Crystalline solids

By

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TYPES OF SOLIDS.

BASED ON STRUCTURE

Crystalline solids

Amorphous solids

Crystalline solids

Highly regular arrangement of atoms, ions, molecules - periodic (repeating)

Example:NaCl,KCl

Amorphous solids

No repeating pattern, only short range order, extensively disordered - non crystalline

Example:glasses

Types of crystalline solids

Metallic

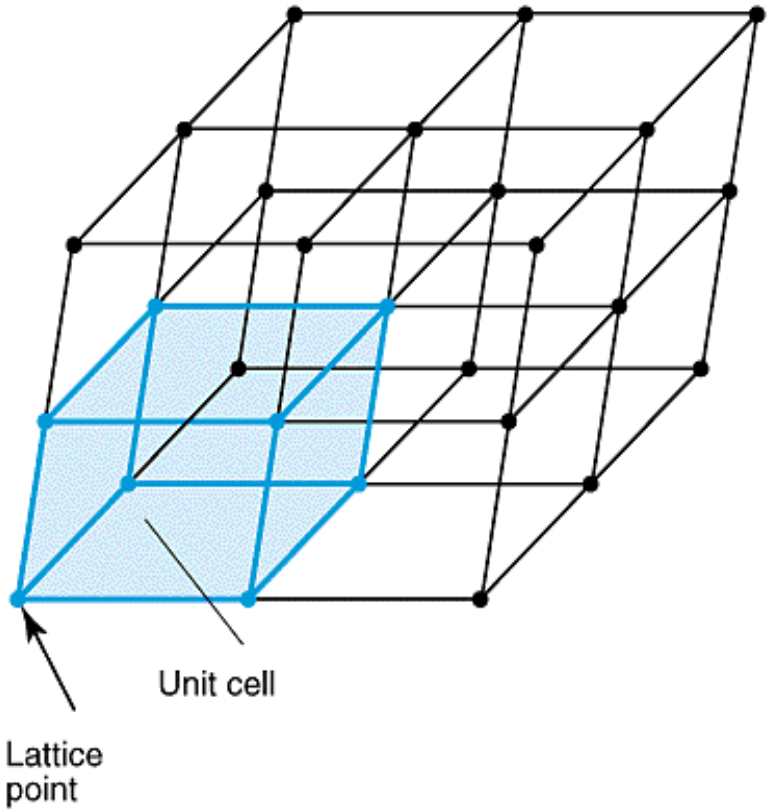
Ionic

Extended covalent (or network)

Molecular

Crystallinity

a repeating unit = **unit cell**



Lattice

is an infinite 1,2, or 3-Dimensional regular arrangement of points, each of which has identical surroundings.

- Any lattice can be described by placing lattice points at equivalent positions within each unit of the pattern.

- To recover original pattern we add the motif to each lattice point.

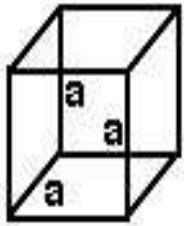
1-D pattern -------- Line

2-D patterns -------- Planar lattices

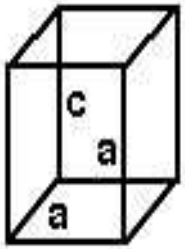
3-D pattern -------- space lattices

The Seven Crystal Systems

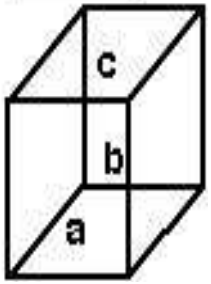
Cubic $a = b = c$, $\alpha = \beta = \gamma = 90^\circ$



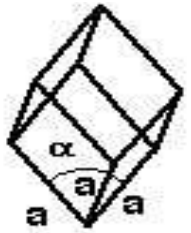
Tetragonal $a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$



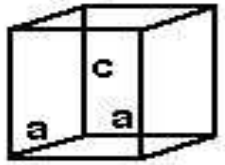
Orthorhombic $a \neq b \neq c$, $\alpha = \beta = \gamma = 90^\circ$



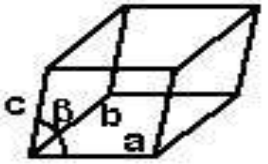
Rhombohedral $a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$



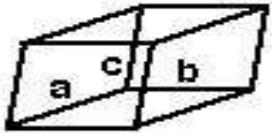
Hexagonal $a = b \neq c$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$



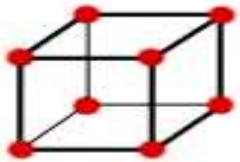
Monoclinic $a \neq b \neq c$, $\alpha = \gamma = 90^\circ \neq \beta$



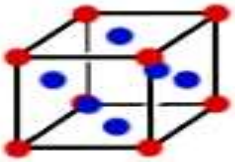
Triclinic $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^\circ$



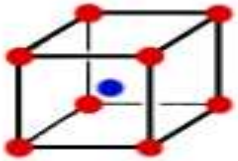
Bravais Lattices



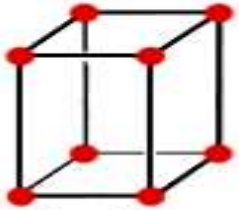
Simple cubic



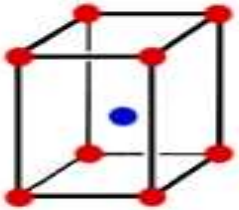
Face-centered cubic



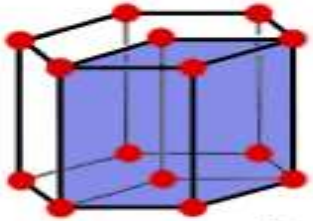
Body-centered cubic



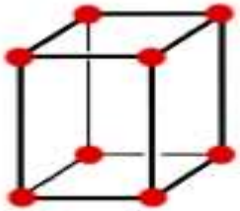
Simple tetragonal



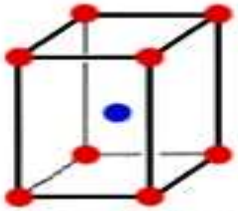
Body-centered tetragonal



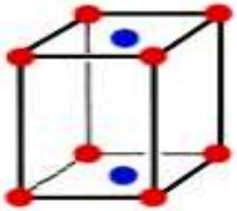
Hexagonal



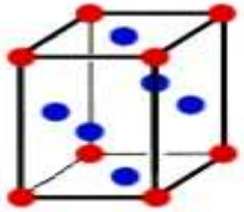
Simple orthorhombic



Body-centered orthorhombic

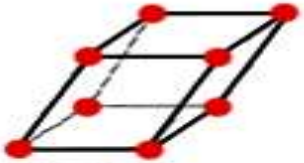


Base-centered orthorhombic

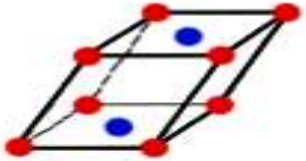


Face-centered orthorhombic

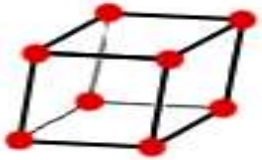
Rhombohedral



Simple Monoclinic



Base-centered monoclinic



Triclinic

Bravais lattices of Cubic Lattice

- Simple cubic (also called primitive cubic), lattice points only at corners
- Body Centered Cubic (BCC), lattice points at corners and in middle of cube.
- Face Centered Cubic (FCC) lattice points at the corners and in the middle of each face

Unit Cells

How many lattice points "belong" to a unit cell ?

