Chapter 8 The structures and properties of metals and alloys

8.1 Metallic bond and general properties of metals

8.1.1 The “free-electron” model of metal

i) A bulk of metal = valence electrons in free-motions & cationic cores;

ii) neglecting the interactions between valence electrons and atomic cores;

iii) neglecting the interactions between free electrons.

A metal solid can be regarded as cationic cores floating in a sea of free electrons.

Like an electron confined within a zero-potential 3D box, the Schrödinger equation for a “free electron” is

$$\hat{H}\varphi = E\varphi; \qquad \hat{H} = \hat{T} + \hat{V} = -\frac{h^2}{8\pi^2 m}\nabla^2 \qquad (\text{i.e.}, \hat{V} = 0)$$

Thus the behavior of free electrons can be described by a plane wave function: $\varphi_k(r) = \sqrt{\frac{1}{V}}\exp(i\vec{k}r)$ with $E_k = h^2|\vec{k}|^2/(2m)$

V-the volume of metal, k-wave vector.

The highest occupied energy level is the Fermi level ***E_F***:

$$E_F = h^2 k_F^2/(2m)$$

This model works well for such metals as Na, K, Rb etc, e.g., for Na

E_F(calc.)= 5.04*10^{-19} J or 3.15eV vs. ***Expt. value ~ 3.2 eV***

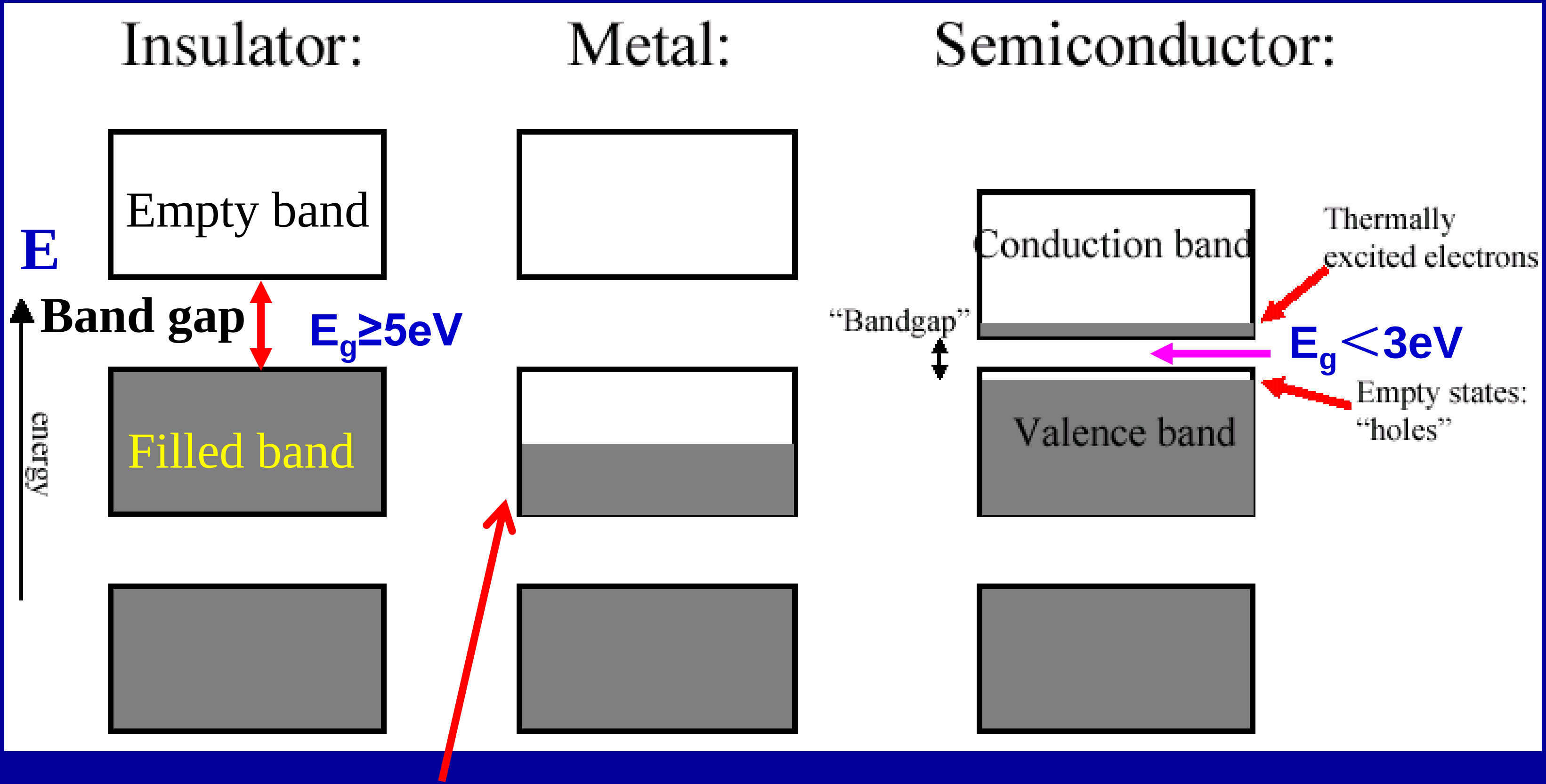
More accurate model: by using pseudo-potentials for cationic cores and by taking into account of the electrostatic interactions between free-electrons and a 3D array of cationic cores.

8.1.2 The Band Theory of Solids

Considering the electrons moving in a periodic potential field of the metal atoms, the Schrödinger equation is

(One-particle equation)

$$\hat{H}\varphi = E\varphi; \qquad \hat{H} = \hat{T} + \hat{V} = -\frac{h^2}{8\pi^2 m}\nabla^2 + V$$



Insulator:

Metal:

Semiconductor:

E

Band gap

energy

Empty band

Filled band

$E_g \geq 5\text{eV}$

Conduction band

Valence band

"Bandgap"

Thermally excited electrons

$E_g < 3\text{eV}$

Empty states: "holes"

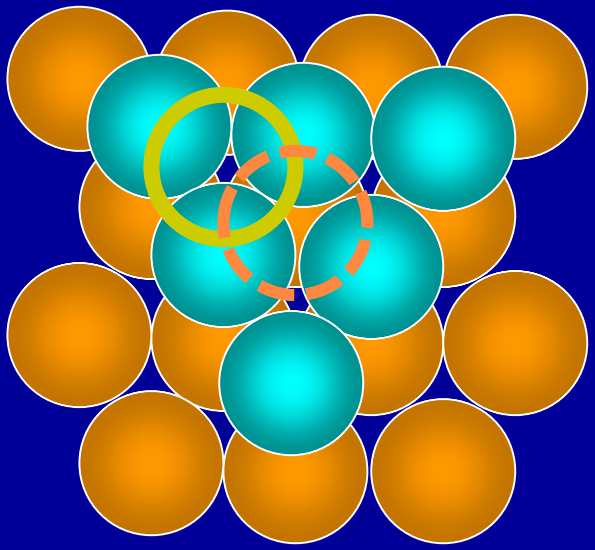
Partially filled bands -- conduction bands!

