Symmetry Operations and Space Groups

Crystal Symmetry

32 point groups of **crystals** compatible with **7 crystal systems**

crystallographers use **Hermann-Mauguin** symmetry symbols

Carl Hermann
German
1898 - 1961

Charles-Victor Mauguin
French
1878 - 1958

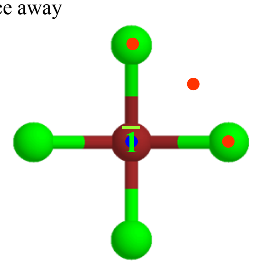
Symmetry Elements

there are **5 types** in point symmetry

1. **center of symmetry** (or inversion): point $\bar{1}$
2. **rotation** (or proper) **axis** : line **n**
3. **mirror** : plane ***m***
4. **rotation–inversion axis** : line $\bar{n}$
5. **identity** : no element **1**

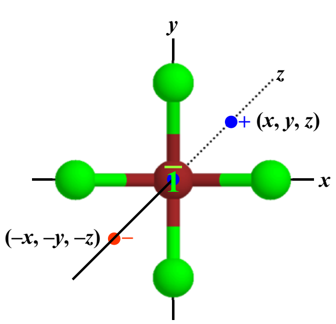
Center of Symmetry: $\bar{1}$

a **point** in the molecule through which if another **point** on the molecule is taken, will meet an identical **point** on the molecule an equal distance away



Center of Symmetry: $\bar{1}$

all points (x, y, z) → ($-x$, $-y$, $-z$) if $\bar{1}$ is placed at the origin



Rotation Axis: n

n is an integer which gives the degrees of rotation: $\frac{2\pi}{n}$ or $\frac{360^o}{n}$

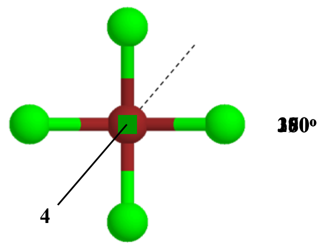
n is the number of times molecule is rotated, each time stopping at an identical **appearance**, before returning to the starting point

n is the **foldness** of the rotation axis

only **2**, **3**, **4**, and **6-fold** axes allowed in **crystal symmetry**

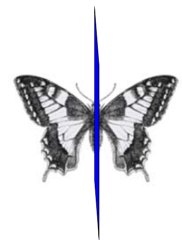
Rotation Axis: 4

$$\frac{360^{o}}{4} = 90^{o}$$



Mirror: *m*

plane **within** the molecule that, when acting as a mirror, reflects the molecule into itself



Rotation-Inversion $\bar{n}$

rotation followed by **inversion**

this is a different definition than **Schoenflies** system

Arthur Moritz Schönflies – German 1891

rotation followed by **reflection**

Representation of Symmetry

point symmetry often represented symbolically in the form of points on a circle (projection of a sphere)

a point above plane is a **filled** circle: ●

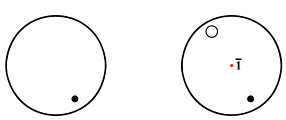
a point below plane is an **open** circle: ○

two points directly on top of each other: ◉

starting with one point, find other points **generated** by symmetry

32 point groups compatible with **7 crystal systems**

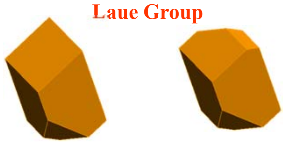
Triclinic



1 (C_1) $\bar{1}$ (C_i)

highest symmetry in **each** crystal system is called:

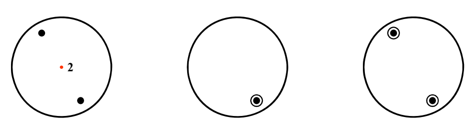
Laue Group



(**Schoenflies** symbol)

have center of symmetry

Monoclinic



2 (C_2) ***m*** (C_s) **2/*m*** (C_{2h})

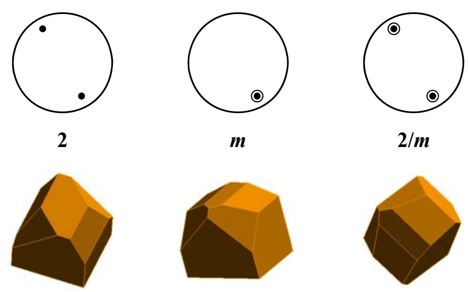
monoclinic convention: symmetry located wrt **b** axis

