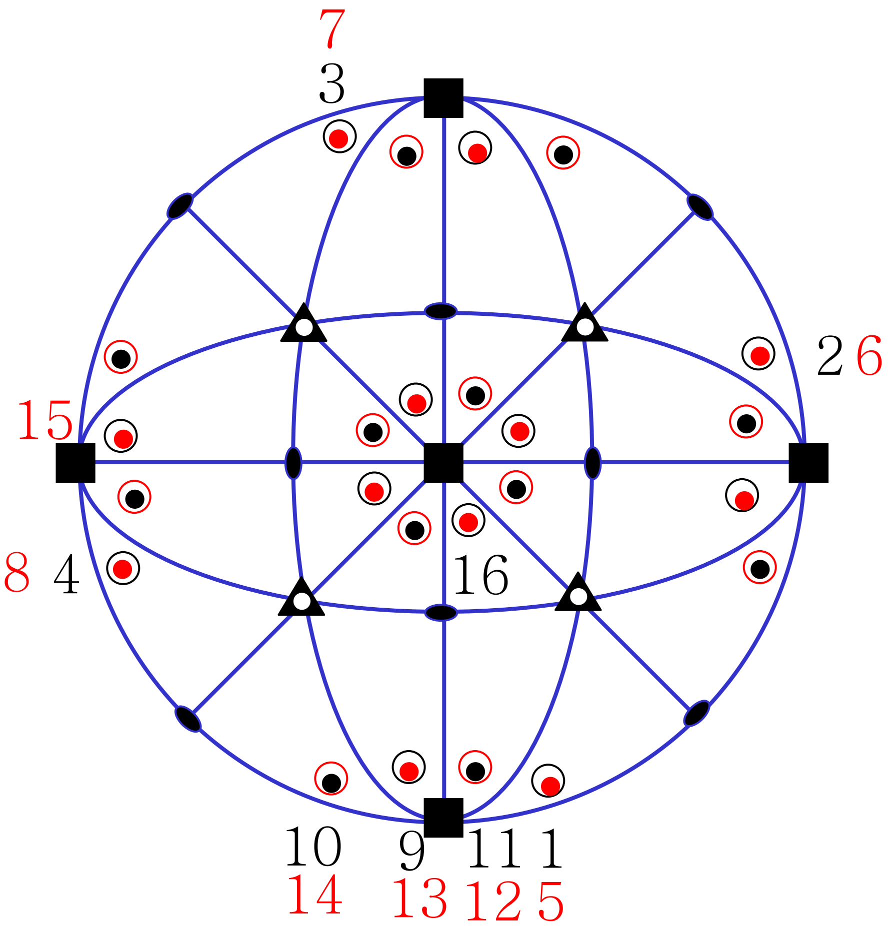
– $\frac{2}{m}\bar{3}(\equiv m3)$

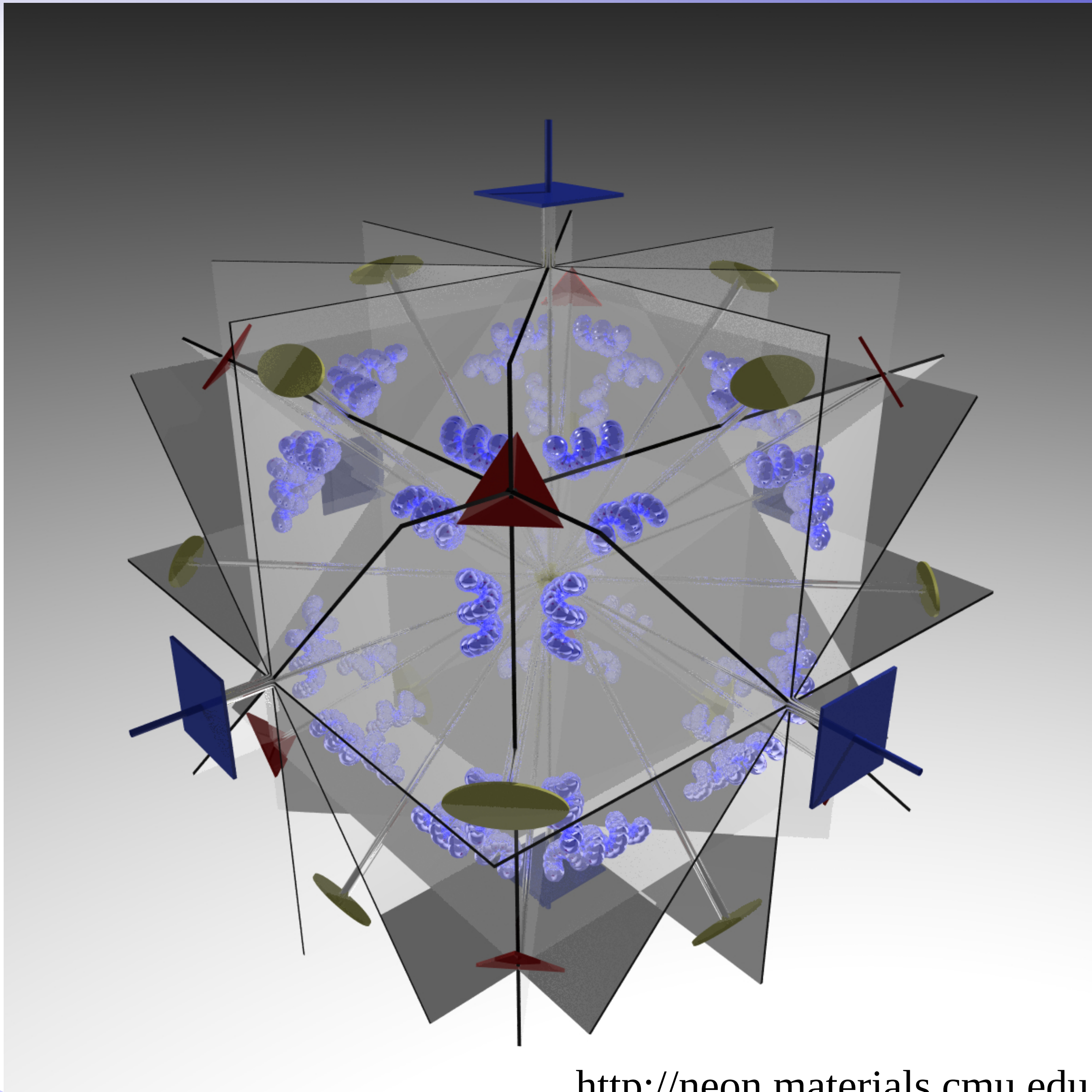


– $\bar{4}3m$



$$-\frac{4}{m}\bar{3}\frac{2}{m}(\equiv m3m)$$





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32 Point Group

- Schonflies symbol vs. International symbol

C_n: n-fold rotation axis; identical with X

C_n	C_1	C_2	C_3	C_4	C_6
X	1	2	3	4	6

C_{ni}: odd-order rotation axis and inversion centre $i \equiv \bar{X}$ (odd)
C_s: (s for German Spiegelebene) = mirror plane;
S_n: n-fold rotoreflection axis (only S_4 and S_6 used)

	C_i	C_s	$C_{3i} \equiv S_6$	S_4	
$\bar{X}$	$\bar{1}$	$(\bar{2} \equiv)$ m	$\bar{3}$	$\bar{4}$	