8.2 Close-packing of spheres and the structure of pure metals

Packing of metal atoms → Crystal of metal

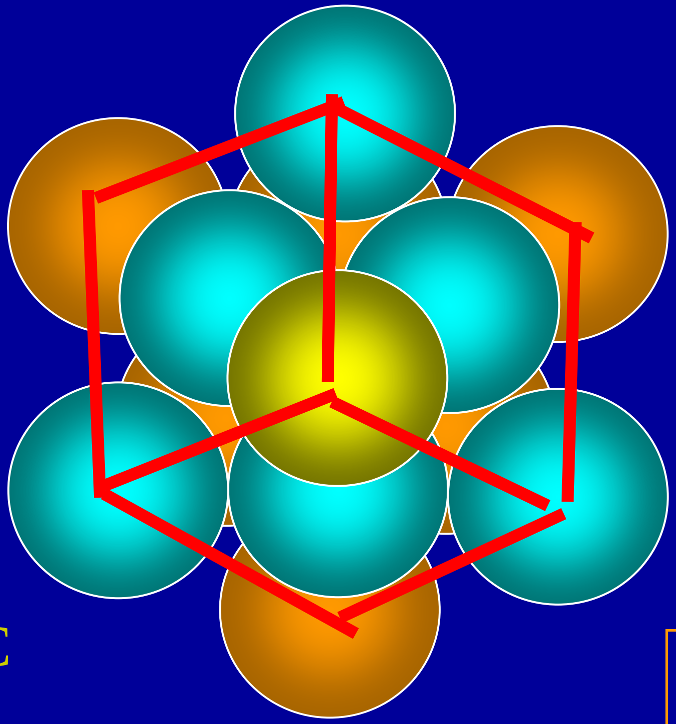
8.2.1 packing of identical spheres

1. Cubic close packing (ccp): Type A1 or ABCABC

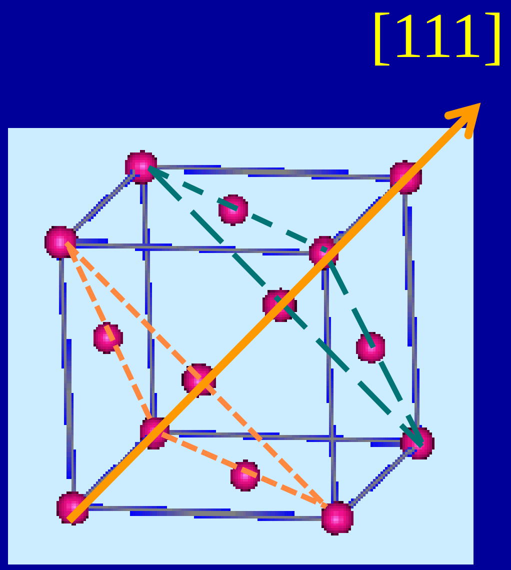


Layer-A Layer-B Layer-C

Layered packing of hexagonal 2D lattices



$N_C=12$



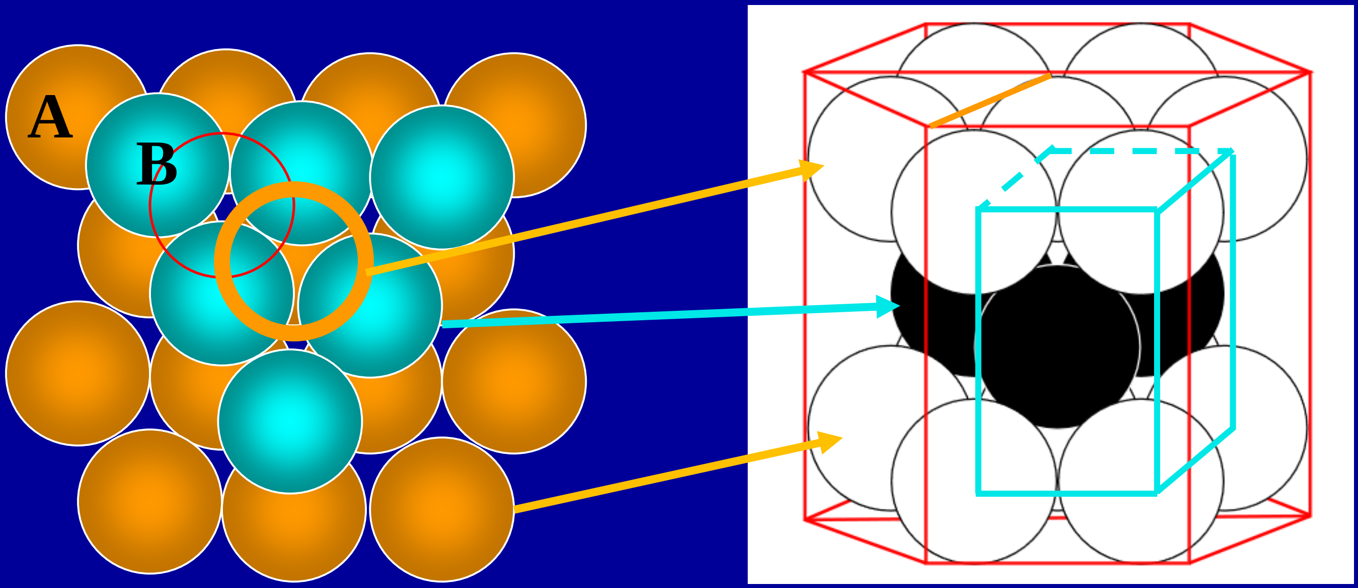
Each unit cell has 4 spheres (atoms)!

Also being face-centered cubic (fcc)!

2. Hexagonal close packing (*hcp*) ABAB or *Type A3*

(A1 and A3: The two most common close-packed structures)

Lattice: hp



Each unit cell has two spheres (atoms).

N_C=12

hcp

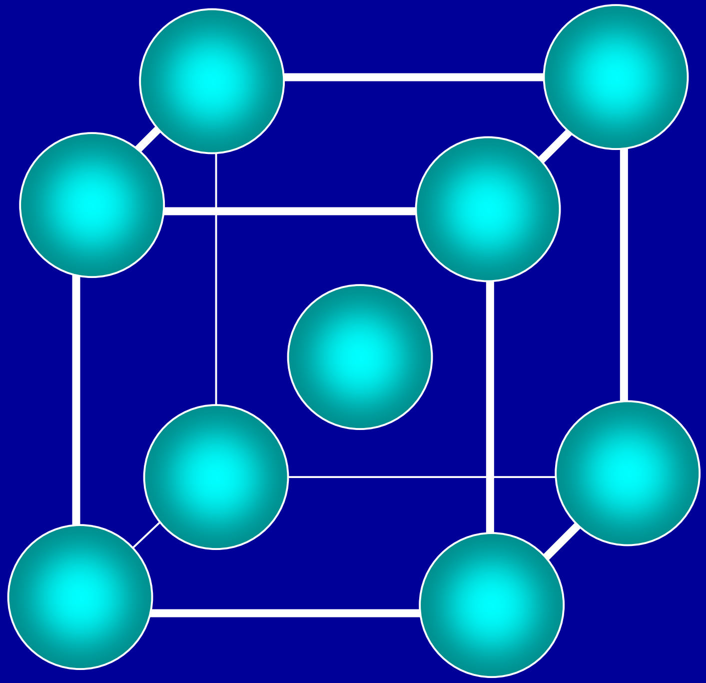
hexagonal close packing

3. Other types of close-packed structures:

ABAC….., ABABCBCAC…….., etc.

(Each layer belongs to a hexagonal 2D lattice!)

4. Body-centred cubic packing (bcp or bcc) A2



Each unit cell has two spheres(atoms).

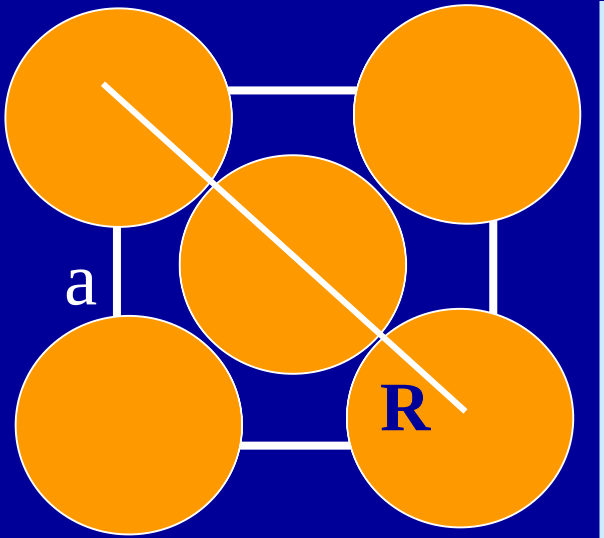
(0,0,0), (0.5,0.5,0.5)

