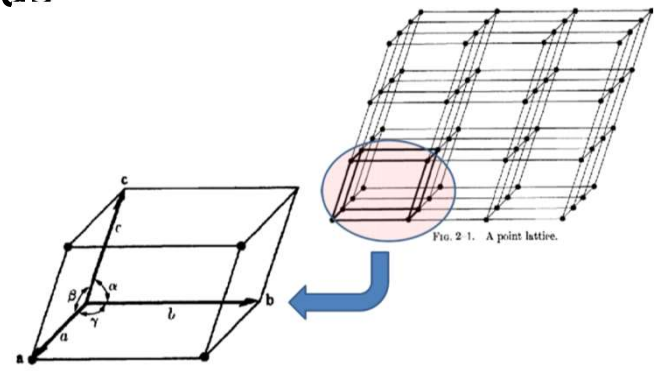
The Solid state

- Crystalline, Quasicrystalline, Amorphous
- Translational symmetry
- Long range periodicity



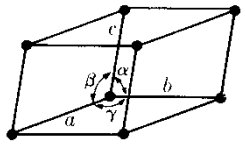
- Lattice parameter in Angstrom 1 Å = 10^{-10} m
- Even micron sized crystal has 10^4 unit cells
- Short range order in amorphous
- Aperiodic nature of quasicrystals

Crystalline materials

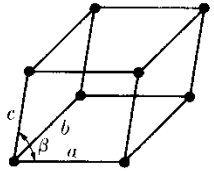
- Regular arrangement of atoms in space
- Directional dependence of properties
- Crystallographic directions and planes are important
- Just like 3D crystal decides properties say triclinic is less symmetric than cubic, planes and directions in cubic/triclinic have different properties
- Bonding is important

Crystallographic directions

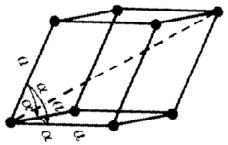
- Directions in crystals
- Co-ordinate system of the crystal system
- Different unit vectors and different angles



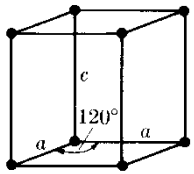
Tri



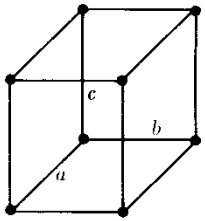
M



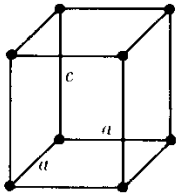
R



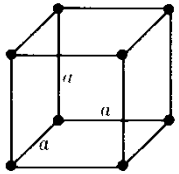
H



O



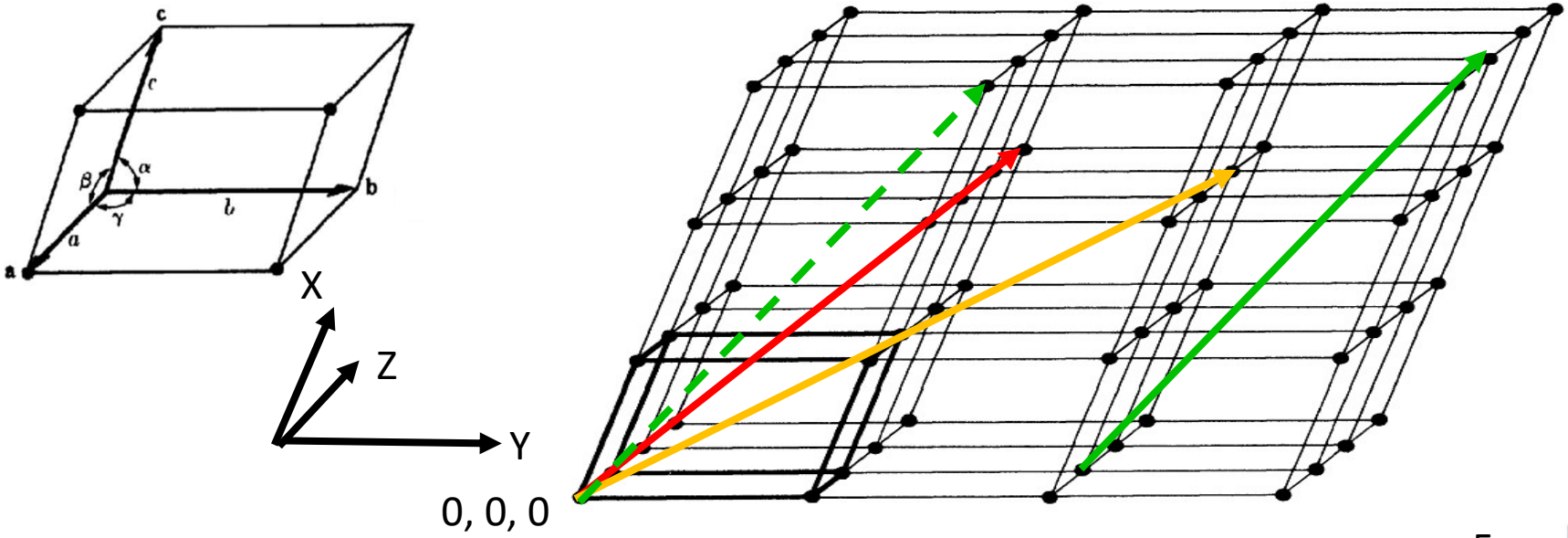
Tetra



C

- To draw a direction, fix origin
- For a direction $la\hat{\imath} + mb\hat{\jmath} + nc\hat{k}$ passing through origin
- l steps along $a\hat{\imath}$ followed with m steps along $b\hat{\jmath}$ and finally n steps along $nc\hat{k}$ to reach point P
- Join origin O and point P
- $\overrightarrow{OP} = la\hat{\imath} + mb\hat{\jmath} + nc\hat{k}$
- For cubic, all three unit vectors have same dimensions
- For cubic, tetragonal and orthorhombic, all three basis vectors are orthogonal to each other

- Red arrow [213]
- Orange arrow [222] not 2 * [111]
- Green arrow foes not pass through origin so draw a parallel line (dashed) from origin and get [310]



Crystallographically equivalent directions

- Use of square bracket to indicate direction
- Negative direction represented by bar over indices
- $[\bar{1}\bar{1}\bar{1}]$ is opposite to [111]
- Symmetry introduces concept of equivalent directions
- Generally parallel directions are considered equivalent geometrically
- Symmetry makes [100], [010], [001], $[\bar{1}00]$, $[0\bar{1}0]$, $[00\bar{1}]$ equivalent
- All are unit vectors of a cubic crystal

- For cubic crystals

  Family of direction <uvw>

  One direction [uvw]

