CRYSTAL STRUCTURE

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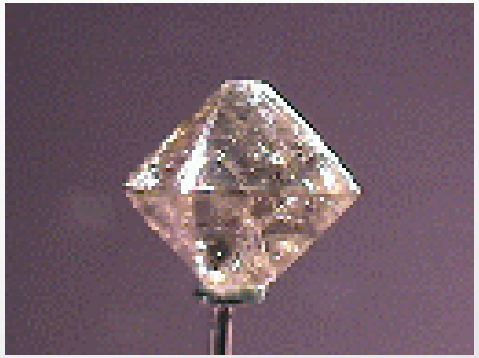
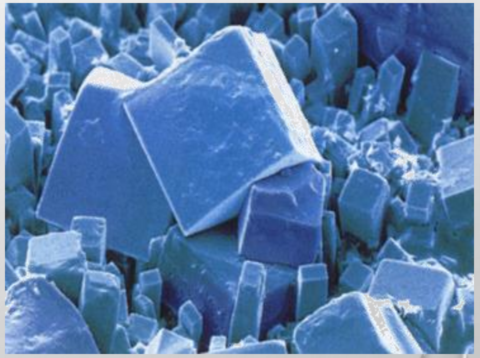
What is Crystallography

The branch of science that deals with the geometric description of crystals and their internal arrangement.



- Symmetry of a crystal can have a profound influence on its properties.
- Any crystal structure should be specified completely, concisely and unambiguously.
- Structures should be classified into different types according to the symmetries they possess.



To describe a crystal, it is necessary to specify three things:

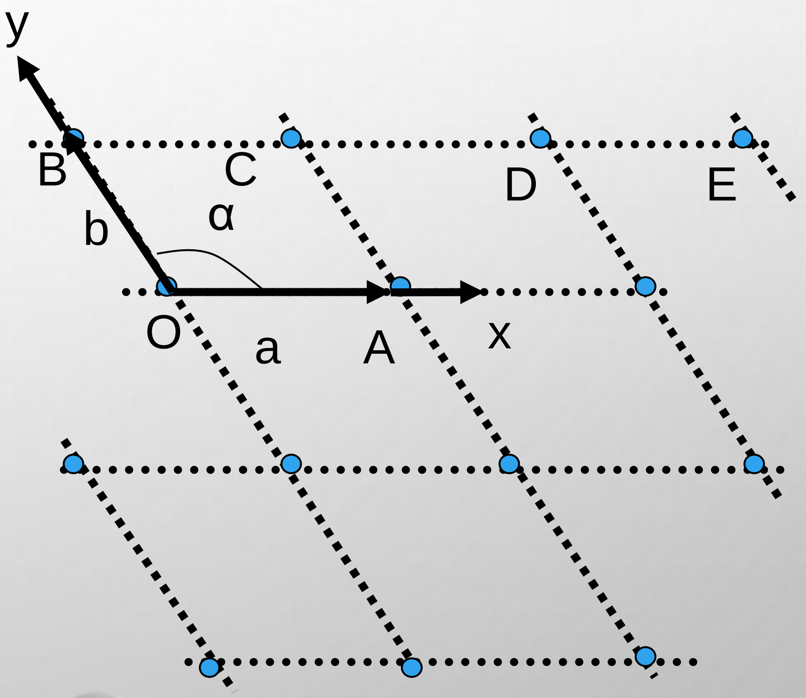
1. **What is the lattice**
2. **What are the lattice translation vectors**
3. **What is the basis**

Crystal Lattice

What is crystal (space) lattice?

In crystallography, only the geometrical properties of the crystal are of interest, therefore one replaces each atom by a geometrical point located at the equilibrium position of that atom.

- An infinite array of points in space,
- Each point has identical surroundings to all others.
- Arrays are arranged exactly in a periodic manner.

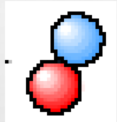


Crystal Lattice

Crystal = Lattice + Motif

Lattice :the underlying periodicity of the crystal •

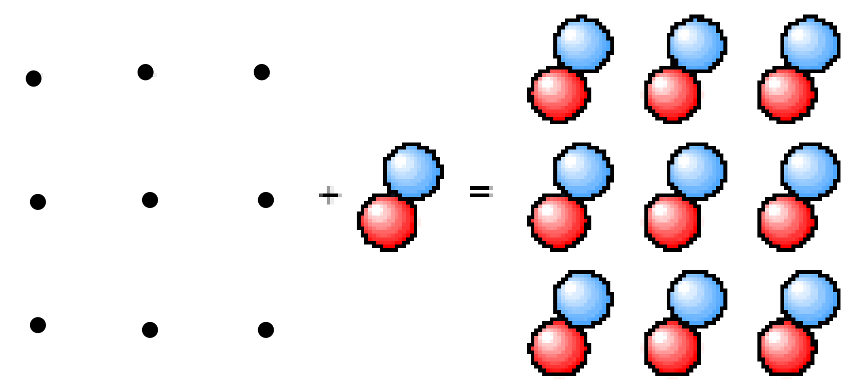
Motif or basis: an atom or a group of atoms associated with each lattice point



Lattice ➢ how to repeat

Motif ➢ what to repeat

Don't mix up atoms with lattice points!!!!



Lattice Translations Vectors

- The lattice and the lattice translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are primitive if any two points satisfy:

$$\mathbf{r}' = \mathbf{r} + u_1\mathbf{a}_1 + u_2\mathbf{a}_2 + u_3\mathbf{a}_3$$

where u_1, u_2 and u_3 are integers.

- The primitive lattice translation vectors specify unit cell of smallest volume.
- A lattice translation operator is defined as a displacement of a crystal with a crystal translation operator.

Basis

- A **basis** of atoms is attached to a lattice point and each atom in the basis is specified by:

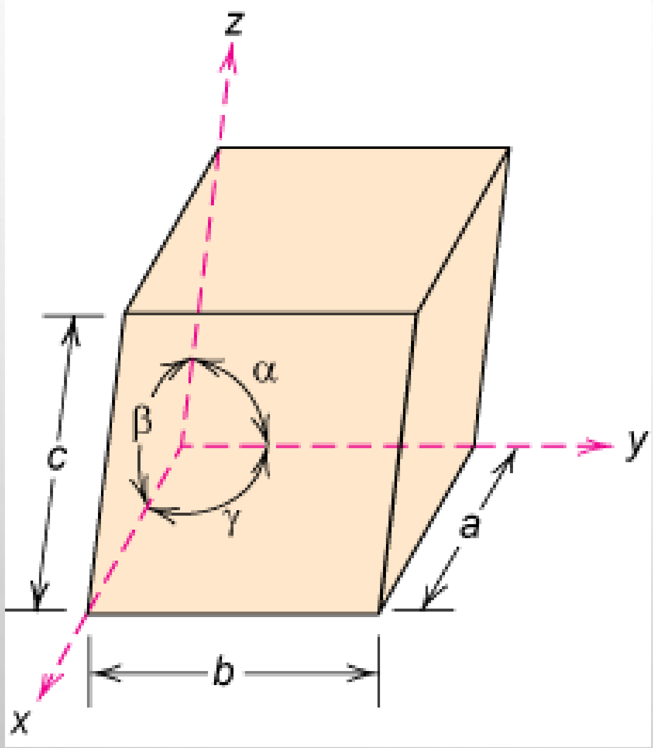
$$\mathbf{r}_j = x_j\mathbf{a}_1 + y_j\mathbf{a}_2 + z_j\mathbf{a}_3$$

where $0 \le x_j, y_j, z_j \le 1$.

The basis consists of one or several atoms.