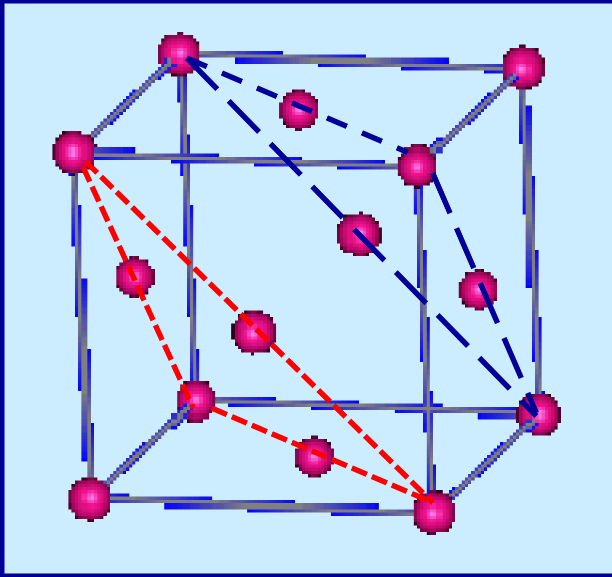
8.2.2 Packing density

1) ccp ---fcc

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

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





The volume of the unit cell : $V_{cell} = a^3 = (4R/\sqrt{2})^3 = 16\sqrt{2}R^3$

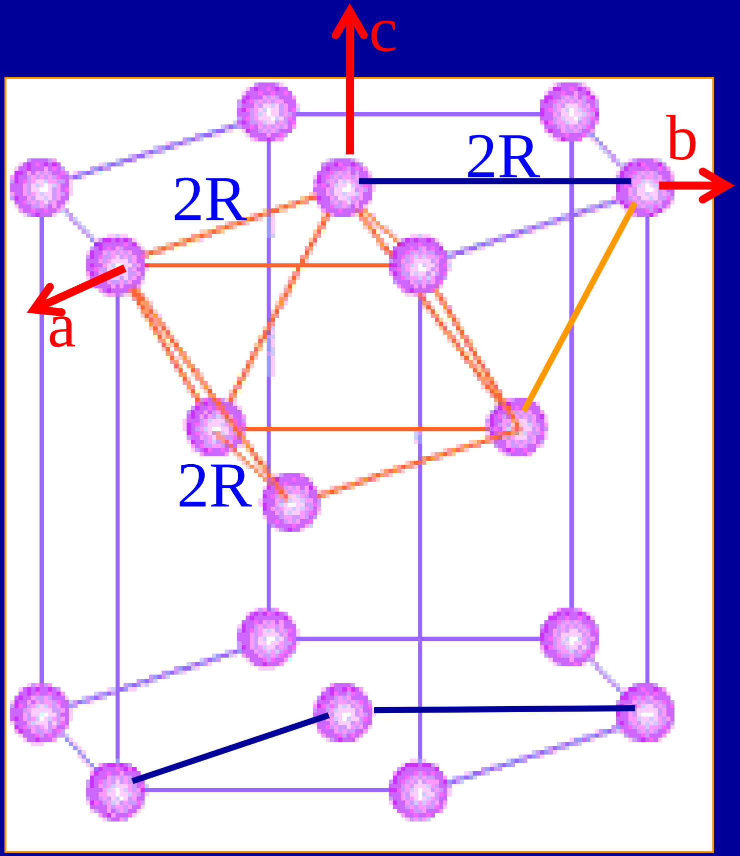
The total volume of the four spheres in the unit cell:

$$V_{spheres} = 4 \times (4\pi R^3/3) = 16\pi R^3/3$$

Packing coefficient: $V_{spheres}/V_{cell} = \pi/(3\sqrt{2}) = 74.05\%$

Note: The hexagonal close packing (hcp) of identical spheres gives the same packing density. (74.05%)

hcp structure



$$a = b = 2R, \quad \gamma = 2\pi/3$$

$$c = 4\sqrt{2}R/\sqrt{3}$$

$$V_{cell} = ca^2\cos\gamma = (4R/\sqrt{2})^3 = 8\sqrt{2}R^3$$

$$V_{sphere} = 2(4\pi R^3/3) = 8\pi R^3/3$$

$$V_{sphere}/V_{cell} = \pi/(3\sqrt{2}) = 74.05\%$$

2) Body-centred cubic packing (bcp or bcc)

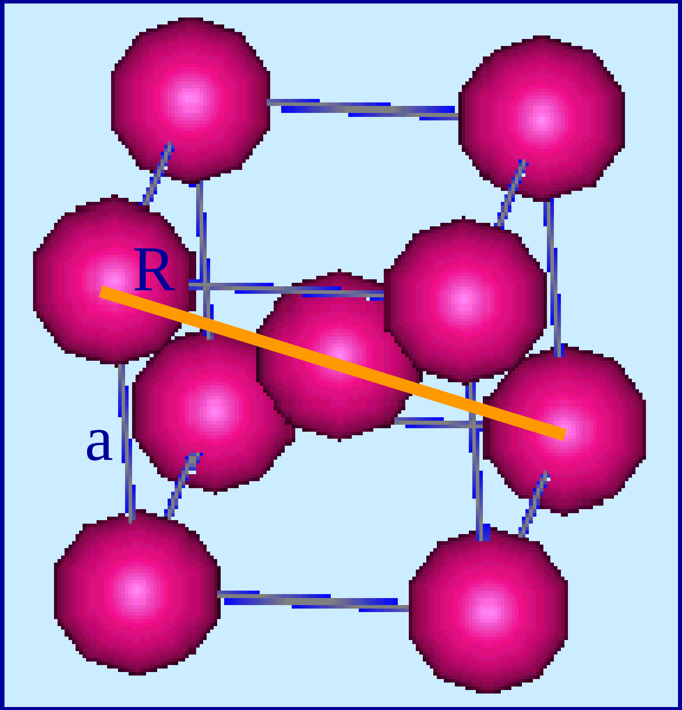
$$4R = \sqrt{3}a \Rightarrow a = \frac{4}{\sqrt{3}}R$$

$$V_{spheres} = 2 \times \left(\frac{4}{3}\right)\pi R^3; \quad V_{cell} = a^3 = \frac{64}{9\sqrt{3}}R^3$$

$$V_{spheres}/V_{cell} = 2 \times \left(\frac{4}{3}\right)\pi R^3 / \left(\frac{64}{9\sqrt{3}}R^3\right)$$

$$= \frac{\sqrt{3}}{8}\pi = 68.02\%$$

Two spheres in a unit cell.



- Thus bcp has a lower density than ccp.
- bcp is not a close-packed structure!

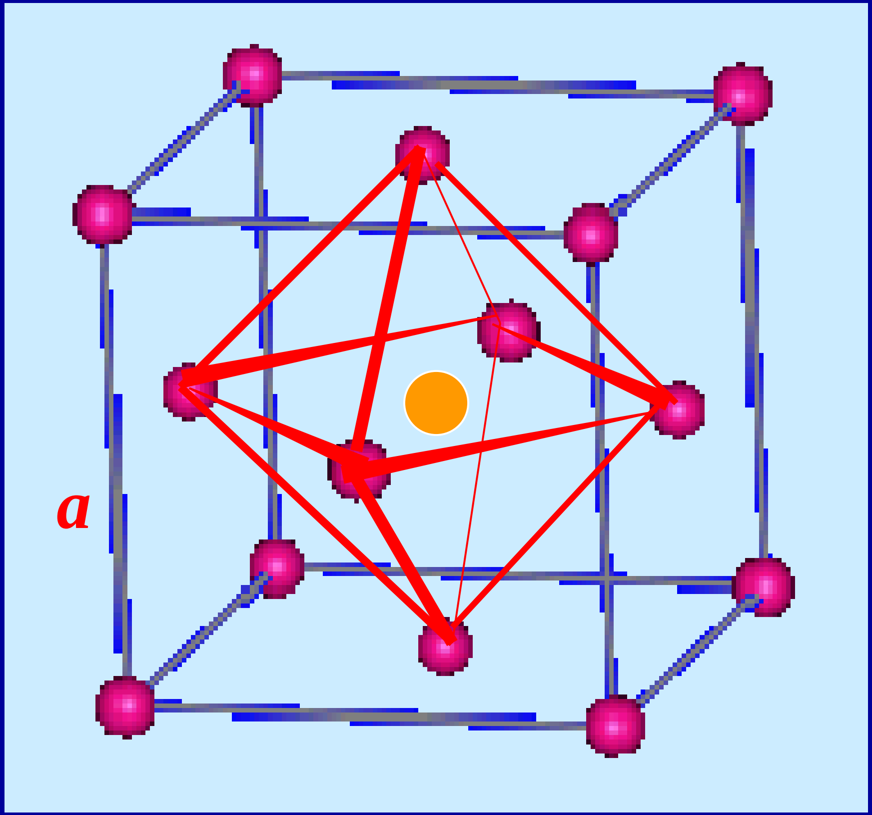
8.2.3 Interstices

a) octahedral holes in ccp

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

Hole radius:

a/2 – R = 0.414 R



For a close-packed structure formed from identical spheres of radius ***R***, the octahedral hole size is ***0.414R***.