  <100> comprises of

  [100], [010], [001], $[\bar{1}00]$, $[0\bar{1}0]$, $[00\bar{1}]$

- For tetragonal

  <100> comprises of [100], [010], $[\bar{1}00]$, $[0\bar{1}0]$

  Remember c is not equal to a = b

- For orthorhombic

  <100> comprises of [100], $[\bar{1}00]$

  Remember a ≠ b ≠ c

Multiplicity of directions

- Higher the symmetry, more the number of equivalent directions

- <123> has 48 equivalent directions in cubic

- <123] has 16 equivalent directions in tetragonal

- [123] has only 8 equivalent directions

- Notice the bracket in tetragonal showing that c is different from a and b

Crystallographic planes

- Crystalline materials in 3D have different crystallographic planes
- Different planes have different properties in the same crystal
- Planes are essentially surfaces
- Number of atoms per plane different
- Understanding of planes and the sub dimensional information like number of atoms, planar packing density important
- Same is true for directions

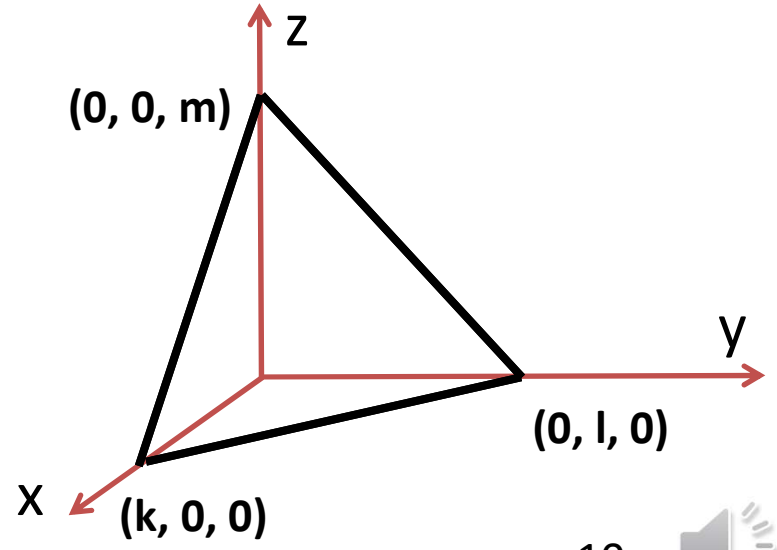
Miller indices for planes

1. Intercept with X, Y, and Z axis
2. (k, 0, 0); (0, l, 0) and (0, 0, m)
3. Determine k/a, l/b, m/c, where a, b, c are lattice parameters along X, Y and Z resp.
4. Determine a/k, b/l, c/m
5. If fractions then multiply each of these by lowest common multiple (LCM), let say it is N

Or, if the three numbers have a common factor then divide them with this highest common factor (HCF)

The Miller indices of the plane are

$$\left(\frac{a}{k}N\ \frac{b}{l}N\ \frac{c}{m}N\right)$$

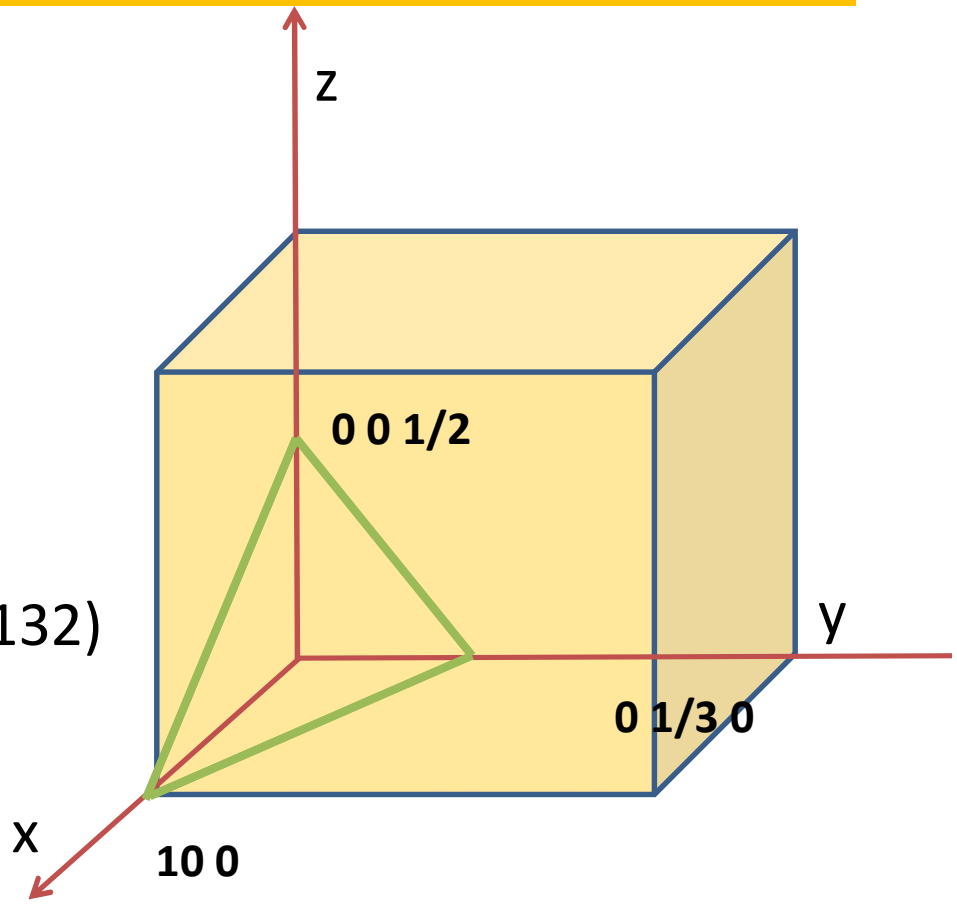


Intercepts are a, b/3, c/2

Finding fractions in terms of
Unit cell dimensions: 1, 1/3, ½

Take inverse: 1, 3, 2

Miller indices of the plane are (132)



