Crystallography

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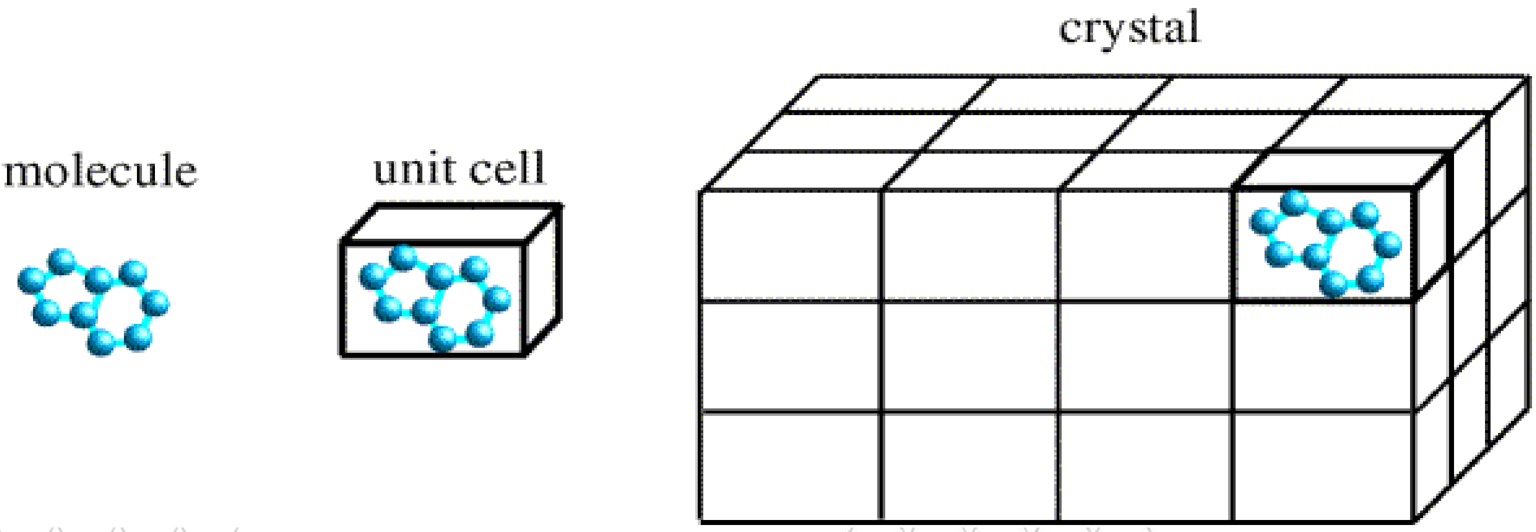
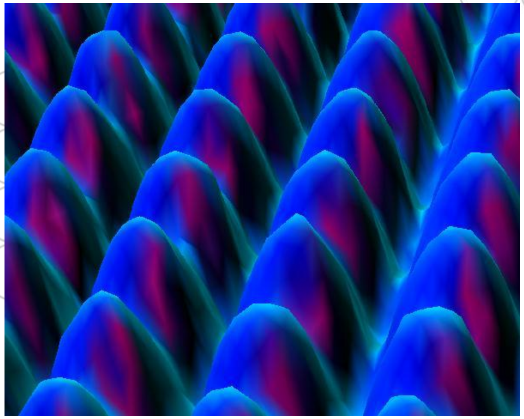
Crystal

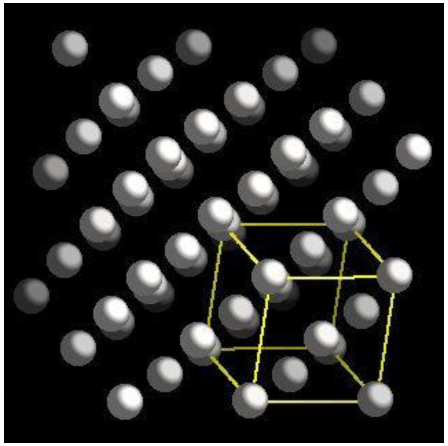
- Buerger (1956): “a region of matter within which the atoms are arranged in a three-dimensional translationally periodic pattern.”
- Periodic arrangement of molecules in three dimensions.
- A crystal structure is like a three-dimensional wallpaper design in that it is an endless repetition of some motif (i.e., a group of atoms or molecules).



Platinum

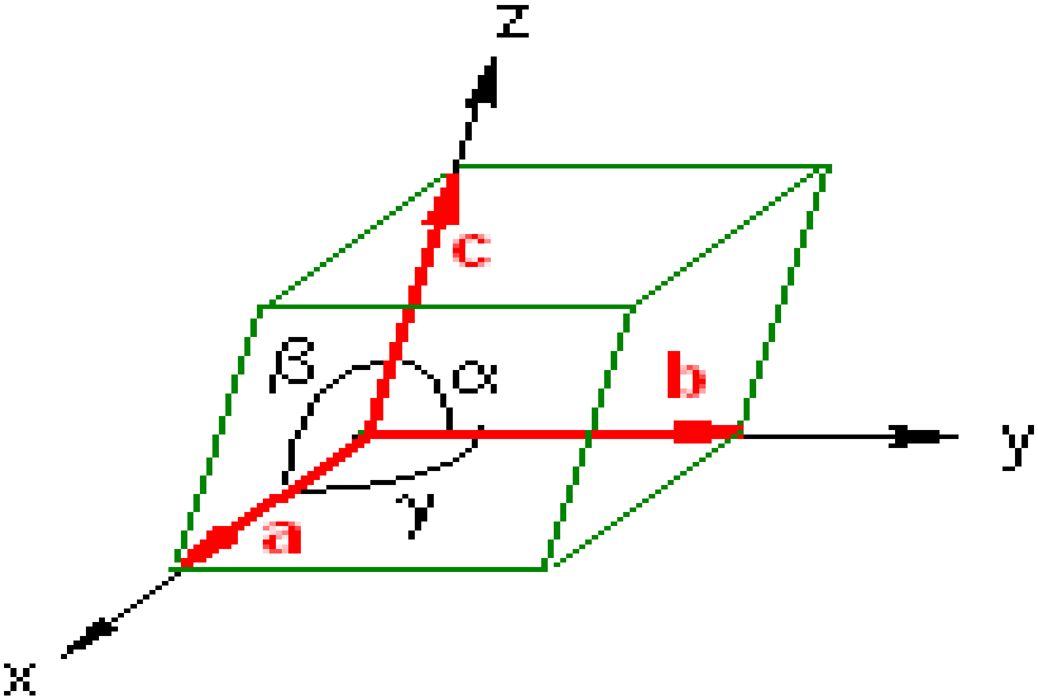


Platinum surface
(scanning tunneling microscope)



Crystal lattice and structure of Platinum

Unit cell



Unit cell is the smallest unit of a crystal, which, if repeated, could generate the whole crystal.

The length of the unit cell edges – a, b, c

Interaxial angles - α, β, γ

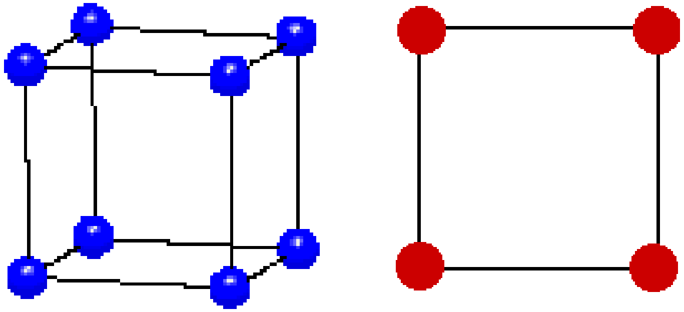
UNIT CELL

Primitive

- Single lattice point per cell
- Smallest area in 2D, or
- Smallest volume in 3D

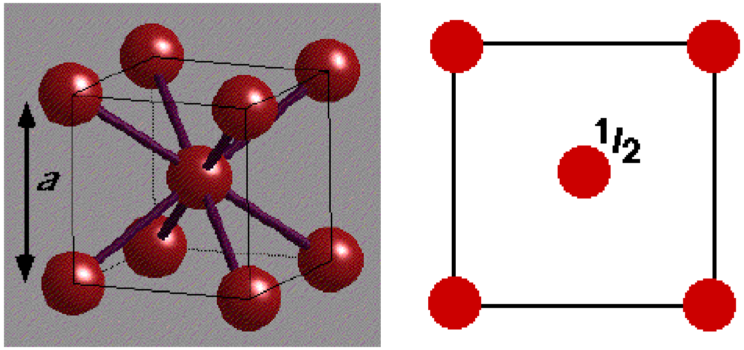
Conventional & Non-primitive

- More than one lattice point per cell
- Integral multibles of the area of primitive cell



Simple cubic(sc)

Conventional = Primitive cell

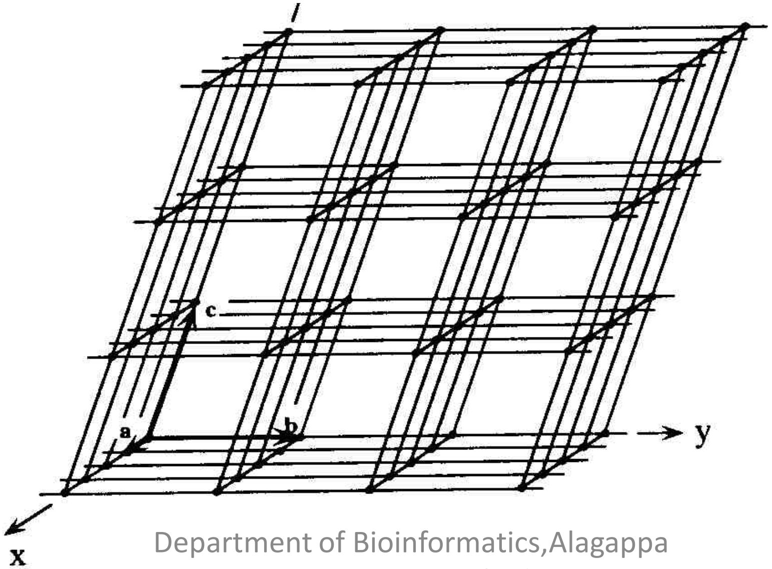


Body centered cubic(bcc)

Conventional ≠ Primitive cell

Lattice

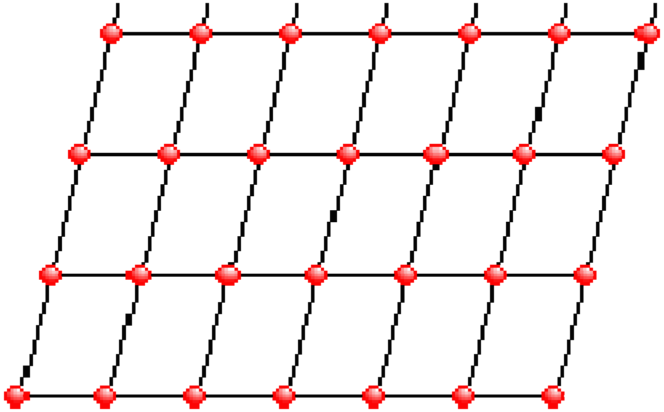
- Klein (2002) defines a lattice as “an imaginary pattern of points (or nodes) in which every point (node) has an environment that is identical to that of any other point (node) in the pattern.
- A lattice has no specific origin, as it can be shifted parallel to itself.”



Crystal Lattice

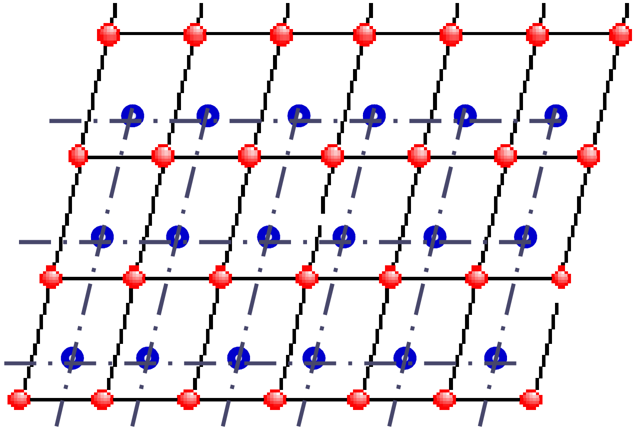
Bravais Lattice (BL)

- All atoms are of the same kind
- All lattice points are equivalent



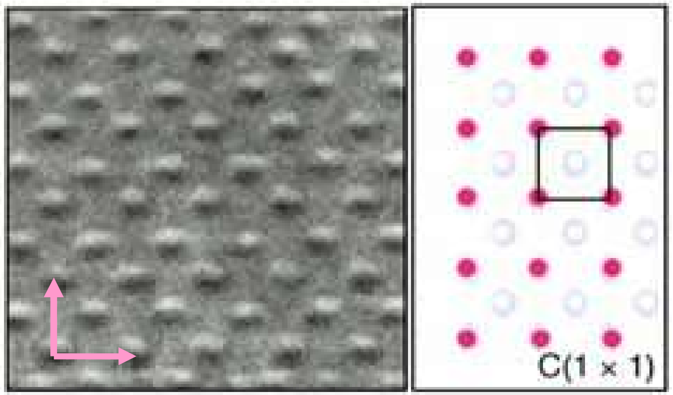
Non-Bravais Lattice (non-BL)

- Atoms can be of different kind
- Some lattice points are not equivalent
- A combination of two or more BL



Types Of Crystal Lattices

1) Bravais lattice is an infinite array of discrete points with an arrangement and orientation that appears exactly the same, from whichever of the points the array is viewed.



Types Of Crystal Lattices

2) Non-Bravais Lattice:
Not only the arrangement but also the orientation must appear exactly the same from every point in a bravais lattice.

Miller Indices

Miller Indices are a symbolic vector representation for the orientation of an atomic plane in a crystal lattice and are defined as the reciprocals of the fractional intercepts which the plane makes with the crystallographic axes.

