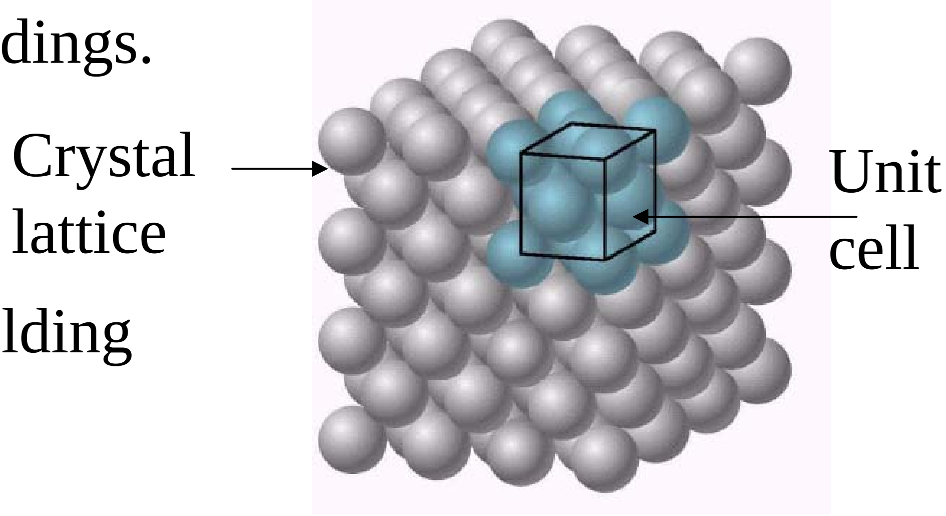
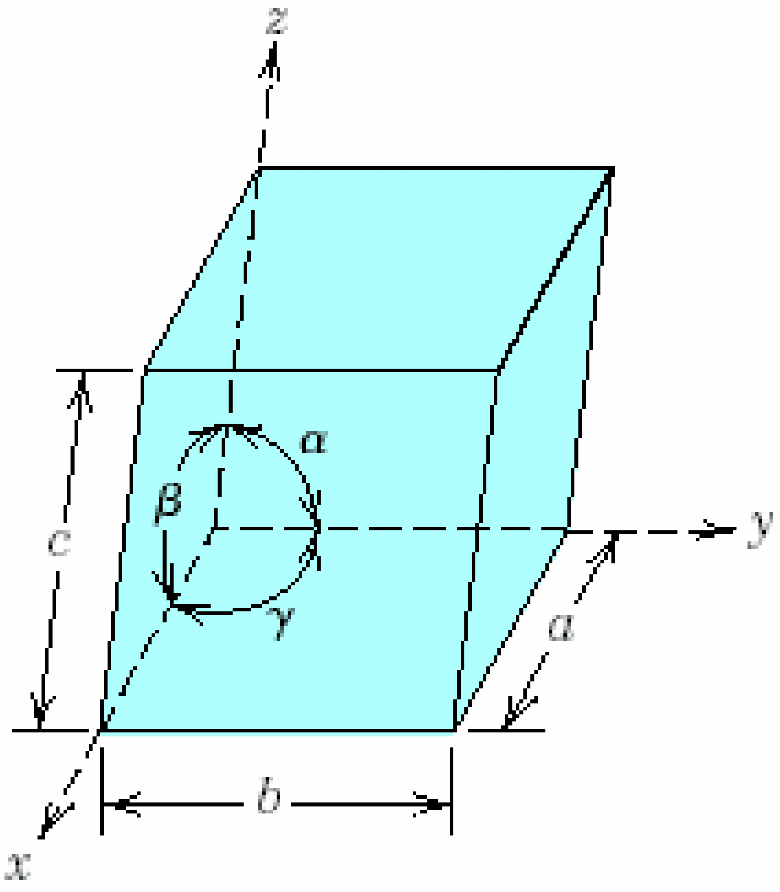
Crystal Structure

- All metals are crystalline solids (special atomic arrangements that extend through out the entire material)
- Amorphous solids: atoms are arranged at random positions (rubber)
- Crystal structure: atoms form a repetitive pattern called lattice.
- Crystal lattice: arrays of points (atoms) arranged such that each point has an identical surroundings.



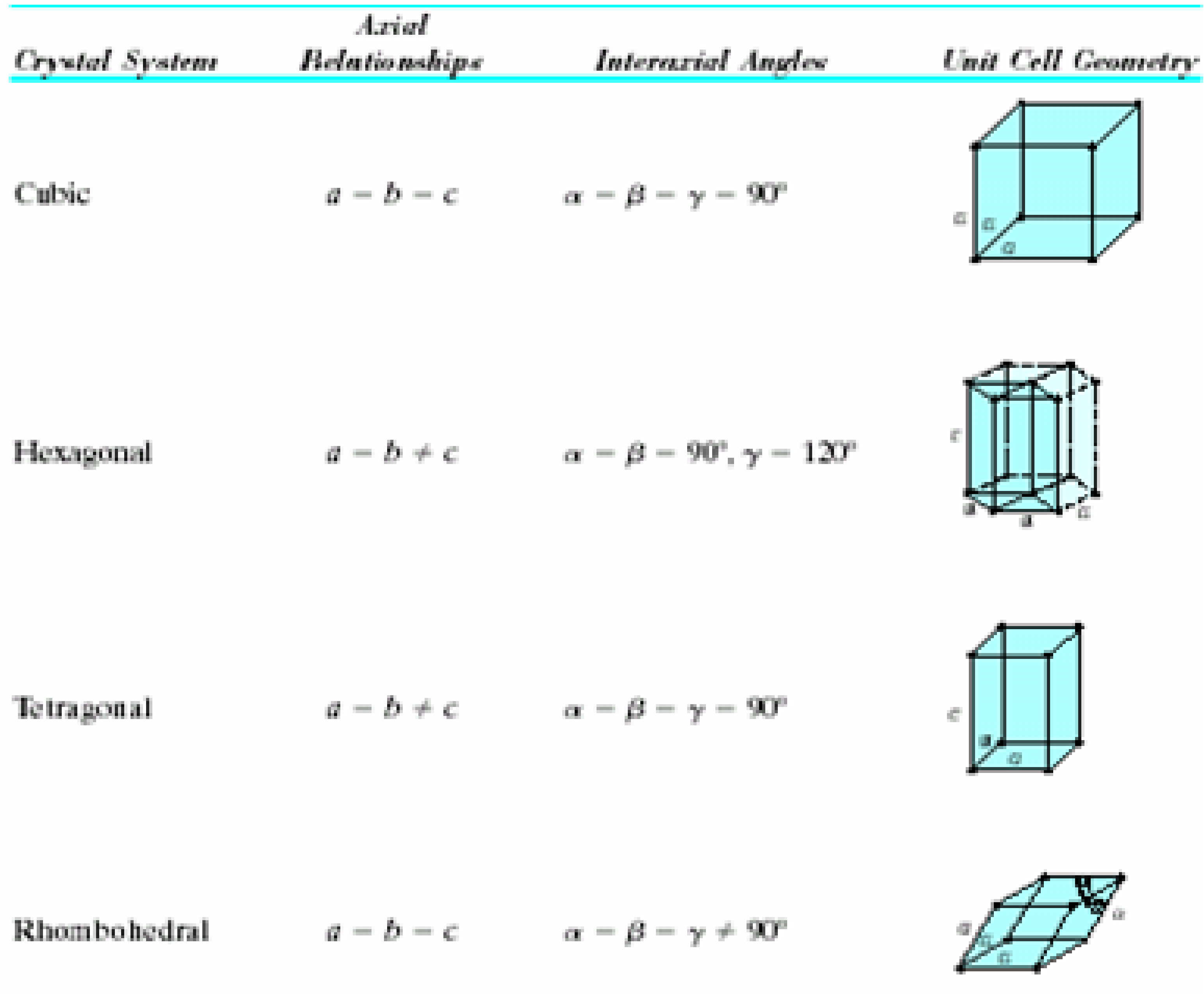
*Unit cell: The smallest building block of the crystal lattice



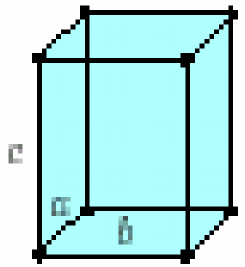
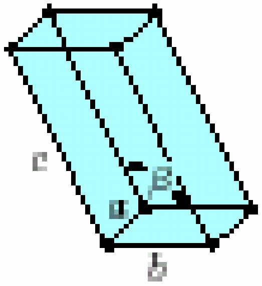
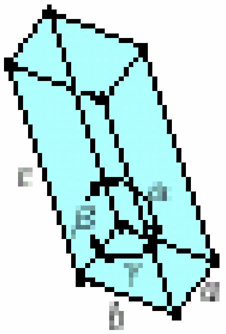
Lattice parameters: parameters that completely defines the unit cell geometry.

There are seven possible combinations of a,b,c and α,β,γ that give rise to seven crystal systems

* There are 14 types of unit cell that stems from 7 crystal systems:

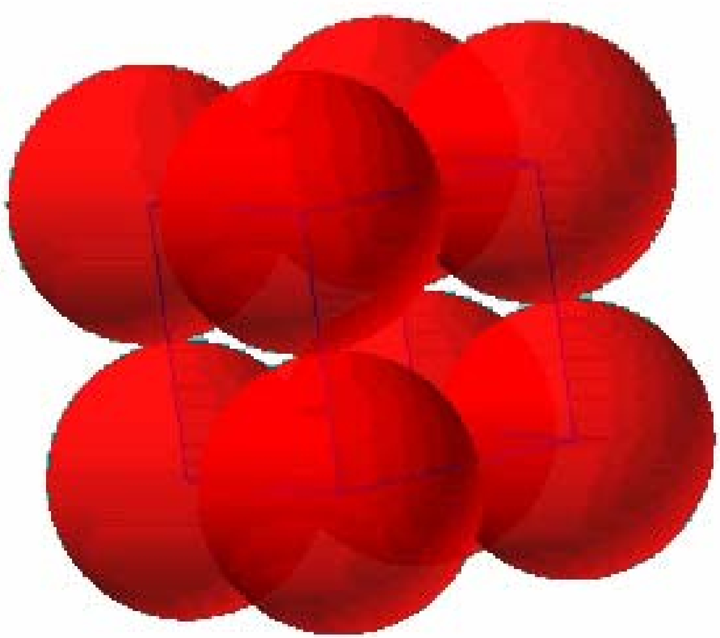


Crystal System	*Axial Relationships*	*Interaxial Angles*	*Unit Cell Geometry*
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°, \gamma = 120°$	
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	

