Chem 241

Lecture 19

Announcement

March 26 → Second Exam

Recap

Water Redox
Comp/Disproportionation
Latimer Diagram
Frost Diagram
Pourbaix Diagram

Ellingham Diagram

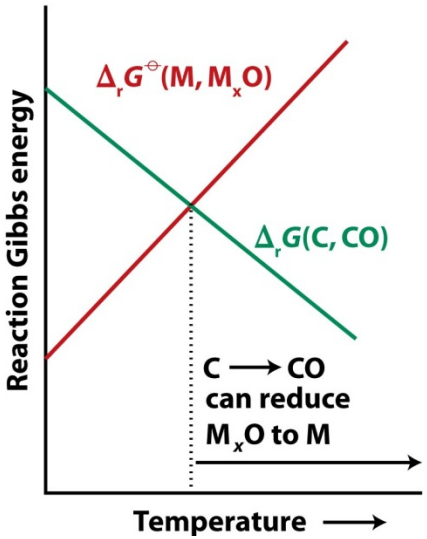
$M_xO + C(s) + \text{heat} \rightarrow xM(s,l) + CO(g)$

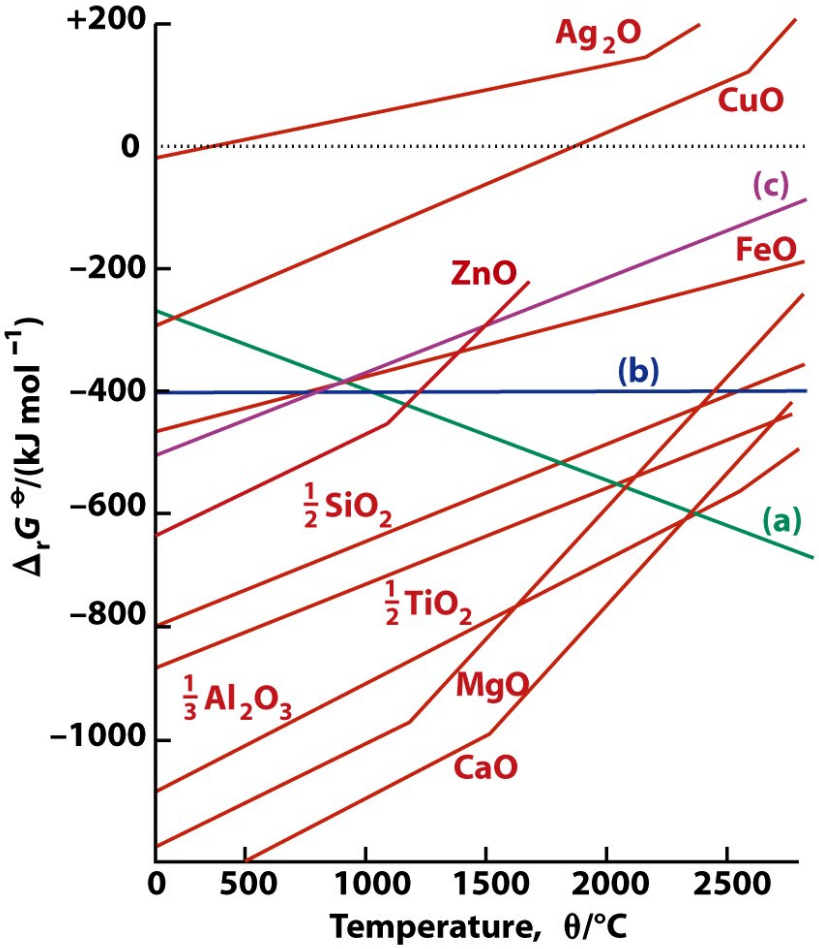
$C(s) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

$\frac{1}{2}C(s) + \frac{1}{2}O_2(g) \rightarrow \frac{1}{2}CO_2(g)$

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$

$M_xO(s) \rightarrow xM(s,l) + \frac{1}{2}O_2(g)$





Homework

Chapter 5

Exercises: 2, 3, 6, 7, 9

Inorganic Solids

What? And Why?

