

Inorganic Chemistry I (CH331)

Solid-state Chemistry I

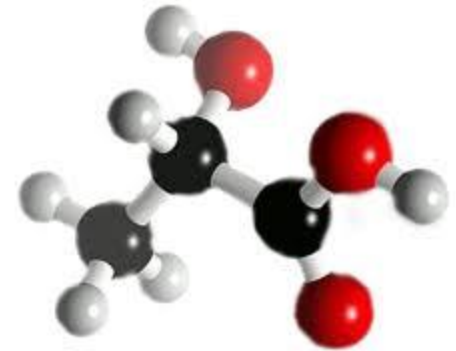
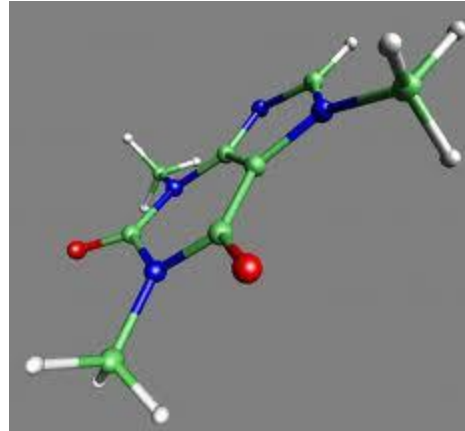
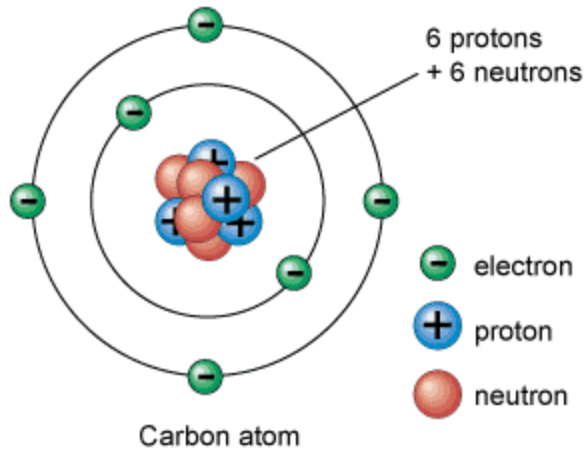
(Crystal structure)

Nattapol Laorodphan
(Chulabhorn Building, 4th Floor)

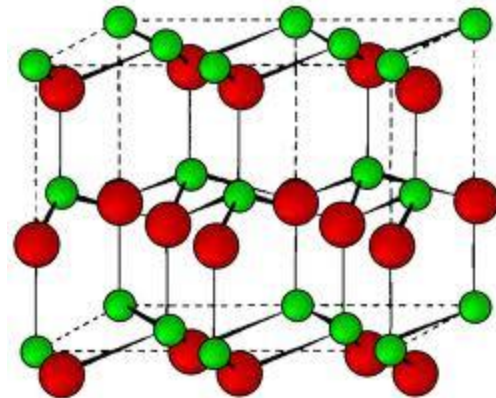
Text books :

1. D.F. Sheiver, P.W. Atkins & C.H. Langford “Inorganic Chemistry” 2nd Edition (1994), Oxford University Press
2. Alan G. Sharpe “Inorganic Chemistry” 3rd edition (1992), Longman
3. R.B. Heslop & P.L. Robinson “Inorganic Chemistry : A Guide to Advance Study” 3rd edition (1967), Elsevier
4. F.A. Cotton & G. Wilkinson “Advanced Inorganic Chemistry: A Comprehensive Text” (1964), Interscience Publishers
5. K.M. Mackay & R.A. Mackay “Introduction to Modern Inorganic Chemistry” 2nd Edition (1972), Intertext Books

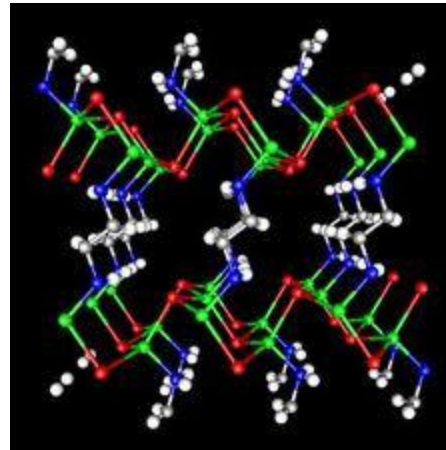
Introduction



Atom(s)



Molecule(s)



Crystal structure of solid(s)

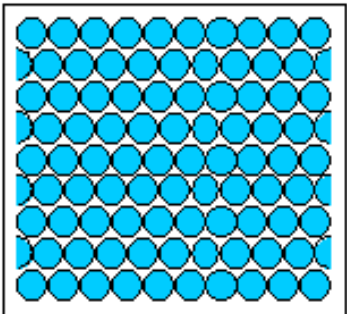
Introduction : crystalline solid vs Amorphous (non-crystalline) solid

Crystalline solid or crystal: Solids that possess long-range order of their atomic position in 3D.

Polycrystalline: Solids that contain many crystallite (crystalline phase) of various size and direction or orientation, e.g. ceramics.

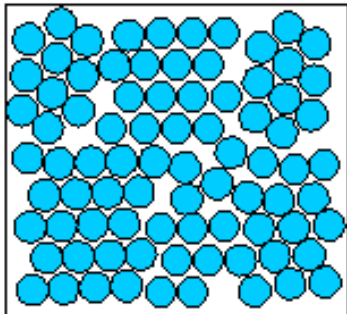
Amorphous: Solids that lack of long-range order or that possess short-range order of their atomic position.

Introduction : crystalline solid vs Amorphous (non-crystalline) solid



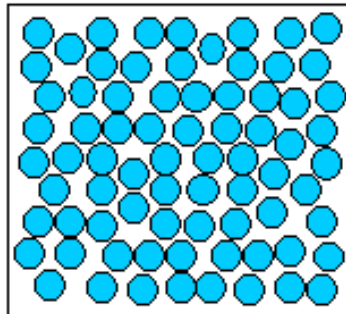
Single crystal

Periodic across the whole volume.



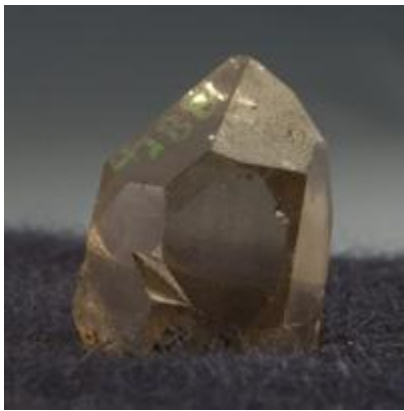
Polycrystal

Periodic across each grain.



Amorphous solid

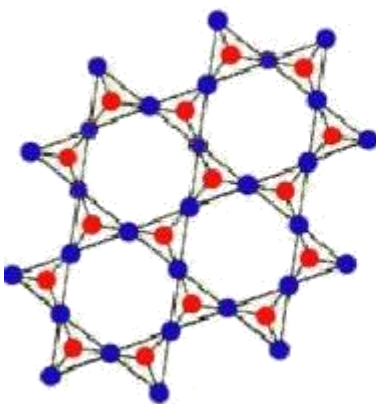
Not periodic.



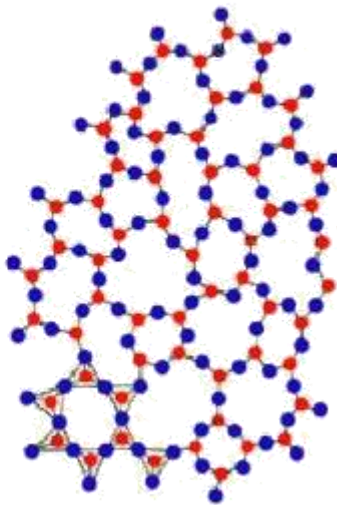
Single crystal of Quartz

<http://www.doitpoms.ac.uk/tlplib/atomic-scale-structure/index.php>

Crystalline SiO₂ (Quartz)



Amorphous SiO₂ (Glass)



● Si ● O

[http://www.steelguru.com/article/details/MjU=/Solid State Structure.html](http://www.steelguru.com/article/details/MjU=/Solid%20State%20Structure.html)

Introduction : crystalline solids

1. Ionic Bond : electrostatic interaction between positive and negative charged species e.g. Na^+ and Cl^- . In this case, at a point between those two species, the approximately zero electron density is found, leading to the possibility to calculate the ionic radii (radius of cation or anion).

- Ionic crystal structure
- Ionic radii/radius ratio
- Lattice Energy and Madelung Constant

Introduction : crystalline solids

2. Van der Waals bonding: weak force (dispersion force) between non-polar molecules, which arises from asymmetric electron distributions; leading to a dipole moment of molecules. The binding energy proportional to α^2/r^6 , where α is polarisability and r is intermolecular separation. The polarisability could be calculated from the dipole moment, μ , where

$$\mu = 4\pi\epsilon_0\alpha E$$

ϵ_0 is permittivity of a vacuum, E is an electric field.

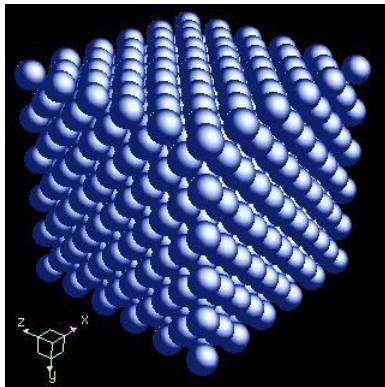
Thus in this case, study of the structure of solid is difficult.

Introduction : crystalline solids

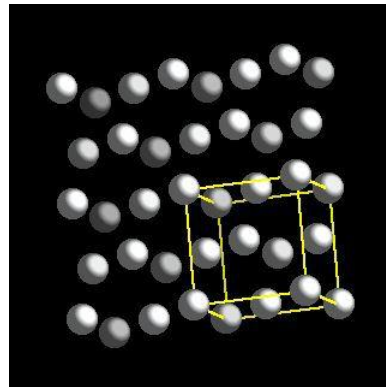
3. Metallic bond: Strong cohesive force and high electrical conductivity, which implies to the electron delocalisation. Metal, in which the whole crystal is regarded as a large molecule, could be structurally studied as the position of the nucleus of the metal atoms present periodically in long-range order.

The radii of the metal is half the distance between the nuclei or neighbouring atoms, in this case, also depending on the coordination number of the lattice.

