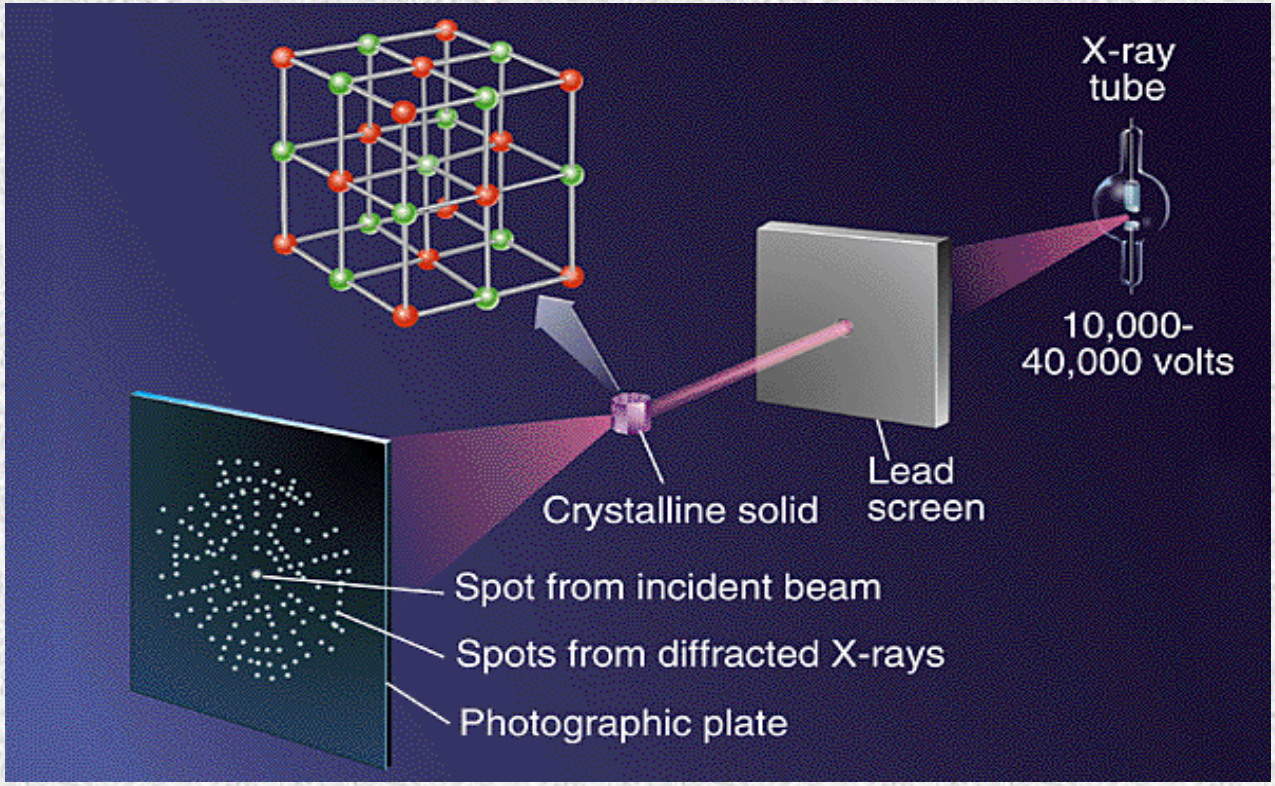
Atomic Arrangement



Primer in Materials

Spring 2018

12.4.2018

Levels of atomic arrangements

➢ No order

In gases, for example the atoms have no order, they are randomly distributed filling the volume to which the gas is confined

➢ Short-range order

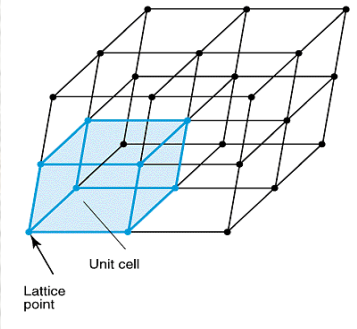
A material displays short-range order if the special arrangement of the atoms extends only to atom's nearest neighbors (**Amorphous Material/Glass**)

➢ Long-range order

Metals, semi-conductors and many ceramics have crystalline structure in which the special atomic arrangement extends throughout the entire material. The atoms form a regular repetitive, grid-like pattern, or **Lattice**.

The lattice differs from material to material in both **shape** and **size**

Lattice



❖Unit cell

is the subdivision of the crystalline lattice that still retains the overall characteristics of the entire lattice.

❖Lattice points

Located at the corners of the unit cell and, in some cases, at either faces or the in the unit cell.

❖Lattice parameter

describes the length of one side of the unit cell

Typically in order of nanometer (1nm=1*10^{-9} m)

❖Number of atoms per unit cell

A specific number of lattice points that define each of the unit cells, when counting one must recognize that lattice points may be shared by more than one unit cell