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

Most common types of unit cell

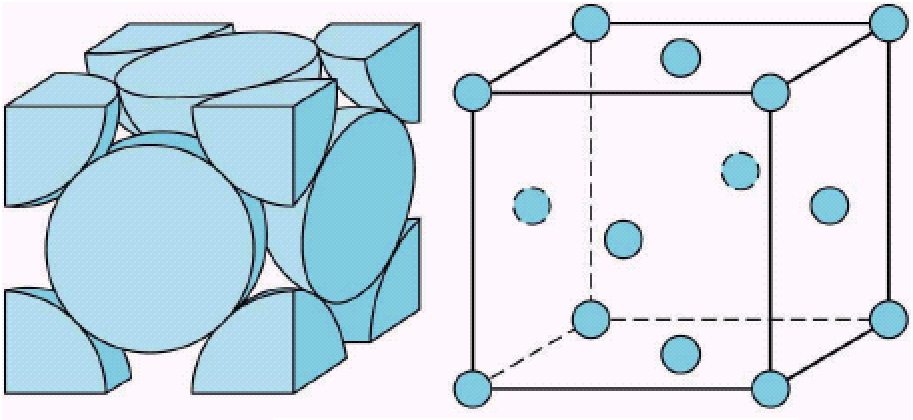
Simple cube



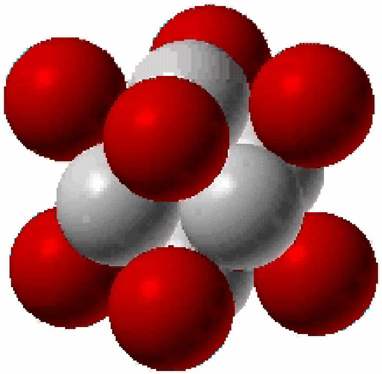
Number of atoms per unit cell : 8 (corner atoms) x 1/8 =1 atom / unit cell

Face center cubic (FCC)

CRYSTAL STRUCTURE



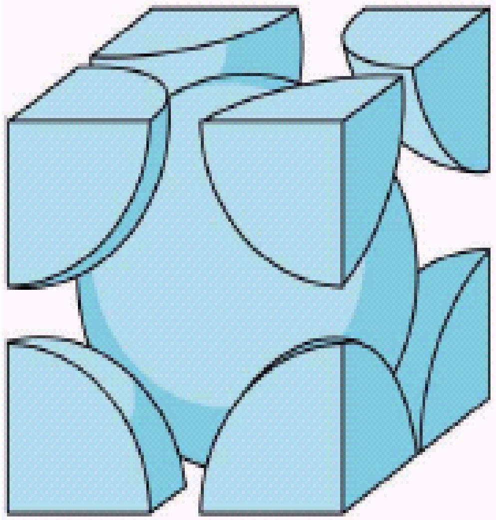
(a)

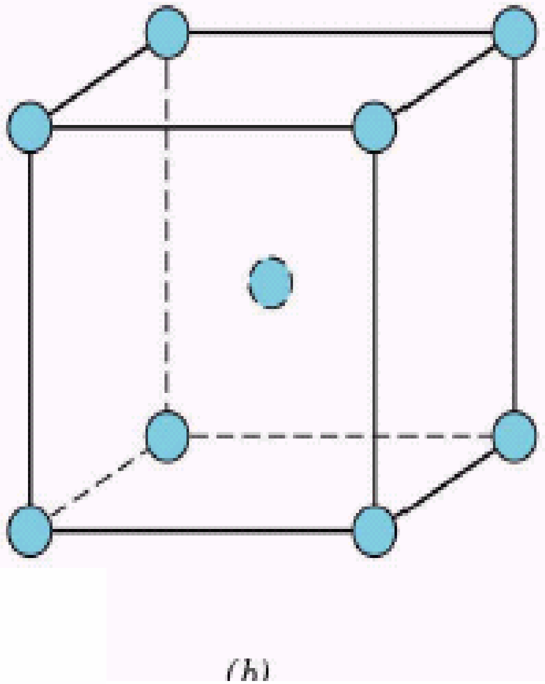


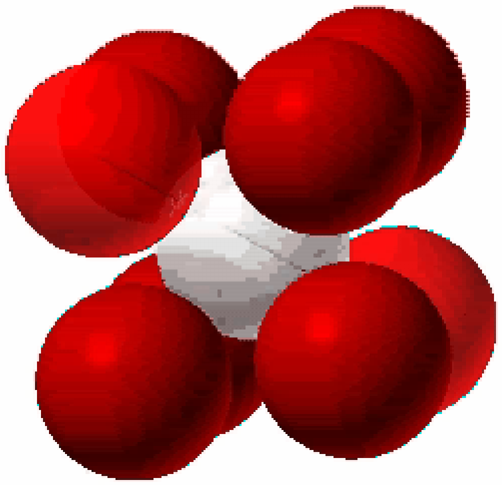
Number of atoms per unit cell : 8 (corner atoms) x 1/8 + 6 (face atoms) x 1/2 =4 atoms / unit cell

Body Center Cube
BCC

CRYSTAL
STRUCTURE





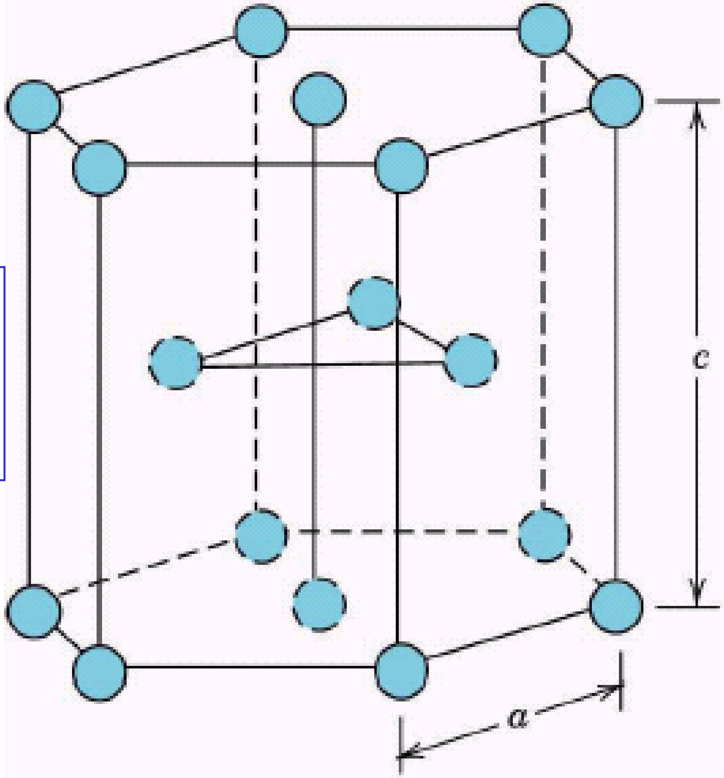


Number of atoms per unit cell : 8 (corner atoms) x 1/8 + 1 (interior atom) = 2 atoms / unit cell

Hexagonal close packed (HCP) crystal structure

c/a = 1.63

For most HCP metals

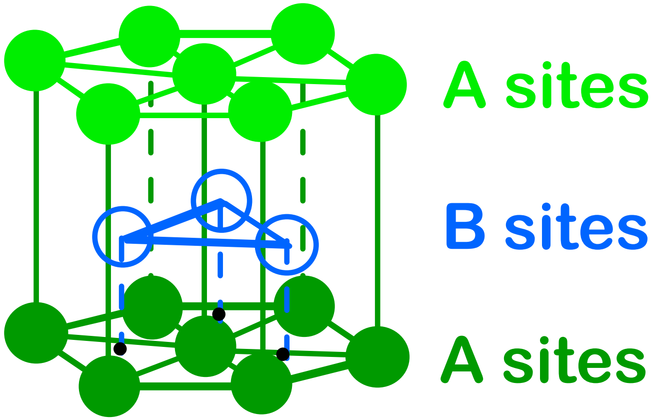


(a)

Number of atoms per unit cell :

12 (corner atoms) x 1/6 + 3 (interior atoms)

+ 2 (face atoms) x 1/2= 6 atoms / unit cell



Atomic radius versus lattice parameter:

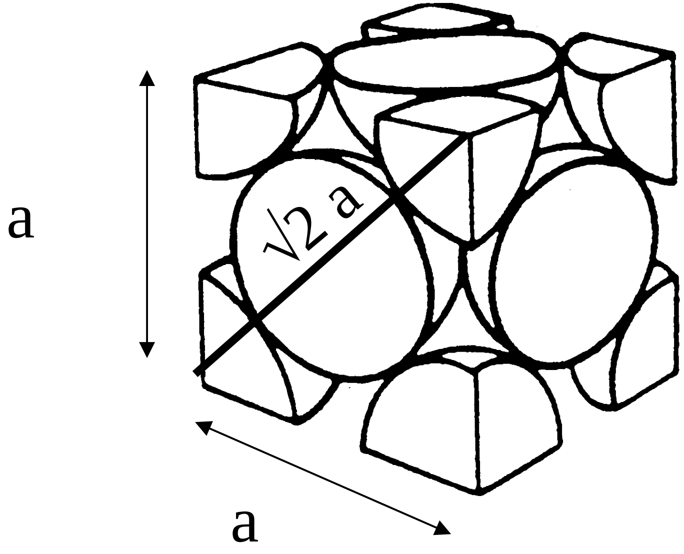
(Look for the close packed directions in the unit cell)

Close packed direction: Directions in the unit cell in which atoms are in continuous contact.