Tetrahedral holes

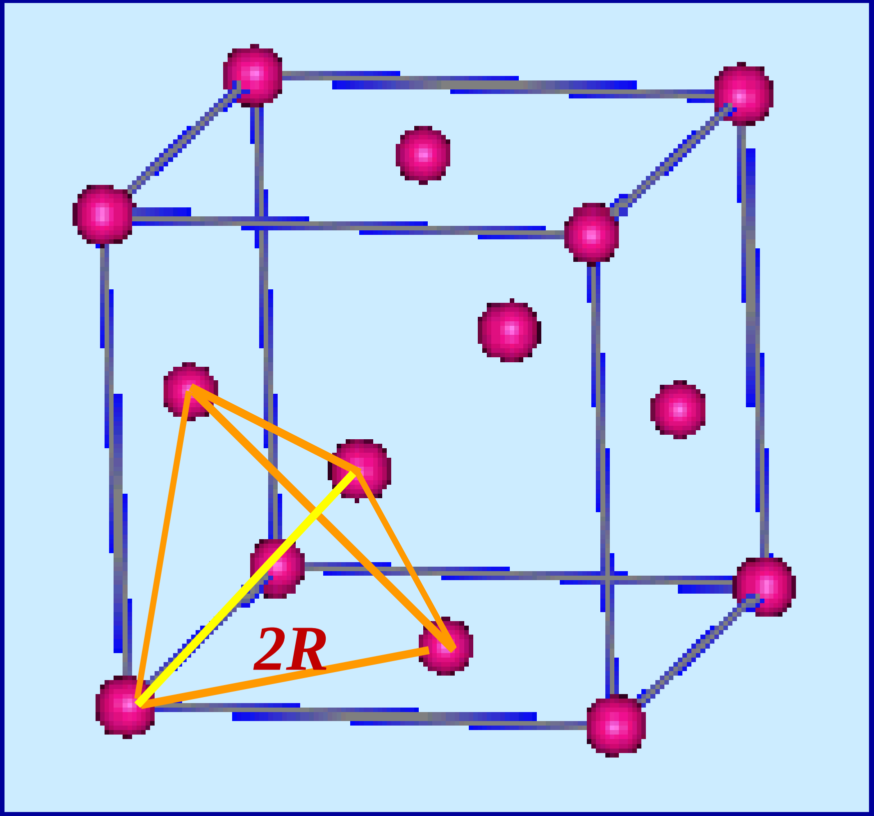
$$\because a = 4R/\sqrt{2}$$

The distance between the center of the tetrahedral hole and its apex is

$$\sqrt{3}a/4 = \sqrt{3}R/\sqrt{2}$$

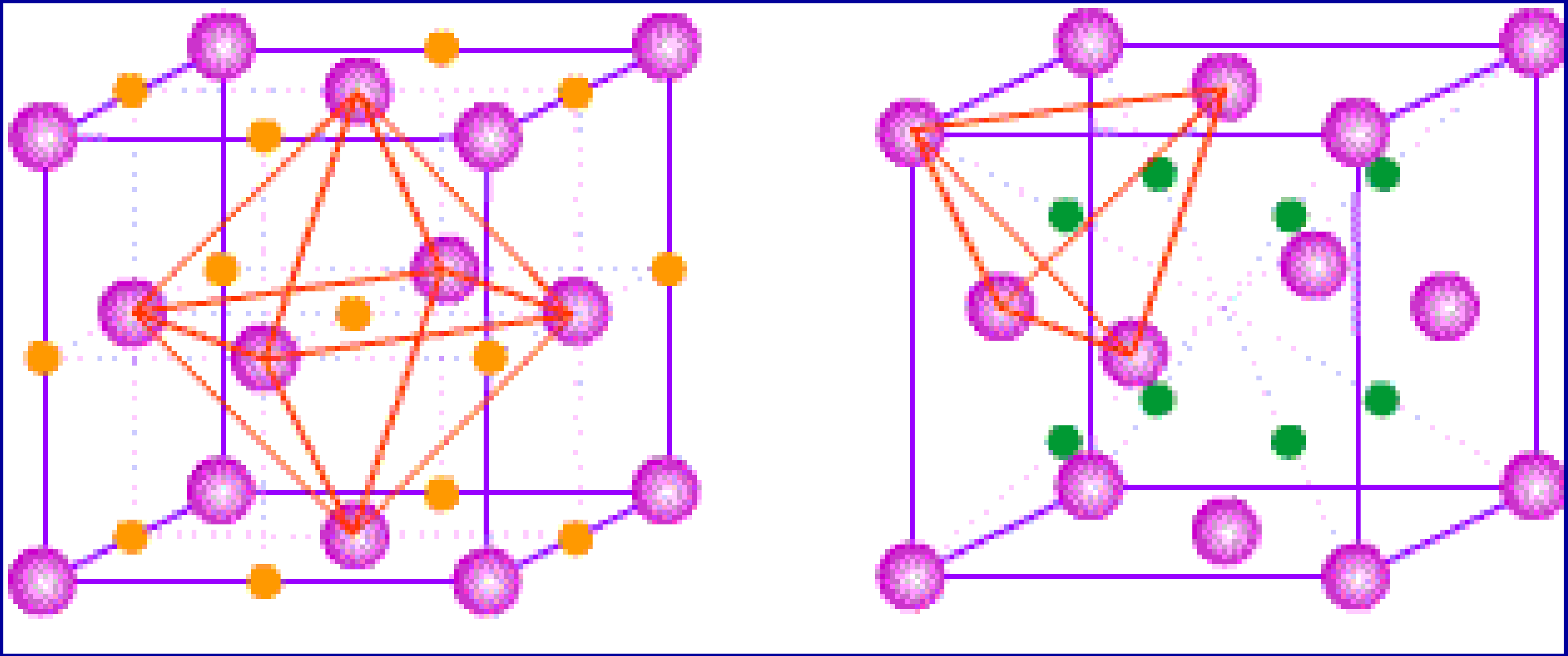
Radius of the tetrahedral hole is

$$\sqrt{3}R/\sqrt{2} - R \approx 0.225R$$



For a close-packed structure formed from N spheres of radius ***R***, the tetrahedral hole size is ***0.225R***.

ccp (fcc) structure



A fcc unit cell contains ***4*** octahedral holes and ***8*** tetrahedral holes.