2: **2-fold** axis **along b**

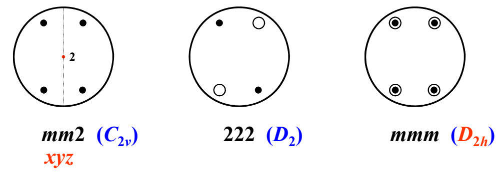
m: **mirror perpendicular** to **b**

2/*m*: **2-fold** axis along **b**, perpendicular to a mirror

Monoclinic

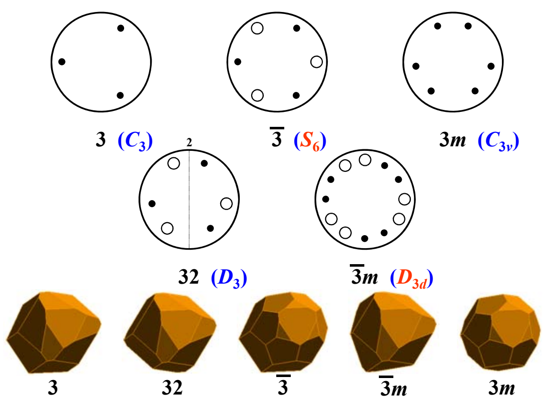


Orthorhombic

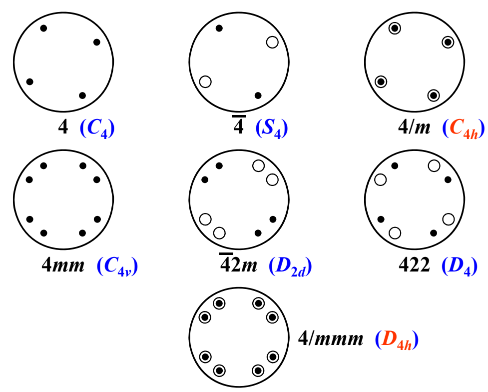


3 symbols refer to: **axes along a, b, or c**
mirrors perpendicular to **a**, **b**, or **c**

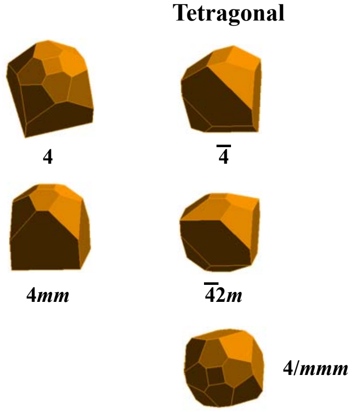
Rhombohedral (Trigonal)