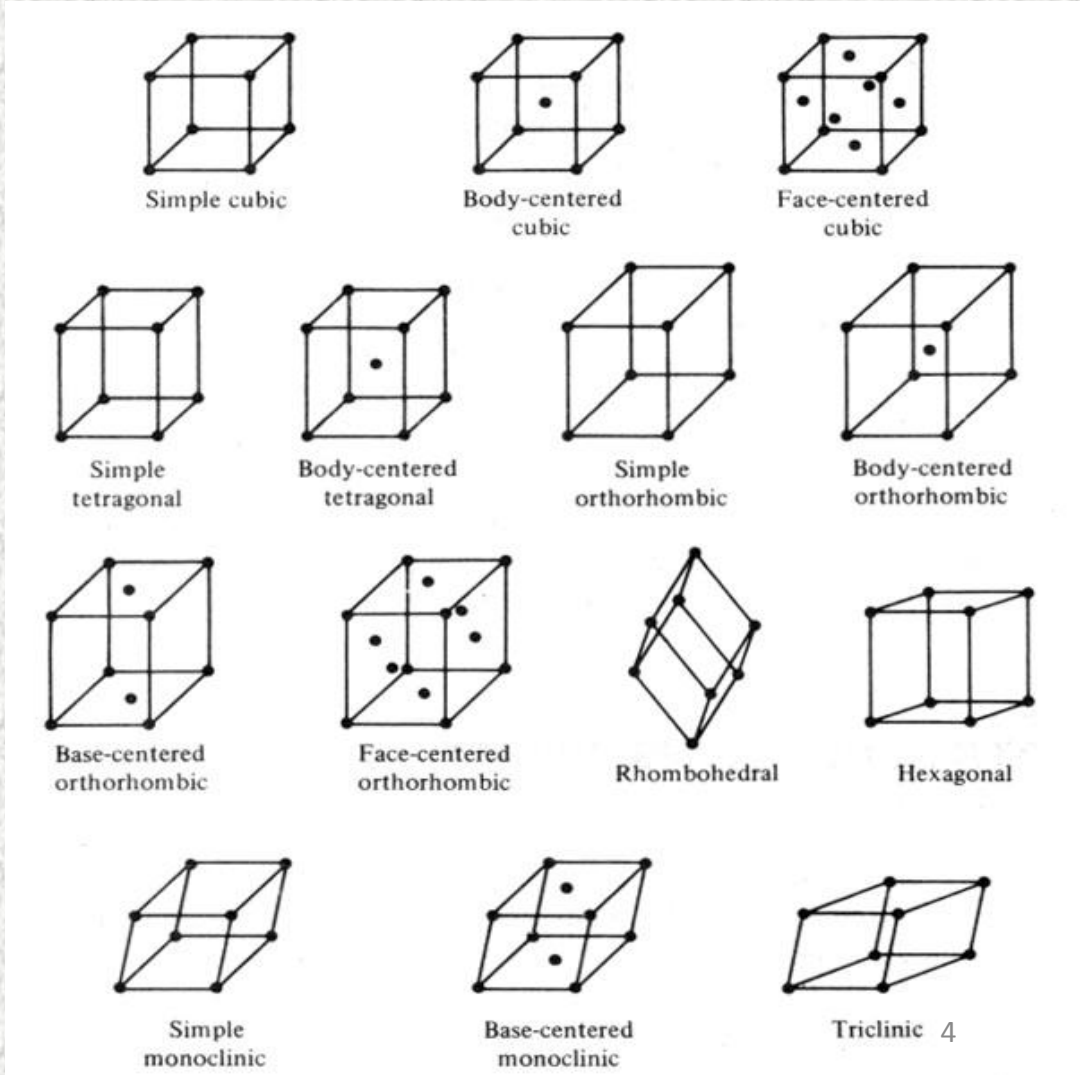
❖Coordination Number

The number of the closest neighbor atoms to a lattice point

Bravais lattices

- There are 14 different lattices in 3D divided into 7 crystal systems

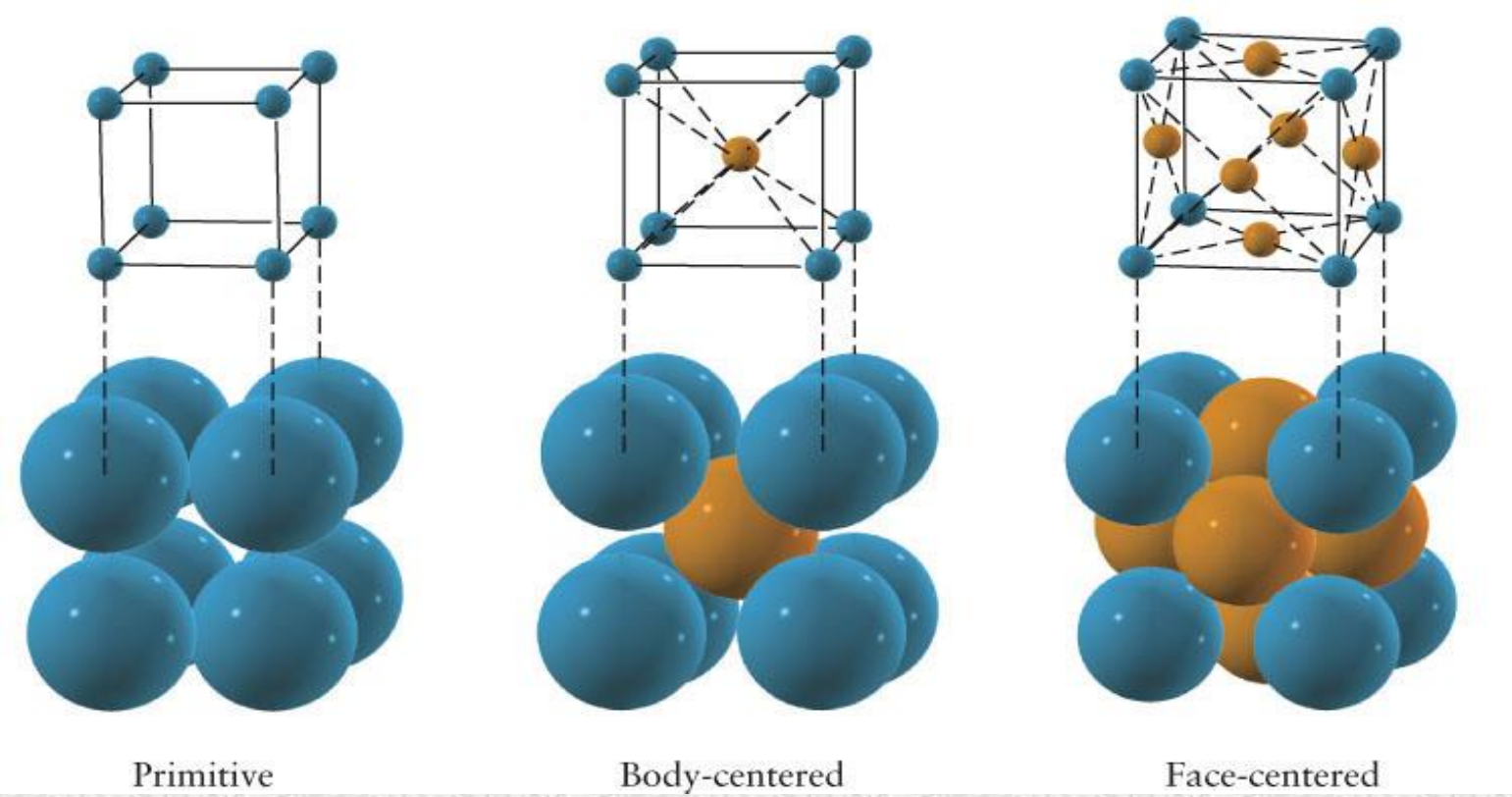
Structure	axes	Angles between axes
Cubic	a=b=c	$\alpha=\beta=\gamma=90^o$
Tetragonal	a=b≠c	$\alpha=\beta=\gamma=90^o$
Orthorhombic	a≠b≠c	$\alpha=\beta=\gamma=90^o$
Hexagonal	a=b≠c	$\alpha=\beta=90^o$, $\gamma=120^o$
Rhombohedral	a=b=c	$\alpha=\beta=\gamma\neq90^o$
Monoclinic	a≠b≠c	$\alpha=\beta=90^o$, $\gamma\neq90^o$
Triclinic	a≠b≠c	$\alpha\neq\beta\neq\gamma\neq90^o$



