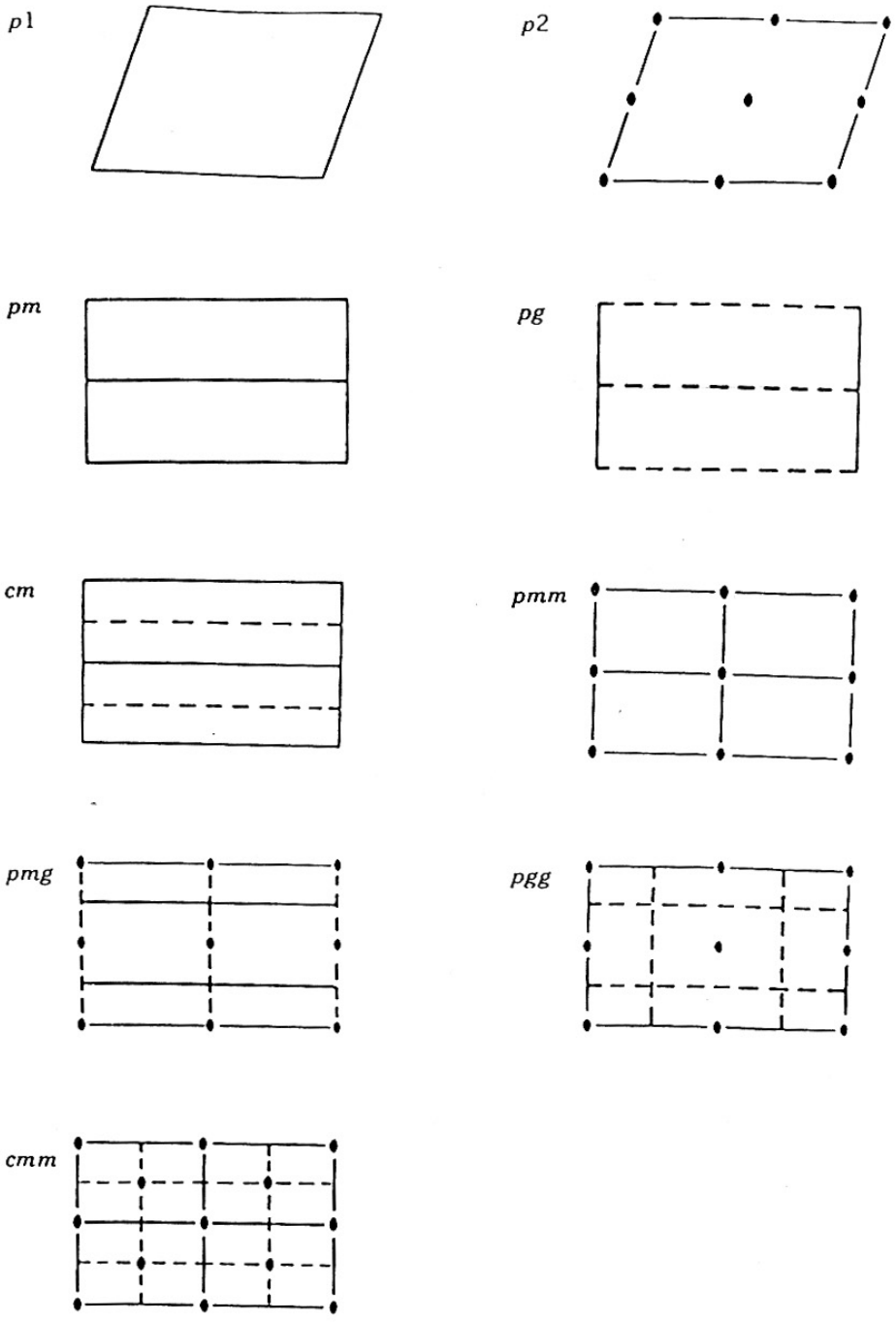
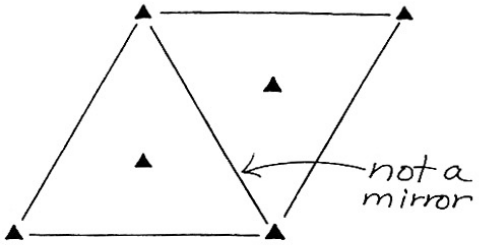