A. Understanding the structure and bonding of solid state compounds is important for understanding

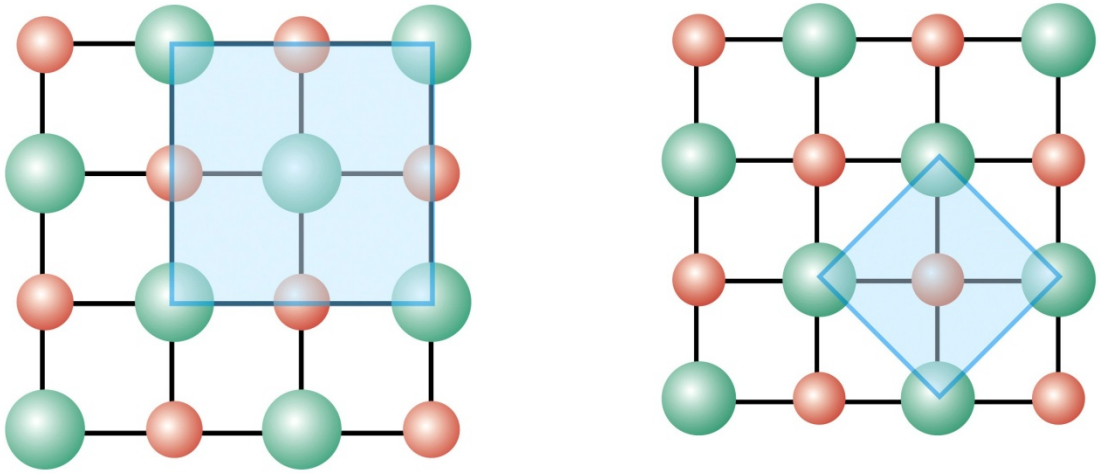
1. inorganic materials such as metals, alloys, salts, such as
   a. Pigments
   b. Nanostructured materials (zeolites)
   c. High-temperature super conductors
   d. minerals
2. Trends in structure and reactivity.
3. Electronic structures of conductors, semi-conductors and insulators.

Inorganic Solids

Aarrangement of atoms (or ions) in a simple solid structure can often be represented by different arrangements of **hard spheres.**

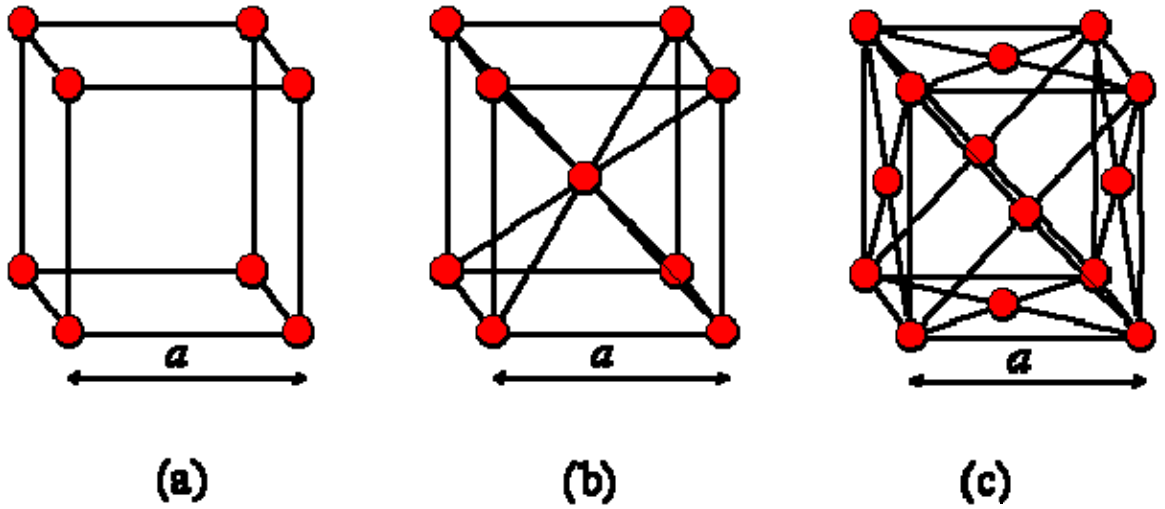
A crystal of an element or compound is constructed from repeating elements. The **crystal lattice** is the pattern formed by these repeating structural elements.