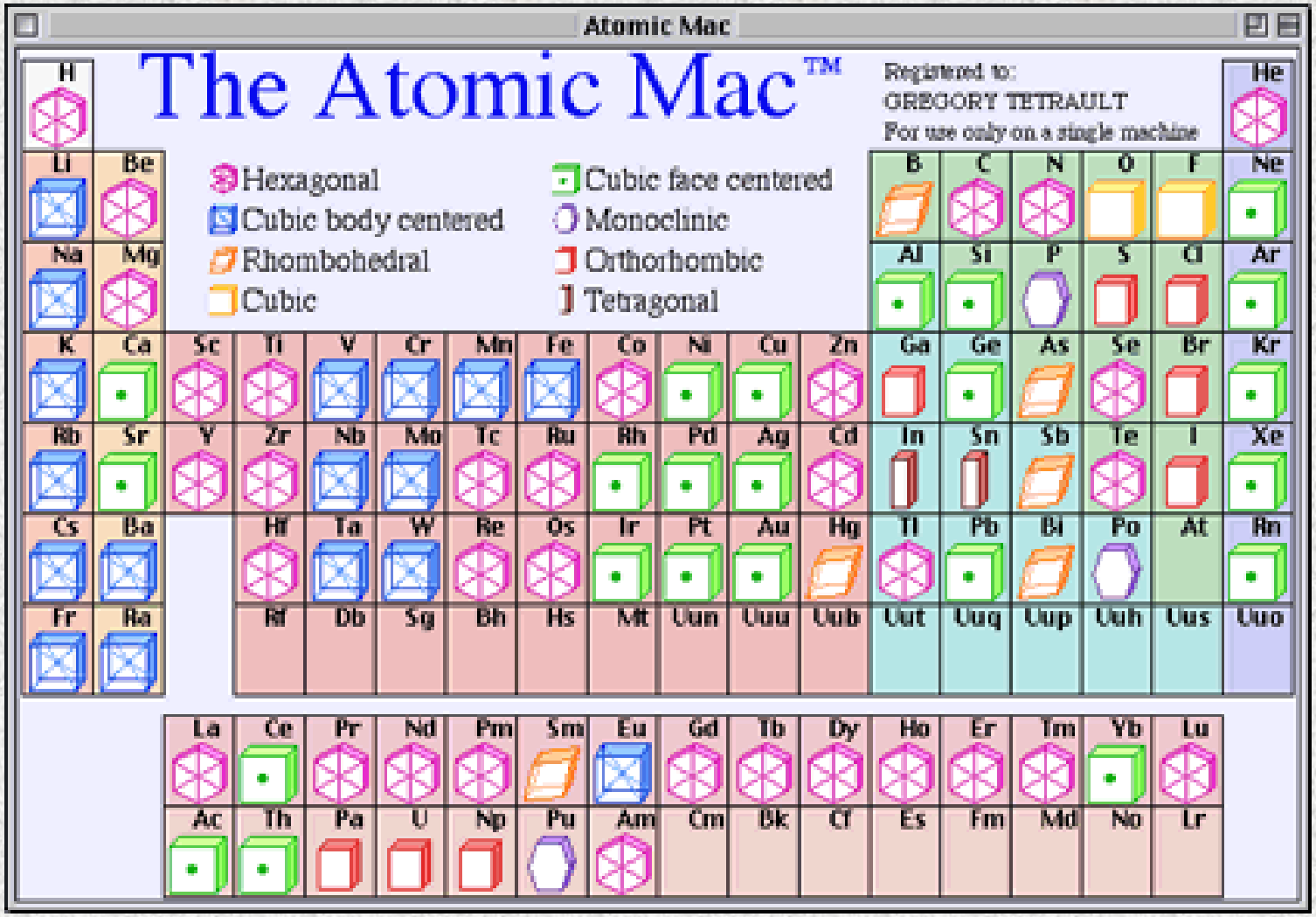
Hard spheres model

Assumptions:

- All the atoms are hard spheres that can not be distorted
- The atoms in the most dense direction are touch each other



Crystal Structure of Elements



Crystal Structure and atomic radii of some selected metals

Table 3.1 Atomic Radii and Crystal Structures for 16 Metals

Metal	*Crystal Structure*[a]	*Atomic Radius*[b] *(nm)*	*Metal*	*Crystal Structure*	*Atomic Radius (nm)*
Aluminum	FCC	0.1431	Molybdenum	BCC	0.1363
Cadmium	HCP	0.1490	Nickel	FCC	0.1246
Chromium	BCC	0.1249	Platinum	FCC	0.1387
Cobalt	HCP	0.1253	Silver	FCC	0.1445
Copper	FCC	0.1278	Tantalum	BCC	0.1430
Gold	FCC	0.1442	Titanium (α)	HCP	0.1445
Iron (α)	BCC	0.1241	Tungsten	BCC	0.1371
Lead	FCC	0.1750	Zinc	HCP	0.1332

[a] FCC = face-centered cubic; HCP = hexagonal close-packed; BCC = body-centered cubic.

[b] A nanometer (nm) equals 10^{-9} m; to convert from nanometers to angstrom units (Å), multiply the nanometer value by 10.