* FCC (close packed directions are the face diagonals)

$\sqrt{2}\,a = 4R$

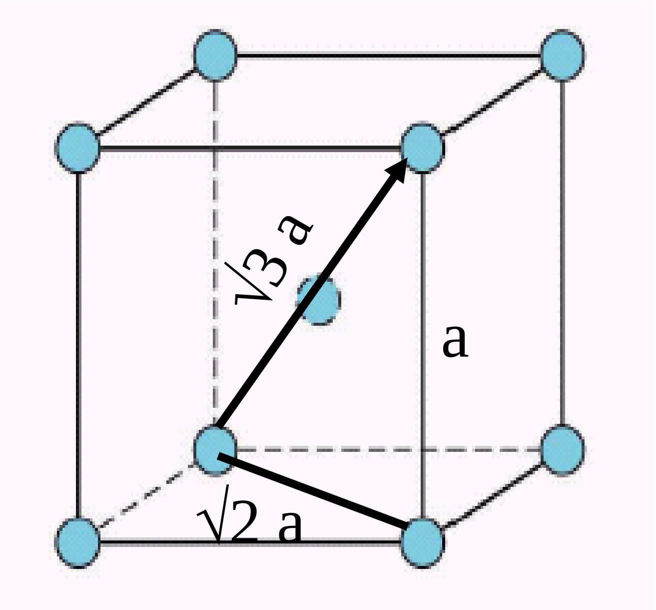
$a = 4R/\sqrt{2} = 2\sqrt{2}\,R$



*BCC (close packed direction are body diagonals)

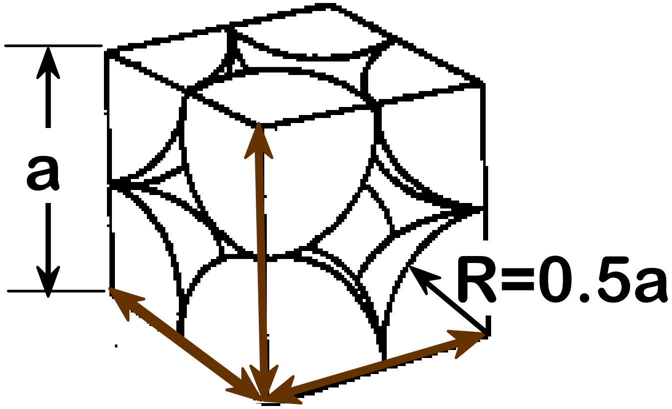
√3 a = 4R

a = 4R/ √3



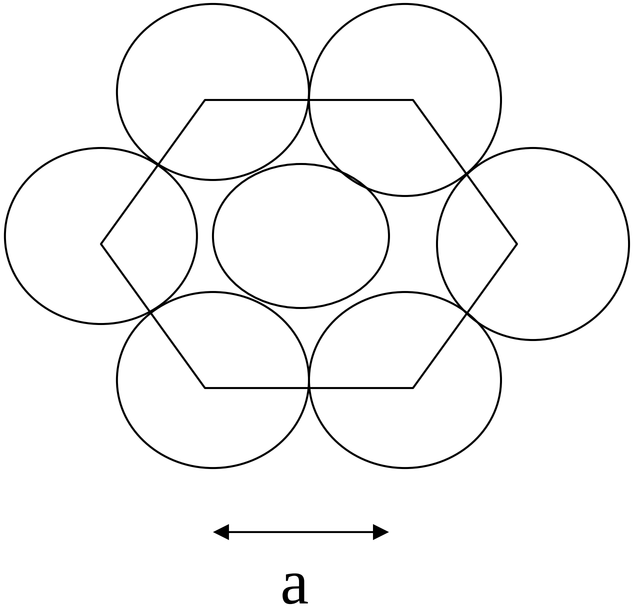
* SC (close packed direction is any edge of the cube)

a= 2R



- HCP (close packed directions are the edges and the diagonals of the upper and lower faces)

$a=2R$



Atomic packing factor (APF)

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

*assume hard spheres

$$\frac{\text{(No.of atoms/unit cell) * volume of each atom}}{\text{Volume of unit cell}}$$

Simple Cube

$$\text{APF} = \frac{\underbrace{1}_{\frac{\text{atoms}}{\text{unit cell}}}\ \overbrace{\frac{4}{3}\pi\,(0.5a)^3}^{\frac{\text{volume}}{\text{atom}}}}{\underbrace{a^3}_{\frac{\text{volume}}{\text{unit cell}}}} =0.52$$

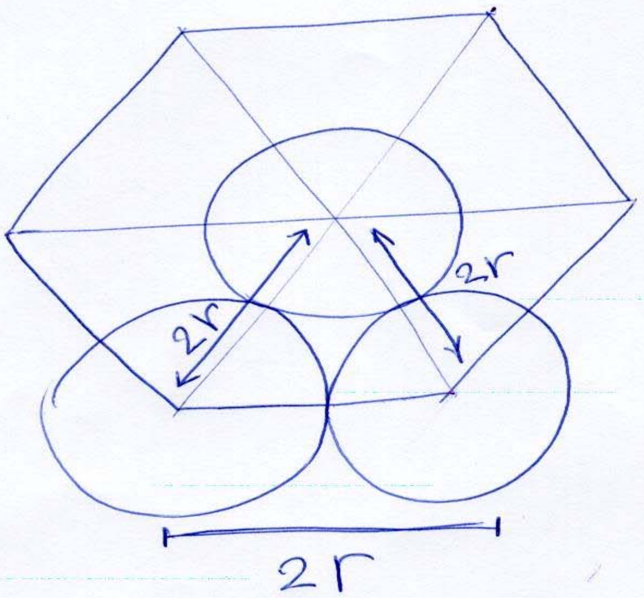
BCC

$$\text{APF} = \frac{\underbrace{2}_{\frac{\text{atoms}}{\text{unit cell}}}\ \underbrace{\frac{4}{3}\pi\left(\sqrt{3}a/4\right)^3}_{\frac{\text{volume}}{\text{atom}}}}{\underbrace{a^3}_{\frac{\text{volume}}{\text{unit cell}}}} = 0.68$$

FCC

$$\text{APF} = \frac{\underbrace{4}_{\frac{\text{atoms}}{\text{unit cell}}}\ \underbrace{\frac{4}{3}\pi\left(\sqrt{2}a/4\right)^3}_{\frac{\text{volume}}{\text{atom}}}}{\underbrace{a^3}_{\frac{\text{volume}}{\text{unit cell}}}} = 0.74$$

Atomic Packing factor for Hcp



$$V = 6 \times \frac{1}{2} \times 2r \times 2r \sin 60 \times 1.63(2r)$$

$$V = 6 \times \frac{1}{2} \times 2r \times 2r \sin 60 \times C$$

$$APf = \frac{6 \times \frac{4}{3} \pi r3}{12 r^2 \frac{\sqrt{3}}{2} \times 1.63(2r)} = 0.74$$

THEORETICAL DENSITY, ρ

atoms/unit cell

Atomic weight (g/mol)

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

Volume/unit cell
(cm^3/unit cell)

Avogadro's number
(6.023 x 10^{23} atoms/mol)

Example: Copper

Data from Table inside front cover of Callister

- crystal structure = FCC: 4 atoms/unit cell
- atomic weight = 63.55 g/mol (1 amu = 1 g/mol)
- atomic radius R = 0.128 nm (1 nm = 10^{-7}cm)

$V_C = a^3$; For FCC, $a = 4R/\sqrt{2}$; $V_C = 4.75 \times 10^{-23}\text{cm}^3$

Result: theoretical $\rho_{Cu} = 8.89$ g/cm^3
Compare to actual: $\rho_{Cu} = 8.94$ g/cm^3

ALLOTROPY: Ability of the material to have more than one crystal structure depending on temperature and pressure.

e.g. Pure iron has a BCC crystal structure at room temperature which changes to FCC at 912 C.

Example: Determine the volume change of a 1 cm3 cube iron when it is heated from 910C, where it is BCC with a lattice parameter of 0.2863 nm, to 915 C, where it is FCC with a lattice parameter of 0.3591.

VBcc= a3 = (0.2863)3 Vfcc= (0.3591)3

On the basis of equivalent number of atoms: 1 fcc unit cell has 4 atoms, while 1 bcc unit cell has 2 atoms

$$\text{Volume change} = \frac{\text{V fcc} - \text{2V Bcc}}{\text{2 VBcc}} = \frac{0.046307 - 2\,(0.023467}{2\,(0.023467)}\ \text{x100}$$

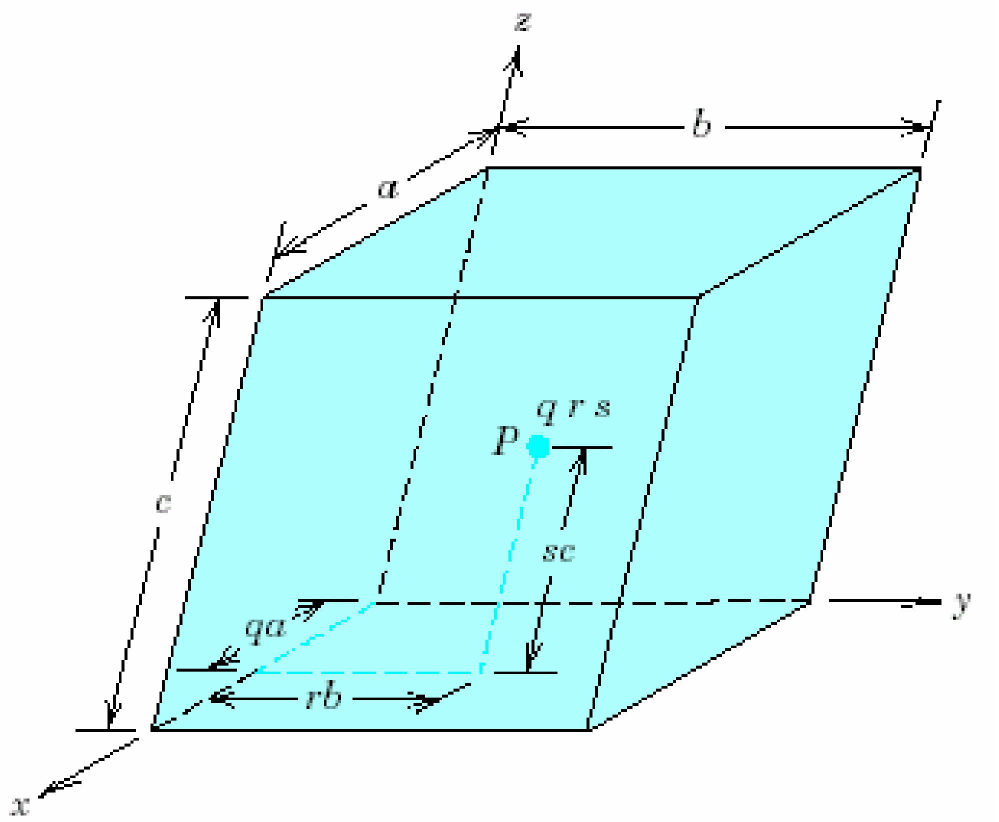
$$\boxed{= -1.34\ \%}$$

Iron contracts upon heating

Determine the volume change in cobalt when it transforms from HCP at room temperature to FCC at higher temperatures.