C_{nh}: n-fold axis normal to mirror plane $\equiv$ X/m

C_{nh}		C_{2h}	C_{3h}	C_{4h}	C_{6h}
X/m		2/m	$(3/m \equiv)$ $\bar{6}$	4/m	6/m

C_{nv}: n-fold axis parallel to n mirror planes ≡ Xm

C_{nv}		C_{2v}	C_{3v}	C_{4v}	C_{6v}
Xm		mm2	3m	4mm	6mm

D_n: n-fold axis normal to n 2-fold axes ≡ X2

D_n		D_2	D_3	D_4	D_6
X2		222	32	422	622

D_{nd}: as D_n plus mirror planes bisecting 2-fold axes

D_{nd}		D_{2d}	D_{3d}		
$\bar{X}m$		$\bar{4}2m$	$\bar{3}m$		

D_{nh}: as D_n plus mirror plane normal to n-fold axis

D_{nh}		D_{2h}	D_{3h}	D_{4h}	D_{6h}
X/mm		mmm	(3/mm ≡) $\bar{6}$m2	4/mmm	6/mmm

T (tetrahedral) and O (octahedral) groups

	T	T_h	O	T_d	O_h
	23	m$\bar{3}$	432	$\bar{4}3m$	m$\bar{3}$m

Table 8.2. The 32 point groups

Crystal system	Point groups	
Triclinic	$\bar{1}$	1
Monoclinic	2/m	m, 2
Orthorhombic	2/m 2/m 2/m (mmm)	mm2, 222
Tetragonal	4/m 2/m 2/m (4/mmm)	$\bar{4}$2m, 4mm, 422 4/m, $\bar{4}$, 4
Trigonal	$\bar{3}$ 2/m ($\bar{3}$m)	3m, 32, $\bar{3}$, 3
Hexagonal	6/m 2/m 2/m (6/mmm)	$\bar{6}$m2, 6mm, 622 6/m, $\bar{6}$, 6
Cubic	4/m $\bar{3}$ 2/m (m$\bar{3}$m)	$\bar{4}$3m, 432, 2/m$\bar{3}$, 23 (m$\bar{3}$)

Table 7.1. The seven crystal systems

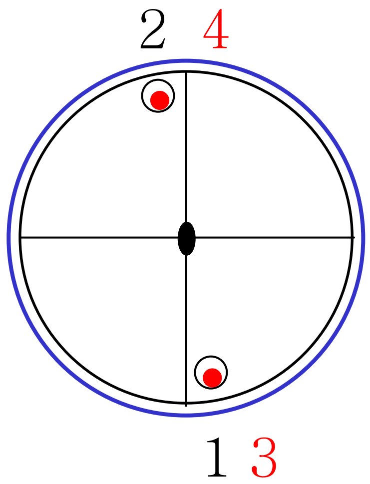
<table>
<tr><th>Crystal system</th><th>Restrictions on the axial system</th></tr>
<tr><td>Triclinic</td><td>$a \neq b \neq c \quad \alpha \neq \beta \neq \gamma$ [a]</td></tr>
<tr><td>Monoclinic</td><td>$a \neq b \neq c \quad \alpha = \gamma = 90°, \quad \beta > 90°$</td></tr>
<tr><td>Orthorhombic</td><td>$a \neq b \neq c \quad \alpha = \beta = \gamma = 90°$</td></tr>
<tr><td>Tetragonal</td><td>$a = b \neq c \quad \alpha = \beta = \gamma = 90°$
$(a_1 = a_2 \neq c)$</td></tr>
<tr><td>Trigonal [b]</td><td rowspan="2">$a = b \neq c \quad \alpha = \beta = 90°, \quad \gamma = 120°$
$(a_1 = a_2 \neq c)$</td></tr>
<tr><td>Hexagonal</td></tr>
<tr><td>Cubic</td><td>$a = b = c \quad \alpha = \beta = \gamma = 90°$
$(a_1 = a_2 = a_3)$</td></tr>
</table>

Table 7.2. Symmetry directions in the seven crystal systems

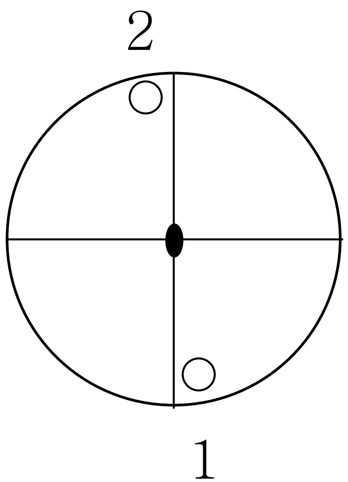
	Position in the international symbol		
	1st	2nd	3rd
Triclinic		–	
Monoclinic		b	
Orthorhombic	a	b	c
Tetragonal	c	⟨a⟩	⟨110⟩
Trigonal	c	⟨a⟩	–[c]
Hexagonal	c	⟨a⟩	⟨210⟩
Cubic	⟨a⟩	⟨111⟩	⟨110⟩

