Point Groups

Read

Ott Chapter 9 (9.2, 9.6, 9.7 제외, Fig 9.4 포함)

Hammond Chapter 2.1 ~ 2.4; 3.1 ~ 3.3; 4.1 ~ 4.3, 4.5; 5.1 ~ 5.6

Sherwood & Cooper Chapter 3.7

Krawitz Chapter 1.1 ~ 1.6; 2.1 ~ 2.4

Lattice, Basis

- Lattice – an array of points in space in which the environment of each point is identical
- Basis (motif) – repeating unit of pattern
- Lattice + basis → crystal structure

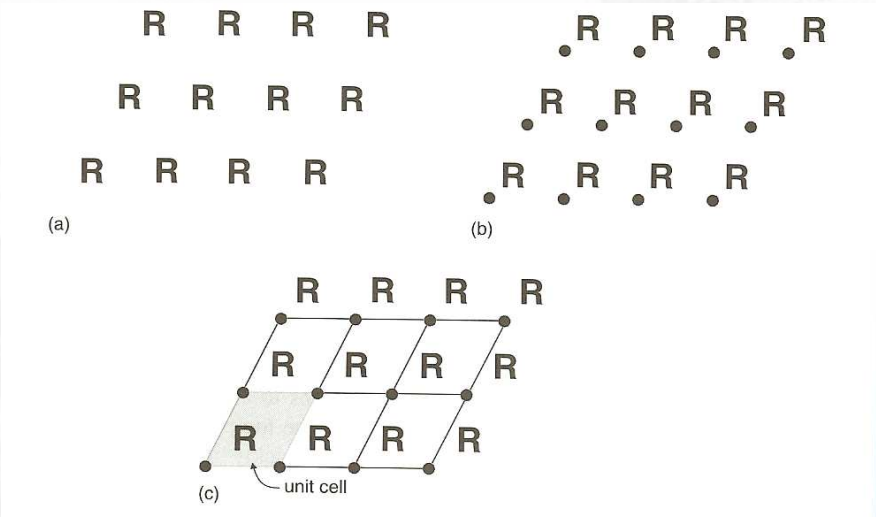


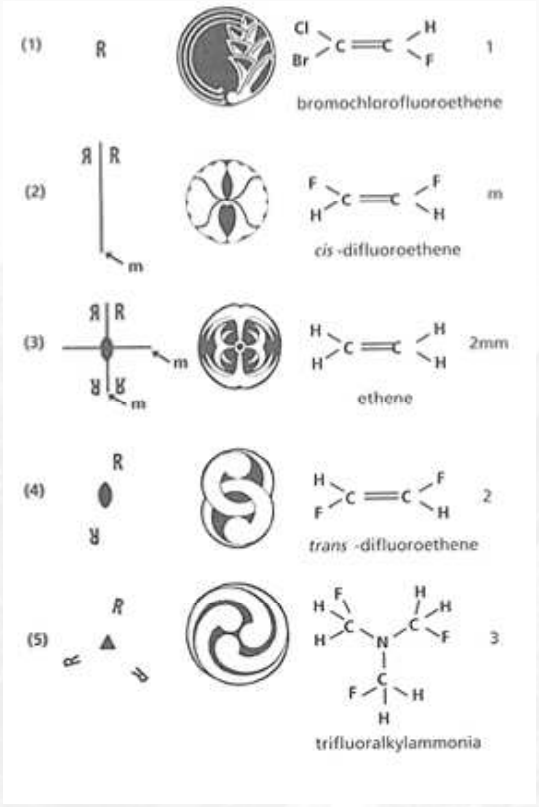
Fig. 2.1. (a) A pattern with the motif R, (b) with the lattice points indicated and (c) the lattice and a unit cell outlined (Drawn by K. M. Crennell).

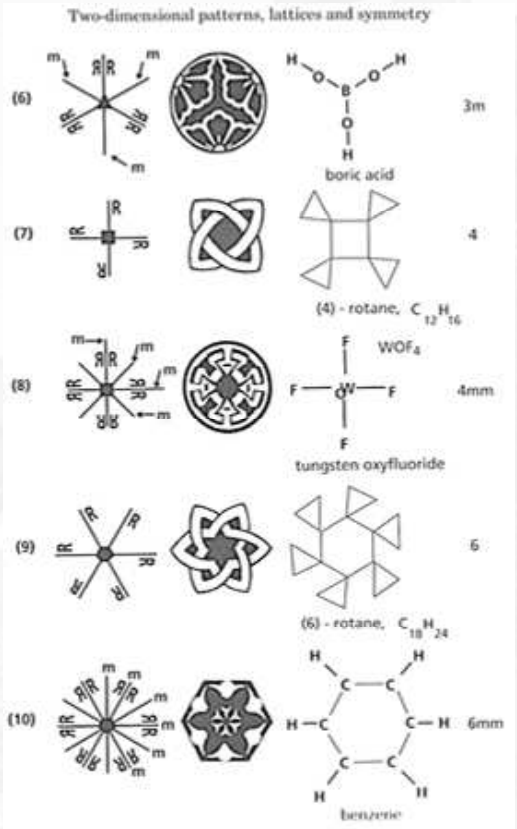
- **Ten** 2-D point groups (plane point groups)
  - ✓ 1, 2, 3, 4, 6, m, 2mm, 3m, 4mm, 6mm
  - ✓ Only these combinations of axes & mirror lines can occur in regular repeating patterns in two dimensions (Hammond 2.3)
- **5 lattices in 2-D** (5 plane lattices) (Hammond 2.4)
- A basis (motif) can possess one of 10 point group symmetries in 2-D
- There are only 10 different types of 2-D patterns, distributed among the 5 plane lattices (**10** plane point groups)
- 7 more 2-D patterns from glide lines → **17 plane groups** (Hammond 2.5)
  - ✓ p1, p2, p3, p4, p6, pm, pg, cm, p2mm, p2mg, c2mm, p2gg, p4mm, p4gm, p31m, p3m1, p6mm

- **3-D, 14 possible lattices, 7 different axis systems**
- The application and permutation of all symmetry elements to patterns in space give rise to **230 space groups** (instead of **17** plane groups) distributed among **14 space lattices** (instead of **5** plane lattices) and **32 point group symmetries** (instead of **10** plane point group symmetries)

- Space group symmetry – the way things are packed together and fill space
- Space group – translational component = point group