Crystrallographic points:

First put the three axes (X,Y,Z) at one of the corners.

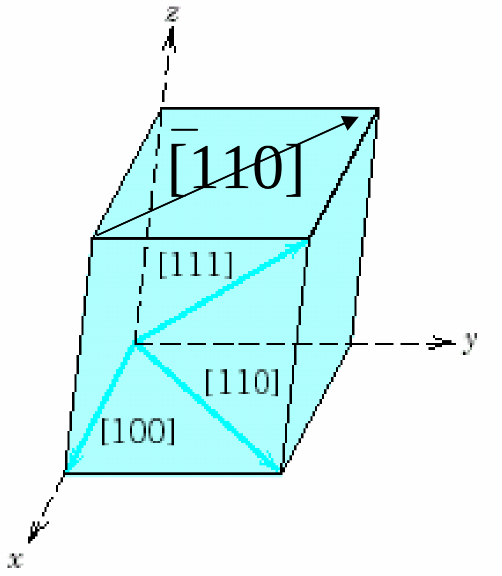


Coordinates of a point is given as a fraction of length a (x-axis), fraction of length b (y-axis) and fraction of length c (z-axis)

Example:

Directions in unit cell:

1. Subtract the coordinates of the tail point from the coordinates of the head point.
2. Clear fractions by multiplying or dividing by a common factor and reduce to lowest integers.



- A direction and its multiple is identical, [100] is identical to [200], the second was not reduced to lowest integer.
- Changing the sign of all indices produces a vector that is opposite in direction.
- Parallel vectors have same indices

Equivalent Directions:

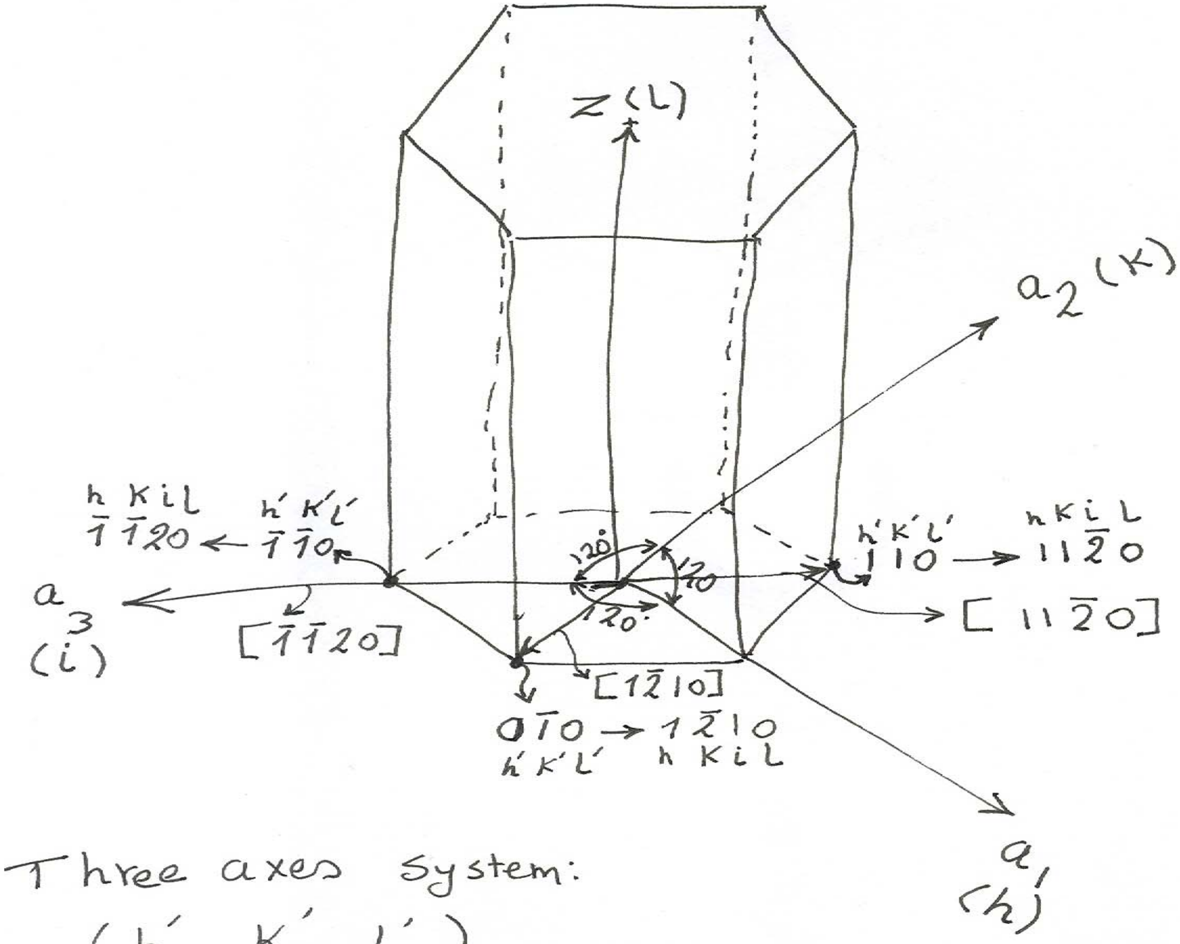
- Directions along which spacing of atoms is the same are considered equivalent directions, they create family of directions.

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

- Directions having the same indices with out regard to order or sign are equivalent: [123] is equivalent to [$\bar{2}$1$\bar{3}$]

Example: Sketch the following directions: [111], [121], $[\bar{1}10]$

Hexagonal crystals:



* Three axes system:

(h', K', l')

a_1 a_2 Z

* Four axes system:

(h, K, i, L)

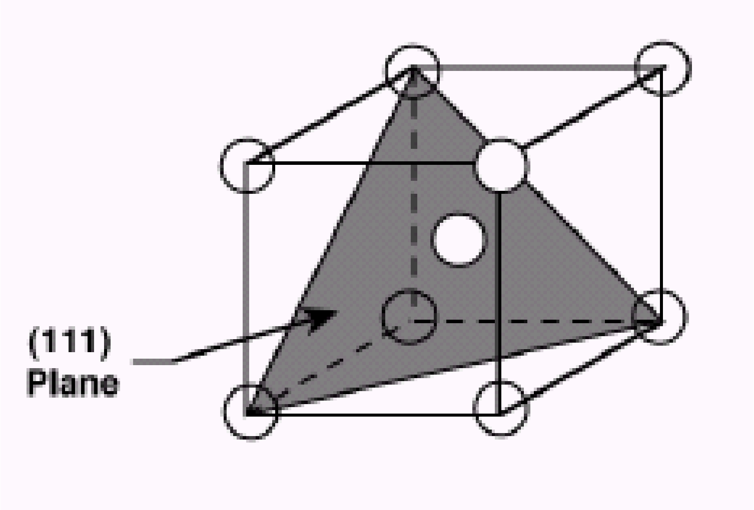
a_1 a_2 a_3 Z

- $h = \frac{1}{3}(2h' - k')$
- $K = \frac{1}{3}(2K' - h')$
- $i = -\frac{1}{3}(h' + K')$
- $L = L'$

$\boxed{* \; h + K = -i}$

*Planes in Unit cell

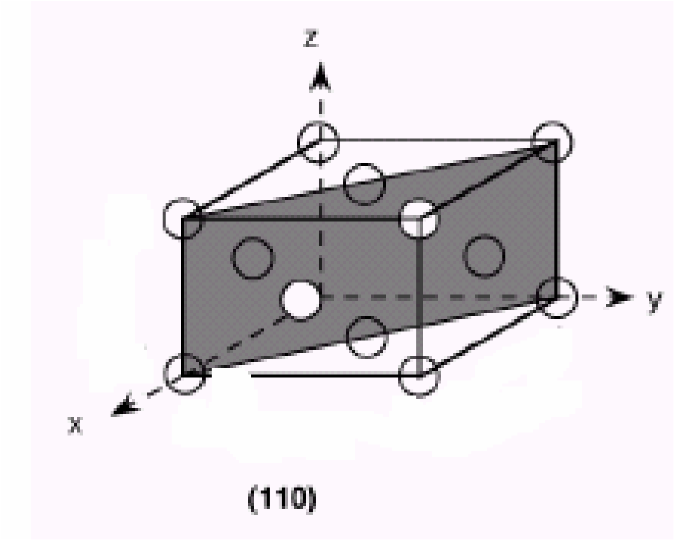
1. Identify the intercept of the plane with the three axes in terms of a, b and c
2. Take the reciprocal of these numbers.
3. Clear fractions by multiplying or dividing by a common factor.



Intercepts: 1 1 1

Reciprocal: 1 1 1

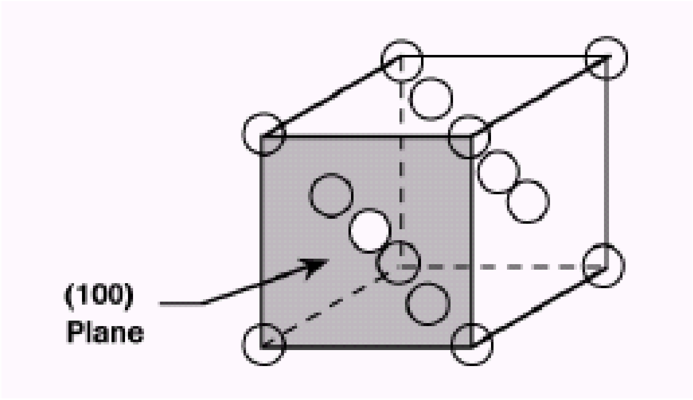
Plane: (111)



Intercept: 1 1 ∞

Reciprocal: 1 1 0

Plane : (110)