- Corners: The points at the corner of the cell are shared by 8 unit cells in total and is only "worth" 1/8 to each cell.
- Faces : - these lattice points are shared by 2 cells, each one is "worth" 1/2 to each cell.
- Body : - this is the sole possesion of that cell, worth 1.
- Total number lattice points:

Primitive cubic = 8(1/8) = 1

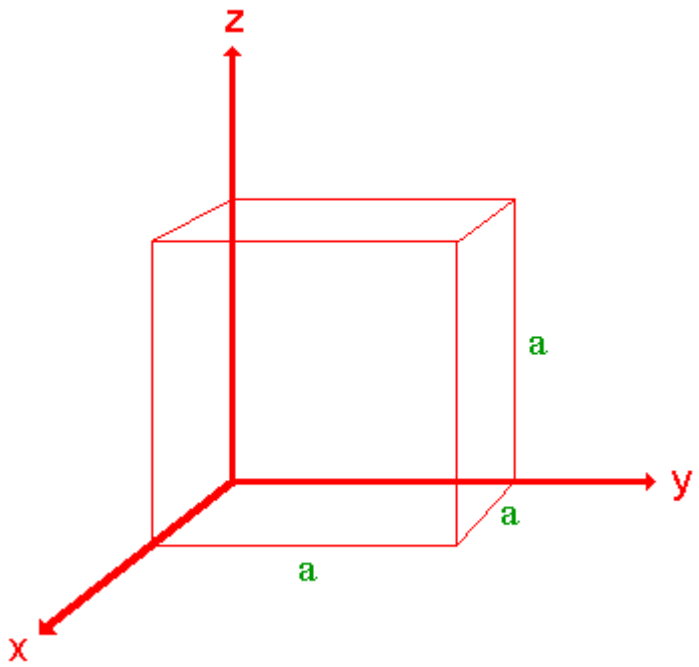
FCC = 6x1/2 + 8(1/8) = 4

BCC = 8(1/8) + 1 = 2

- Law of constancy of interfacial angles
- Law of reciprocal indices

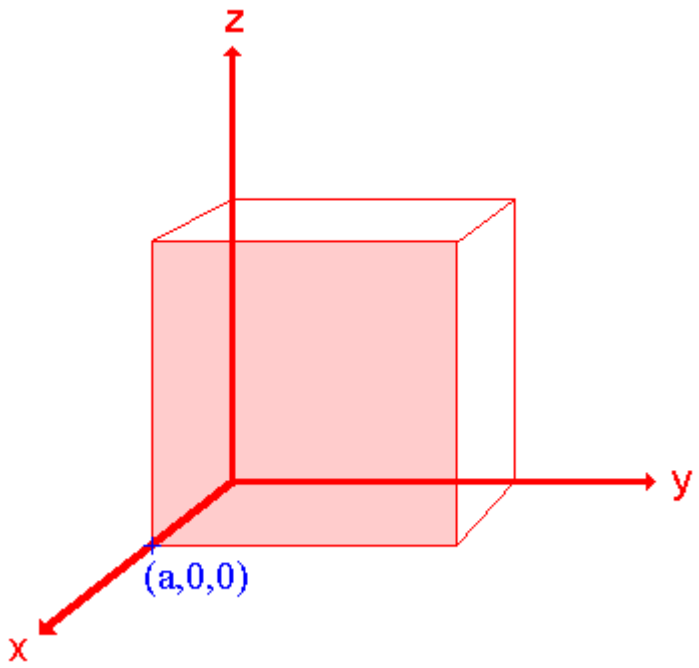
Lattice dimensions

- Directions

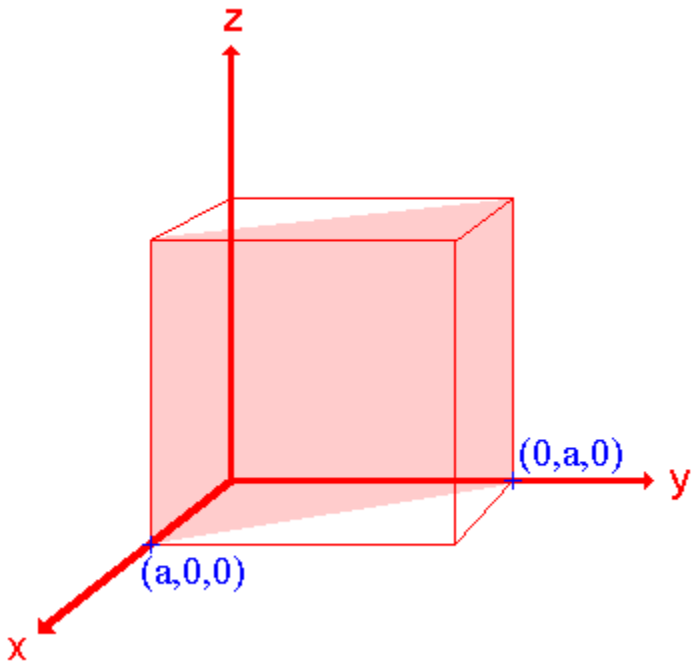


Miller Planes

(100)



(110)