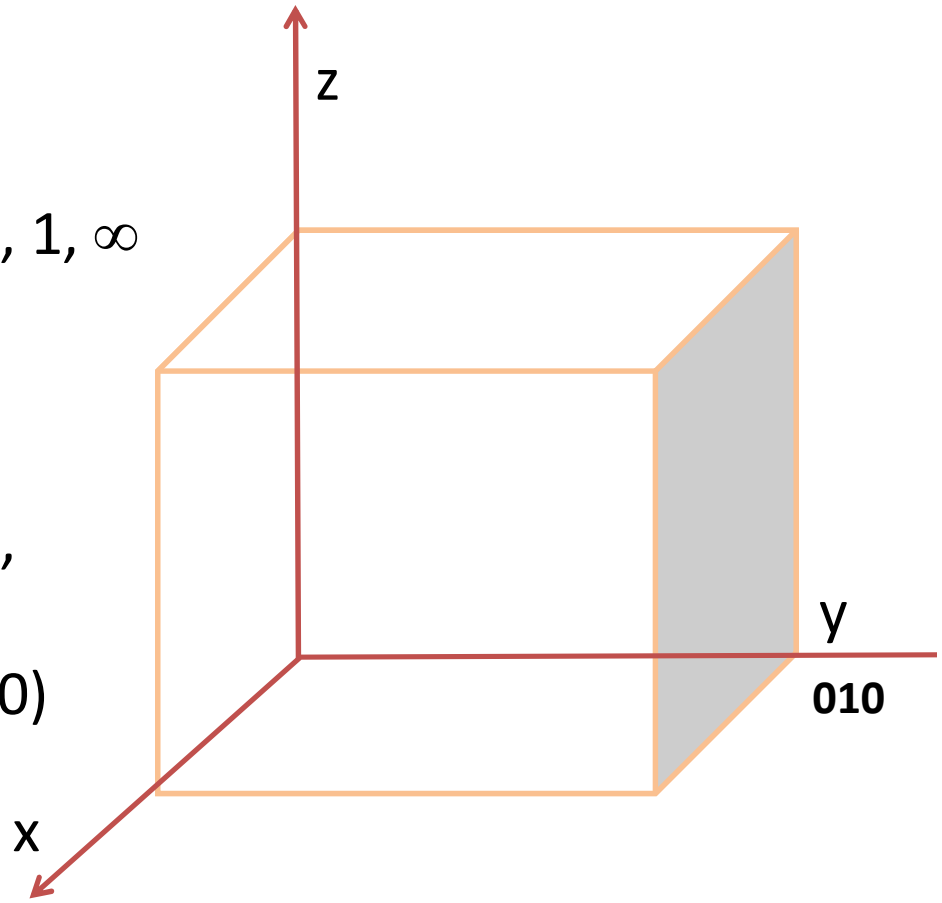
Intercepts: ∞, b, ∞

Divide by unit cell dimensions: ∞, 1, ∞

Inverse of these: 0, 1, 0

No fractions, no common factors,

Therefore, Miller indices are (010)



Multiplicity of planes

- Just like directions, planes too have the concept of equivalent planes

- There is nothing like positive or negative plane

- Shift the origin if needed

- {hkl} is family of planes for cubic

- {111} comprises of

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

- No negative planes so multiplicity/2

- For cubic

  {123} has 24 equivalent planes

Just like directions, planes too have the concept of equivalent planes

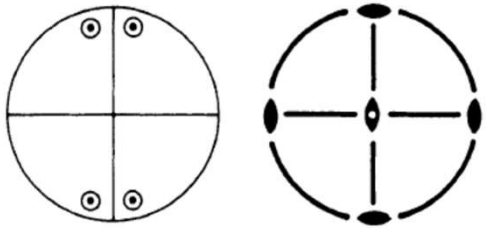
- For tetragonal

  {123) has 8 equivalent planes

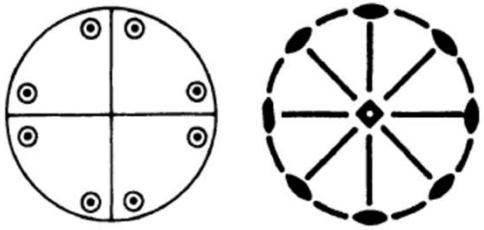
- For orthorhombic

  (123) only 4

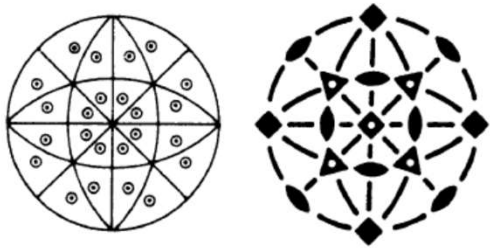
Symmetry is not just beautiful but also useful



(hkl) $(\bar{h}\bar{k}l)$ $(\bar{h}k\bar{l})$ $(h\bar{k}\bar{l})$
$(\bar{h}\bar{k}\bar{l})$ $(hk\bar{l})$ $(h\bar{k}l)$ $(\bar{h}kl)$



(hkl) $(\bar{h}\bar{k}l)$ $(\bar{k}hl)$ $(k\bar{h}l)$
$(\bar{h}kl)$ $(h\bar{k}l)$ $(k\bar{h}l)$ $(\bar{k}\bar{h}l)$
$(\bar{h}k\bar{l})$ $(h\bar{k}\bar{l})$ $(k\bar{h}\bar{l})$ $(\bar{k}h\bar{l})$
$(h\bar{k}l)$ $(\bar{h}kl)$ $(\bar{k}\bar{h}l)$ (khl)



(hkl) $(\bar{h}kl)$ $(h\bar{k}l)$ $(hk\bar{l})$ (khl) $(\bar{k}\bar{h}l)$ $(k\bar{h}l)$ $(\bar{k}hl)$
(lhk) $(\bar{l}hk)$ $(l\bar{h}k)$ $(lh\bar{k})$ (lkh) $(\bar{l}\bar{k}h)$ $(l\bar{k}h)$ $(\bar{l}kh)$
(klh) $(\bar{k}lh)$ $(kl\bar{h})$ $(\bar{k}\bar{l}h)$ (hlk) $(\bar{h}\bar{l}k)$ $(\bar{h}lk)$ $(h\bar{l}k)$

$(\bar{h}k\bar{l})$ $(hk\bar{l})$ $(h\bar{k}l)$ $(\bar{h}kl)$ $(\bar{k}hl)$ (khl) $(\bar{k}\bar{h}l)$ $(k\bar{h}l)$
$(\bar{l}hk)$ (lhk) $(\bar{l}\bar{h}k)$ $(\bar{l}h\bar{k})$ $(\bar{l}kh)$ (lkh) $(\bar{l}\bar{k}h)$ $(l\bar{k}h)$
$(k\bar{l}h)$ $(kl\bar{h})$ $(\bar{k}\bar{l}h)$ $(\bar{k}lh)$ $(\bar{h}lk)$ (hlk) $(\bar{h}\bar{l}k)$ $(h\bar{l}k)$

Single crystal linear elasticity

- Hard sphere vs. ball and spring model
- Stress and strain are rank 2 tensors so 9 components
- Symmetric so only 6 components
- Stiffness has 36 components

$$\begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \tau_{23} \\ \tau_{13} \\ \tau_{12} \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix} \begin{bmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \varepsilon_{33} \\ \gamma_{23} \\ \gamma_{13} \\ \gamma_{12} \end{bmatrix}$$

$$\begin{bmatrix} 11 & 12 & 13 & 0 & 0 & 0 \\ . & 22 & 23 & 0 & 0 & 0 \\ . & . & 33 & 0 & 0 & 0 \\ . & . & . & 44 & 0 & 0 \\ . & . & . & . & 55 & 0 \\ . & . & . & . & . & 66 \end{bmatrix}, \begin{bmatrix} 11 & 12 & 13 & 0 & 0 & 16 \\ . & 11 & 13 & 0 & 0 & -16 \\ . & . & 33 & 0 & 0 & 0 \\ . & . & . & 44 & 0 & 0 \\ . & . & . & . & 44 & 0 \\ . & . & . & . & . & 66 \end{bmatrix}$$

$$\begin{bmatrix} \varepsilon_{11} \\ \varepsilon_{22} \\ \varepsilon_{33} \\ \gamma_{23} \\ \gamma_{13} \\ \gamma_{12} \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{11} & S_{12} & 0 & 0 & 0 \\ S_{12} & S_{12} & S_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & S_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & S_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & S_{44} \end{bmatrix} \begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \tau_{23} \\ \tau_{13} \\ \tau_{12} \end{bmatrix}$$

$$\frac{1}{E_{hkl}} = S_{11} - 2\left[(S_{11} - S_{12}) - \frac{S_{44}}{2}\right](l_1^2 l_2^{2+} l_2^2 l_3^2 + l_3^2 l_2^{2)})$$