Unit Cell



Centering the Unit Cell

A. **Primitive (P)**
B. **Body Centered (I)**
C. **Face Centered (F)**
D. **Base Centered (C)**

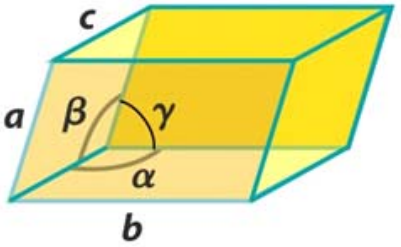


Seven Crystal Systems

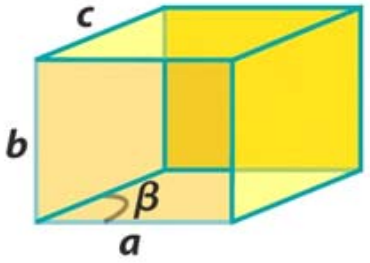
Unit Cell is the repeating parallelepiped

Table 3.1 The seven crystal systems

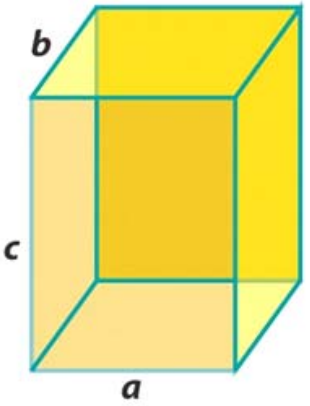
System	Relations between lattice parameters	
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90° \ \beta \neq 90°$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$
Hexagonal	$a = b \neq c$	$\gamma = 120°$
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$



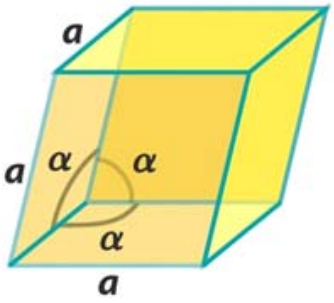
Triclinic



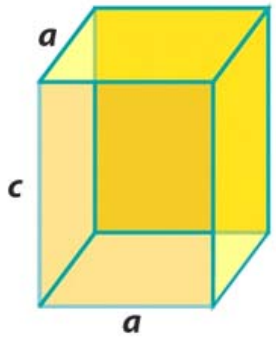
Monoclinic



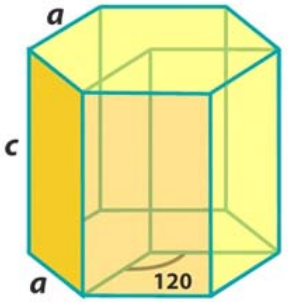
Orthorhombic



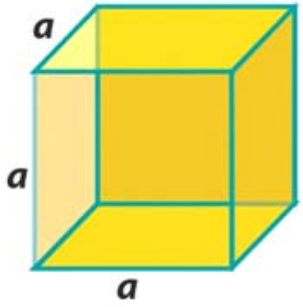
Trigonal



Tetragonal



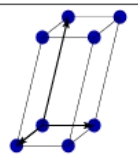
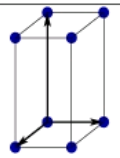
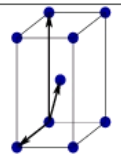
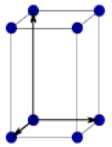
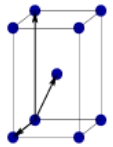
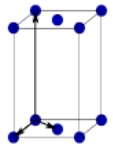
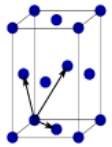
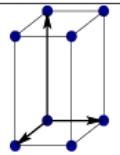
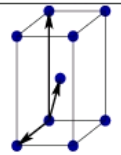
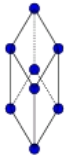
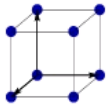
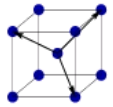
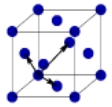
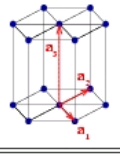
Hexagonal