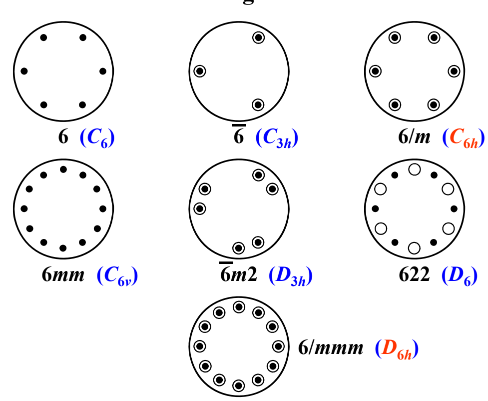
Tetragonal



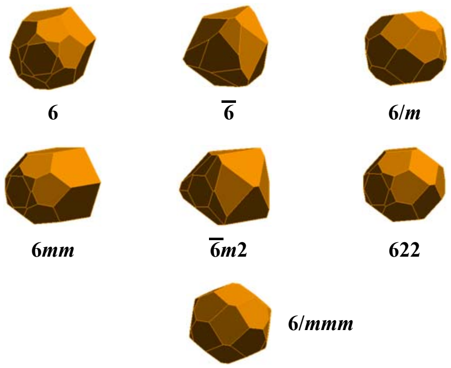
Tetragonal



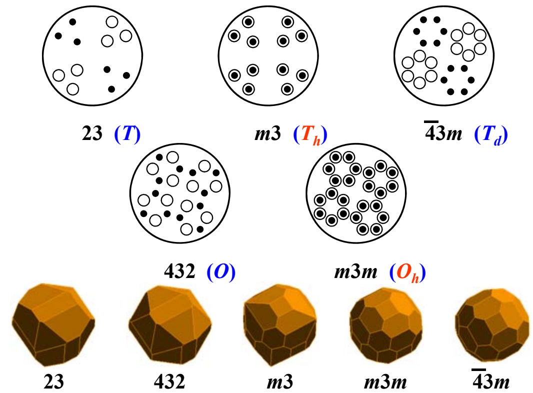
Hexagonal



Hexagonal



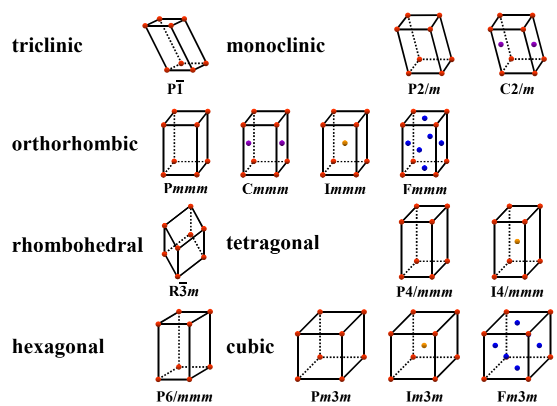
Cubic



Lattices

14 Bravais lattices have **Laue** symmetry

14 Bravais Lattices



Lattices

14 Bravais lattices have **Laue** symmetry

all have a **center of symmetry**

center of symmetry very important in crystallography:

centrosymmetric or **noncentrosymmetric**

Translational Symmetry

in **repeating** lattices, two **additional** symmetry elements

translational elements

1. **screw axis** rotation **and** translation: $\mathbf{n_r}$

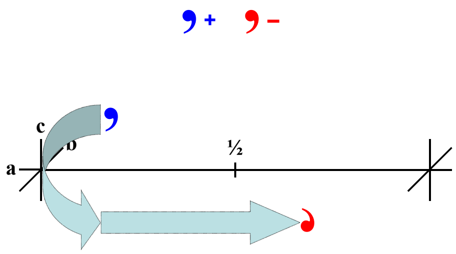
   rotation by **360º/n**;
   followed by translation of **r/n** along **that axis** (**a**, **b** or **c**)

   2-fold screw axis most common: $\mathbf{2_1}$

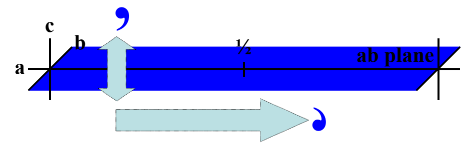
2. **glide plane** reflection **and** translation: ***a***, ***b***, ***c***, ***n*** or ***d***

   reflection across plane;
   followed by translation of **1/2** (usually) unit cell parallel to plane along **a**, **b**, **c**, **face diagonal** (***n***), or **body diagonal** (***d***)

Screw Axis - 2_1



Glide Plane - *a*



a-glide ⊥ c

http://www.cut-the-knot.org/Curriculum/Geometry/GlideReflection.shtml

Space Groups

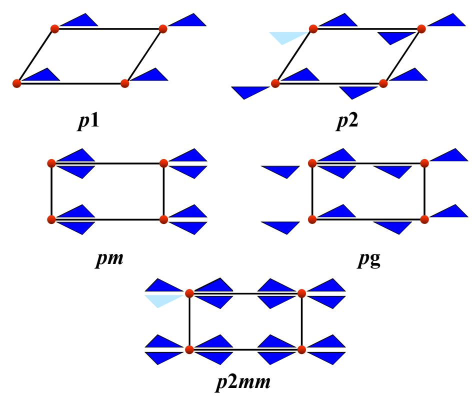
translational elements + point symmetry ⇒ **space groups**

in 2-D, referred to as **plane groups**

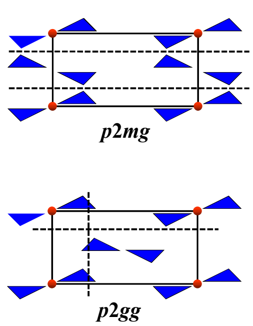
there are 17 **distinct** ways of packing repeating object in **2-D**