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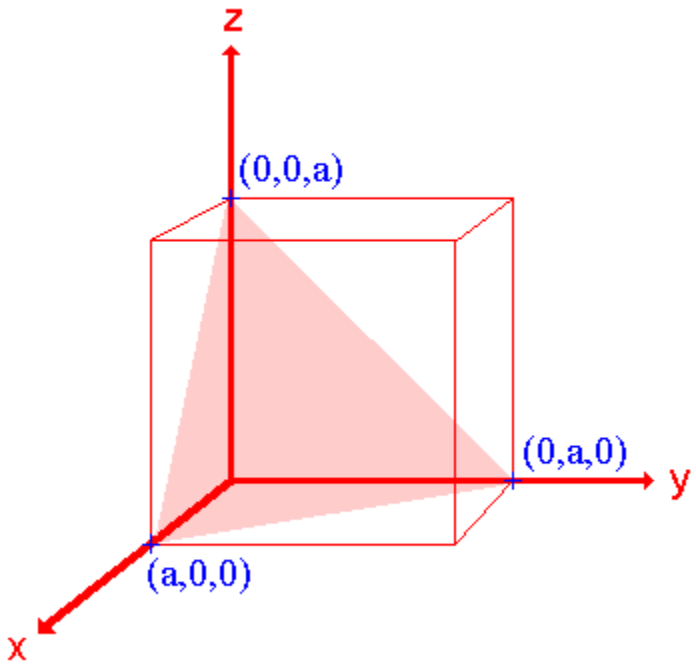
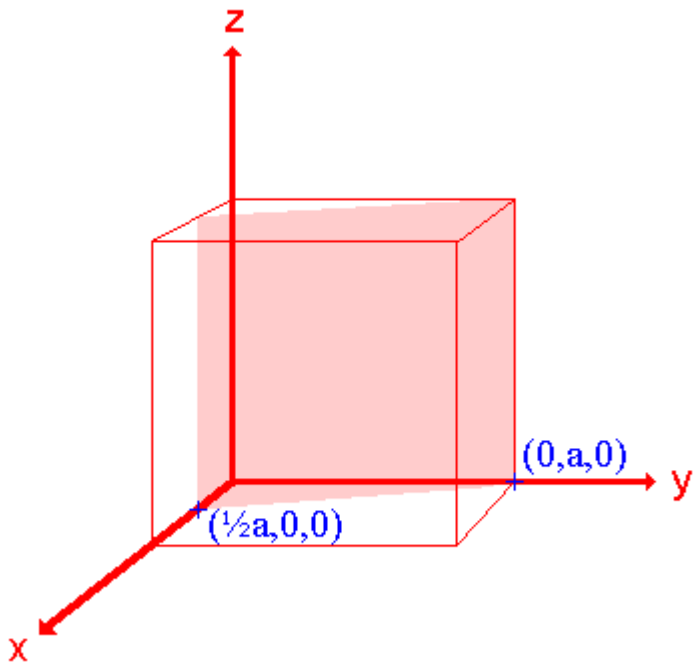
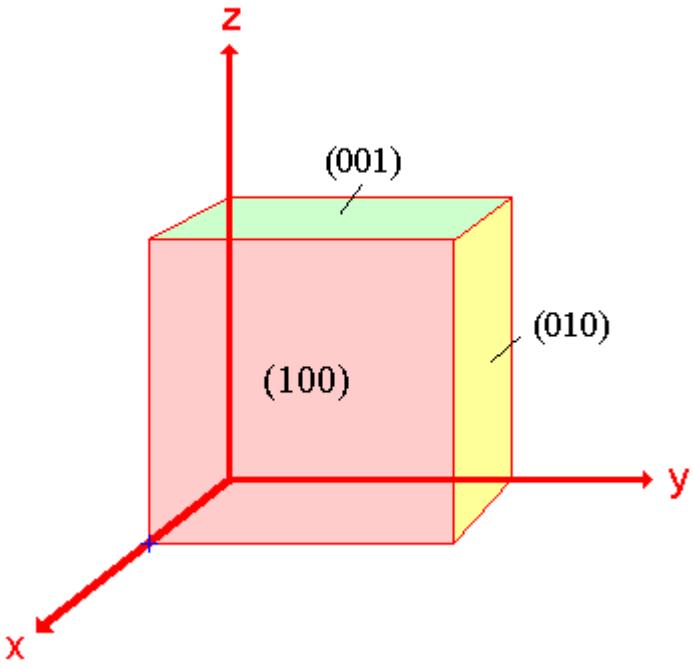


(210)




z
(001)
(010)
(100)
y
x

Theoretical Density

Density=nM/NV n=No of particles

M=Atomic mass

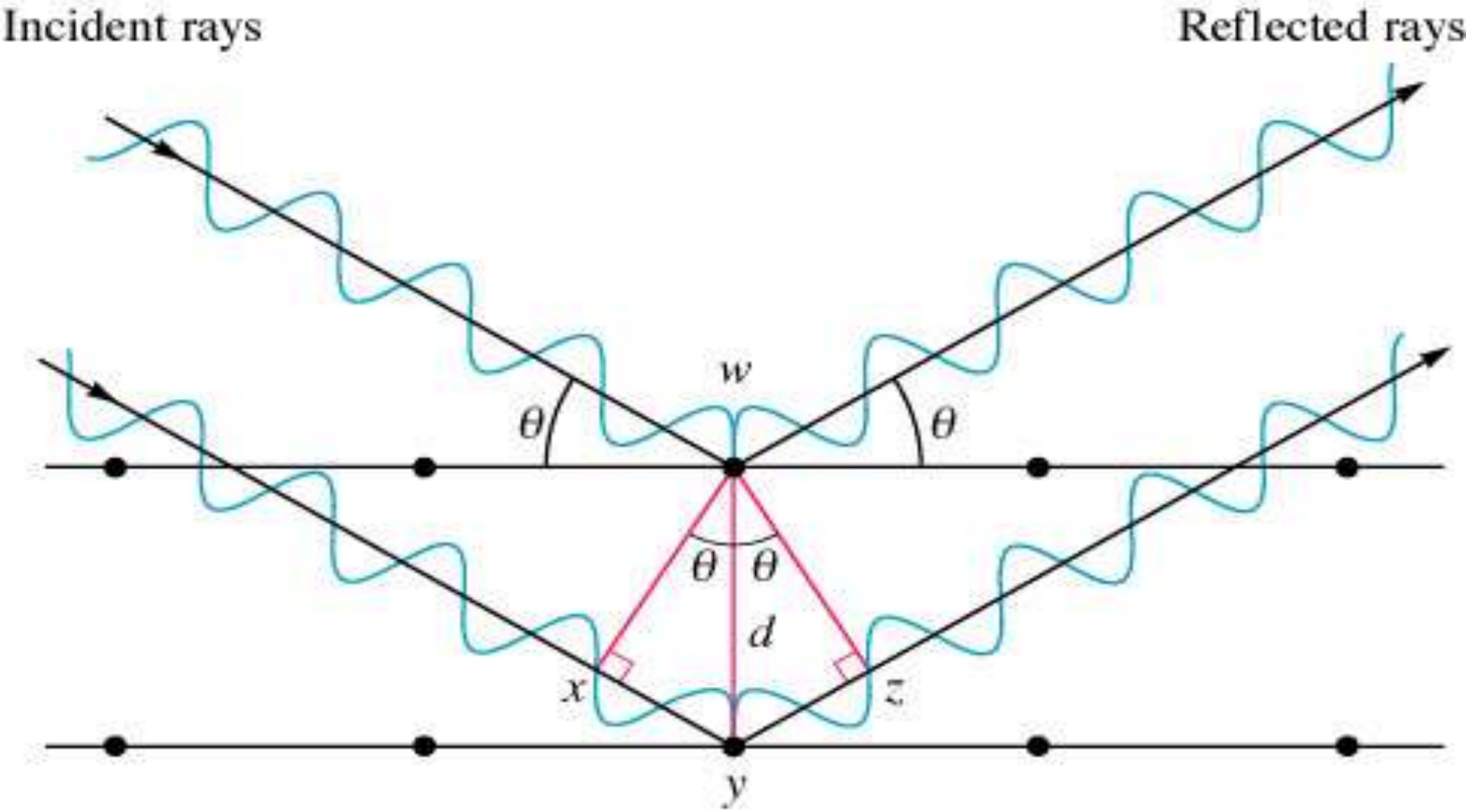
N=Avagadro number

V=Volume of unit cell

How can we study their structures ?