- Copper wire to carry electricity
- $E_{111} = 1.5 * E_{100}$
- Good electrical conductivity
- Electrical conductivity is a 2nd rank tensor but not much directional dependence
- So yes copper is good but …

Unit cell volume

Cubic $V = a^3$

Tetragonal $V = a^2 c$

Orthorhombic $V = abc$

Hexagonal $V = \left(\sqrt{3}a^2 c\right)/2 = 0.866 a^2 c$

Monoclinic $V = abc \sin\beta$

Triclinic $V = abc\left(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma\right)^{1/2}$

Interplanar distance

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

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

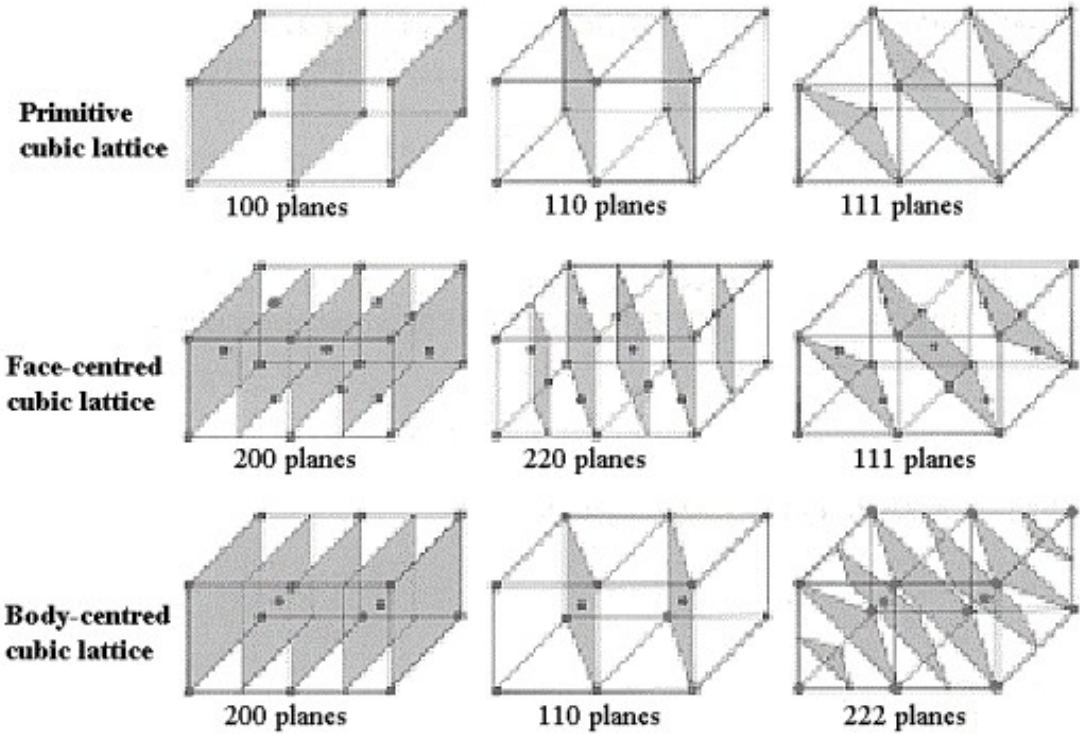
Orthorhombic $$\frac{1}{d^2}=\frac{h^2}{a^2}+\frac{k^2}{b^2}+\frac{l^2}{c^2}$$

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

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

Triclinic $$\frac{1}{d^2}=\frac{1}{V^2}[h^2b^2c^2\sin^2\alpha+k^2a^2c^2\sin^2\beta$$
$$+l^2a^2b^2\sin^2\gamma+2hkabc^2(\cos\alpha\cos\beta-\cos\gamma)$$
$$+2kla^2bc(\cos\beta\cos\gamma-\cos\alpha)+2hlab^2c(\cos\alpha\cos\gamma-\cos\beta)]$$

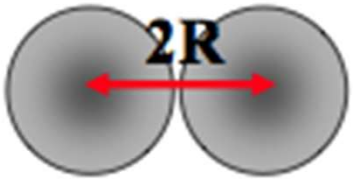
Where, V is the cell volume.



Miller indices for three types of cubic lattices.

$$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2}}$$

- Crystal = Lattice + Motif
- Analysis till this point on lattice
- Let us put atoms
- Hard sphere model
- Same size



- hard-sphere model

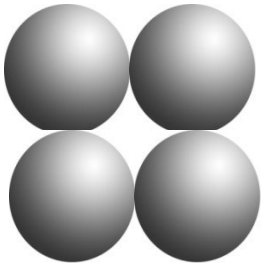
- Let us focus on the cubic crystal system

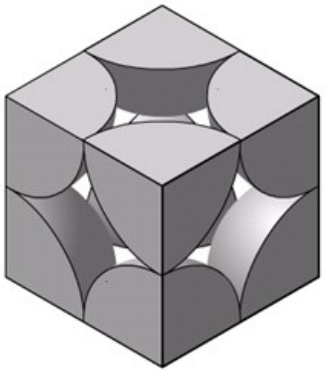
- Simple cubic (SC): 1 lattice point per unit cell
  (0, 0, 0)

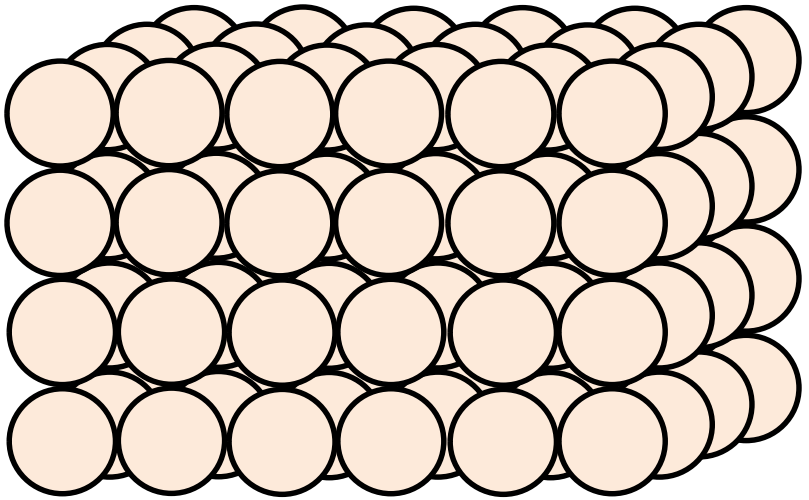
(0, 0, 0) represents (0, 0, 0); (1, 0,0); (0, 1, 0); (0, 0, 1); (1, 1, 0); (10, 1, 1); (1, 0, 1); (1, 1,1) due to translational symmetry. These are coordinates of the corners of the cube.