Figure 11.8. Diagrams showing all symmetry elements for the 17 two-dimensional symmetry classes; continuation on page 364. (Adapted from the International Tables for X-ray Crystallography, 1965.)

p3



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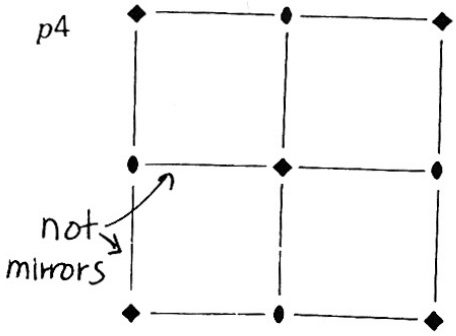
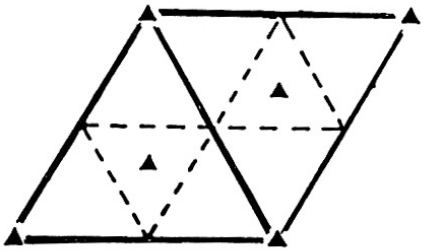
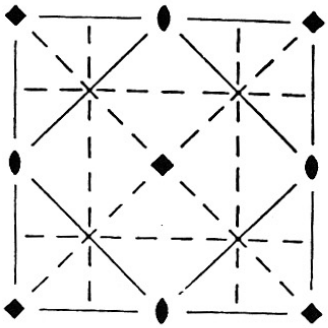


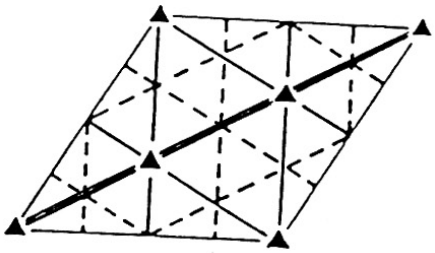
p31m



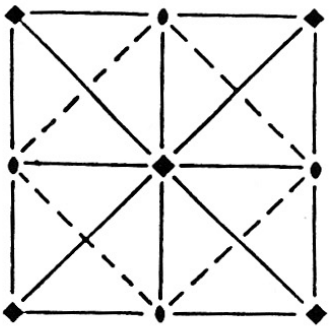
p4g



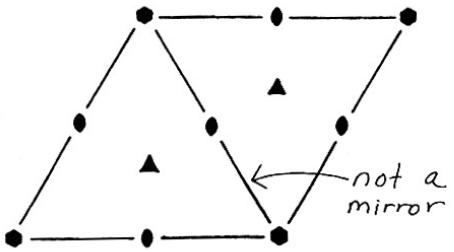
p3m1



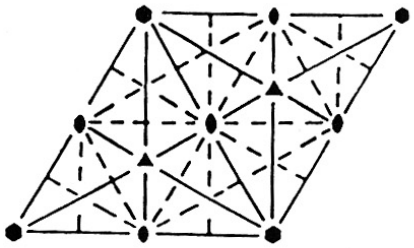
p4m



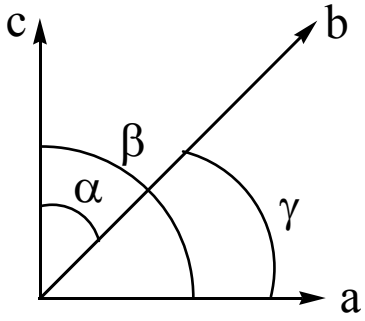
p6



p6m



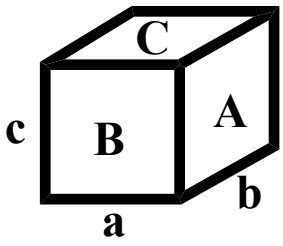
3-D unit cell (six parameters)



