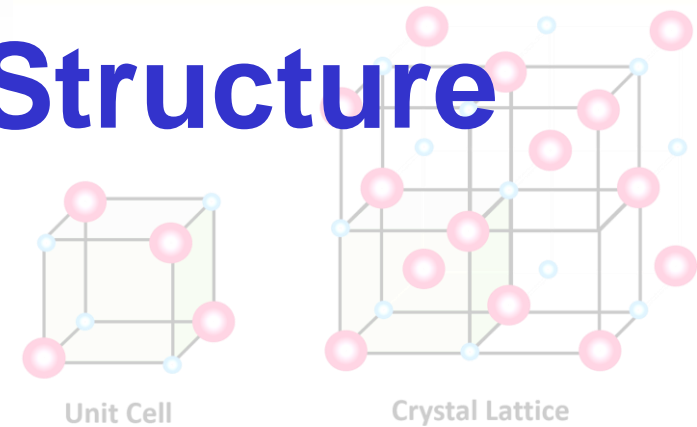




MS31007: Materials Science

Chapter 3 (Part-II): Crystal Structure



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Crystal Structure : Solid State Materials


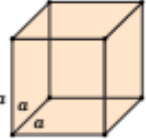

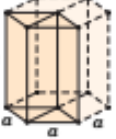

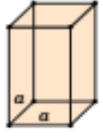



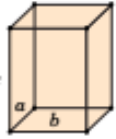

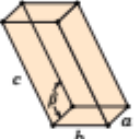

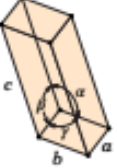
- Lattice structures of common chemical elements.
Concept of Bravais lattice, definition and examples.
Primitive vectors of Bravais lattice.
Primitive/Conventional unit cell.
- Coordination number.
- Examples of common crystal structures.
 - ☐ Body-centered cubic lattice.
 - ☐ Face-centered cubic lattice.
 - ☐ Crystal systems
 - ☐ Lattice planes and Miller indices.
- Ceramic Crystal Structures
- Determination of Lattice Spacing : X-ray Diffraction

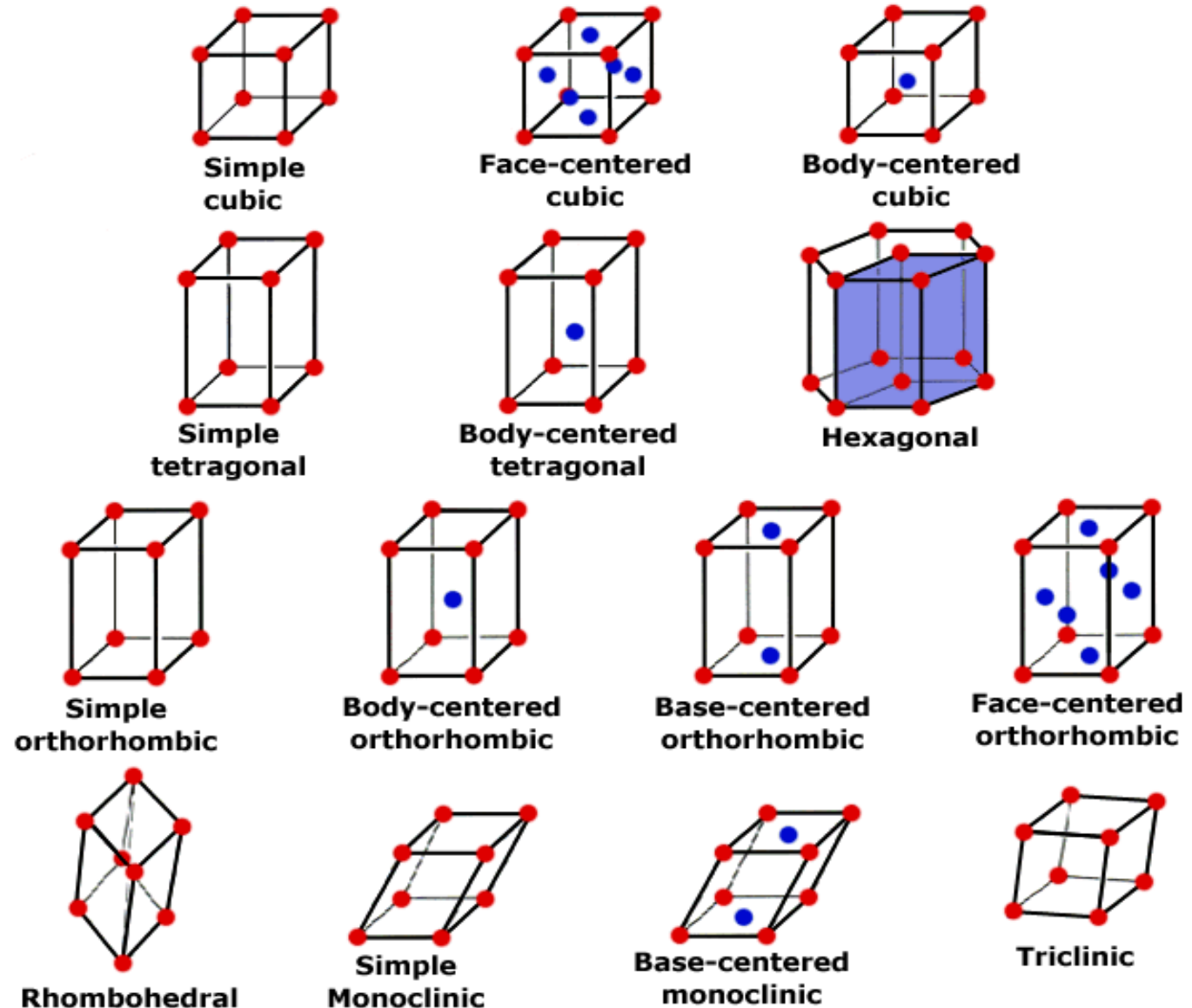




Bravais Lattice

14 types of unit cells under seven crystal systems

Crystal System	Axial Relationships	Interaxial Angles	Unit Cell Geometry
 Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	
 Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	
 Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
 Rhombohedral (Trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	
 Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	
 Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	
 Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	

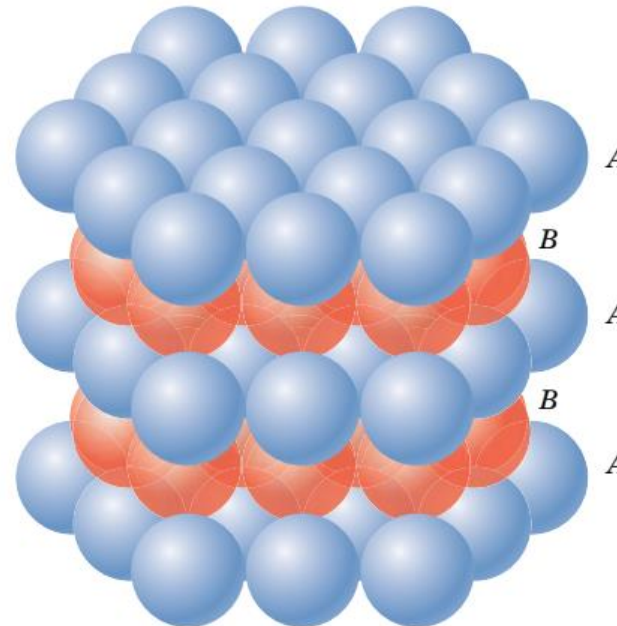
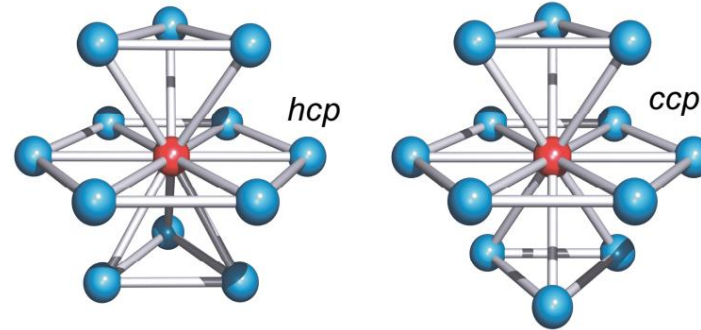
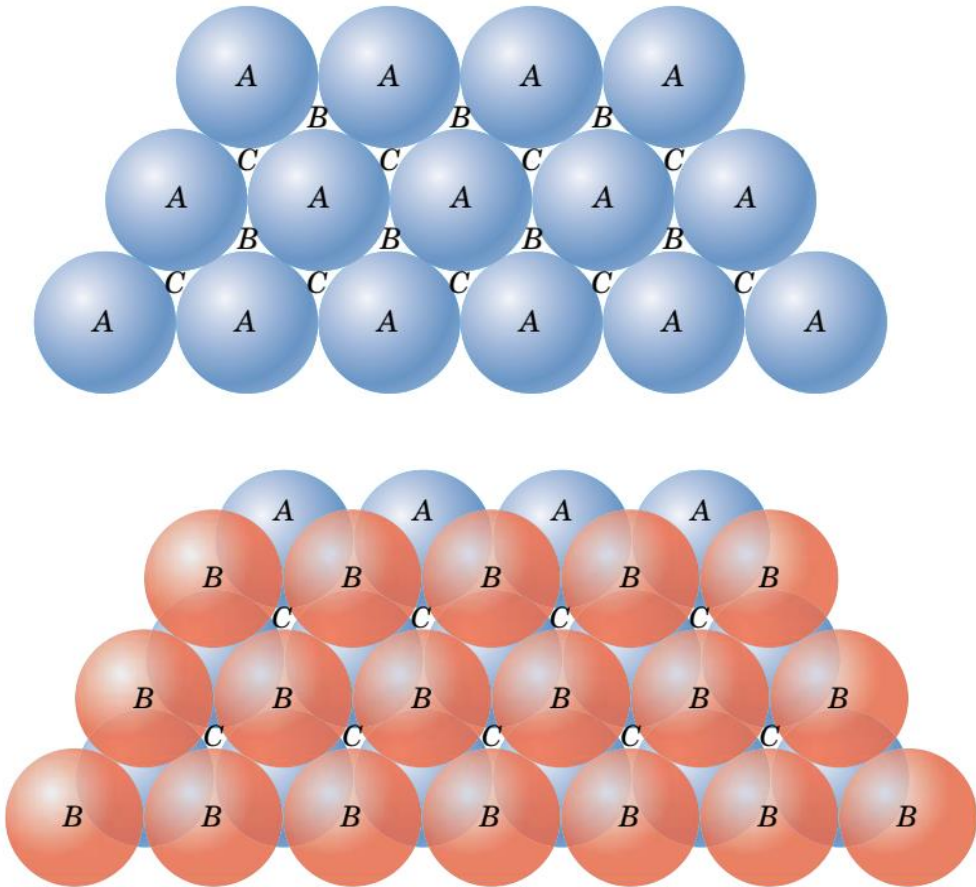