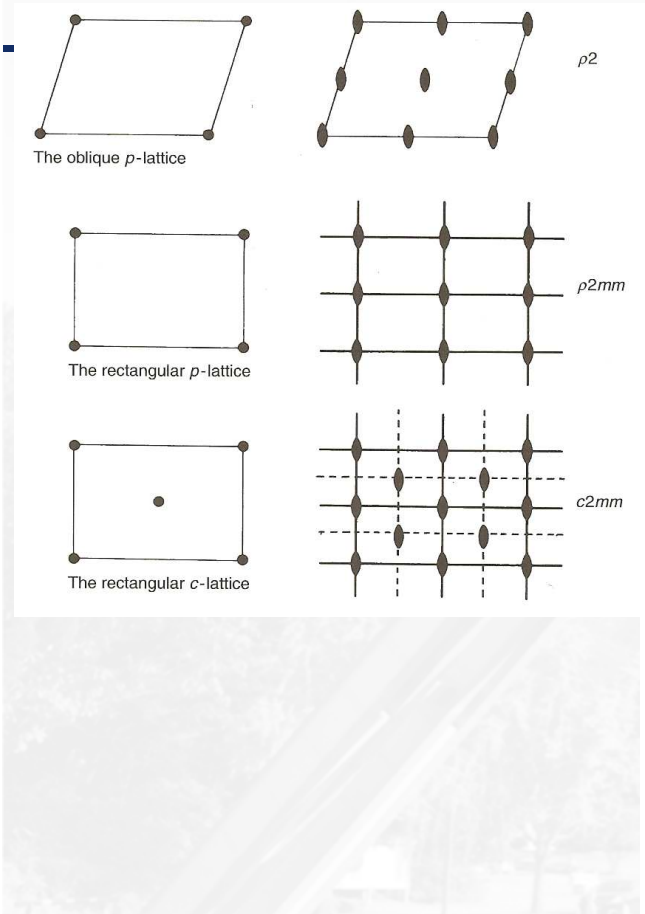
Ten 2D (plane) point groups



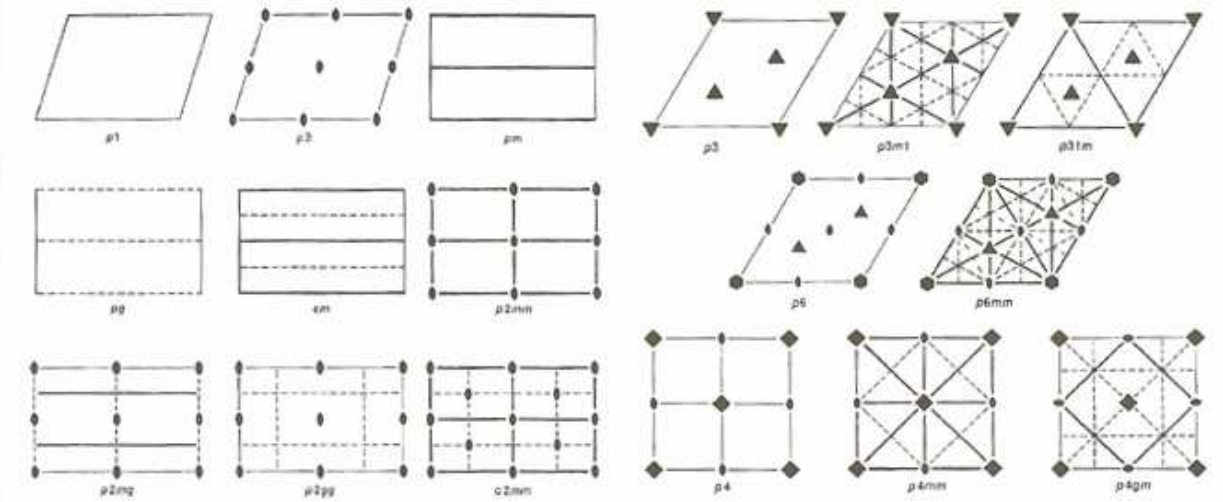


Hammond page 60, 61

5 plane lattices



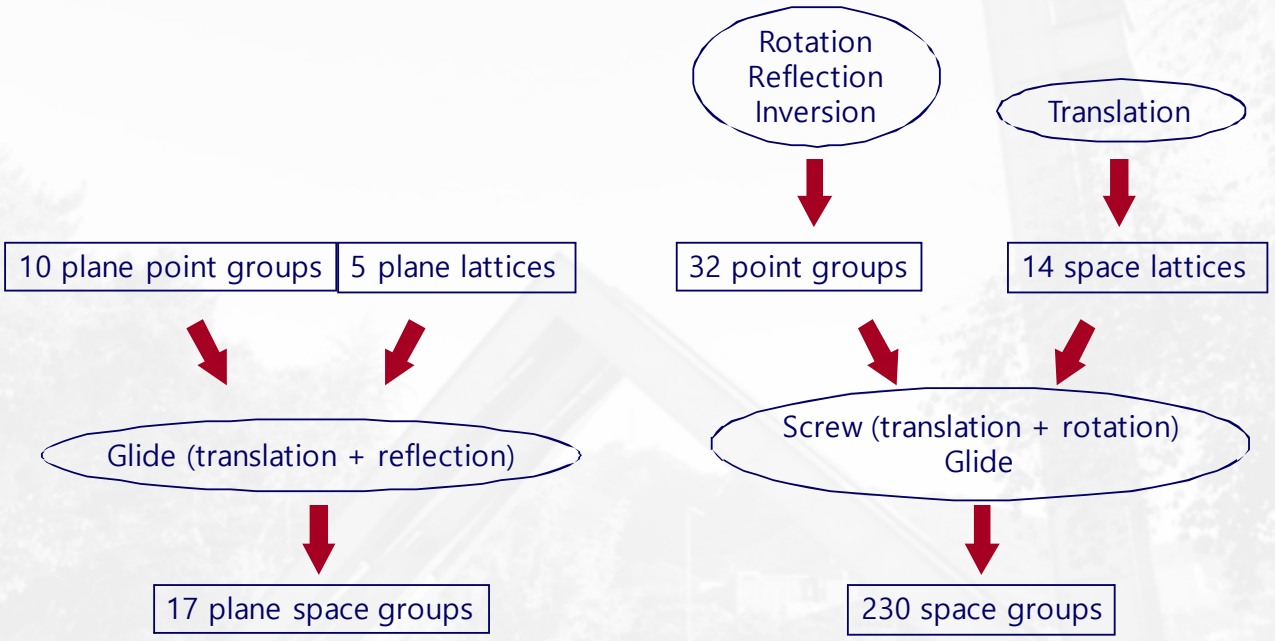
17 plane groups



Two-dimensional patterns, lattices and symmetry

Fig. 2.6. (a) The seventeen plane groups (from *Point and Plane Groups* by K. M. Crennell). The numbering 1–17 is that which is arbitrarily assigned in the International Tables. Note that the 'shorthand' symbols do not necessarily indicate all the symmetry elements which are present in the patterns. (b) The symmetry elements outlined within (conventional) unit cells of the seventeen plane groups, heavy solid lines and dashed lines represent mirror and glide lines respectively (from *Manual of Mineralogy* 21st edn, by C. Klein and C. S. Hurlbut, Jr., John Wiley, 1999).

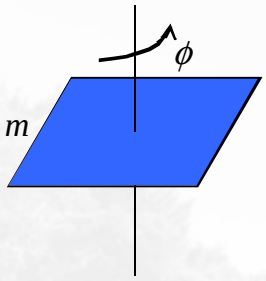
Plane groups vs. Space groups



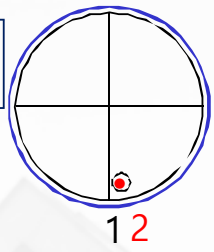
Point group

- A group of point symmetry operations whose operation leaves at least one point unmoved
  - ✓ **Lattice translation is not considered in the point group.**
- A **Point Group** describes all the symmetry operations that can be performed on a molecule that result in a conformation indistinguishable from the original.
- 32 unique combination of symmetry operations about a point in space
  → 32 point groups (32 3D point groups; ten 2D point groups)

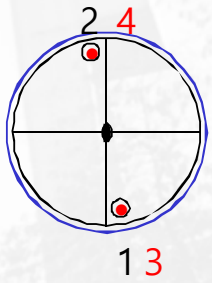
➢ a mirror plane is added normal to the rotation axis, $\frac{X}{m}$



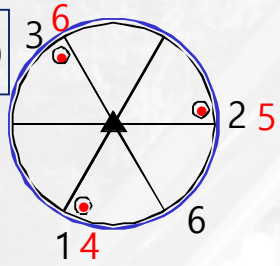
$\frac{1}{m}(\equiv m)$



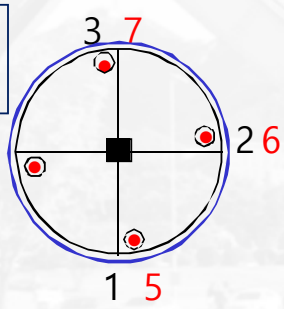
$\frac{2}{m}$



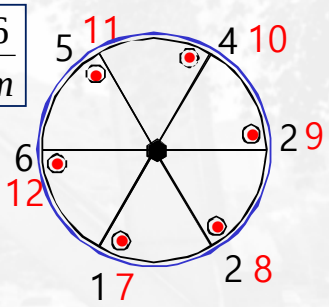
$\frac{3}{m}(\equiv \bar{6})$



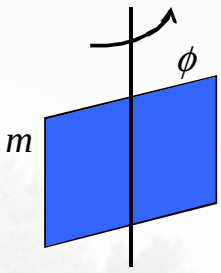
$\frac{4}{m}$



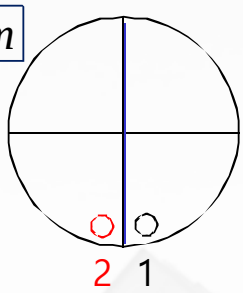
$\frac{6}{m}$



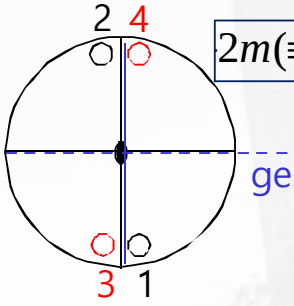
➢ a mirror plane is added parallel to the rotation axis, Xm



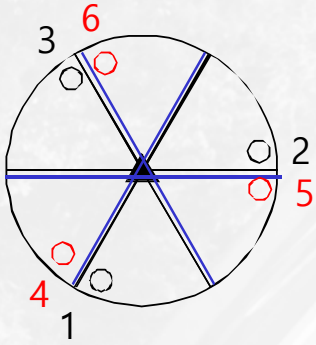
$1m$



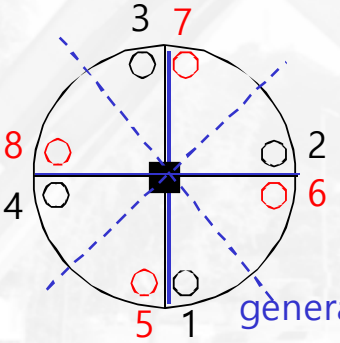
$2m(\equiv 2mm, mm2)$



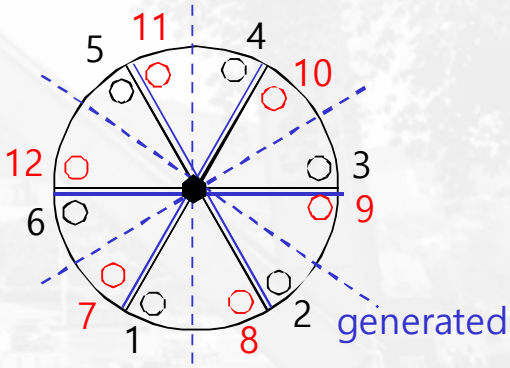
$3m$



$4m(\equiv 4mm)$

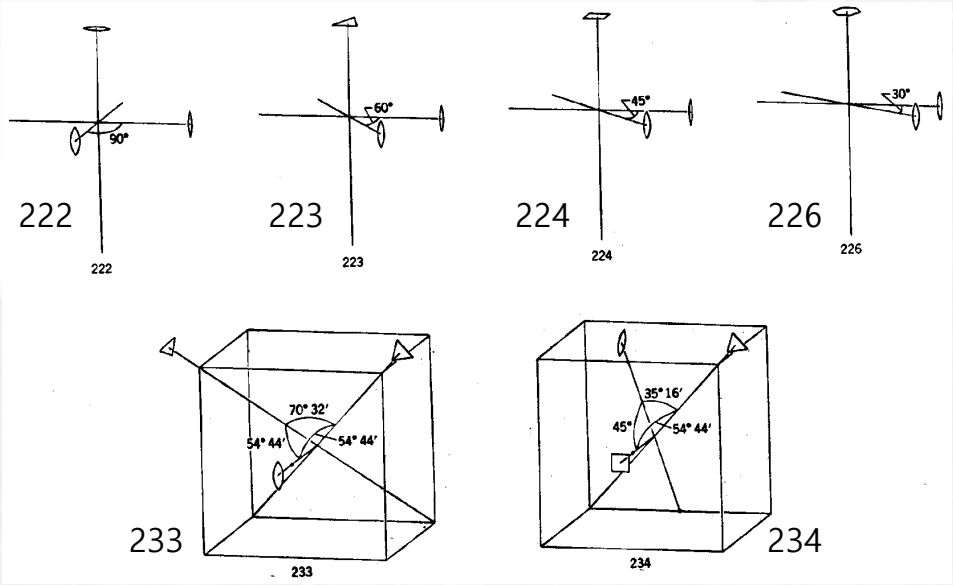


$6m(\equiv 6mm)$



Combination of rotation axes – **should be mutually consistent**

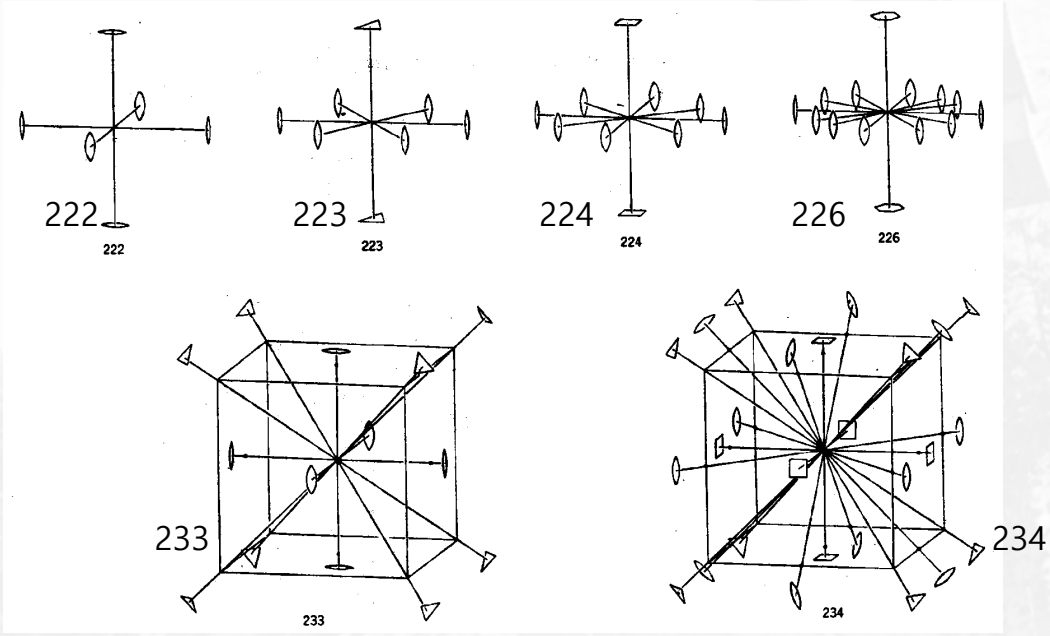
Allowed sets of simultaneous rotational symmetries passing thru a point