α is the angle between b and c

β is the angle between a and c

γ is the angle between a and b



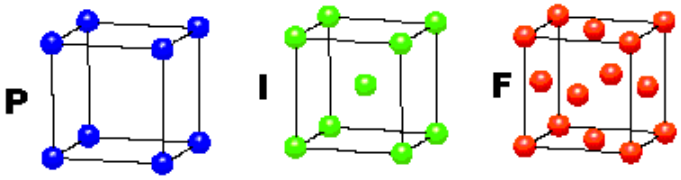
The faces of the unit cell are labeled as shown with A, B, C designations

As in the 2-D lattices, we can define unit cells with no symmetry on up to high symmetry

CUBIC

$a = b = c$

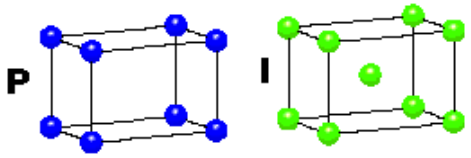
$\alpha = \beta = \gamma = 90°$



TETRAGONAL

$a = b \neq c$

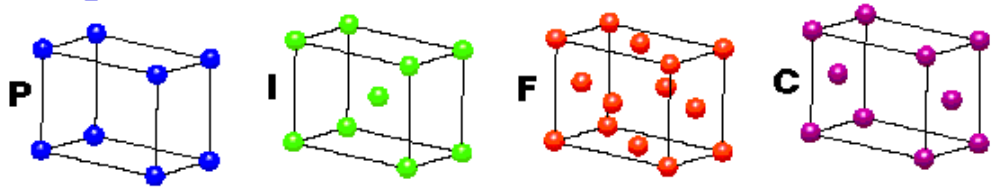
$\alpha = \beta = \gamma = 90°$



ORTHORHOMBIC

$a \neq b \neq c$

$\alpha = \beta = \gamma = 90°$

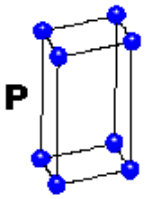


HEXAGONAL

$a = b \neq c$

$\alpha = \beta = 90°$

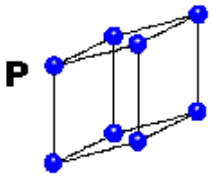
$\gamma = 120°$



TRIGONAL

$a = b = c$

$\alpha = \beta = \gamma \neq 90°$

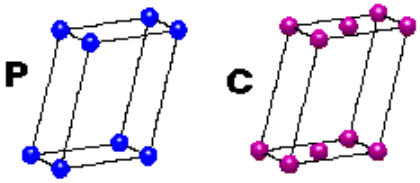


MONOCLINIC

$a \neq b \neq c$

$\alpha = \gamma = 90°$

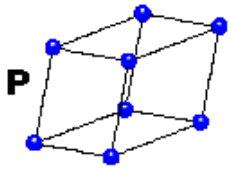
$\beta \neq 120°$



TRICLINIC

$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma \neq 90°$



4 Types of Unit Cell
P = Primitive
I = Body-Centred
F = Face-Centred
C = Side-Centred
+
7 Crystal Classes
→ 14 Bravais Lattices

DEVELOPING THE 14 BRAVAIS LATTICES

ONE WILL ENCOUNTER BOTH MOLECULAR SYMMETRY SYMBOLS (SCHÖENFLIES) AND CRYSTALLOGRAPHIC SYMBOLS (HERMANN-MAUGIN)

Molecular point group symmetry (Schönflies)

TRICLINIC

C_i $\bar{1}$ ← Crystallographic point group $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$

3-D OBLIQUE LATTICE P

No unique way to define vectors so one chooses the shortest vectors

THE ONLY SYMMETRY IS AN INVERSION CENTER

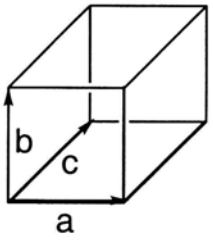
MONOCLINIC

C_{2h}	2/m	$a \neq b \neq c$, $\alpha = \gamma = 90$
molecular symbol	crystallographic symbol	$\beta \neq 90°$
		P, I, C (A,B)