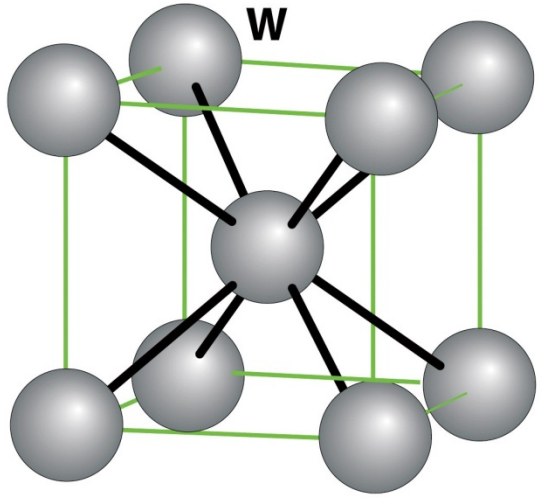
Cubic

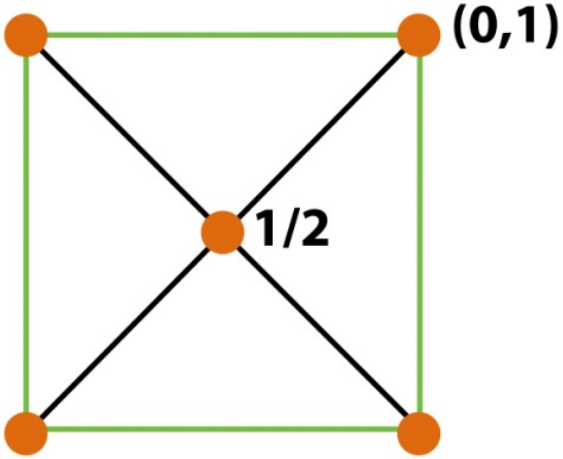
Bravais Lattice

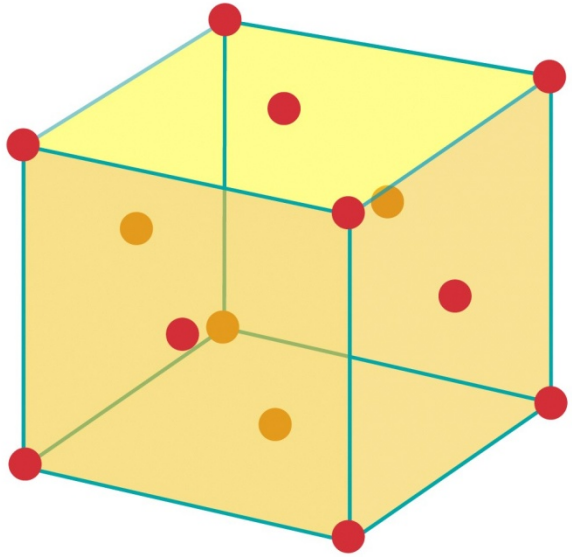
A. **Primitive (P)**
B. **Body Centered (I)**
C. **Face Centered (F)**
D. **Base Centered (C)**

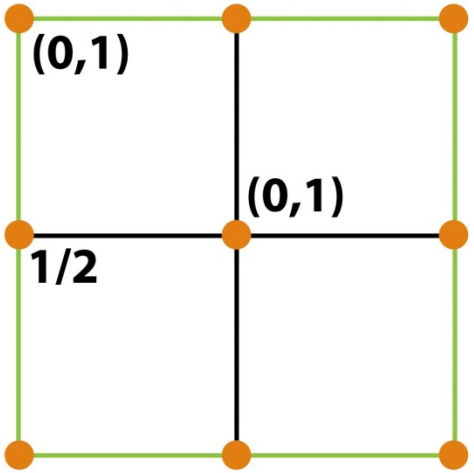
Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				