Spatial arrangements for the six permissible combinations of 3 rotational symmetry axes passing through a point in crystals

Page 149, Allen & Thomas, The Structure of Materials (MIT Series in Materials Science and Engineering) (1999)
Page 43, Buerger, Elementary Crystallography: An introduction to the fundamental geometric features of crystals (1978)

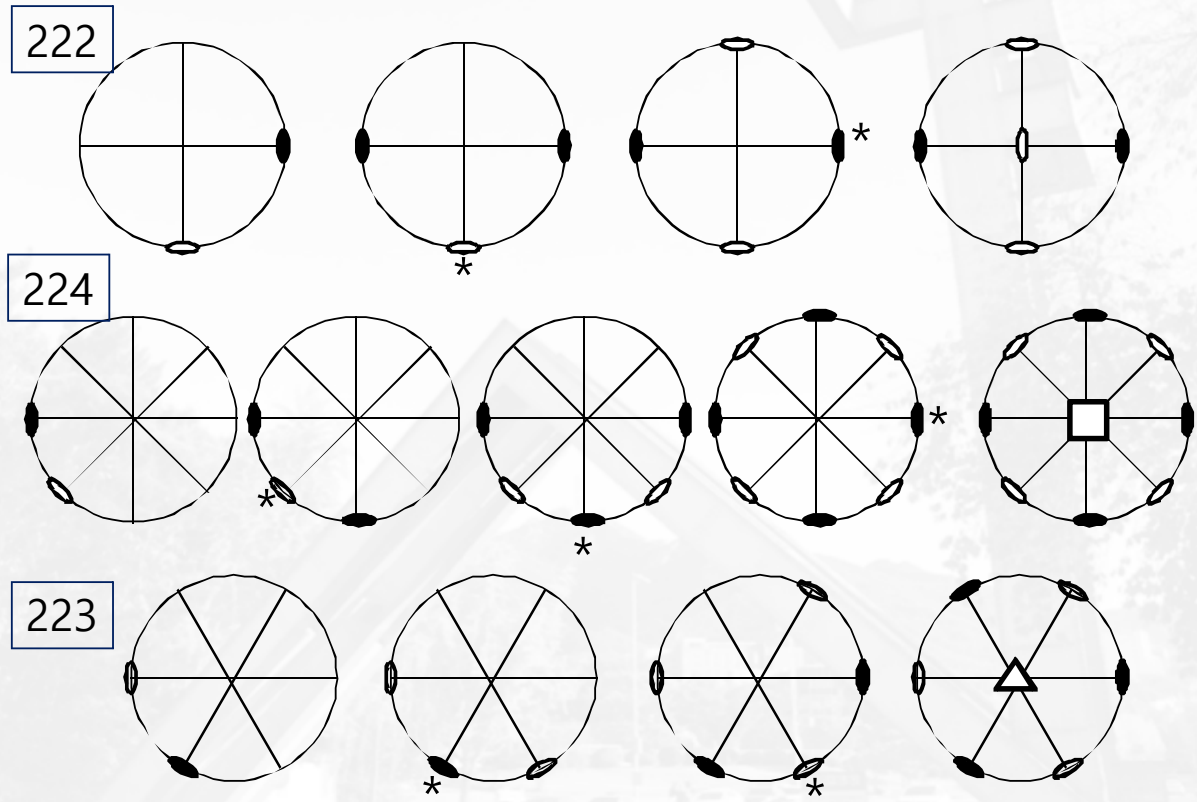
Combination of rotation axes



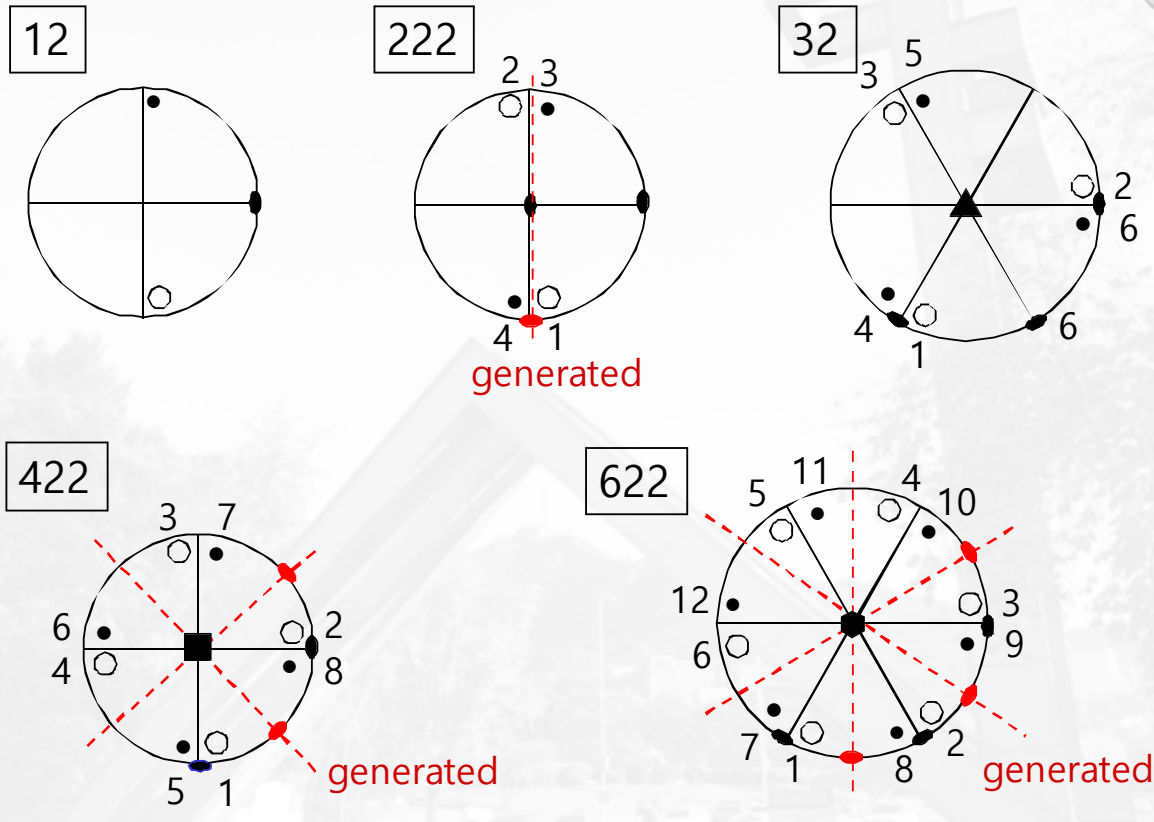
Spatial arrangements for the 6 permissible combinations of rotational symmetry axes passing through a point in crystals after allowing all rotational repetitions

Page 150, Allen & Thomas, The Structure of Materials (MIT Series in Materials Science and Engineering) (1999)
Page 44, Buerger, Elementary Crystallography: An introduction to the fundamental geometric features of crystals (1978)

Combination of rotation axes

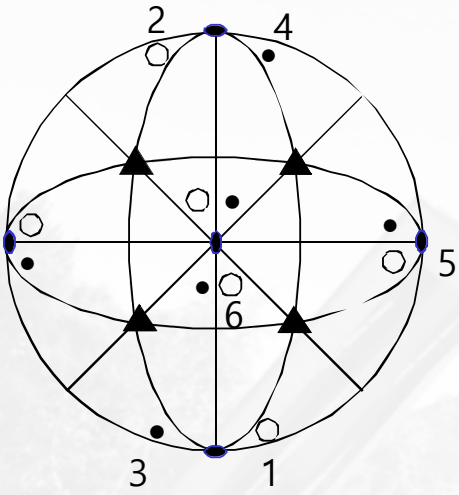


Combination of rotation axes > n2

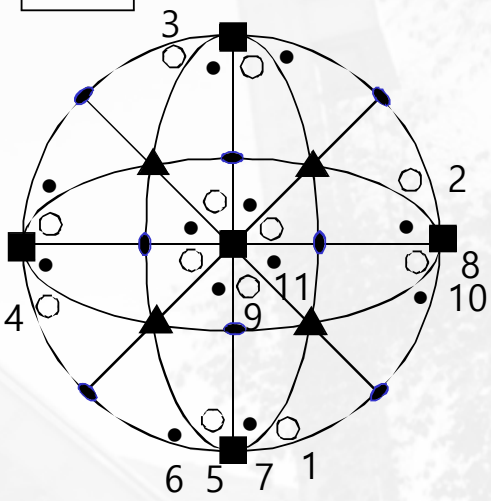


Combination of rotation axes

23



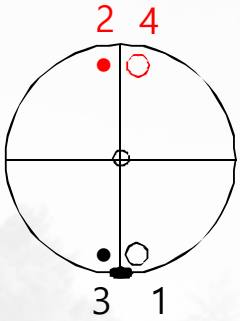
432



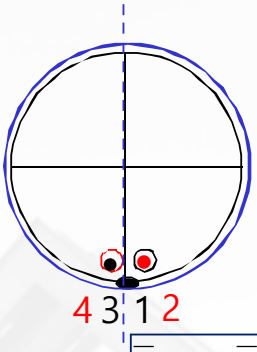
- 3-fold rotation axes are in non-orthogonal directions
- body-diagonal directions in cubes (see page 14 of Krawitz)