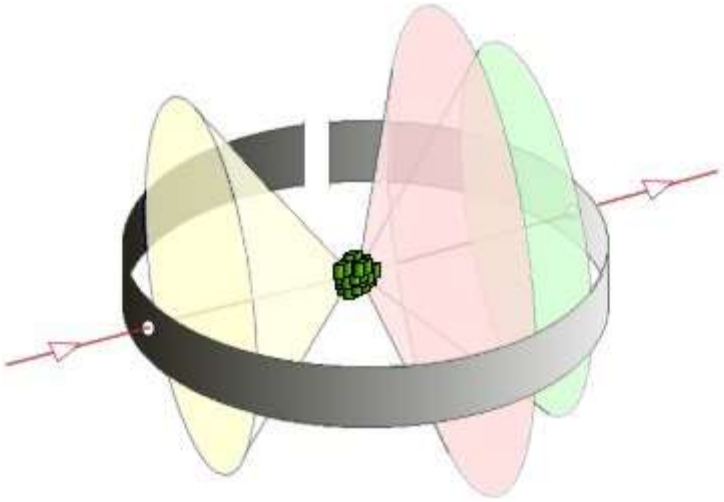
By x-ray diffraction

Bragg's Law



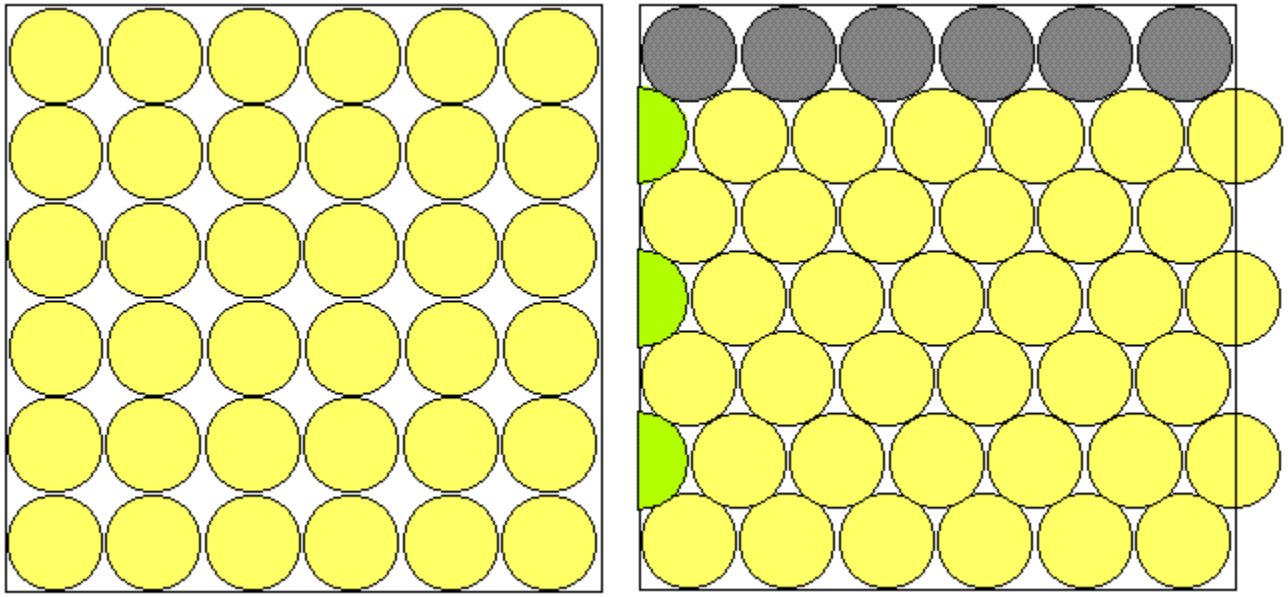
X-Ray Diffraction

Debye



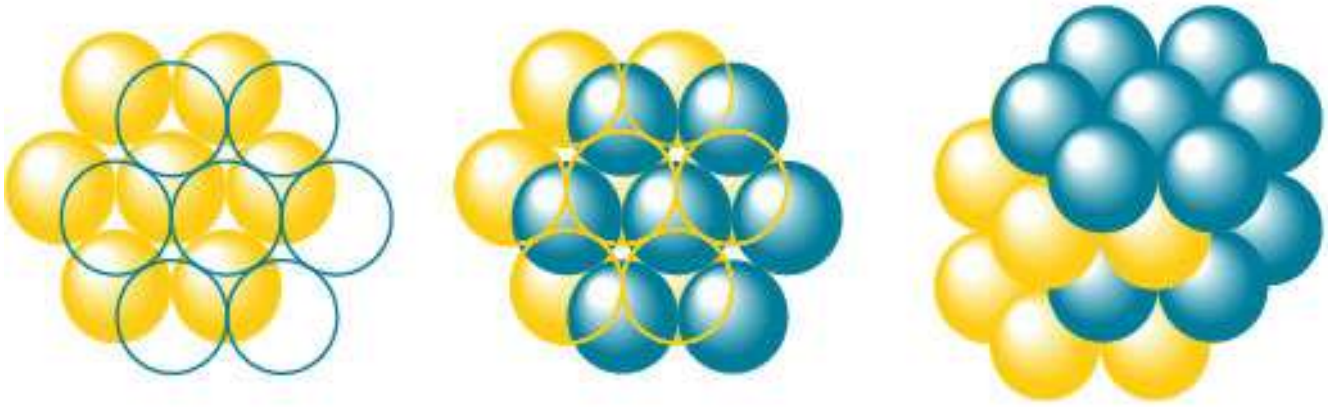
Close packing of spheres

The vacant spaces are called interstitial holes



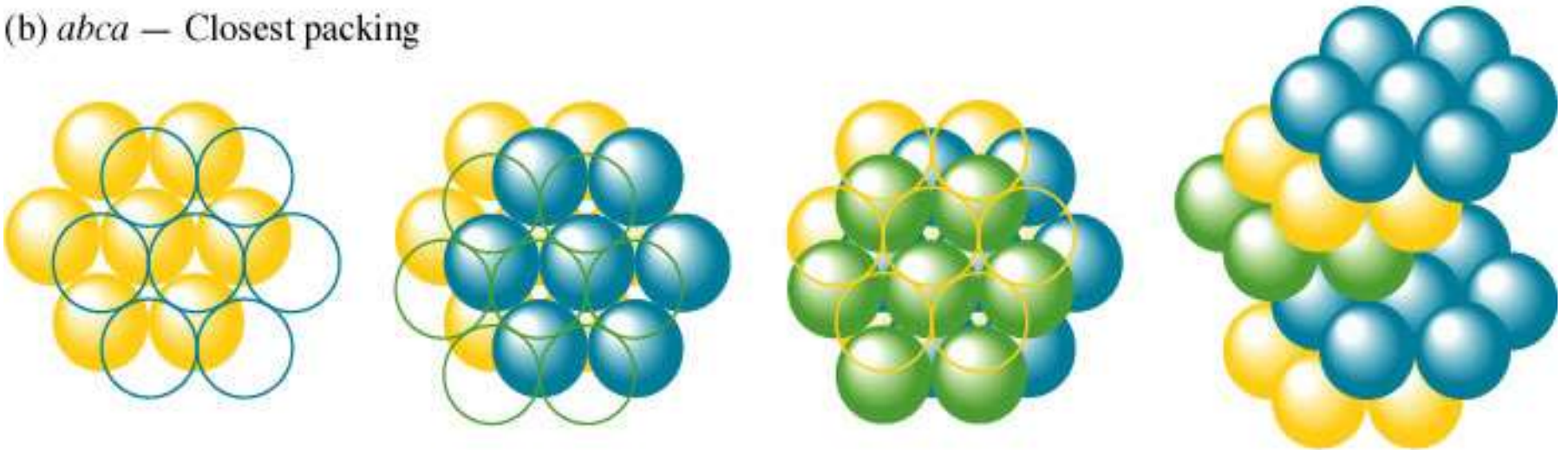
Most effective

(a) *abab* — Closest packing