Intercept: 1 ∞ ∞

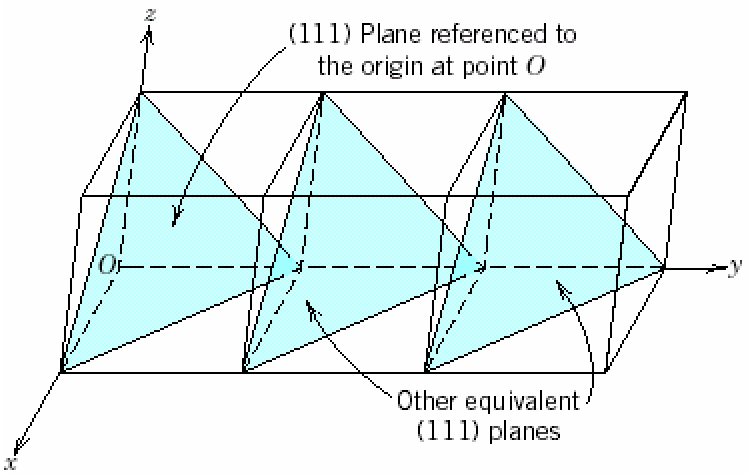
Reciprocal: 1 0 0

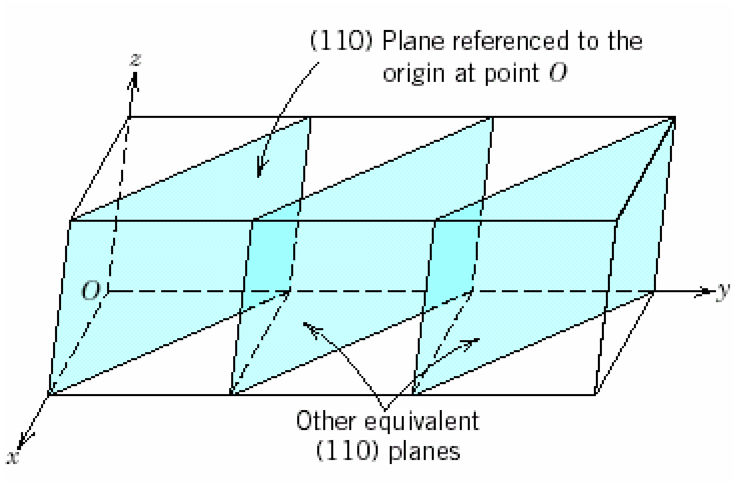
Plane: (100)

- If the plane passes through the origin, then the origin point has to be shifted by one lattice parameter to another corner.

Example:

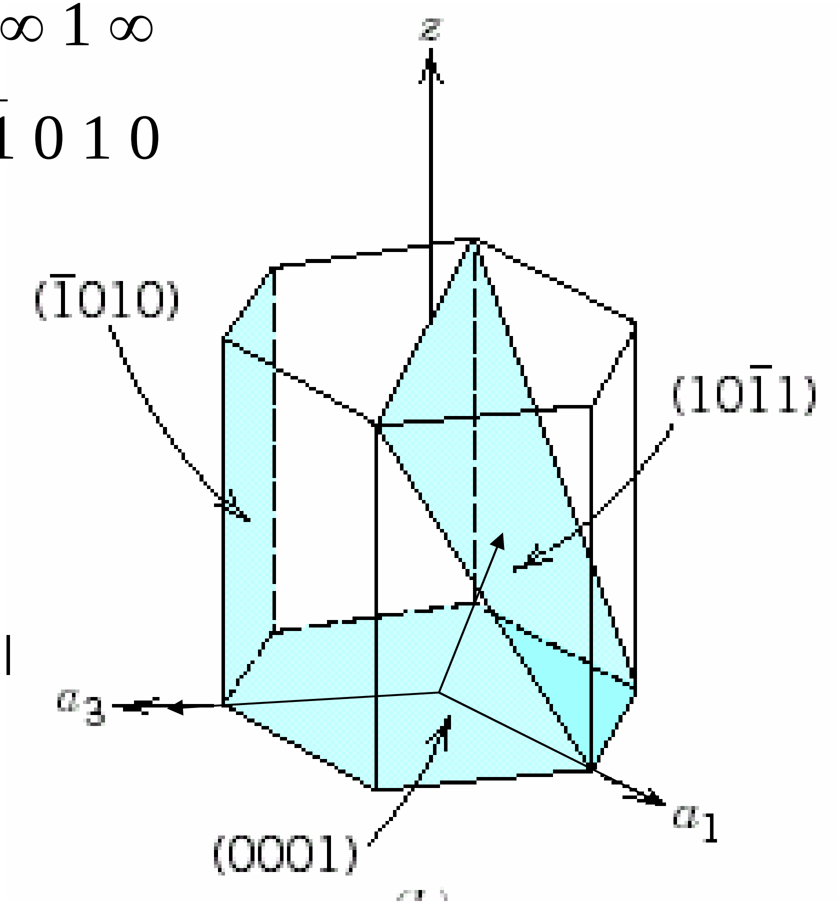
Equivalent planes





Intercept: $\bar{1}$ ∞ 1 ∞

Reciprocal: $\bar{1}$ 0 1 0



Intercepts: 1 ∞ $\bar{1}$ 1

Reciprocal: 1 0 $\bar{1}$ 1

Plane: (10$\bar{1}$1)

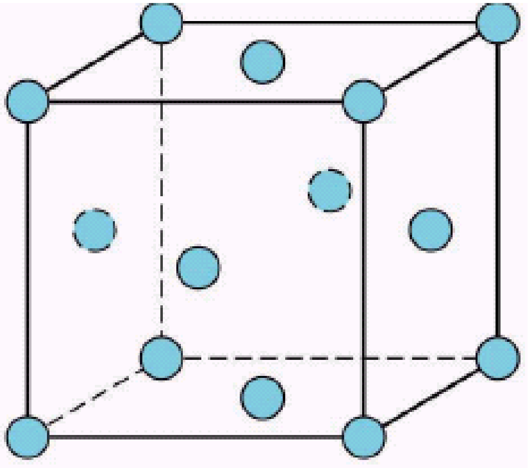
Linear density: $$\frac{\text{No. of atoms}}{\text{Magnitude of the direction}}$$

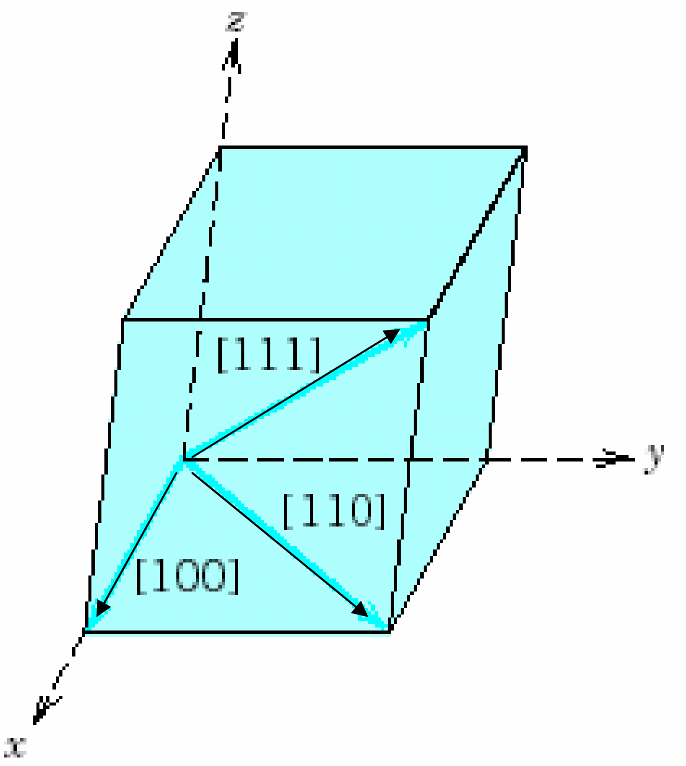
Linear Packing: $$\frac{\text{Length occupied by atoms}}{\text{Magnitude of the direction}}$$

Example: Calculate the linear density and linear packing factor

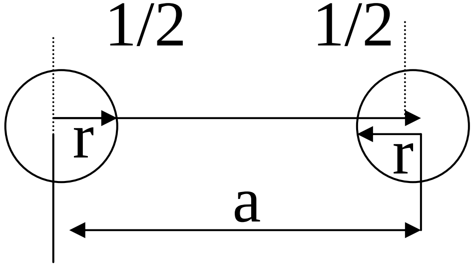
Choose which would be a possible slip direction :

[100], [110] and [111] in FCC unit cell.





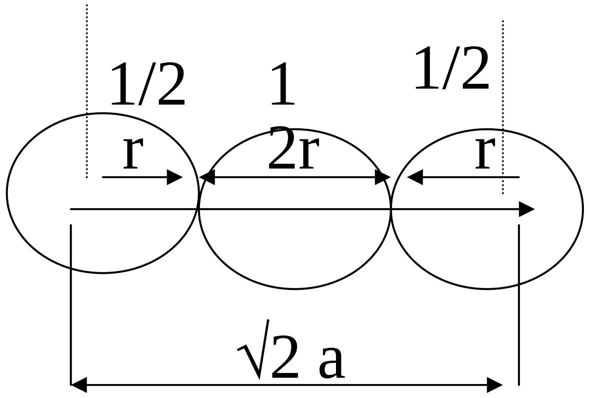
[100]



L.D= $1/a = 1/\ 2\ \sqrt{2}\ r$

L.P= $2r\ /\ 2\ \sqrt{2}\ r\ =\ 0.71$

[110]



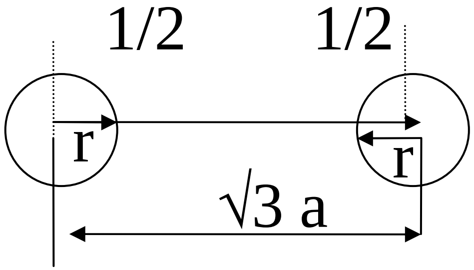
$L.D= 2 / \sqrt{2}\, a$

$L.P= 4r/ \sqrt{2}\; 2\, \sqrt{2}\, r= 1.0$

Length of burgers vector is $\sqrt{2}\, a /2$

½ the face diagonal

[111]



$L.D= 1 / \sqrt{3}\, a$

$L.P= 2r/ \sqrt{3}\; 2\, \sqrt{2}\, r= 0.4$

In FCC unit cell any face diagonal is highly packed with atoms referred to as close packed direction.