Fractional Coordinates

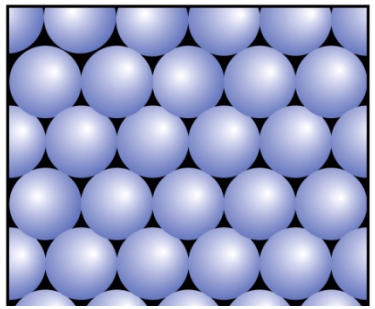




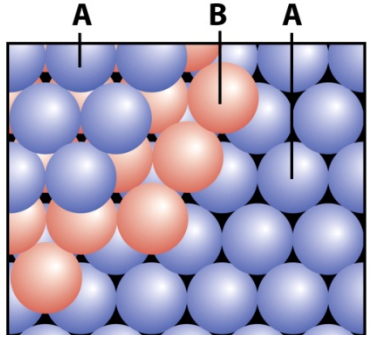




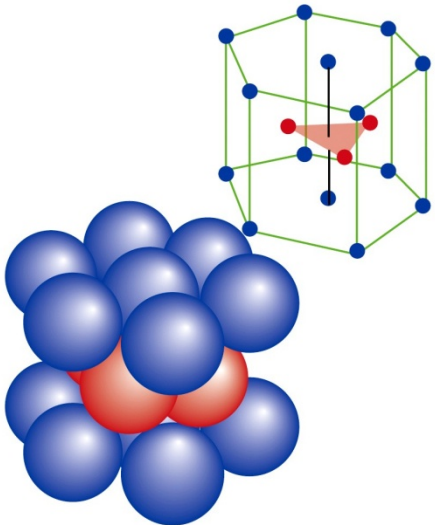
Packing

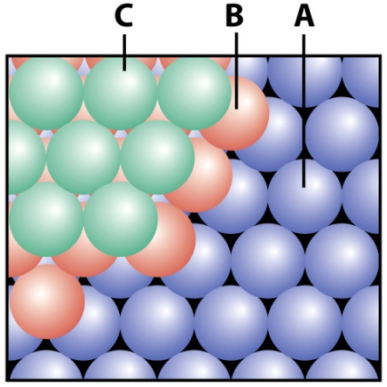


1st Layer

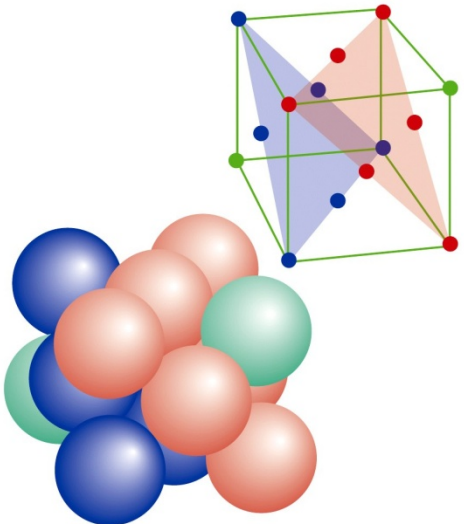


two layers (ABAB…) is hcp



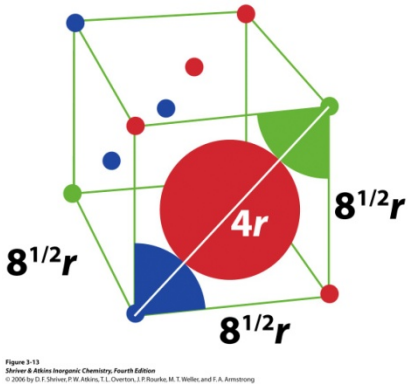


packing in three layers (ABCABC…) is ccp.



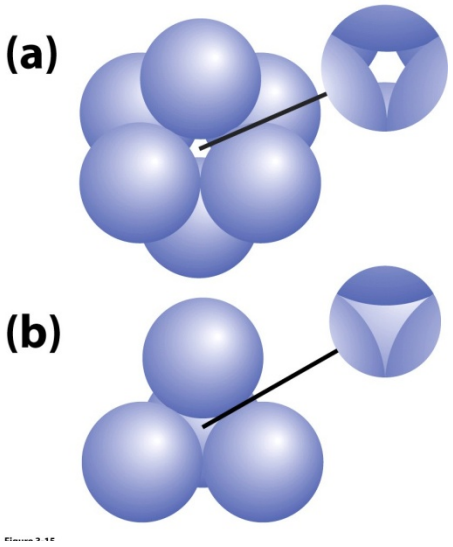
Inorganic Solids

26% of the volume of a close packed structure is space.



The space is made up of T_d and O_h holes.

a. There are 4 Oh holes in the unit cell and 8 Td holes.
b. Sizes of holes are 0.414r (Oh) and 0.225r (Td).