Monoclinic

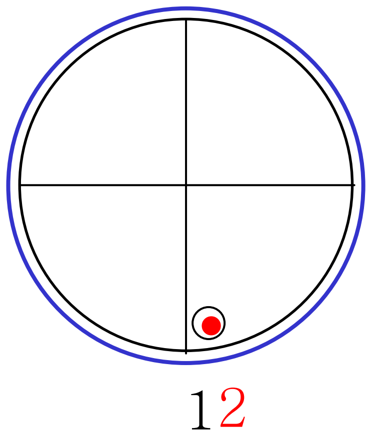
$-\frac{2}{m}$

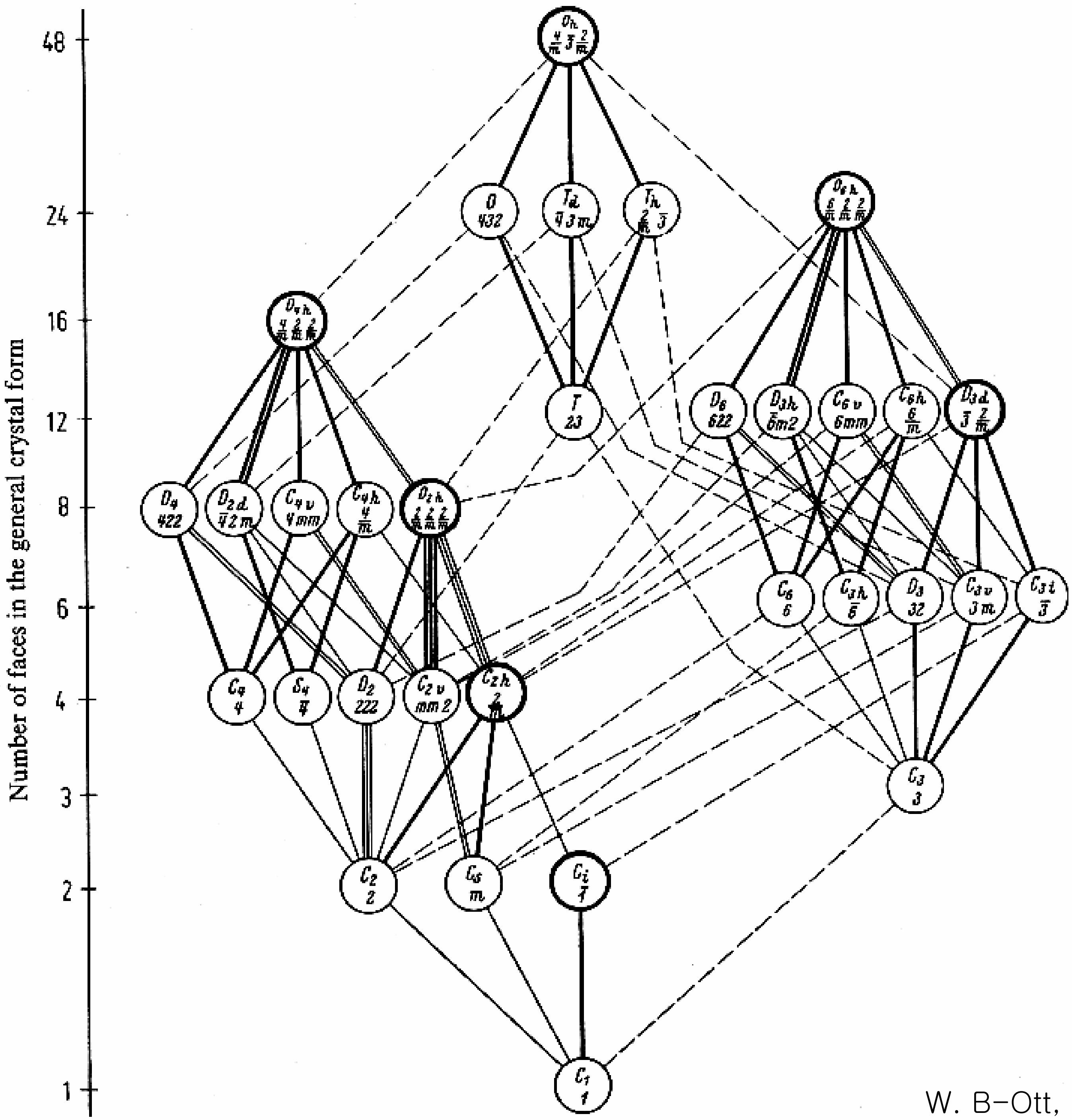


-2



$-m$