Unit cell

- **A unit cell is defined as a fundamental building block of a crystal structure, which can generate the complete crystal by repeating its own dimensions in various directions**



These systems are built by changing the lattice parameters:

a, b, and *c* are the edge lengths

α, β, and γ are interaxial angles

Permitive Cell

- The **primitive cell** is a parallelepiped specified by the primitive translation vectors. It is a **minimum volume cell** and there is **one lattice point** per primitive cell.
- The volume of the primitive cell is:

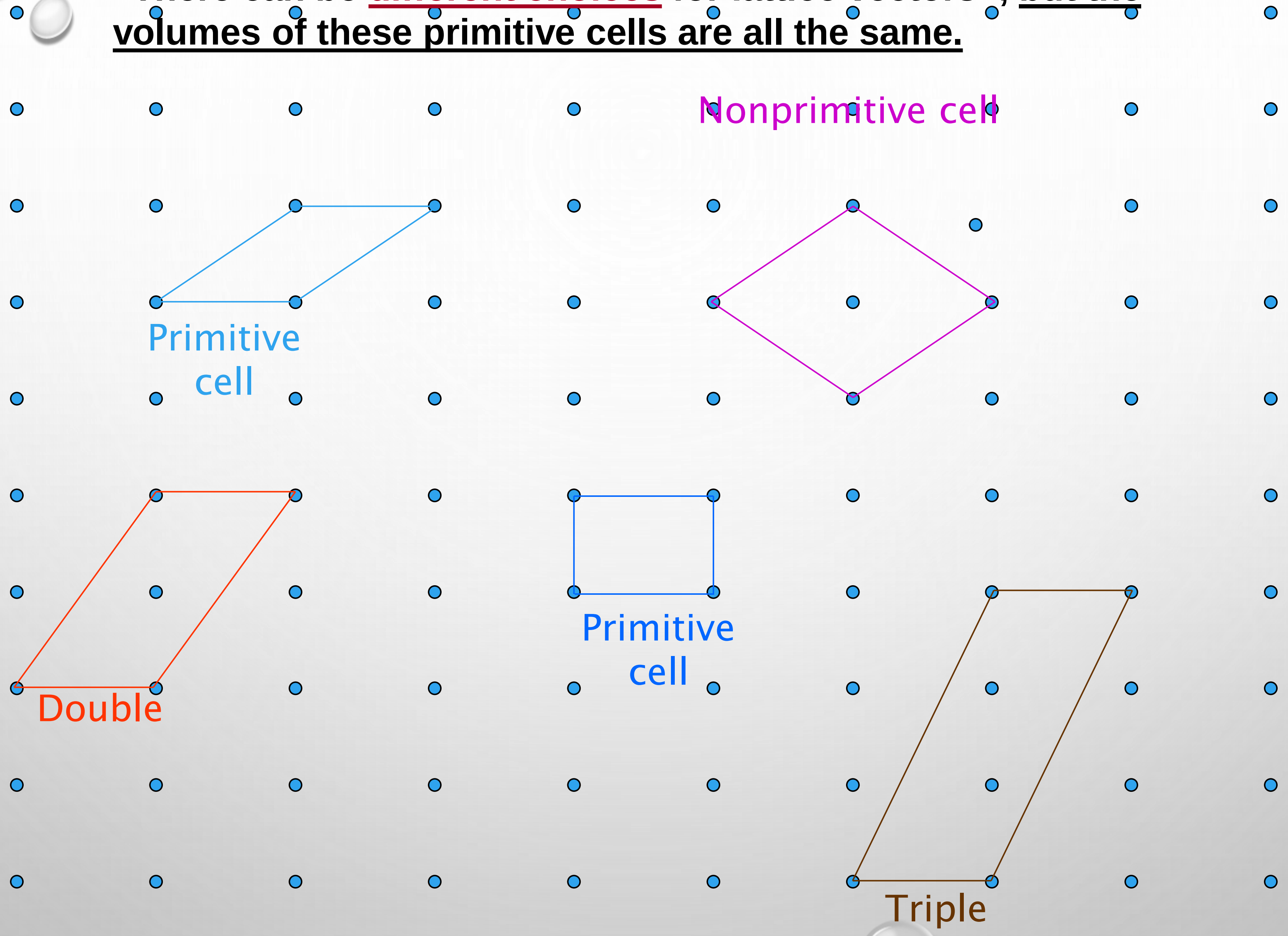
$$\mathbf{V}_c = \left| \mathbf{a}_1 \cdot (\mathbf{a}_2 \times \mathbf{a}_3) \right|$$

Basis associated with a primitive cell is called a primitive basis and contains the least # of atoms.

- If the lattice points are only at the corners, the cell is **primitive.**
- If there are lattice points in the cell other than the corners, the cell is **nonprimitive**.

The primitive unit cell must have only one lattice point

- **There can be different choices for lattice vectors , but the volumes of these primitive cells are all the same.**



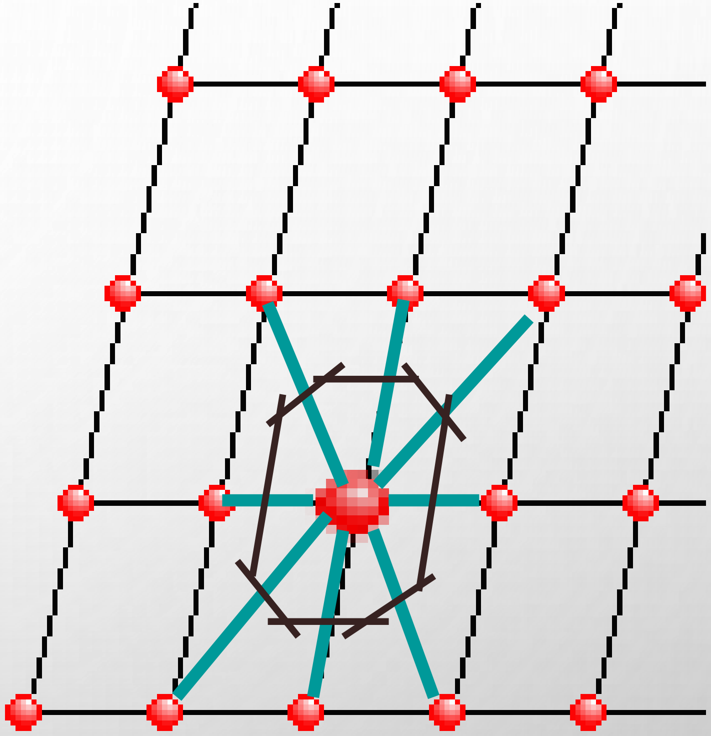
Symmetry of the Lattice or the crystal is not altered by our choice of unit cell!!

Wigner-Seitz cell

a particular kind of primitive cell which has the same symmetry as the lattice.

A simply way to find the primitive cell which is called **Wigner-Seitz** cell can be done as follows;

1. Choose a lattice point.
2. Draw lines to connect this lattice point to its neighbours.
3. At the mid-point and normal to these lines draw new lines.

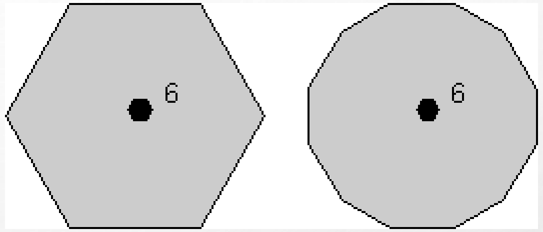


The volume enclosed is called as a Wigner-Seitz cell.

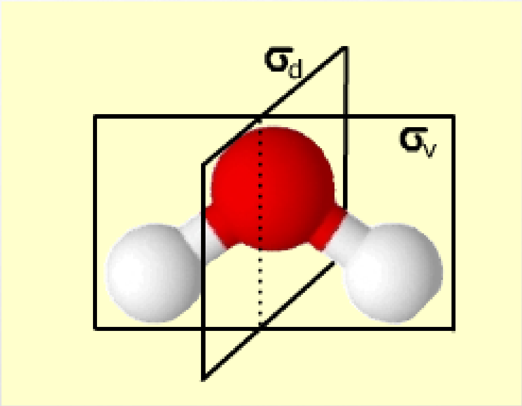
Symmetry Operations

- Translational
- Reflection at a plane
- Rotation about an axis
  - Inversion through a point
- Glide (=reflection + translation)
- Screw (=rotation + translation)

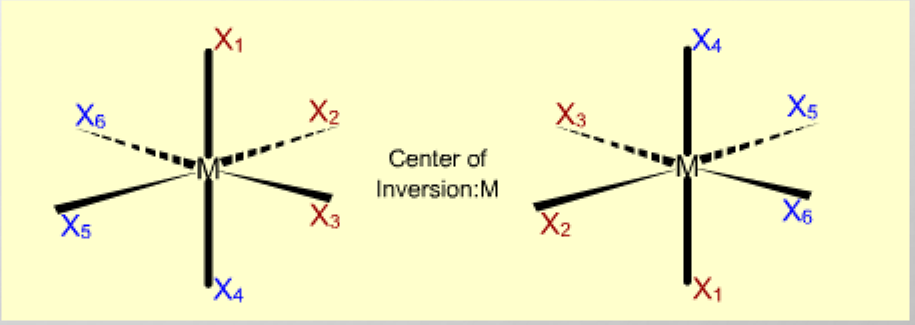
rotation



reflection



inversion



The most common symmetry operations are listed below:

- C_2 = two-fold rotation or a rotation by 180°
- C_3 = three-fold rotation or a rotation by 120°
- C_4 = four-fold rotation or a rotation by 90°
- C_6 = six-fold rotation or a rotation by 180°
- s = reflection about a plane through a lattice point
- i = inversion, I.e. rotation by 180° that is followed by a reflection in a plane normal to rotation axis.