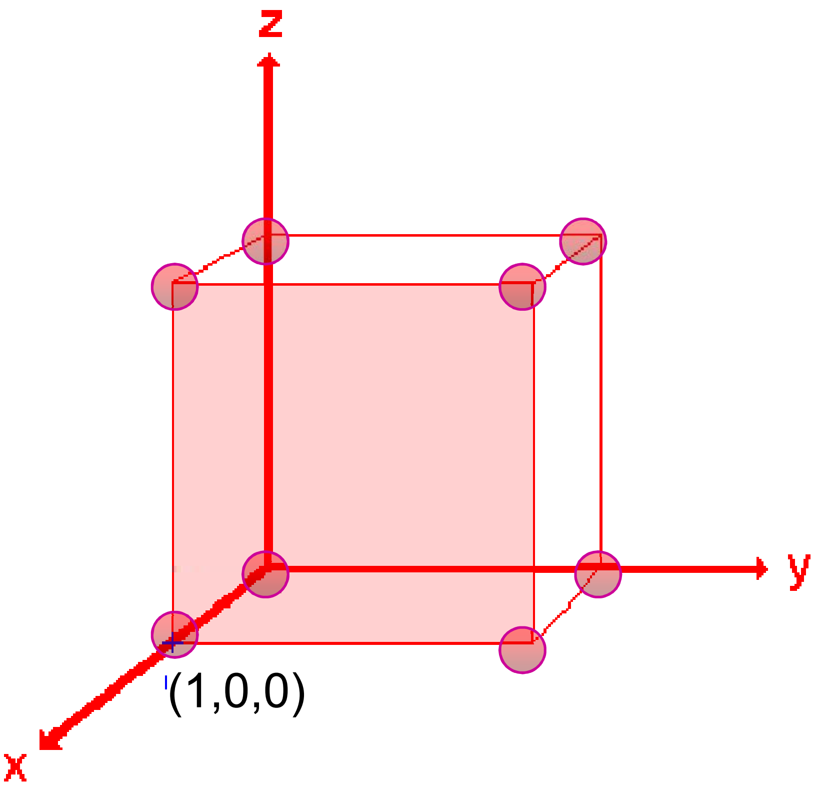
To determine Miller indices of a plane, take the following steps;

1) Determine the intercepts of the plane along each of the three crystallographic directions

2) Take the reciprocals of the intercepts

3) If fractions result, multiply each by the denominator of the smallest fraction

Example-1



Axis	X	Y	Z
Intercept points	1	∞	∞
Reciprocals	1/1	1/ ∞	1/ ∞
Smallest Ratio	1	0	0
Miller İndices (100)			

Where does a protein crystallographer see the Miller indices?

- **Common crystal faces are parallel to lattice planes**

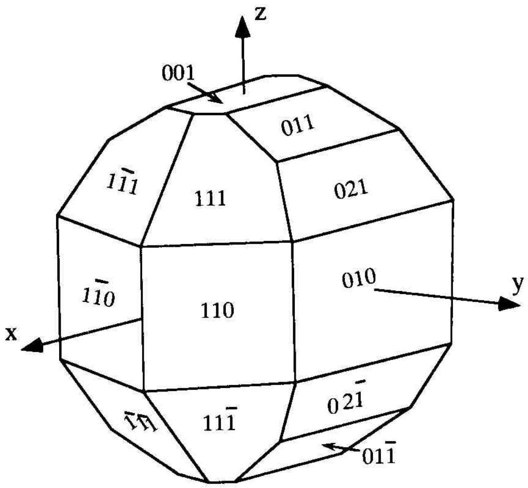
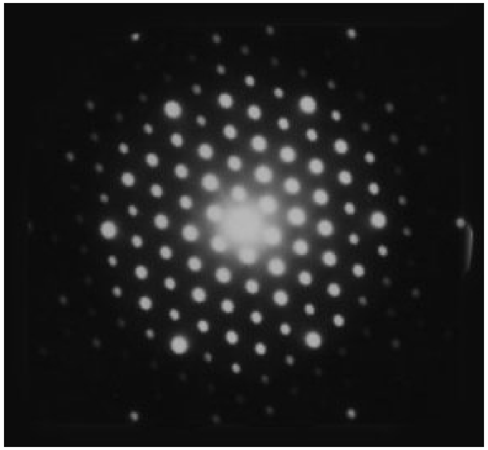


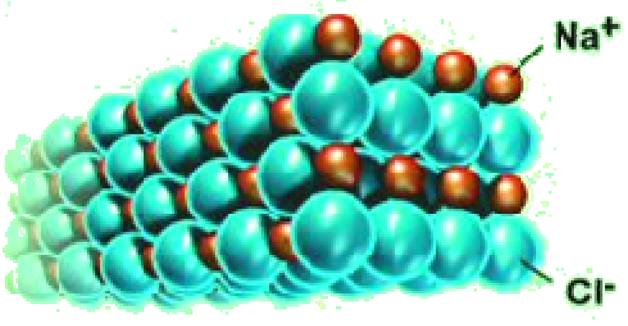
Figure 3.7. A crystal showing several faces.

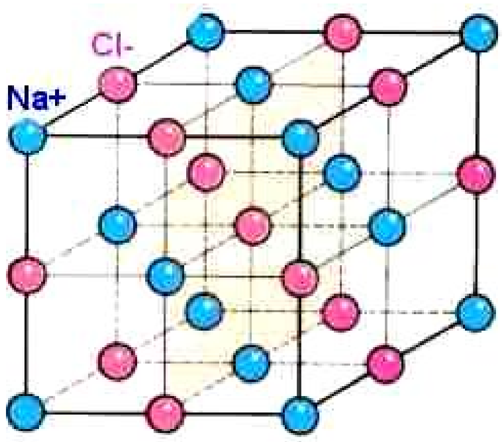
- **Each diffraction spot can be regarded as a X-ray beam reflected from a lattice plane, and therefore has a unique Miller index.**

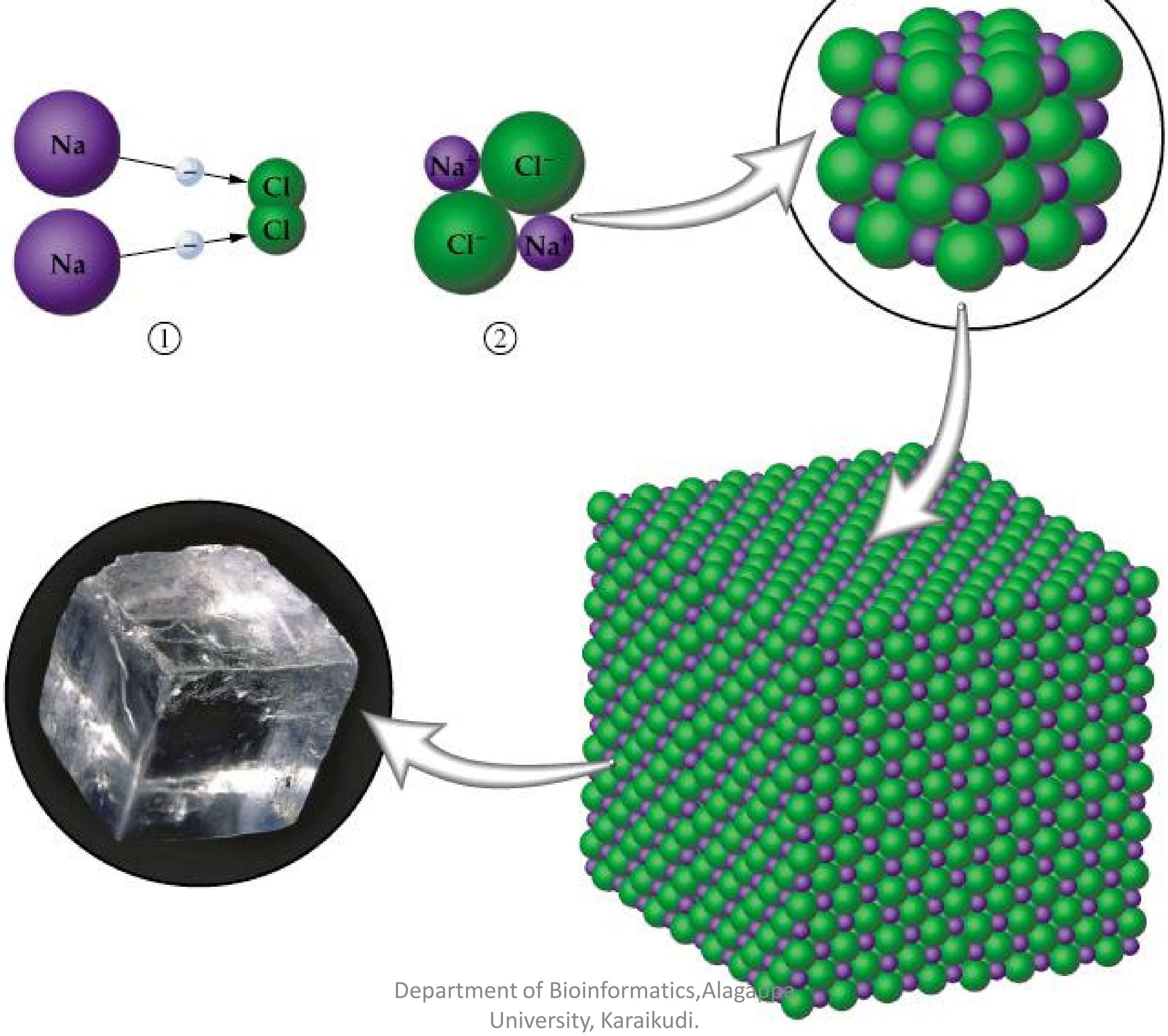


Sodium Chloride Structure

- Sodium chloride also crystallizes in a cubic lattice, but with a different unit cell.
- Sodium chloride structure consists of equal numbers of sodium and chlorine ions placed at alternate points of a simple cubic lattice.
- Each ion has six of the other kind of ions as its nearest neighbours.






Na
Cl
Cl
Na
①
Na^+
Cl^-
Cl^-
Na^+
②

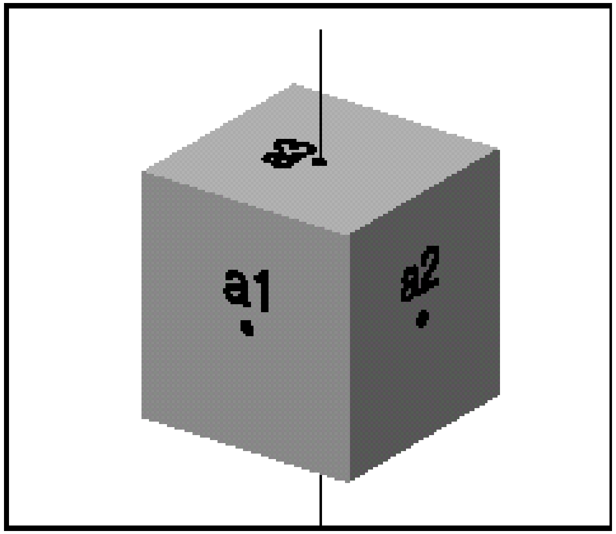
Crystal systems and symmetry

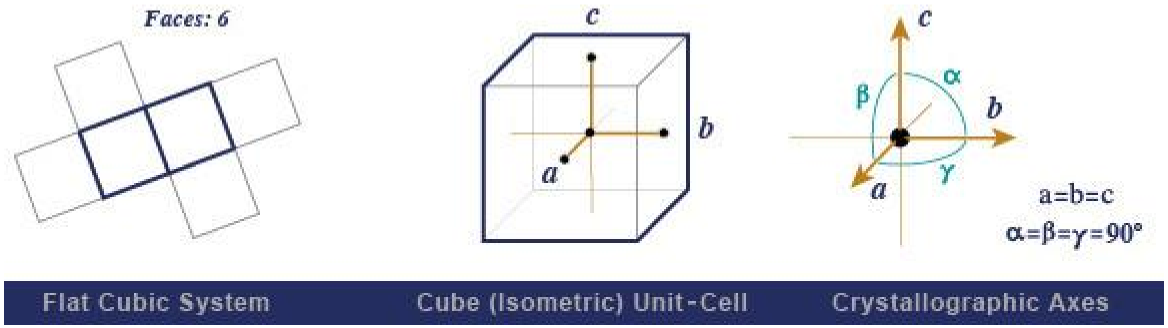
- There are 7 crystal systems, which include
  - ✓ Triclinic
  - ✓ Monoclinic
  - ✓ Orthorhombic
  - ✓ Tetragonal
  - ✓ Trigonal(rhombhohedral)
  - ✓ Hexagonal
  - ✓ Cubic

Cubic

- The three crystallographic axes a1, a2, a3 (or a, b, c) are all equal in length and intersect at right angles (90 degrees) to each other.

Cubic	P	$a_1 = a_2 = a_3$	
	I	$\alpha = \beta = \gamma = 90°$	m3m
	F		





Tetragonal

- Three axes, all at right angles, two of which are equal in length (a and b) and one (c) which is different in length (shorter or longer).
- Note: If c was equal in length to a or b, then we would be in the cubic system

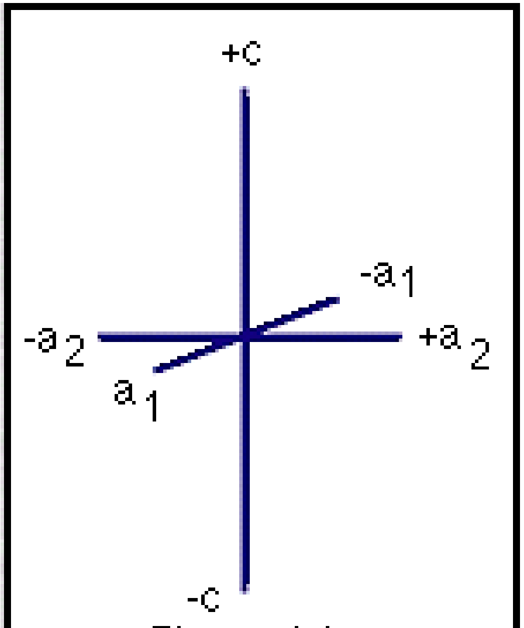
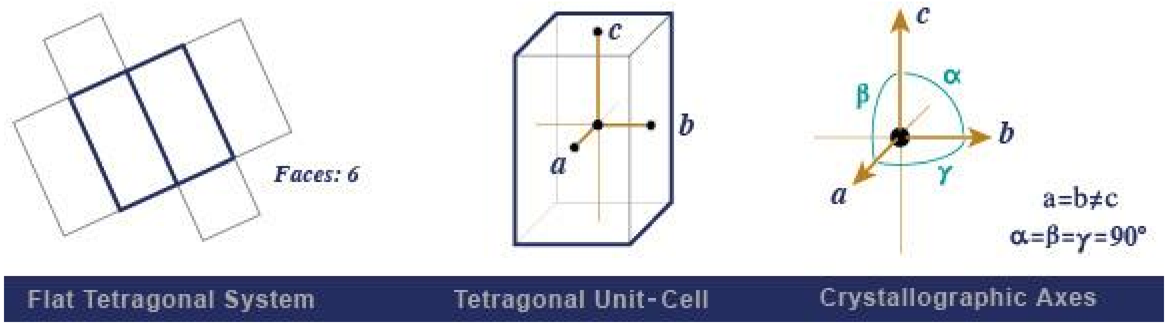