Example 1.1

Determine the number of lattice atoms per cell and the coordination number in the cubic crystal systems

SC – one point at each corner i.e. 8 points per unit cell. BUT each point is been shared by 8 unit cells so: (8 corners)·(⅛)=1; CN=6

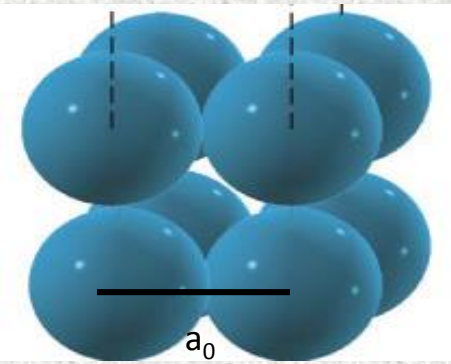
BCC – one point at each corner (shared by other 8 unit cells) and another point in the center. (8 corners)·(⅛)+(1 center)=2 ; CN=8

FCC – again, one shared point at each corner plus one point at each face (shared by two unit cells). (8 corners)·(⅛)+(6 faces) · (½)=4 ; CN=12

Example 1.2

Determine the relationship between the atomic radius and the lattice parameter in SC and BCC

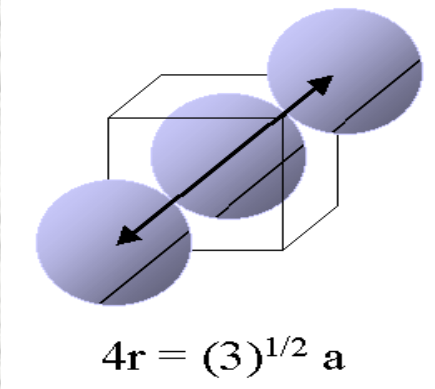
Let r be the radii of the atom and a_0 the side of the cube:



<u>SC</u>: $a_0 = 2r$

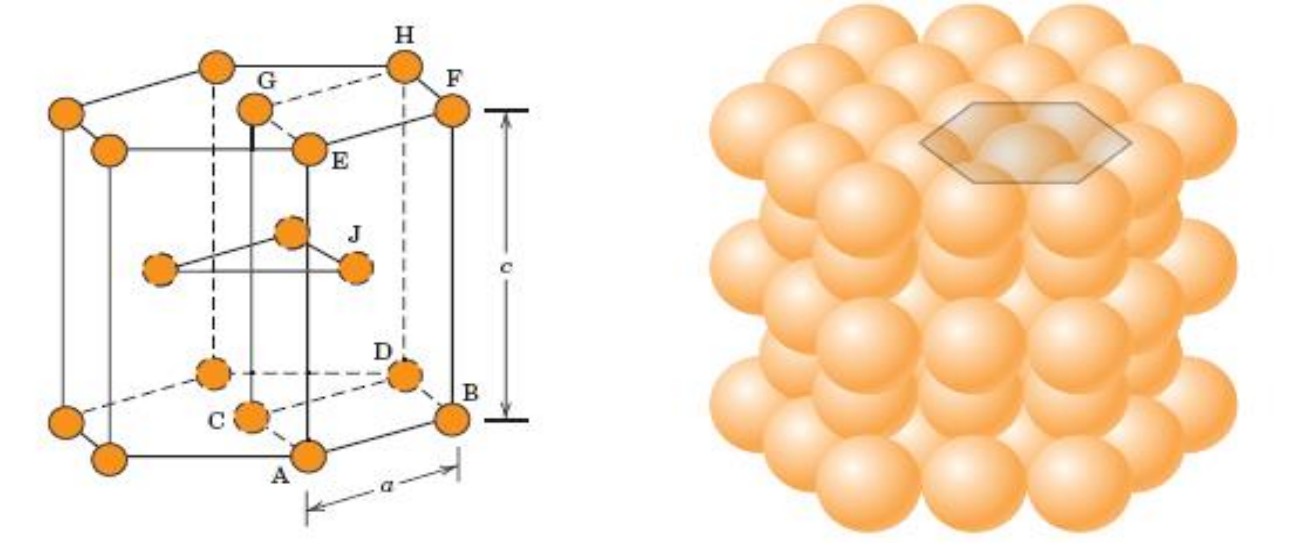
<u>BCC</u>: the atoms along the main diagonal touches each other

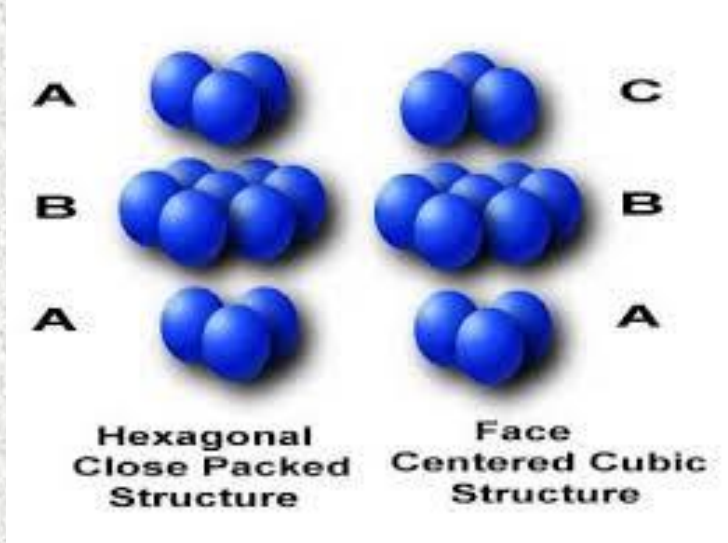
$$a0 := \frac{4r}{\sqrt{3}}$$



Hexagonal Close-Pack (HCP)

Not all metals have unit call with cubic symmetry. Some has a unit cell that is hexagonal (Co, Ti, Zn)





c/a ratio should be 1.633; however, for some HCP metals this ratio deviates from the ideal value

Packing factor

The packing factor is the fraction of space occupied by atoms, assuming that atoms are hard spheres

$$\text{APF} = \frac{\text{volume of atoms in a unit cell}}{\text{total unit cell volume}}$$

Examplele 1.3

Calculate the packing factor for the FCC cell

There are 4 lattice points per cell and one atom per unit cell giving total 4 atoms per unit cell. The volume each atom is ⅓($4\pi R^3$) and the volume of the unit cell is a_0^3:

$$\text{Packing factor} = \frac{(4 \text{ atoms / cell})(\frac{4}{3}\pi r^3)}{a_0^3}$$

