Crystal Structures

Lecture 6

1- **Revision some points in the last lecture**

- Hexagonal closed packing (HCP)
- Symmetry
- Symmetry Operations
- Octahedral and tetrahedral voids or holes

2- Element of Symmetry

3- Point group & Space group

Symmetry

A state in which parts on opposite sides of a plane, line, or point display arrangements that are related to one another via a symmetry operation such as translation, rotation, reflection or inversion.

Application of the symmetry operators leaves the entire crystal unchanged.

Symmetry Operations

- Rotation about an axis
- Translational
- **Reflection at a plane**
- Inversion, or center of symmetry
- Mirror plane
- Screw (=rotation + translation)
- Glide (=reflection + translation)

2- Symmetry Elements

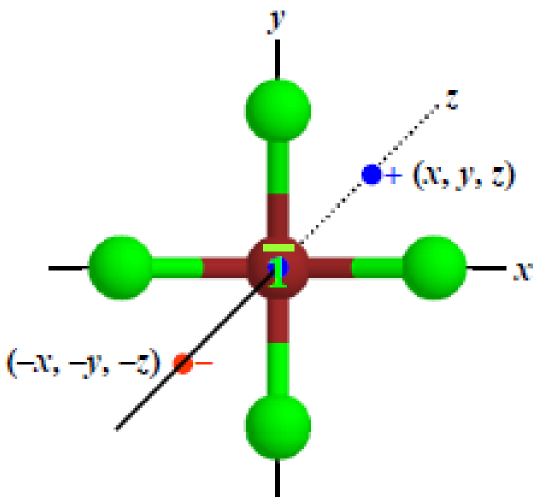
Symmetry Elements

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: $\bar{1}$

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



Rotation Axis: n

n is an integer which gives the degrees of rotation: $\dfrac{2\pi}{n}$ or $\dfrac{360°}{n}$

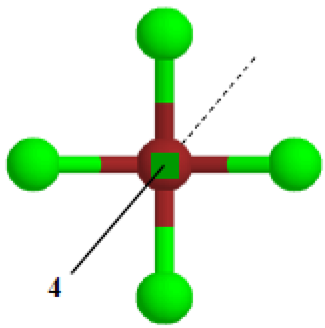
n is the number of times molecule is rotated, each time stopping at an identical appearance, before returning to the starting point

n is the foldness of the rotation axis

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

Rotation Axis: 4

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



Mirror: *m*

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

Translational Symmetry

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

translational elements

1. **screw axis** rotation **and** translation: n_r

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

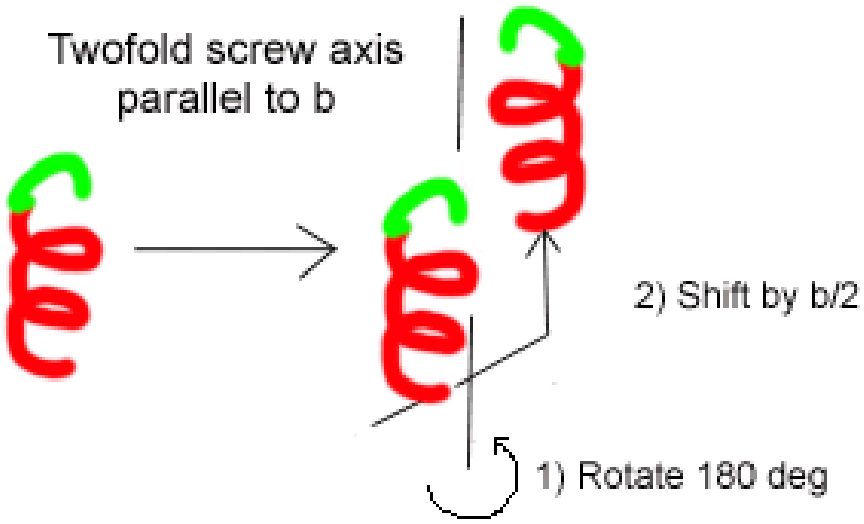
   2-fold screw **axis** most common: 2_1

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*)

Symmetry Elements

Screw axes (rotation + translation)



rotation about the axis of symmetry by 360°/n, followed by a translation parallel to the axis by r/n of the unit cell length in that direction. (r < n)

Symmetry Elements

Glide reflection (mirror plane + translation)

reflects the asymmetric unit across a mirror and then translates parallel to the mirror. A glide plane changes the handedness of figures in the asymmetric unit. There are no invariant points (points that map onto themselves) under a glide reflection.

A point group is described by a characteristic assembly of symmetry operations. A certain number of symmetry operations with defined geometrical relations among themselves can be found for any given object. The object is said to have symmetry described by the given point group.

3- Point group and Space group

The combination of the 32 crystallographic point groups and the 14 Bravais lattices (which are again combinations of different crystal systems and non-centred or centred lattices) give rise to 230 different space groups

Space Groups

translational elements + 32 crystal point groups;

230 **space groups**

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

32 point symmetries

- – 2 triclinic
- – 3 monoclinic
- – 3 orthorhombic
- – 7 tetragonal
- – 5 cubic
- – 5 trigonal
- – 7 hexagonal

plus the Bravais lattices yields 73 simple 3D Space Groups

+

plus compound operations (glide and screw operations) yields 157 more

= 230 space symmetry

Space Groups

cubic

23	P23	F23	I2
$m3$	P$m3$	P$n3$	Fm
432	P432	P$4_2$32	F4
	P$4_1$32	I$4_1$32	
$\bar{4}3m$	P$\bar{4}3m$	F$\bar{4}3m$	I$\bar{4}$
$m3m$	P$m3m$	P$n3n$	Pn
	F$d3m$	F$d3c$	Im

Space Groups

triclinic

1	P1	
$\bar{1}$	P$\bar{1}$	Centrosymmetric space groups

monoclinic

2	P2	P2_1	C2			
m	Pm	Pc	Cm	Cc		
$2/m$	P$2/m$	P$2_1/m$	C$2/m$	P$2/c$	P$2_1/c$	C$2/c$

orthorhombic

222	P222	P222_1	P2_12_12	P$2_12_12_1$	C222_1	C222	F222	I222
	I$2_12_12_1$							
$mm2$	P$mm2$	P$mc2_1$	P$cc2$	P$ma2$	P$ca2_1$	P$nc2$	P$mn2_1$	P$ba2$
	P$na2_1$	P$nn2$	C$cc2$	A$mm2$	A$bm2$	A$ma2$	A$ba2$	F$mm2$
	C$mm2$	C$mc2_1$	F$dd2$	I$mm2$	I$ba2$	I$ma2$		
mmm	Pmmm	Pnnn	Pccm	Pban	Pmma	Pnna	Pmna	Pcca
	Pbam	Pccn	Pbcm	Pnnm	Pmmn	Pbcn	Pbca	Pnma
	Cmcm	Cmca	Cmmm	Cccm	Cmma	Ccca	Fmmm	Fddd
	Immm	Ibam	Ibca	Imma				

Lattices

14 Bravais lattices have **Laue** symmetry

all have a **center of symmetry**

center of symmetry very important in crystallography:

centrosymmetric or **noncentrosymmetric**