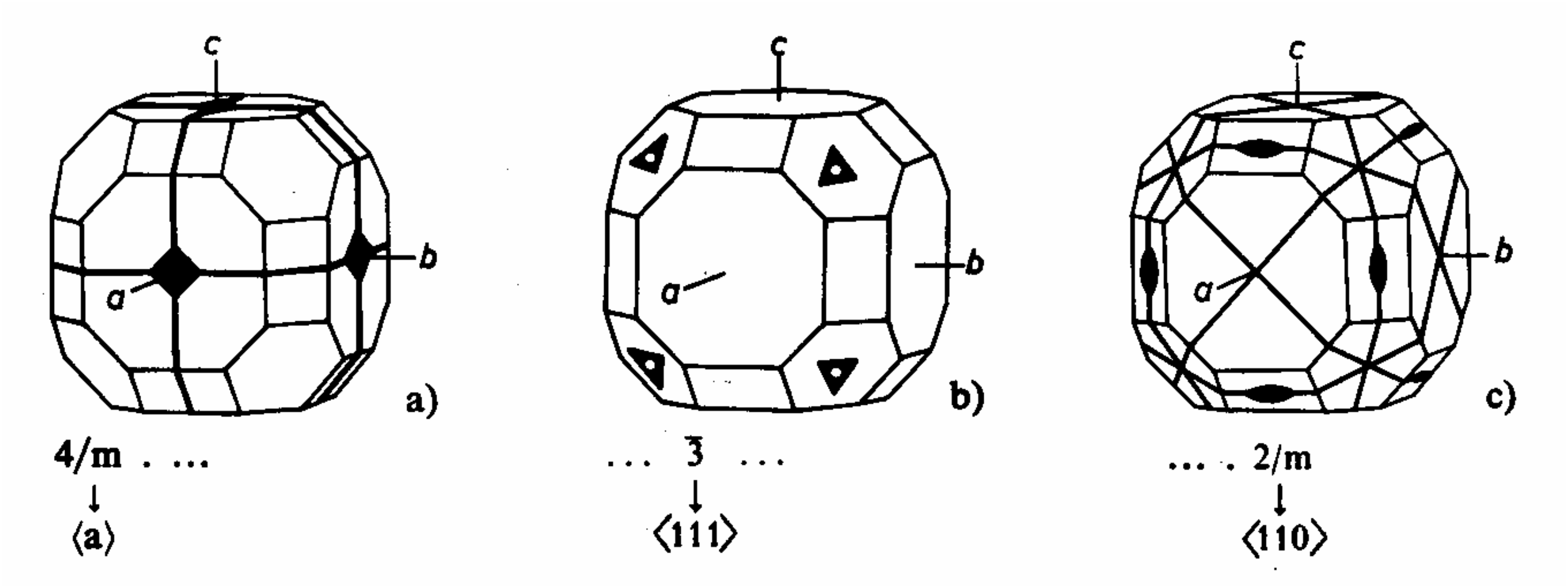


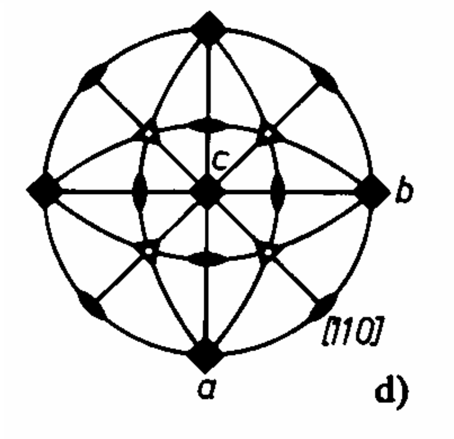


W. B-Ott, Crystallography

Crystal Symmetry

-galena (PbS) $\frac{4}{m}\bar{3}\frac{2}{m}$