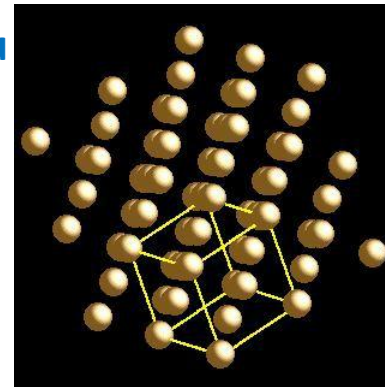
Cu



Ag



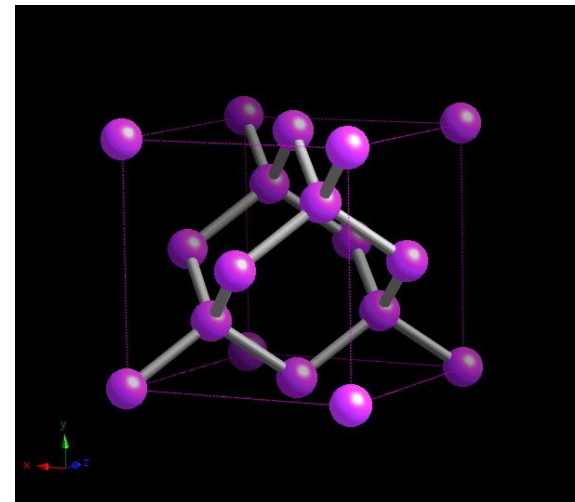
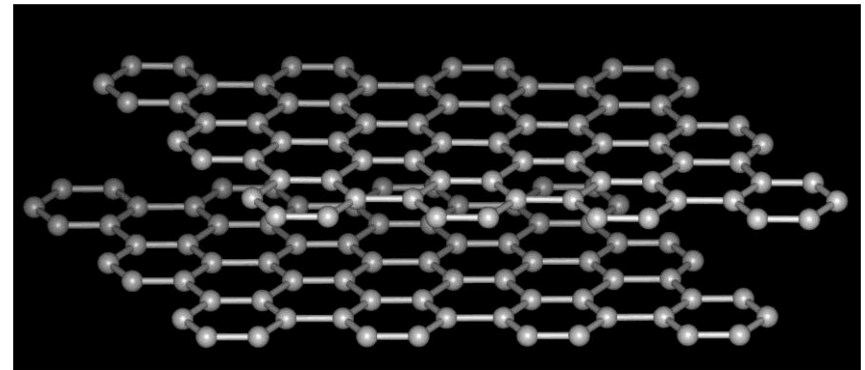
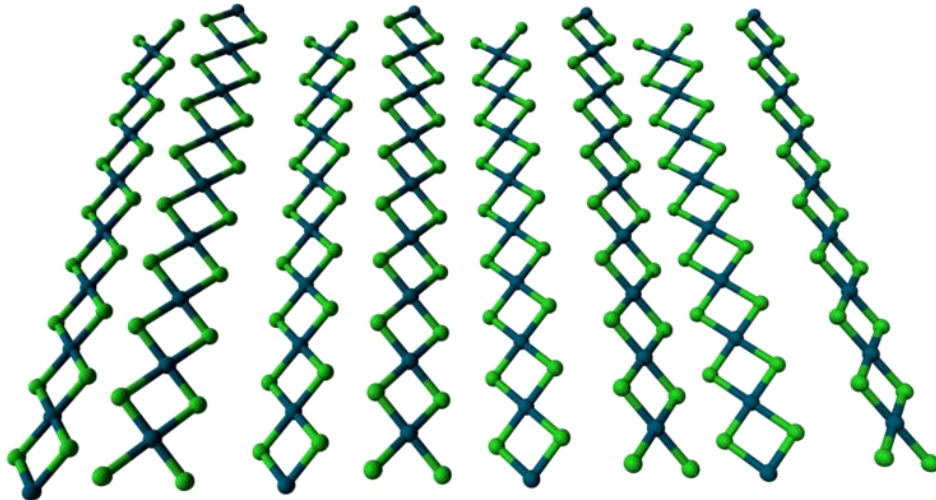
Au



www.webelements.com

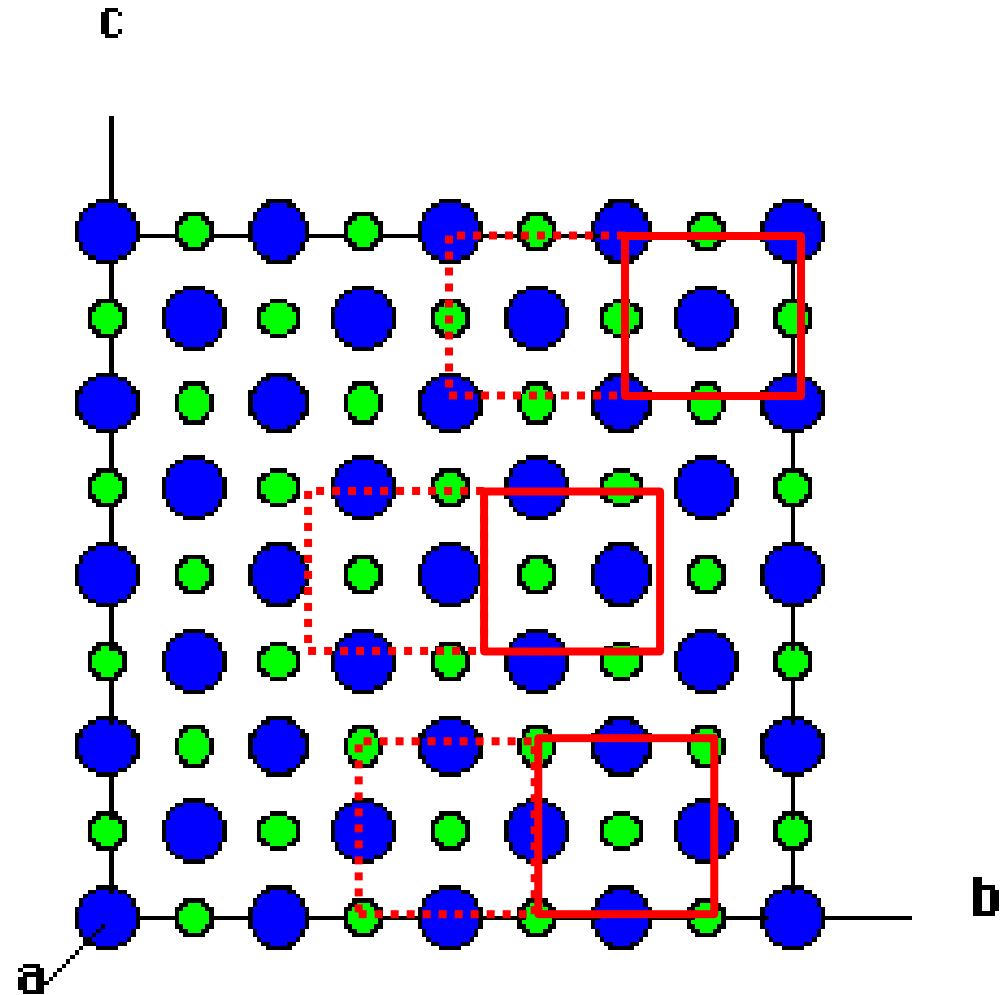
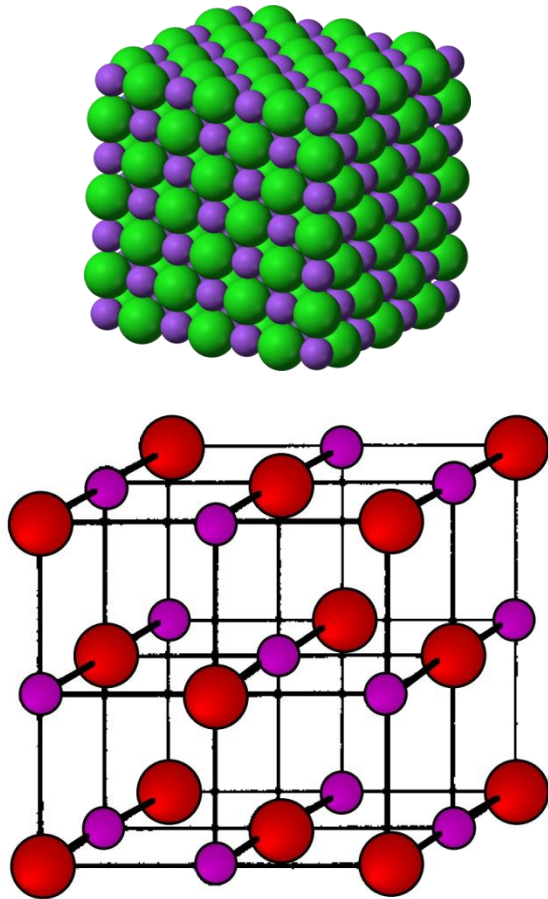
Introduction : crystalline solids

4. Covalent bond: the crystal structure may be in one, two or three dimensions depending on the molecule, e.g. PdCl_2 , graphite and diamond in which the molecule are extended in 1D, 2D and 3D, respectively.



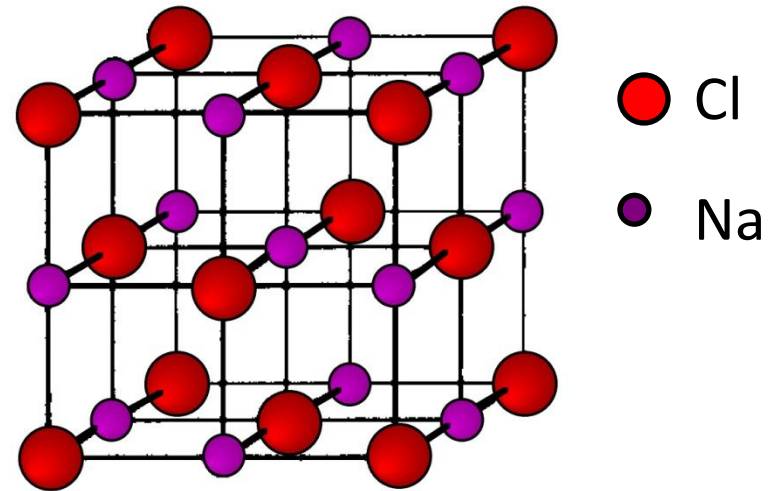
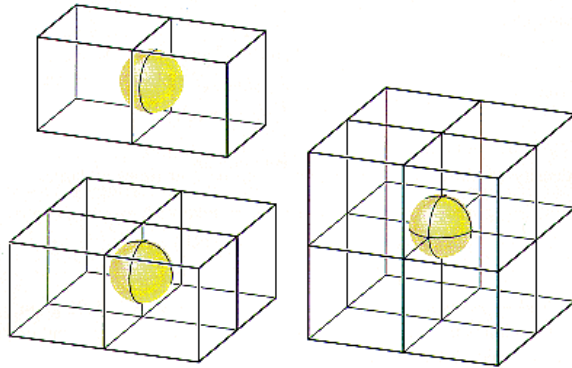
Introduction : Fundamental concepts

Unit Cell: the smallest repeating unit of the structure that produces the structure of the whole crystalline solid.