ONE VECTOR ALONG b DIRECTION IS UNIQUE AND THE LATTICE HAS 2-FOLD ROTATIONAL SYMMETRY ABOUT THE "b" DIRECTION AND PLANES OF SYMMETRY PERPENDICULAR TO IT

TYPE I - PRIMITIVE CELL

NOTE: COTTON'S BOOK USES ANOTHER CONVENTION USE THIS ONE



The Seven Crystal Systems

Crystal system	Characteristic symmetry	Lattice symmetry (highest symmetry of lattice)	Axial and angular constraints from symmetry* (cell constraints)
1. *Triclinic*	*Identity or inversion (onefold rotation or rotatory-inversion axis) in any direction*	$\bar{1}$	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$
2. *Monoclinic*	*A single 2-fold rotation or rotatory-inversion axis along* b	$2/m$	$a \neq b \neq c$ $\alpha = \gamma = 90°$, $\beta \neq 90°$
3. *Orthorhombic*	*Three mutually perpendicular 2-fold rotation or rotatory-inversion axes along* a, b *and* c	mmm	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90°$
4. *Tetragonal*	*A single 4-fold rotation or rotatory-inversion axis along* c	$4/mmm$	$a = b \neq c$ $\alpha = \beta = \gamma = 90°$
5. *Cubic*	*Four 3-fold axes along* a+b+c, −a+b+c, a−b+c, −a−b+c	$m\bar{3}m$	$a = b = c$ $\alpha = \beta = \gamma = 90°$
6. *Trigonal* (same as Rhomb.)	*A single 3-fold rotation or rotatory-inversion axis along* a+b+c	$\bar{3}m$	$a = b = c$ $\alpha = \beta = \gamma \neq 90°$ $\gamma < 120°$
7. *Hexagonal*	*A single 6-fold rotation or rotatory-inversion axis (along* c)	$6/mmm$	$a = b \neq c$ $\alpha = \beta = 90°$ $\gamma = 120°$

* *These follow from the definition given in the characteristic symmetry column, rather than being the direct definition of the crystal system. Note that the symbol* ≠ *means that values are not equal for symmetry reasons; they may, however, accidentally be equal.*

(7) CRYSTAL SYSTEM

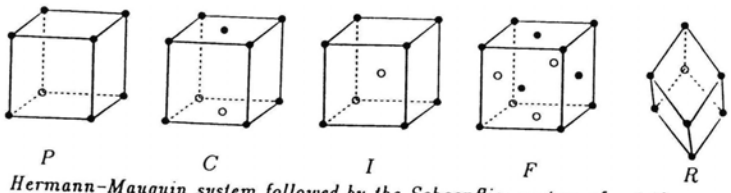
(14) Bravais Lattices

(32) Crystallographic Point Groups

Sample Space Groups

	Crystal system (7)	*Bravais Lattices* (14)*	*Crystallographic Point Groups* (32)**	*Common and/or representative space groups* (*out of* 230)
Hermann-Mauguin Symbol →	1. *Triclinic*	P	$1, \bar{1}$ (C_1, C_i)	$P1$, $P\bar{1}$
	2. *Monoclinic*	P, C	$2, m, 2/m$ (C_2, C_S, C_{2h})	$P2_1$ $C2/c, P2_1/c$
Schönflies molecular Symbol →	3. *Orthorhombic*	P, C, I, F	$222, mm2, mmm$ (D_2, C_{2v}, D_{2h})	$P2_12_12_1, Pbca$ $I222, I2_12_12_1$
	4. *Tetragonal*	P, I	$4, \bar{4}, 4/m, 422,$ $4mm, \bar{4}2m, 4/mmm$ $(C_4, S_4, C_{4h}, D_4,$ $C_{4v}, D_{2d}, D_{4h})$	$P4$, $P4_1$, $I\bar{4}$ $P4_12_12$, $I4_1/amd$
	5. *Cubic*	P, I, F	$23, m3, 432,$ $\bar{4}3m, m3m$ (T, T_h, O, T_d, O_h)	$Fm3m$, $P23$ $Pa3$, $I2_13$
Same	6. *Trigonal*	R	$3, \bar{3}, 32, 3m, \bar{3}m$ $(C_3, C_{3i}, D_3, C_{3v}, D_{3d})$	$P3$, $P3_121$, $R3c$
Same	7. *Hexagonal*	P	$6, \bar{6}, 6/m, 622,$ $6mm, \bar{6}m2, 6/mmm$ $(C_6, C_{3h}, C_{6h}, D_6$ $C_{6v}, D_{3h}, D_{6h})$	$P6_1$, $P6_222$