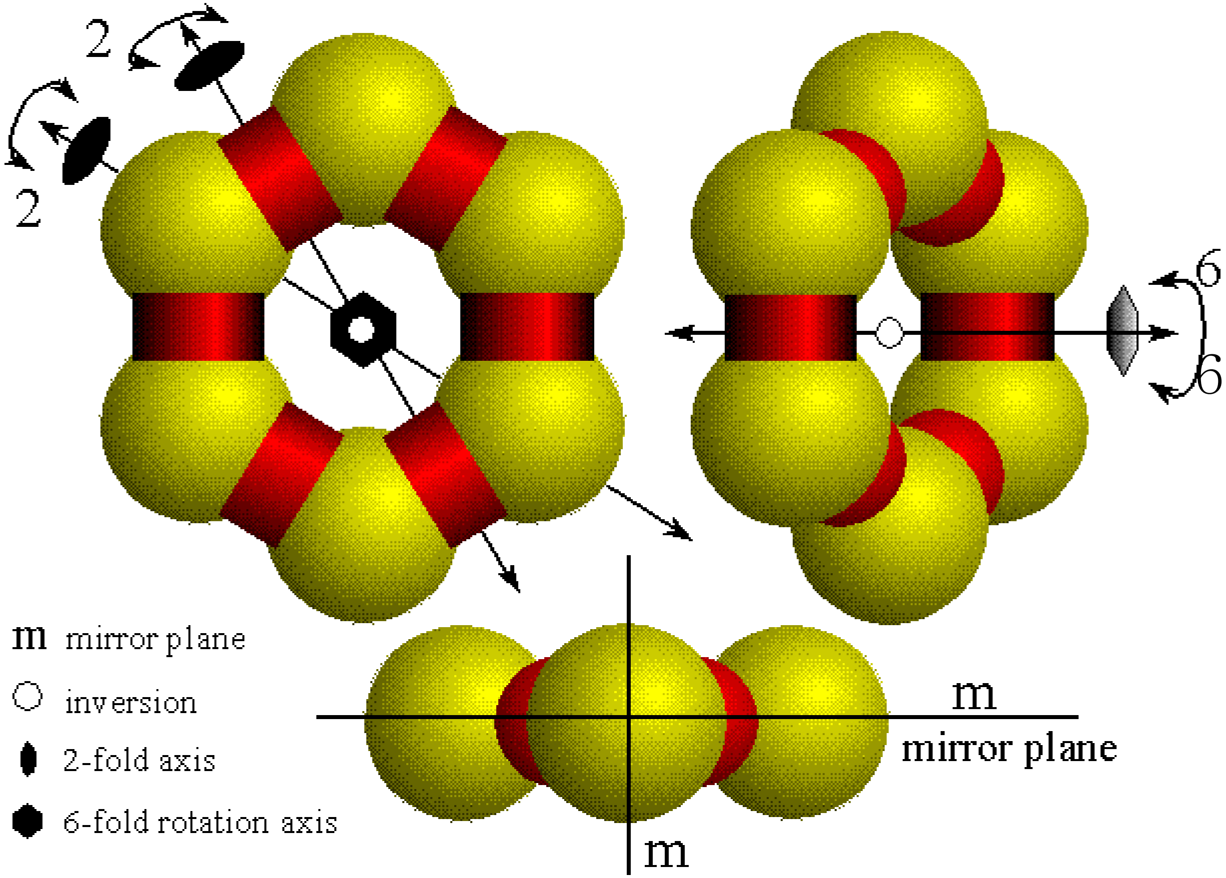


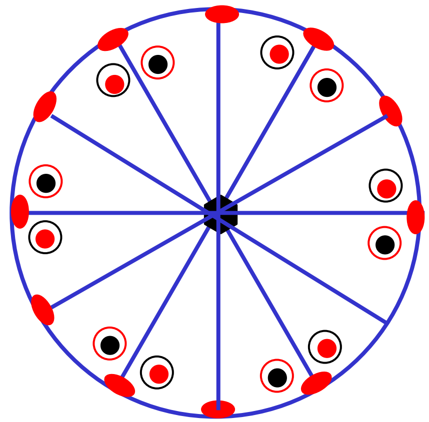


Molecular Symmetry

– benzene(C_6H_6)