Introduction : Fundamental concepts

Number of Atom(s) in the Unit Cell:



$\frac{1}{8}$ atom at 8 corners



Simple cubic

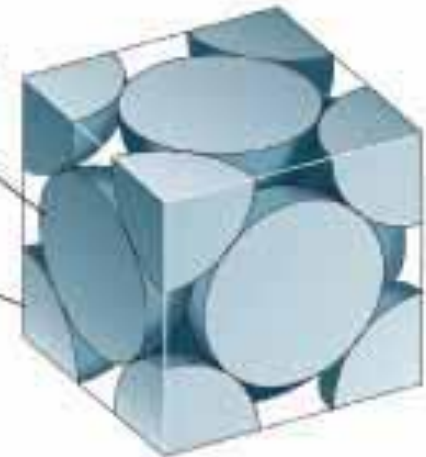
$\frac{1}{8}$ atom at 8 corners
1 atom at center



Body-centered cubic

$\frac{1}{2}$ atom at 6 faces

$\frac{1}{8}$ atom at 8 corners

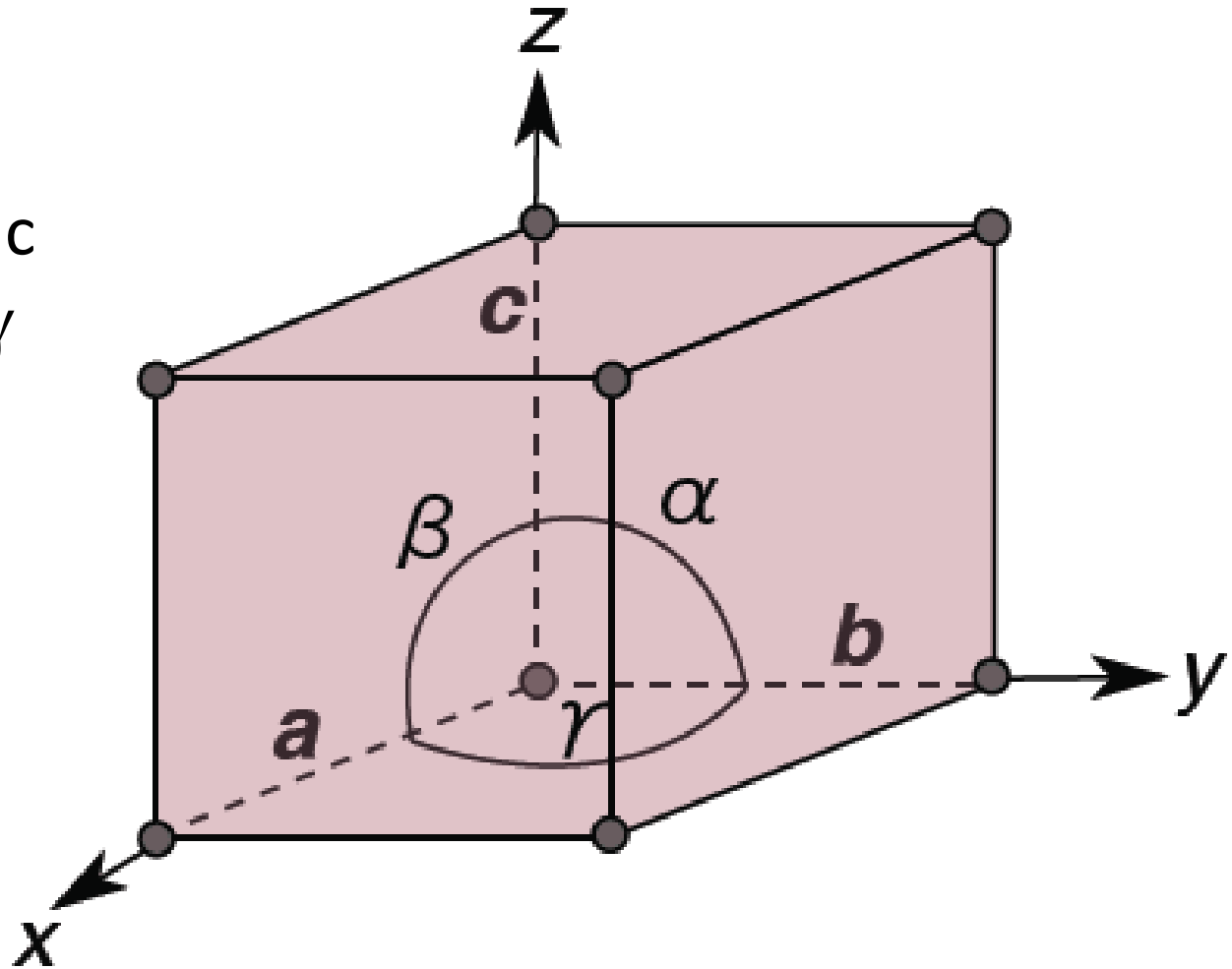


Face-centered cubic

Introduction : Fundamental concepts

Unit cell parameters: length, angle and plane

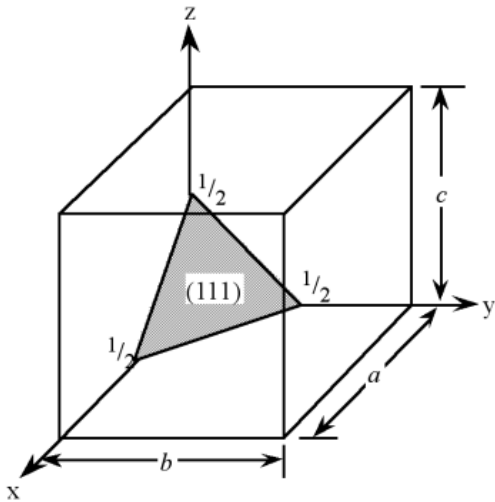
Length : a, b, c
Angle : α, β, γ



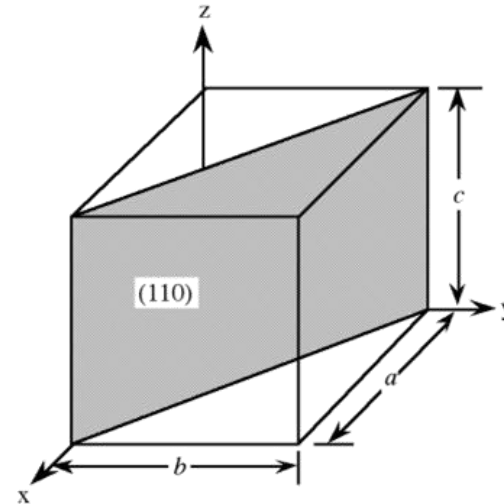
Introduction : Fundamental concepts

Unit cell parameters: Plane

- 1) Find the intercept of x, y and z
- 2) Do the reciprocal ($1/a$, $1/b$ and $1/c$)
- 3) Make it simple (clear fraction)



$$\begin{array}{c} h \quad k \quad l \\ \frac{1}{1/2}, \frac{1}{1/2}, \frac{1}{1/2} = (222) = (111) \end{array}$$



$$\begin{array}{c} h \quad k \quad l \\ \frac{1}{1}, \frac{1}{1}, \frac{1}{\infty} = (110) \end{array}$$

Introduction : Fundamental concepts

Crystal system:

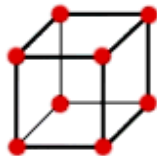
1) There are 7 crystal classes

System	Cell edges	Cell angles
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Rhombohedral (trigonal)	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ \gamma = 120^\circ$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \beta \neq 90^\circ$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$

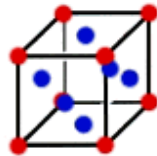
Introduction : Fundamental concepts

Crystal system:

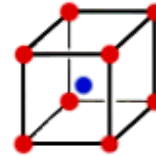
2) There are 14 Bravais Lattices



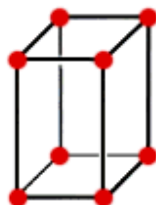
Simple cubic



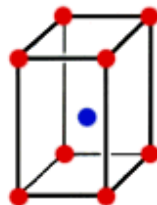
Face-centered cubic



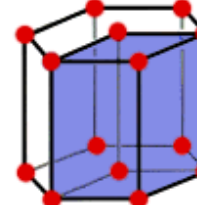
Body-centered cubic



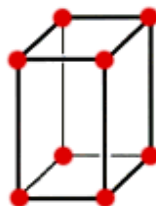
Simple tetragonal



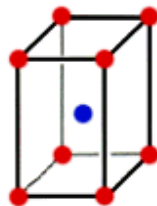
Body-centered tetragonal



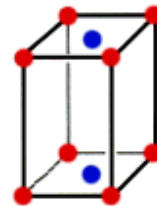
Hexagonal



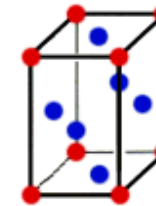
Simple orthorhombic



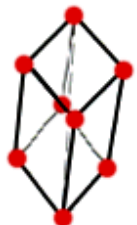
Body-centered orthorhombic



Base-centered orthorhombic



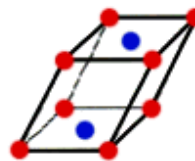
Face-centered orthorhombic



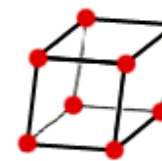
Rhombohedral



Simple Monoclinic



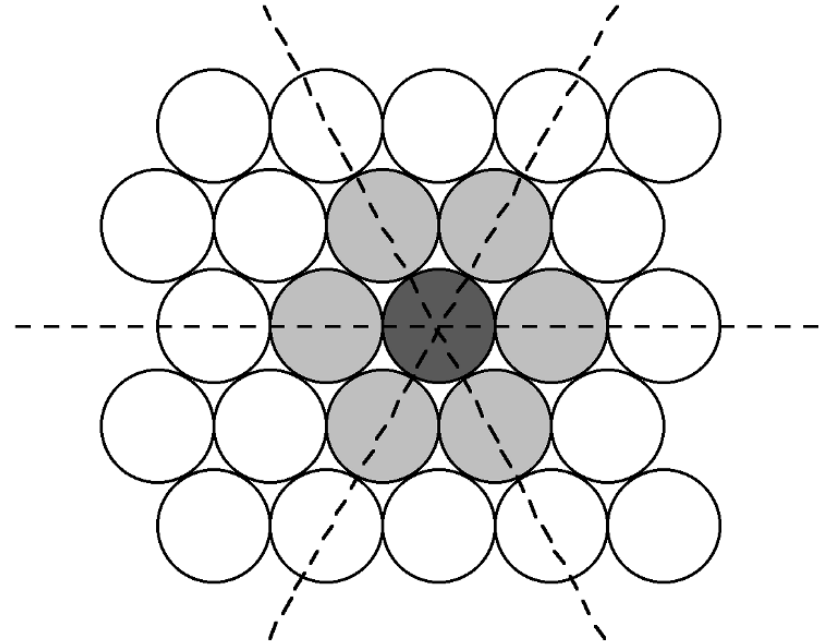
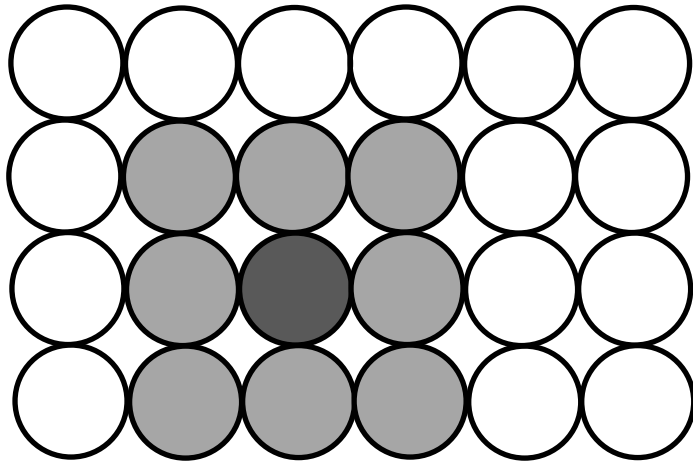
Base-centered monoclinic



Triclinic

Introduction : Close packing of spheres

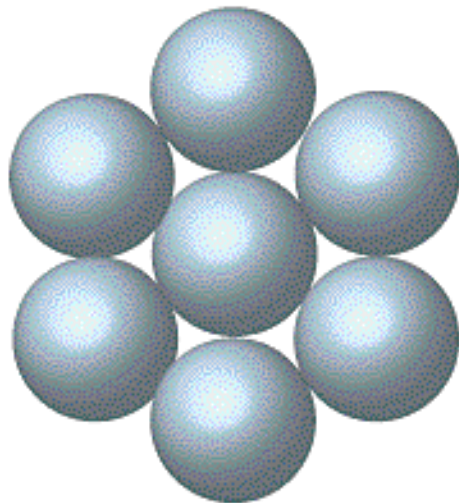
Highest efficiency of packing, when one atom is surrounded by other **6 atoms** in the same plane (Coordination No. = 6).