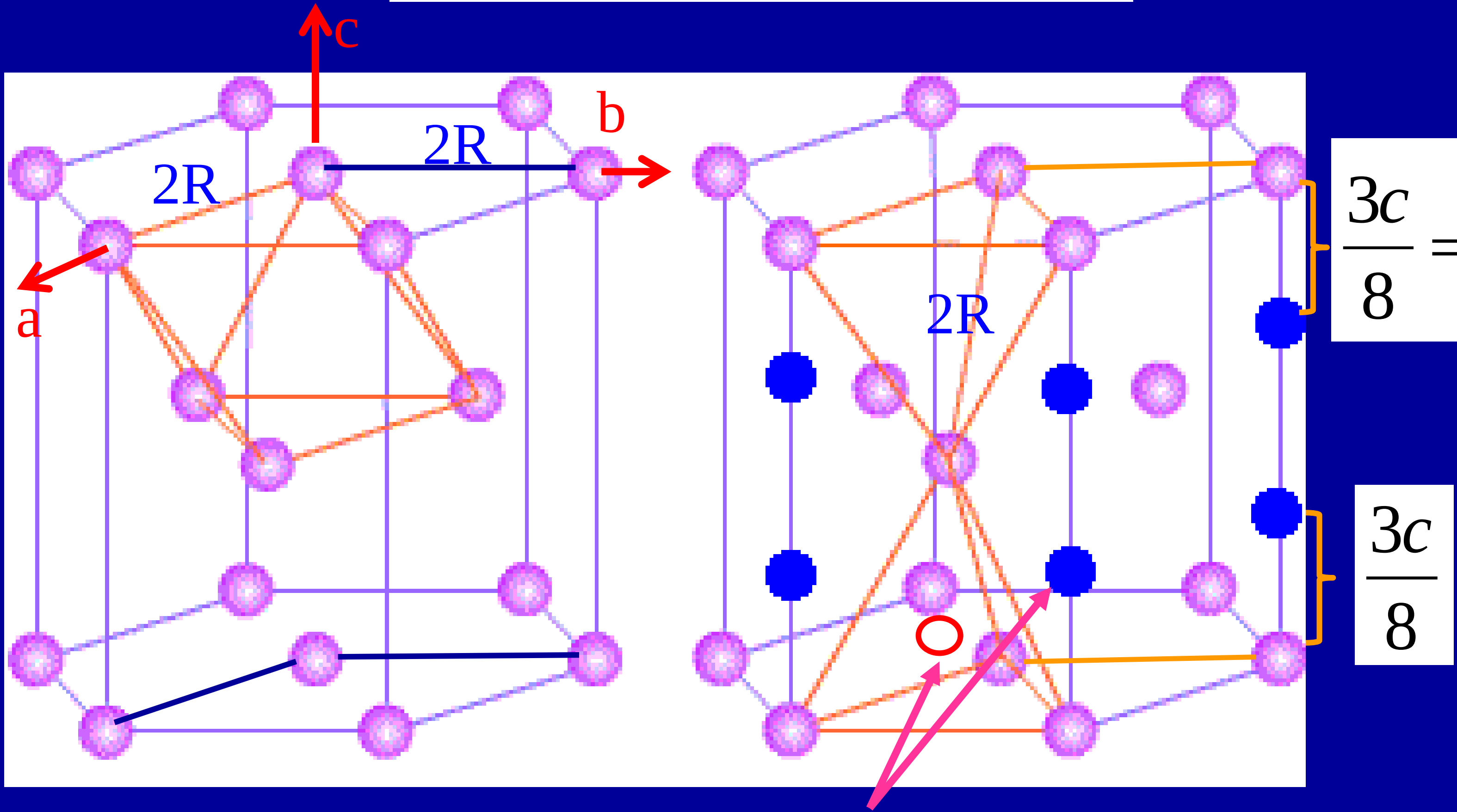
- Octahedral holes: ***(0.5,0.5,0.5), (0.5,0,0), (0,0.5,0),(0,0,0.5)***

  at edge centers and body center of the fcc unit cell.

- Tetrahedral holes: ***(+/-0.25,+/-0.25,+/-0.25)***

hcp structure

$$a = b = 2R, c = 4\sqrt{2}R / \sqrt{3}$$



$$\frac{3c}{8} = \sqrt{\frac{3}{2}}R$$

$$\frac{3c}{8}$$

Octahedral holes (2)

$$R_{hole} = (\sqrt{2} - 1)R$$

Tetrahedral holes (2 + 8x(1/4)= 4)

$$R_{hole} = (\sqrt{3}/\sqrt{2} - 1)R$$

(2/3,1/3,1/8), (2/3,1/3,-1/8);
(0,0,3/8), (0,0,-3/8)

Interstices in bcp structure

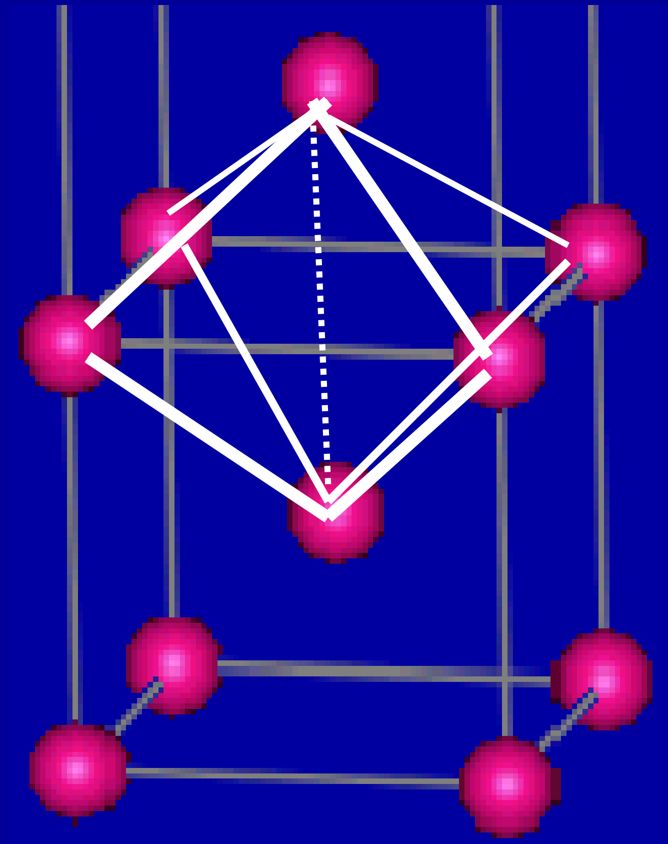
- There are ***3 octahedral holes*** at the face centers in a unit cell.

- They are not regular octahedra, but partially compressed along the c-axis.

$$\because a = 4R/\sqrt{3},$$

$$\therefore r_h = (a - 2R)/2$$

$$= 0.154R$$



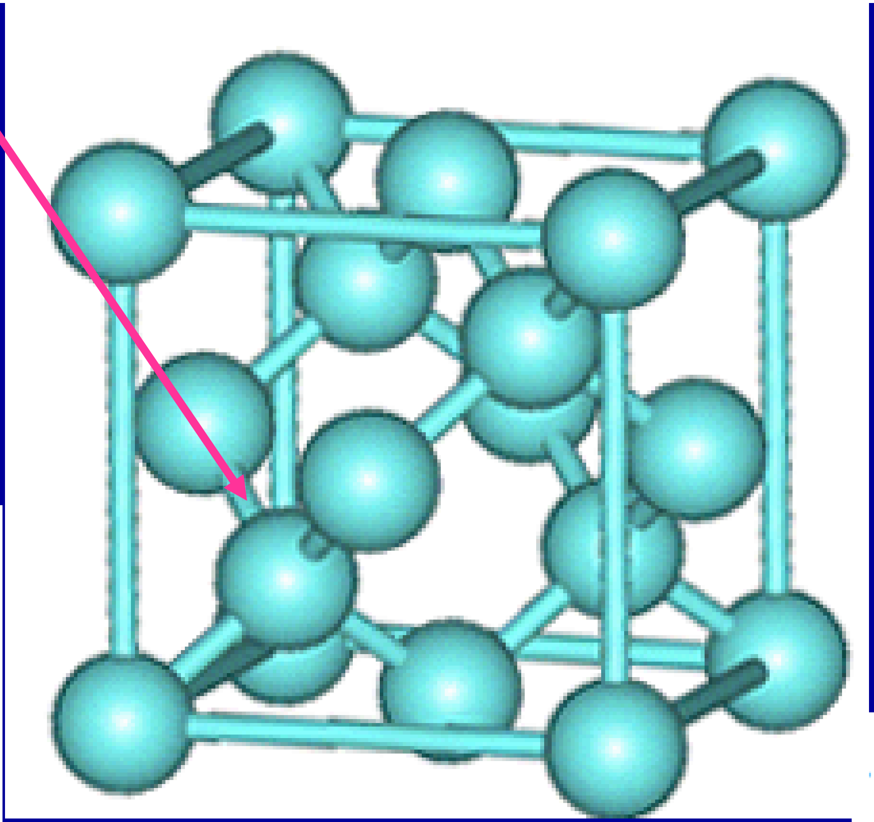
8.2.4 A structural survey of pure metals

Most of pure metals adopt A1 (ccp/fcc), A2 (bcp), or A3 (hcp) type of (close-)packed structure.

A4 (The diamond structure): Ge, Sn, Pb.

4 out of 8 tetrahedral holes of a normal ccp structure are occupied!

- ***fcc*** lattice with 2 atoms in a structure motif (lattice point)
- Can be regarded as two sets of intercalated fcc structures!