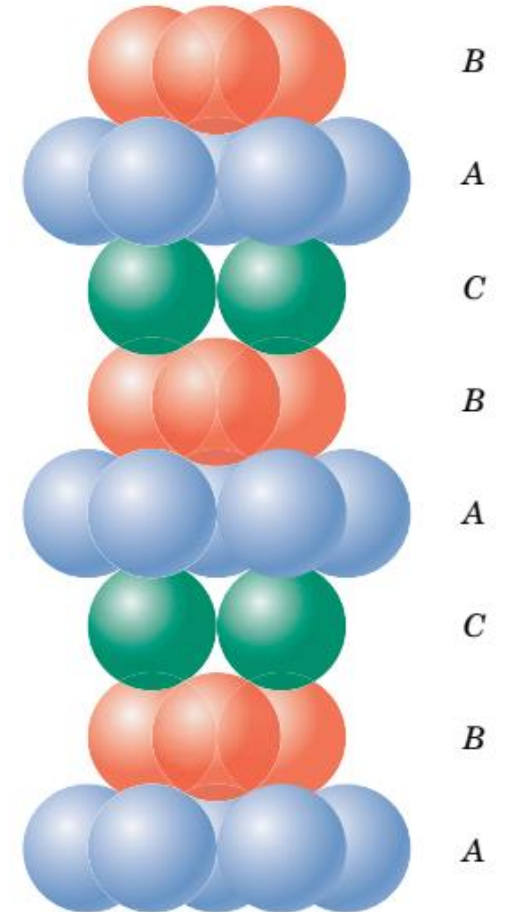
Close-packed Structures (FCC and HCP)

- ❑ Both FCC and HCP crystal structures have atomic packing factors of 0.74
- ❑ Both FCC and HCP crystal structures may be generated by the stacking of close-packed planes

The difference between the two structures is in the stacking sequence



HCP: ABABAB...

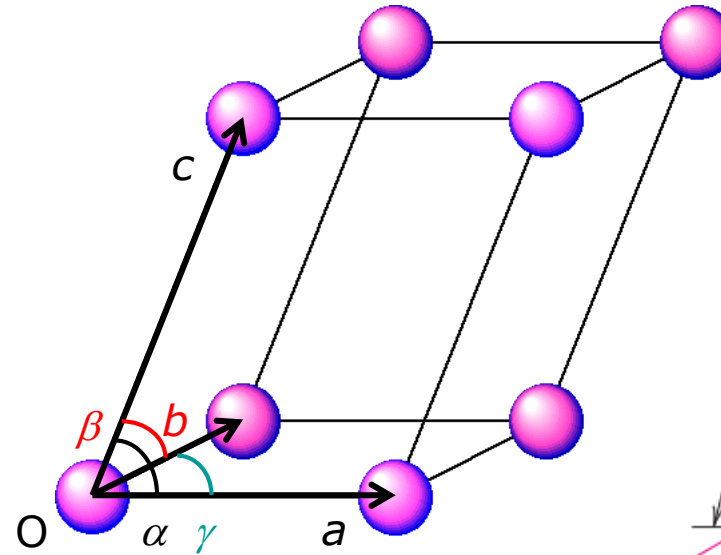
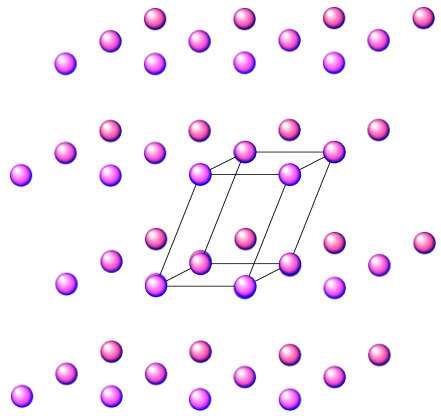


FCC: ABCABCABC...



Unit Cell : Point Coordinates

Unit cell in a crystal :



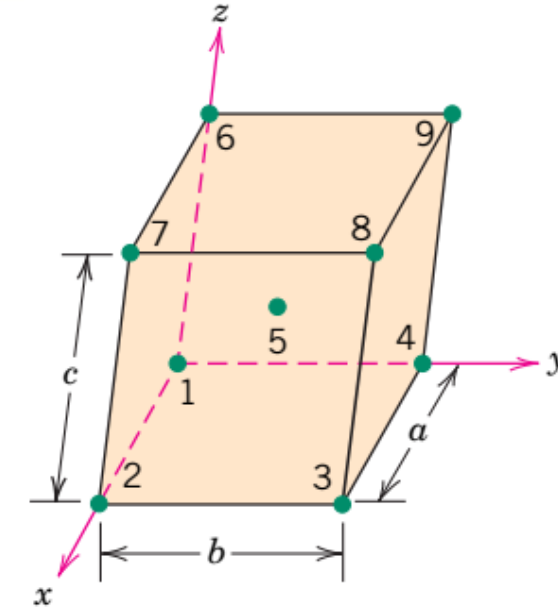
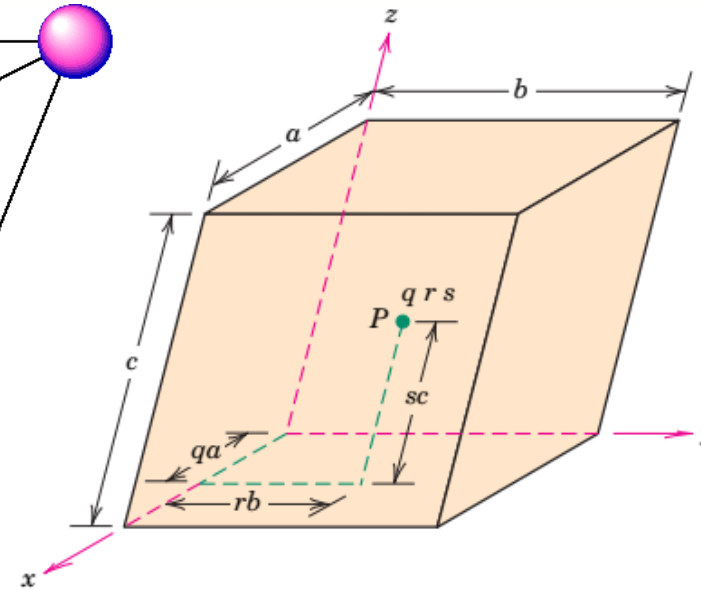
a , b and c : crystal axes

$|a|$, $|b|$, $|c|$, α , β and γ : lattice constants

- It is necessary to specify a lattice position using three *point coordinate indices*: q , r , and s .
- These indices are fractional multiples of a , b , and c unit cell edge lengths

a/q , b/r , c/s : ratios \rightarrow smallest integers

q , r and s : coordinates (\bar{u} : negative)



Point Number	q	r	s
1	0	0	0
2	1	0	0
3	1	1	0
4	0	1	0
5	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
6	0	0	1
7	1	0	1
8	1	1	1
9	0	1	1

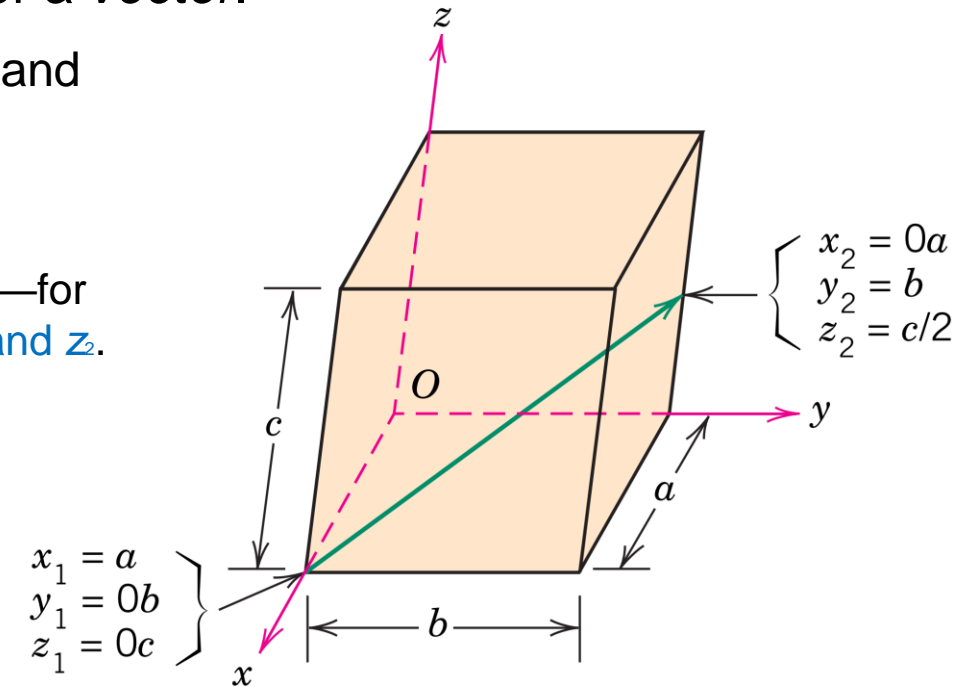


Directions in the Unit Cell

Crystallographic direction: a line directed between two points, or a *vector*.