In 3D packing, some layers of the densest layer are stacked, leading only **two ways** of stacking that give the densest 3D structure, which is so called “**close packing**”.

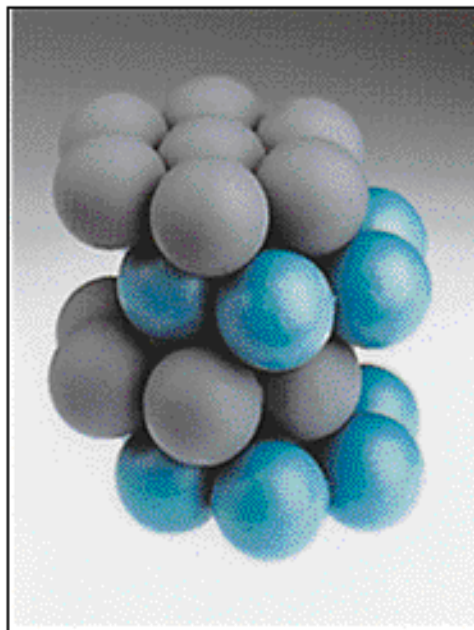
Introduction : Close packing of spheres

In close packing of some layers together, the coordination number (CN) of one atom is 12 (there are 12 atoms surrounding central atom, 3 atoms from each of the above and lower layers).

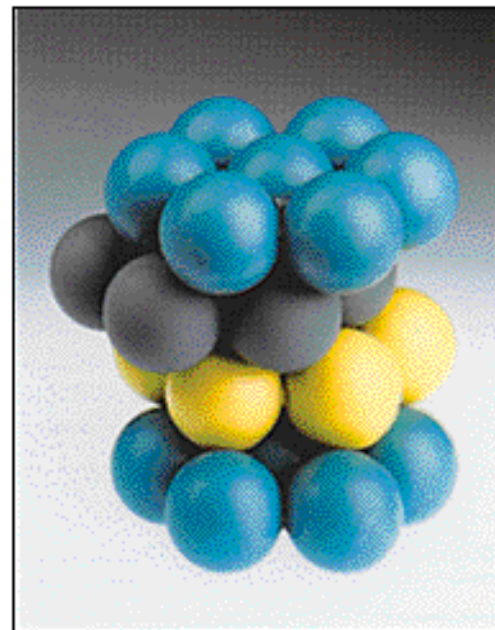


Close-packed layer of spheres

(a)



(b)



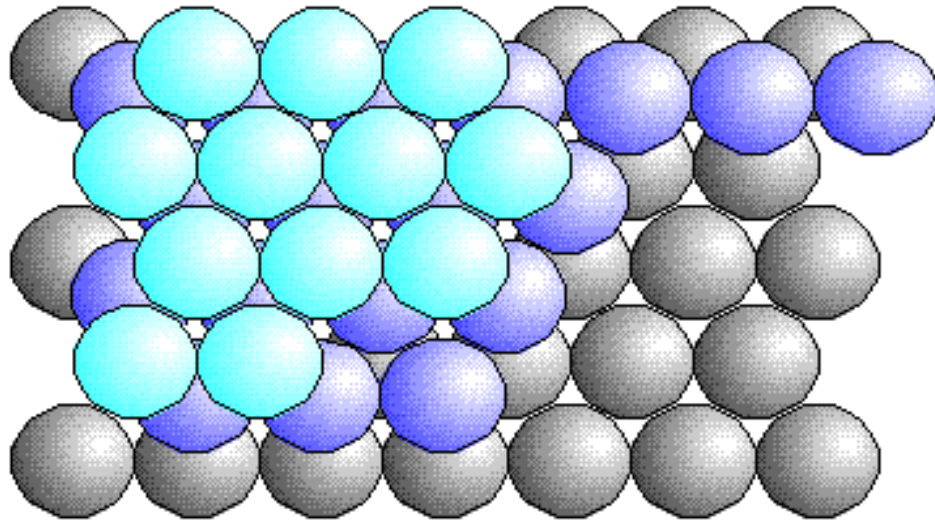
(c)

http://www.chem.ufl.edu/~itl/2045/lectures/lec_h.html

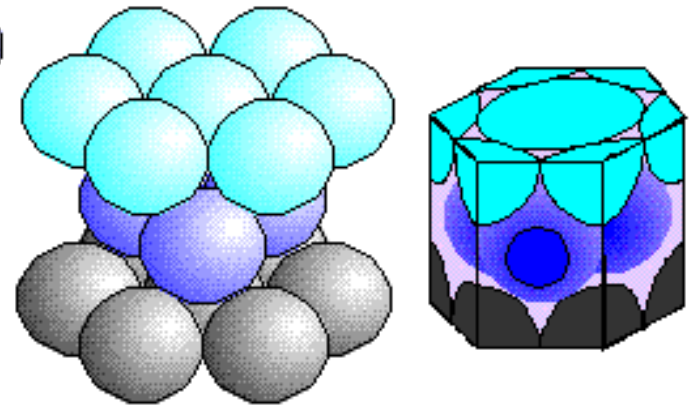
Introduction : Close packing of spheres

1) Hexagonal Close Packing (HCP)

ABABAB....



ABAB Layer Stacking

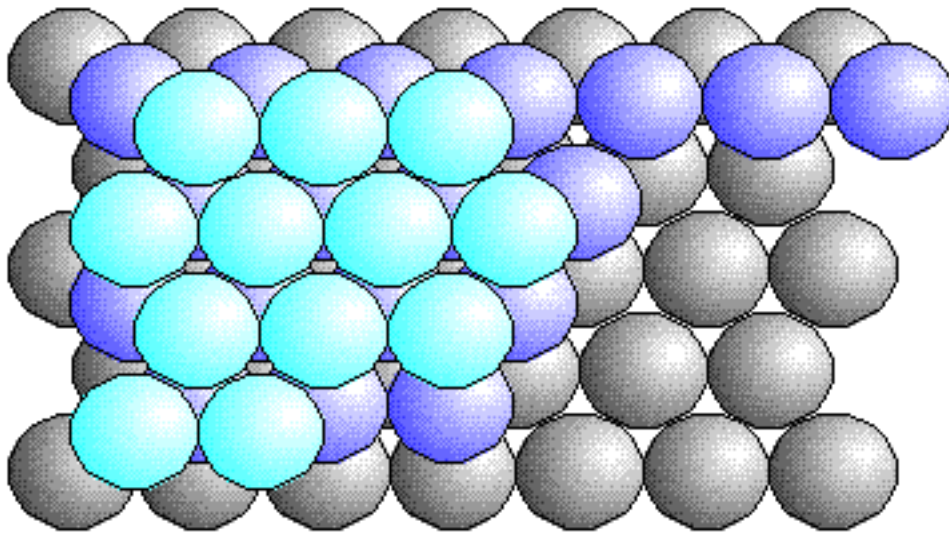


Hexagonal Structure

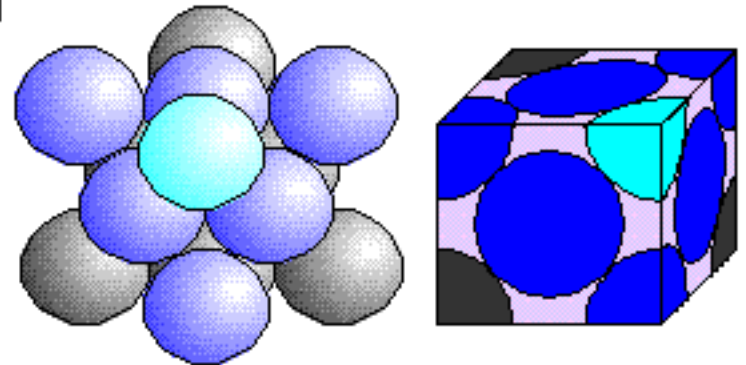
http://www.chem.ufl.edu/~itl/2045/lectures/lec_h.html

Introduction : Close packing of spheres

2) Cubic Close Packing (CCP) or face-centred cubic (fcc) ABCABCABC....



ABC Layer Stacking



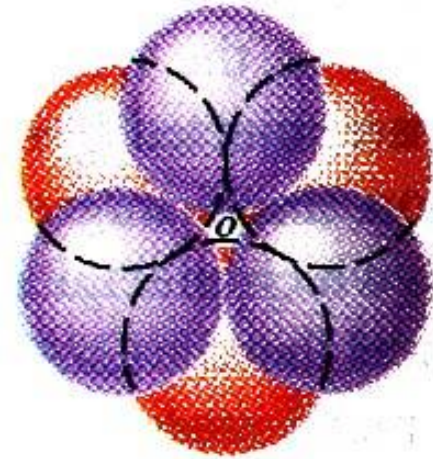
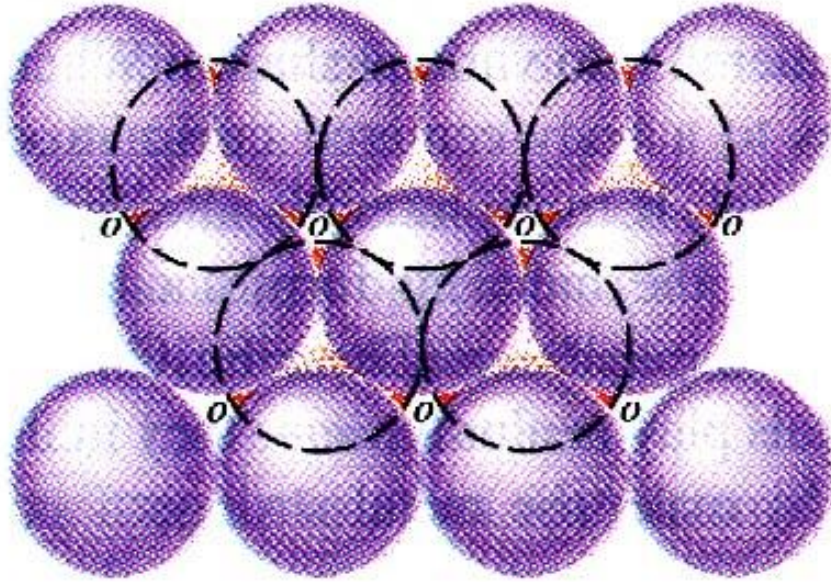
Cubic Unit Cell

http://www.chem.ufl.edu/~itl/2045/lectures/lec_h.html

Introduction : Close packing of spheres

Interstitial Sites or Holes in close packing of spheres.