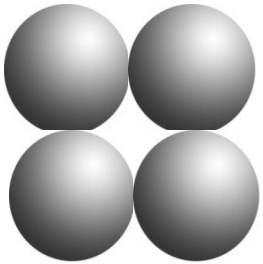
- Body centered Cubic: 2 lattice points/unit cell
  (0, 0,0) and (½, ½, ½)

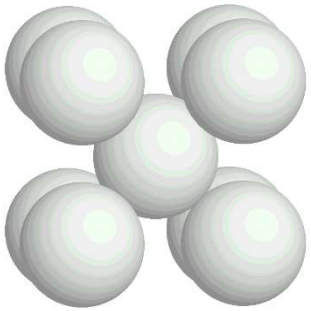
- Face Centered Cubic (FCC): 4 lattice points per unit cell
  (0, 0,0); (½, ½, 0); (0, ½, ½); (½, 0, ½)

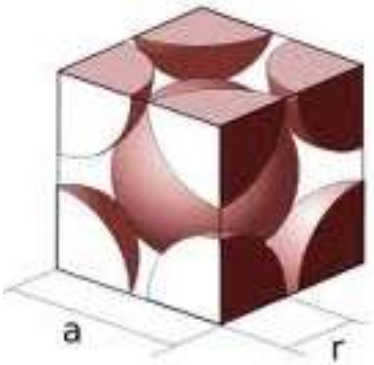


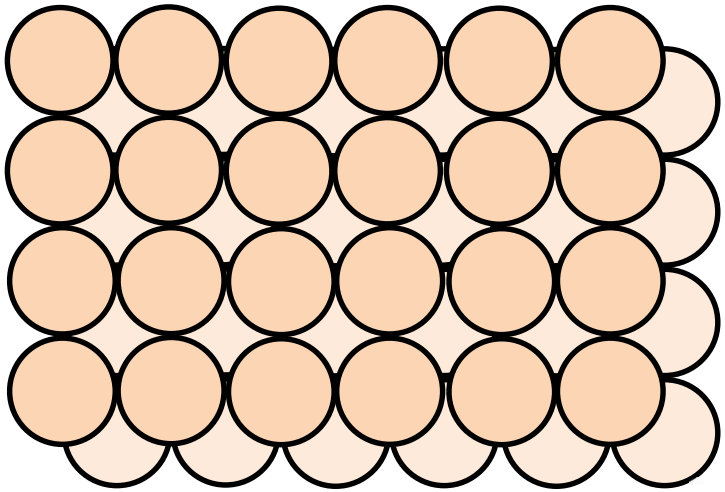


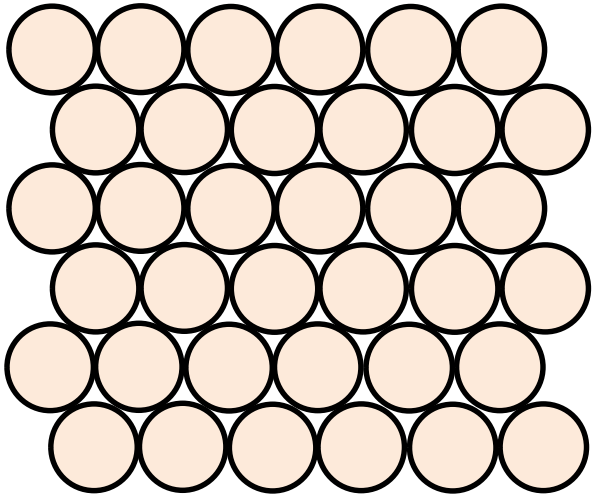




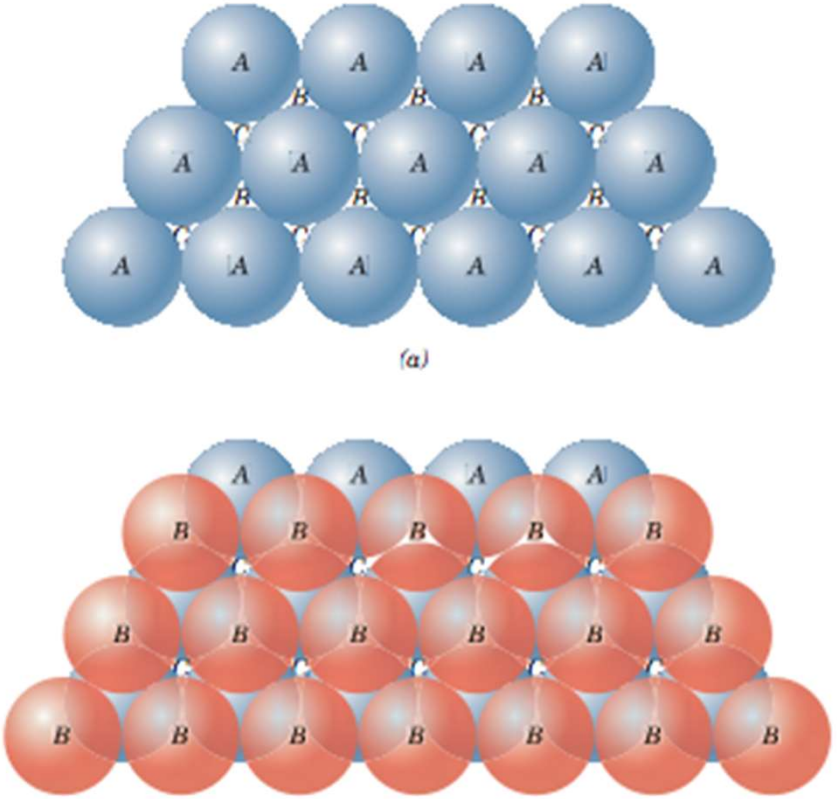



a
r



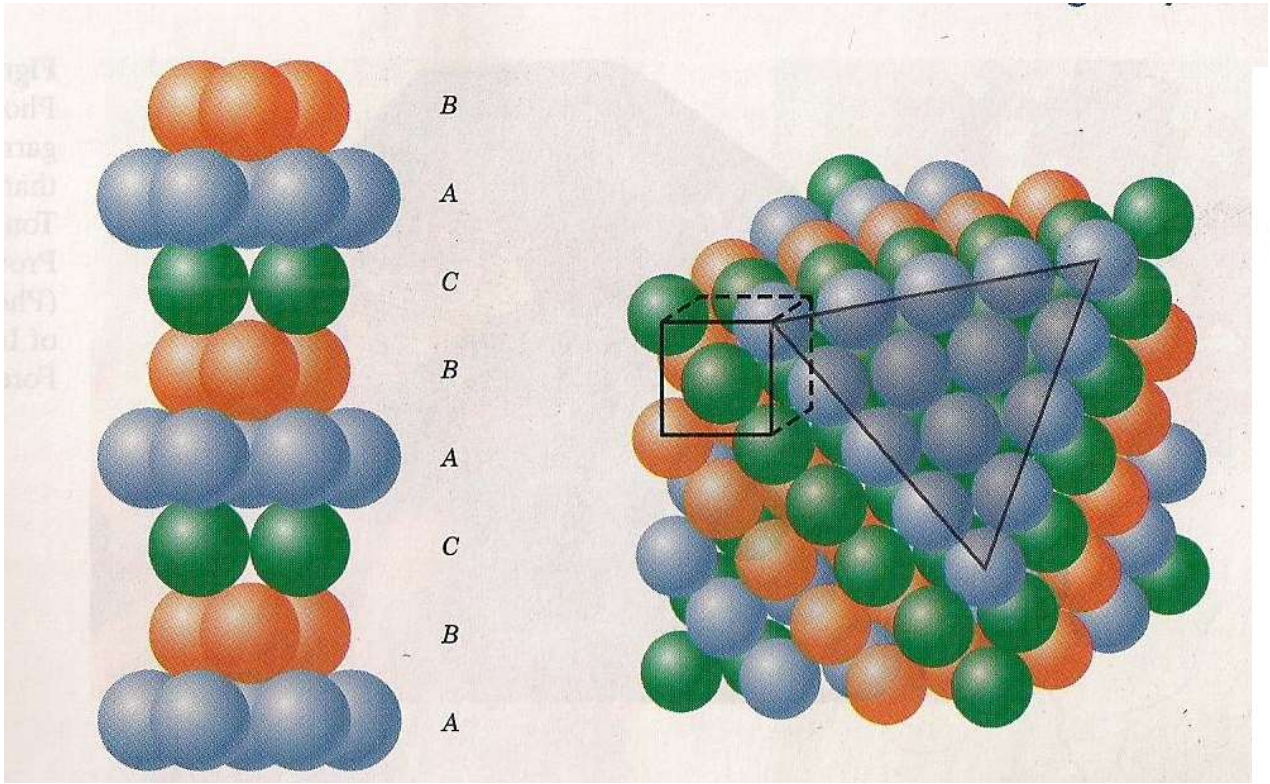


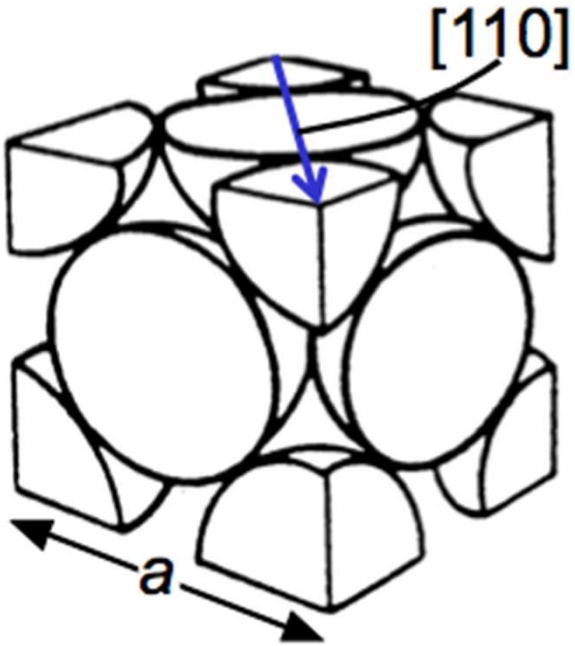
(Adapted from W. G. Moffatt, G. W. Pearsall, and J. Wulff, The Structure and Properties of Materials, Vol. I, Structure, p. 50.)



(a) A portion of a close-packed plane of atoms; A, B, and C positions are indicated.