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

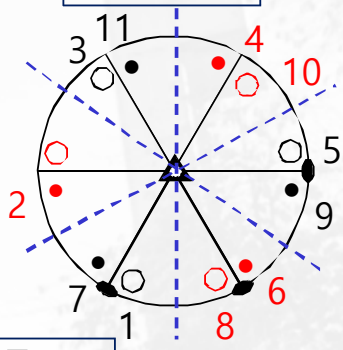
$\bar{1}2(\equiv \frac{2}{m})$



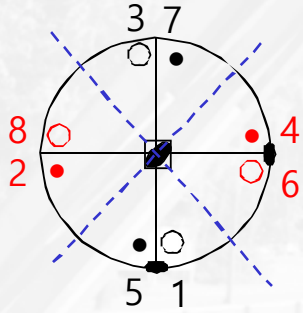
$\bar{2}2(\equiv 2mm)$



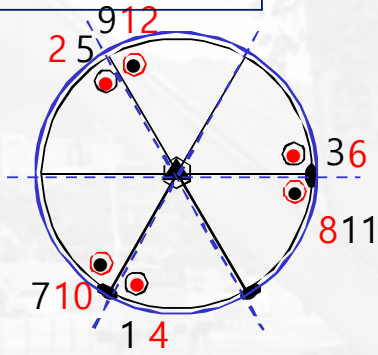
$\bar{3}2(\equiv \bar{3}\frac{2}{m})$



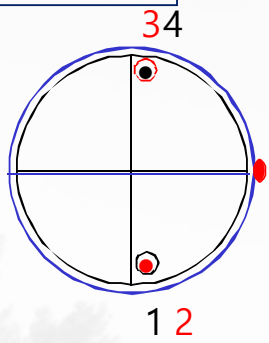
$\bar{4}2(\equiv \bar{4}2m)$



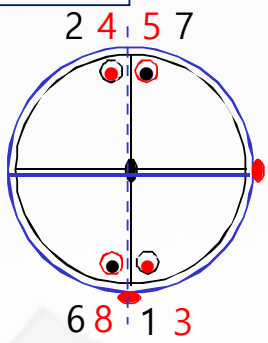
$\bar{6}2(\equiv \bar{6}2m \equiv \bar{6}m2)$



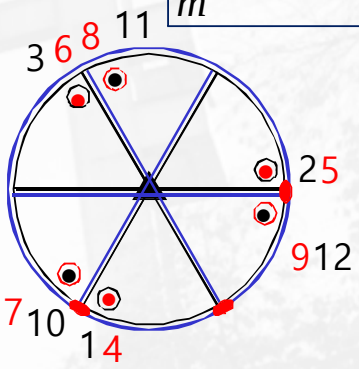
$\frac{1}{m}m(\equiv 2mm)$



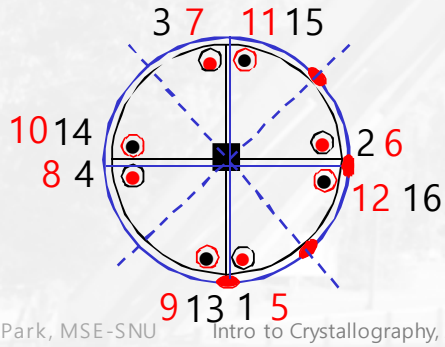
$\frac{2}{m}m(\equiv \frac{2}{m}\frac{2}{m}\frac{2}{m}) = mmm$



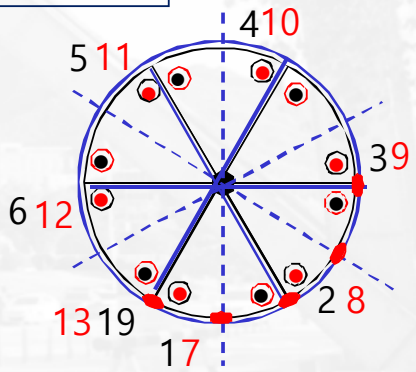
$\frac{3}{m}m(\equiv \bar{6}m2)$



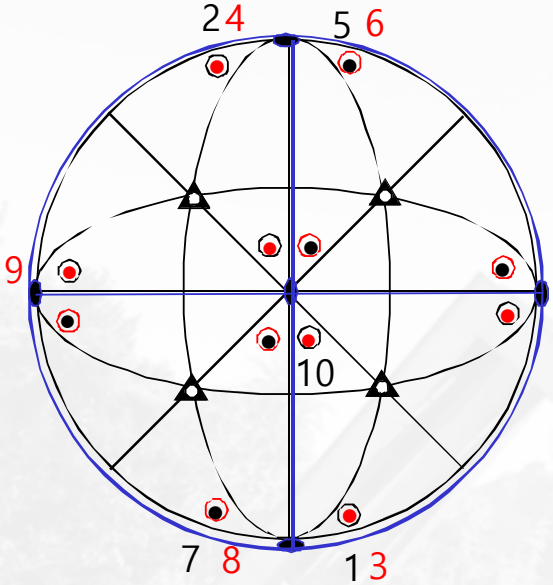
$\frac{4}{m}m(\equiv \frac{4}{m}\frac{2}{m}\frac{2}{m}) = 4/mmm$



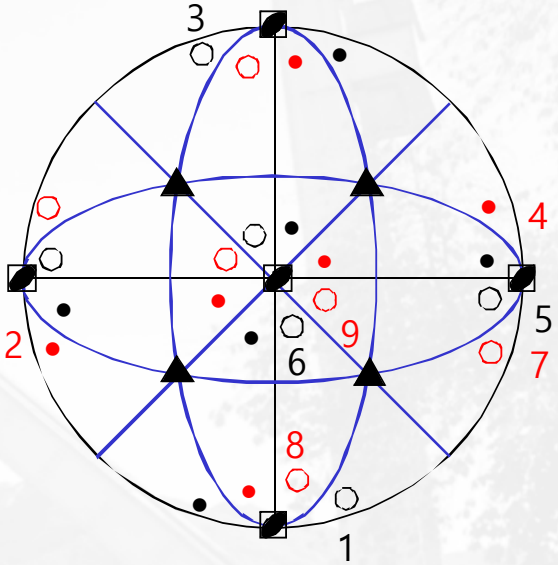
$\frac{6}{m}m(\equiv \frac{6}{m}\frac{2}{m}\frac{2}{m}) = 6/mmm$

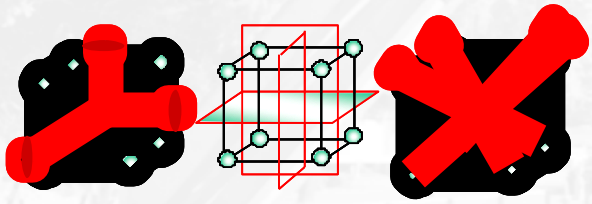


$\frac{2}{m}\bar{3}(\equiv m\bar{3})$

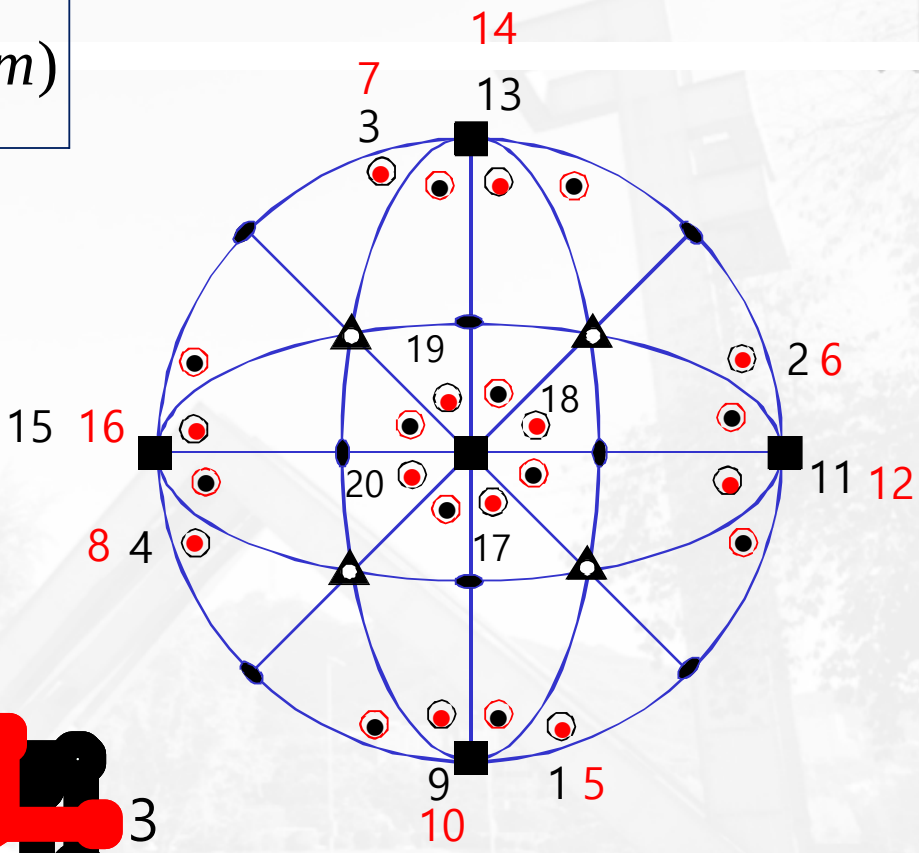


$\bar{4}3m$





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



Symmetry directions & Characteristic symmetry elements

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Xtal systems	Symmetry directions			Characteristic symmetry elements
Triclinic				$\bar{1}$ or 1 only
Monoclionic	b			2 and/or m in one direction
Orthorhombic	a	b	c	2 and/or m in 3 orthogonal directions
Tetragonal	c	<a>	<110>	1 ■ or 1 ◪
Trigonal	c	<a>		1 ▲
Hexagonal	c	<a>	<210>	⬢ or ⬡
Cubic	<a>	<111>	<110>	4 ▲

Notations in the "International Tables for Crystallography"

Table 1.1. Notation for Asymmetric Units Used to Represent Point Group Symmetry

Notation	Description
○	Asymmetric unit in the plane of the page
○+ ○−	Asymmetric unit above (+) or below (−) the plane of the page
⚲	Apostrophe indicating a left-handed asymmetric unit and clear circle indicating righthandedness.
−◐+	Two asymmetric units directly on top of one another, with the "+" meaning above the plane and the "−" meaning below the plane.
◑	Two asymmetric units directly on top of one another, one left-handed and the other right-handed

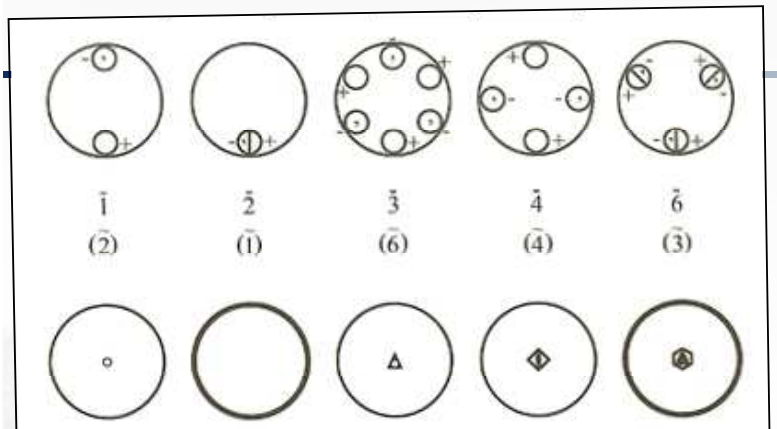
Note: The notation derives from the *International Tables for Crystallography*.