Fundemental types of lattices

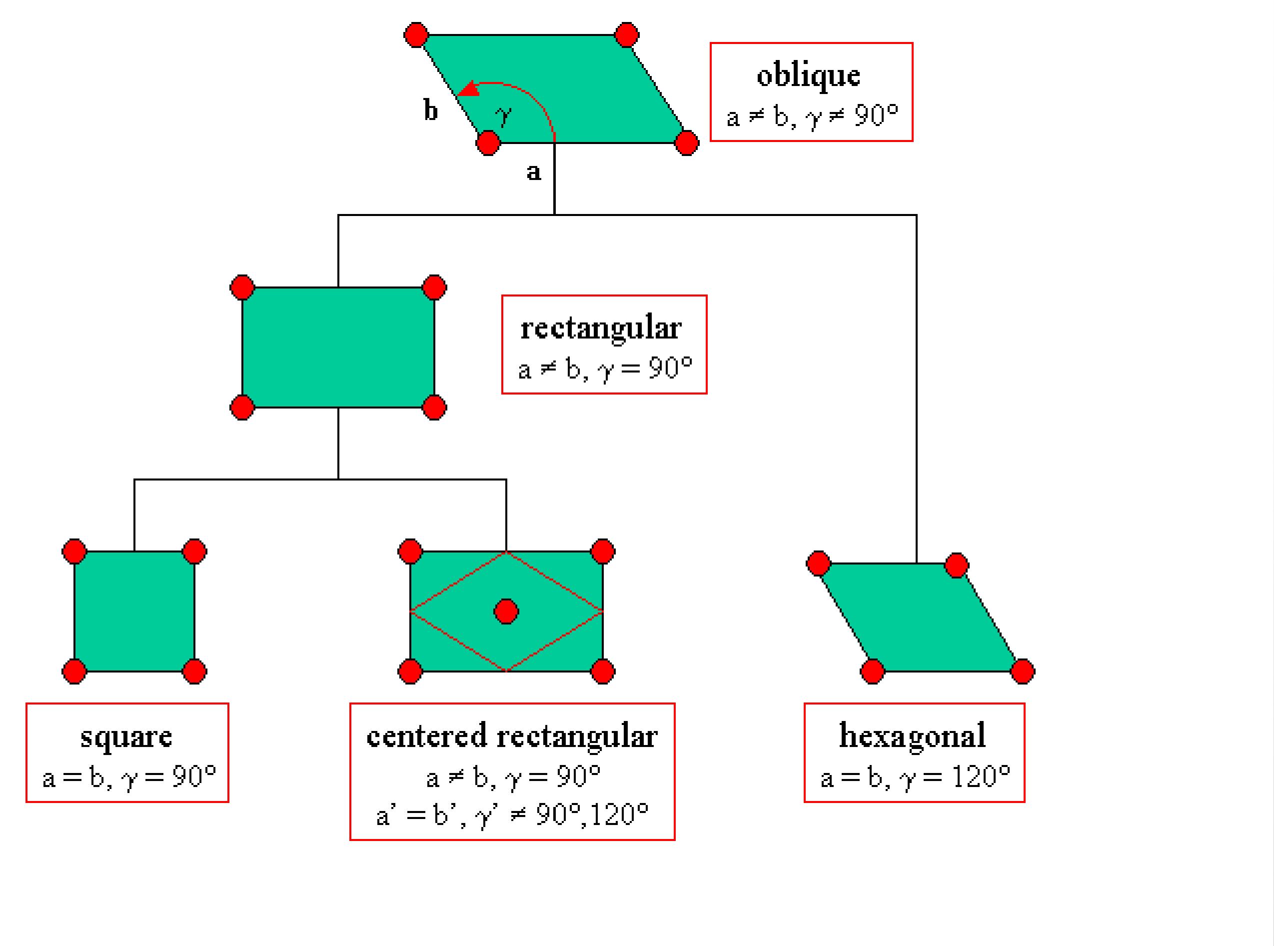
- crystal lattices can be mapped into themselves by the lattice translations **t** and by various other symmetry operations.
- a typical symmetry operation is that of rotation about an axis that passes through a lattice point. allowed rotations of : 2 π, 2π/2, 2π/3,2π/4, 2π/6
- (note: lattices do not have rotation axes for 1/5, 1/7 …) times 2π

Two Dimensional Lattices

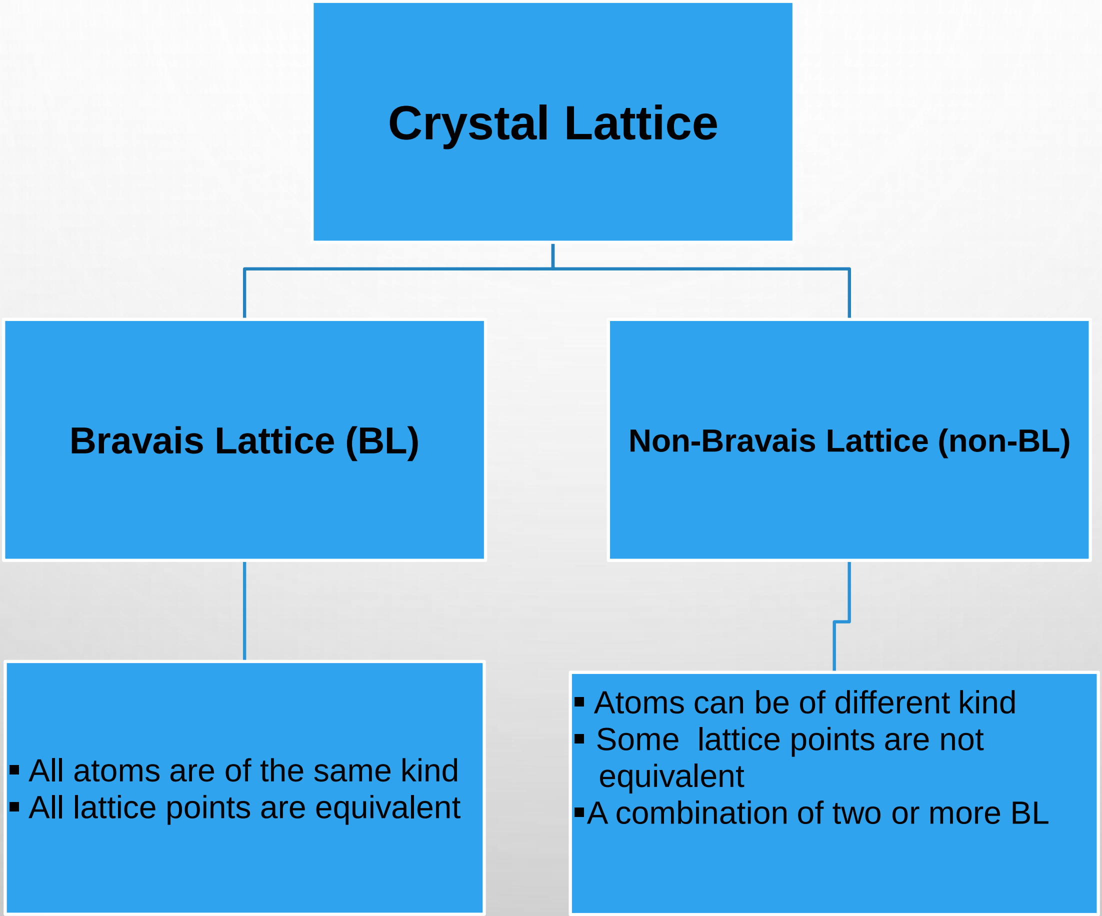
- there is an unlimited number of possible lattices, since there is no restriction on the lengths of the lattice translation vectors or on the angle between them. an **oblique lattice** has arbitrary **a1** and **a2** and is invariant only under rotation of π and 2 π about any lattice point.