(a) The AB stacking sequence for close-packed atomic planes.

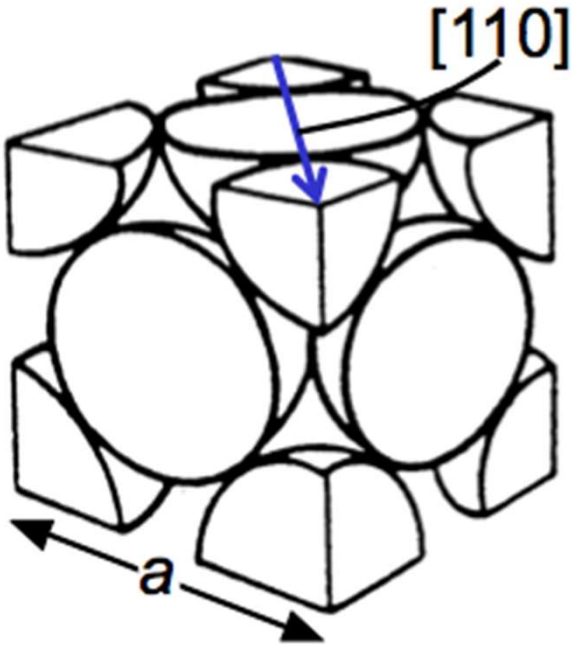




Adapted from Fig. 3.1(a), *Callister & Rethwisch 8e.*

Linear density

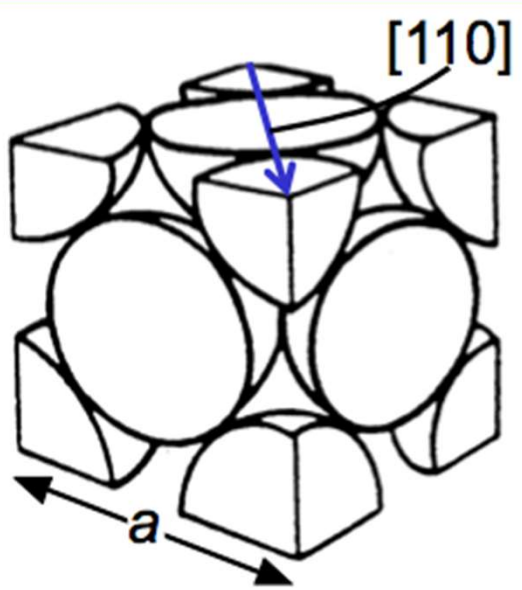
- Linear density of atoms
- Packing density of directions
- Number of atoms per unit length
- Linear density for FCC along [110]
- 2 (0.5 + 1 + 0.5) atoms for $\sqrt{2}a$ where a is the lattice parameter
- Linear density for [110] is $2/\sqrt{2}a$
- Linear density for [100] is 1/a



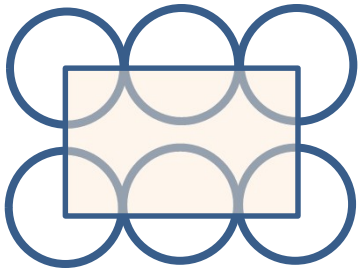
Adapted from Fig. 3.1(a), *Callister & Rethwisch 8e.*

Planar density

- No. of atoms/Area of plane
- Packing density of planes
- Number of atoms per unit area
- Planar density for FCC (110)