Inorganic solids

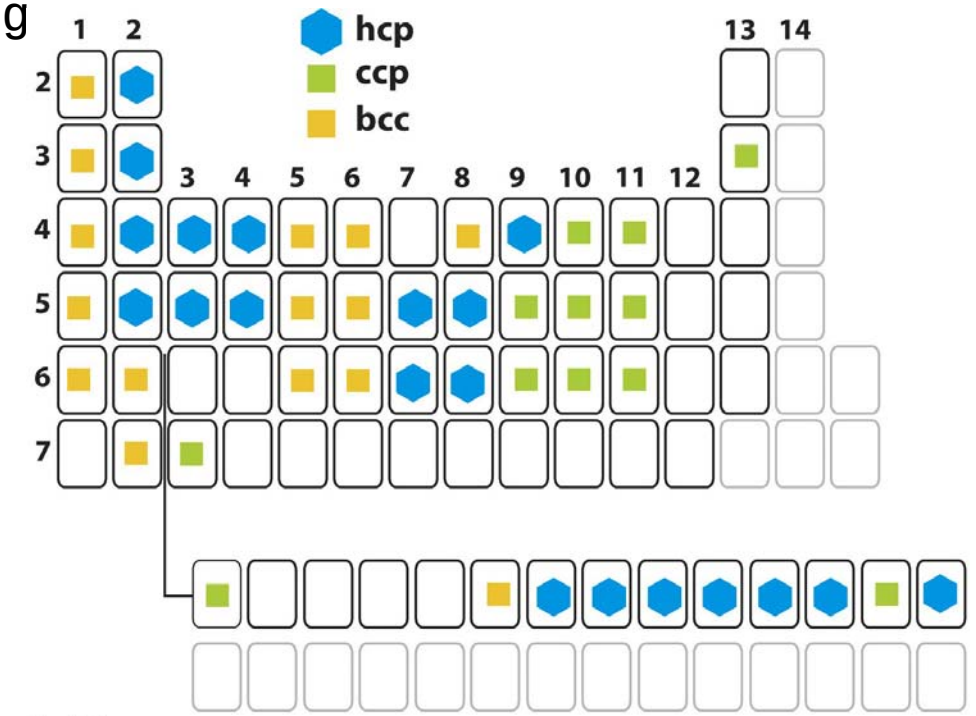
Metals and Alloys

- 1. often adopt close-packed structures
  - a. accounts for the high density of metals (Ir and Os are the most dense elements at STP.
  - b. Implies a lack of directional covalent bonds
    - Metallic bonding (cations in a sea of electrons, metals generally have low IE)
    - Or effectively enormous molecules with MOs that extend throughout the sample.
  - c. Good conductors because electrons are delocalized
  - d. Malleable and ductile: no directional bonding, electrons rapidly relocate. Forces between atoms is small.

Inorganic Solids

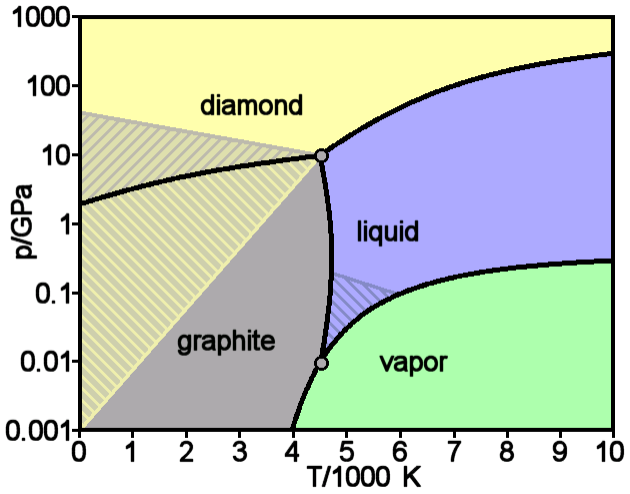
Which close packed arrangement is adopted by a metal depends on the electronic structure.