Krawitz page 10

- down
- up

Black & Red; enantiomorphs

- down, left
- up, right



RE 1.7. Rotoinversion point groups (with equivalent rotoreflection operations inc

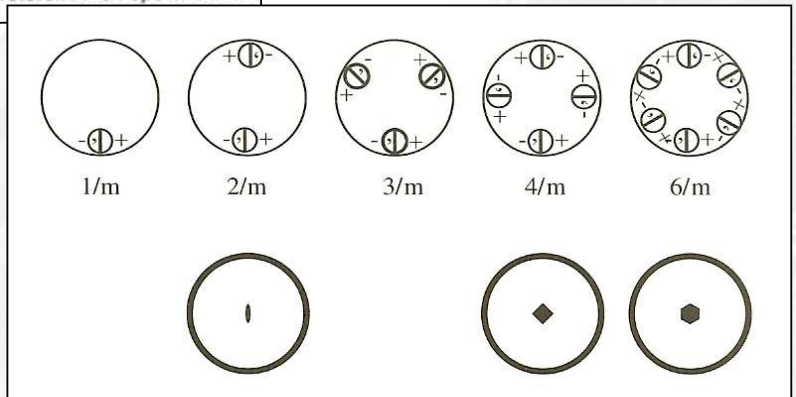


FIGURE 1.8. Point groups resulting from mirror planes normal to rotation axes.

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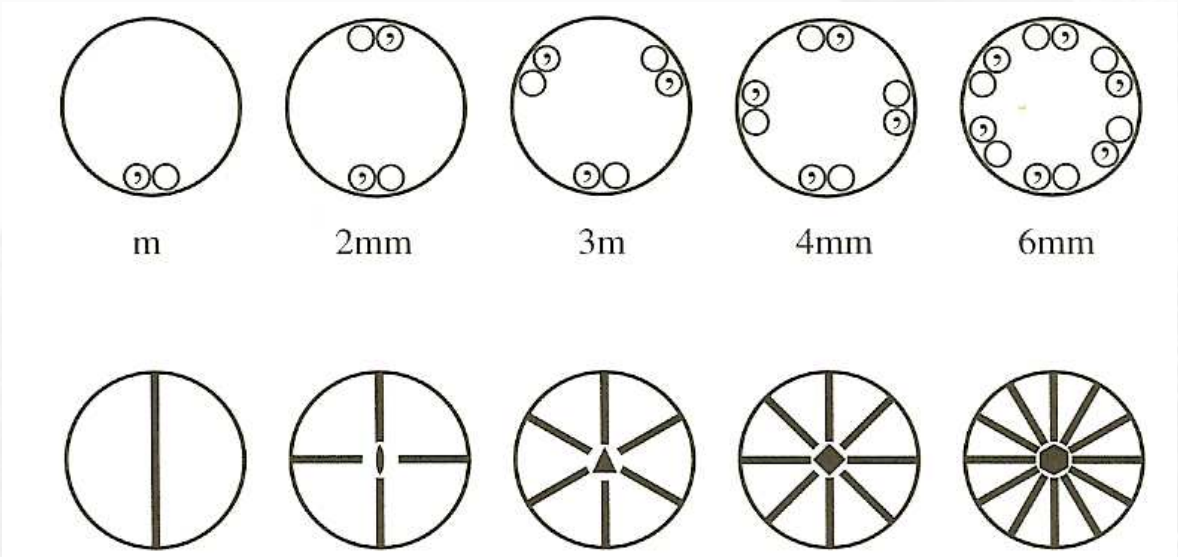

FIGURE 1.9. Point groups resulting from mirror planes parallel to rotation axes

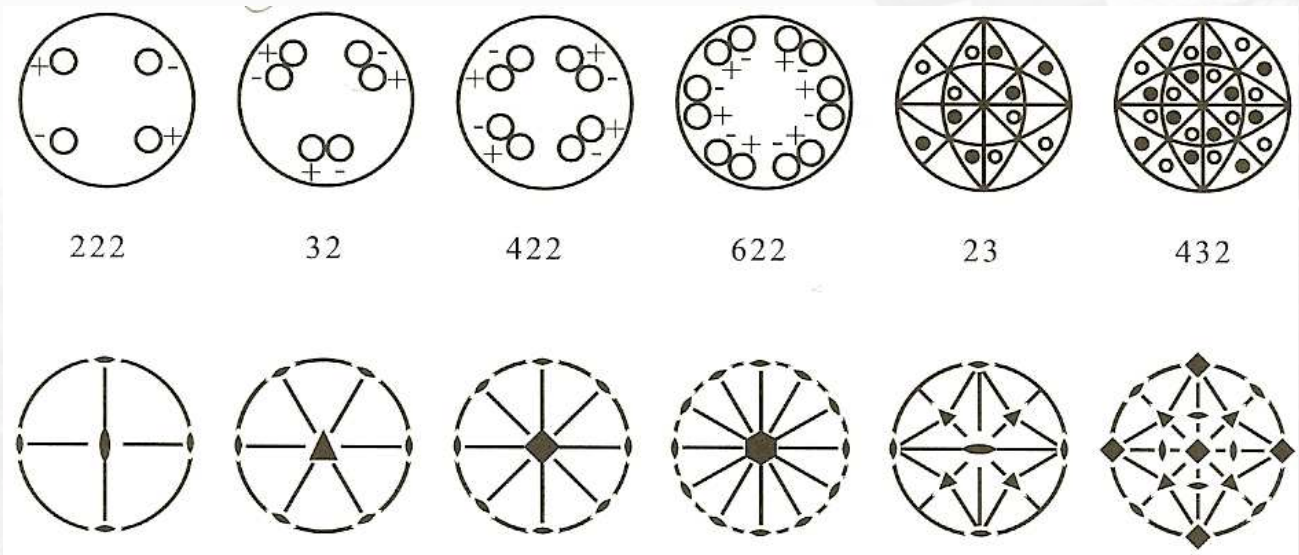

FIGURE 1.10. Point groups resulting from combined rotation axes.

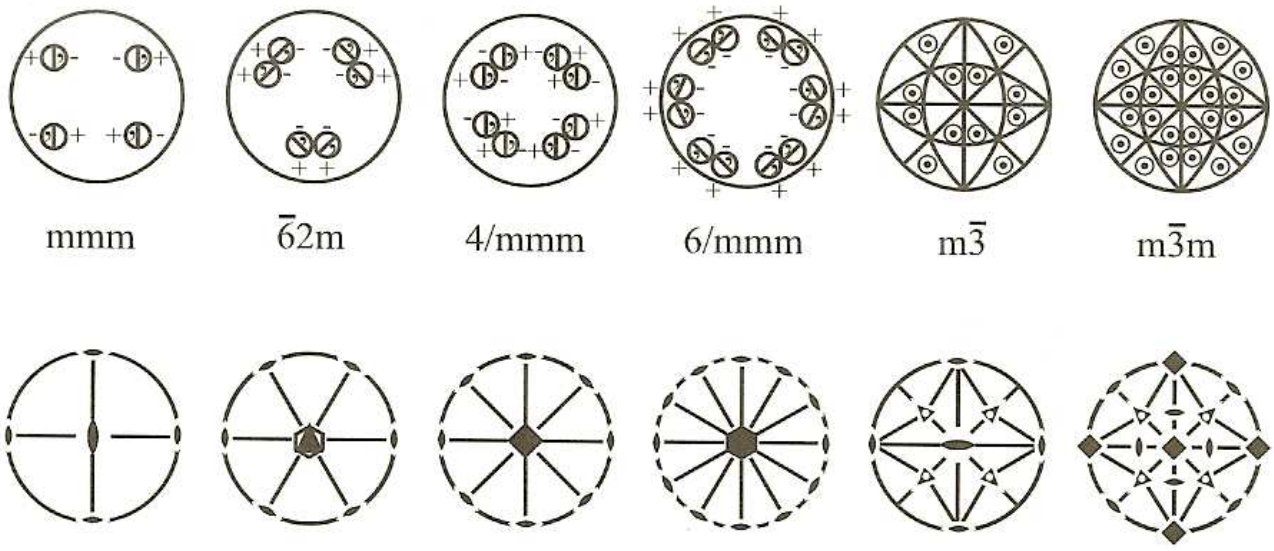

FIGURE 1.11. Point groups resulting from multiple n/m axes combined with rotation.