- 1) Tetrahedral Hole (CN = 4)
- 2) Octahedral Hole (CN=6)



These holes could be filled by other smaller balls (ions) in which the size of ion could be $0.225r$ and $0.414r$ in the tetrahedral and octahedral holes, respectively, where r is the size of the larger ion radius.

Introduction : Close packing of spheres

Interstitial sites (holes)

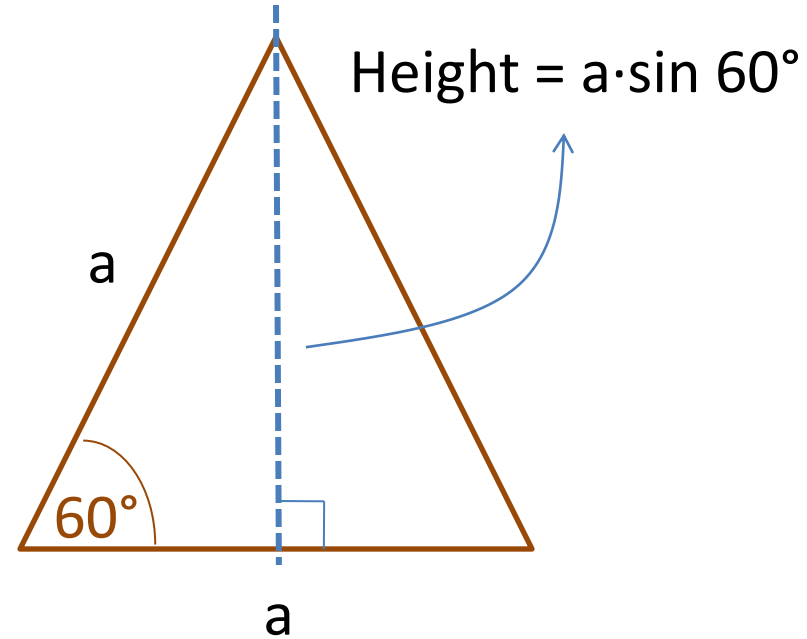
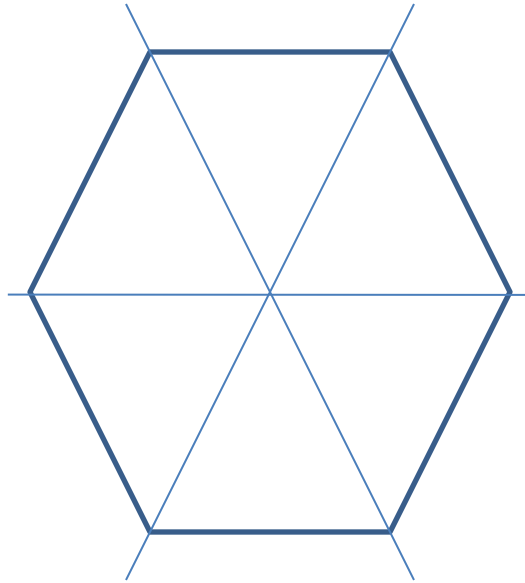
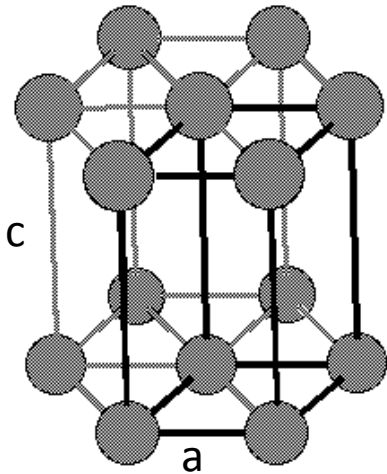
The number of each types of holes are different, as there are two tetrahedral holes and one octahedral hole per atom, when the close packing is achieved whether it is hexagonal close packing (hcp) or cubic close packing (ccp).

Packing efficiency could be calculated in order to consider how dense the crystal is. This could be done using this equation;

$$\text{Packing Efficiency} = \frac{\text{Volume of sphere}}{\text{Volume of unit cell}}$$

It may be reported in percent (%).

e.g. calculate the packing efficiency of HCP.



Ideal HCP ; $c = 1.633a$

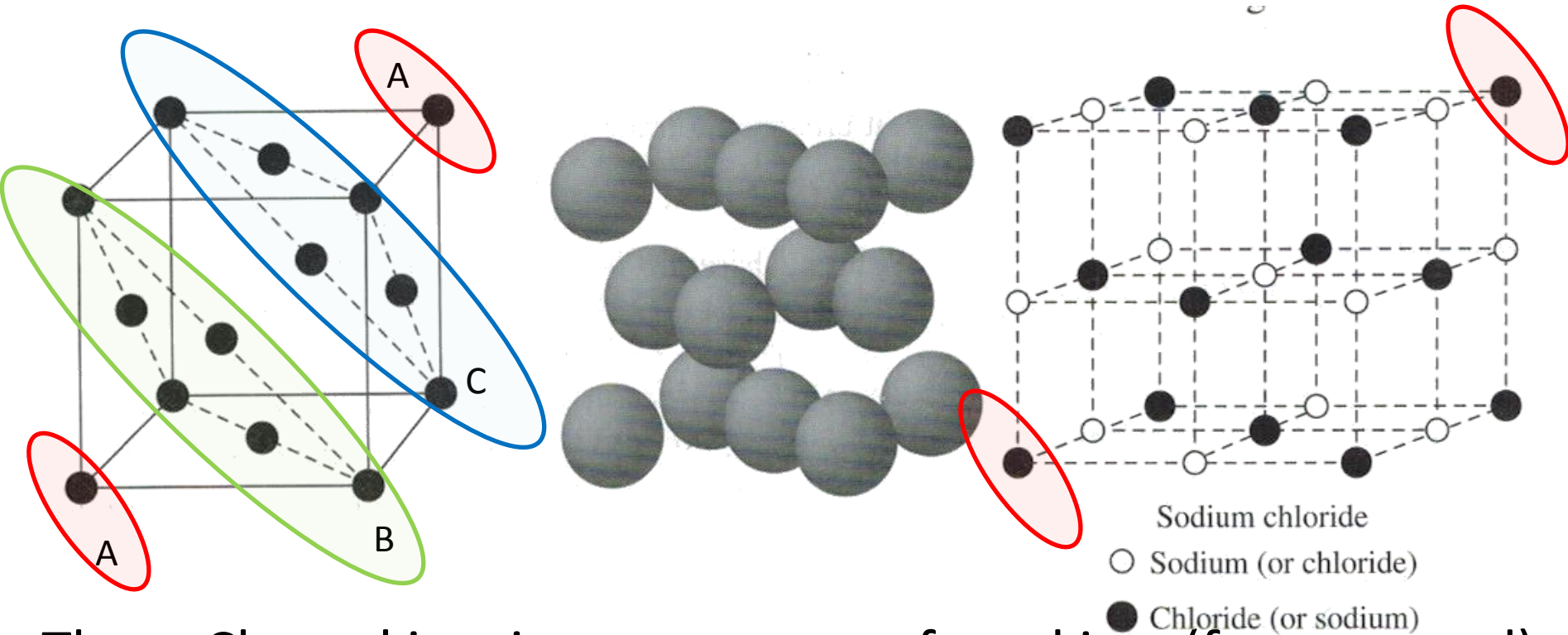
No. of atoms in the unit cell = $(1/6 \times 12) + (1/2 \times 2) = 6$ atoms

Volume of the unit cell = area of the base \times height

$$\text{Packing efficiency} = \frac{6 \times \left(\frac{4}{3}\pi r^3\right)}{3a^2 \sin 60^\circ c} = 0.74 \text{ or equivalent to } 74\%$$

Introduction : Close packing of spheres

Example of using the close packing is the packing of NaCl structure.



Thus, Cl⁻ packing is a ccp type of packing (face-centred), allowing Na⁺ ions sit in the octahedral holes (Na⁺ radius = 0.695 times of Cl⁻ ion)

Structure of Binary compounds ,e.g. ionic compound

As previously mentioned that there are two types of holes in the close packing of spheres (analogous to the ions). The ions that are close packed together are typically *larger in size (Anion)*, leaving the small spaces (holes) for smaller ions (typically Cation). Where should the cation be? In tetrahedral holes or octahedral holes.....

Depending on

- 1) Radius ratio (r_+/r_-); considers the NaCl structure***
- 2) Relatives Numbers of cations and anions.***

Remark that the numbers of tetrahedral holes are more than octahedral holes in the close packing. M_2X compound has too many cations, thus they should be sit in the tetrahedral holes.

Radius Ratio (r_+/r_-)

is a simple (but good) approximation method used to predict the coordination number or structure of the crystal structure of solids, in which the r_+/r_- ratio is calculated (where the r_+ and r_- are the radius of cation and anion, respectively).

Radius Ratios and Coordination Numbers

<i>Radius Ratio Limiting Values</i>	<i>Coordination Number</i>	<i>Geometry</i>	<i>Ionic Compounds</i>
0.414	4	Tetrahedral	ZnS
0.732	4	Square planar	None
	6	Octahedral	NaCl, TiO ₂ (rutile)
1.00	8	Cubic	CsCl, CaF ₂ (fluorite)
	12	Cubooctahedron	No ionic examples, but many metals are 12-coordinate

Radius Ratio (r_+/r_-)

Ionic radii depends on the coordination number, in which depending on the bond length between two ions (+ and -). Thus many values of ionic radius are reported.

e.g.1 NaCl structure, Na^+ ions are in octahedral holes.

e.g.2 ZnS structure, Zn^{2+} ions are in tetrahedral holes.

Exercise : Calculation the radius ratio of CaCl_2 and predict the coordination number of Ca^{2+} .

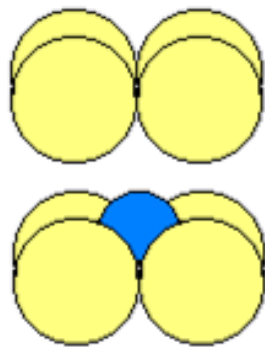
$\text{Cl}^- \rightarrow 167 \text{ pm}$, $\text{Ca}^{2+} \rightarrow 114 \text{ pm}$ (for $\text{CN}=6$) and 116 pm (for $\text{CN}=8$).

Use with caution as the ion is not a hard sphere thus it is flexible. Moreover some cases the prediction is incorrect.