wallpaper patterns

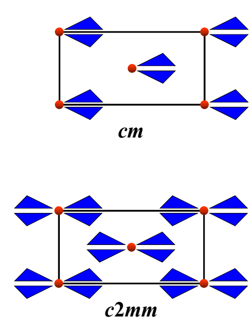
Plane Groups



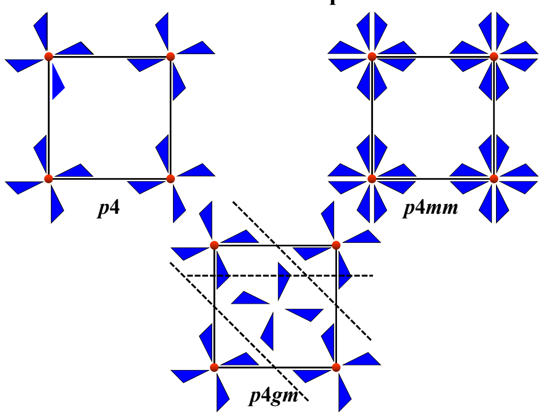
Plane Groups



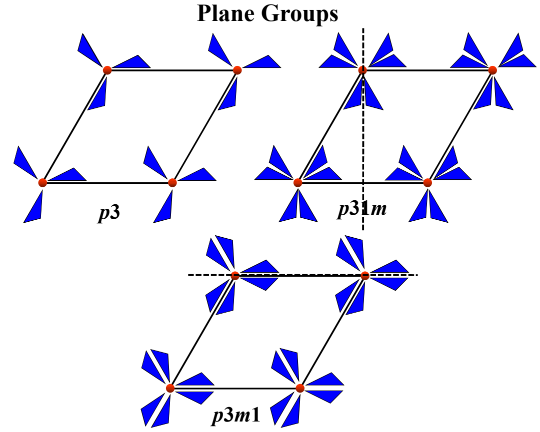
Plane Groups



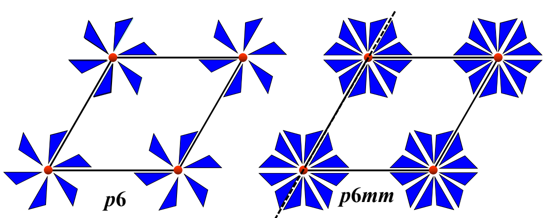
Plane Groups



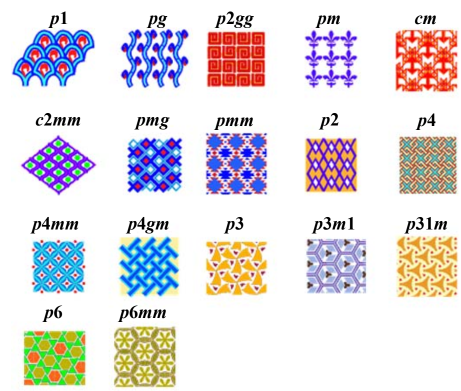
Plane Groups



Plane Groups



Plane Groups



Space Groups

translational elements + 32 crystal point groups;

230 **space groups**

230 **distinct** ways of packing repeating object in **3-D**

Space Groups

triclinic								
1	P1							
$\bar{1}$	$P\bar{1}$	Centrosymmetric space groups						
monoclinic								
2	P2	$P2_1$	C2					
m	P*m*	P*c*	C*m*	C*c*				
2/*m*	P2/*m*	$P2_1/m$	C2/*m*	P2/*c*	$P2_1/c$	C2/*c*		
orthorhombic								
222	P222	$P222_1$	$P2_12_12$	$P2_12_12_1$	$C222_1$	C222	F222	I222
	$I2_12_12_1$							
*mm*2	P*mm*2	$Pmc2_1$	P*cc*2	P*ma*2	$Pca2_1$	P*nc*2	$Pmn2_1$	P*ba*2
	$Pna2_1$	P*nn*2	C*cc*2	A*mm*2	A*bm*2	A*ma*2	A*ba*2	F*mm*2
	C*mm*2	$Cmc2_1$	F*dd*2	I*mm*2	I*ba*2	I*ma*2		
mmm	P*mmm*	P*nnn*	P*ccm*	P*ban*	P*mma*	P*nna*	P*mna*	P*cca*
	P*bam*	P*ccn*	P*bcm*	P*nnm*	P*mmn*	P*bcn*	P*bca*	P*nma*
	C*mcm*	C*mca*	C*mmm*	C*ccm*	C*mma*	C*cca*	F*mmm*	F*ddd*
	I*mmm*	I*bam*	I*bca*	I*mma*				