Two-dimensional lattices, invariant under C_3, C_4 or C_6 rotations are classified into five categories:

5 Bravais lattice in 2D



Fundemental types of lattices



Crystal Lattice

Bravais Lattice (BL)

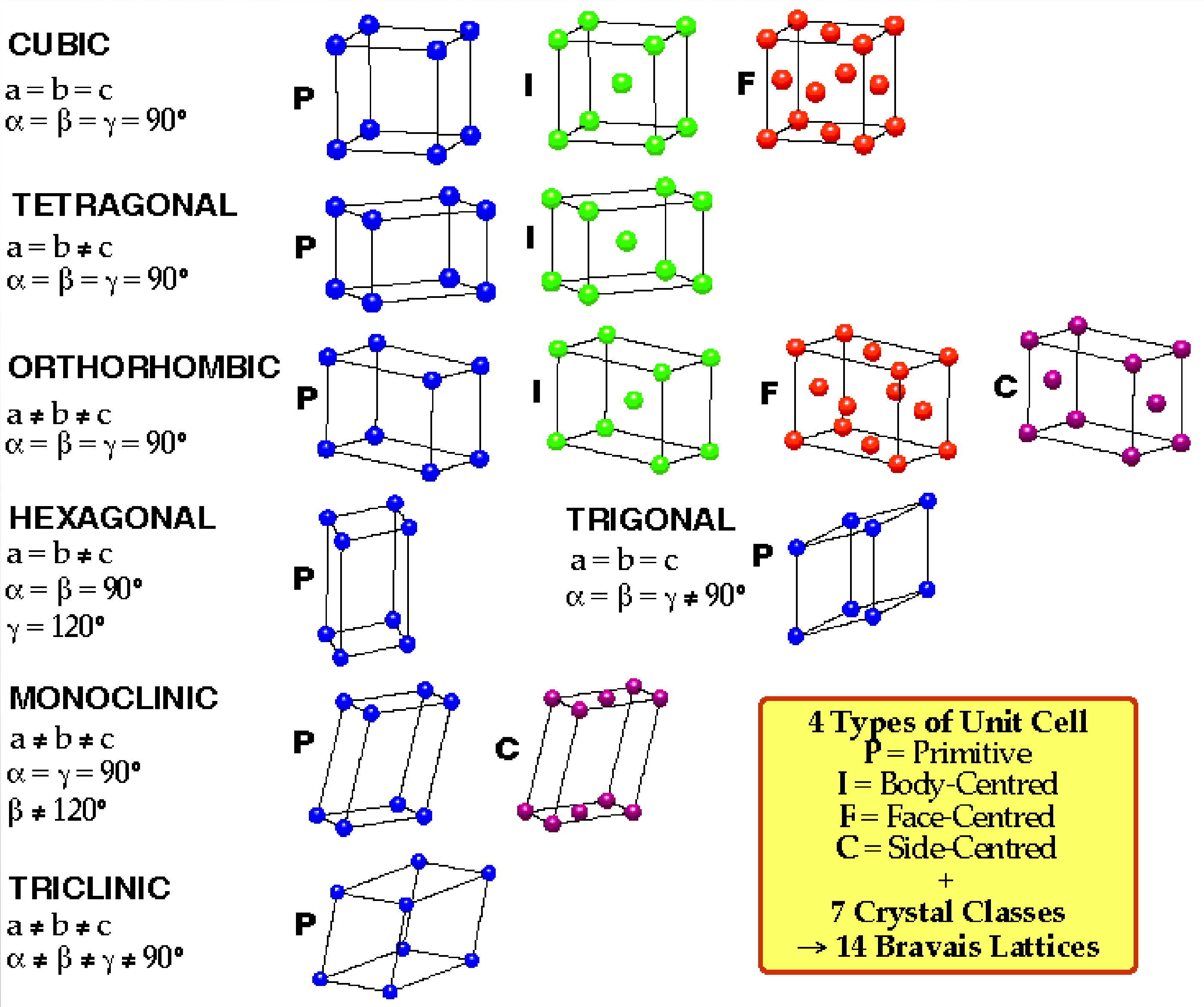
- All atoms are of the same kind
- All lattice points are equivalent

Non-Bravais Lattice (non-BL)

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

14 Bravais lattice in 3D

Crystals are grouped under seven systems on the basis of the shape of the unit cell.



Coordination number

- Coordination Number (CN) : The Bravais lattice points closest to a given point are the nearest neighbours.
- Because the Bravais lattice is periodic, all points have the same number of nearest neighbours or coordination number. It is a property of the lattice.
- A simple cubic has coordination number 6; a body-centered cubic lattice, 8; and a face-centered cubic lattice,12.

Atomic Packing Factor

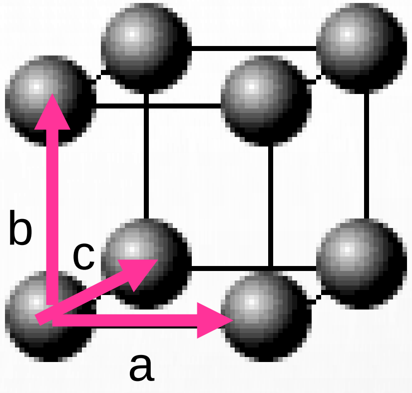
Atomic Packing Factor (APF) is defined as the volume of atoms within the unit cell divided by the volume of the unit cell.

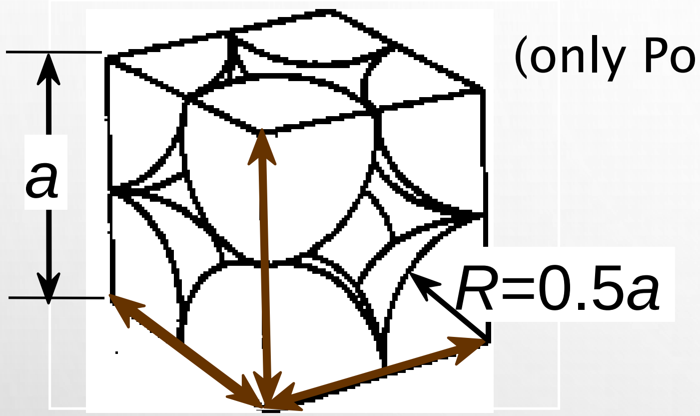
$$\text{APF} = \frac{\text{Volume of atoms in unit cell*}}{\text{Volume of unit cell}}$$

*assume hard spheres

Simple Cubic Structure (SC)

- Simple Cubic has one lattice point so its primitive cell.

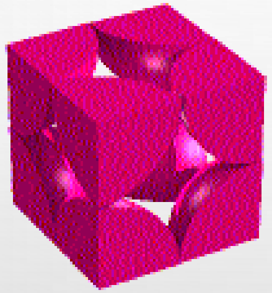




(only Po – Polonium -- has this structure)

close-packed directions

contains (8 x 1/8) =
1 atom/unit cell

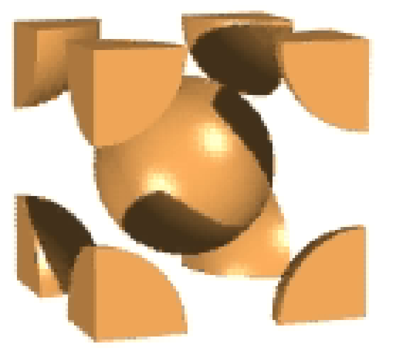


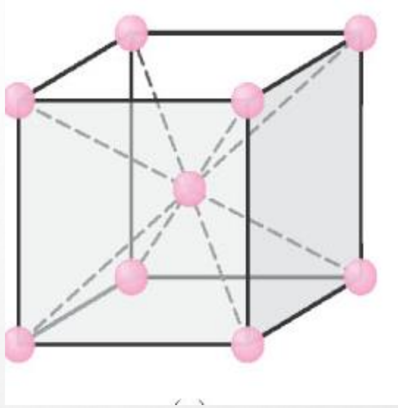
$$\text{APF} = \frac{\underbrace{1}_{\frac{\text{atoms}}{\text{unit cell}}}\ \underbrace{\frac{4}{3}\pi(0.5a)^3}_{\frac{\text{volume}}{\text{atom}}}}{\underbrace{a^3}_{\frac{\text{volume}}{\text{unit cell}}}}$$