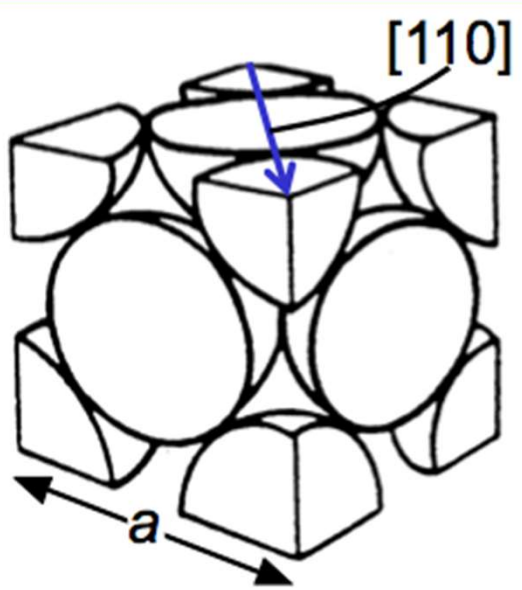
- 2 [(2 * 0.5) + (4 * 0.25)] atoms for area od $\sqrt{2}a^2$
- Planar density for (110) is $2/\sqrt{2}a^2$
- Planar density for (100) is $2/a^2$



Packing density

- Volume of atoms/Volume of unit cell
- FCC [<110> closest packed direction
- $\sqrt{2}\,\mathrm{a} = 4\mathrm{R}$

  R is radius of atom



No. of atoms/Area of plane

- 4 atoms per unite cell in FCC
- Packing fraction = $\frac{4 * (\frac{4}{3}\pi R^3)}{a^3}$ = 0.74

$$\text{Density} = \rho = \frac{\text{Mass of Atoms in Unit Cell}}{\text{Total Volume of Unit Cell}}$$

$$\rho = \frac{n A}{V_C N_A}$$

where n = number of atoms/unit cell

A = atomic weight

V_C = Volume of unit cell = a^3 for cubic

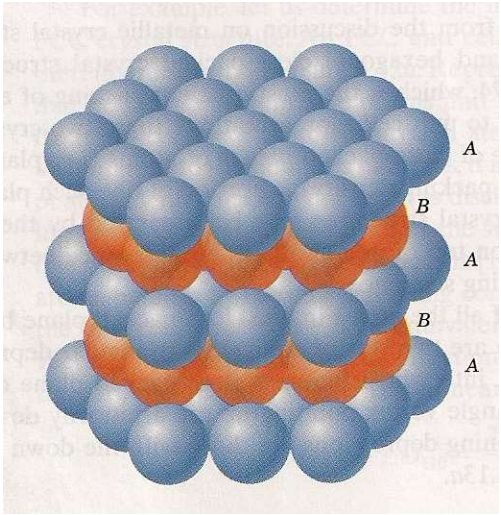
N_A = Avogadro's number

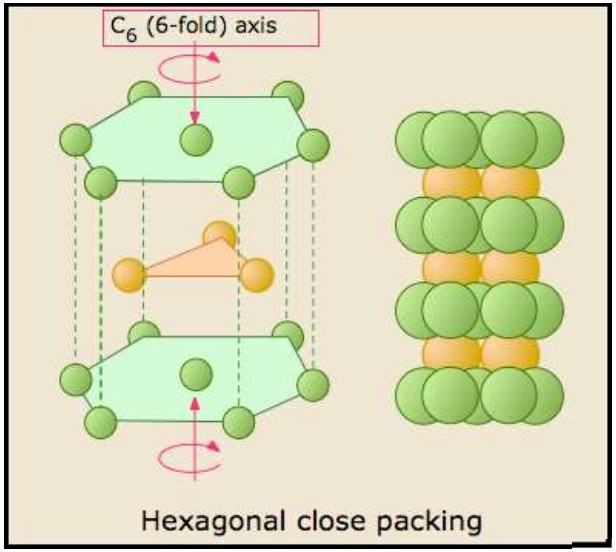
= 6.022×10^{23} atoms/mol

Crystal	APF (%)	Co-ordination number NN	NN distance
SC	52 %	6	a
BCC	68%	8	$\sqrt{3}a/2$
FCC	74%	12	$a/\sqrt{2}$

Hexagonal close packed crystal structure

- Hexagonal lattice
- Stack ABAB unlike ABCABC for FCC
- Hexagonal closed packed crystal structure
- There is nothing like HCP lattice
- Space group P63/mmc
- Titanium and magnesium





- Lattice is hexagonal obtained by combining three rhombic cells

- c/a ratio

- Determine ideal c/a ratio assuming close packing

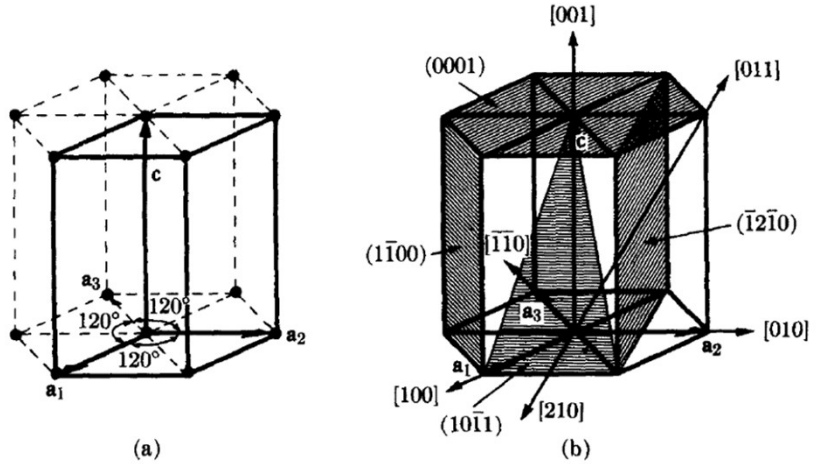
- 74% packing like FCC

- Not all elements have 74% packing if crystal structure is FCC or HCP

- Stacking of rhombic layers give hexagonal lattice

Planes and directions in hexagonal lattice

- 4 index notation for planes in Miller-Bravais indices
- a1, a2, a3 and c such that a1 = -(a2+a3)
- Third index is redundant for plane (hkil)
- Drop the third index and put dot (hk.l)



l = - (h + k)

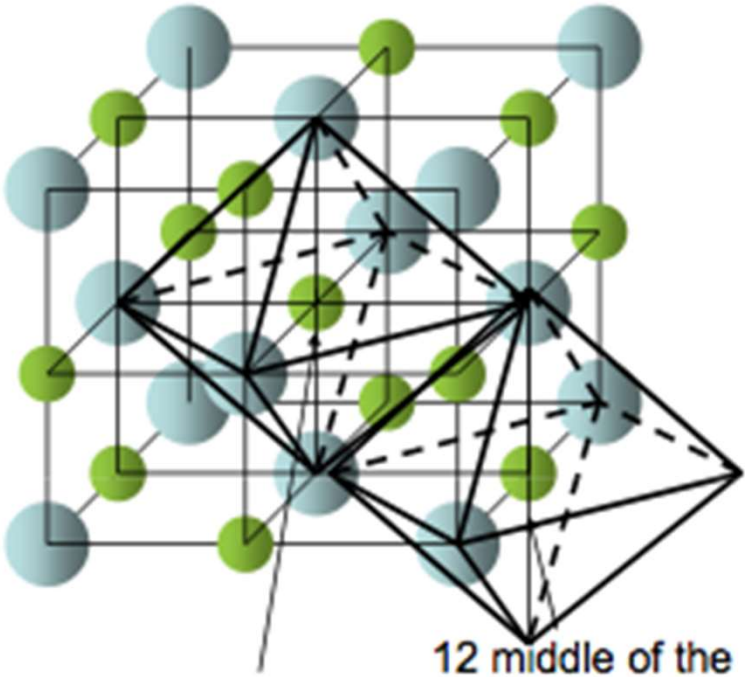
Fig. 2–11 (a) The hexagonal unit cell (heavy lines) and (b) indices of planes and directions.