Miller-indices - notation to describe certain crystallographic directions and planes in a material

1. **First construct** x-y-z coordinate system
2. The coordinates of two points that lie on the direction vector are determined—for example, **Point 1: x_1 , y_1 , and z_1** ; whereas for the vector head, **Point 2: x_2 , y_2 , and z_2** .
3. Tail point coordinates are subtracted from head point components—that is, **$x_2 - x_1$, $y_2 - y_1$, and $z_2 - z_1$** .
4. These coordinate differences are then normalized by a , b , and c lattice parameters



$$\frac{x_2 - x_1}{a} \quad \frac{y_2 - y_1}{b} \quad \frac{z_2 - z_1}{c}$$

$$u = n \left(\frac{x_2 - x_1}{a} \right)$$

$$v = n \left(\frac{y_2 - y_1}{b} \right)$$

$$w = n \left(\frac{z_2 - z_1}{c} \right)$$

$$x_2 = ua + x_1$$

$$y_2 = vb + y_1$$

$$z_2 = wc + z_1$$

5. Reduce them to the smallest integer values.
6. The three resulting **indices, $[uvw]$** . The u , v , and w integers correspond to the normalized coordinate differences referenced to the x , y , and z axes, respectively.





A direction in a unit cell

a , b and c : axes of coordinate/ lattice constants

a/u , b/v , c/w : ratios \rightarrow smallest integers

u , v and w : coordinates (\bar{u} : negative)

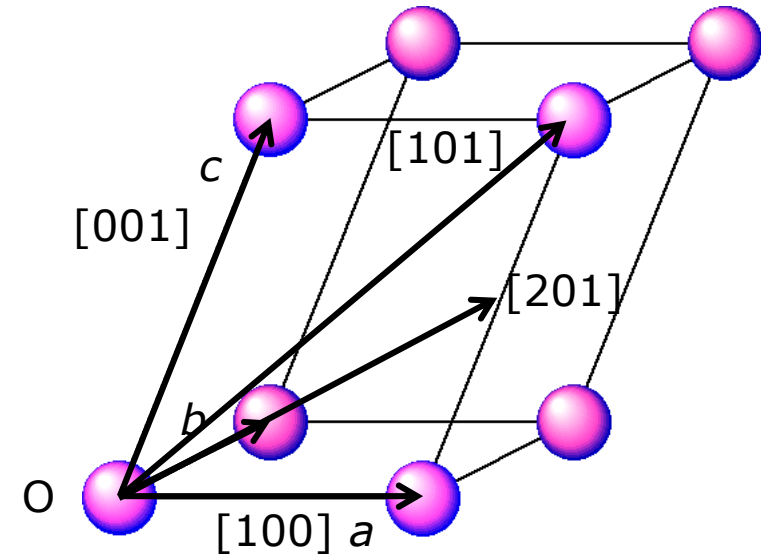
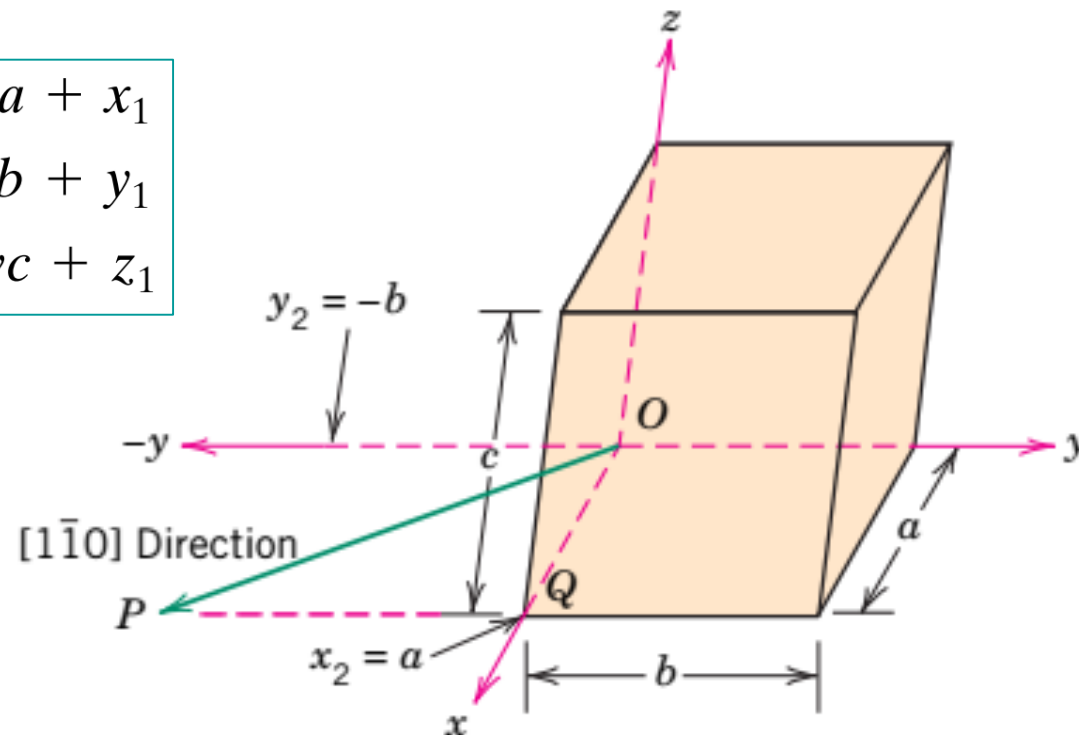
$[x\ y\ z]$: lattice directions

$\langle x\ y\ z \rangle$: directions of a form $\langle 100 \rangle = [100], [010], [001], \dots$

$$x_2 = ua + x_1$$

$$y_2 = vb + y_1$$

$$z_2 = wc + z_1$$



Construction of a Specified Crystallographic Direction

Within the following unit cell draw a $[1\bar{1}0]$ direction with its tail located at the origin of the coordinate system, point O.



Miller Indices : Indexing planes

Crystallographic planes are specified by three Miller indices as (hkl)

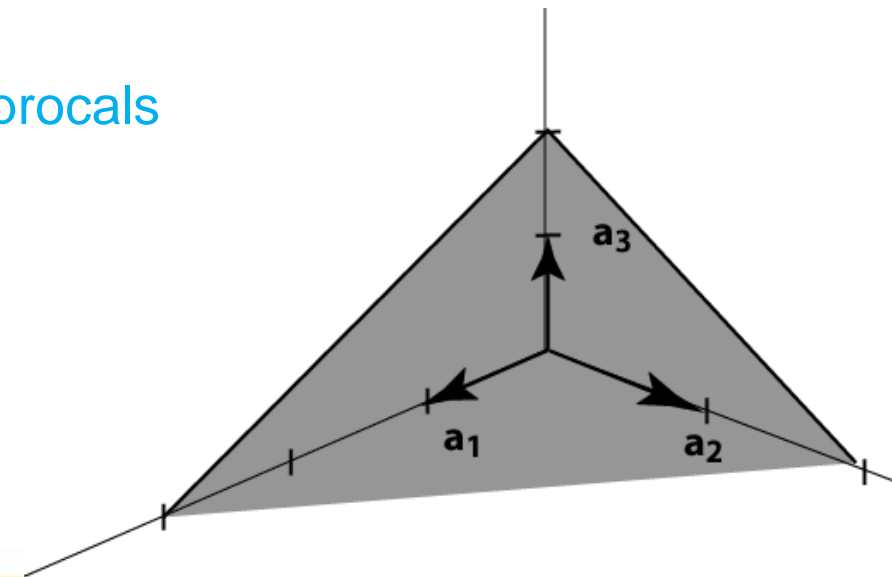
1. If the plane passes through the selected origin- a new origin must be established
2. Determine the coordinate for the intersection of the crystallographic plane with each of the axes. Designates the intercepts for the x , y , and z axes by A , B , and C , respectively.
3. The reciprocals of these numbers are taken. (plane that is parallel to an axis - zero index).
4. The reciprocals of the intercepts are then normalized respectively by a , b , and c lattice parameters.
5. It is necessary to change the numbers to a set of smallest integers
6. The integer indices are **Miller indices (hkl)** .

$$h = \frac{na}{A}$$
$$k = \frac{nb}{B}$$
$$l = \frac{nc}{C}$$

The h , k , and l integers correspond to the normalized intercept reciprocals referenced to the x , y , and z axes, respectively.