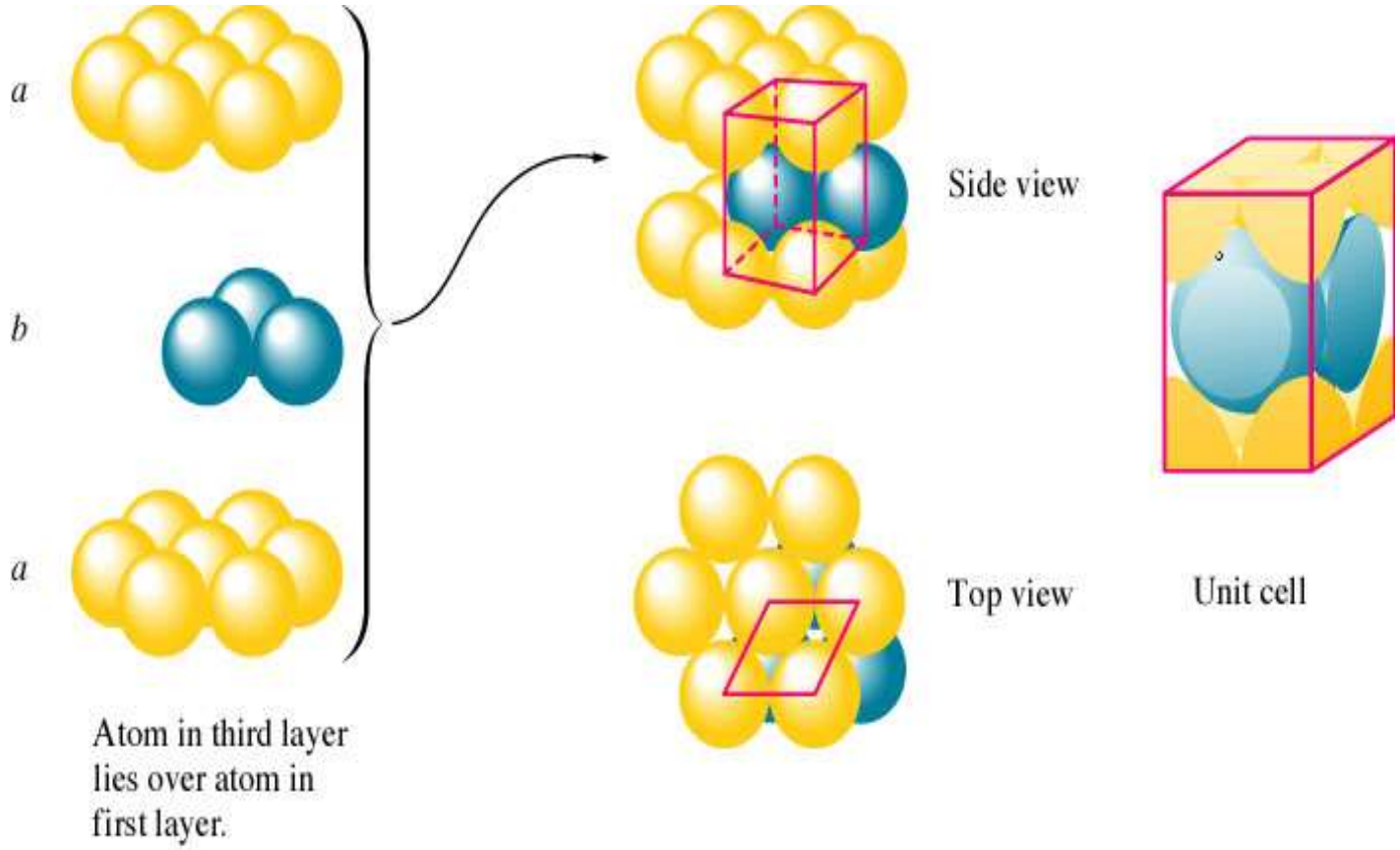
Top view Top view Side view

(b) *abca* — Closest packing

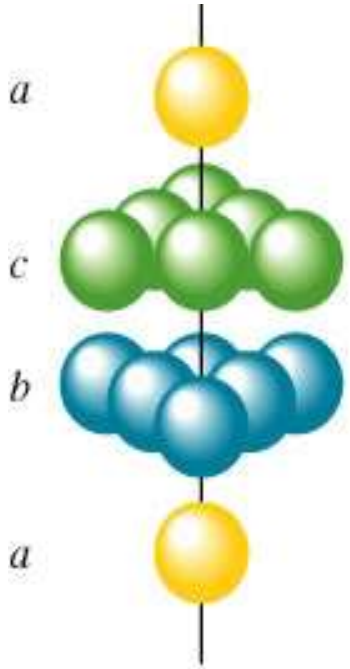


Top view Top view Top view Side view

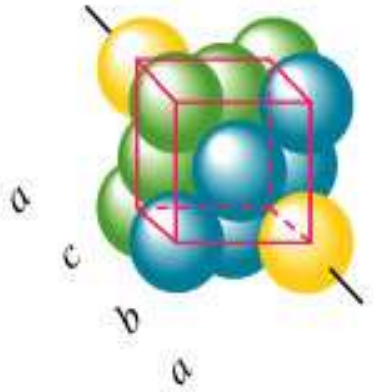
Hexagonal Closest Packing

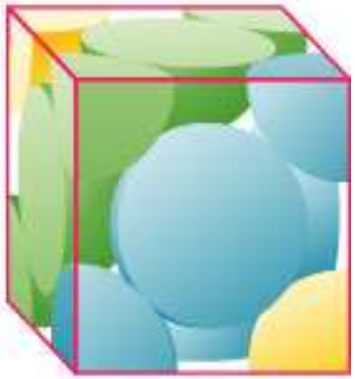


Cubic Closest Packing (FCC)



An atom in every fourth layer lies over an atom in the first layer.