Since, for FCC unit cells, $a_0 = 4r/\sqrt{2}$:

$$\text{Packing factor} = \frac{(4)(\frac{4}{3}\pi r^3)}{(4r/\sqrt{2})^3} = 0.74$$

More about PF

The packing factor of 0.74 in the fcc unit cell is the most efficient packing possible

Lattice type	PF
FCC	0.74
BCC	0.68
SC	0.52
HCP	0.74

No common engineering metals have the SC structure

Density

The theoretical density of a material can be calculated using the properties of the crystal structure. The general formula is:

$$\rho = \frac{nA}{V_C N_A}$$

where

n = number of atoms associated with each unit cell
A = atomic weight
V_C = volume of the unit cell
N_A = Avogadro's number (6.023×10^{23} atoms/mol)

Example 1.4

Calculate the theoretical density of copper

$r := 0.1278\text{nm} \quad Mw := 63.546 \frac{\text{gm}}{\text{mol}} \quad n := 4 \quad Av := 6.022 \cdot 10^{23} \frac{1}{\text{mol}}$

$a0 := \frac{4 \cdot r}{\sqrt{2}} \qquad a0 = 0.361\ \text{nm}$

$Vc := a0^3 \qquad Vc = 4.723 \times 10^{-29}\ \text{m}^3$

$\rho := \frac{n \cdot Mw}{Vc \cdot Av} \qquad \rho = 8.937 \times 10^3 \frac{\text{kg}}{\text{m}^3}$

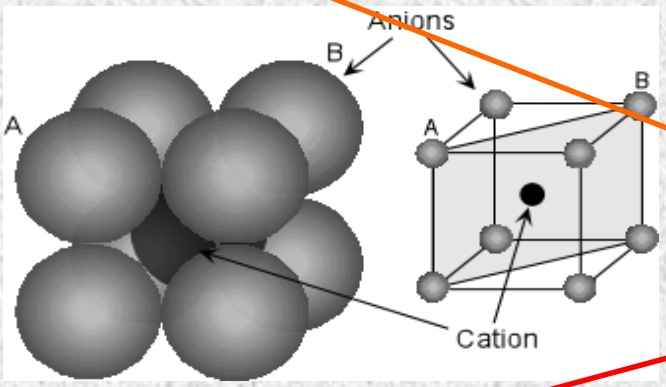
The theoretical density is higher than the measured one (ρ=8.93) why?

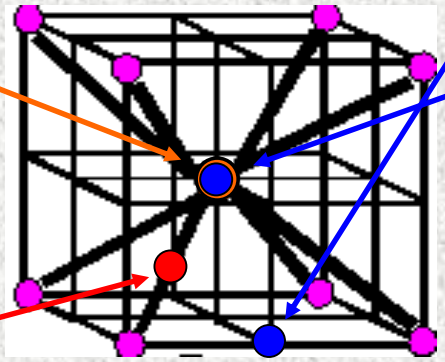
Interstitial sites

Interstitial sites are small voids between the basic lattice atoms into which smaller atoms may be places

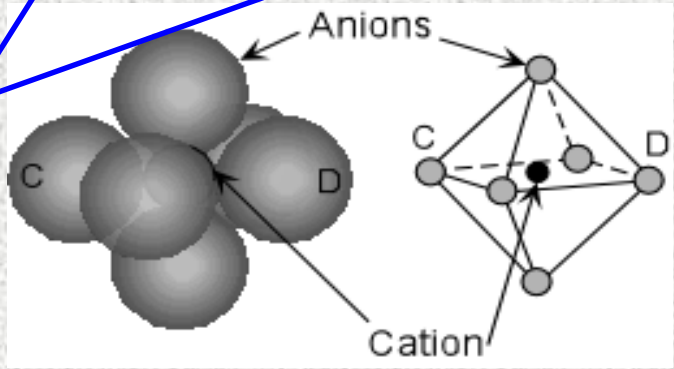
Coordination number

SC: Cubic (1, CN=8)

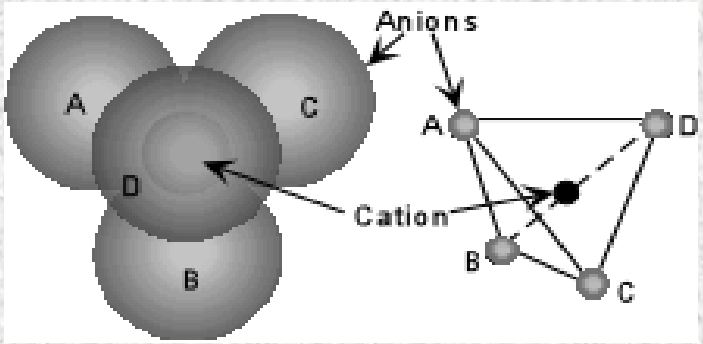




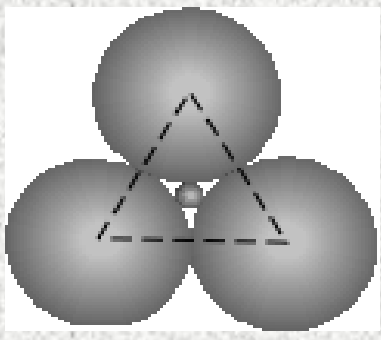
BCC & FCC: Octahedral (BCC-12/4;FCC 12/4+1, CN=6)



FCC: Tetrahedral(8, CN=4)



Triangular(3)



The Ratio Between The Interstitial Atom Radius (r) and The Lattice Atom (R)

SC: cubic- $r \leq 0.732R$

FCC: octahedron- $r \leq 0.414R$

tetrahedron- $r \leq 0.224R$

BCC: octahedron- $r \leq 0.154R$

Ionic crystals (> 50% ionic*)

*The fraction of bonding that is covalent can be estimated form the equation:
Fraction covalent = $Exp(-0.25 \cdot \Delta E^2)$
ΔE –difference in electronegativity

Many ceramics materials contain ionic bonds between the anions and the cations. These ionic materials must have crystal structure that ensures electrical neutrality, yet permit ions of different size to be packed. The crystal structure of ionic bonded compounds often can be described by placing the anions at the normal lattice points of a unit cell, with the cations then located at one or more of the interstitial sites

- **Coordination Number (in ionic material)**

  The number of ions with opposite charge that surround the ion.