■ Miller index : example

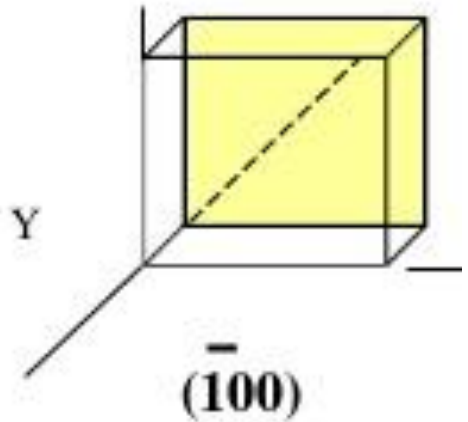
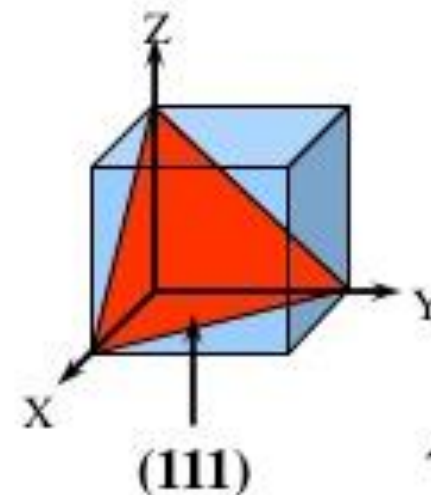
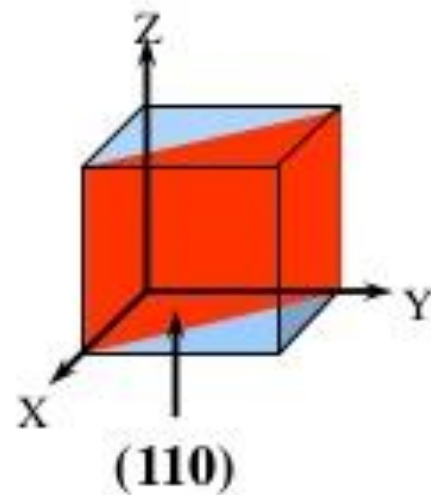
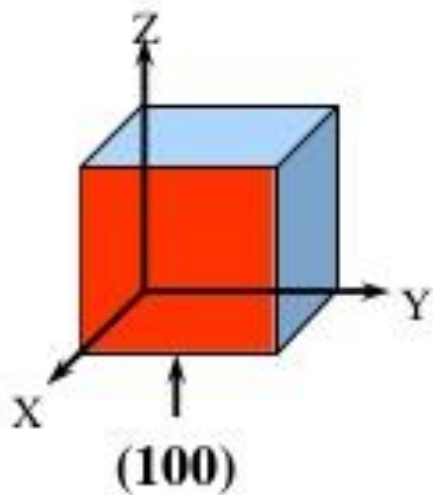
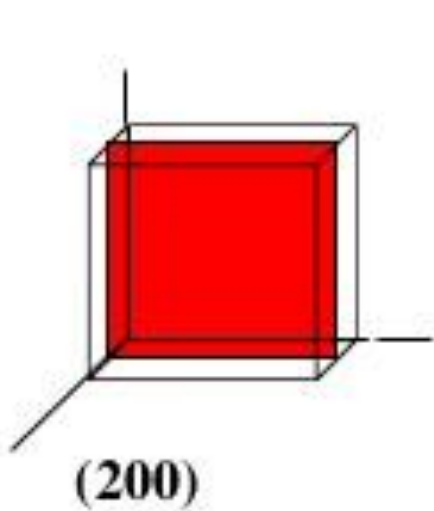
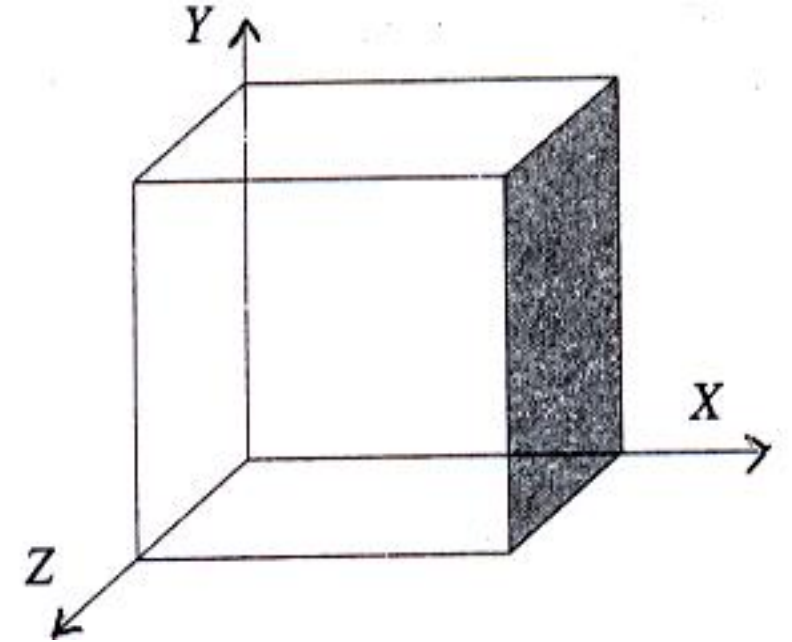
- plane intercepts axis : $3a_1$, $2a_2$, $2a_3$
- inverses : $1/3$, $1/2$, $1/2$
- integers : 2, 3, 3
- $h=2$, $k=3$, $l=3$
- Index of planes : $(2,3,3)$





Miller Indices : **Indexing planes**

- intercepts are **1, ∞ and ∞ .**
- reciprocals of the intercepts are **$1/1$, $1/\infty$ and $1/\infty$.**
- Miller indices for the plane is **(1 0 0).**

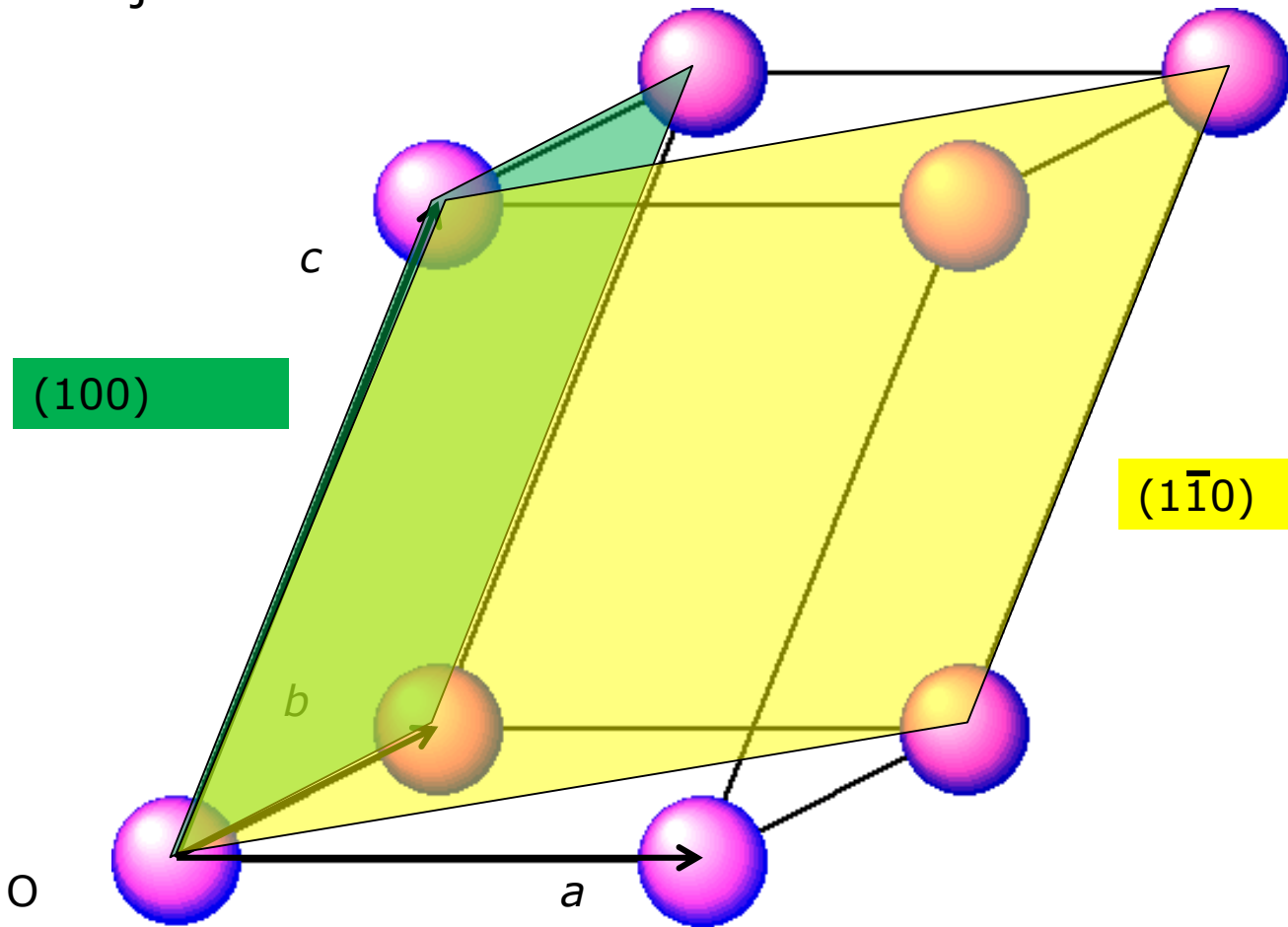




Miller Indices : A direction in a unit cell

In case a plane crossing the origin, then shift the origin to a new lattice point

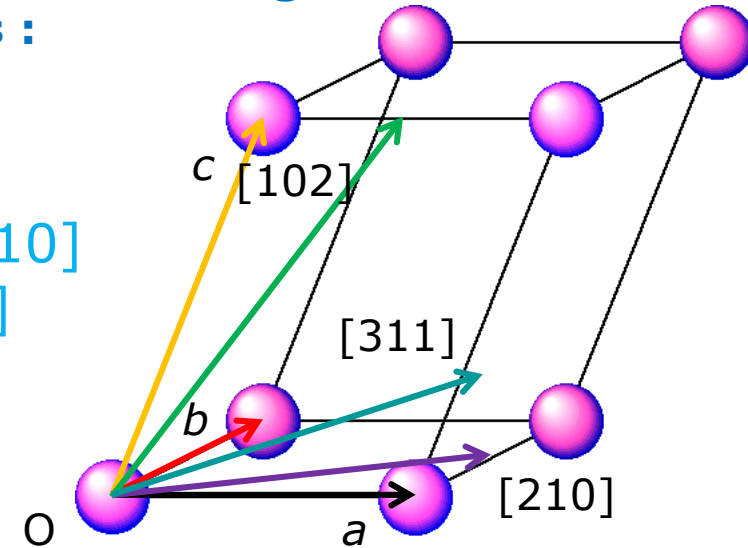
it is just a mathematical convenience !