- APF for a simple cubic structure = 0.52

Body catered Cubic Structure (BCC)

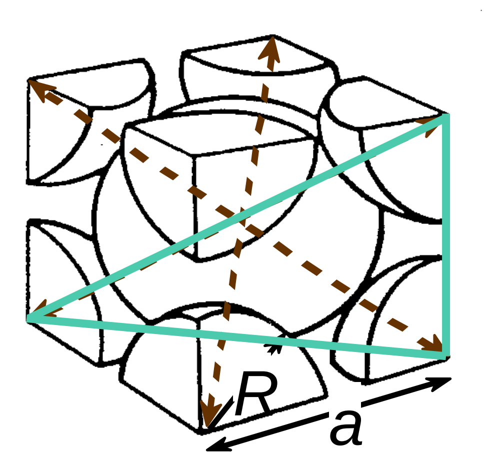
- BCC has two lattice points so BCC is a non-primitive cell.



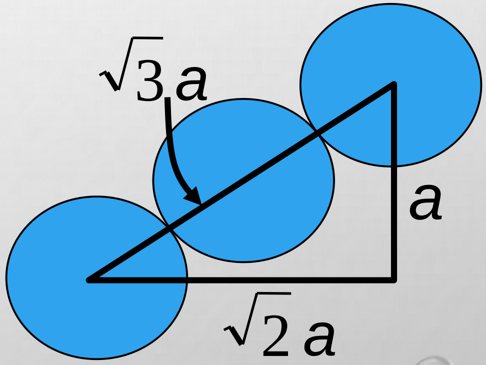


- BCC has eight nearest neighbors. Each atom is in contact with its neighbors only along the body-diagonal directions. (Coordination#)

ex: Cr, W, Fe (α), Tantalum, Molybdenum,



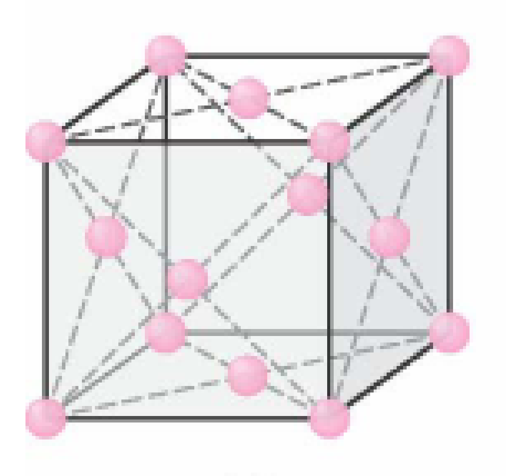
$$\text{APF} = \frac{\overbrace{2}^{\text{atoms}/\text{unit cell}}\ \overbrace{\frac{4}{3}\pi(\sqrt{3}a/4)^3}^{\text{volume}/\text{atom}}}{\underbrace{a^3}_{\text{volume}/\text{unit cell}}}$$



- APF for a body-centered cubic structure = 0.68

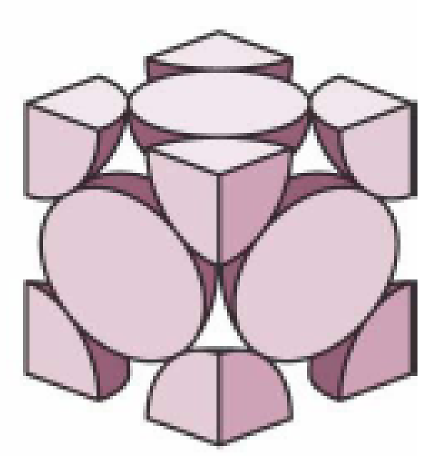
Face catered Cubic Structure (FCC)
Cubic Close Packed (ccp)

- ❑ There are atoms at the corners of the unit cell and at the centre of each face.
- ❑ Face centred cubic has 4 atoms so its non primitive cell.



ex: Al, Cu, Au, Pb, Ni, Pt, Ag

- ❑ Atoms touch each other along *face diagonals*.



Unit cell contains:

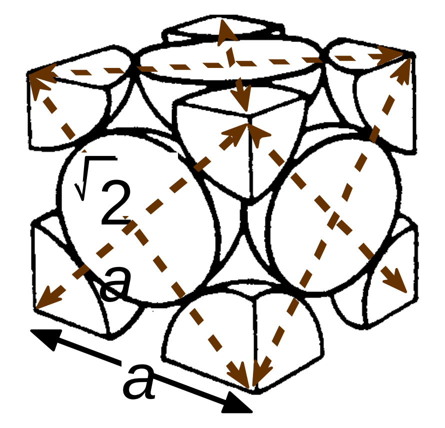
6 x 1/2 + 8 x 1/8

= 4 atoms/unit cell

$$\frac{\text{atoms}}{\text{unit cell}} \qquad \frac{\text{volume}}{\text{atom}}$$

$$\text{APF} = \frac{4 \;\; \frac{4}{3}\pi(\sqrt{2}a/4)^3}{a^3}$$

$$\frac{\text{volume}}{\text{unit cell}}$$



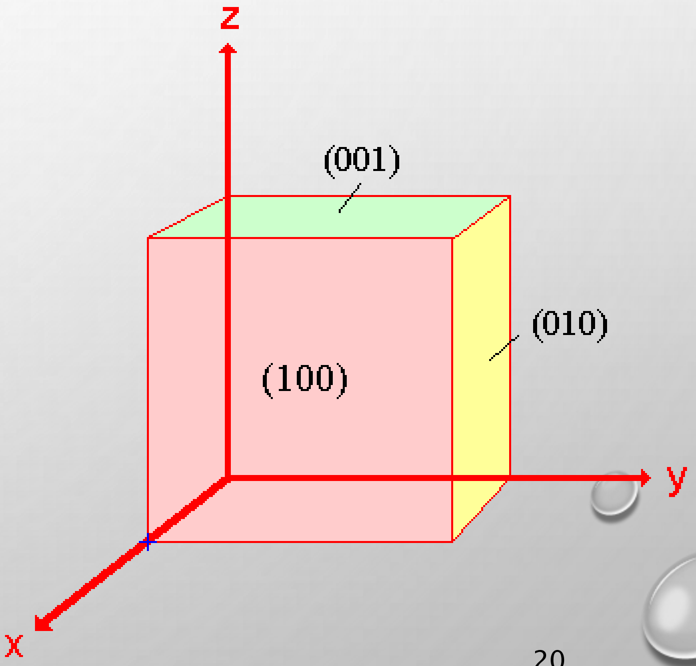
- APF for a face-centered cubic structure = 0.74

Basic definitions – Lattice sites

Define basic terms and give examples of each:

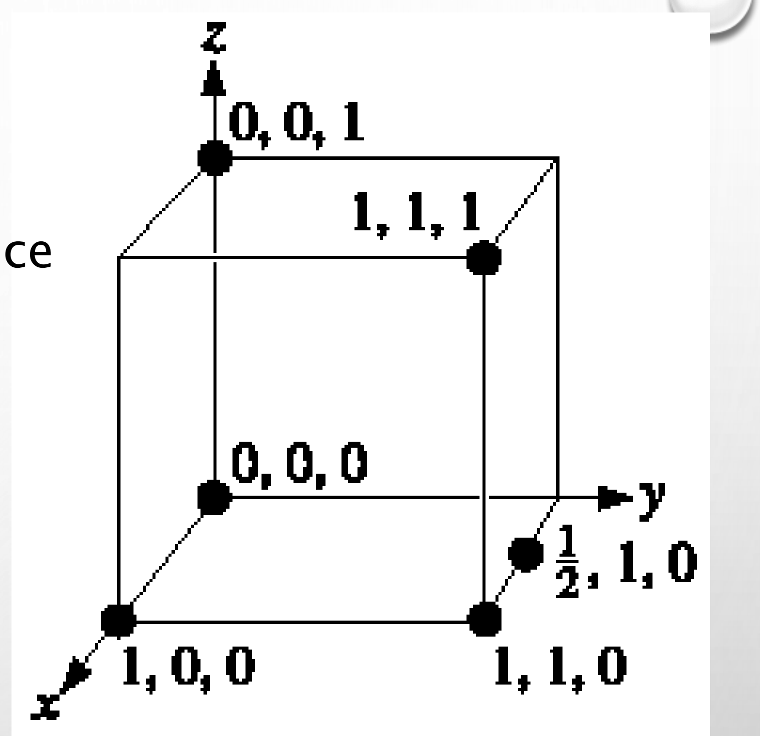
- **Points** (atomic positions)
- **Vectors** (defines a particular *direction - plane normal*)
- **Miller Indices** (defines a particular plane)
  - relation to diffraction
  - 3-index for cubic and 4-index notation for HCP

☐ Miller indices - A shorthand notation to describe certain crystallographic directions and planes in a material. Denoted by [ ], <>, ( ) brackets. A negative number is represented by a bar over the number.