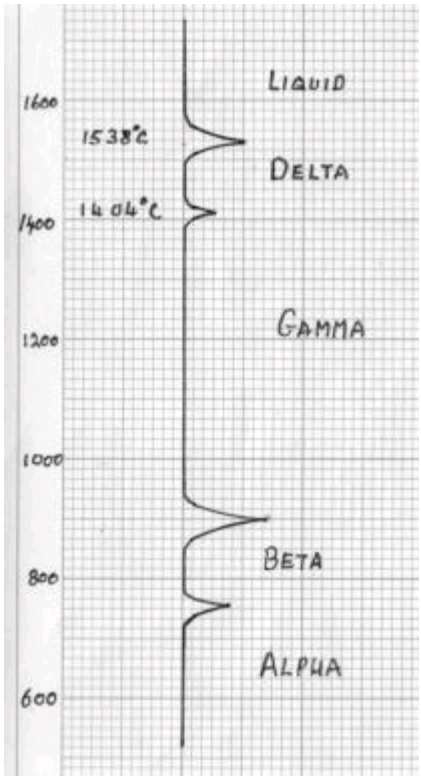
- a. hcp and ccp are not required. Another common arrangement is body-centered cubic (bcc).
- b. Polytypism is common. Ex. Above 500 C Co is ccp, but adopts a more random arrangement of layers upon cooling



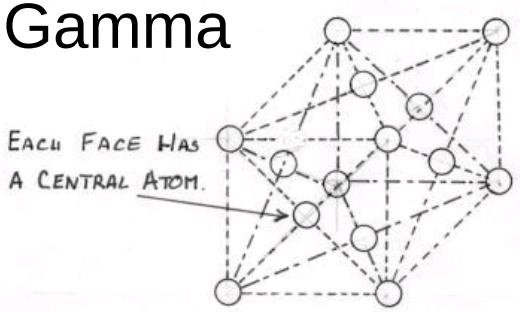
Polymorphism

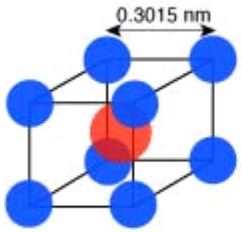
The ability to adopt different crystal forms under different conditions of pressure and temperature,