$\{h\ k\ l\}$: planes of a form
 $\{100\} = (100), (010), (001), \dots$

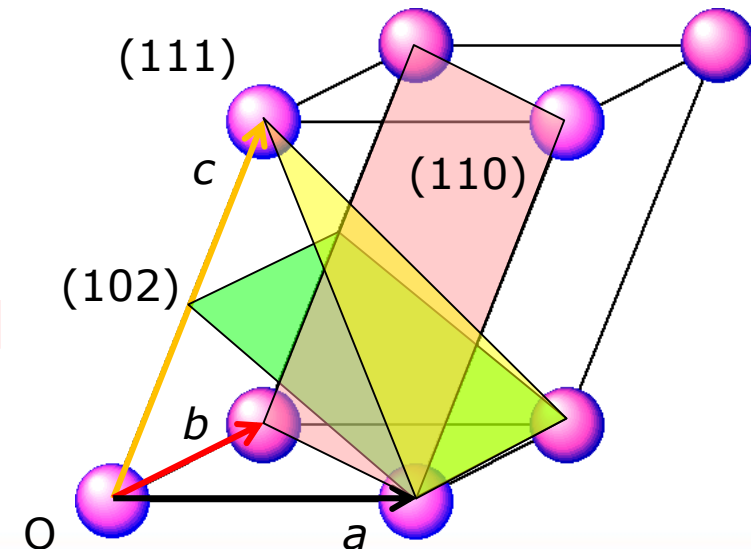
1. Indicate the following lattice orientations :

$[102]$, $[210]$
and $[311]$



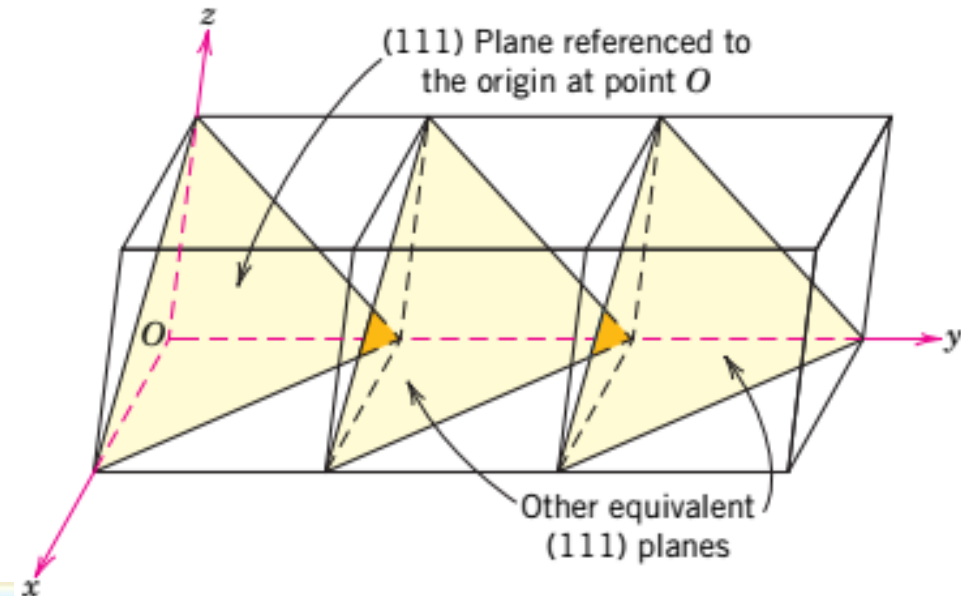
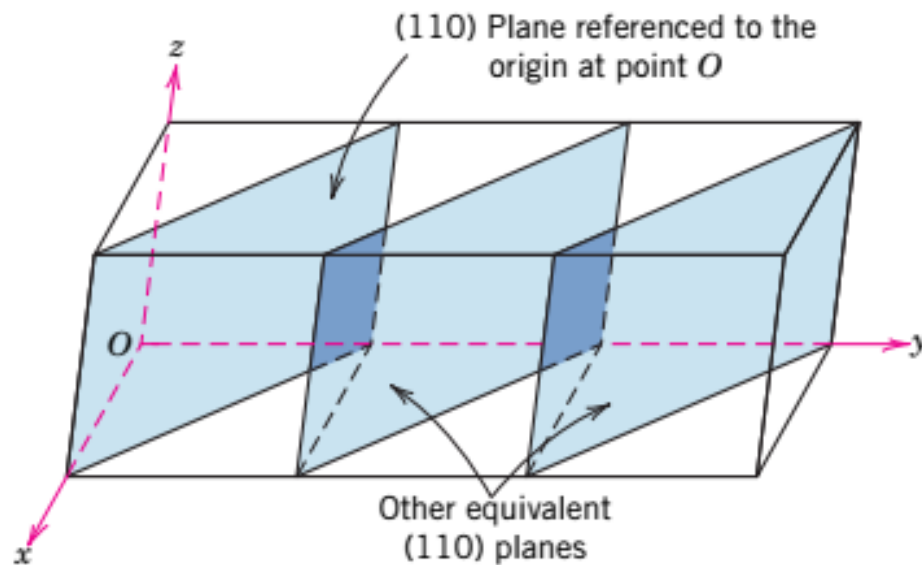
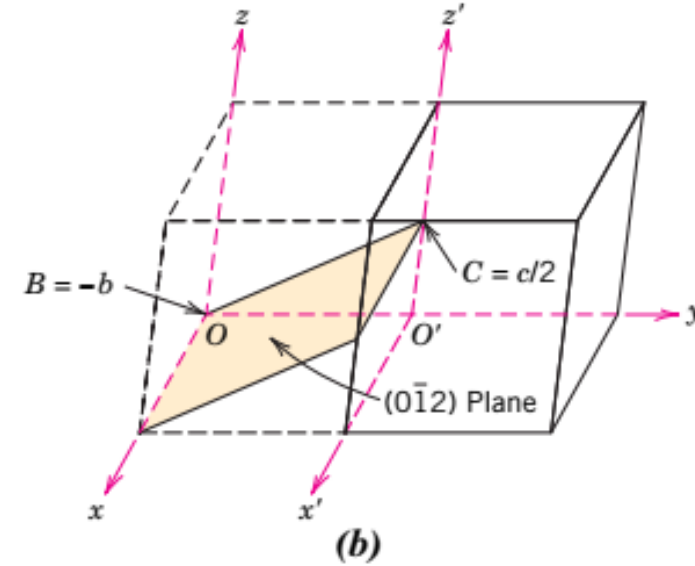
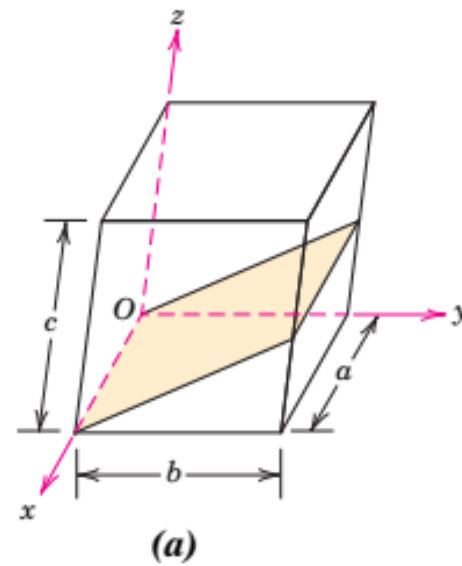
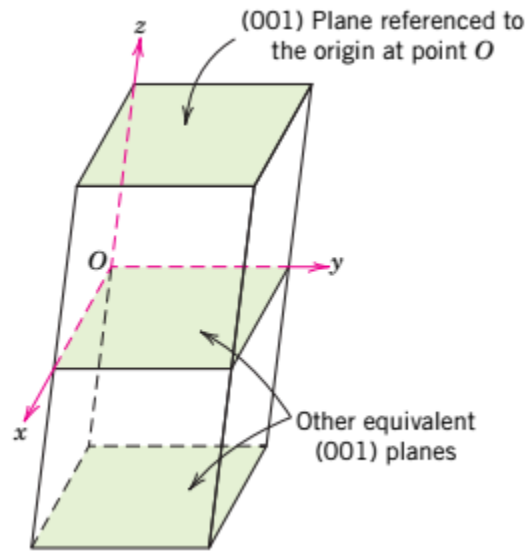
2. Indicate the following lattice planes :

(102) ,
 (110) and
 (111)





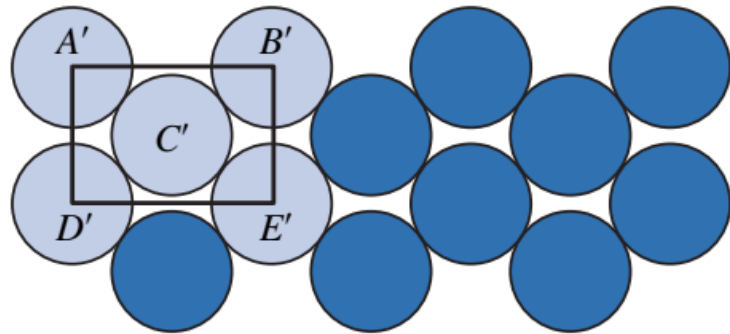
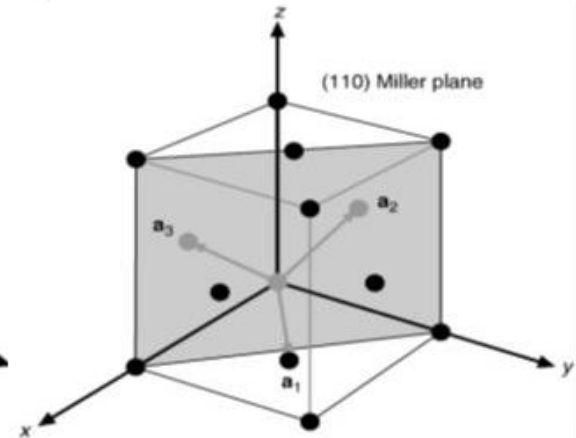
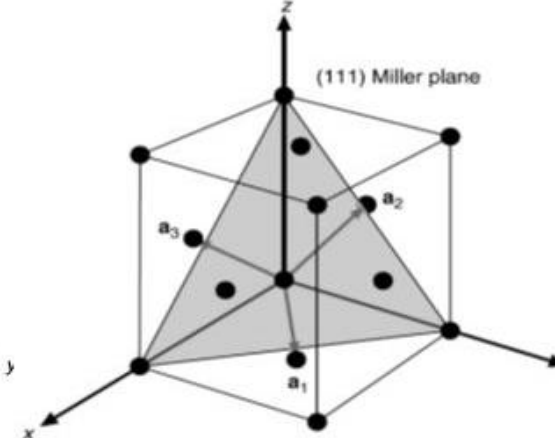
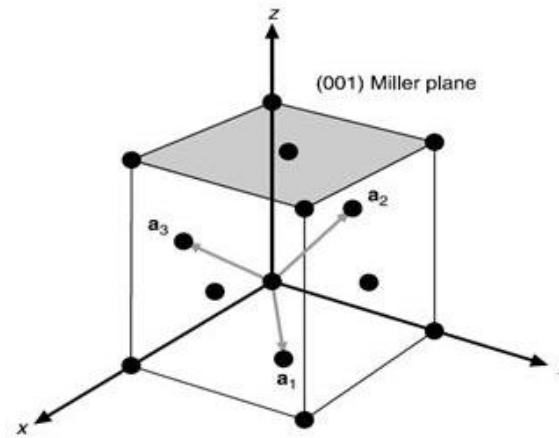
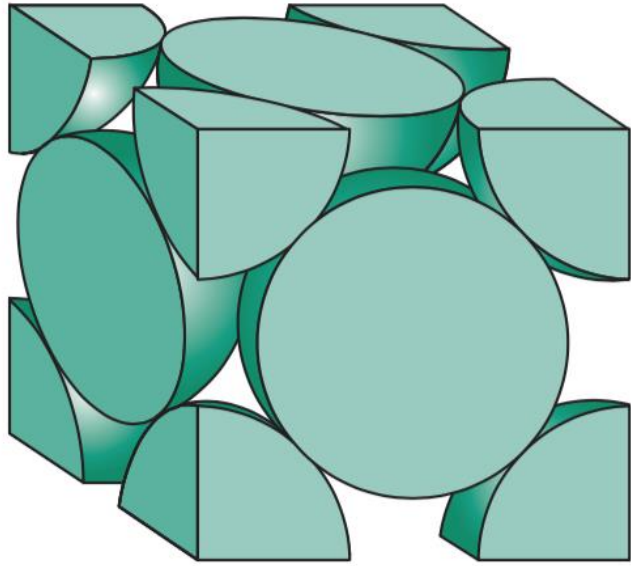
Miller Indices : A direction in a unit cell