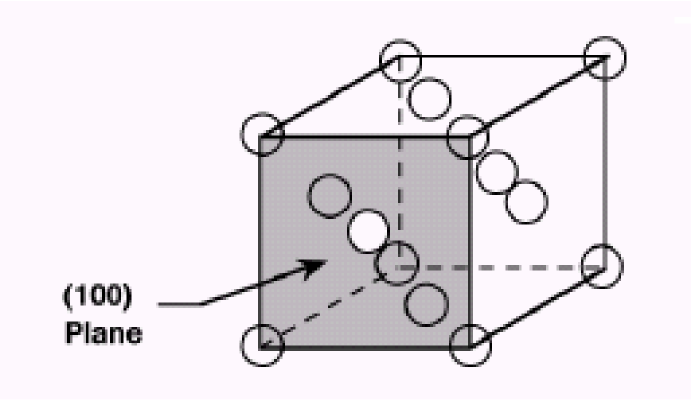
Planar density: $\dfrac{\text{No. of atoms}}{\text{Area of plane}}$

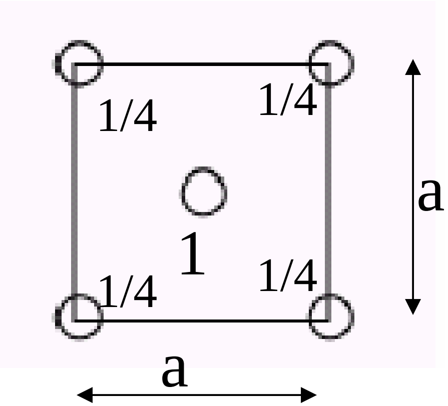
Planar Packing: $\dfrac{\text{Area occupied by atoms}}{\text{Area of plane}}$

Example: Calculate the planar density and planar packing factor

Choose which would be a possible slip plane :

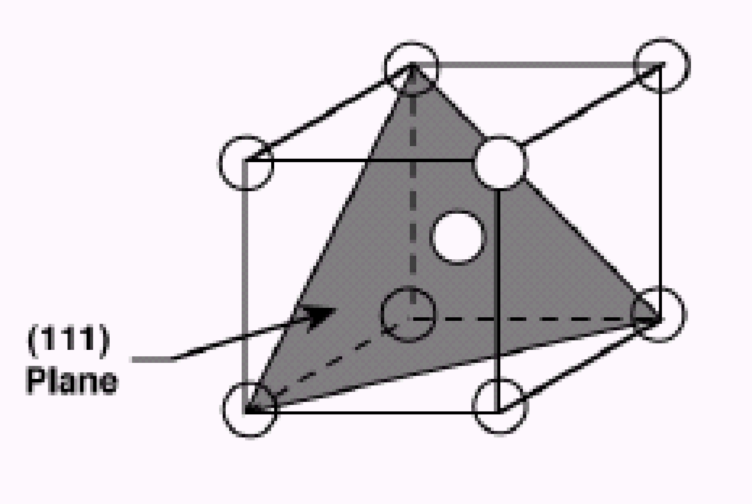
(100), (110) and (111) in FCC unit cell.

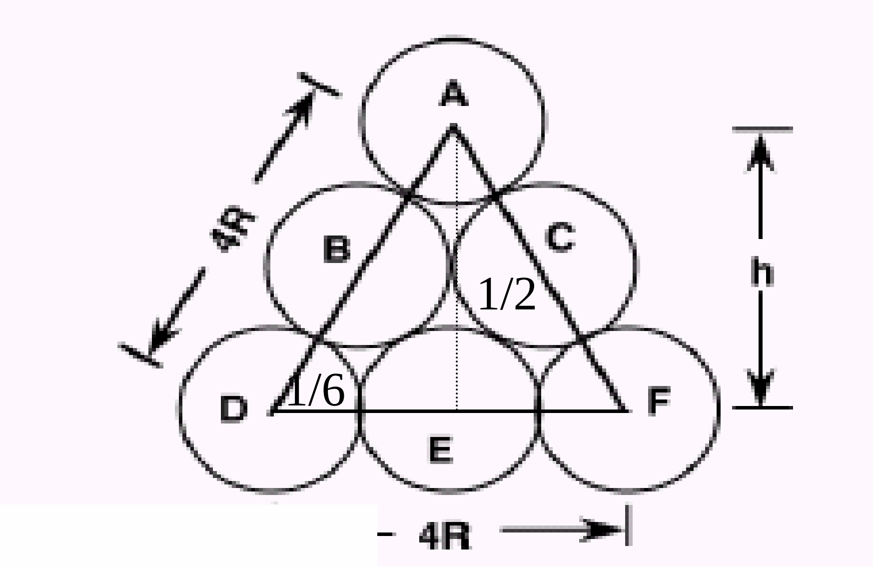




P.D = 2/ a^2= 2/ $8r^2$

P.F=2 πr^2 / $8r^2$ = 0.79





$$(2R)^2 + h^2 = (4R)^2$$

No. of atoms= 3x 1/6 +3x 1 / 2

which leads to $h = 2R\sqrt{3}$. Thus, the area is equal to

$$\text{Area} = \frac{4R(h)}{2} = \frac{(4R)\left(2R\sqrt{3}\right)}{2} = 4R^2\sqrt{3}$$

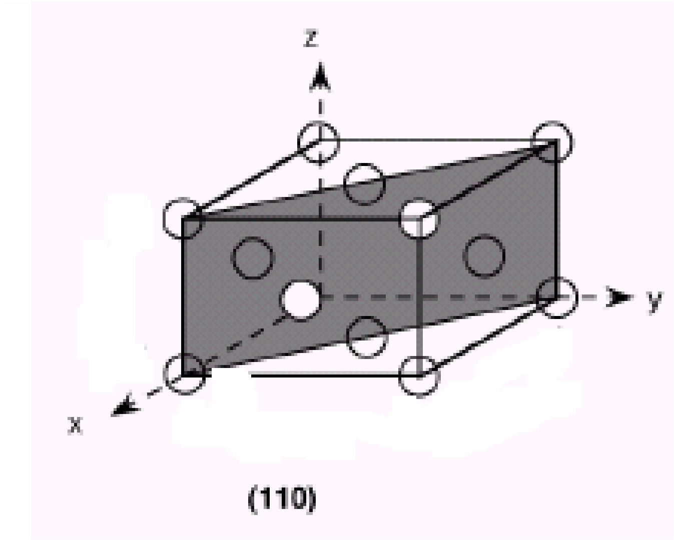
= ½ x base x height

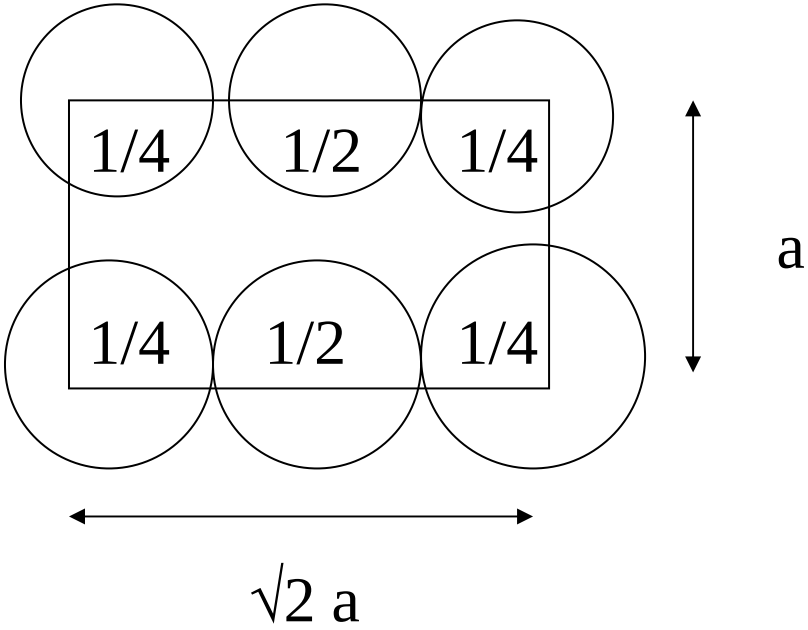
And, thus, the planar density is

$$PD_{111} = \frac{\text{number of atoms centered on (111) plane}}{\text{area of (111) plane}}$$

$$= \frac{2\text{ atoms}}{4R^2\sqrt{3}} = \frac{1}{2R^2\sqrt{3}}$$

$\text{P.F} = 2\pi r^2 / 4r^2\sqrt{3} = 0.9$





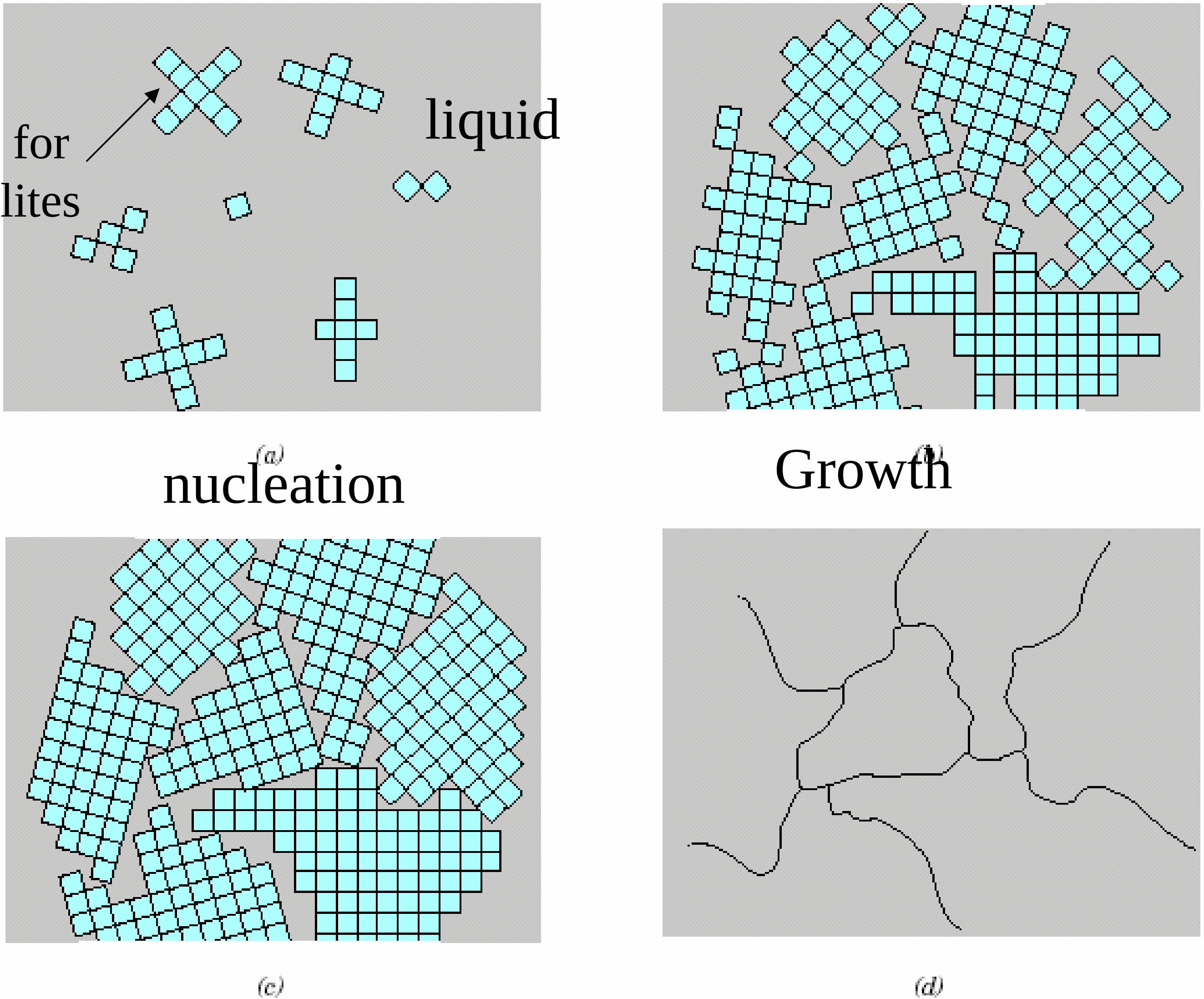
$\text{P.D} = 2/\sqrt{2}\, a^2 = 2/\, 8\sqrt{2}\, r^2$