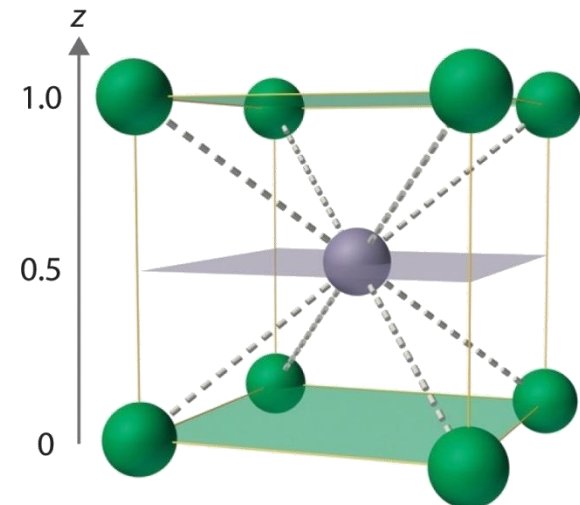
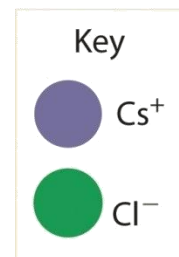
Radius Ratio (r_+/r_-)

Remarks****

- Use with caution as the ion is not a hard sphere thus it is flexible. Moreover some cases the prediction is incorrect.
- Sometimes the cation size is larger than anion, so that the application of this radius ratio **must be modified**.
- When both cation and anion have nearly the same size, a ***cubic*** arrangement of anions with cation in the body centre results, e.g. CsCl (CN=8).



Cubic Hole



Lattice Energy and Madelung Constant

Lattice energy of a crystal may just consider only every pair of ions and calculate the sum of the electrostatic of each pair using;

$$\Delta U = \frac{Z_i Z_j}{r_0} \left(\frac{e^2}{4\pi\epsilon_0} \right)$$

where

Z_i and Z_j are ionic charges

r_0 is distance between centre of two ions

e is electronic charge = 1.602×10^{-19} C

$4\pi\epsilon_0$ is permittivity of a vacuum

$$= 1.11 \times 10^{-10} \text{ C}^2 \text{ J}^{-1} \text{ m}^{-1}$$

Lattice Energy and Madelung Constant

But in the whole unit cell or crystal not only cation and anion interact (or not only the nearest-neighbour), but there is also an interaction from the longer distance ions. Thus the corrected equation is created with the term of Madelung Constant.

$$\Delta U = \frac{NMZ_+Z_-}{r_0} \left(\frac{e^2}{4\pi\epsilon_0} \right) \left(1 - \frac{\rho}{r_0} \right)$$

where

N is Avogadro's number

M is Madelung Constant

ρ is constant = 30 pm

Lattice Energy and Madelung Constant

Lattice Energy (ΔH_{xtal}) could be calculated from

$$\Delta H_{xtal} = \Delta U + \Delta(PV) = \Delta U + \Delta(nRT)$$

But the values of $\Delta(nRT)$ is so small, e.g. = -4.95 kJ/mol for any MX compounds or -7.43 kJ/mol for MX₂ compounds.

Thus it should be safely state that

$$\Delta H_{xtal} \approx \Delta U$$

e.g. Calculate the lattice energy for NaCl.

Structure of the simple compounds

Homework II (1 pt)

- 1) NaCl
- 2) CsCl
- 3) ZnS (Zinc Blende)
- 4) ZnS (Wurtzite)
- 5) Fluorite (CaF_2)

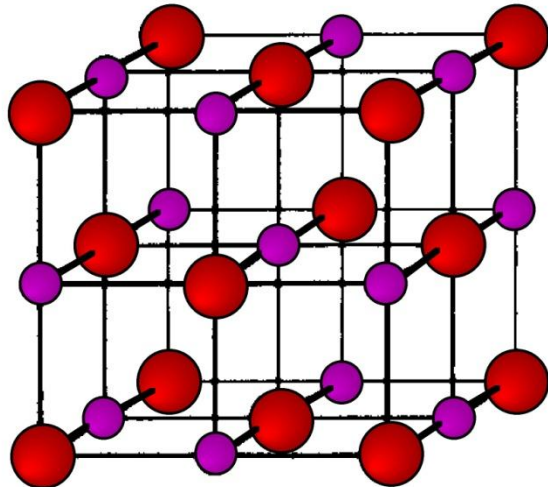
Find the length of the unit cell, and calculate the density of the crystals.

2&3 ID ends with odd No. and 4&5 ID ends with even No.
Deadline : 26th July 2013

e.g. The edge length of the NaCl unit cell is 564 pm. What is the density of NaCl in g/cm^3 ?

a (length of unit cell) = 564 pm = 564×10^{-10} cm

Consider the number of ions in one unit cell



consider mass of atoms in unit cell
as $m = nM / N_A$

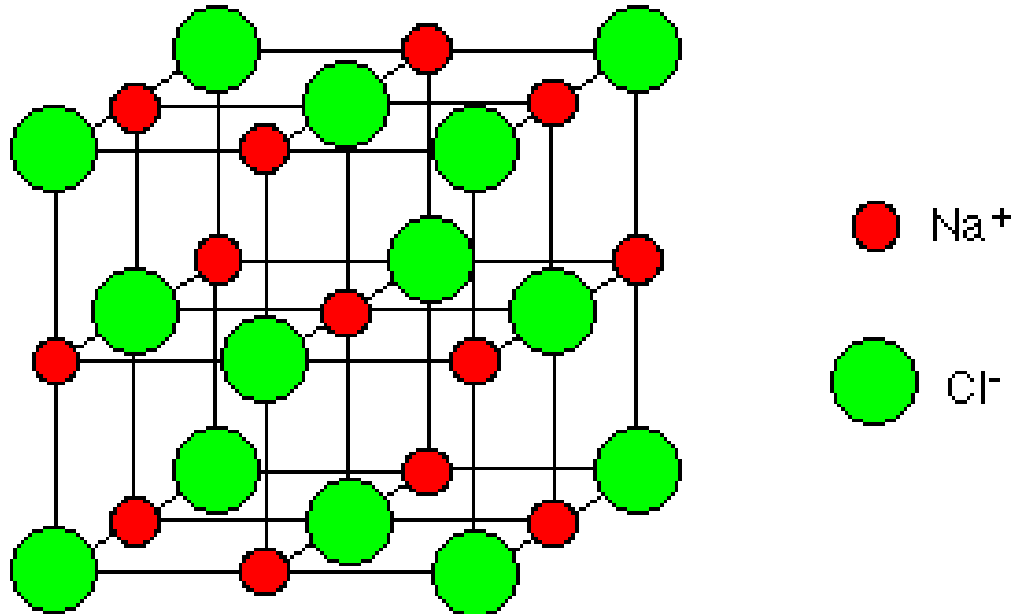
calculate density
 $\rho = m/V$

Coordination Number (CN) is number of next-nearest neighbour units surround the central unit, i.e. number of ions that attach the central atom. From the picture above the CN of smaller ion (Na^+) is 6 meaning that there are 6 ions of larger ions (Cl^-) around it.

Structure of the common compounds

1) Sodium Chloride or rock salt structure

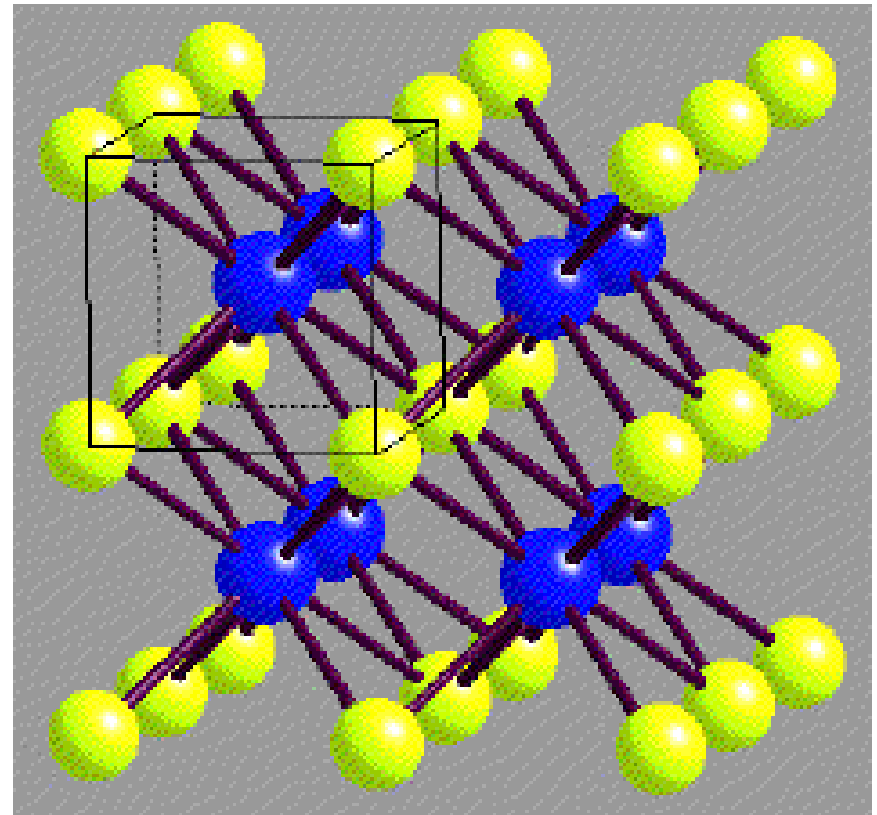
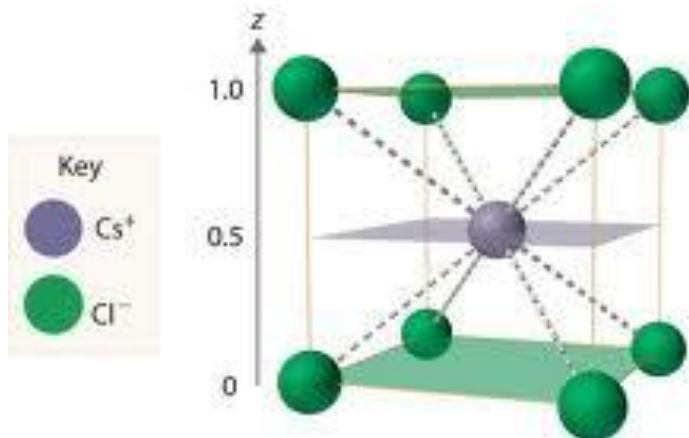
- e.g. NaCl, LiCl, KBr, RbI, AgCl, AgBr, MgO, CaO, TiO, FeO, NiO, SnAs, UC and ScN.
- fcc packing of larger ion (e.g. Cl⁻)
- Smaller ions occupy the octahedral holes.
- CN of Na⁺ and Cl⁻ = 6 : 6 [NaCl has (6,6)-coordination].