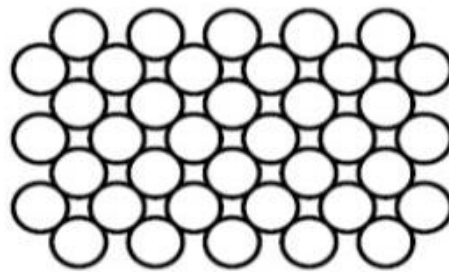


Atomic Arrangements

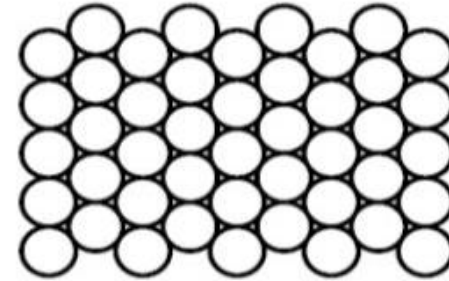
Different planes in FCC



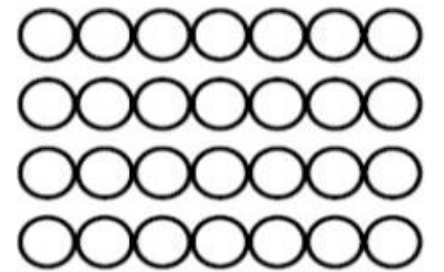
Top views



(100)



(111)



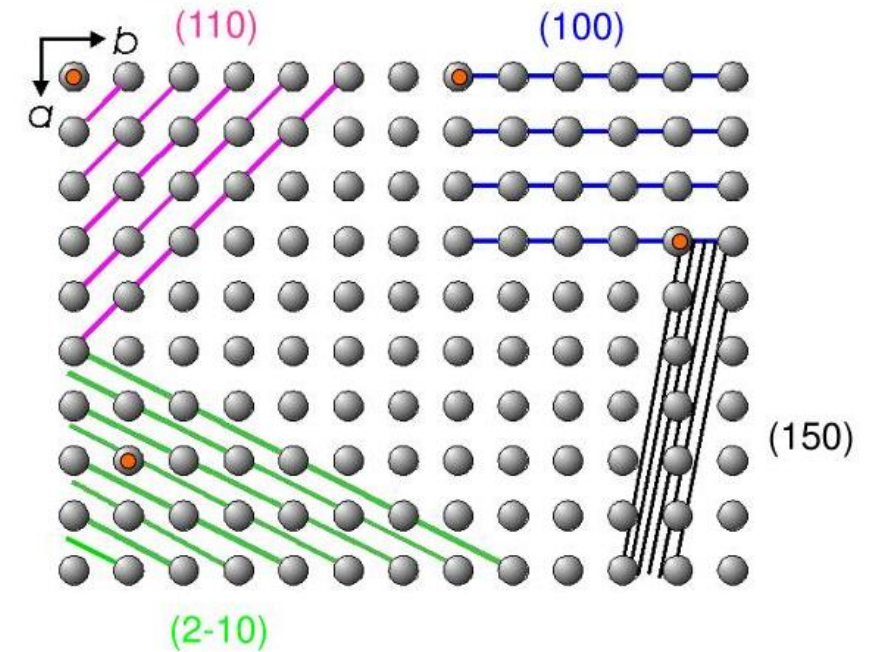
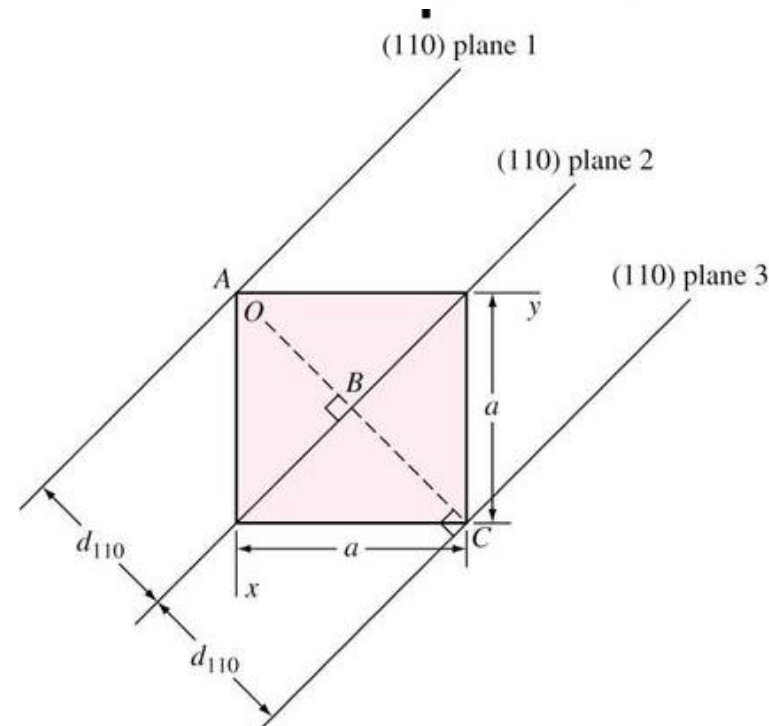
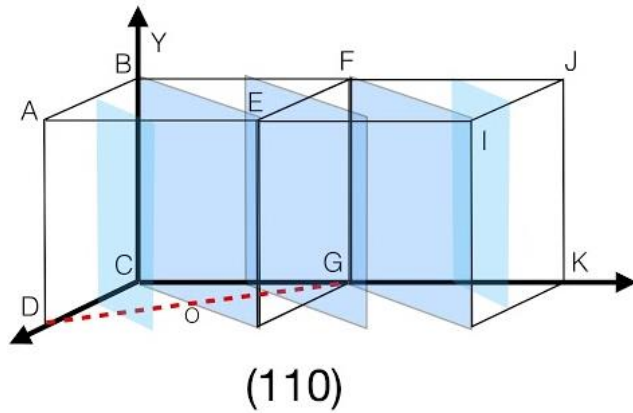
(110)



Distance Between parallel planes

What is Inter planar distance in Face Centred Cubic lattice.

Thus, the ratio of these inter planar distances for face centred cubic lattice can be given as,



- Interplanar spacing between parallel closest planes with same miller indices is given by

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

d_{hkl} = Interplanar spacing between parallel planes

a = Lattice constant

h, k, l = miller indices of cubic planes





Distance Between parallel planes

Cubic:

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Hexagonal:

$$\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2}$$

Rhombohedral:

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2) \sin^2 \alpha + 2(hk + kl + hl)(\cos^2 \alpha - \cos \alpha)}{a^2(1 - 3 \cos^2 \alpha + 2 \cos^3 \alpha)}$$

Orthorhombic:

$$\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

Monoclinic:

$$\frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left(\frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$$

$$S_{11} = b^2 c^2 \sin^2 \alpha$$

$$S_{22} = a^2 c^2 \sin^2 \beta$$

$$S_{33} = a^2 b^2 \sin^2 \gamma$$

Triclinic:

$$\frac{1}{d^2} = \frac{1}{V^2} \left(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl \right) \text{ where}$$

$$S_{12} = abc^2(\cos \alpha \cos \beta - \cos \gamma)$$

$$S_{23} = a^2 bc(\cos \beta \cos \gamma - \cos \alpha)$$

$$S_{13} = ab^2 c(\cos \gamma \cos \alpha - \cos \beta)$$

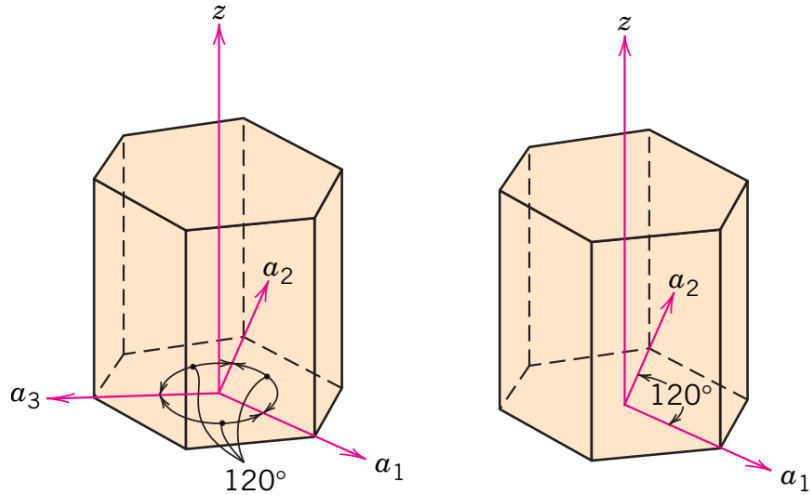




Miller Indices for Hexagonal Crystal : **Directions**

Some equivalent crystallographic directions do not have the same set of indices.