Figure 4.1a

Tetragonal	P I	$a_1 = a_2 \neq c$ $\alpha = \beta = \gamma = 90°$	4/mmm



Orthorhombhic

- Three axes, all at right angles, and all three of different lengths.
- Note: If any axis was of equal length to any other, then we would be in the tetragonal system

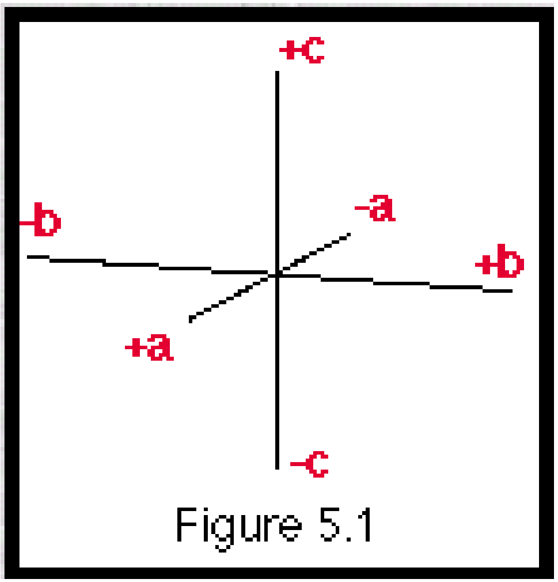
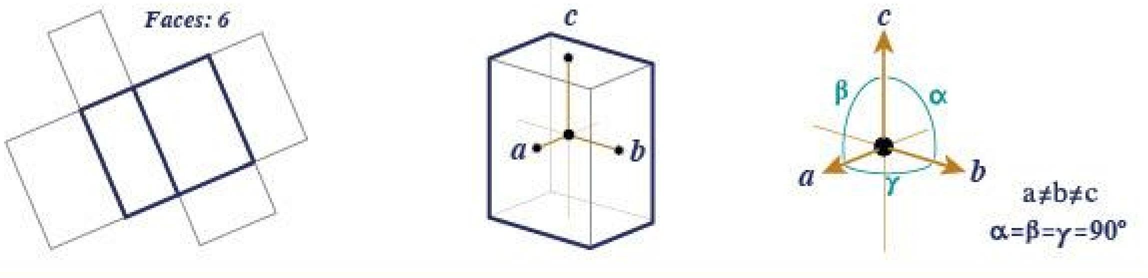


Figure 5.1

Orthorhombic	P C (or A, B) I F	a ≠ b ≠ c α = β = γ = 90°	mmm



Flat Monoclinic System   Orthorhombic Unit-Cell   Crystallographic Axes

Hexagonal

- Four axes! Three of the axes fall in the same plane and intersect at the axial cross at 120 degrees between the positive ends. These 3 axes, labeled a1, a2, and a3, are the same length. The fourth axis, termed c, may be longer or shorter than the a axes set. The c axis also passes through the intersection of the a axes set at right angle to the plane formed by the a set.

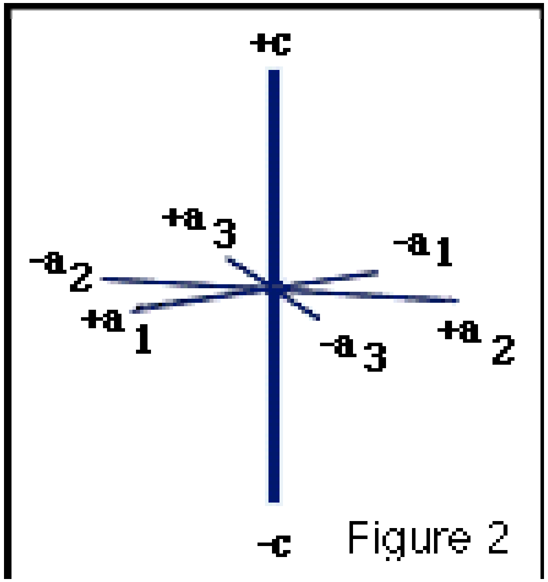


Figure 2

Hexagonal	R P	$a_1 = a_2 \neq c$ $\alpha = \beta = 90°, \gamma = 120°$	m 6/mmm

Monoclinic

- Three axes, all unequal in length, two of which (a and c) intersect at an oblique angle (not 90 degrees), the third axis (b) is perpendicular to the other two axes.
- Note: If a and c crossed at 90 degrees, then we would be in the orthorhombic system

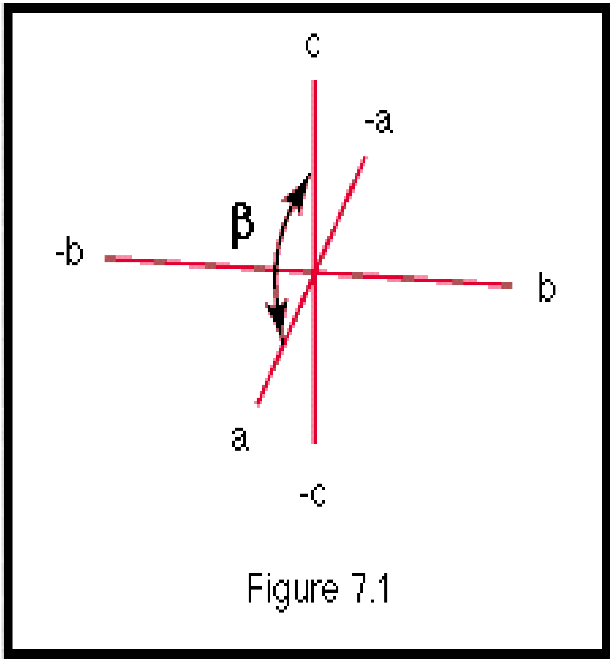
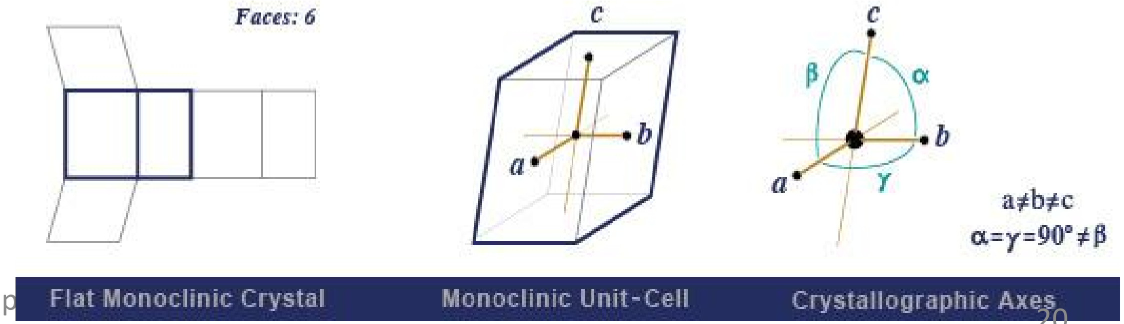


Figure 7.1

Monoclinic	P (b = twofold axis) C	a ≠ b ≠ c α = γ = 90° ≠ β	2/m



Triclinic

- The three axes are all unequal in length and intersect at three different angles (any angle but 90 degrees).
- Note: If any two axes crossed at 90 degrees, then we would be describing a monoclinic crystal

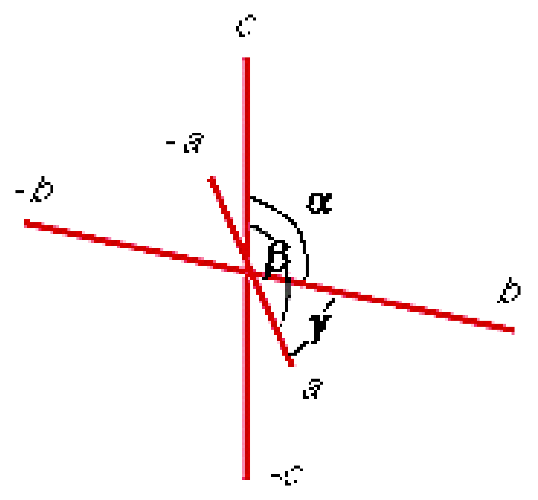
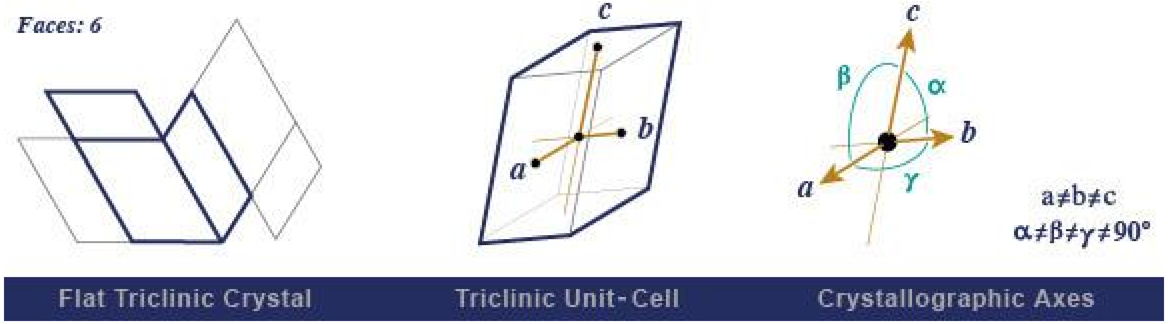


Figure 8.1

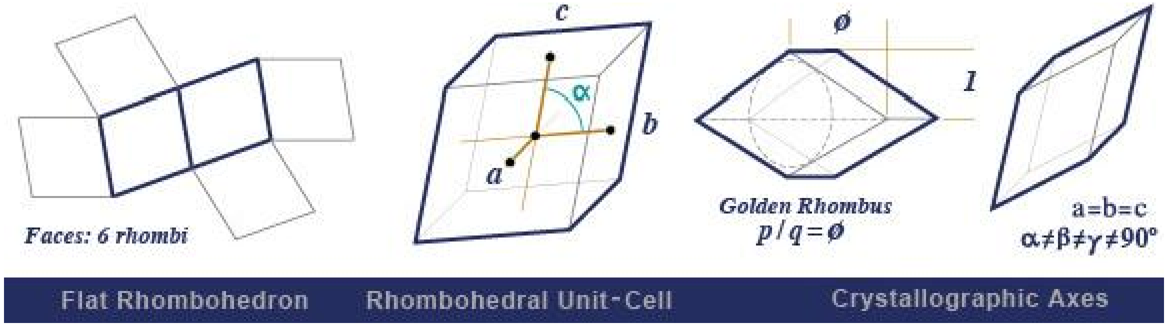
Triclinic	P	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	$\bar{1}$



Flat Triclinic Crystal — Triclinic Unit-Cell — Crystallographic Axes

Rhombohedral

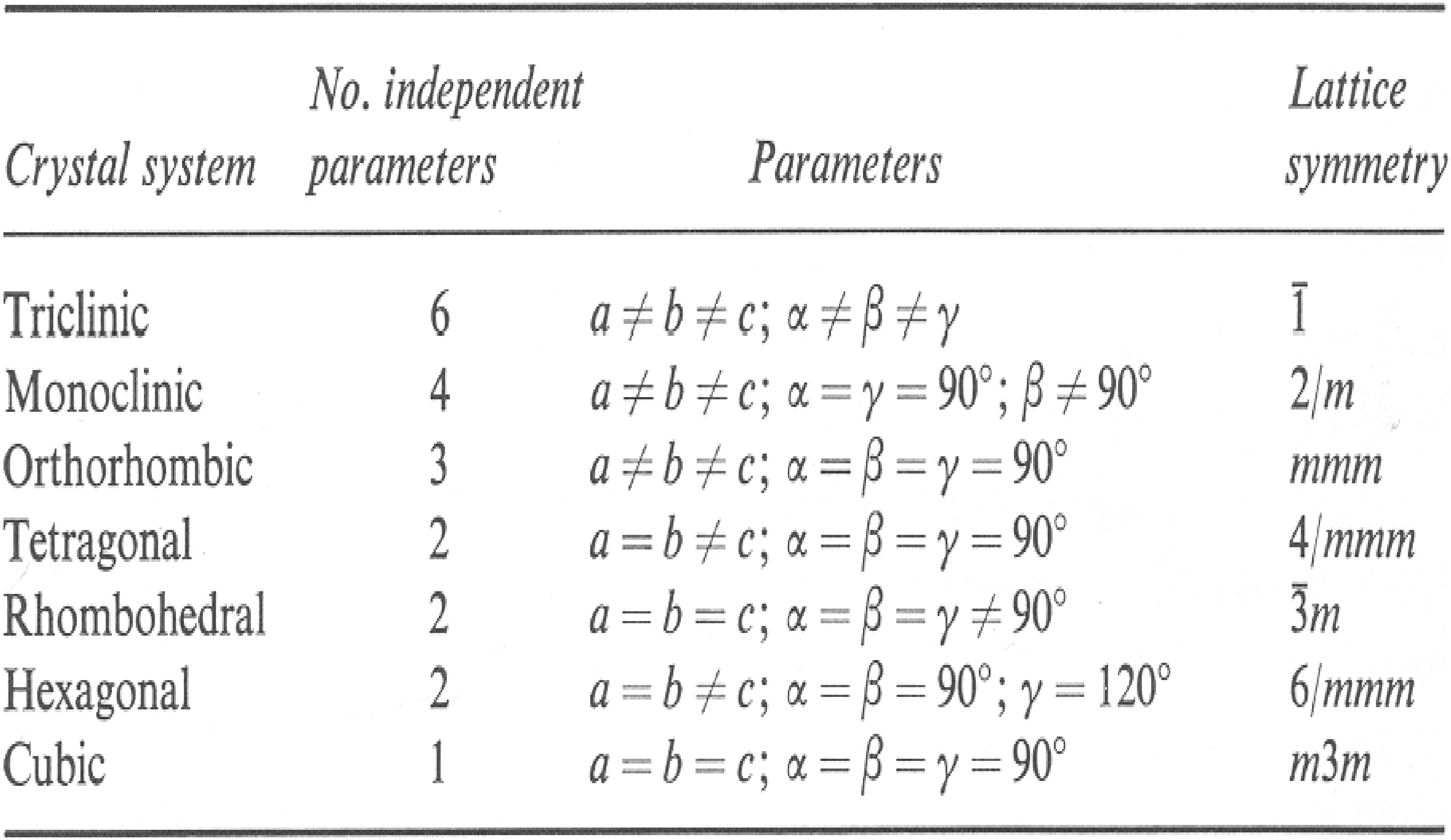
- The three crystallographic axes a1, a2, a3 (or a, b, c) are all equal in length and intersect at right angles (90 degrees) to each other.