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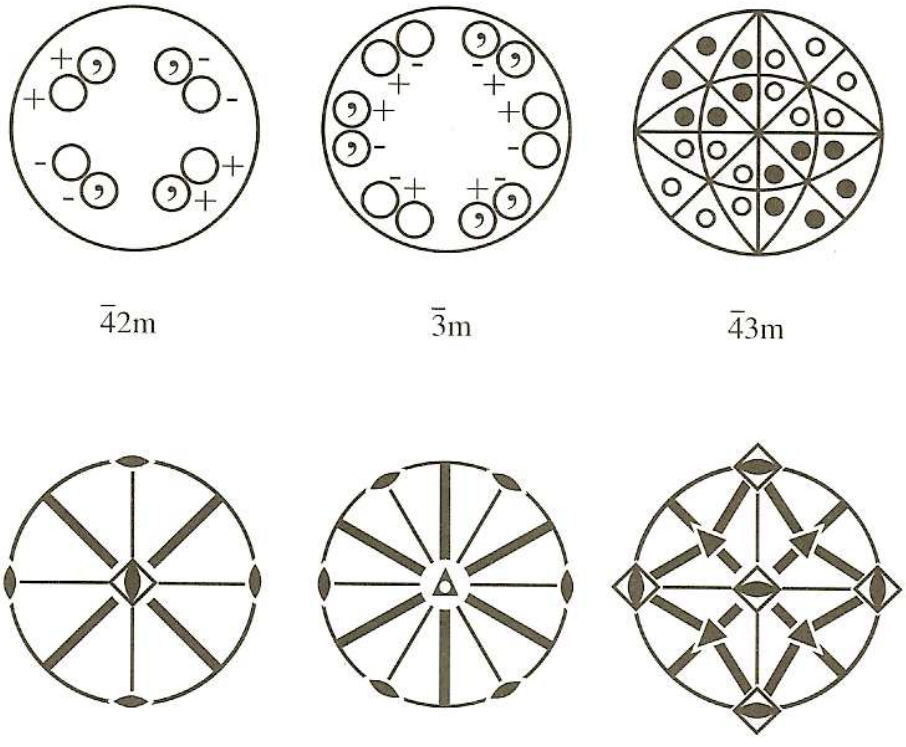

FIGURE 1.12. Point groups resulting from rotoinversion combined with rotation.

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32 point groups

- The point groups are made up from point symmetry operation and combinations of them (translation is excluded)
- X : x-fold rotation axis
- m : mirror plane
- $\bar{1}$: inversion centre
- $\bar{X}$: rotoinversion axis
- X2 : X-fold rotation axis + 2-fold rotation axis (X⊥2)
- Xm(m) : X + m (X // m)
- $\bar{X}$2(2) : $\bar{X}$ + 2-fold axis ($\bar{X}$⊥2)
- $\bar{X}$m : $\bar{X}$ + m (X // m)
- $\frac{X}{m}$m : X + m1 + m2 (X ⊥ m1, X // m2)

32 point group > Schönflies symbol vs. International (Hermann-Mauguin) 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 ≡ X/m

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

Symmetry directions

Xtal systems	Symmetry directions			
Triclinic				a1 ≠ a2 ≠ a3, α ≠ β ≠ γ ≠ 90°
Monoclionic	b			a1 ≠ a2 ≠ a3, α = γ = 90° ≠ β
Orthorhombic	a	b	c	a1 ≠ a2 ≠ a3, α = β = γ = 90°
Tetragonal	c	<a>	<110>	a1 = a2 ≠ a3, α = β = γ = 90°
Trigonal	c	<a>		a1 = a2 = a3, α = β = γ < 120° ≠ 90°
Hexagonal	c	<a>	<210>	a1 = a2 ≠ a3, α = β = 90° , γ = 120°
Cubic	<a>	<111>	<110>	a1 = a2 = a3, α = β = γ = 90°

Table 8.2. The 32 point groups

Crystal system	Point groups		
Triclinic	$\bar{1}$	1	2
Monoclinic	2/m	m, 2	3
Orthorhombic	2/m 2/m 2/m (mmm)	mm2, 222	3
Tetragonal	4/m 2/m 2/m (4/mmm)	$\bar{4}$2m, 4mm, 422 4/m, $\bar{4}$, 4	7
Trigonal	$\bar{3}$ 2/m ($\bar{3}$m)	3m, 32, $\bar{3}$, 3	5
Hexagonal	6/m 2/m 2/m (6/mmm)	$\bar{6}$m2, 6mm, 622 6/m, $\bar{6}$, 6	7
Cubic	4/m $\bar{3}$ 2/m (m$\bar{3}$m)	$\bar{4}$3m, 432, 2/m$\bar{3}$, 23 ($\bar{m3}$)	5

full symbols
(short symbols)

Total 32

Laue class, Laue group; 11 point groups with center of symmetry

Table 2.9 The 11 Laue classes and six "powder" Laue classes.

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

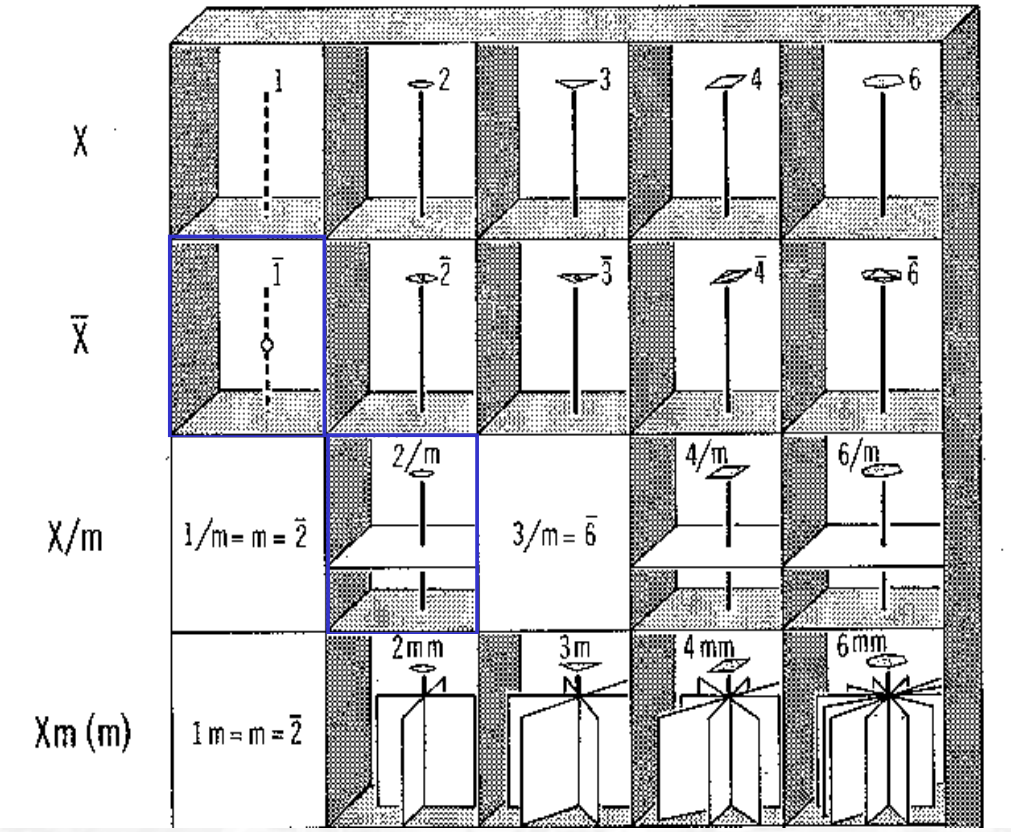
11

32

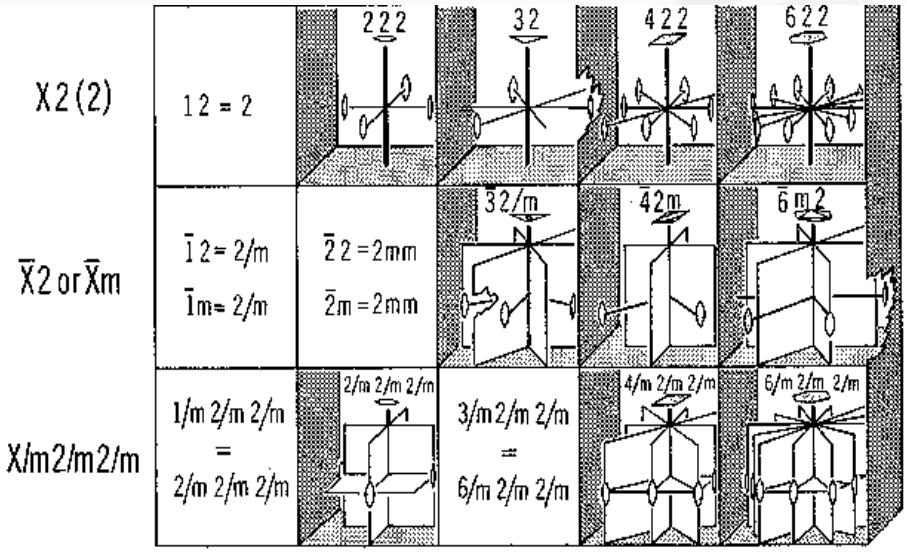
Table 2.10 Lattice symmetry and unit cell shapes.

Crystal family	Unit cell symmetry	Unit cell shape/parameters
Triclinic	$\bar{1}$	$a \neq b \neq c$; $\alpha \neq \beta \neq \gamma \neq 90°$
Monoclinic	2/m	$a \neq b \neq c$; $\alpha = \gamma = 90°, \beta \neq 90°$
Orthorhombic	mmm	$a \neq b \neq c$; $\alpha = \beta = \gamma = 90°$
Tetragonal	4/mmm	$a = b \neq c$; $\alpha = \beta = \gamma = 90°$
Hexagonal and Trigonal	6/mmm	$a = b \neq c$; $\alpha = \beta = 90°, \gamma = 120°$
Cubic	m$\bar{3}$m	$a = b = c$; $\alpha = \beta = \gamma = 90°$