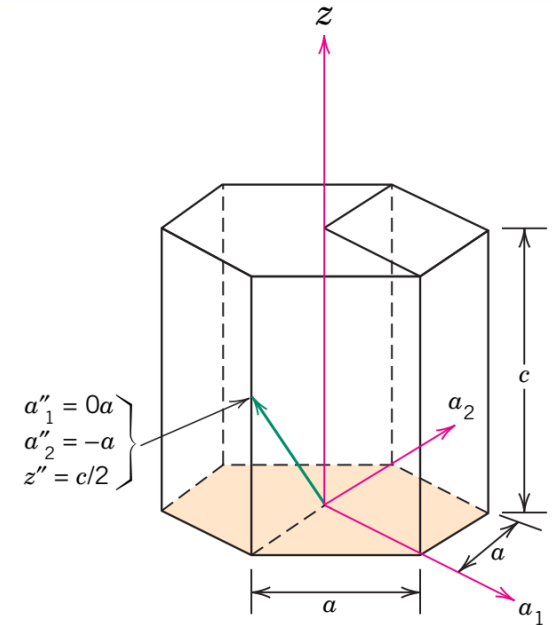
Using a four-axis, or *Miller–Bravais*, coordinate system



$$U = n \left(\frac{a_1'' - a_1'}{a} \right)$$

$$V = n \left(\frac{a_2'' - a_2'}{a} \right)$$

$$W = n \left(\frac{z'' - z'}{c} \right)$$



Conversion from the **three-index system** : (a_1 – a_2 – z coordinate axes) to the **four-index system**

$$u = \frac{1}{3}(2U - V)$$

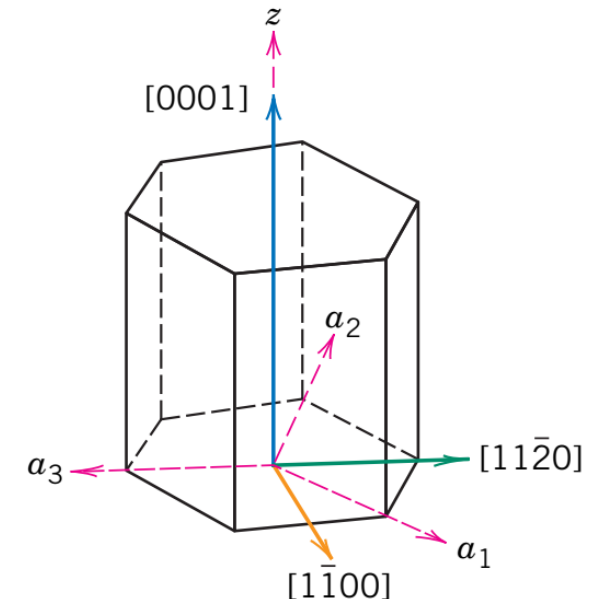
$$v = \frac{1}{3}(2V - U)$$

$$t = -(u + v)$$

$$w = W$$

$$[UVW] \rightarrow [uvw]$$

the u , v , and t relate to vector coordinate differences referenced to the respective a_1 , a_2 , and a_3 axes in the basal plane, the fourth index pertains to the z axis.





Problem : Determination of Directional Indices for a Hexagonal Unit Cell

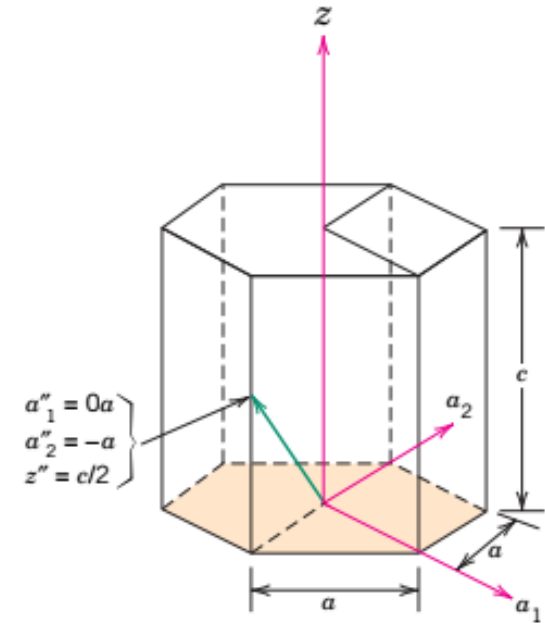
For the direction shown in the accompanying figure, do the following:

- Determine the directional indices referenced to the three-axis coordinate system of Figure.
- Convert these indices into an index set referenced to the four-axis scheme.

Solution

The first thing we need to do is determine U , V , and W indices for the vector referenced to the three-axis scheme represented in the sketch;

Because the vector passes through the origin, $a'_1 = a'_2 = 0a$ and $z' = 0c$.



3 index

$$a''_1 = 0a$$

$$a''_2 = -a$$

$$z'' = \frac{c}{2}$$

$n=2$



$$U = n \left(\frac{a''_1 - a'_1}{a} \right) = 2 \left(\frac{0a - 0a}{a} \right) = 0$$

$$V = n \left(\frac{a''_2 - a'_2}{a} \right) = 2 \left(\frac{-a - 0a}{a} \right) = -2$$

$$W = n \left(\frac{z'' - z'}{c} \right) = 2 \left(\frac{c/2 - 0c}{c} \right) = 1$$



4 index

$$u = \frac{1}{3}(2U - V) = \frac{1}{3}[(2)(0) - (-2)] = \frac{2}{3}$$

$$v = \frac{1}{3}(2V - U) = \frac{1}{3}[(2)(-2) - 0] = -\frac{4}{3}$$

$$t = -(u + v) = -\left(\frac{2}{3} - \frac{4}{3}\right) = \frac{2}{3}$$

$$w = W = 1$$



the direction vector $[\bar{2}4\bar{2}3]$.



Miller Indices for Hexagonal Crystal : Plane

Hexagonal symmetry, the convention leads to the four-index **(*h k i l*)**

$$i = -(h + k)$$

$$i = -(h + k) = -[1 + (-1)] = 0$$

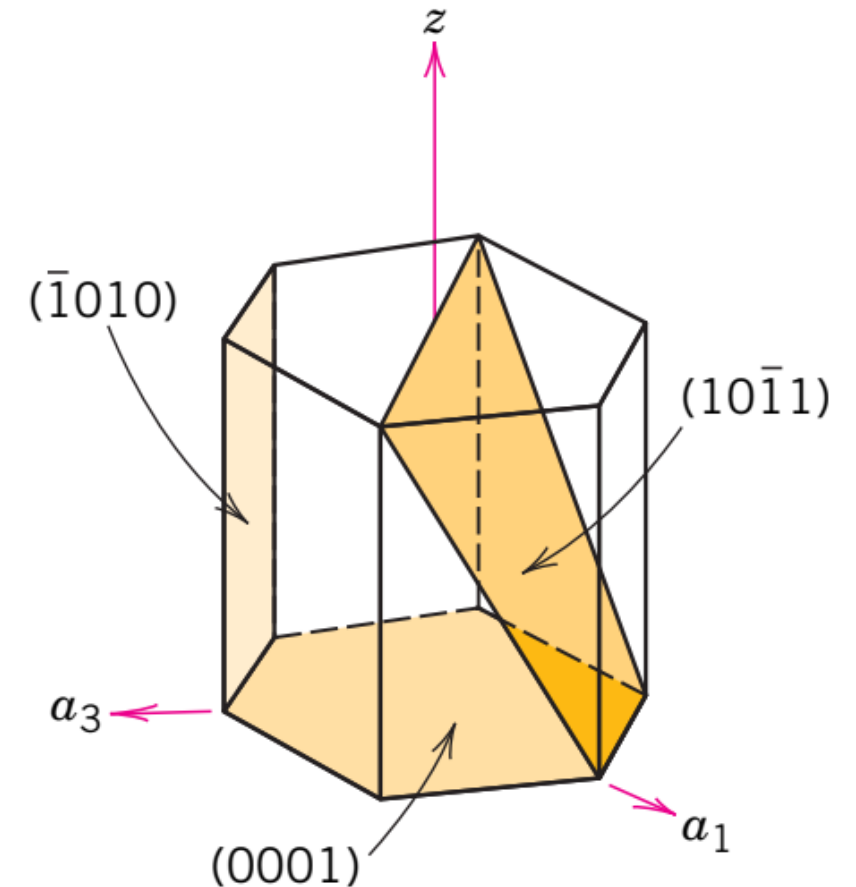
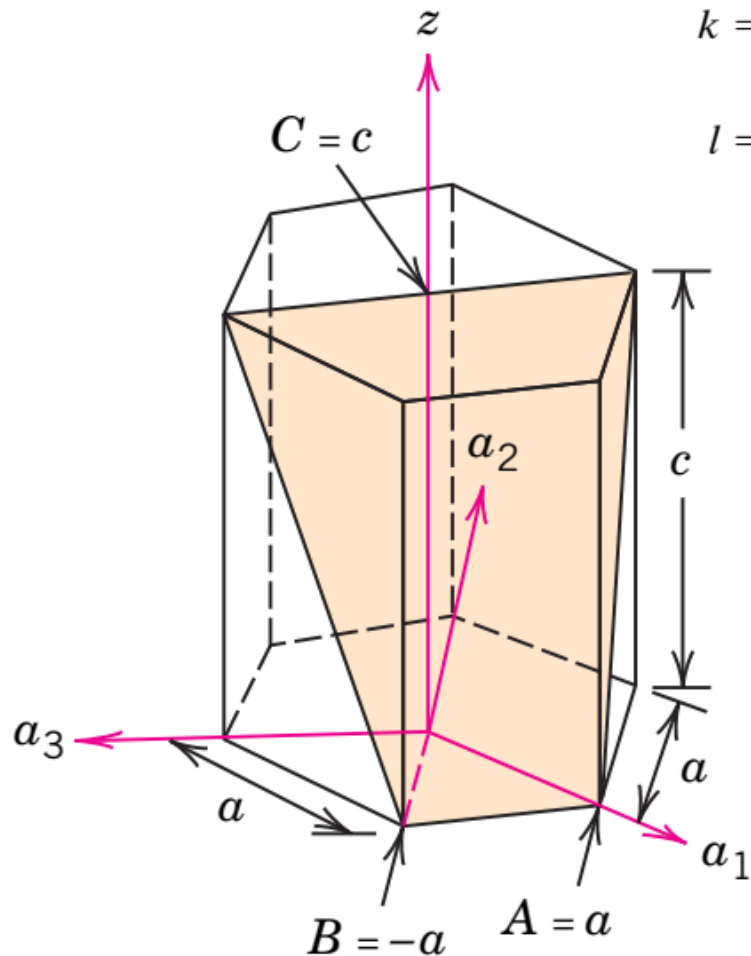
(*h k i l*) indices are ($1\bar{1}01$)