$\bar{3}m$

Rhombohedral	P	$a_1 = a_2 = a_3$ $\alpha = \beta = \gamma \neq 90°$

Crystal systems

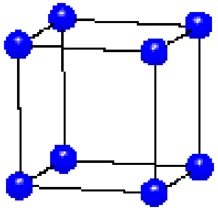


Crystal system	No. independent parameters	Parameters	Lattice symmetry
Triclinic	6	$a \neq b \neq c;\ \alpha \neq \beta \neq \gamma$	$\bar{1}$
Monoclinic	4	$a \neq b \neq c;\ \alpha = \gamma = 90°;\ \beta \neq 90°$	$2/m$
Orthorhombic	3	$a \neq b \neq c;\ \alpha = \beta = \gamma = 90°$	mmm
Tetragonal	2	$a = b \neq c;\ \alpha = \beta = \gamma = 90°$	$4/mmm$
Rhombohedral	2	$a = b = c;\ \alpha = \beta = \gamma \neq 90°$	$\bar{3}m$
Hexagonal	2	$a = b \neq c;\ \alpha = \beta = 90°;\ \gamma = 120°$	$6/mmm$
Cubic	1	$a = b = c;\ \alpha = \beta = \gamma = 90°$	$m3m$

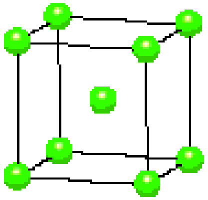
CUBIC

$a = b = c$
$\alpha = \beta = \gamma = 90°$

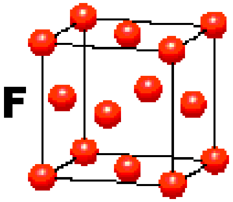
P



I



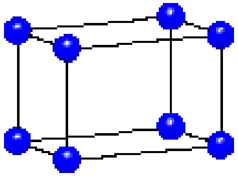
F



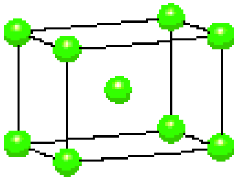
TETRAGONAL

$a = b \neq c$
$\alpha = \beta = \gamma = 90°$

P



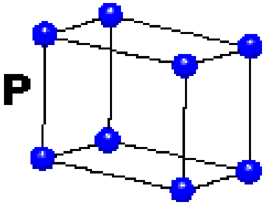
I



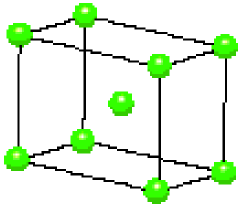
ORTHORHOMBIC

$a \neq b \neq c$
$\alpha = \beta = \gamma = 90°$

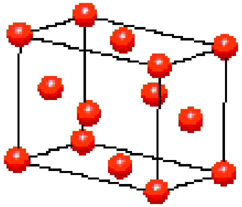
P



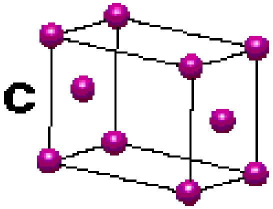
I



F



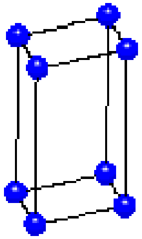
C



HEXAGONAL

$a = b \neq c$
$\alpha = \beta = 90°$
$\gamma = 120°$

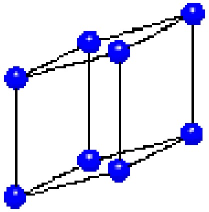
P



TRIGONAL

$a = b = c$
$\alpha = \beta = \gamma \neq 90°$

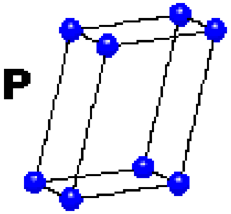
P



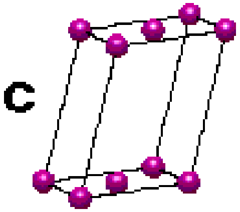
MONOCLINIC

$a \neq b \neq c$
$\alpha = \gamma = 90°$
$\beta \neq 120°$

P



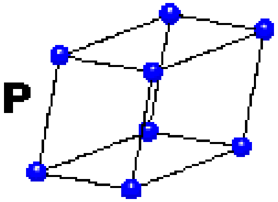
C



TRICLINIC

$a \neq b \neq c$
$\alpha \neq \beta \neq \gamma \neq 90°$

P



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

Notation

P: Primitive (lattice points only at the corners of the unit cell)

I: Body-centred (lattice points at the corners + one lattice point at the centre of the unit cell)

F: Face-centred (lattice points at the corners + lattice points at centres of all faces of the unit cell)

C: End-centred or base-centred (lattice points at the corners + two lattice points at the centres of a pair of opposite faces)

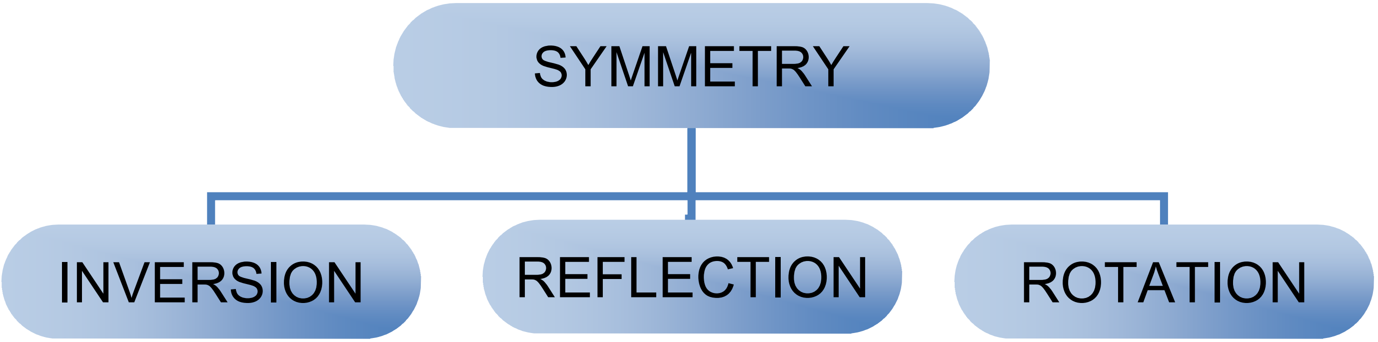
Point groups

- The crystallographic point group or *crystal class* is the mathematical group comprising the symmetry operations that leave at least one point unmoved and that leave the appearance of the crystal structure unchanged. These symmetry operations include

1. ***Reflection:*** which reflects the structure across a *reflection plane*
2. ***Rotation:*** which rotates the structure a specified portion of a circle about a *rotation axis*
3. ***Inversion:*** which changes the sign of the coordinate of each point with respect to a *center of symmetry* or *inversion point*
4. ***Improper rotation(rotoinversion):*** which consists of a rotation about an axis followed by an inversion.

ELEMENTS OF SYMMETRY

- Each of the unit cells of the 14 Bravais lattices has one or more types of symmetry properties, such as inversion, reflection or rotation,etc.



SYMMETRY

INVERSION

REFLECTION

ROTATION

Lattice goes into itself through Symmetry without translation(point group)

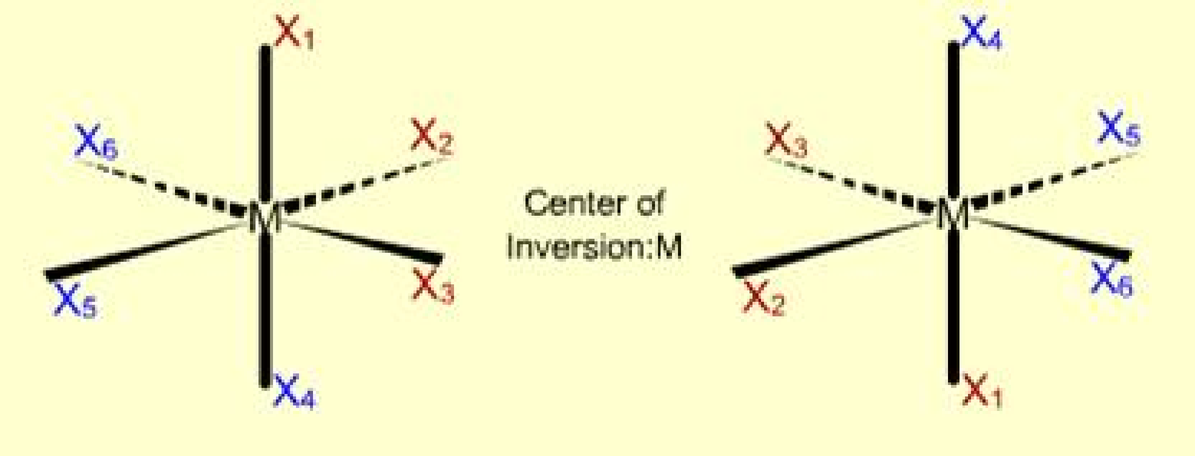
Operation	Element
Inversion	Point
Reflection	Plane
Rotation	Axis
Rotoinversion	Axis

Inversion Center

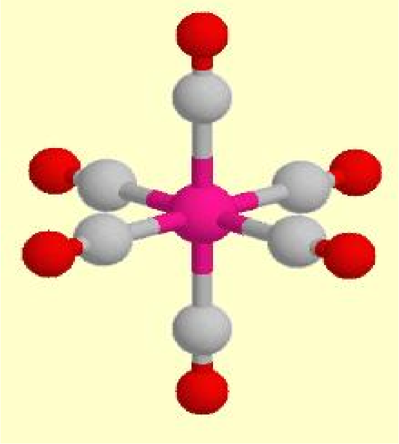
- A center of symmetry: A point at the center of the molecule.

(x,y,z) --> (-x,-y,-z)

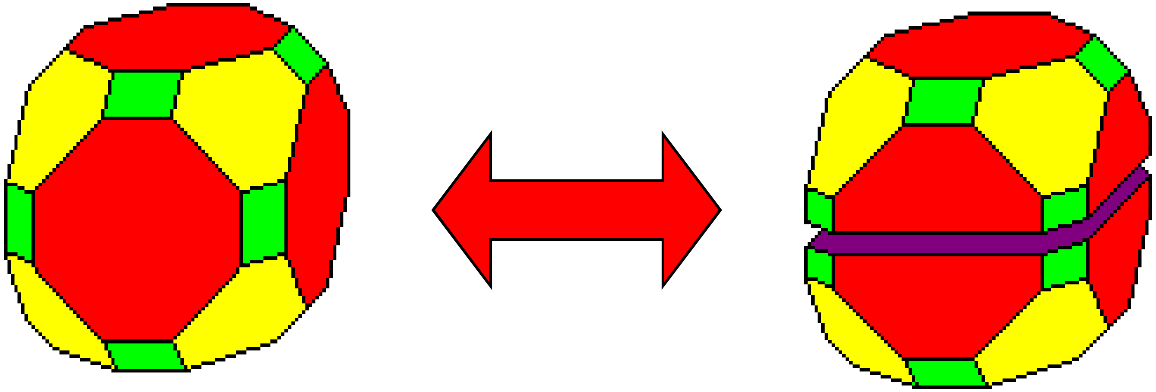
- Center of inversion can only be in a molecule. It is not necessary to have an atom in the center (benzene, ethane). Tetrahedral, triangles, pentagons don't have a center of inversion symmetry. All Bravais lattices are inversion symmetric.



Mo(CO)6

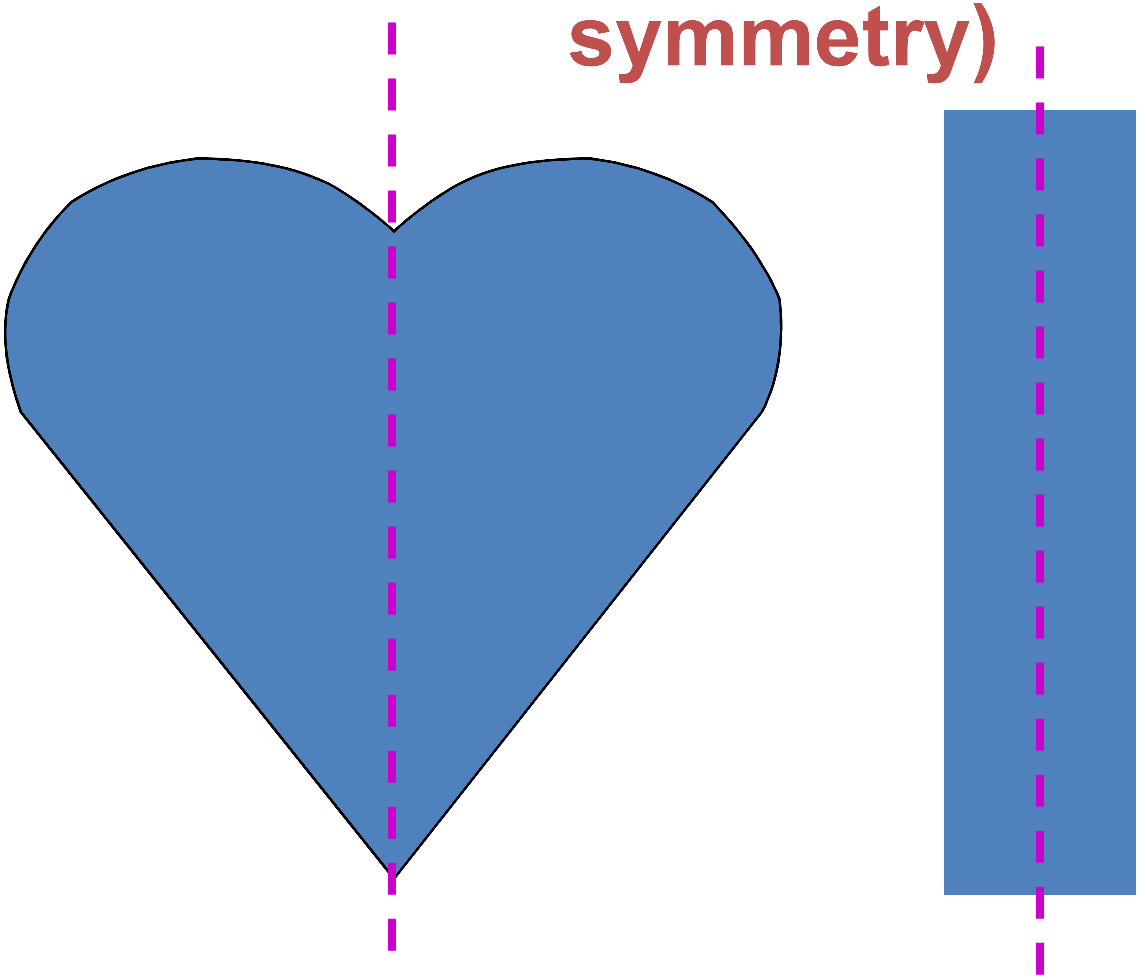


Reflection Plane

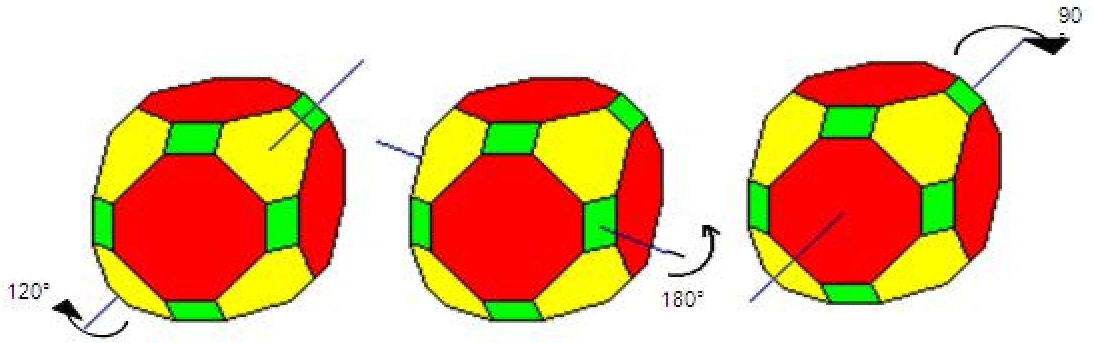


- A plane in a cell such that, when a mirror reflection in this plane is performed, the cell remains invariant.