Directions in hexagonal lattice

- UVTW direction
- T = - (U + V)
- For three index notation
- $$U = u - t \qquad u = (2U - V)/3$$
  $$V = v - t \qquad v = (2V - U)/3$$
  $$W = w \qquad t = -(u + v) = -(U + V)/3$$
  $$w = W.$$

Voids in FCC lattice

Octahedral (O_h) sites



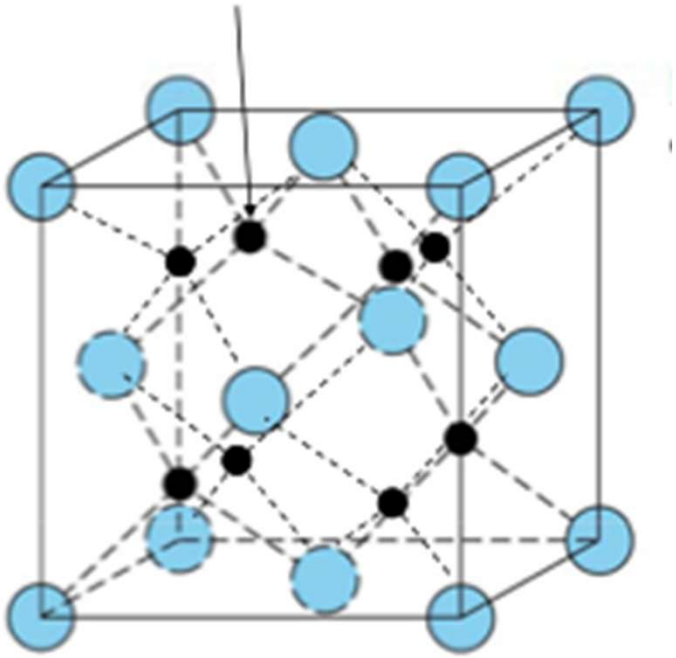
1 at the center

12 middle of the edge sites (each shared by 4 unit cells)

Net 4 O_h sites/unit cell

(½, ½, ½) and (½, 0, 0)

Tetrahedral (T_d) sites

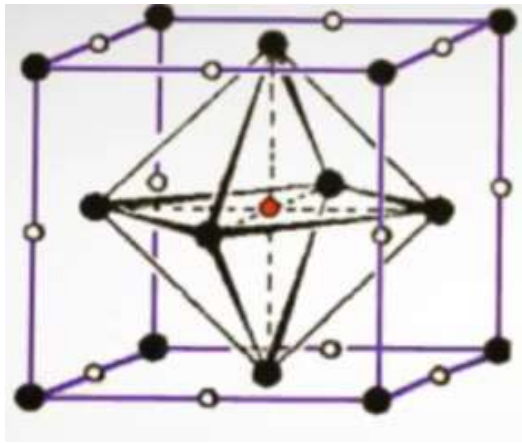
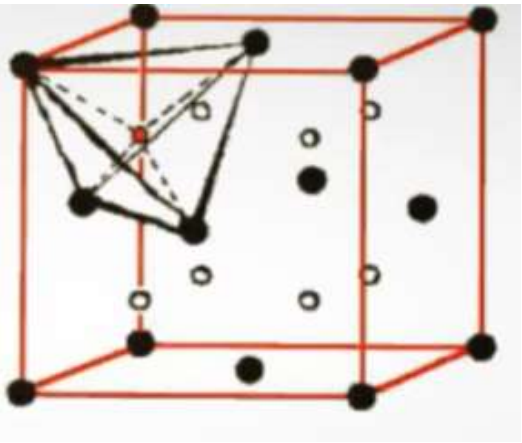
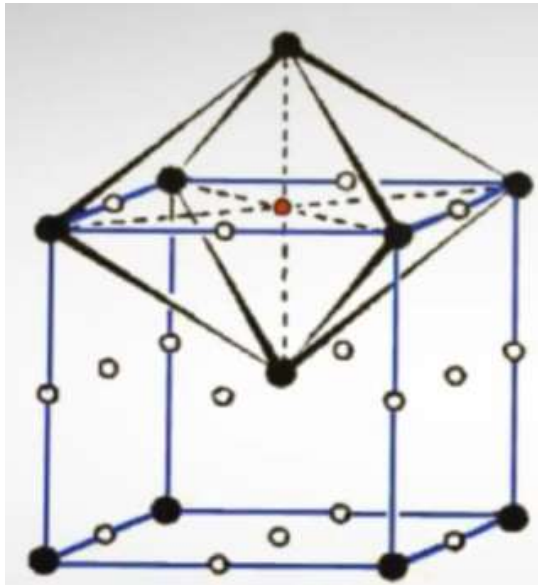
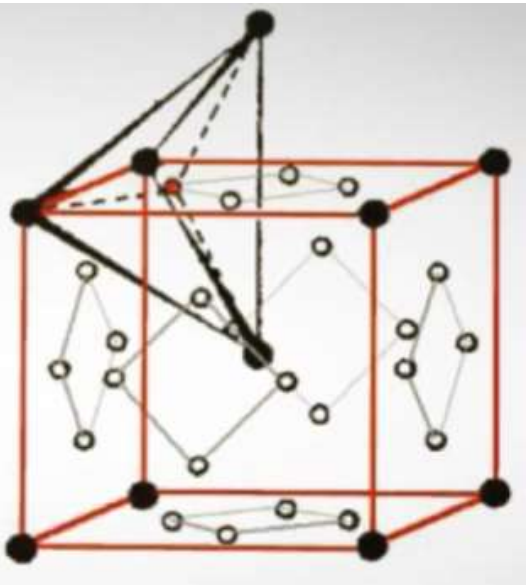


Net 8 T_d sites/unit cell

(¼, ¼, ¼)

Irregular voids in BCC lattice

- FCC has regular octahedral and tetrahedral voids
- BCC has irregular octahedral and tetrahedral voids
- BCC octahedral voids are at face centers and edge centers
- 6*0.5 + 12 * * 0.25 = 6 octahedral voids
- Tetrahedral voids are also on face centers at (½, ¼. 0)
- 4 voids on each face
- 12 tetrahedral voids in BCC

	Octahedral	Tetrahedrall
FCC		
BCC		

- Steels are the biggest marvel of engineering
- C in iron
- Solubility of carbon is higher in FCC gamma iron than BCC alpha iron
- FCC is more densely packed but has few large voids
- BCC is less closely packed but has many small voids
- Size and co-ordination number matters when we have atoms/ions of different sizes

- Introducing atoms of different sizes allows alloying
- Compound formation
- Solid solutions
- Explore the entire palette of elements
- Iron alloys, copper alloys
- Superalloys