Space Groups

tetragonal

4	P4	$P4_1$	$P4_2$	$P4_3$	I4	$I4_1$
$\bar{4}$	$P\bar{4}$	$I\bar{4}$				
4/*m*	P4/*m*	$P4_2/m$	P4/*n*	$P4_2/n$	I4/*m*	$I4_1/a$
422	P422	$P42_12$	$P4_122$	$P4_12_12$	$P4_222$	$P4_22_12$
	$P4_322$	$P4_32_12$	I422	$I4_122$		
4*mm*	P4*mm*	P4*bm*	$P4_2cm$	$P4_2nm$	P4*cc*	P4*nc*
	$P4_2mc$	$P4_2bc$	I4*mm*	I4*cm*	$I4_1md$	$I4_1cd$
$\bar{4}2m$	$P\bar{4}2m$	$P\bar{4}2c$	$P\bar{4}2_1m$	$P\bar{4}2_1c$	$P\bar{4}m2$	$P\bar{4}c2$
	$P\bar{4}b2$	$P\bar{4}n2$	$I\bar{4}m2$	$I\bar{4}c2$	$I\bar{4}2m$	$I\bar{4}2d$
4/*mmm*	P4/*mmm*	P4/*mcc*	P4/*nbm*	P4/*nnc*	P4/*mbm*	P4/*mnc*
	P4/*nmm*	P4/*nnc*	$P4_2/mmc$	$P4_2/mcm$	$P4_2/nbc$	$P4_2/nnm$
	$P4_2/mbc$	$P4_2/mnm$	$P4_2/nmc$	$P4_2/ncm$	I4/*mmm*	I4/*mcm*
	$I4_1/amd$	$I4_1/acd$				

Space Groups

trigonal/rhombohedral

3	P3	$P3_1$	$P3_2$	R3			
$\bar{3}$	$P\bar{3}$	$R\bar{3}$					
32	P312	P321	$P3_112$	$P3_121$	$P3_212$	$P3_221$	R32
3*m*	P3*m*1	P31*m*	P3*c*1	P31*c*	R3*m*	R3*c*	
$\bar{3}m$	$P\bar{3}1m$	$P\bar{3}1c$	$P\bar{3}m1$	$P\bar{3}c1$	$R\bar{3}m$	$R\bar{3}c$	

hexagonal

6	P6	$P6_1$	$P6_5$	$P6_2$	$P6_4$	$P6_3$	
$\bar{6}$	$P\bar{6}$						
6/*m*	P6/*m*	$P6_3/m$					
622	P622	$P6_122$	$P6_522$	$P6_222$	$P6_422$	$P6_322$	
6*mm*	P6*mm*	P6*cc*	$P6_3cm$	$P6_3mc$	6*m*2	P6*m*2	P6*c*2
	P62*m*	P62*c*					
$\bar{6}m2$	$P\bar{6}m2$	$P\bar{6}c2$	$P\bar{6}2m$	$P\bar{6}2c$			
6/*mmm*	P6/*mmm*	P6/*mcc*	$P6_3/mcm$	$P6_3/mmc$			

Space Groups

cubic

23	P23	F23	I23	$P2_13$	$I2_13$	
*m*3	P*m*3	P*n*3	F*m*3	F*d*3	I*m*3	P*a*3
432	P432	$P4_232$	F432	$F4_132$	I432	$P4_332$
	$P4_132$	$I4_132$				
$\bar{4}3m$	$P\bar{4}3m$	$F\bar{4}3m$	$I\bar{4}3m$	$P\bar{4}3n$	$F\bar{4}3c$	$I\bar{4}3d$
*m*3*m*	P*m*3*m*	P*n*3*n*	P*m*3*n*	P*n*3*m*	F*m*3*m*	F*m*3*c*
	F*d*3*m*	F*d*3*c*	I*m*3*m*	I*a*3*d*		

Symmetry

7 crystal systems: point symmetry of external **lattice**

14 Bravais lattices: translational symmetry of **lattice points**

32 point groups: point symmetry of external **crystal**

230 space groups: translational symmetry inside **crystal**

molecules

Space Groups

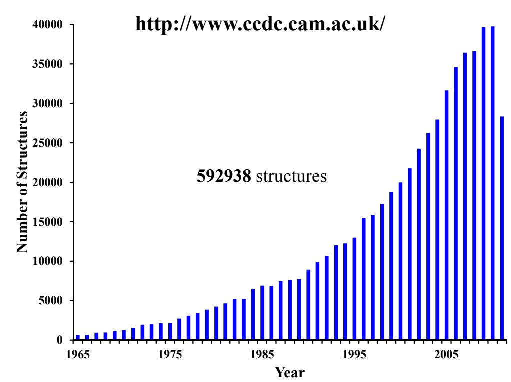
all compounds crystallize in one or more of these space groups usually possible to find **P1**, but **always** try to find the **highest possible symmetry**.