Reflection (or mirror symmetry)



Rotation Symmetry

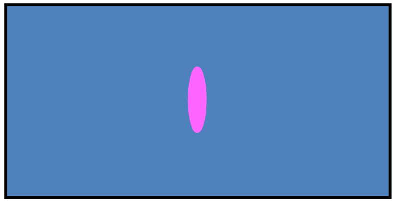


- This is an axis such that, if the cell is rotated around it through some angles, the cell remains invariant.
- The axis is called n-fold if the angle of rotation is $2\pi/n$.

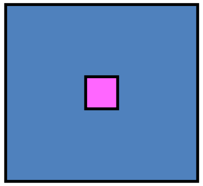
Rotation Axis

If an object come into self-coincidence through smallest non-zero rotation angle of θ then it is said to have an n-fold rotation axis where

$$\theta = \frac{360^0}{n}$$

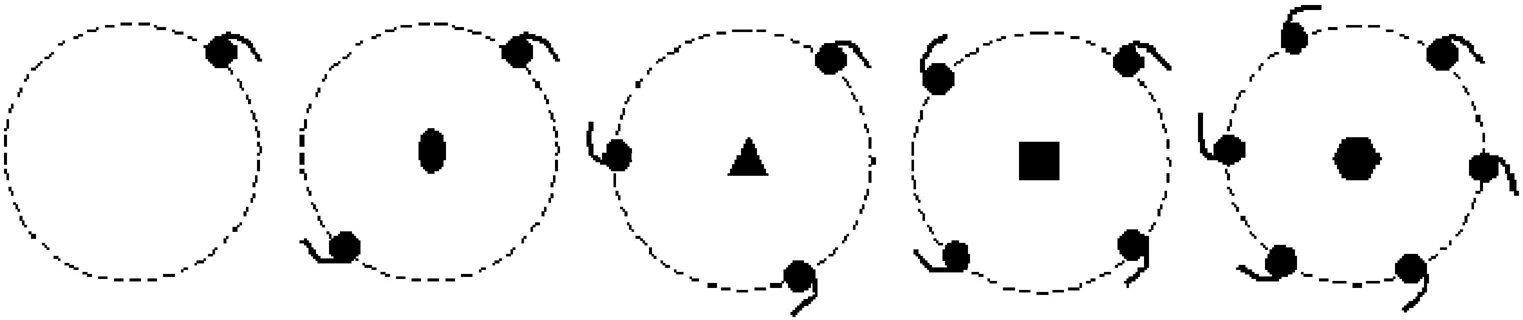


$\theta=180^\circ$ $n=2$ 2-fold rotation axis



$\theta=90^\circ$ $n=4$ 4-fold rotation axis

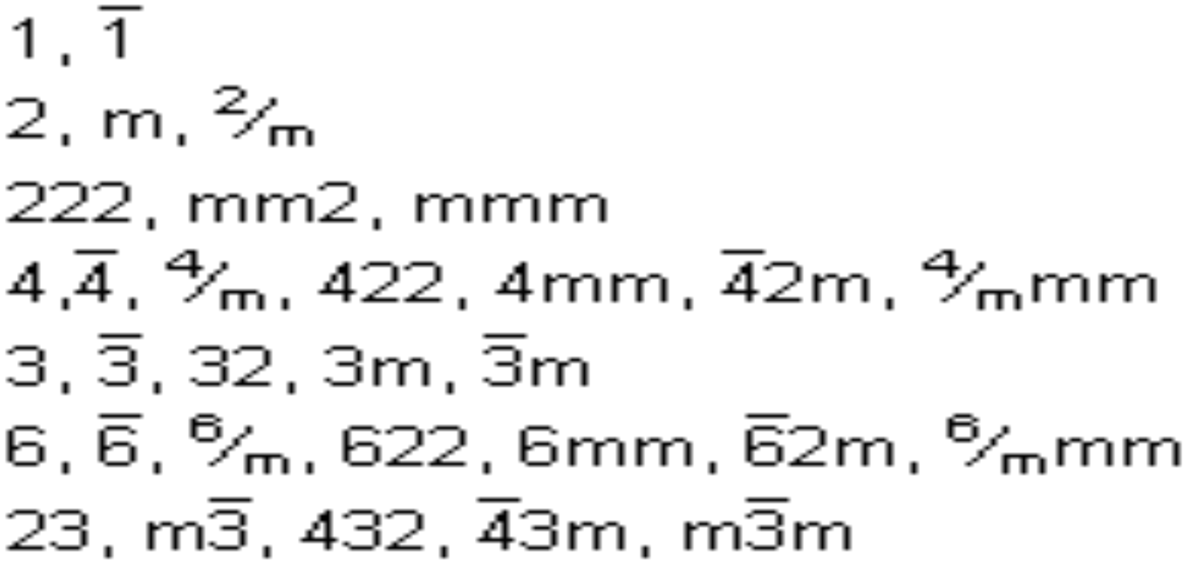
Axis of Rotation



Fold (n)	1	2	3	4	6
Angles	360	180	120	90	60

The 32 Point Groups

- Operation of translation-free symmetry operations on the 14 Bravais lattices produces the 32 Point Groups
- These are also known as the “Crystal Classes”



$1, \bar{1}$

$2, m, 2/m$

$222, mm2, mmm$

$4, \bar{4}, 4/m, 422, 4mm, \bar{4}2m, 4/mmm$

$3, \bar{3}, 32, 3m, \bar{3}m$

$6, \bar{6}, 6/m, 622, 6mm, \bar{6}2m, 6/mmm$

$23, m\bar{3}, 432, \bar{4}3m, m\bar{3}m$

There are a total of 32 point groups

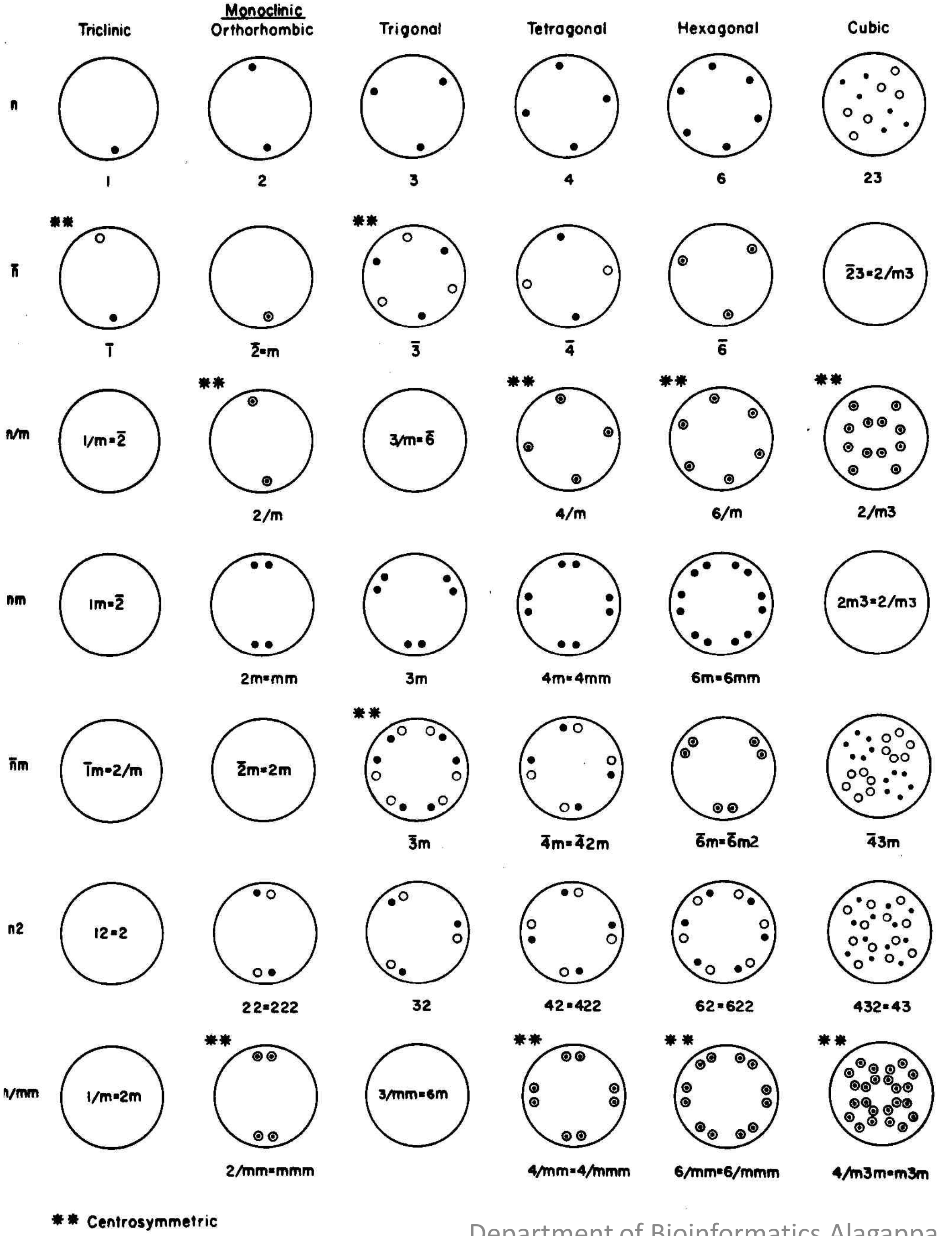
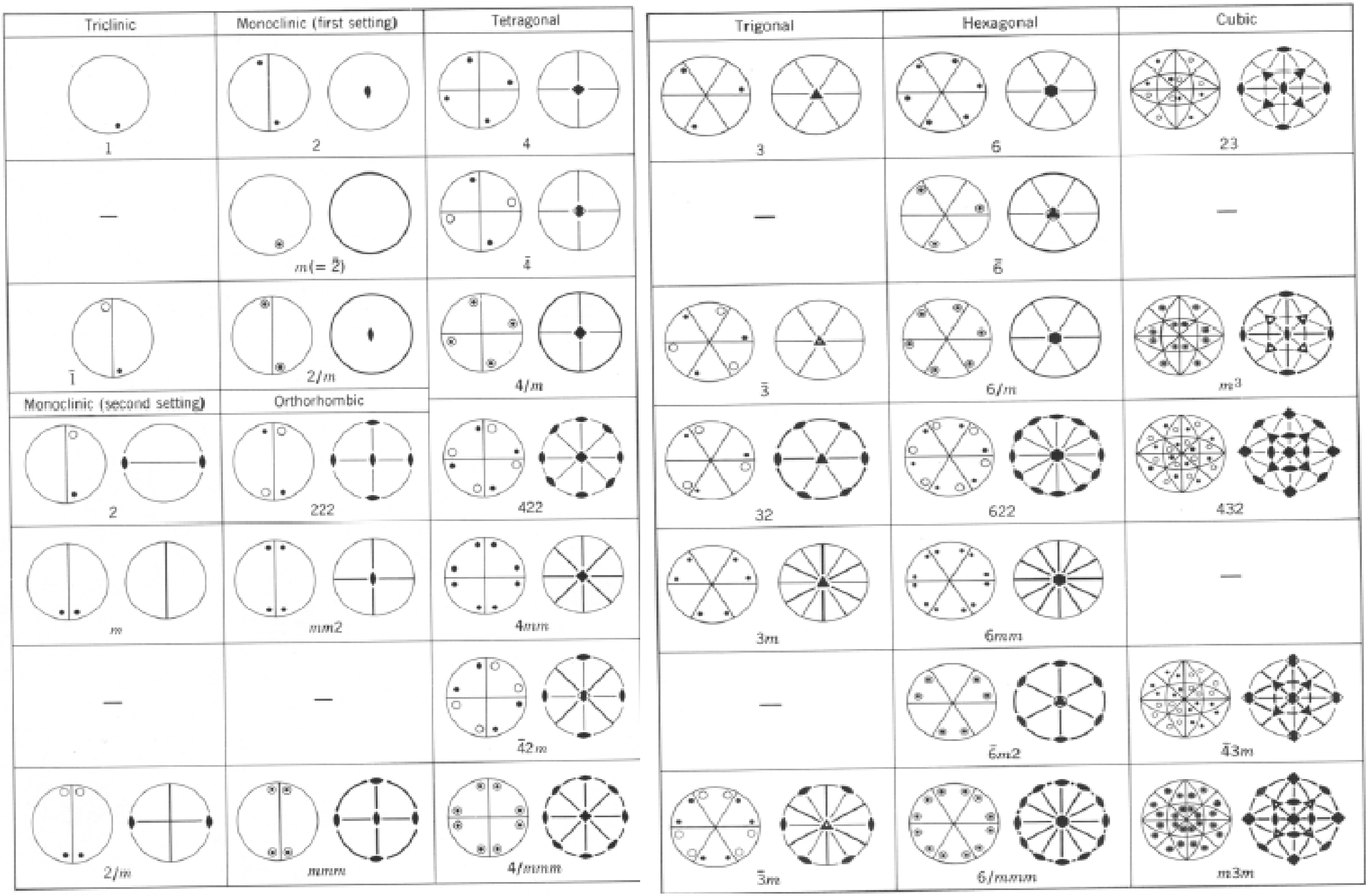
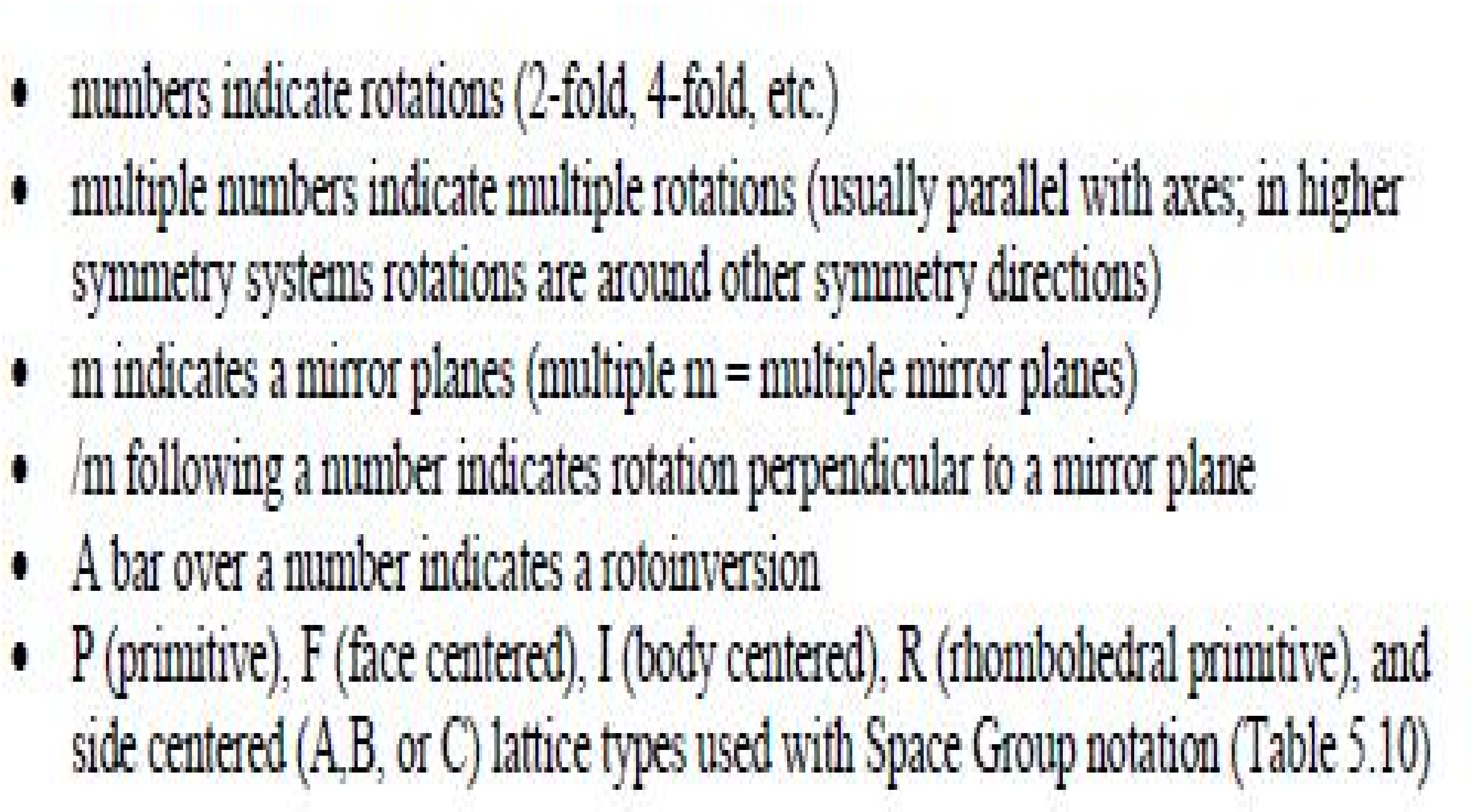