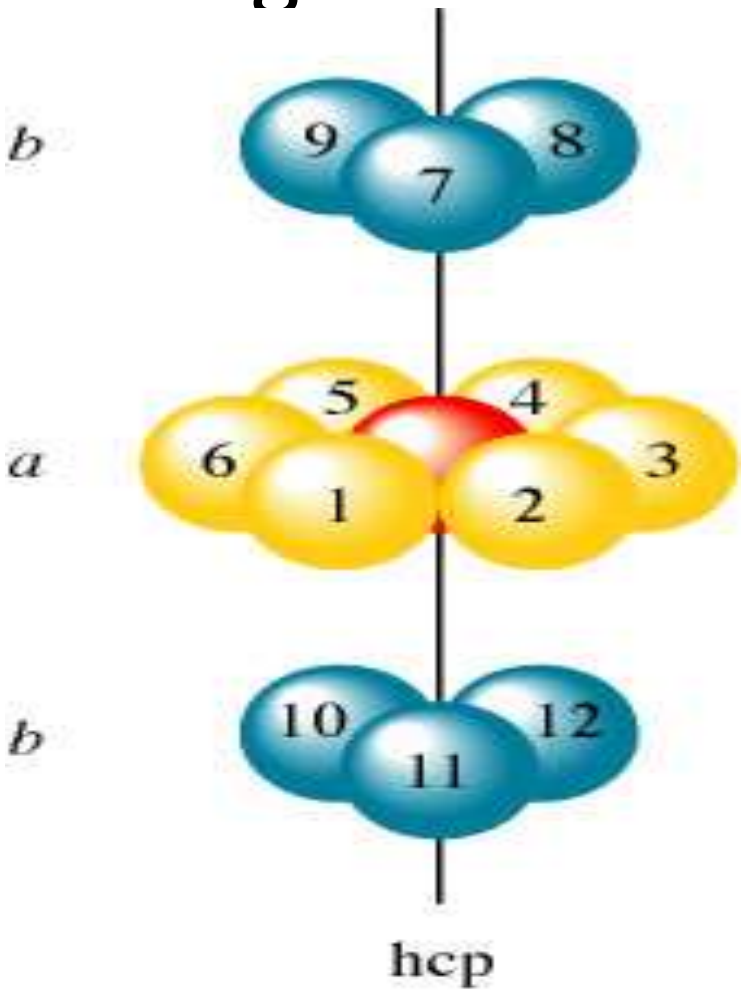




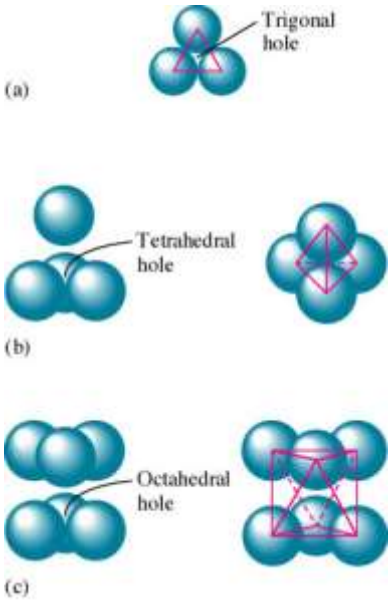
Unit cell

- Each sphere is surrounded by 12 other spheres (6 in one plane, 3 above and 3 below).
- Coordination number: the number of spheres directly surrounding a central sphere.
- If unequally sized spheres are used, the smaller spheres are placed in the interstitial holes.

The Indicated Sphere Has 12 Nearest Neighbors



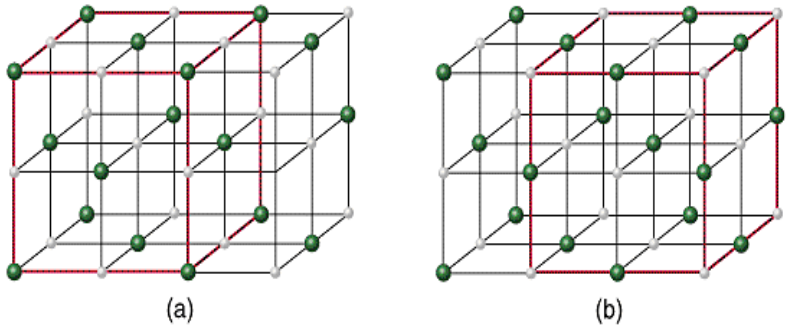
The Holes that Exist Among Closest Packed Uniform Spheres



Crystal Structure of Sodium Chloride

Face-centered cubic lattice.

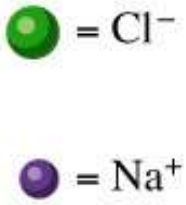
- Two equivalent ways of defining unit cell:
  - Cl^- (larger) ions at the corners of the cell, or
  - Na^+ (smaller) ions at the corners of the cell.

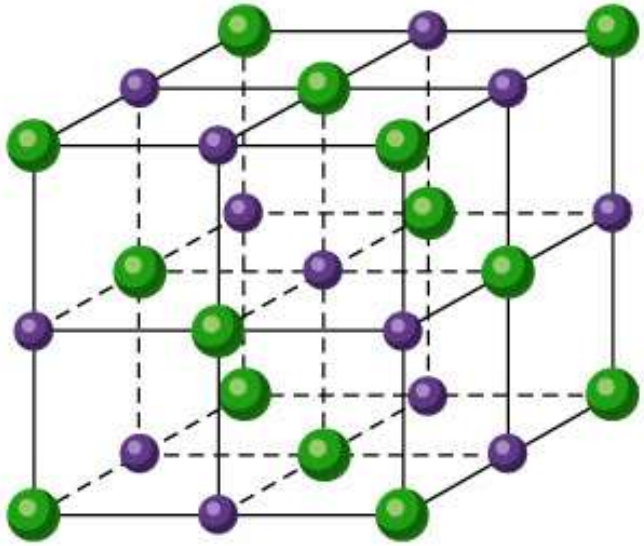


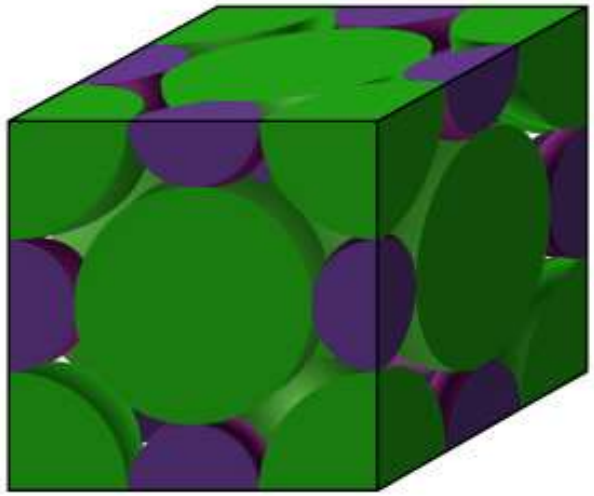
- The cation to anion ratio in a unit cell is the same for the crystal. In NaCl each unit cell contains same number of Na^+ and Cl^- ions.
- Anions ccp (fcc). Radius Na+ = 1.02Å, radius Cl- = 1.81Å; radius ratio = 0.563.
- Therefore Na octahedral.
- 1 octahedral / anion therefore 100% octahedral sites are filled.
- Coordination # Na = 6; coordination # Cl = 6.