Point Coordinates

- Coordinates of selected points in the unit cell.
- The number refers to the distance from the origin in terms of lattice parameters.



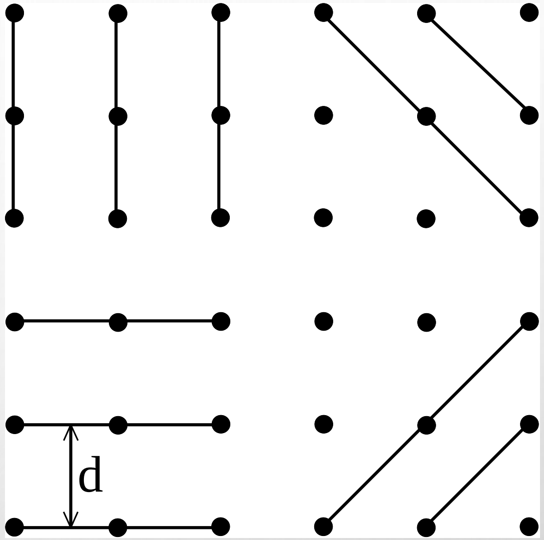
Point coordinates for unit cell center are

a/2, *b*/2, *c*/2 ½½½

Point coordinates for unit cell corner are 111

Miller Indices

- The orientation of planes or faces in a crystal can be described in terms of their intercepts on the three axes.
- Miller introduced a system to designate a plane in a crystal. It is a set of three numbers, to specify a plane in a crystal, known as '***Miller Indices***'
- Miller indices is defined as the reciprocals of the intercepts made by the plane on the three axes.
- An essential concept required to understand the diffraction of X-rays by crystal lattices (at least using the Bragg treatment) is the presence of planes and families of planes in the crystal lattice.



different lattice planes

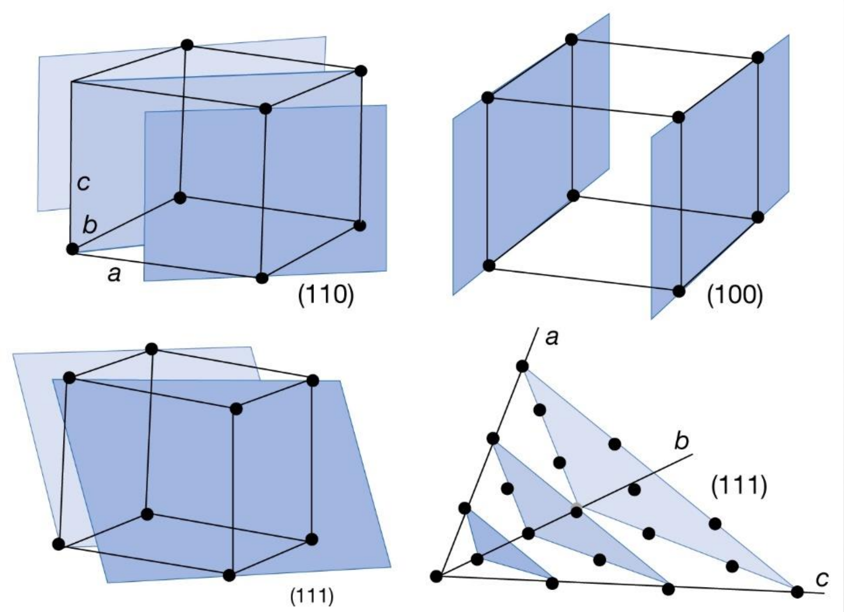
The orientation of planes is best represented by a vector normal to the plane. The direction of a set of planes is indicated by a vector denoted by square brackets containing the Miller indices of the set of planes. Miller indices are also used to describe crystal faces.

Procedure for finding Miller Indices

- **Step 1:** Determine the intercepts of the plane along the axes X,Y and Z in terms f the lattice constants a,b and c.

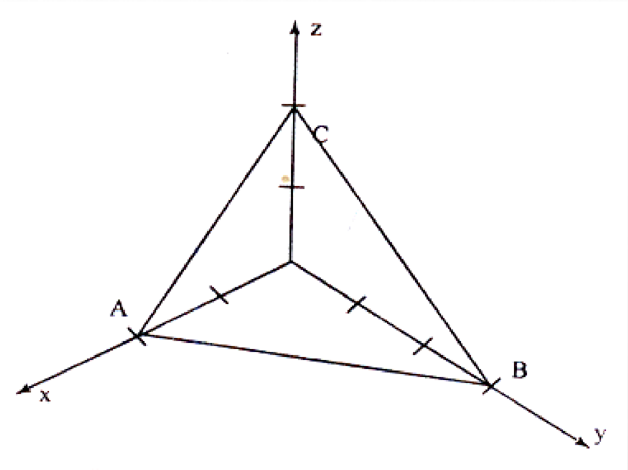
- **Step 2:** Determine the reciprocals of these numbers.

- **Step 3:** Find the least common denominator (*lcd*) and multiply each by this *lcd*.**OR** If fractions result, multiply each by the denominator of the smallest fraction.
- **Step 4:**The result is written in paranthesis. This is called the `Miller Indices' of the plane in the form (h k l).



Note: If a plane does not intersect an axis, the intercept would be ∞ and the reciprocal is 0.

Example



Step 1: The intercepts are 2,3 and 2 on the three axes.

Step 2: The reciprocals are 1/2, 1/3 and 1/2.

Step 3: The least common denominator is ‘6’.
Multiplying each reciprocal by lcd,
we get, 3,2 and 3.

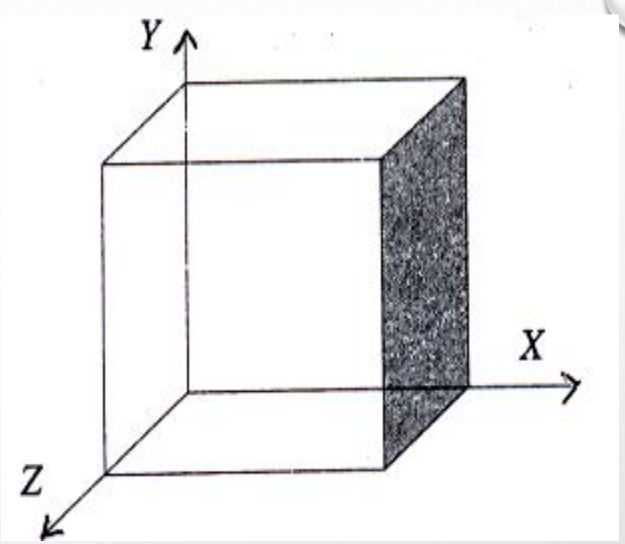
Step 4: Hence Miller indices for the plane ABC is (3 2 3)

Note: If a plane cuts an axis on the negative side of the origin, corresponding index is negative. It is represented by a bar, like $(\bar{1}\ 0\ 0)$. i.e. Miller indices $(\bar{1}\ 0\ 0)$ indicates that the plane has an intercept in the –ve X –axis.