Structure of the common compounds

2) Cesium-Chloride Structure

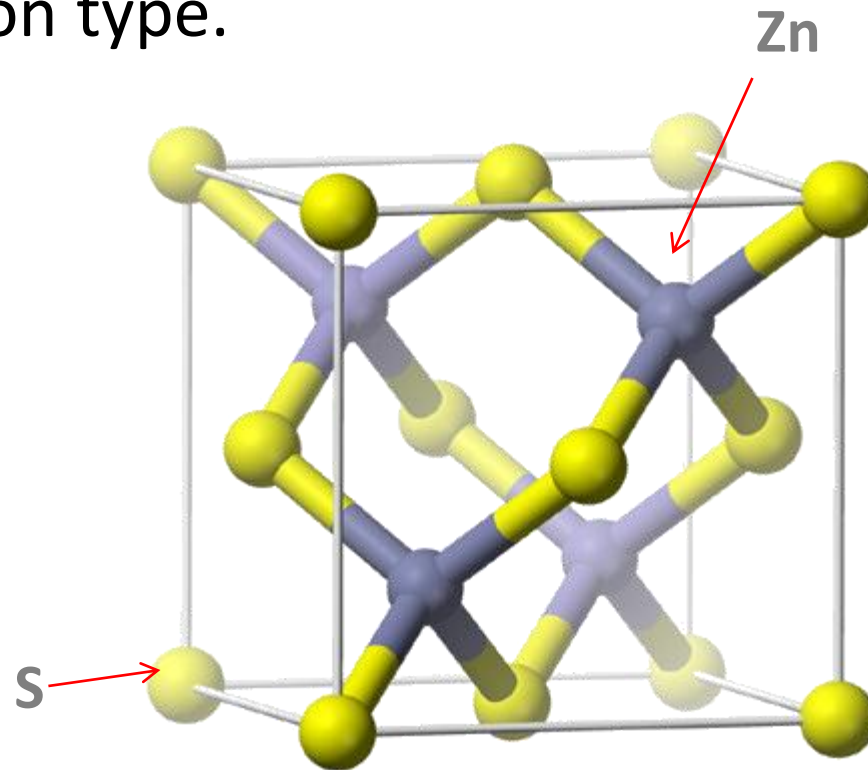
- e.g. CsCl, CaS, TlSb, CsCN and CuZn
- Cubic unit cell (not a close packing) where the first ions (e.g. Cl^-) occupied. The second ion (e.g. Cs^+) is at the unit cell centre.
- (8,8)-coordination
- Both ions or atoms have similar size.



Structure of the common compounds

3) Zinc Blende or Sphalerite structure (ZnS)

- e.g. ZnS, CuCl, CdS, HgS, GaP, InAs
- From this example, FCC anion (S^{2-}) is formed, and the cations (Zn^{2+}) occupy one type of the tetrahedral sites.
- (4,4)-coordination type.



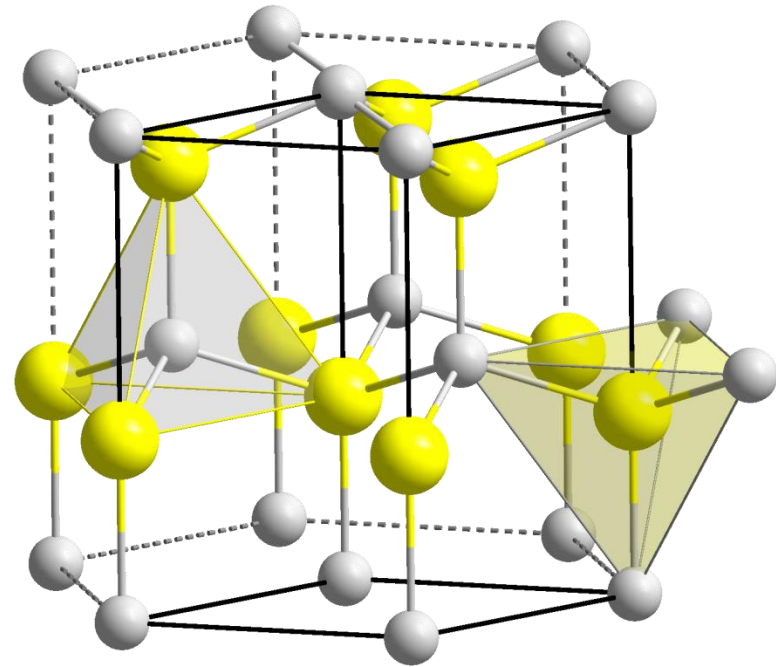
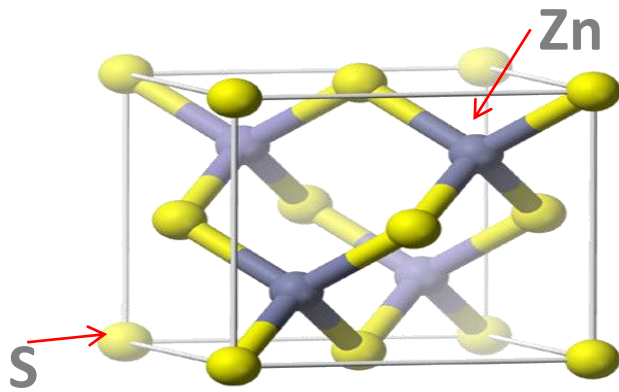
Structure of the common compounds

4) Wurtzite (ZnS)

-e.g. ZnS, ZnO, BeO, MnS, AgI, AlN, SiC and NH_4F

-Instead of the FCC likes in Zinc Blende structure, the HCP anion is formed. And as in Zinc Blende structure, one type of tetrahedral is occupied by cations.

-(4,4)-coordination



Structure of the common compounds

5) Fluorite (CaF_2)

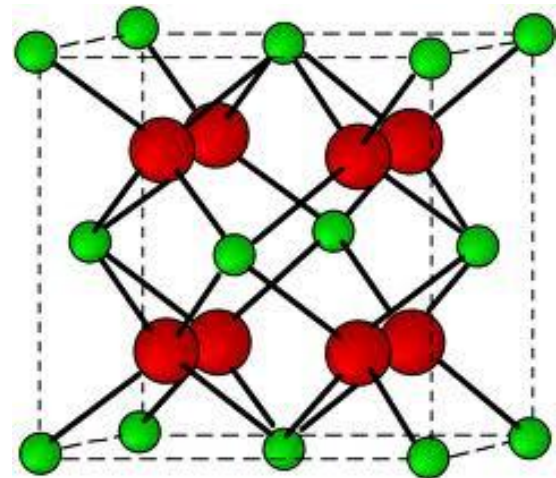
- e.g. CaF_2 , UO_2 , BaCl_2 , HgF_2 , and PbO_2

- Expanded FCC of previous structure (Ca^{2+} size is usually smaller than F^-)

- Ca^{2+} ions are located at the FCC packing unit and the F^- are in both types of tetrahedral holes.

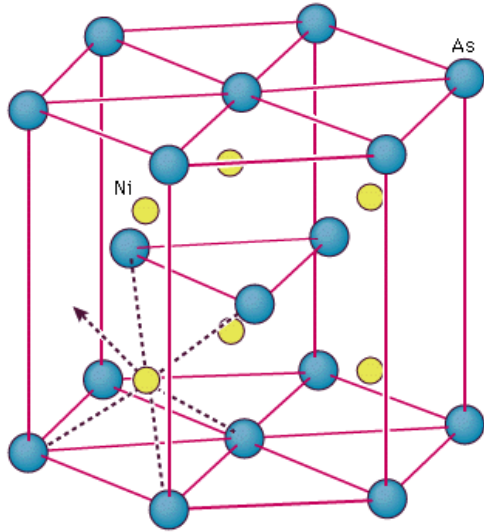
• *Number of F^- ions are twice a number of Ca^{2+} ions.*

• *There is a antifluorite structure where the position of cation and anion are reversed, e.g. K_2O , K_2S , Li_2O , Na_2O , Na_2Se and Na_2S .*

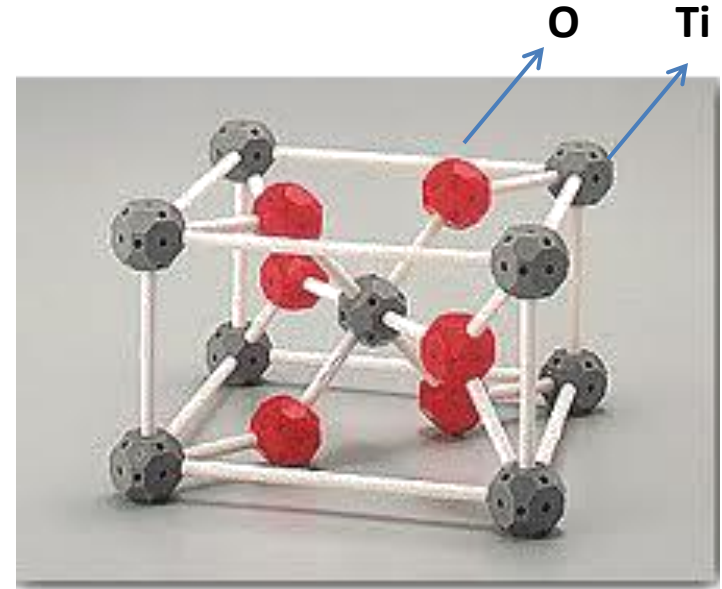


Structure of the common compounds

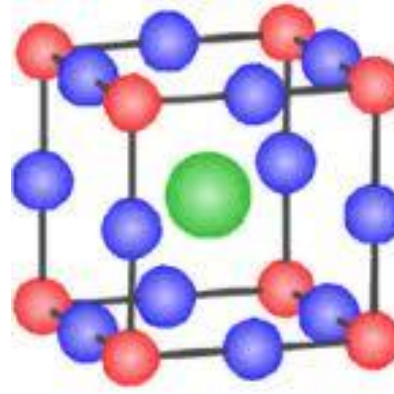
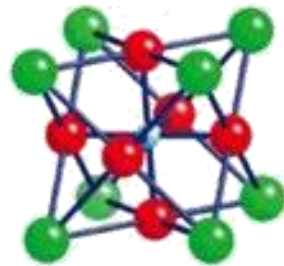
6) Nickel-Arsenide Structure



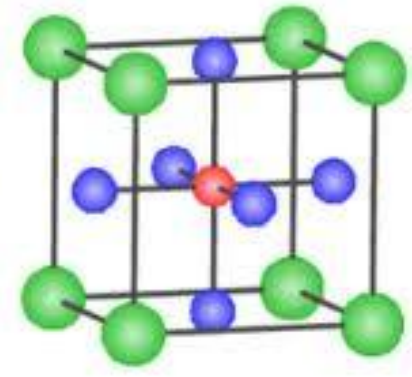
7) Rutile Structure



8) Perovskite Structure



Perovskite A-type



Perovskite B-type

Structure of the Metal and Alloy

The crystal structures adopted by some metallic elements at 25 °C and 1 bar

Crystal structure

Element

Hexagonal close-packed (hcp)

Be, Cd, Co, Mg, Ti, Zn

Cubic close-packed (fcc)