$$\frac{6}{m}\frac{2}{m}\frac{2}{m}$$



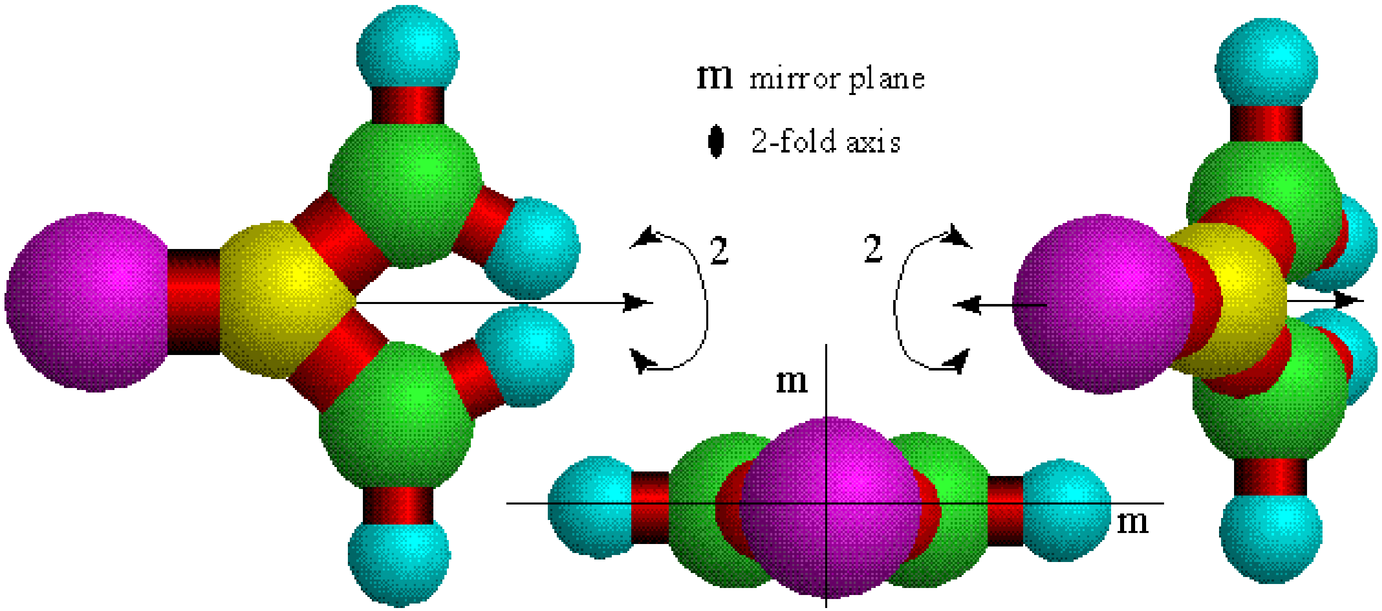


http://www.gh.wits.ac.za/craig/diagrams/benze.gif

Molecular Symmetry

– thiourea

*mm*2



http://www.gh.wits.ac.za/craig/diagrams/thiou.gif

Molecular Symmetry

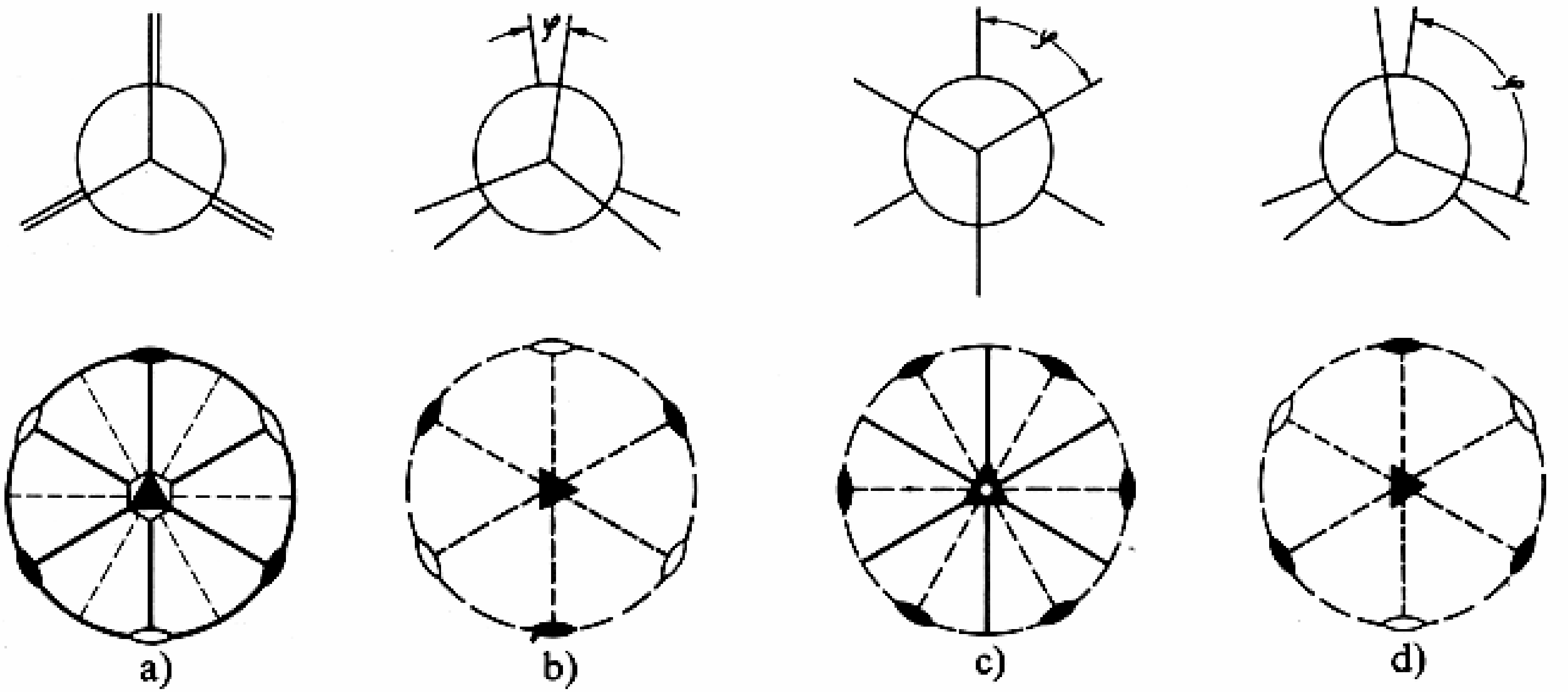


Fig. 8.20 a–d. Conformations of ethane. **a** Eclipsed: $\varphi = 0$ or 120 or 240°: ($\bar{6}m2 - D_{3h}$). **b** Skew: $0 < \varphi < 60°$, $120 < \varphi < 180°$ or $240 < \varphi < 300°$: ($32 - D_3$). **c** Staggered: $\varphi = 60$ or 180 or 300°: ($\bar{3}m - D_{3d}$). **d** Skew: $60 < \varphi < 120°$, $180 < \varphi < 240°$ or $300 < \varphi < 360°$: ($32 - D_3$). The conformations in **b** and **d** are enantiomorphs