The NaCl Unit Cell Contains 4 Na^+ and 4Cl^-

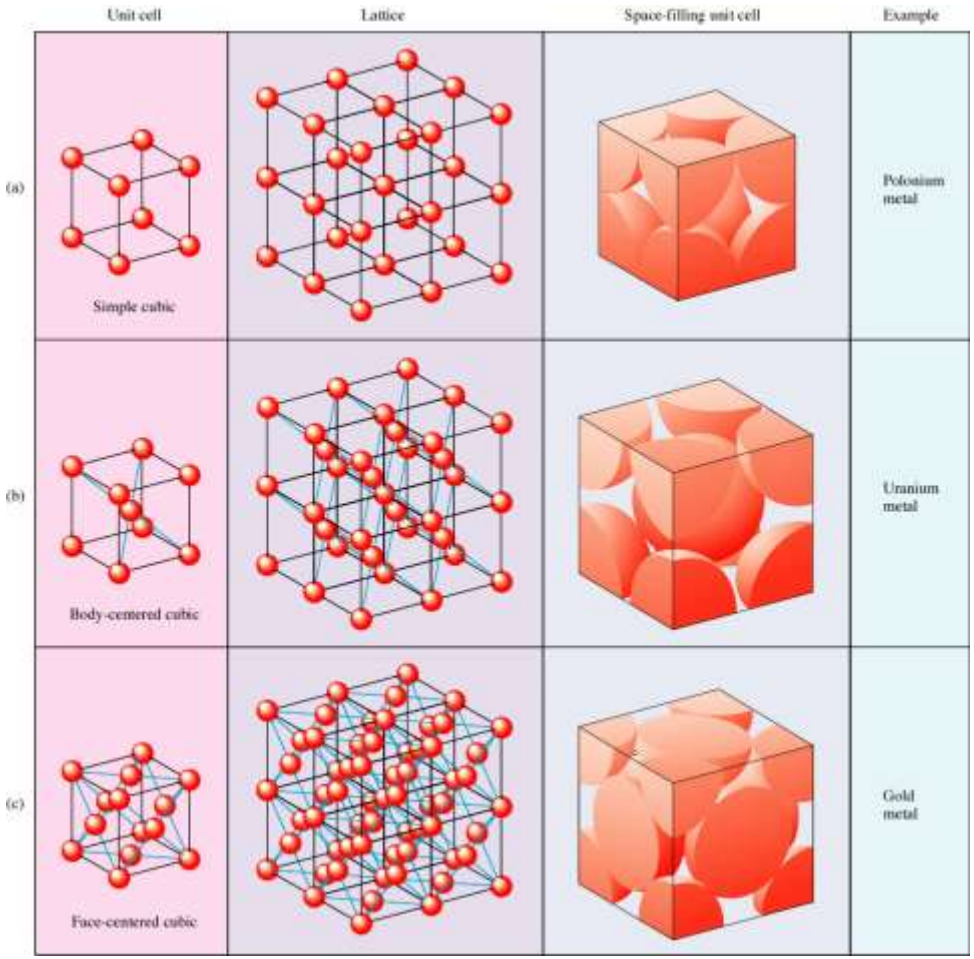
Can you see them?????



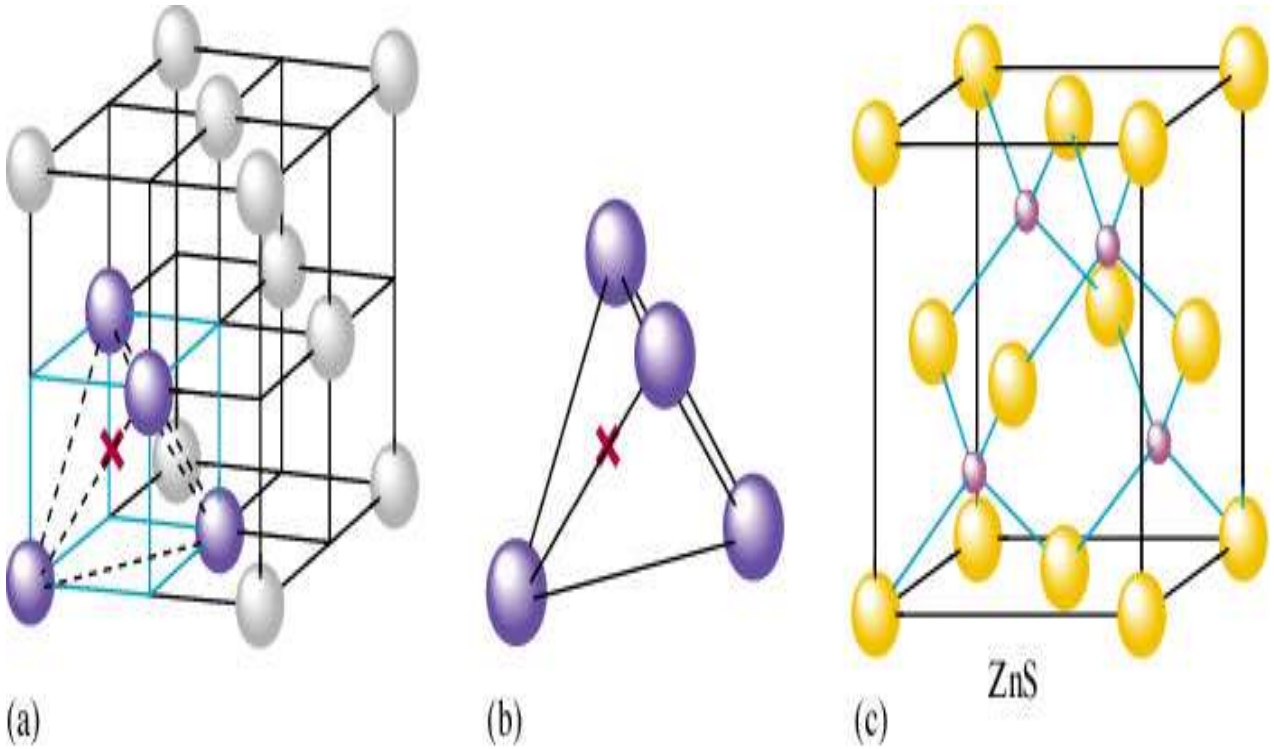




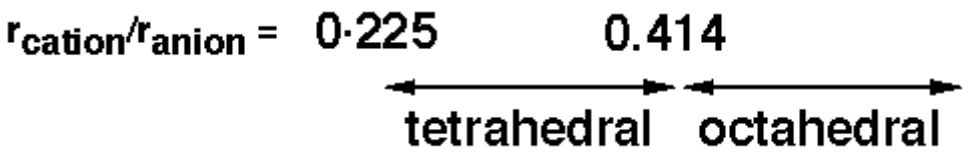
Three Cubic Unit Cells and the Corresponding Lattices