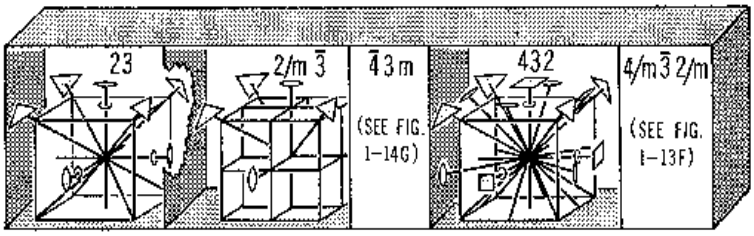
32 point groups



32 point groups

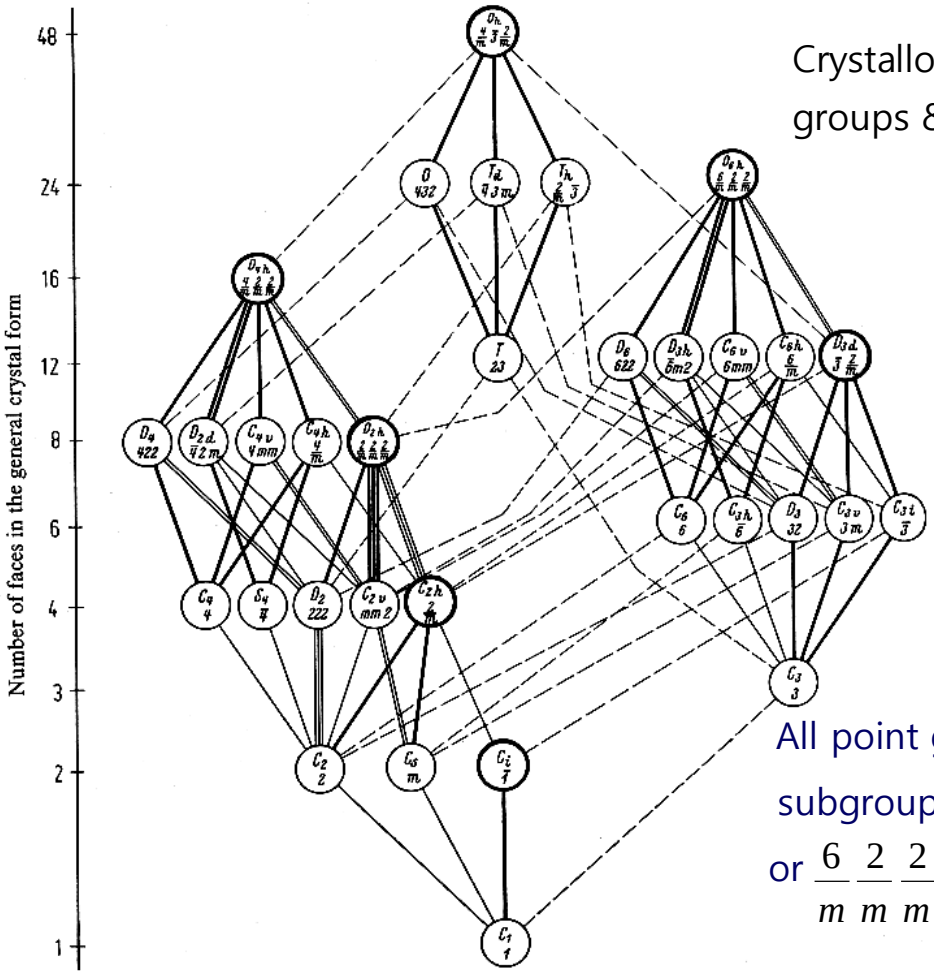


Combinations referable to Guide-Cube



X3

Geometric relationships between the symmetry elements in the 32 point groups.



Crystallographic point groups & their subgroups

All point groups are subgroups of either $\frac{4}{m}\bar{3}\frac{2}{m}$ or $\frac{6}{m}\frac{2}{m}\frac{2}{m}$ or both.

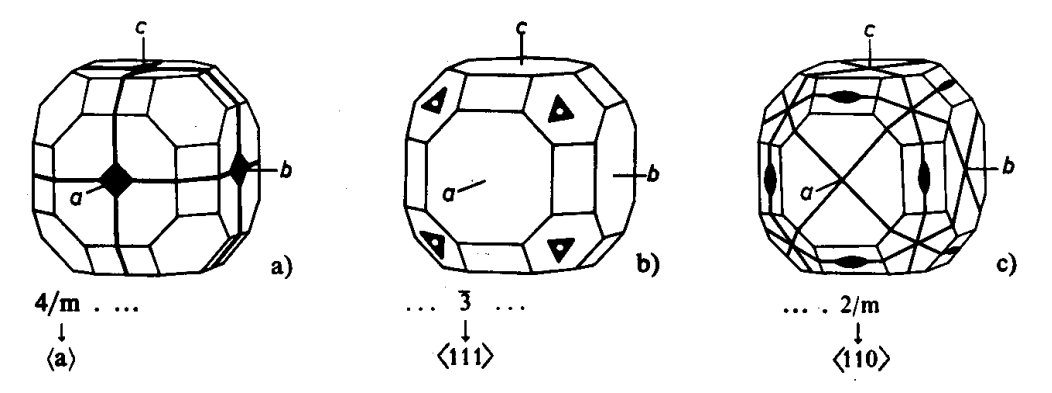
Trigonal	Hexagonal	Cubic
3	6	23
$\bar{3}$	$\bar{6}$	–
–	6/m	m3
32	622	432
3m	6mm	–
–	$\bar{6}$m2	$\bar{4}$3m
$\bar{3}$m	6/mmm	m3m

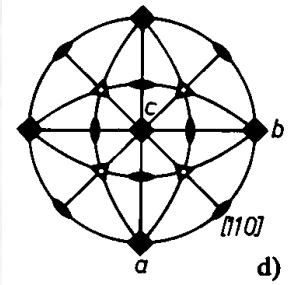
	Triclinic	Monoclinic	Tetragonal
X	1	2	4
$\bar{X}$	$\bar{1}$	m (=$\bar{2}$)	$\bar{4}$
X+$\bar{1}$	–	2/m	4/m
		Orthorhombic	
X2	–	222	422
Xm	–	mm2	4mm
$\bar{X}$m	–	–	$\bar{4}$2m
X2+$\bar{1}$		mmm	4/mmm

Fig. The 32 crystallographic point group. Each pari of stereograms shows (left) the poles of a general form , (righr) the symmetry elements of the point group

Crystal symmetry

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



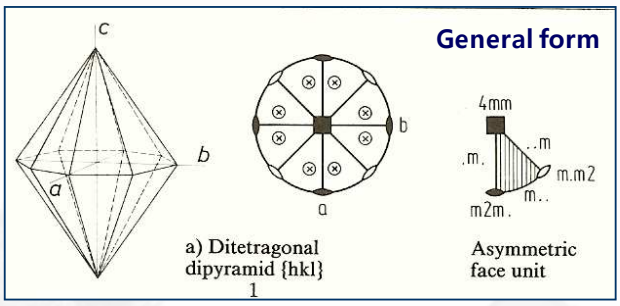


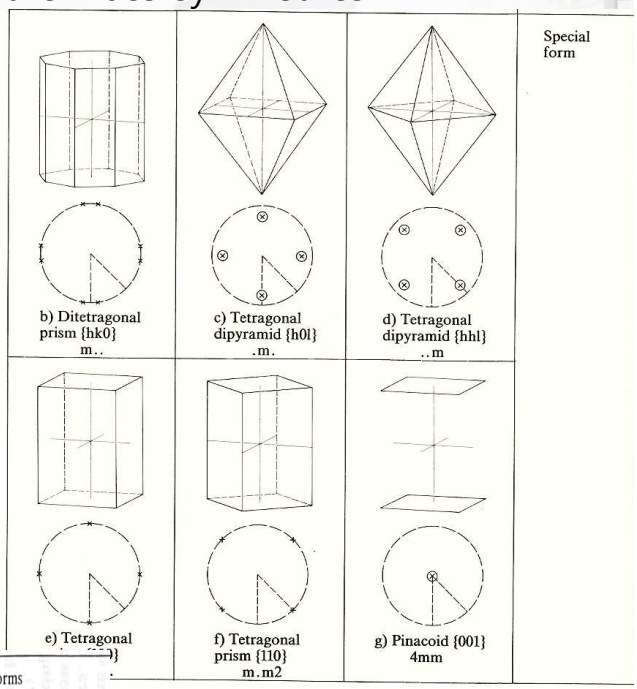
Crystal Symmetry

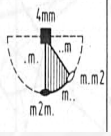
- Crystal form (family of planes): a set of equivalent faces
- General form : a set of equivalent faces, each of which has symmetry 1
- Special form : a set of equivalent faces, each of which has symmetry higher than 1
- Limiting form : A special case of either a general or a special form. It has the same number of faces, each of which has the same face symmetry, but the faces are differently arranged.
- Asymmetry face unit : The smallest part of the surface of the sphere which, by the application of the symmetry operations, will generate the entire surface of the sphere

Crystal forms in 4/mmm (tetragonal) & their face symmetries

<c> <a> <110>

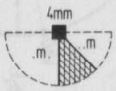




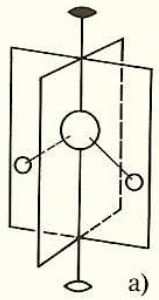
Point group	Asymmetric face unit and face symmetry	Special forms {hhl}	Special forms {h0l}	General and limiting forms {hkl}	Special and limiting forms {hk0}	Special and limiting forms {100}	Special and limiting forms {110}	Special and limiting forms {001}
4/m 2/m 2/m (4/mmm)		Tetragonal dipyramid ..m	Tetragonal dipyramid .m.	Ditetragonal dipyramid 1	Ditetragonal prism m..	Tetragonal prism m2m.	Tetragonal prism m.m2	Pinacoid 4mm

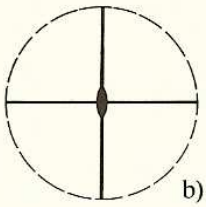
Crystal forms in tetragonal system & their face symmetries

Table 8.4. Crystal forms in the tetragonal system and their face symmetries

Point group	Asymmetric face unit and face symmetry	Special forms {hhl}	Special forms {h0l}	General and limiting forms {hkl}	Special and limiting forms {hk0}	Special and limiting forms {100}	Special and limiting forms {110}	Special and limiting forms {001}
4/m 2/m 2/m (4/mmm)		Tetragonal dipyramid ..m	Tetragonal dipyramid .m.	Ditetragonal dipyramid 1	Ditetragonal prism m..	Tetragonal prism m2m.	Tetragonal prism m.m2	Pinacoid 4mm
4mm		Tetragonal pyramid ..m	Tetragonal pyramid .m.	Ditetragonal pyramid 1		Tetragonal prism .m.	Tetragonal prism ..m	Pedion 4mm
$\bar{4}$2m		Tetragonal disphenoid ..m		Tetragonal scalenohedron 1	Ditetragonal prism 1	Tetragonal prism .2.		Pinacoid 2.mm
422		Tetragonal dipyramid 1		Tetragonal trapezohedron 1			Tetragonal prism ..2	Pinacoid 4..