Example

- In this plane, the intercept along X axis is 1 unit.
- The plane is parallel to Y and Z axes. So, the intercepts along Y and Z axes are '∞'.
- Now the intercepts are 1, ∞ and ∞.
- The reciprocals of the intercepts are = 1/1, 1/∞ and 1/∞.
- Therefore the Miller indices for this plane is (1 0 0).

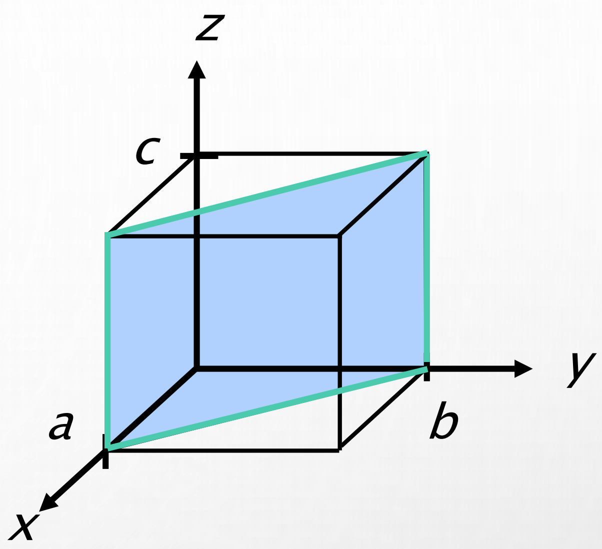
Note: It is only the ratio of the indices which is important in this notation. The (6 2 2) planes are the same as (3 1 1) planes.



Plane parallel to Y and Z axes

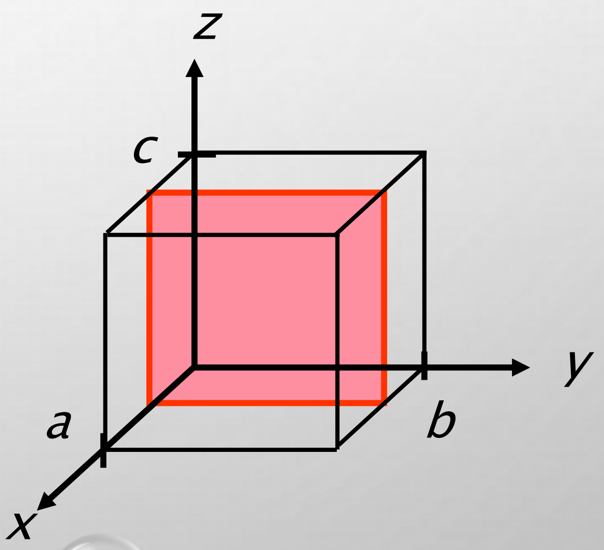
example	*a*	*b*	*c*
1. Intercepts	1	1	∞
2. Reciprocals	1/1	1/1	1/∞
	1	1	0
3. Reduction	1	1	0

4. Miller Indices (110)



example	*a*	*b*	*c*
1. Intercepts	1/2	∞	∞
2. Reciprocals	1/½	1/∞	1/∞
	2	0	0
3. Reduction	2	0	0

4. Miller Indices (200)



Family Of Planes

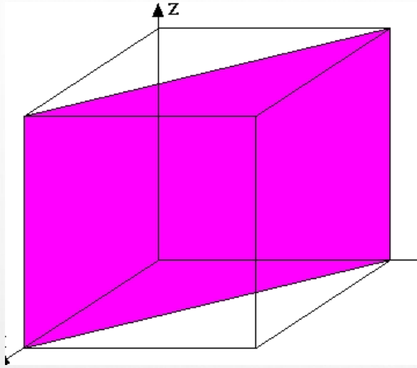
- Planes that are crystallographically equivalent have the same atomic packing.
- Also, in cubic systems only, planes having the same indices, regardless of order and sign, are equivalent.

- Ex: $\{111\}$

$$= (111),\ (11\bar{1}),\ (1\bar{1}1),\ (\bar{1}\bar{1}\bar{1}),\ (\bar{1}1\bar{1}),\ (\bar{1}\bar{1}1),\ (1\bar{1}\bar{1}),\ (\bar{1}11)$$

Ex: $\{100\} = (100)(0,10),(001),(\bar{1}00),(0\bar{1}0),(00\bar{1})$

Family of planes{1 1 0}



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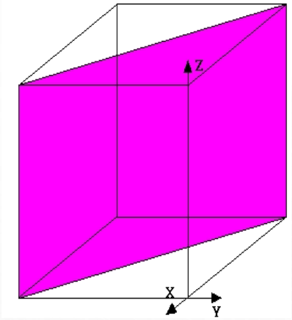
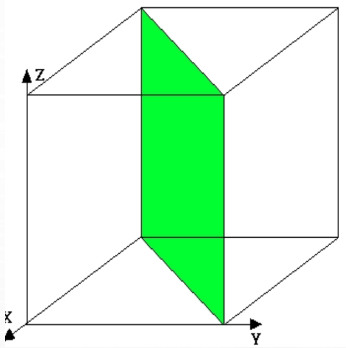
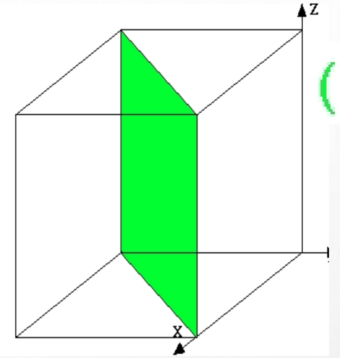


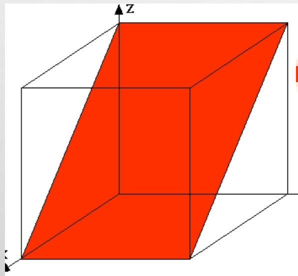
$(\bar{1}\bar{1}0)$



$(\bar{1}10)$



$(1\bar{1}0)$



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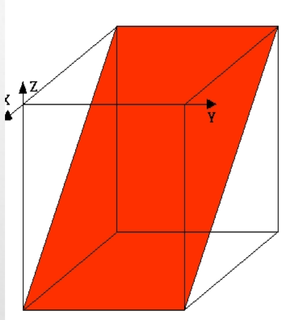
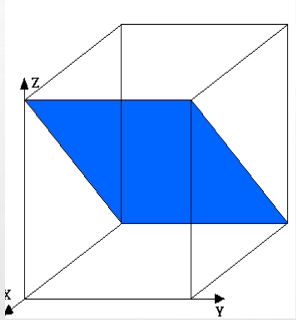
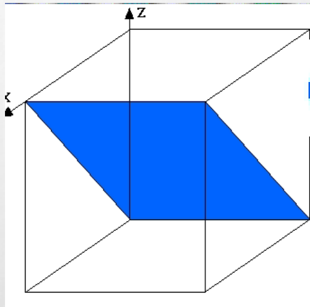


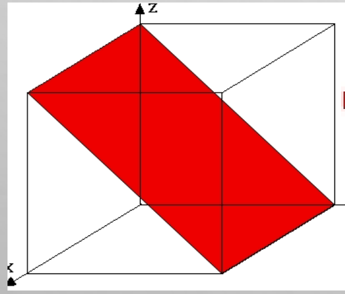
$(\bar{1}0\bar{1})$



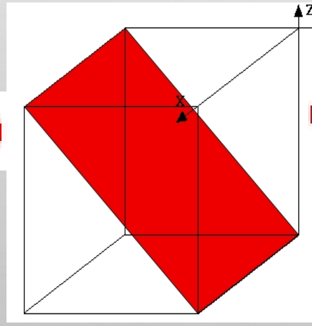
$(\bar{1}01)$



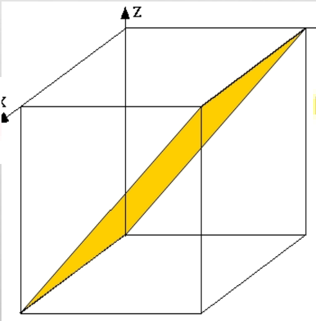
$(10\bar{1})$



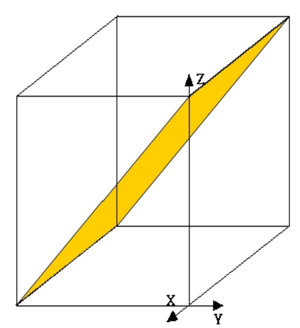
(011)



$(0\bar{1}\bar{1})$



$(01\bar{1})$



$(0\bar{1}1)$

Questions

1- Calculate the miller indices for the plane with intercepts 2a, - 3b and 4c the along the crystallographic axes. $\left(6\ \bar{4}\ 3\right)$

2- A certain crystal has lattice parameters of 4.24, 10 and 3.66 Å on X, Y, Z axes respectively. Determine the Miller indices of a plane having intercepts of 2.12, 10 and 1.83 Å on the X, Y and Z axes.