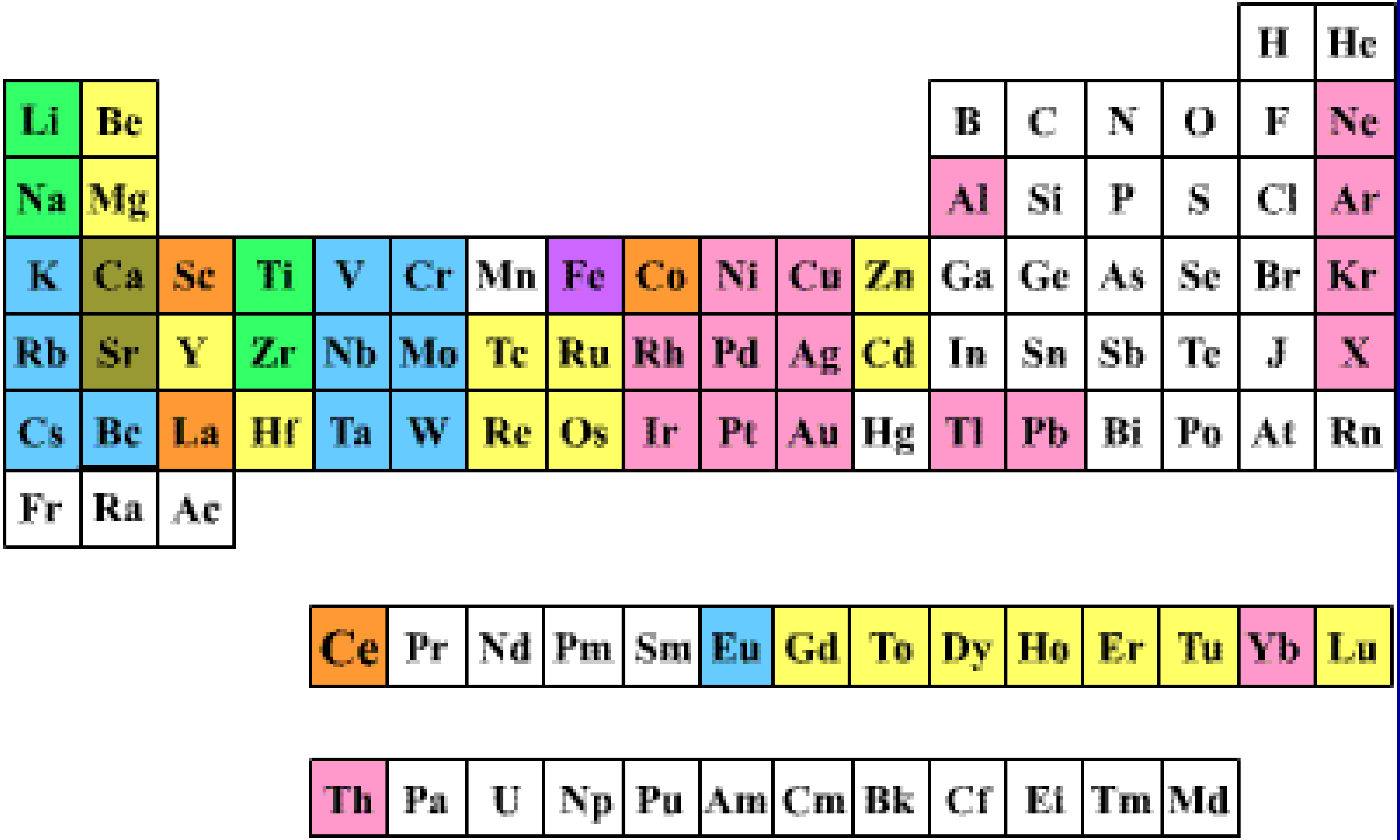


$$\sqrt{3}a/4 = 2R \Rightarrow a = 8R/\sqrt{3}$$

$$V_{spheres} = 8 \times (4\pi R^3/3) = 32\pi R^3/3$$

$$V_{cell} = a^3 = 512R^3/3\sqrt{3}$$

$$P = V_{spheres}/V_{cell} = \sqrt{3}\pi/16 = 34.01\%$$



																H	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	J	X
Cs	Be	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															
				Ce	Pr	Nd	Pm	Sm	Eu	Gd	To	Dy	Ho	Er	Tu	Yb	Lu
				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Ei	Tm	Md		

bcp

fcc

hcp

The number of electrons in the s and p orbitals affects the type of structure:

When the average number of s and p electrons for each atoms

is small, type **A2** is preferred Na $[Ne]3s^1$

is large, type **A1** is preferred Al $3s^2 3p^1$

is an intermediate value, **A3** is preferred Mg $3s^2$

8.2.5 Atomic radii of metals

(1) Within a family, the atomic radius increases as the atomic number increases.

(2) Within the same period, the atomic radius decreases as the atomic number increases

(3) For transition metals within the same period, the atomic radius first decreases steadily and then increase slightly.

(4) **“lanthanide contraction” effect**

- The screening exerted by 4f electrons is weak!
- Yet ~10% of the “lanthanide contraction” is due to relativistic effects.
- Relativistic contraction of valence shell of heavy atoms: electrons of inner shells exert smaller screening effects onto those of valence shell than expected due to relativistic effects!

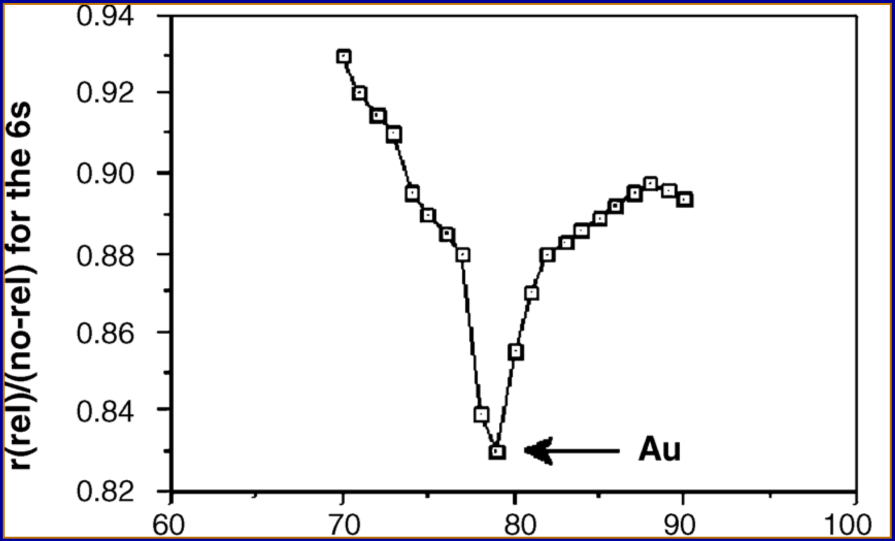
Relativistic effects on the valence shell of heavy atoms:

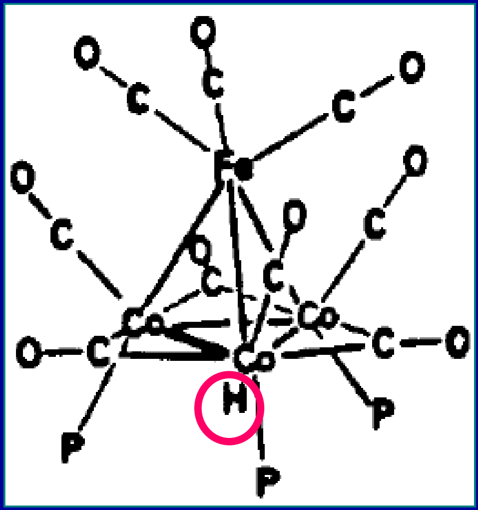
- Relativistic-effect (RE) contraction of 6s AO.
- The largest RE contraction of 6s AO occurs at Au for Z < 100:

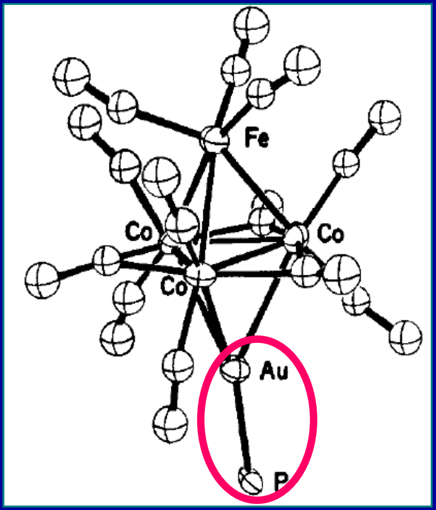
i) High electronegativity (Pauling: I~2.66>Au~2.54>H~2.20).

ii) Gold-halogen analogy, e.g., M^+Au^- (M=Na, K, Cs).

iii) Gold-hydrogen analogy, e.g., $[AuPR_3]$ ~ H







Pyykkö P, *Angew Chem Int Ed*, **2002**, *41*, 3573; **2004**, *43*, 4412.