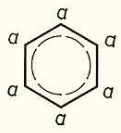
H_2O molecule
mm2

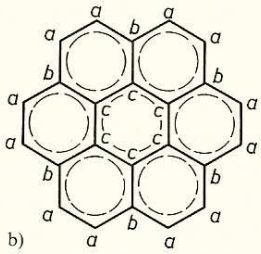


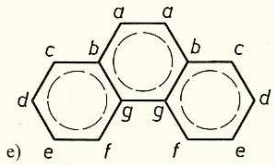


6/mmm

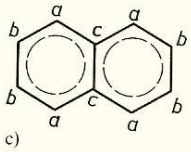
Benzene
6/mmm



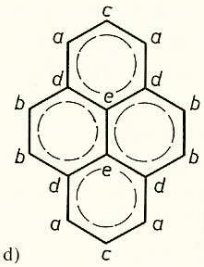




mm2



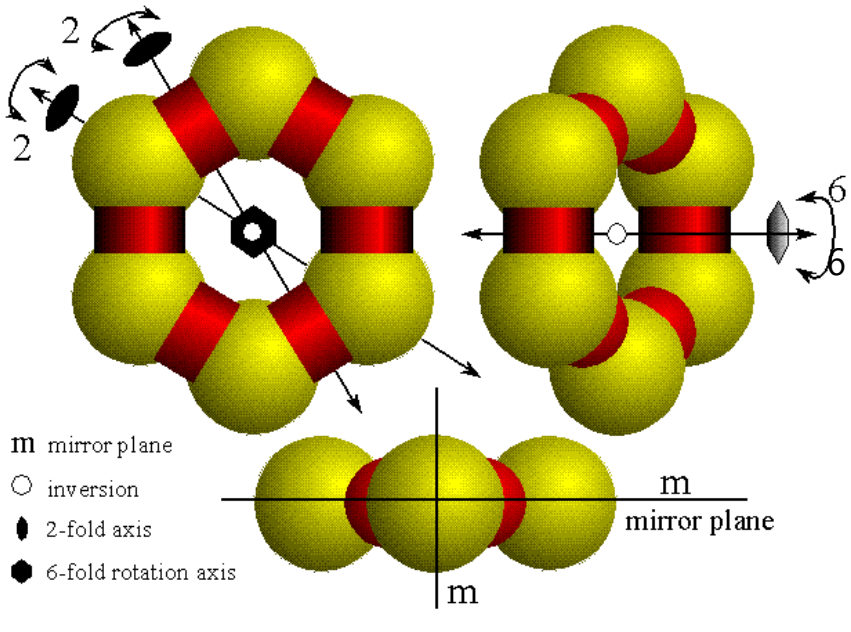
mmm

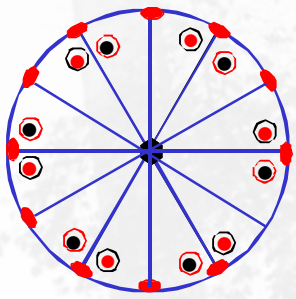


mmm

Fig. 8.18a–e. Equivalence within molecules. Equivalent atoms have the same letter symbols; equivalent bonds have the same pair of letters. **a** Benzene and **b** coronene (6/mmm – D_{6h}); **c** naphthalene and **d** pyrene (mmm – D_{2h}); **e** phenanthrene (mm2 – C_{2v})

benzene(C_6H_6) $\frac{6}{m}\frac{2}{m}\frac{2}{m}$ = 6/mmm





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

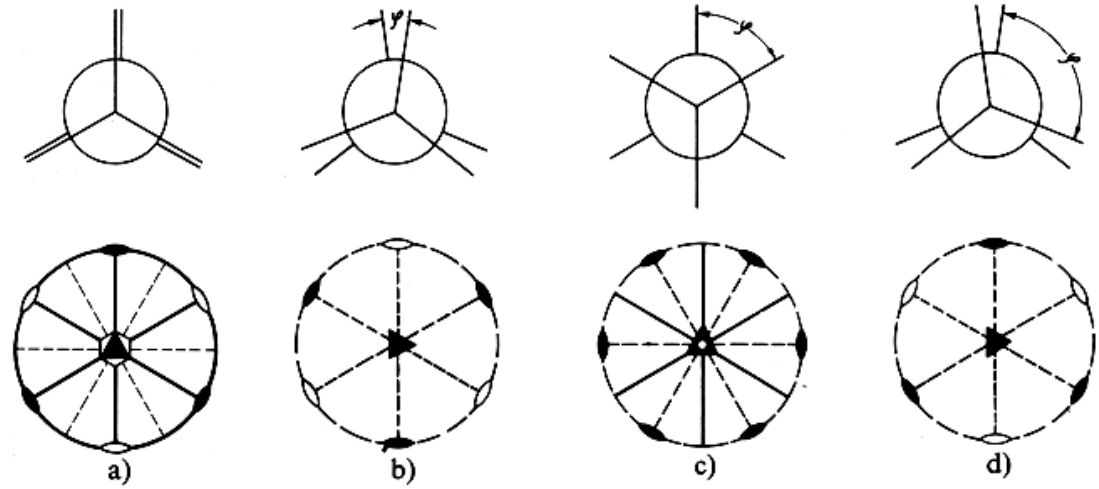
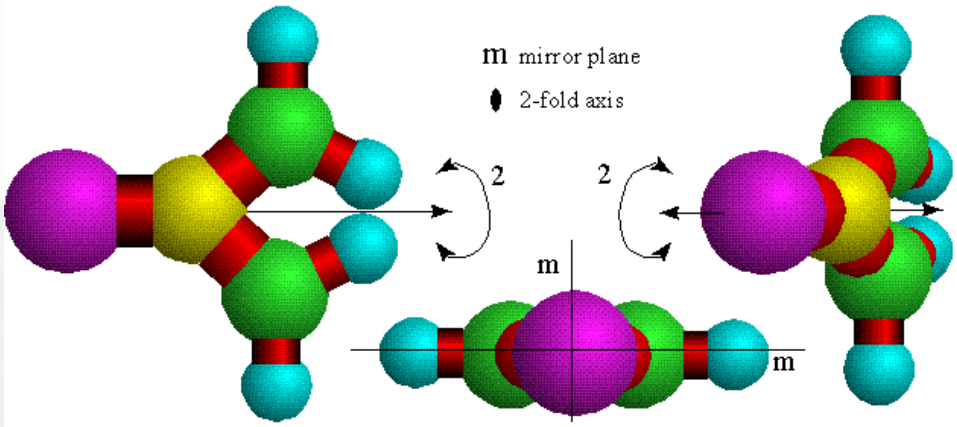


Fig. 8.20 a–d. Conformations of ethane. **a** Eclipsed: $\varphi = 0$ or 120 or 240°: ($\bar{6}$m2 – D_{3h}). **b** Skew: $0 < \varphi < 60°$, $120 < \varphi < 180°$ or $240 < \varphi < 300°$: (32 – D_3). **c** Staggered: $\varphi = 60$ or 180 or 300°: ($\bar{3}$m – D_{3d}). **d** Skew: $60 < \varphi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

Thiourea *mm2*

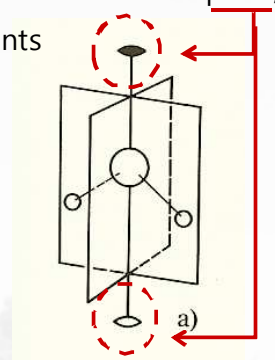


http://www.gh.wits.ac.za/craig/diagrams/thiou.gif

Check other examples in the Table 9.11, Ott

Determination of point groups

➢all rotation axes are polar, which can be destroyed by the presence of certain symmetry elements



➢ which one of the 7 crystal system?

← characteristic symmetry elements

➢ Are rotation axes higher than 2 present? → 3, 4 or 6?

➢ Are these axes polar? Or is there an inversion center?

Table 8.9. Characteristic symmetry elements of the seven crystal systems

Crystal system	Point groups[a]	Characteristic symmetry elements
Cubic	$\underline{4}/m\ \underline{\bar{3}}\ \underline{2}/m$ $\underline{\bar{4}3m}, \underline{432}, \underline{2}/m\underline{\bar{3}}, \underline{23}$	4 ▲
Hexagonal	$\underline{6}/m\ \underline{2}/m\ \underline{2}/m$ $\underline{\bar{6}m2}, \underline{6mm}, \underline{622}$, $\underline{6}/m, \underline{\bar{6}}, \underline{6}$	⬢ or ⬣
Tetragonal	$\underline{4}/m\ \underline{2}/m\ \underline{2}/m$ $\underline{\bar{4}2m}, \underline{4mm}, \underline{422}$, $\underline{4}/m, \underline{\bar{4}}, \underline{4}$	1 ■ or 1 ◪ (3 ■ or 3 ◪ ⇒ cubic)
Trigonal	$\underline{\bar{3}}\ \underline{2}/m$ $\underline{3m}, \underline{32}, \underline{\bar{3}}, \underline{3}$	1 ▲ (remember that m normal to 3 gives $\bar{6}$ ⇒ hexagonal
Orthorhombic	$\underline{2}/m\ \underline{2}/m\ \underline{2}/m$ $\underline{mm2}, \underline{222}$	2 and/or m in three orthogonal directions
Monoclinic	$\underline{2}/m$ $\underline{m}, \underline{2}$	2 and/or m in one direction
Triclinic	$\underline{\bar{1}}$ $\underline{1}$	$\bar{1}$ or 1 only

[a] Characteric symmetry elements are underlined.

Must see examples in Ott Chap 9.4

todos

- Movies and images of 32 point groups → http://neon.mems.cmu.edu/degraef/pg/pg.html#AGM
- Table 9.11 of Ott
  - ✓ Spend a lot of time to understand point groups of molecules & crystals
  - ✓ Need to be able to determine point groups of most molecules & crystals
- Read
  - ✓ Ott Chapter 9 (9.2, 9.6, 9.7 제외, Fig 9.4 포함)
  - ✓ Hammond Chapter 2.1 ~ 2.4; 3.1 ~ 3.3; 4.1 ~ 4.3, 4.5; 5.1 ~ 5.6
  - ✓ Sherwood & Cooper Chapter 3.7
  - ✓ Krawitz Chapter 1.1 ~ 1.6; 2.1 ~ 2.4
- Point group HW (due in 1 week)
  - ✓ Ott chapter 9 --- 1, 2, 3, 4, 5, 8, 9, 10, 11 (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 22, 23, 35, 36, 37, 38), 15(exclude c & d)(exclude figure 17~20)