$\text{P.F} = 2\pi r^2 / 8\sqrt{2}\, r^2 = 0.56$

(111) Plane in fcc is the slip plane because it has the highest atomic packing density

Example

Solidification of a polycrystalline metal



Nuclei for crystallites

liquid

nucleation

Growth

Grains are formed

liquid	nucleation	growth	Grain with different lattice orientations

- Different grains have different orientations of atoms separated by grain boundaries.
- Anistropy: Properties depend on crystallographic direction.
- Isotropic: Properties are independent of directions.

POLYCRYSTALS

- *Most* engineering materials are polycrystals.

Adapted from Fig. K, color inset pages of *Callister 6e*.
(Fig. K is courtesy of Paul E. Danielson, Teledyne Wah Chang Albany)

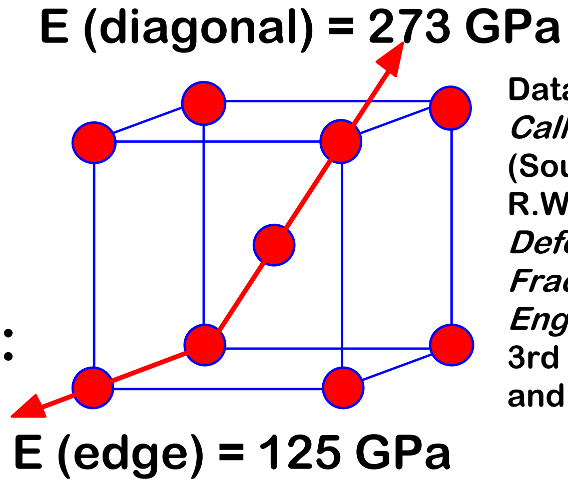
- Nb-Hf-W plate with an electron beam weld.
- Each "grain" is a single crystal.
- If crystals are randomly oriented,
  overall component properties are not directional.
- Crystal sizes typ. range from 1 nm to 2 cm
  (i.e., from a few to millions of atomic layers).

SINGLE VS POLYCRYSTALS

- **Single Crystals**

  -Properties vary with direction: anisotropic.

  -Example: the modulus of elasticity (E) in BCC iron:



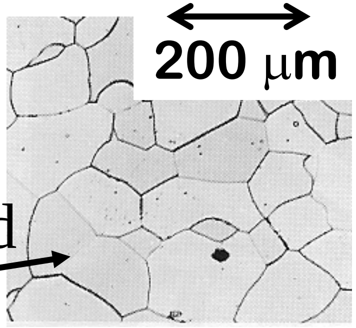
Data from Table 3.3, *Callister 6e*. (Source of data is R.W. Hertzberg, *Deformation and Fracture Mechanics of Engineering Materials*, 3rd ed., John Wiley and Sons, 1989.)

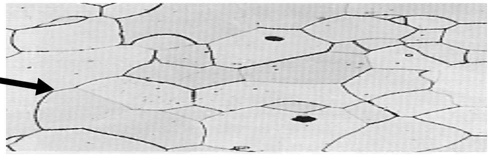
- **Polycrystals**

  -Properties may/may not vary with direction.

  -If grains are randomly oriented: isotropic. ($E_{\text{poly iron}}$ = 210 GPa)

  -If grains are textured, anisotropic.





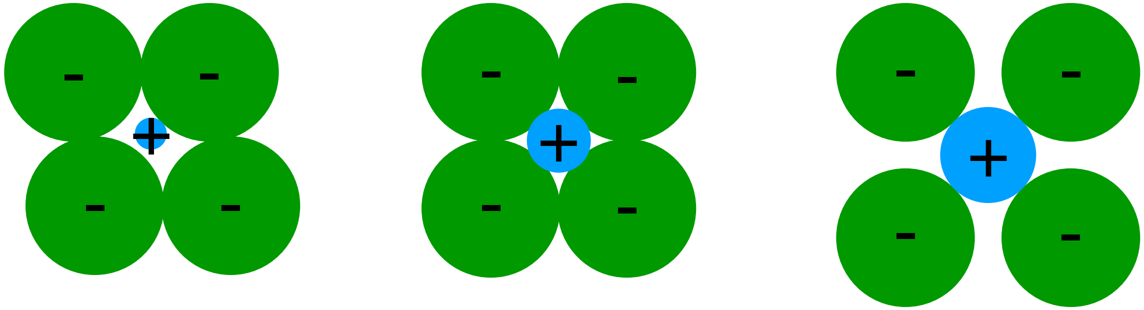
Adapted from Fig. 4.12(b), *Callister 6e*. (Fig. 4.12(b) is courtesy of L.C. Smith and C. Brady, the National Bureau of Standards, Washington, DC [now the National Institute of Standards and Technology, Gaithersburg, MD].)

Structure of Ceramic Materials

Factors that Determine Crystal Structure

1. Relative sizes of ions – Formation of stable structures:

--maximize the # of oppositely charged ion neighbors.

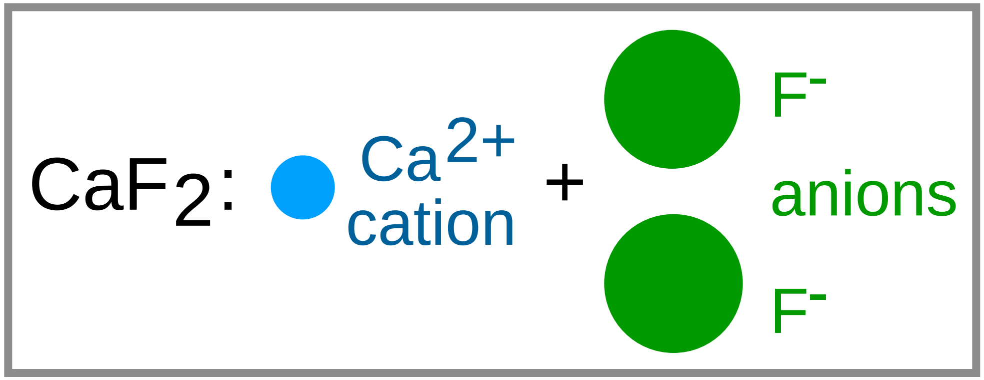


unstable stable stable

2. Maintenance of Charge Neutrality :

--Net charge in ceramic should be zero.

--Reflected in chemical formula:



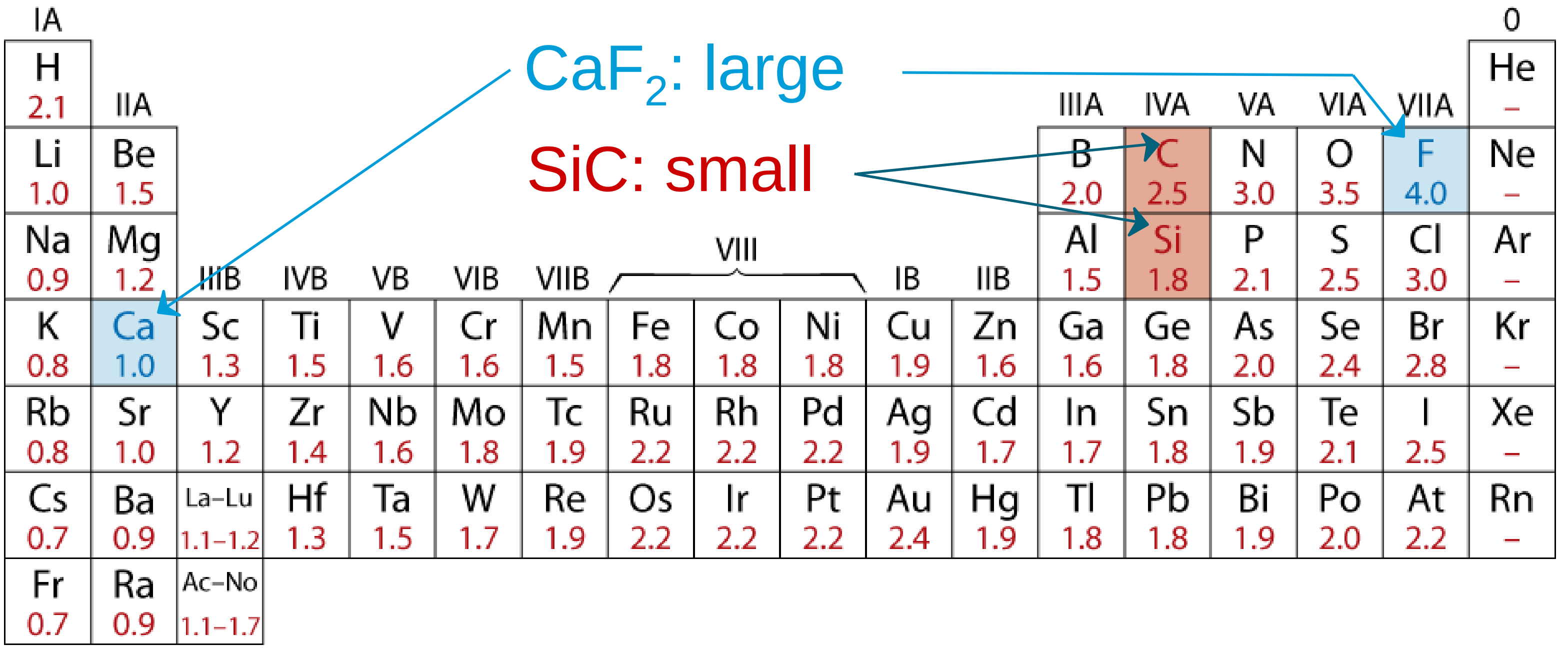
CaF_2: Ca^{2+} cation + F^- anions F^-

$A_m X_p$

m, p values to achieve charge neutrality

Atomic Bonding in Ceramics

- Bonding:
  - -- Can be ionic and/or covalent in character.
  - -- % ionic character increases with difference in electronegativity of atoms.
- Degree of ionic character may be large or small:



CaF_2: large

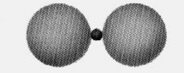
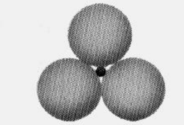
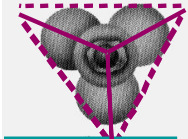
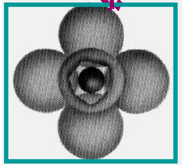
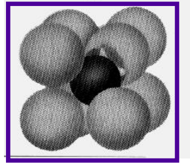
SiC: small

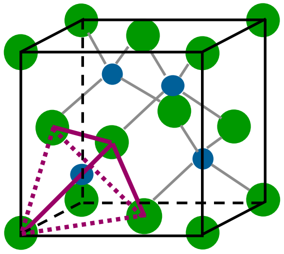
IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIII			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0
H 2.1																	He –
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne –
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar –
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr –
Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	Xe –
Cs 0.7	Ba 0.9	La–Lu 1.1–1.2	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	Rn –
Fr 0.7	Ra 0.9	Ac–No 1.1–1.7															

Coordination # and Ionic Radii

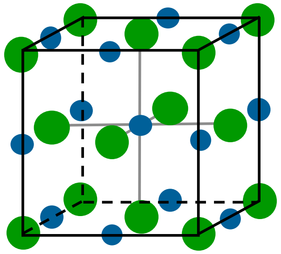
- Coordination # increases with $\frac{r_{cation}}{r_{anion}}$

To form a stable structure, how many anions can surround a cation?

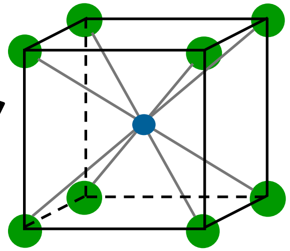
$\frac{r_{cation}}{r_{anion}}$	Coord #		
< 0.155	2	linear	
0.155 - 0.225	3	triangular	
0.225 - 0.414	4	tetrahedral	
0.414 - 0.732	6	octahedral	
0.732 - 1.0	8	cubic	



ZnS (zinc blende)

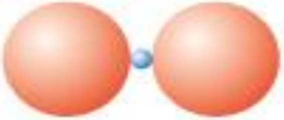
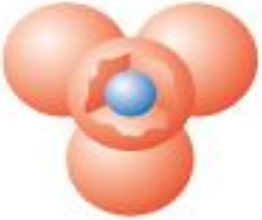
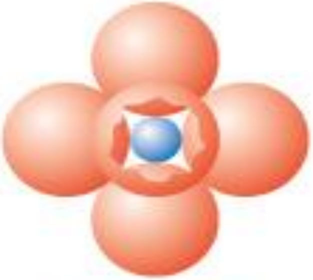
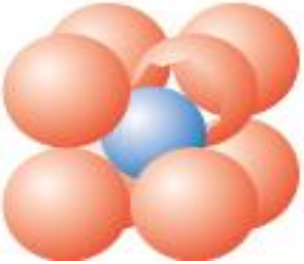


NaCl (sodium chloride)



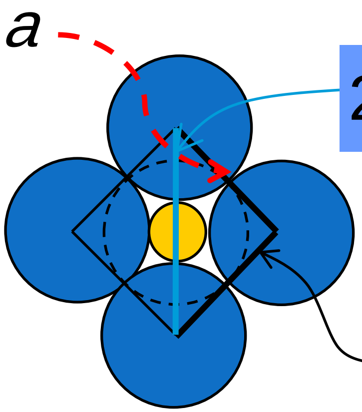
CsCl (cesium chloride)

Table 3.3 **Coordination Numbers and Geometries for Various Cation–Anion Radius Ratios (r_C/r_A)**

Coordination Number	*Cation–Anion Radius Ratio*	*Coordination Geometry*
2	<0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	

Computation of Minimum Cation-Anion Radius Ratio

- Determine minimum r_{cation}/r_{anion} for an octahedral site (C.N. = 6)



$$2r_{anion} + 2r_{cation} = \sqrt{2}a$$

Measure the radii (blue and yellow spheres)

$$a = 2r_{anion}$$

Substitute for **"a"** in the above equation

$$2r_{anion} + 2r_{cation} = 2\sqrt{2}r_{anion}$$

$$r_{anion} + r_{cation} = \sqrt{2}r_{anion}$$

$$r_{cation} = (\sqrt{2} - 1)r_{anion}$$

$$\boxed{\frac{r_{cation}}{r_{anion}} = \sqrt{2} - 1 = 0.414}$$

Example Problem: Predicting the Crystal Structure of FeO

- On the basis of ionic radii, what crystal structure would you predict for FeO?

Cation	Ionic radius (nm)
Al^{3+}	0.053
Fe^{2+}	0.077
Fe^{3+}	0.069
Ca^{2+}	0.100

Anion	
O^{2-}	0.140
Cl^{-}	0.181
F^{-}	0.133

- Answer:

$$\frac{r_{cation}}{r_{anion}} = \frac{0.077}{0.140}$$

$$= 0.550$$

based on this ratio,
-- coord # = 6 because

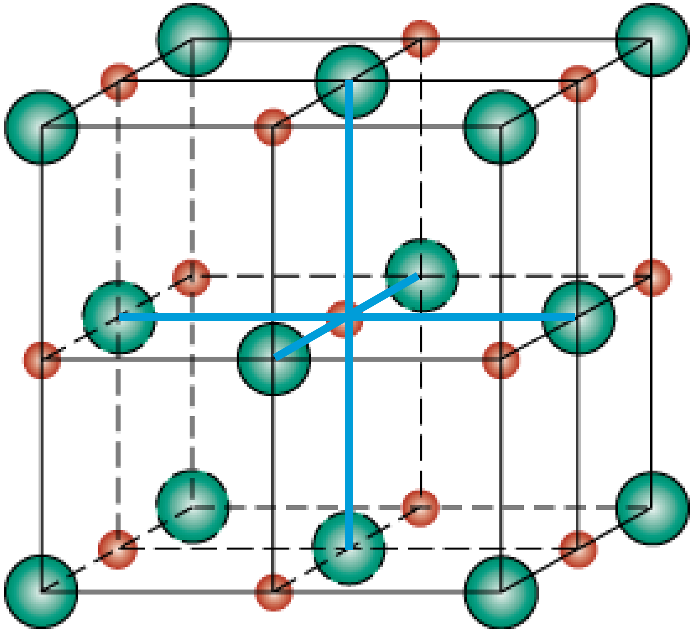
$0.414 < 0.550 < 0.732$

-- crystal structure is similar to NaCl

Rock Salt Structure

Same concepts can be applied to ionic solids in general.

Example: NaCl (rock salt) structure



● Na^+ $r_{Na} = 0.102$ nm

● Cl^- $r_{Cl} = 0.181$ nm

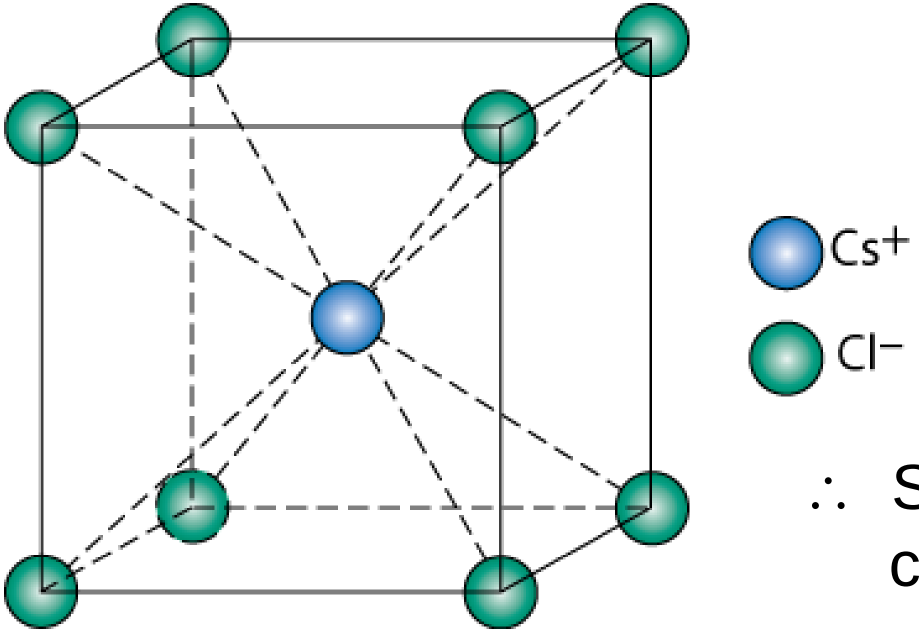
$r_{Na}/r_{Cl} = 0.564$

∴ cations (Na^+) prefer octahedral sites

AX Crystal Structures

AX–Type Crystal Structures include NaCl, CsCl, and zinc blende

Cesium Chloride structure:



$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{0.170}{0.181} = 0.939$$

$\therefore$ Since $0.732 < 0.939 < 1.0$, cubic sites preferred

So each Cs^+ has 8 neighbor Cl^-

SUMMARY

- Atoms may assemble into crystalline or amorphous structures.
- Common metallic crystal structures are FCC, BCC and HCP. Coordination number and atomic packing factor are the same for both FCC and HCP crystal structures.
- We can predict the density of a material, provided we know the atomic weight, atomic radius, and crystal geometry (e.g., FCC, BCC, HCP).
- Interatomic bonding in ceramics is ionic and/or covalent.
- Ceramic crystal structures are based on:

  -- maintaining charge neutrality

  -- cation-anion radii ratios.