8.3 The structures and properties of alloys

Alloy is the product of two and more metal.

Alloys may be divided into three major categories:

- **Metallic solid solution**
- **Metallic compounds**
- **Metallic interstitial compounds**

8.3.1 The structure of metallic solid solutions

- The structure of a bimetallic solid solution is usually similar to the metals except that fraction of the atoms of one metal is statistically substituted by the atoms of another metal.

The tendency to form a solid solution depends on :

(1) The positions in the periodic table and the similarity in chemical and physical properties.

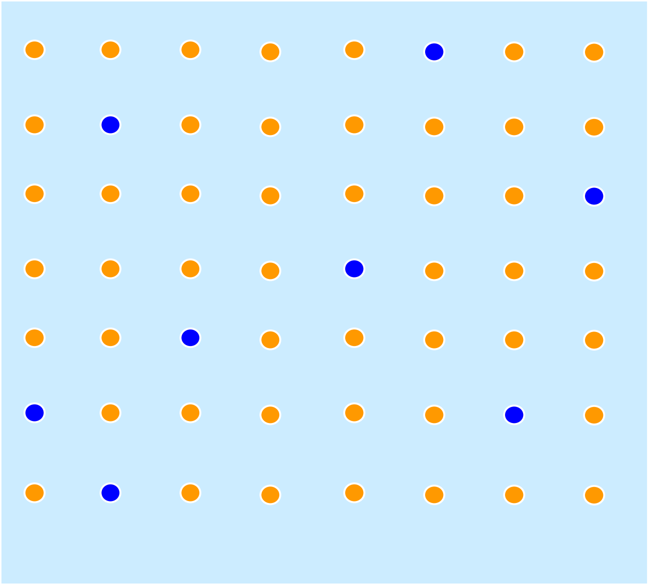
(2) the similarity in atomic radii

(3) the structural type of the pure metals.

ccp: Cu, Ag, Au, Ni, β-Co, γ-Fe, Pt, Ir, Rh, Pd

bcp: α-Fe, V, Cr

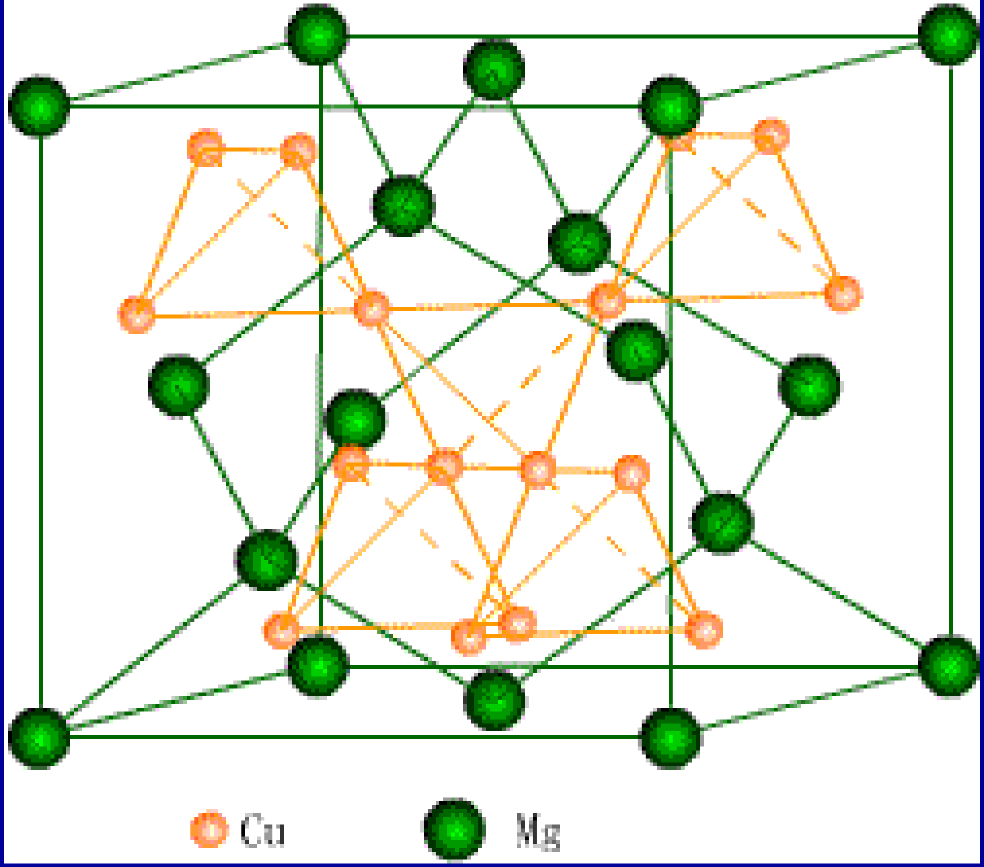
bcp: Mo, W



8.3.2 The structure of metallic compounds

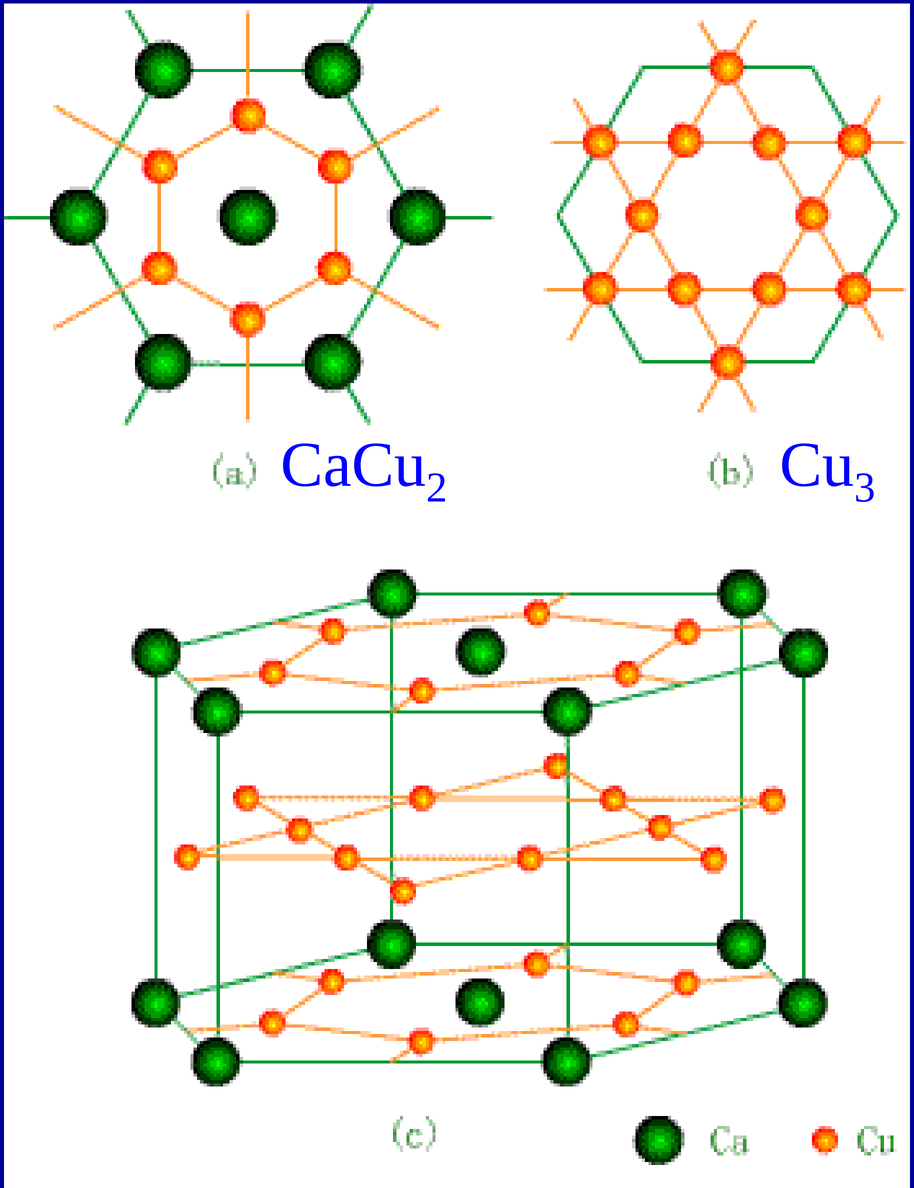
The stoichiometric phase

1. $MgCu_2$ alloy– Laves phase for AB2 type metallic compound.