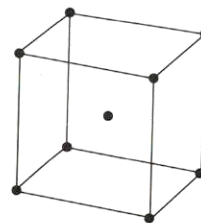
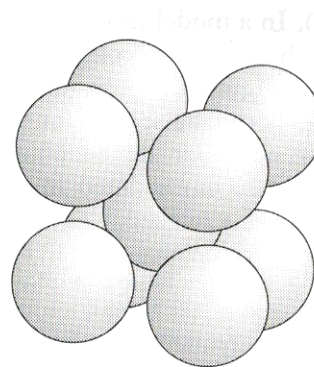
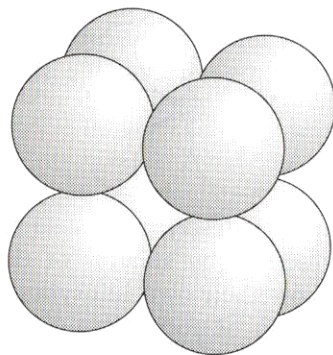
Ag, Al, Au, Ca, Cu, Ni, Pb, Pt

Body-centered cubic (bcc)

Ba, Cr, Fe, W, alkali metals

Primitive cubic (cubic-P)

Po

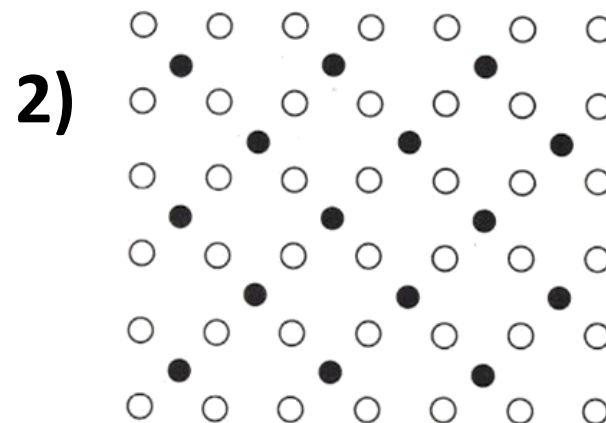
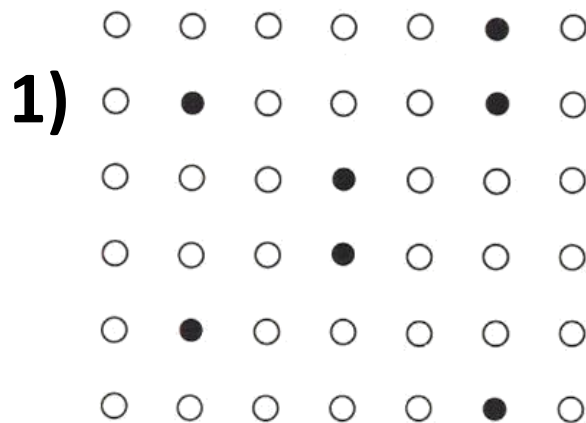


Structure of the Metal and Alloy

Alloy : is a blend of metals, usually prepared by mixing the molten components and cooling the mixture. Alloy may be homogeneous solid solutions, in which the atoms of one metal are distributed randomly. There are two types.

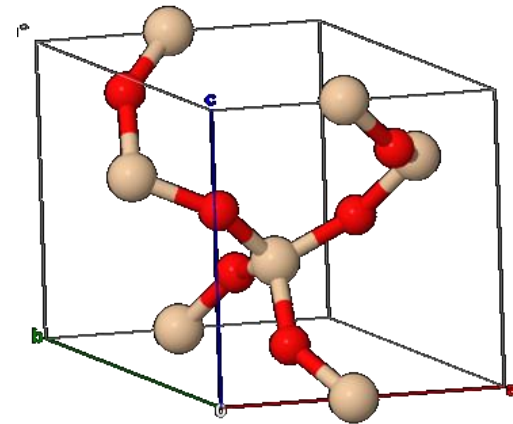
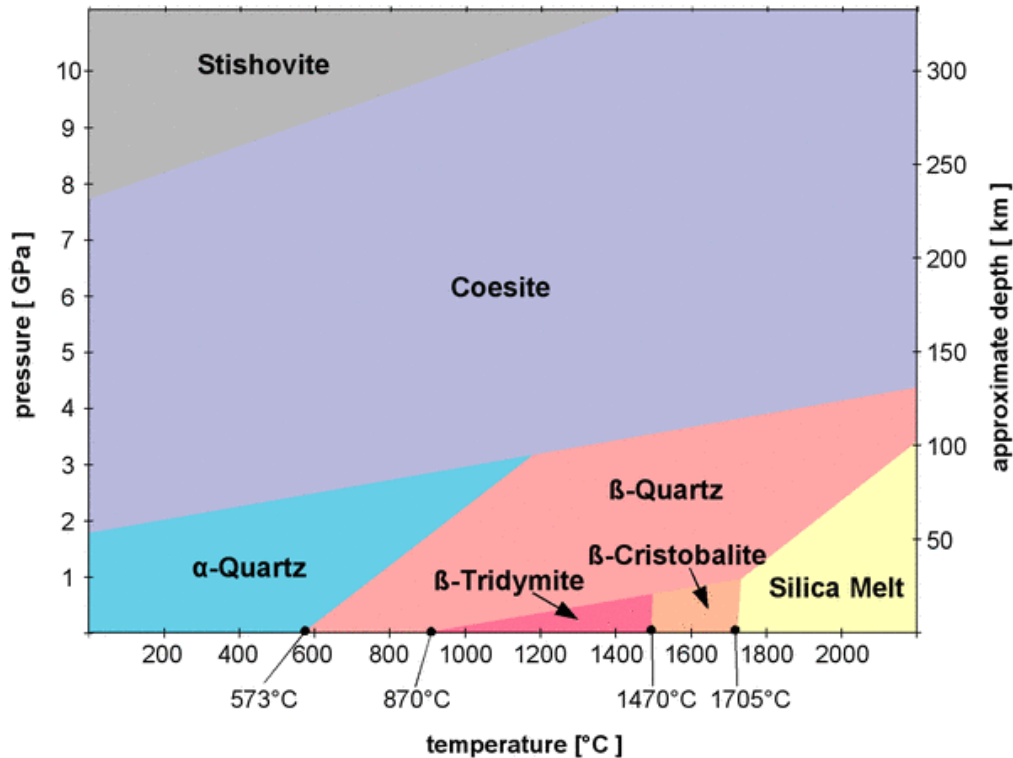
1. Substitution solid solution

2. Interstitial solid solution

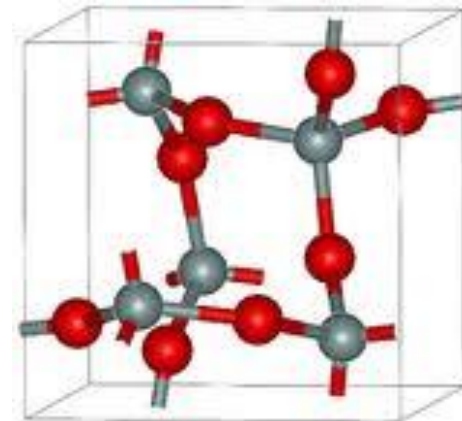


Polymorph

Two minerals that have the same chemical composition, but a different crystal structure are called “*polymorphs*”.



Quartz

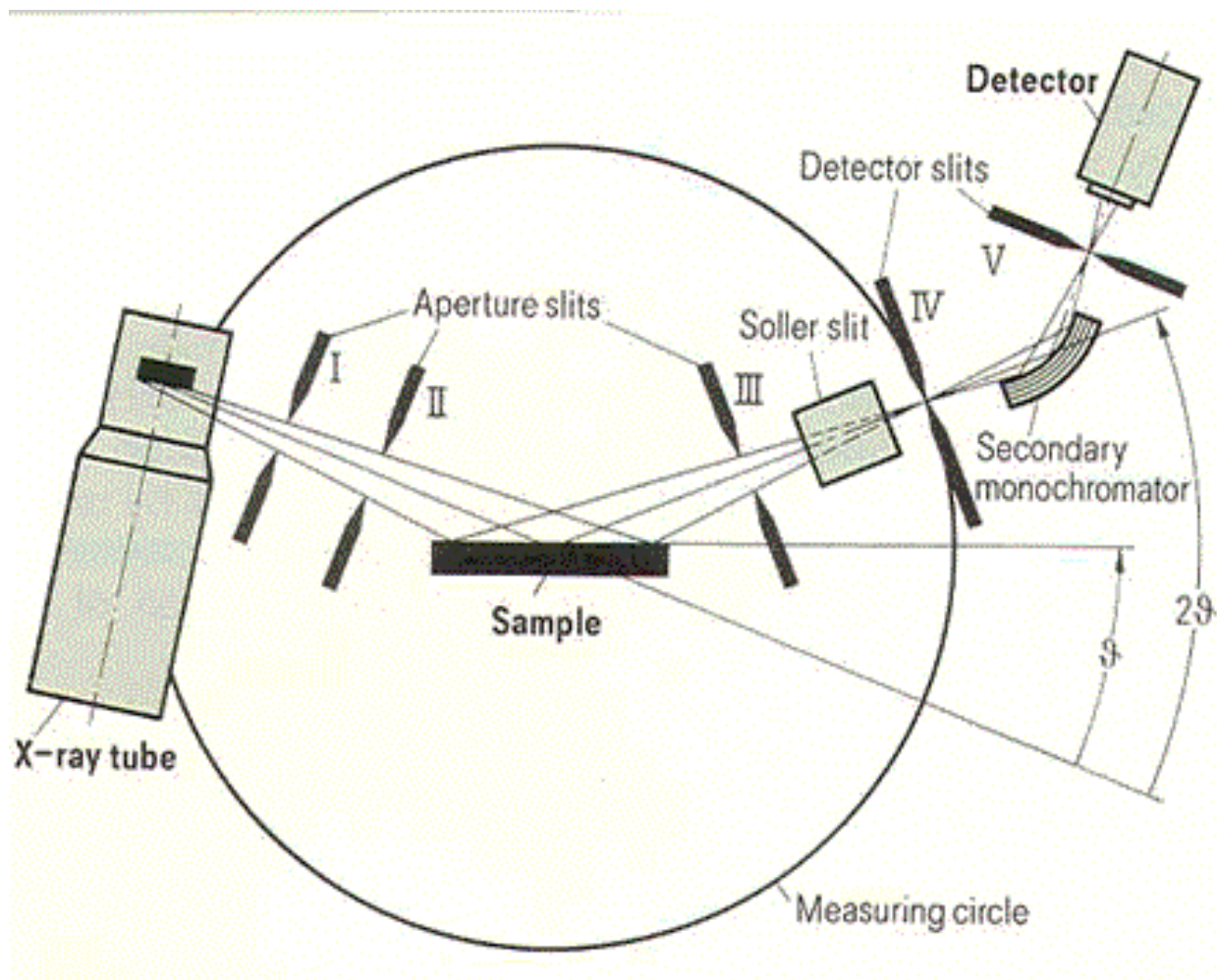


Cristobalite

X-ray Diffraction Techniques



X-ray Diffraction Techniques



X-ray Diffraction Techniques :Bragg's Law

$$\lambda = 2d_{hkl} \sin \theta$$