* *P = primitive, C = centered on the (001) faces, I = body-centered, F = all face-centered, R = primitive rhombohedral.*



P *C* *I* *F* *R*

** *Hermann–Mauguin system followed by the Schoenflies system of notation.*

To fully understand the crystallographic notation used in this table, you need to examine symmetry elements present in 3-D point groups

*Biggest Difference (besides symbols being different sometimes) is that improper rotation axes are defined as a rotation followed by inversion or rotoinversion instead of rotation followed by reflection.

1. five pure rotations $2\pi/n$ where n =1, 2, 3, 4, and 6. Previously they were identified as C_1, C_2, C_3, C_4, C_6. They are now represented by 1, 2, 3, 4, and 6
2. five rotoinversion operations symbolized by $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$, and $\bar{6}$

   remember $\bar{1} \equiv$ i

rotoinversions are related to S_n, m, and i symbols (recall m=s, and i=S_2)

$\bar{1}$ operation:

No net rotation but inverts all the coordinates

$(x, y, z) \longrightarrow (\bar{x}, \bar{y}, \bar{z})$

crystallographers equivalent of i

I. UNIT CELLS/LATTICE TYPES

(a) 7 DISTINCT CRYSTAL SYSTEMS

(b) 7 CRYSTAL SYSTEMS + CENTERING =

14 DISTINCT BRAVAIS *LATTICES*

II. POINT GROUPS

32 CRYSTALLOGRAPHIC *POINT GROUPS*

DESCRIBE THE SYMMETRY OF a

STATIONARY UNIT CELL (same as a molecule)

FOR THIS WE NEED ONLY:

ROTATIONS, REFLECTIONS AND INVERSIONS

III. SPACE GROUPS

14 DISTINCT BRAVAIS *LATTICES* +

32 CRYSTALLOGRAPHIC *POINT GROUPS* =

230 CRYSTALLOGRAPHIC *SPACE GROUPS*

DESCRIBE HOW MOLECULES ARE

ARRANGED IN SPACE

FOR THIS WE NEED:

TRANSLATIONAL SYMMETRY ELEMENTS

(GLIDE PLANES, SCREW AXES)

+

ROTATIONS, REFLECTIONS AND INVERSIONS

WHAT ARE THE 32 CRYSTALLOGRAPHIC POINT GROUPS?

Same as the 32 molecular point groups. These are the total number of unique point groups that one can have by various combinations of rotations (restricted to C_1, C_2, C_3, C_4, and C_6), mirrors and an inversion center.

<u>32 CRYSTALLOGRAPHIC *POINT GROUPS*</u>
(Hermann-Maugin notation)
1, 1, **m**, **2/m**, **mm**, **222**, **mmm**, **4**, 4, **4/m**, **4mm**, 4**2m**, **422**, **4/mmm**, **3**, 3, **3m**, **32**, 3**m**, **6**, 6, **6/m**, **6m2**, **6mm**, **622**, **6/mmm**, **23**, **m3**, 4**3m**, **432**, **m3m**

<u>CORRESPONDING Molecular Point Groups</u>
(Schönflies notation)
C_1, C_i, C_s, C_2, C_{2h}, C_{2v}, D_2, D_{2h}, C_4, S_4, C_{4h}, C_{4v}, D_{2d}, D_4, D_{4h}, C_3, S_6, C_{3v}, D_3, D_{3d}, C_{3h}, C_6, S_3, C_{6h}, D_{3h}, C_{6v}, D_6, D_{6h}, T, T_h, T_d, O, O_h