- Lattice: FCC
- Structure motif: Mg_2Cu_4
- Arrangement of Mg atoms: diamond-like
- Arrangement of Cu: tetrahedrally distributed Cu_4 tetrahedra

2. The structure of the alloy $CaCu_5$



(a) $CaCu_2$ (b) Cu_3

Layered-stacking structure!

Many alloys which act as reservoirs for hydrogen such as $LaNi_5$, $LaCo_5$ and $CeCo_5$ have the same structure as $CaCu_5$.

e.g., **$LaNi_5 + xH_2 \rightarrow LaNi_5H_y$ (y ~4.5)**

8.3.3 The structure of interstitial metallic compounds

The term interstitial compound is given to compounds of metals with B, C, N, etc.. $R_{nonmetal}/R_{metal} < 0.59$

- The salient characteristics of interstitial compounds are:

(1) Most interstitial compounds adopt the NaCl structure irrespective of the original structure of the pure metals.

(2) These compounds are very hard and melt at very high temperatures.

(3) They have good conductivity.

The structure and properties of steel

Steel is an alloy system consisting of iron and carbon and is a basic industrial material.

Iron that contains less than 0.02% C is known as pure iron, with more than 2.0% C pig iron or cast iron, and with intermediate concentration between these two limits steel.

Pure iron: A2 (bcp) structure α-Fe (room temperature)

A1 (fcc) structure γ -Fe (910°C)

(bcp) structure δ-Fe (1390°C)

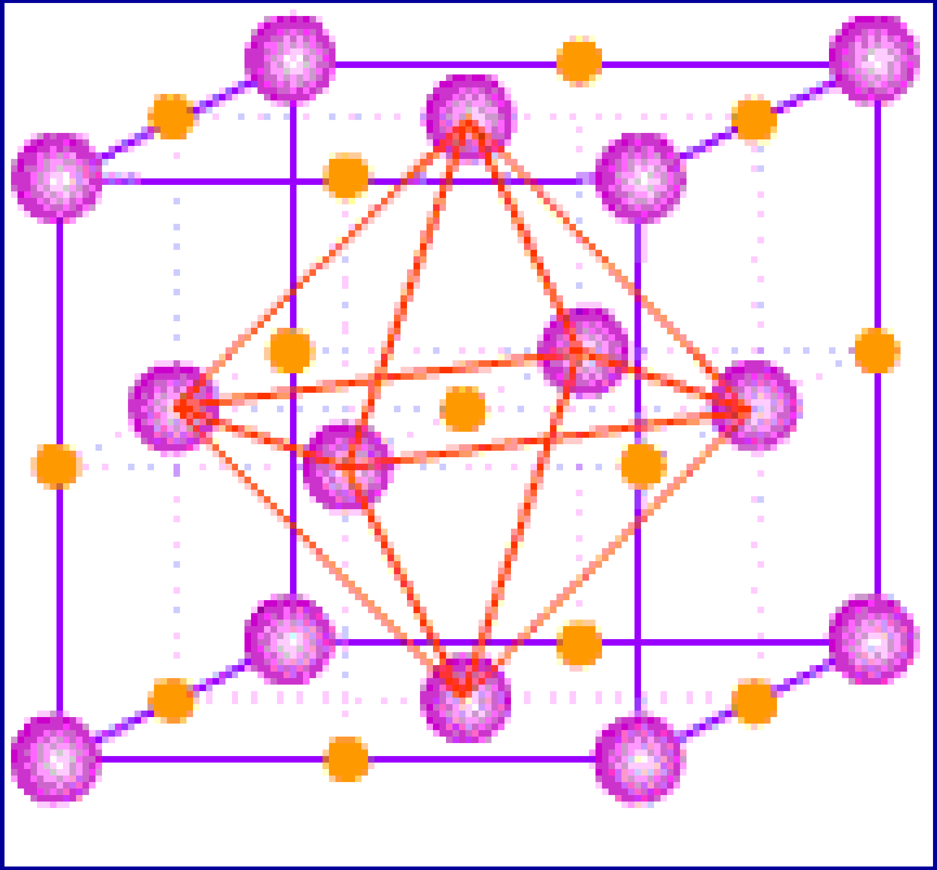
melting point 1535°C

Iron is ferromagnetic below 760°C and non-ferromagnetic above this temperature.

a. Austenite (奥氏体):

An interstitial solid solution of C in γ-Fe (about 0.8% by weight)

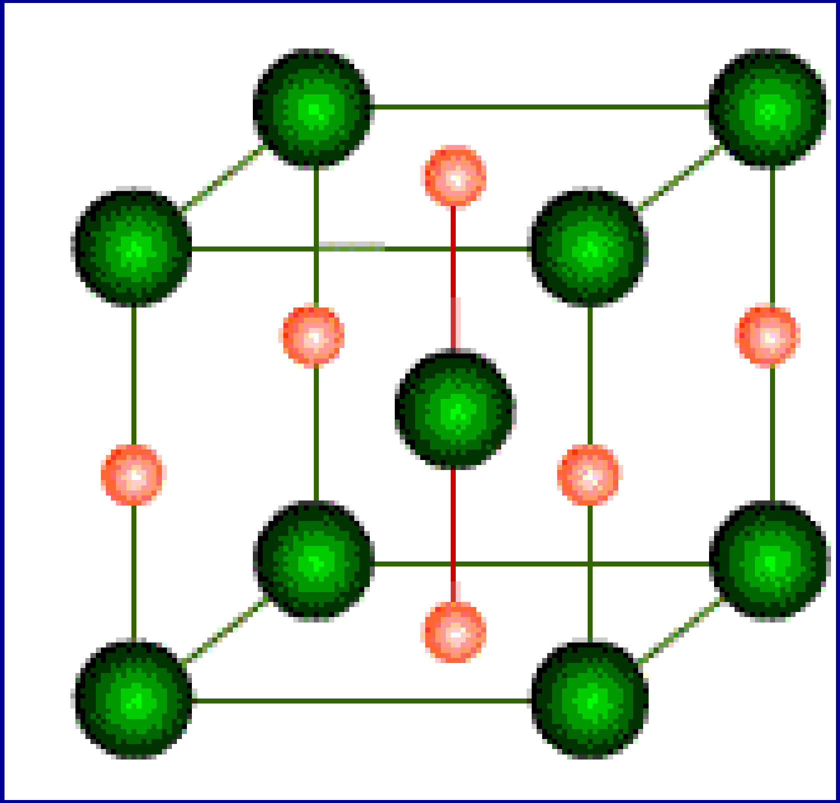
- The C atoms are distributed randomly at the octahedral positions.
- There is one C atom in every six or seven fcc unit cells.



b. **Ferrite**(铁素体): a solid solution of C in α-Fe. Since the size of the octahedral holes is very small in α-Fe, the solubility is very low (the highest solubility is 0.02%)

c. **Cementite** (渗碳体): Fe_3C (6.67%).

d. **Martensite**（马氏体）: a supersaturated solid solution of C in α-Fe. (FeC)



The mechanical properties of the four type of crystals are shown below:

Properties	Ferrite	Austenite	Cementite	Martensite
Hardness	80-100	120-180	800	650-760
Limiting strength (kg/mm^{-1})	20-30	40-85	3.5	175-210
Tensile rate %	30-50	40-60	~0	2-8