Figure 3.19. Plane representations of the 32 point groups.

The 32 Point Groups



The 32 Point Groups

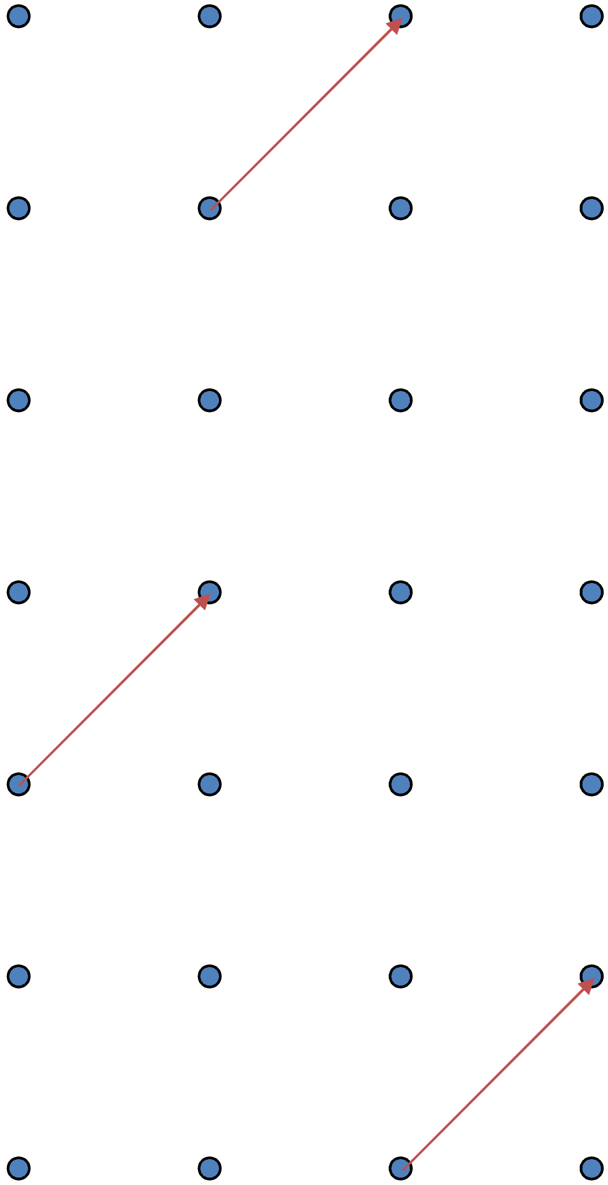


- numbers indicate rotations (2-fold, 4-fold, etc.)
- multiple numbers indicate multiple rotations (usually parallel with axes; in higher symmetry systems rotations are around other symmetry directions)
- m indicates a mirror planes (multiple m = multiple mirror planes)
- /m following a number indicates rotation perpendicular to a mirror plane
- A bar over a number indicates a rotoinversion
- P (primitive), F (face centered), I (body centered), R (rhombohedral primitive), and side centered (A,B, or C) lattice types used with Space Group notation (Table 5.10)

The 230 Space Groups

- Operation of the translation operations on the 32 point groups produces the (somewhat intimidating) space groups (listed on following slides).
- Screw Axes combine rotation about an axis with translation parallel to it. Rotations can be 180º, 120º, 90º or 60º defining 2-, 3-, 4- and 6-fold axes respectively.
- Screw axis=rotation +translation
- Glide Planes combine reflection across a plane combined with translation parallel to it. Glides are expressed as a direction (a,b,c) with a subscript indicating how many glides occur in one unit distance.
- Glide planes=reflection+translation
- Pure *translations* which move a point along a vector

Translational symmetry



Lattices also have **translational symmetry**

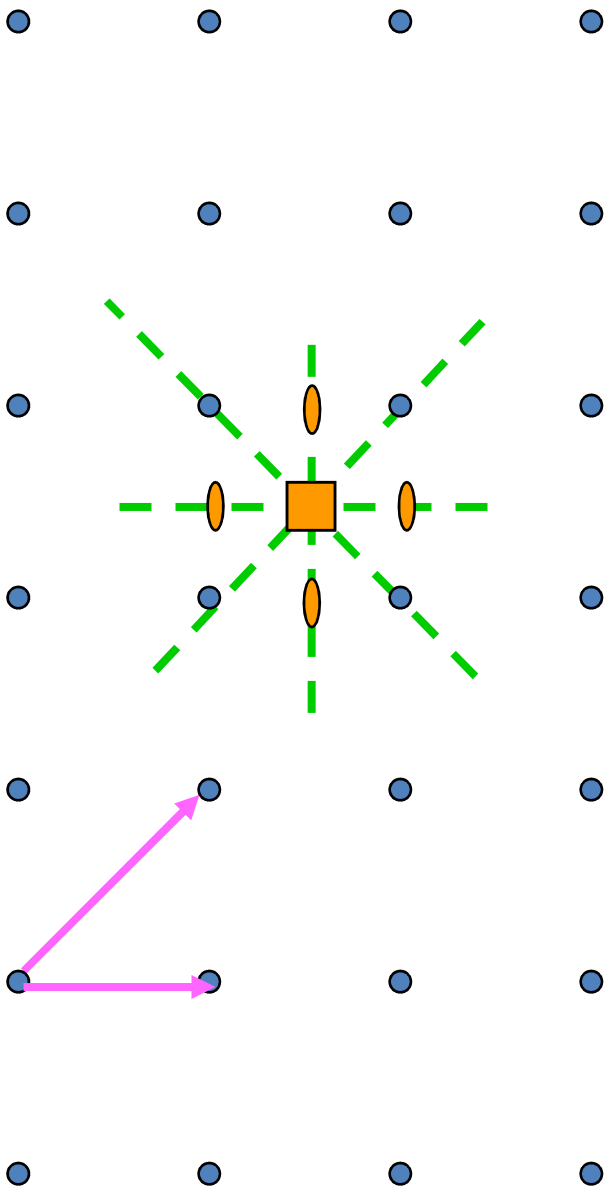
Symmetry of lattices

Lattices have

Translational symmetry

Rotational symmetry

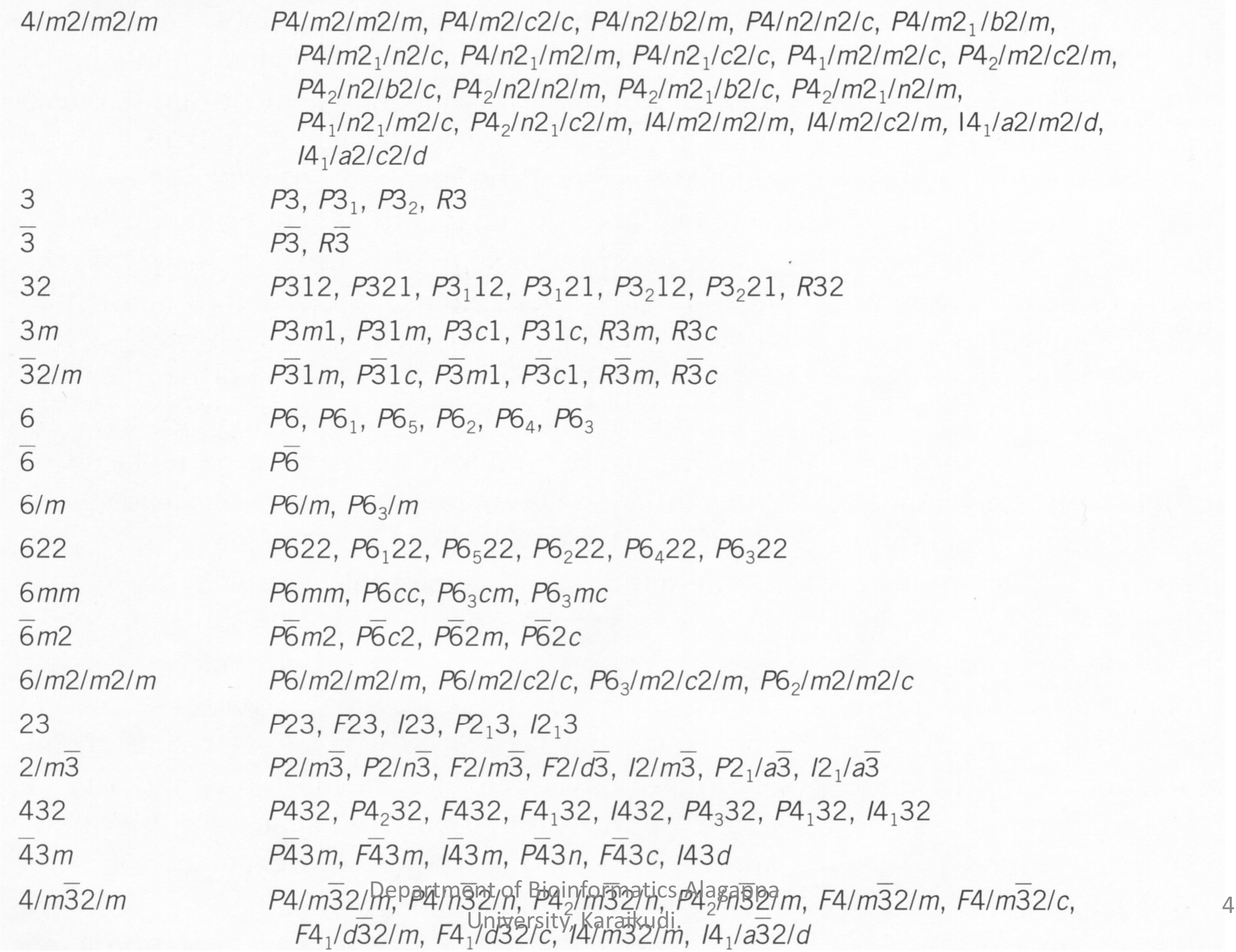
Reflection symmetry



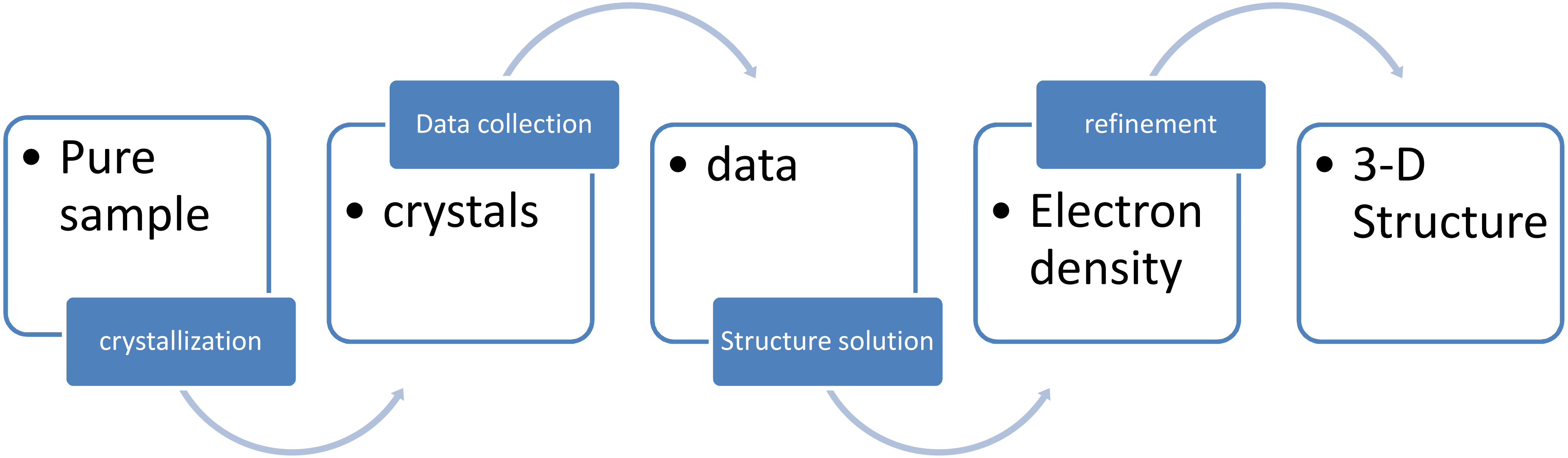
The 230 Space Groups (pt. 1)