- **Electrical neutrality**

  The charge of the anion equals to that of the cations that surround it :

anion valence=∑cation valence/C.N

- **Stoichiometry**

  The unit cell must preserve the material stoichiometry

Electrostatic Energy of Ionic Crystal (Madelung Energy)

Example 1.5

Calculate the Madelung constant for an infinite chain of alternating positive and negative ions + - + - + and so on.

$U = -\frac{z_i e^2 A}{4\pi\varepsilon_0 d}$; z_i is the number of charges on ion i; d is the distance between the nearest neighbor ions.

$$A = \sum_{i\neq J} \frac{N_j z_j d}{z_i r_{ji}} = 2d \sum_{i\neq J} \frac{\pm 1}{r_{ji}} = 2d\left(\frac{1}{d} + \left(-\frac{1}{2d}\right) + \frac{1}{3d} + \left(-\frac{1}{4d}\right) \ldots\right) = 2\left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} \ldots\right) =$$

$$2\ln(2) = \ln(4)$$

Ionic radii

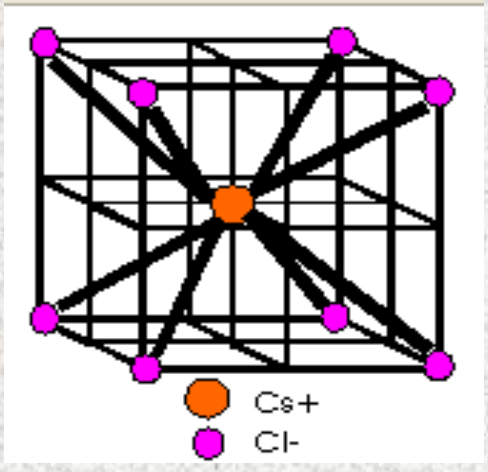
The radius ratio determined the coordination number

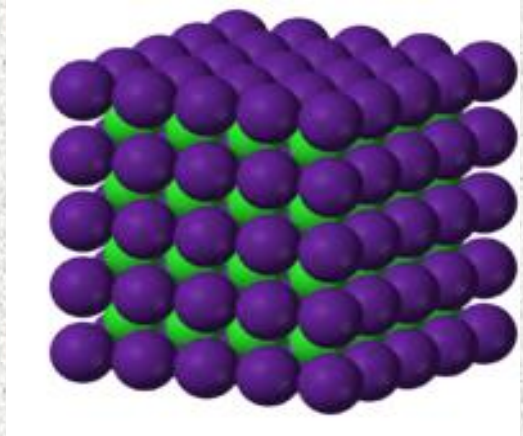
C.N	Type	r/R
12	Hexagonal or Cubic Closest Packing	1.0
8	Cubic	1.0 - 0.732
6	Octahedral	0.732 - 0.414
4	Tetrahedral	0.414 - 0.225
3	Triangular	0.225 - 0.155
2	Linear	<0.155

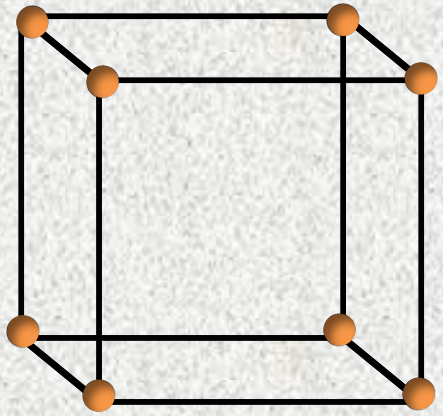
A number of common structures in ceramics compounds are described below:

Caesium Chloride structure (CsCl) (r/R>0.732)

The Chloride antions forms SC with one Cs cation occupied cubic interstitial site; Or, two SC structures that are shifted by ½ main diagonal. Coordination number: Cl= 8 , Cs=8
Number of atoms per unit cell=2







Example 1.6

For KCl, (a) verify that the compound has the CsCl structure and (b) calculate the PF for the compound (the ionic radii are: r_K=0.133nm r_{Cl}=0.181 nm and the electronegativity: K=0.8, Cl=3)

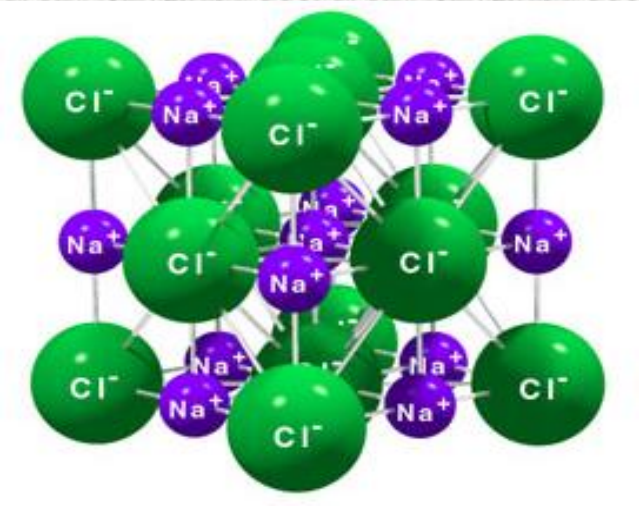
- r_K/r_{Cl}=0.133/0.181=0.735. this ration corresponds to coordination number of 8, the difference in the electronegativity is 2.2(70%< ionic) and the valance of each ion is 1 so the compound will be CsCl structure.
- First lets find the lattice parameter and the volume of the unit cell. The ions touches each other along the main diagonal so: $\sqrt{3}\cdot a_0=2r_K+2r_{Cl}$. Therefore a 0=0.363nm.