The Position of Tetrahedral Holes in a Face-Centered Cubic Unit Cell

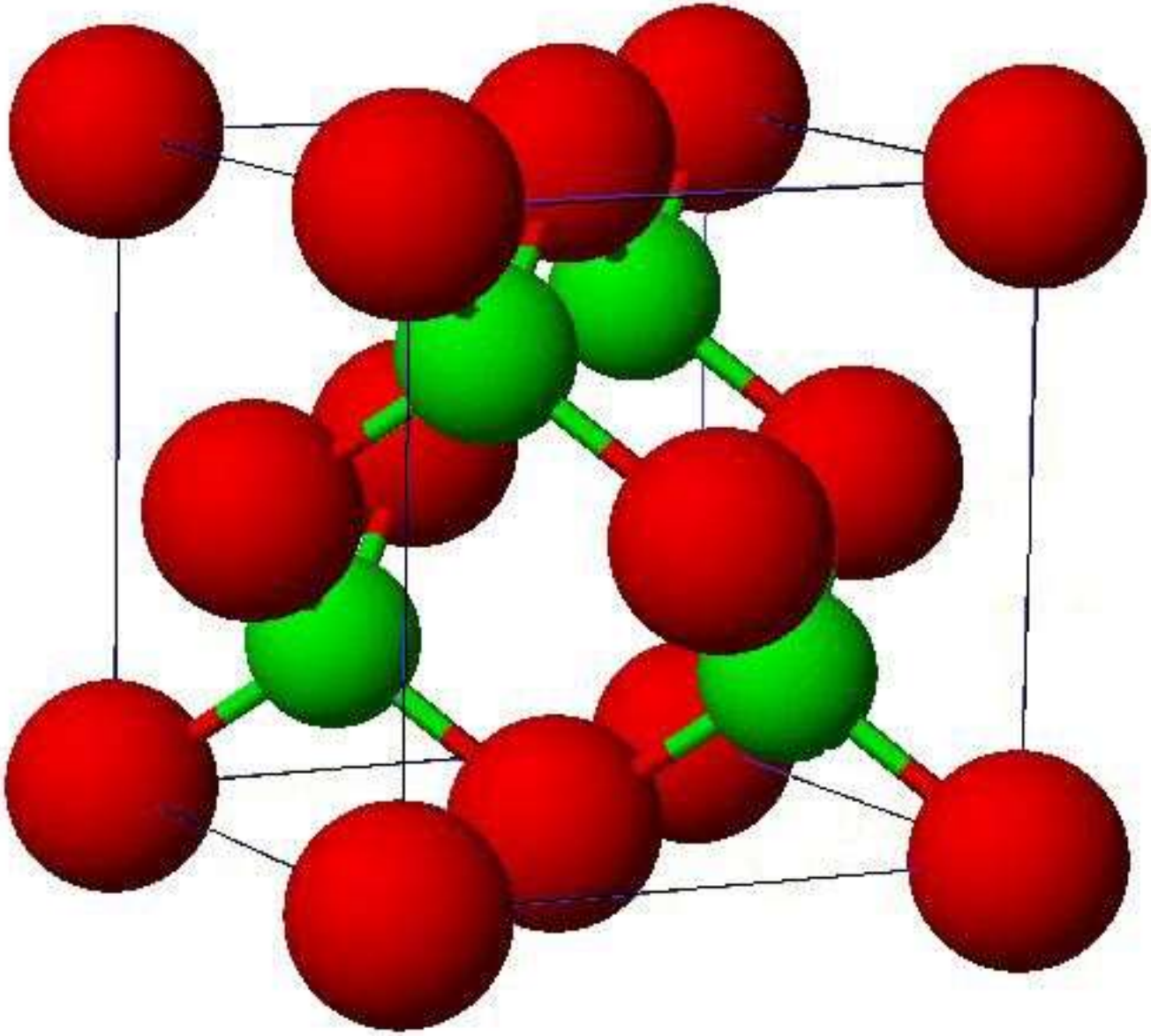


Radius Ratio rules.

- 

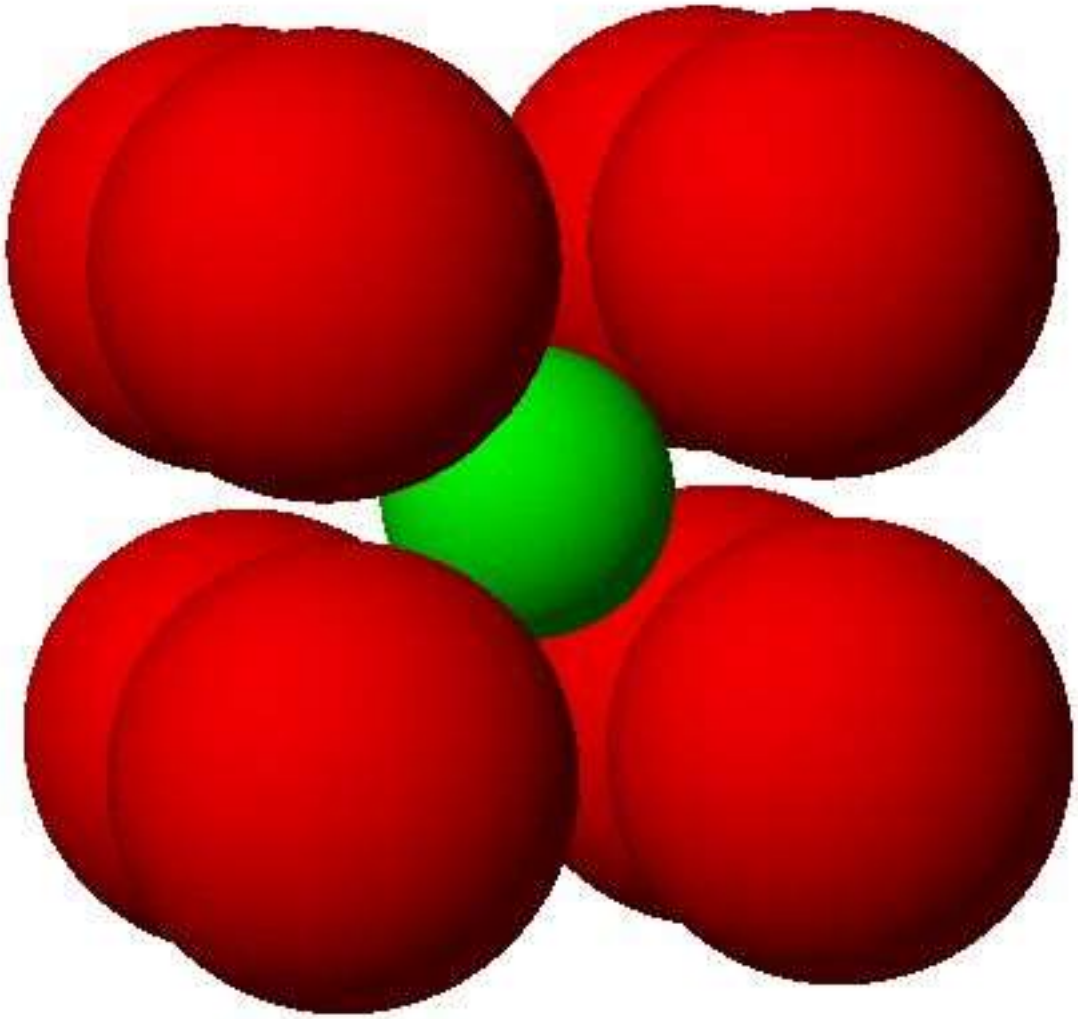
Zincblende (Zinc sulfide, ZnS) structure

- Anions ccp (fcc). Radius Zn2+ = 0.6Å, radius S2- = 1.84Å; radius ratio = 0.33 Æ Zn tetrahedral.
- Have 2 tetrahedral sites/ anion, therefore from formula of ZnS only 50% of the tetrahedral sites can be filled.
  Coordination # Zn = 4; coordination # S = 4.
- Which sites are filled ?: see picture below.
  Note the filling of diagonally opposite sites to maximize the cation-cation separations



Cesium Chloride Structure

- CsCl: radius Cs+ = 1.74Å, radius Cl- = 1.81Å: radius ratio = 0.96 Æ predict cubic coordination.
  All cubic sites are filled by Cs cations.
  Coordination numbers: Cs = 8; Cl = 8.
  Note Cs and Cl are in contact along the body diagonal



FLUORITE STRUCTURE (CaF2).

- Simple cubic arrangement of anions - 50% cubic sites filled.
  e.g.CaF2
  ionic radius Ca2+ = 1.12Å; radius F- = 1.31Å; radius ratio = 0.85
  Æ Ca2+ cubic coordination. One cubic site per F anion; from stoichiometry only 50% cubic sites filled by Ca cations.
  Arrangement of the filled cubic sites is such that the Ca-Ca distances are as large as possible (compare the Ca distribution to that of Zn in ZnS)
  Coordination numbers: Ca2+ surrounded by 8 F- 's; F- surrounded by 4 Ca2+'s.
  Other examples: ZrO2