Crystal Class	Space Group
1	$P1$
$\bar{1}$	$P\bar{1}$
2	$P2$, $P2_1$, $C2$
m	Pm, Pc, Cm, Cc
$2/m$	$P2/m$, $P2_1/m$, $C2/m$, $P2/c$, $P2_1/c$, $C2/c$
222	$P222$, $P222_1$, $P2_12_12$, $P2_12_12_1$, $C222_1$, $C222$, $F222$, $I222$, $I2_12_12_1$
$mm2$	$Pmm2$, $Pmc2_1$, $Pcc2$, $Pma2$, $Pca2_1$, $Pnc2$, $Pmn2_1$, $Pba2$, $Pna2_1$, $Pnn2$, $Cmm2$, $Cmc2_1$, $Ccc2$, $Amm2$, $Abm2$, $Ama2$, $Aba2$, $Fmmc$, $Fdd2$, $Imm2$, $Iba2$, $Ima2$
$2/m2/m2/m$	$P2/m2/m2/m$, $P2/n2/n2/n$, $P2/c2/c2/m$, $P2/b2/a2/n$, $P2_1/m2/m2/a$, $P2/n2_1/n2/a$, $P2/m2/n2_1/a$, $P2_1/c2/c2/a$, $P2_1/b2_1/a2/m$, $P2_1/c2_1/c2/n$, $P2/b2_1/c2_1/m$, $P2_1/n2_1/n2/m$, $P2_1/m2_1/m2/n$, $P2_1/b2/c2_1/n$, $P2_1/b2_1/c2_1/a$, $p2_1/n2_1/m2_1/a$, $C2/m2/c2/m$, $C2/m2/c2_1/a$, $C2/m2/m2/m$, $C2/c2/c2/m$, $C2/m2/m2/a$, $C2/c2/c2/a$, $F2/m2/m2/m$, $F2/d2/d2/d$, $I2/m2/m2/m$, $I2/b2/a2/m$, $I2/b2/c2/a$, $I2/m2/m2/a$
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	$P422$, $P42_12$, $P4_122$, $P4_12_12$, $P4_222$, $P4_22_12$, $P4_322$, $P4_32_12$, $I422$, $I4_122$
$4mm$	$P4mm$, $P4bm$, $P4_2cm$, $P4_2nm$, $P4cc$, $P4nc$, $P4_2mc$, $P4_2bc$, $I4mm$, $I4cm$, $I4_1md$, $I4_1cd$
$\bar{4}2m$	$P\bar{4}2m$, $P\bar{4}2c$, $P\bar{4}2_1m$, $P\bar{4}2_1c$, $P\bar{4}m2$, $P\bar{4}c2$, $P\bar{4}b2$, $P\bar{4}n2$, $I\bar{4}m2$, $I\bar{4}c2$, $I\bar{4}2m$, $I\bar{4}2d$

The 230 Space Groups (pt. 2)



Crystal Class	Space Group
$4/m2/m2/m$	$P4/m2/m2/m$, $P4/m2/c2/c$, $P4/n2/b2/m$, $P4/n2/n2/c$, $P4/m2_1/b2/m$, $P4/m2_1/n2/c$, $P4/n2_1/m2/m$, $P4/n2_1/c2/c$, $P4_1/m2/m2/c$, $P4_2/m2/c2/m$, $P4_2/n2/b2/c$, $P4_2/n2/n2/m$, $P4_2/m2_1/b2/c$, $P4_2/m2_1/n2/m$, $P4_1/n2_1/m2/c$, $P4_2/n2_1/c2/m$, $I4/m2/m2/m$, $I4/m2/c2/m$, $I4_1/a2/m2/d$, $I4_1/a2/c2/d$
3	$P3$, $P3_1$, $P3_2$, $R3$
$\bar{3}$	$P\bar{3}$, $R\bar{3}$
32	$P312$, $P321$, $P3_112$, $P3_121$, $P3_212$, $P3_221$, $R32$
$3m$	$P3m1$, $P31m$, $P3c1$, $P31c$, $R3m$, $R3c$
$\bar{3}2/m$	$P\bar{3}1m$, $P\bar{3}1c$, $P\bar{3}m1$, $P\bar{3}c1$, $R\bar{3}m$, $R\bar{3}c$
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	$P622$, $P6_122$, $P6_522$, $P6_222$, $P6_422$, $P6_322$
$6mm$	$P6mm$, $P6cc$, $P6_3cm$, $P6_3mc$
$\bar{6}m2$	$P\bar{6}m2$, $P\bar{6}c2$, $P\bar{6}2m$, $P\bar{6}2c$
$6/m2/m2/m$	$P6/m2/m2/m$, $P6/m2/c2/c$, $P6_3/m2/c2/m$, $P6_2/m2/m2/c$
23	$P23$, $F23$, $I23$, $P2_13$, $I2_13$
$2/m\bar{3}$	$P2/m\bar{3}$, $P2/n\bar{3}$, $F2/m\bar{3}$, $F2/d\bar{3}$, $I2/m\bar{3}$, $P2_1/a\bar{3}$, $I2_1/a\bar{3}$
432	$P432$, $P4_232$, $F432$, $F4_132$, $I432$, $P4_332$, $P4_132$, $I4_132$
$\bar{4}3m$	$P\bar{4}3m$, $F\bar{4}3m$, $I\bar{4}3m$, $P\bar{4}3n$, $F\bar{4}3c$, $I43d$
$4/m\bar{3}2/m$	$P4/m\bar{3}2/m$, $P4/n\bar{3}2/n$, $P4_2/m\bar{3}2/n$, $P4_2/n\bar{3}2/m$, $F4/m\bar{3}2/m$, $F4/m\bar{3}2/c$, $F4_1/d\bar{3}2/m$, $F4_1/d\bar{3}2/c$, $I4/m\bar{3}2/m$, $I4_1/a\bar{3}2/d$



- Pure sample

crystallization

- crystals

Data collection

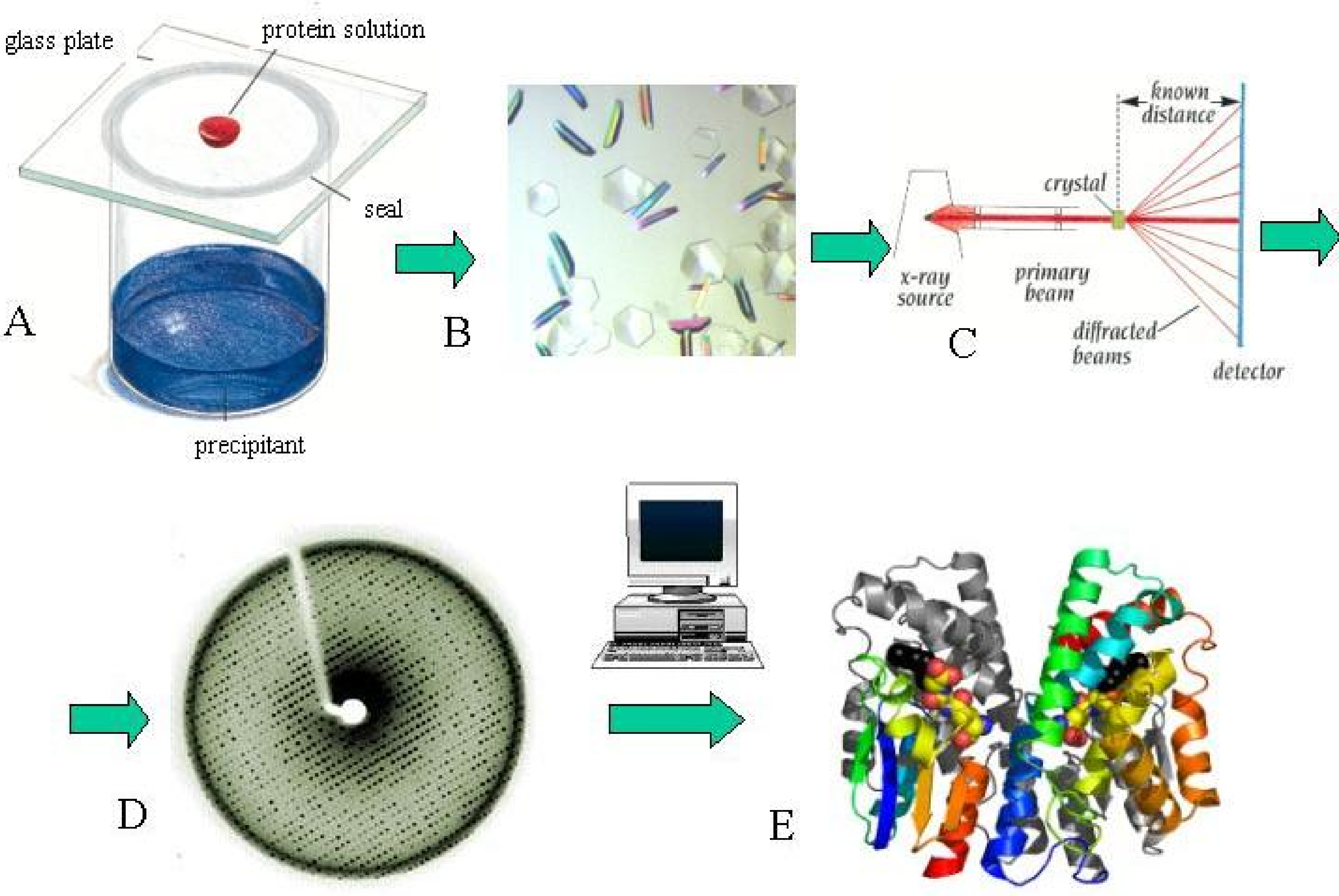
- data

Structure solution

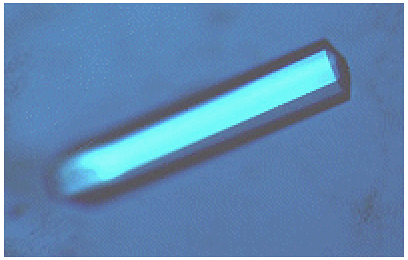
- Electron density

refinement

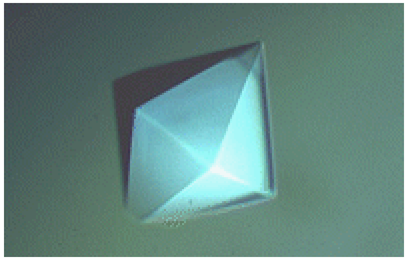
- 3-D Structure


glass plate
protein solution
seal
precipitant
A
B
x-ray source
primary beam
crystal
known distance
diffracted beams
detector
C
D
E