structures observed in all 230 space groups

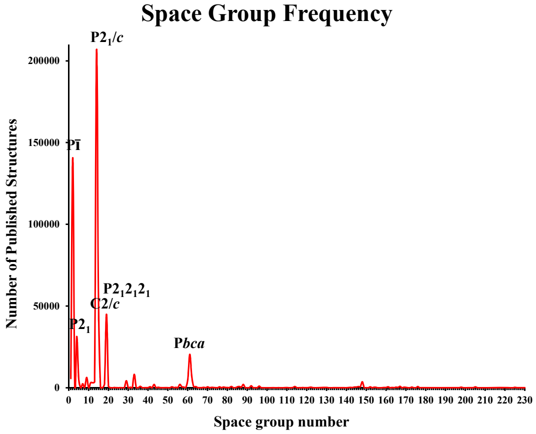
~95% of all structures: **monoclinic**, **triclinic**, **orthorhombic**

~83% of all structures: **$P2_1/c$**, **$P\bar{1}$**, **$P2_12_12_1$**, **C2/*c***, **$P2_1$**, **P*bca***

Cambridge Structural Database (CSD)



Space Group Frequency



Space Group Nomenclature

space group name comes from Bravais lattice symbol, modified for translational symmetry

easy to understand the components of **many** names, especially **monoclinic** and **orthorhombic**:

P2$_1$/*c* (P 2-1 on c)
- **primitive** unit cell (1 lattice point)
- **2-fold screw axis** along **b** (**unique axis**)
- ***c* glide** (translation along **c** axis) in **ac** plane (⊥ to **b**)

P*bca*
- **primitive** unit cell (1 lattice point)
- ***b* glide** (translation along **b** axis) in **bc** plane (⊥ to **a**)
- ***c* glide** (translation along **c** axis) in **ac** plane (⊥ to **b**)
- ***a* glide** (translation along **a** axis) in **ab** plane (⊥ to **c**)

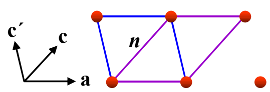
Standard and Non-standard Settings

sometimes a space group that is not on the list of 230 is given in a publication

some space groups can be derived which are identical with another space group ⇒ choice depends on convention

P2$_1$/*a* identical with **P2$_1$/*c*** switching **a** and **c** label in monoclinic does not change the symmetry

P2$_1$/*n* alternate setting of **P2$_1$/*c***
β closer to 90° preferred



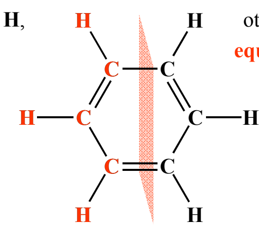
P*nam* same as **P*nma*** switch **b** and **c** label

Equivalent Positions

space groups used to locate **symmetry** related atoms in unit cell

for example, if a benzene ring is located on a **mirror**:

locate 3 **C** and 3 **H**, others at symmetry **equivalent positions**



asymmetric unit is the smallest part that generates the rest of the unit cell contents by **all** symmetry operations of space group

Equivalent Positions, Asymmetric Unit and Z

equivalent positions are divided into:

general positions

special positions

asymmetric unit along with general and special positions allows an interpretation of **Z** (**number** of molecules **in** unit cell), and possible **molecular** symmetry

Equivalent Positions of Symmetry Elements

axis	‖ to	position	plane	⊥ to	position
2	a	$x, \bar{y}, \bar{z}$	*a*	c	$x + ½, y, \bar{z}$
2	b	$\bar{x}, y, \bar{z}$	*b*	a	$\bar{x}, y + ½, z$
2	c	$\bar{x}, \bar{y}, z$	*b*	c	$x, y + ½, \bar{z}$
2_1	a	$x + ½, \bar{y}, \bar{z}$	*c*	a	$\bar{x}, y, z + ½$
2_1	b	$\bar{x}, y + ½, \bar{z}$	*c*	b	$x, \bar{y}, z + ½$
2_1	c	$\bar{x}, \bar{y}, z + ½$	*n*	a	$\bar{x}, y + ½, z + ½$
plane	⊥ to		*n*	b	$x + ½, \bar{y}, z + ½$
m	a	$\bar{x}, y, z$	*n*	c	$x + ½, y + ½, \bar{z}$
m	b	$x, \bar{y}, z$	*d*	a	$\bar{x}, y + ¼ , z + ¼$
m	c	$x, y, \bar{z}$	*d*	b	$x + ¼, \bar{y}, z + ¼$
a	b	$x + ½, \bar{y}, z$	*d*	c	$x + ¼, y + ¼, \bar{z}$

Equivalent Positions from Centering

for **centered** groups, add the following to **each P** general position:

A	$x, y + \frac{1}{2}, z + \frac{1}{2}$
C	$x + \frac{1}{2}, y + \frac{1}{2}, z$
F	$x + \frac{1}{2}, y + \frac{1}{2}, z$
	$x + \frac{1}{2}, y, z + \frac{1}{2}$
	$x, y + \frac{1}{2}, z + \frac{1}{2}$
I	$x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$
R	$x + 2/3, y + 1/3, z + 1/3$
	$x + 1/3, y + 2/3, z + 2/3$

Transforming Coordinates

$\bar{x} - \frac{1}{4} = -(x + \frac{1}{4}) = -(x - \frac{1}{4} + \frac{1}{2}) = -(x + \frac{1}{2}) = \bar{x} - \frac{1}{2} = \bar{x} + \frac{1}{2}$ (by adding **1**)

$y + \frac{1}{4} = y - \frac{1}{4} + \frac{1}{2} = y + \frac{1}{2}$

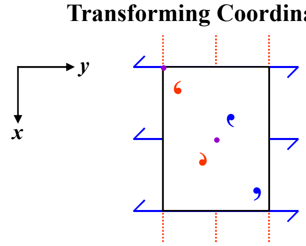
Transforming Coordinates

$\bar{x} - \frac{1}{4} = -(x + \frac{1}{4}) = -(x - \frac{1}{4} + \frac{1}{2}) = -(x + \frac{1}{2}) = \bar{x} - \frac{1}{2} = \bar{x} + \frac{1}{2}$ (by adding **1**)

$y + \frac{1}{4} = y - \frac{1}{4} + \frac{1}{2} = y + \frac{1}{2}$

$\bar{x} + \frac{1}{4} = (\bar{x} - \frac{1}{4}) + \frac{1}{2} = \bar{x} + \frac{1}{2} + \frac{1}{2} = \bar{x}$ (by subtracting **1**)

Transforming Coordinates



P2$_1$/*a*

rename: $x - \frac{1}{4}$ as x $y - \frac{1}{4}$ as y z as z

1. $x - \frac{1}{4}, y - \frac{1}{4}, z$ ➡ x, y, z
2. $\bar{x} - \frac{1}{4}, y + \frac{1}{4}, \bar{z}$ ➡ $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, \bar{z}$
3. $\bar{x} + \frac{1}{4}, \bar{y} + \frac{1}{4}, \bar{z}$ ➡ $\bar{x}, \bar{y}, \bar{z}$
4. $x + \frac{1}{4}, \bar{y} - \frac{1}{4}, z$ ➡ $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, z$

Transforming Coordinates

related by a change in sign: x, y, z and $\bar{x}, \bar{y}, \bar{z}$

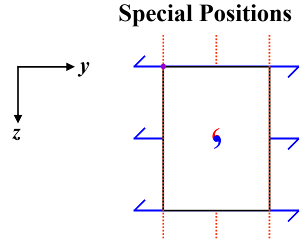
related by a change in sign: $\bar{x} + \frac{1}{2}, y + \frac{1}{2}, \bar{z}$ and $x + \frac{1}{2}, \bar{y} + \frac{1}{2}, z$

finally, change to preferred setting **P2$_1$/*c***; switch ***x*** and ***z***

x, y, z
$\bar{x}, \bar{y}, \bar{z}$
$\bar{x}, y + \frac{1}{2}, \bar{z} + \frac{1}{2}$
$x, \bar{y} + \frac{1}{2}, z + \frac{1}{2}$

general positions
P2$_1$/*c*

Special Positions



2 molecules/cell

if an object is located at x, y, z = **0, 0, 0**;
only unique point generated by symmetry is at **0, ½, ½**

also true for:

0, 0, ½ ➡ **0, ½, 0**
½, 0, ½ ➡ **½, ½, 0**
½, 0, 0 ➡ **½, ½, ½**

Special Positions

0, 0, 0	**0, ½, ½**
0, 0, ½	**0, ½, 0**
½, 0, ½	**½, ½, 0**
½, 0, 0	**½, ½, ½**

note: an object (molecule) at a special position **has** to have the same symmetry as the special position

in **P2$_1$/*c***, a **center of symmetry**

Z = 4 for an object on a **general position** in **P2$_1$/*c***

Z = 2 for an object on a **special position** in **P2$_1$/*c***

asymmetric unit is ½ of the molecule

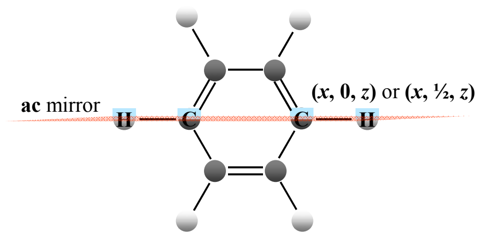
Special Positions

an atom **on** a special position **has** at least **one** fixed coordinate; part of the atom **generates** the rest:

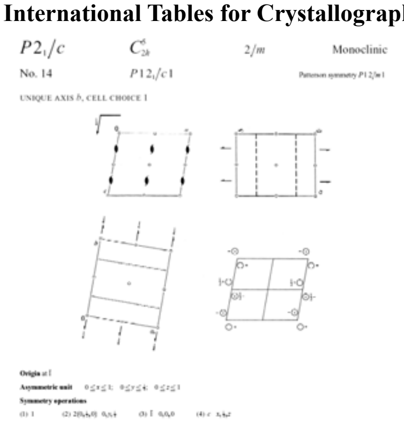
one fixed position (axis ⊥ to plane) for an atom on a **mirror**

two fixed positions (other axes) for an atom on a **rotation axis**

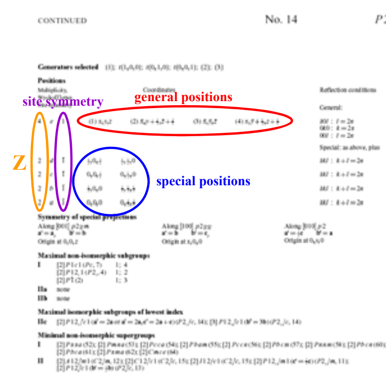
three fixed positions for an atom on an **inversion center**

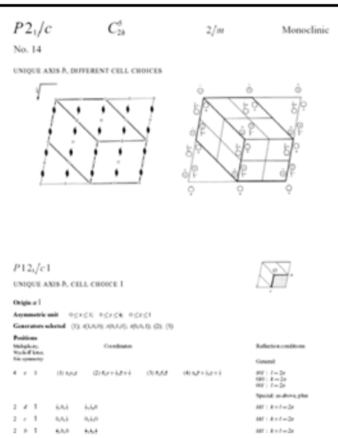


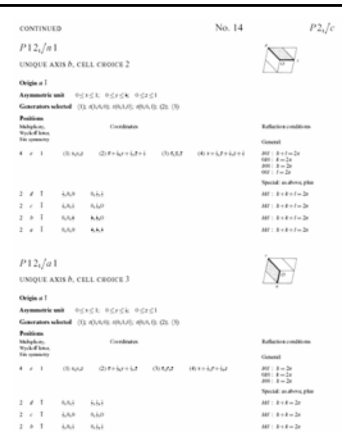
International Tables for Crystallography



International Tables for Crystallography





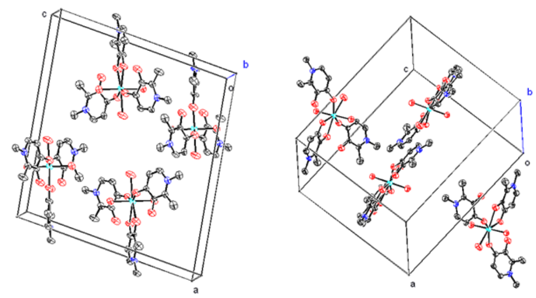


General Positions for Other Space Groups

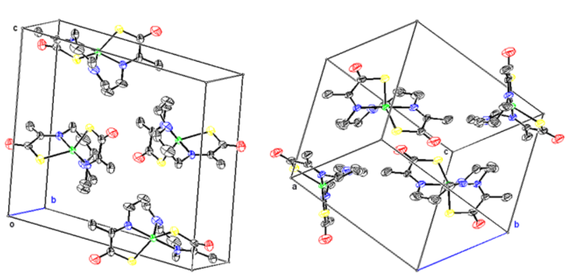
http://www.cryst.ehu.es/cryst/get_gen.html

http://it.iucr.org/A/

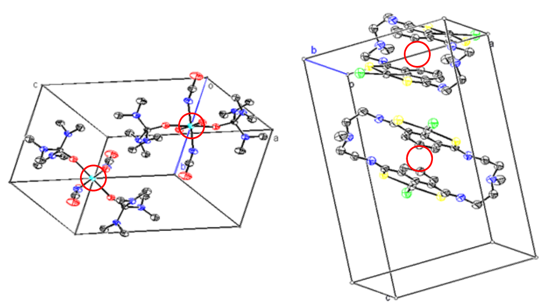
$P2_1/c$: Z = 4



$P2_1/c$: Z = 4



$P2_1/c$: Z = 2



atom on special position **no atom on special position**