$$\frac{a}{A} \quad \frac{a}{B} \quad \frac{c}{C}$$

$$h = \frac{na}{A} = \frac{(1)(a)}{a} = 1$$

$$k = \frac{na}{B} = \frac{(1)(a)}{-a} = -1$$

$$l = \frac{nc}{C} = \frac{(1)(c)}{c} = 1$$





Summary of Equations Used to Determine Crystallographic Point, Direction, and Planar Indices

<i>Coordinate Type</i>	<i>Index Symbols</i>	<i>Representative Equation^a</i>	<i>Equation Symbols</i>
Point	$q\ r\ s$	qa = lattice position referenced to x axis	—
Direction			
Non-hexagonal	$[uvw]$	$u = n \left(\frac{x_2 - x_1}{a} \right)$	x_1 = tail coordinate— x axis x_2 = head coordinate— x axis
Hexagonal	$[UVW]$	$U = n \left(\frac{a_1'' - a_1'}{a} \right)$	a_1' = tail coordinate— a_1 axis a_1'' = head coordinate— a_1 axis
	$[uvtw]$	$u = \frac{1}{3}(2U - V)$	—
Plane			
Non-hexagonal	(hkl)	$h = \frac{na}{A}$	A = plane intercept— x axis
Hexagonal	$(hkil)$	$i = -(h + k)$	—

^aIn these equations a and n denote, respectively, the x -axis lattice parameter, and a reduction-to-integer parameter.





Ceramic Crystal Structures

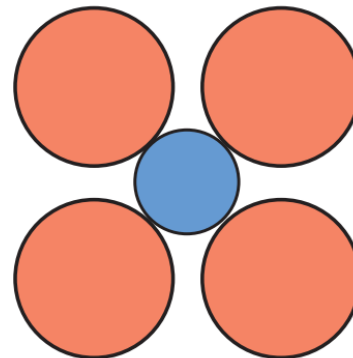
Because ceramics are composed of at least two elements and often more, their crystal structures are generally more complex than those of metals.

- ❖ The atomic bonding in these materials ranges from purely ionic to totally covalent
- ❖ The percentage of ionic character depends on electronegativities of the atoms.
 - Electrical charge of the component ions
 - sizes or ionic radii of the cations and anions, r_C , and r_A

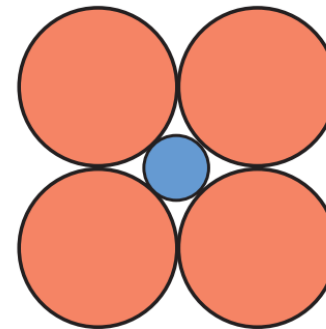
Because the metallic elements give up electrons when ionized, cations are ordinarily smaller than anions,
- consequently, the ratio r_C/r_A is less than unity.

<i>Material</i>	<i>Percent Ionic Character</i>
CaF ₂	89
MgO	73
NaCl	67
Al ₂ O ₃	63
SiO ₂	51
Si ₃ N ₄	30
ZnS	18
SiC	12

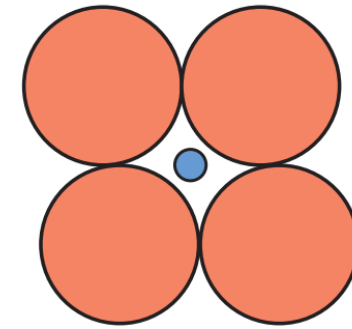
- The **coordination number** (i.e., number of anion nearest neighbors for a cation) is dependent on r_C/r_A .



Stable



Stable



Unstable





Example: Computation of Minimum Cation-to-Anion Radius Ratio for a Coordination Number of 3

Consideration of the right triangle APO makes it clear that the side lengths are related to the anion and cation radii r_A and r_C as

$$\overline{AP} = r_A$$

and

$$\overline{AO} = r_A + r_C$$

Furthermore, the side length ratio $\overline{AP}/\overline{AO}$ is a function of the angle α as

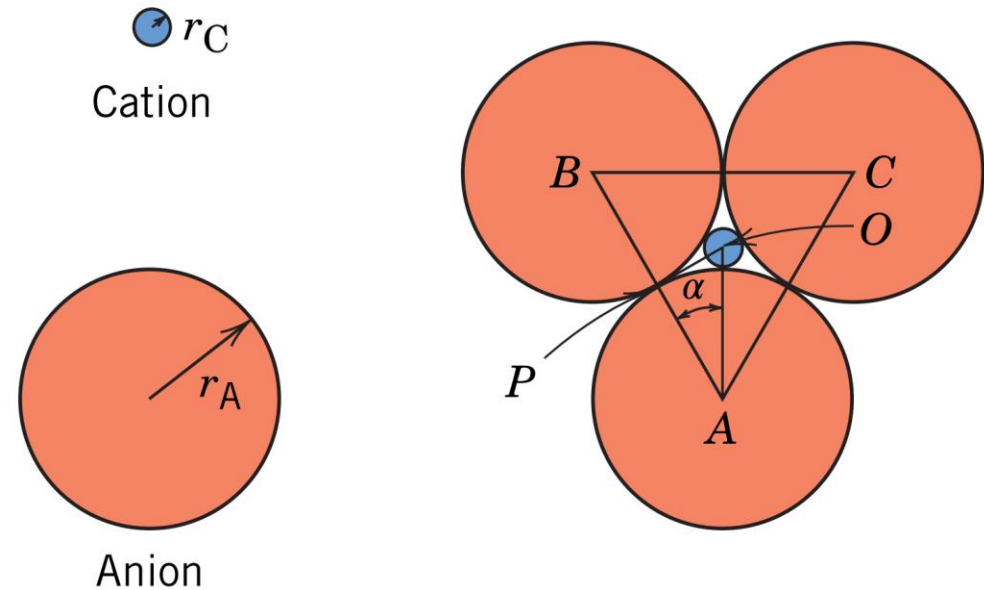
$$\frac{\overline{AP}}{\overline{AO}} = \cos \alpha$$

The magnitude of α is 30° because line \overline{AO} bisects the 60° angle BAC . Thus,

$$\frac{\overline{AP}}{\overline{AO}} = \frac{r_A}{r_A + r_C} = \cos 30^\circ = \frac{\sqrt{3}}{2}$$

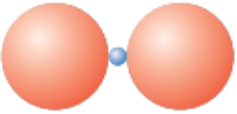
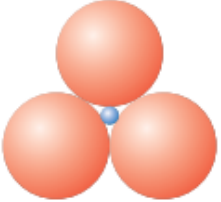
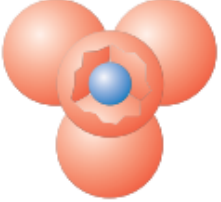
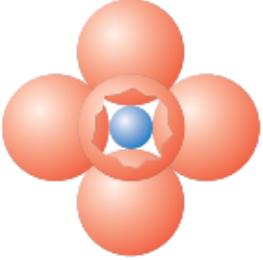

Solving for the cation–anion radius ratio, we have

$$\frac{r_C}{r_A} = \frac{1 - \sqrt{3}/2}{\sqrt{3}/2} = 0.155$$





Ceramic crystal structures

Coordination Number	Cation–Anion Radius Ratio	Coordination Geometry
2	<0.155 linear manner	
3	$0.155-0.225$ Equilateral triangle	
4	$0.225-0.414$ Tetrahedron	
6	$0.414-0.732$ Octahedron	
8	$0.732-1.0$	

For a radius ratio greater than unity, the coordination number is 12.

Coordination number $\sim r_C/r_A$.

For a specific coordination number, there is a critical or minimum r_C/r_A ratio for which this cation–anion contact is established

Ionic radius tends to increase as the number of nearest-neighbor ions of opposite charge increases.

Charge on an ion will influence its radius.

- the radii for Fe^{2+} and Fe^{3+} are 0.077 and 0.069 nm,
- Contrasted to the radius of an iron atom—0.124 nm
- ionic size decreases when electrons are added to the ion



Home Work

Q-C3-1: Show that APF for BCC lattice is 0.68

Q-C3-2: Home assignment : Show that APF for HCP lattice is 0.74.

Q-C3-3: Show that HCP unit cell volume is $V_c = 6R^2c\sqrt{3}$

Q-C3-4: Show that the minimum cation-to-anion radius ratio for the coordination number 3 is 0.155.