(4 2 4) or (2 1 2).

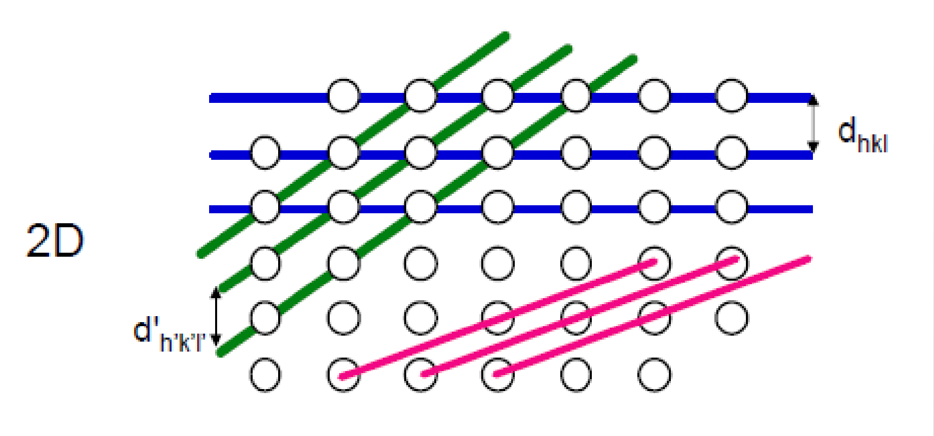
Interplanner distance

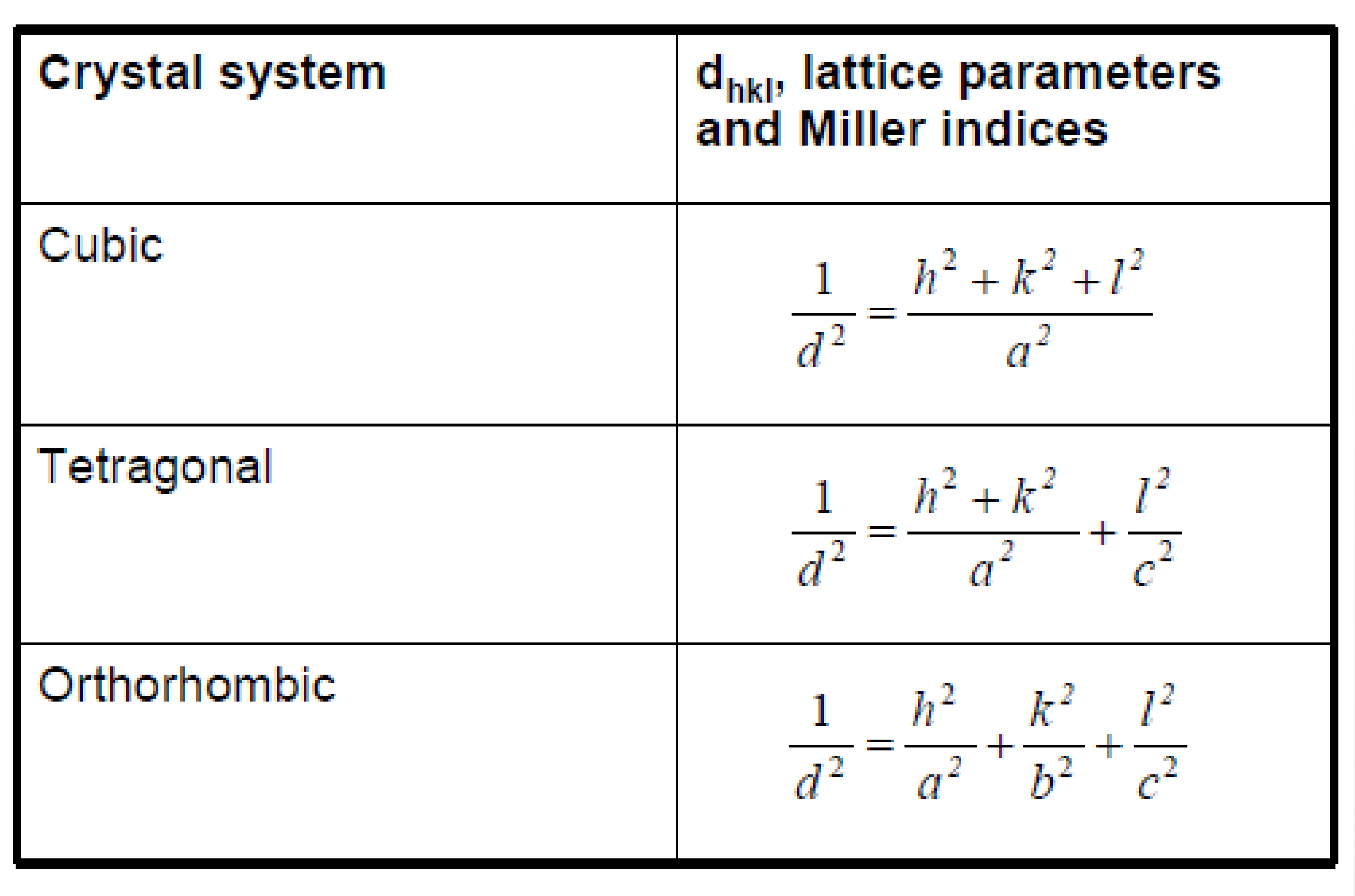
Distances between planes defined by the same set of Miller indices are unique for each material

The relation between the interplanar distance and the interatomic distance is given by,

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

for cubic crystal.





Crystal system	d_{hkl}, lattice parameters and Miller indices
Cubic	$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$
Tetragonal	$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$
Orthorhombic	$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$

The expressions for the remaining crystal systems are more complex

Example

The lattice constant for a unit cell of aluminum is 4.031Å Calculate the interplanar space of (2 1 1) plane.

a = 4.031 Å
(h k l) = (2 1 1)
Interplanar spacing

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{4.031 \times 10^{-10}}{\sqrt{2^2 + 1^2 + 1^2}}$$

∴ d = 1.6456 Å

Example

Find the perpendicular distance between the two planes indicated by the Miller indices (1 2 1) and (2 1 2) in a unit cell of a cubic lattice with a lattice constant parameter 'a'.

We know the perpendicular distance between the origin and the plane is (1 2 1)

$$d_1 = \frac{a}{\sqrt{h_1^2 + k_1^2 + l_1^2}} = \frac{a}{\sqrt{1^2 + 2^2 + 1^2}} = \frac{a}{\sqrt{6}}$$

and the perpendicular distance between the origin and the plane (2 1 2),

$$d_2 = \frac{a}{\sqrt{h_2^2 + k_2^2 + l_2^2}} = \frac{a}{\sqrt{2^2 + 1^2 + 2^2}} = \frac{a}{\sqrt{9}} = \frac{a}{3}$$

The perpendicular distance between the planes (1 2 1) and (2 1 2) are,

$$d = d_1 - d_2 = \frac{a}{\sqrt{6}} - \frac{a}{3} = \frac{3a - \sqrt{6}a}{3\sqrt{6}} = \frac{a(3 - \sqrt{6})}{3\sqrt{6}}$$

(or) **$d = 0.0749$ a.**

Questions

1- Copper has fcc structure. Radius of copper atom is 1.28 Å. Calculate the inter-planar distance for plane (111). [Hint: $a = 4R/\sqrt{2}$

2-What is the family of planes {hkl} with an interplanar spacing of $d = 1.246$ Å in nickel (Ni) with $a = 3.524$ Å?

Notation Summary

- (h,k,l) represents a point – note the exclusive use of commas
- Negative numbers/directions are denoted with a bar on top of the number
- [hkl] represents a direction
- <hkl> represents a family of directions
- (hkl) represents a plane
- {hkl} represents a family of planes