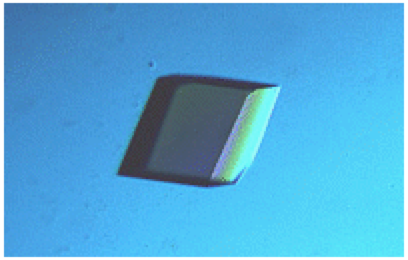
Some crystals



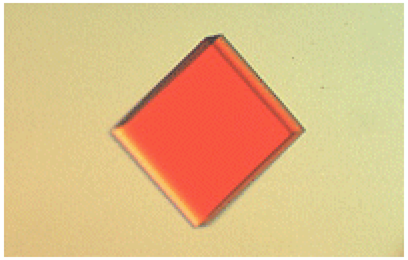
Hexagonal rod crystal



Hexagonal bipyramid crystal

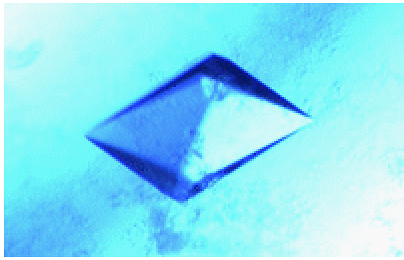


Trigonal crystal

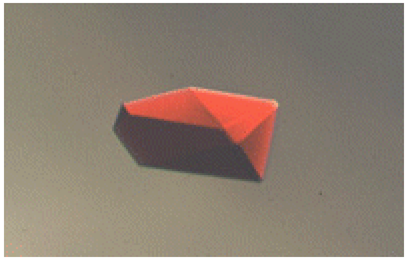


Monoclinic crystal

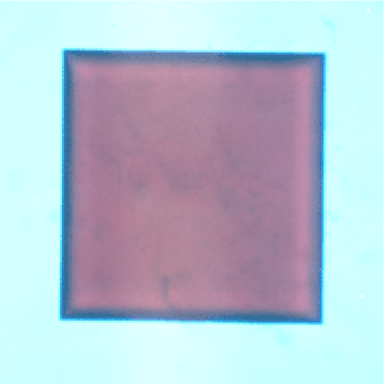
Some crystals



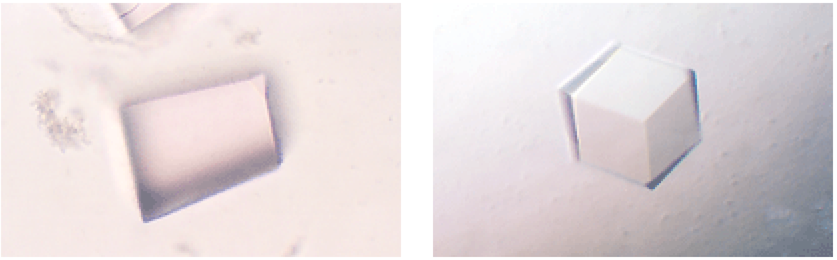
Monoclinic crystal



Orthorhombic crystal



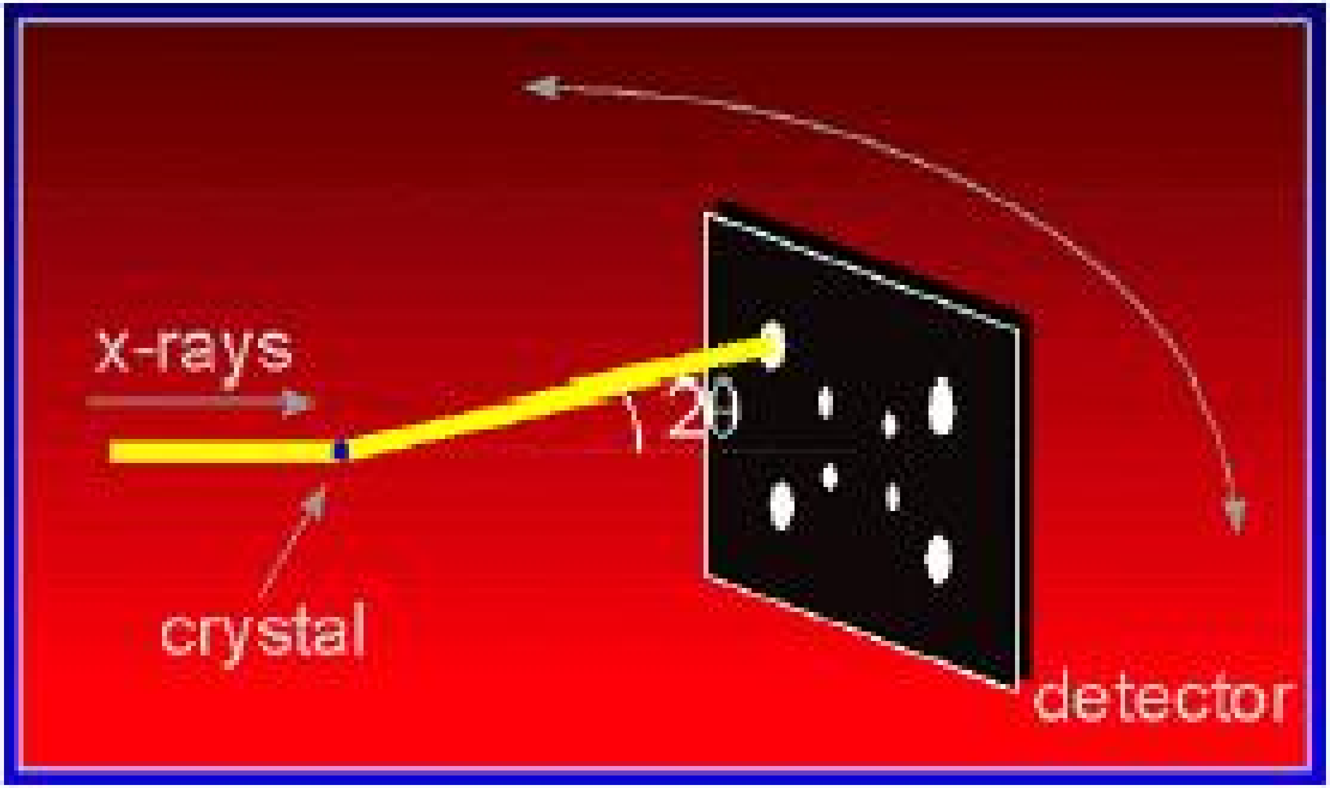
Tetragonal crystal



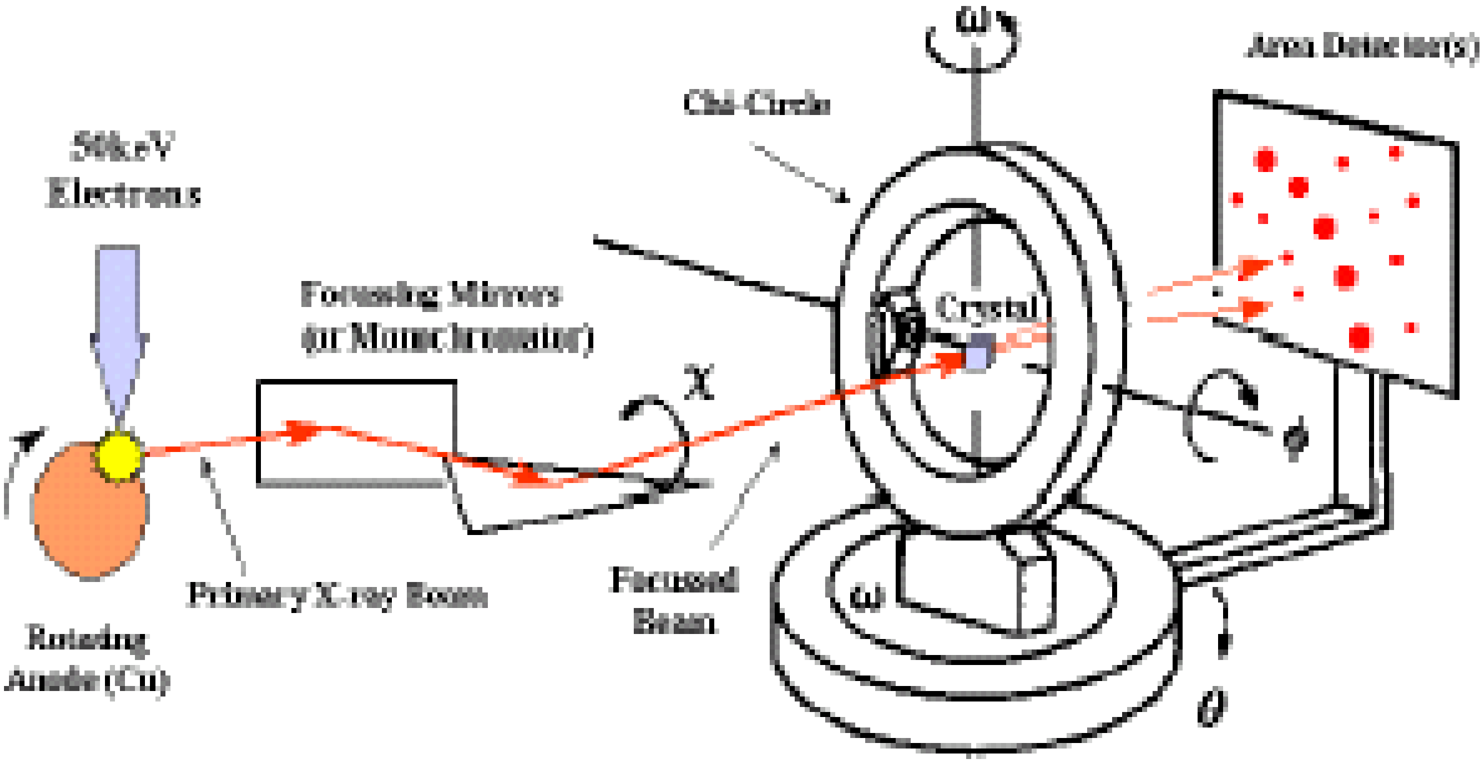
Trigonal and Cubic crystal

Thank you

X-ray diffraction

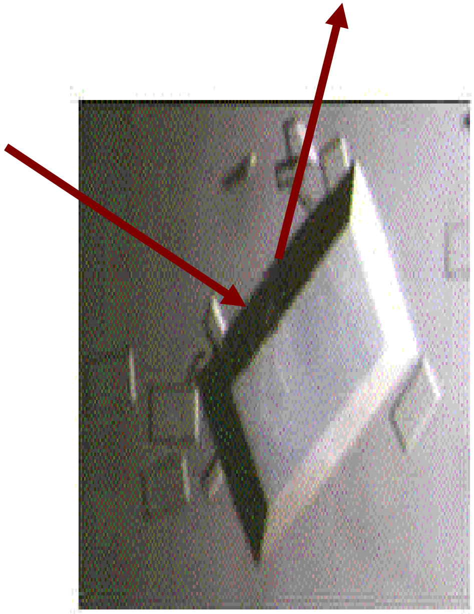


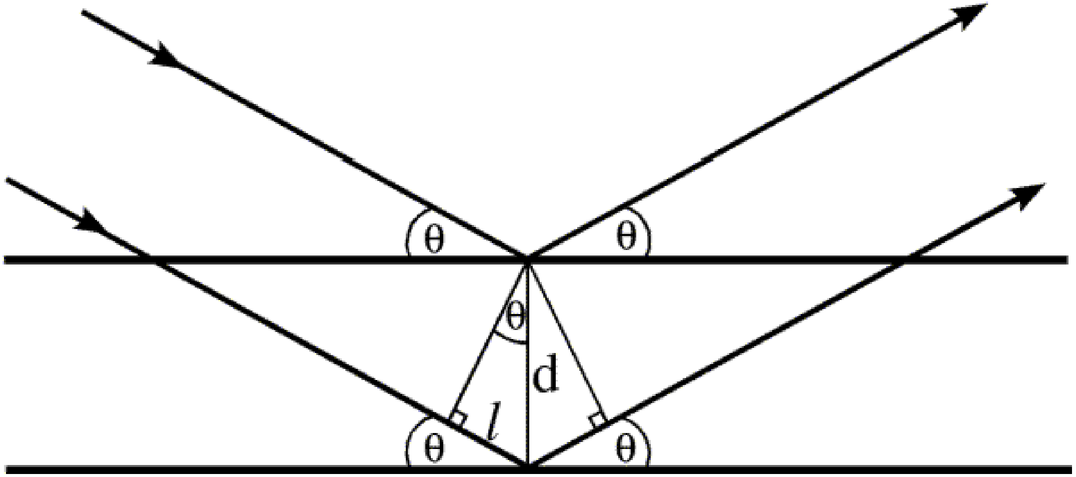
X-ray Diffractometer



4-Circle Goniometer (Eulerian or Kappa Geometry)

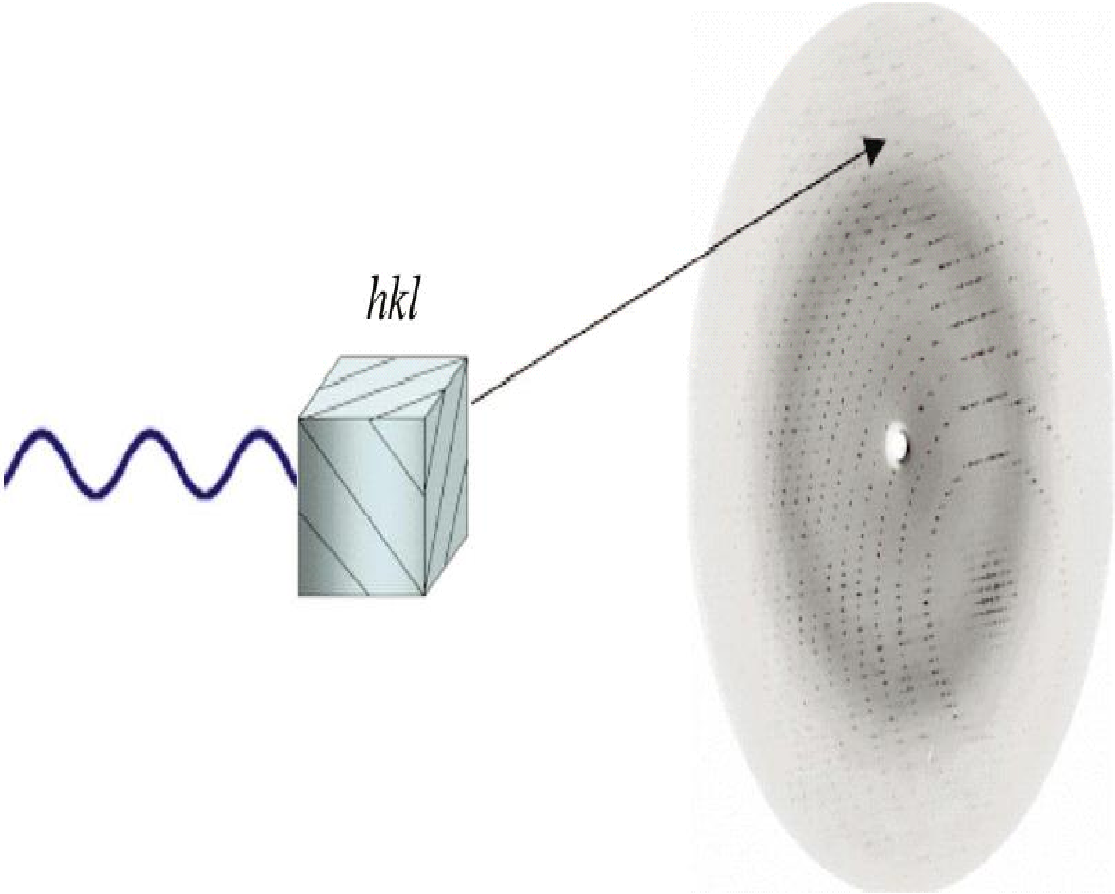
Diffraction Principles





$$2d\sin\theta = n\lambda$$

The Diffraction Experiment



Direct Methods

Direct methods are the mathematical methods (probabilistic methods) using which phase information could be obtained directly from the measured intensities.

First, the probable values of some linear combination of phases called structure invariants and structure semi-invariants are estimated. The individual values of phases are then obtained using tangent formula.

Limitations of direct methods

The validity of probabilistic estimate becomes poor as the number of atoms in the unit cell becomes large.

Thus Direct Methods which are traditionally useful to solve small molecules (less than 200 atoms in a molecule) fail when they are applied as such to solve macromolecular crystal structures. For solving macromolecules, Direct Methods require atomic resolution data.