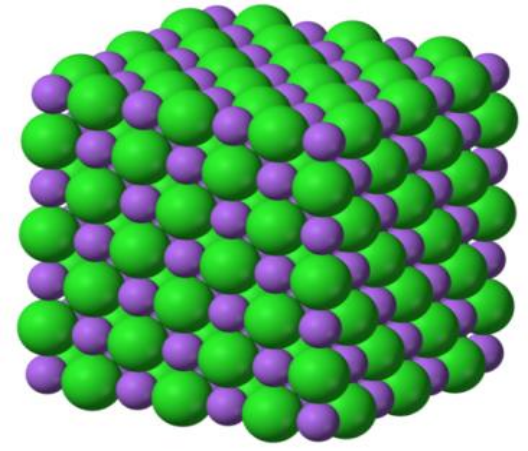
$$\text{Packing factor} = \frac{\frac{4}{3}\pi r_K^3(1\ \text{K ion}) + \frac{4}{3}\pi r_{Cl}^3(1\ \text{Cl ion})}{a_0^3}$$

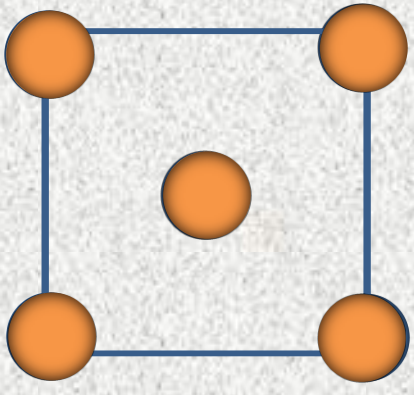
$$= \frac{\frac{4}{3}\pi(0.133)^3 + \frac{4}{3}\pi(0.181)^3}{(0.363)^3} = 0.725$$

Rock Salt structure (NaCl) (0.414<r/R<0.732)

The Chloride antions forms FCC with and Sodium cation occupied all the octahedral interstitial sites; Or, two FCC structures that are shifted by ½ lattice parameter. Coordination number: Cl=6, Na=6
Number of atoms per unit cell=8







- Many ceramics including MgO, CaO and FeO, have this structure

Example 1.7

Show that MgO has the sodium chloride structure and calculate the density of MgO. (the ionic radii are: r_{Mg}=0.066nm r_O=0.132 nm. The atomic weights are: 24.312 and 16 [gm/mol] and the electronegativity 1.2 and 3.5 for Mg and O respectively)

- r_{Mg}/r_O=0.066/0.132=0.50. this ration corresponds to coordination number of 6, the difference in the electronegativity is 2.3(74%< ionic) and the valance of each ion is 2 so the compound will be NaCl structure
- First lets find the lattice parameter and the volume of the unit cell. The ions touches each other along the edge of the cube so: $a_0=2r_{Mg}+2r_O$. Therefore a0=0.396nm. Each unit cell contains 4 O ions and 4 Mg ions:

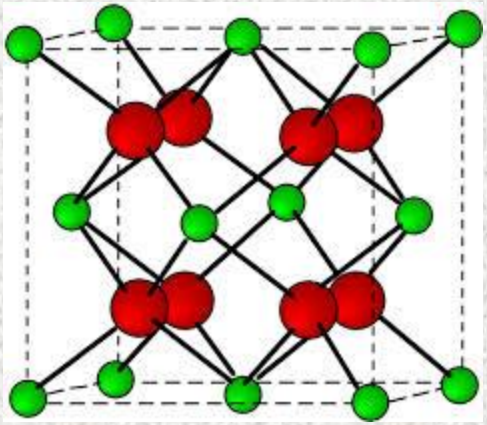
$$\rho = \frac{(4\ \text{Mg ions})(24.312)+(4\ \text{O ions})(16)}{(3.96\times10^{-10}\,\text{m})^3(6.02\times10^{23})} = 4.31\times10^6\,\text{g.m}^{-3} = 4.31\ \text{g/cm}^3$$

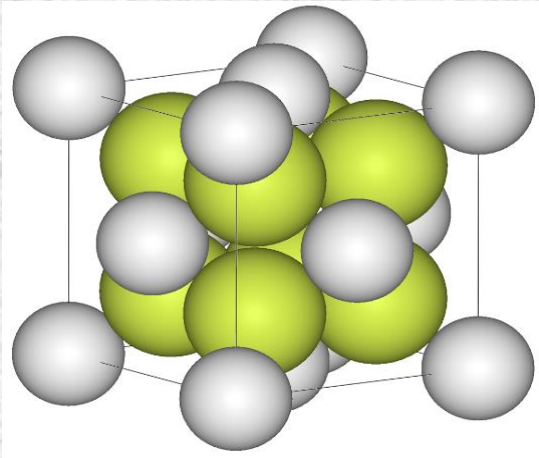
AntiFluorite(Li_2O)/ Fluorite structure (CaF_2)

The antifluorite structure is FCC of the anions, with cations (small) located at all eight of the tetrahedral positions. Coordination number: O= 8 , Li=4

The fluorite structure is FCC of the cations (large), with anions located at all eight of the tetrahedral positions. Coordination number: F= 4 , Ca=8

Number of atoms per unit cell=12

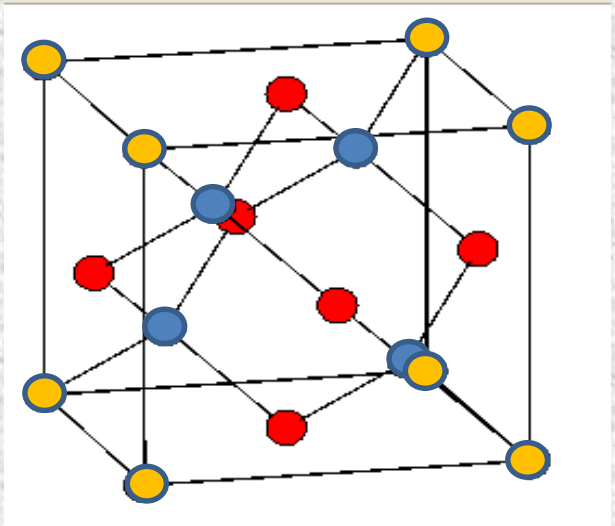


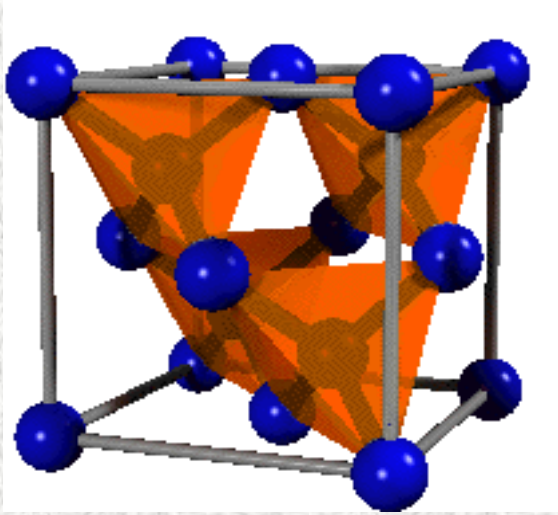


Covalent structure (<45% ionic)