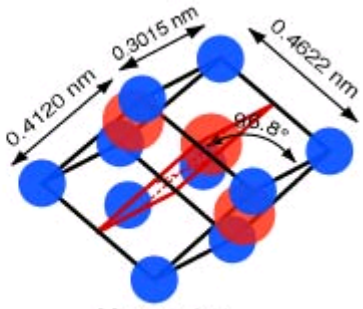


Gamma



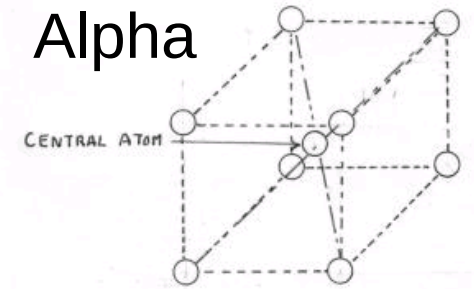


Austenite



Martensite

Alpha

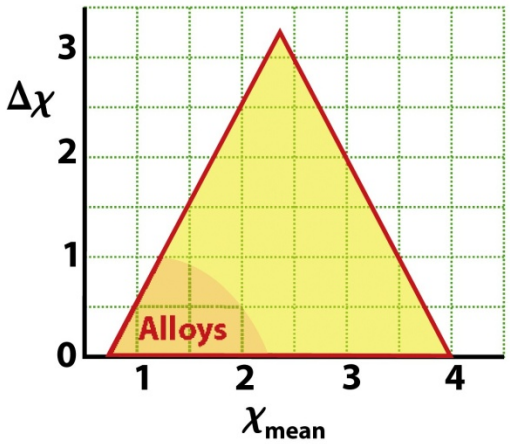


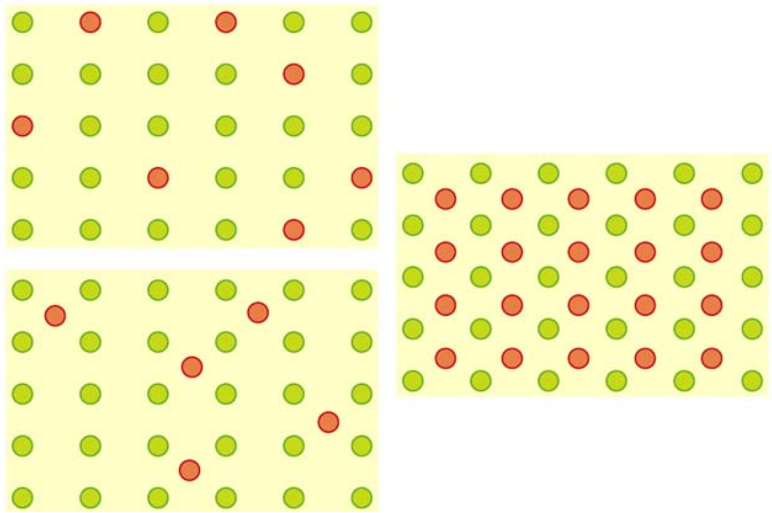
Inorganic Solids

An **alloy** is a blend of metallic elements prepared by mixing the molten components and cooling to produce a solid that has metallic properties.

-Typically form between electropositive metals that have similar electronegativities.

-Solid solutions may be substitutional or interstitial.





Substitutional Solid Solutions

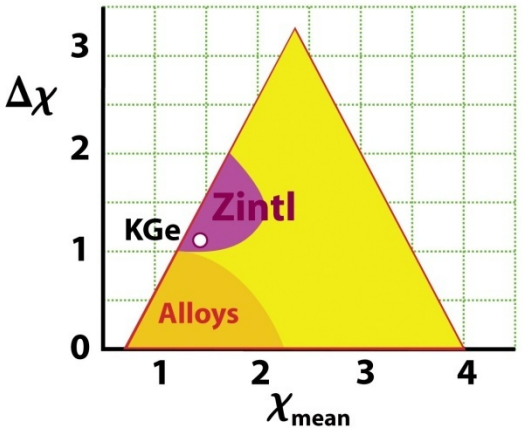
Substitutional solid solutions typically form when:

1. The metals have similar size; the Atomic radii of the elements is within ~ 15%
2. The crystal structures of the pure metals are the same
3. Electronegativity is similar.

Interstitial Solid Solutions

- Formed between metals and smaller atoms (that fit in the holes).
- They can be stoichiometric substances like WC or randomly distributed non-stoichiometric compounds.
- Holes determine what can og in the open sapeces

Intermetallic compounds



- When liquid mixtures cool, they sometimes form phases of stoichiometric composition with definite structures.
- Examples include $MgZn_2$, Cu_3Au, Na_5Zn_{21} etc.
- Often involve elements with a difference in electronegativity (Zintl phases).
- They are in the gray area between metals and ionic solids. They are brittle like ionic materials, but have a luster like metals.

Ionic solids

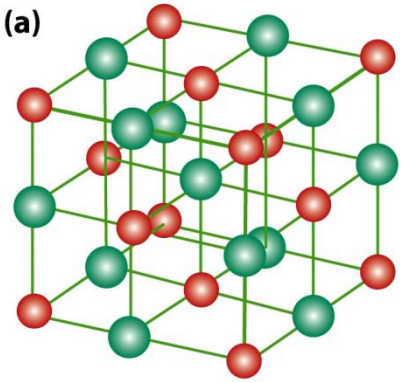
- Many ionic solids adopt one of several prototypical lattices.

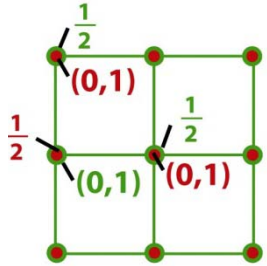
- These lattices can be viewed as having a close-packed structure (ccp or hcp) in one ion, usually the largest, with the smaller ion occupying Oh or Td holes.

- Repulsions between ions of the same charge, generally expand the lattice from a close packed arrangement

Rock Salt

NaCl





- Can be viewed as ccp in Cl^- with Na^+ in all the Oh holes.
- Has 6,6-coordination; the cation and anion have 6 nearest neighbors, respectively.
- Visualize the lattice:
  - The Cl- in the center in entirely within the unit cell=1
  - It has 6 nearest neighbors, all Na+ (first coordination sphere) that occupy faces, (6/2)=3
  - It has 12 Cl- in the second coordination sphere that occupy edges, 12/4 = 3
  - It has 8 Na+ in the third coordination sphere that occupy corners, 8/8 = 1
  - → there are 4 Cl- in the unit cell (ccp) and 4 Na+, the stoichiomentry is 1:1, formula unit = NaCl and Z = 4