Diamond cubic structure

- Elements such as silicon, germanium and carbon in its diamond form are bonded by four covalent bonds and produce a tetrahedron
- This lattice can be describes as an FCC lattice with two atoms associated with each lattice point or two FCC structures that are shifted by ¼ main diagonal. Coordination number 4 ; 8 atoms per unit cell

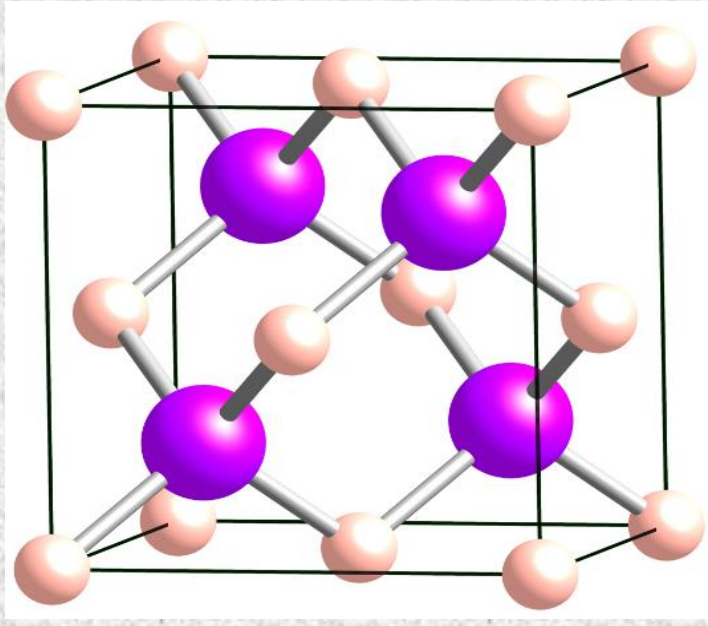




Zinc Blende structure (ZnS)

(covalent, or ionic when r/R<0.414)

Exactly like diamond structure but with two elements Instead of one. This structure is typical for covalent materials and ionic materials with very small cations. The Sulfur atoms enters to tetrahedral sites in the FCC Zink lattice. Sulfur atoms occupies 4 of the 8 sites inside the unit cell. Coordination number: Zn= 4 , S=4



Example 1.8

Would you expect CsBr to have the sodium chloride, zinc blende, CsCl, antifluorite or fluorite structure? Based on your answer, determine:

a. **The lattice parameter**

b. **The density**

c. **The packing factor for CsBr**

Electronegativity: Cs=0.7, Br=2.8

$MwCs := 132.91 \frac{gm}{mol}$ $MwBr := 79.904 \frac{gm}{mol}$

$rCs := 0.167nm$ $rBr := 0.196nm$

The valance of bromine is Br^{-1} and of cesium Cs^{+1} so one might expect an ionic compound

covalent fraction=exp(-0.25·2.1²)=0.33

The ionic radii ratio is: $\frac{rCs}{rBr} = 0.852$ 0.852 is in the range of cubic so CsCl structure is expected.

a. CsCl is like BCC structure with the atoms in contact along the main diagonal. the lattice parameter (side of the lattice unit cell) is:

$$a0 := \frac{(2 \cdot rCs + 2rBr)}{\sqrt{3}} \qquad a0 = 0.419\,nm$$

b. Each unit cell contains one Br and one Cs atom. The volume of the unit cell and the density can be calculate:

$$Vlattice := a0^3 \qquad Vlattice = 0.074\,nm^3$$

$$\rho := \frac{1 \cdot \left(\frac{MwCs}{Av}\right) + 1 \cdot \left(\frac{MwBr}{Av}\right)}{Vlattice} \qquad \rho = 4.799 \times 10^3 \frac{kg}{m^3}$$

c. The PF is the volume occupied by the atoms divided by the volume of the unit cell so:

$$PF := \frac{\frac{4}{3} \cdot \pi \cdot rCs^3 + \frac{4}{3} \cdot \pi \cdot rBr^3}{Vlattice} \qquad PF = 0.693$$

Example 1.9

For the structure that is shown below, determine the:

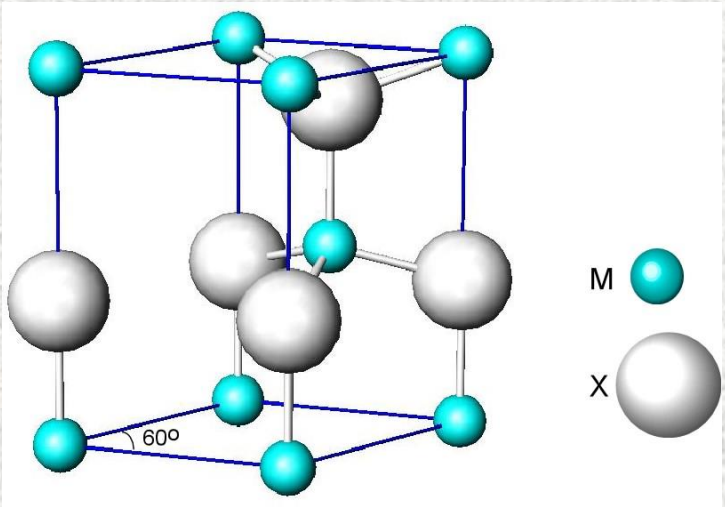
a) Coordination Number

b) Number of ions per unit cell

c) Stoichiometry

a) 4

b) $1 \cdot X + \frac{2 \cdot X}{6} + \frac{2 \cdot X}{3} + 1 \cdot M + \frac{4 \cdot M}{6} + \frac{4 \cdot M}{12} = 4$

c) 1:1

Wurtzite