Crystal Structure (metallic, ionic, and covalent)

Contents

1. Simple metallic structure;

   FCC, HCP and BCC structure

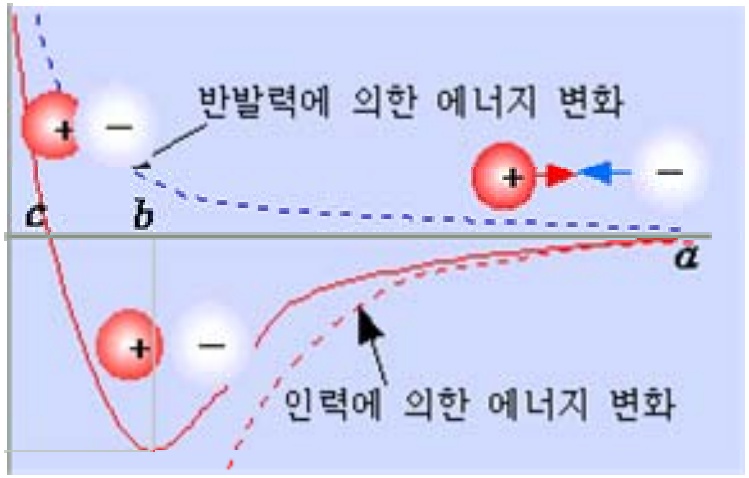
   Stacking sequence, [(110) projection structure]

   Interstitial sites

2. Complicate structure; Ionic and covalent structure

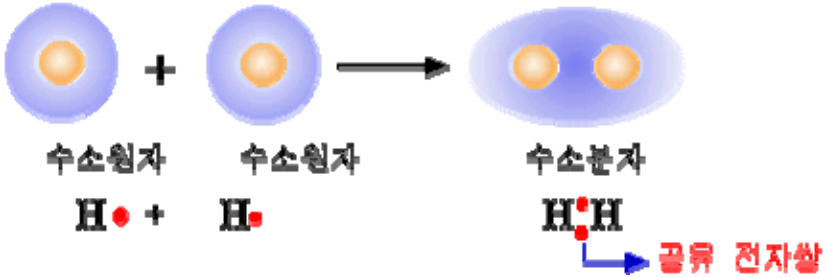
Chemical bonding :

► Ionic bonding

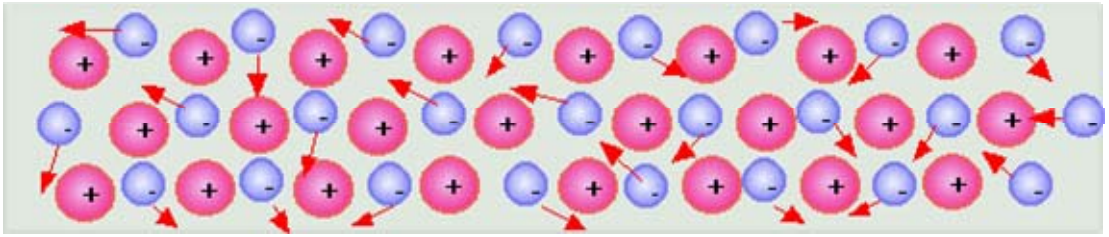


$$F = \frac{1}{\varepsilon} \cdot \frac{e_1 e_2}{r^2}$$

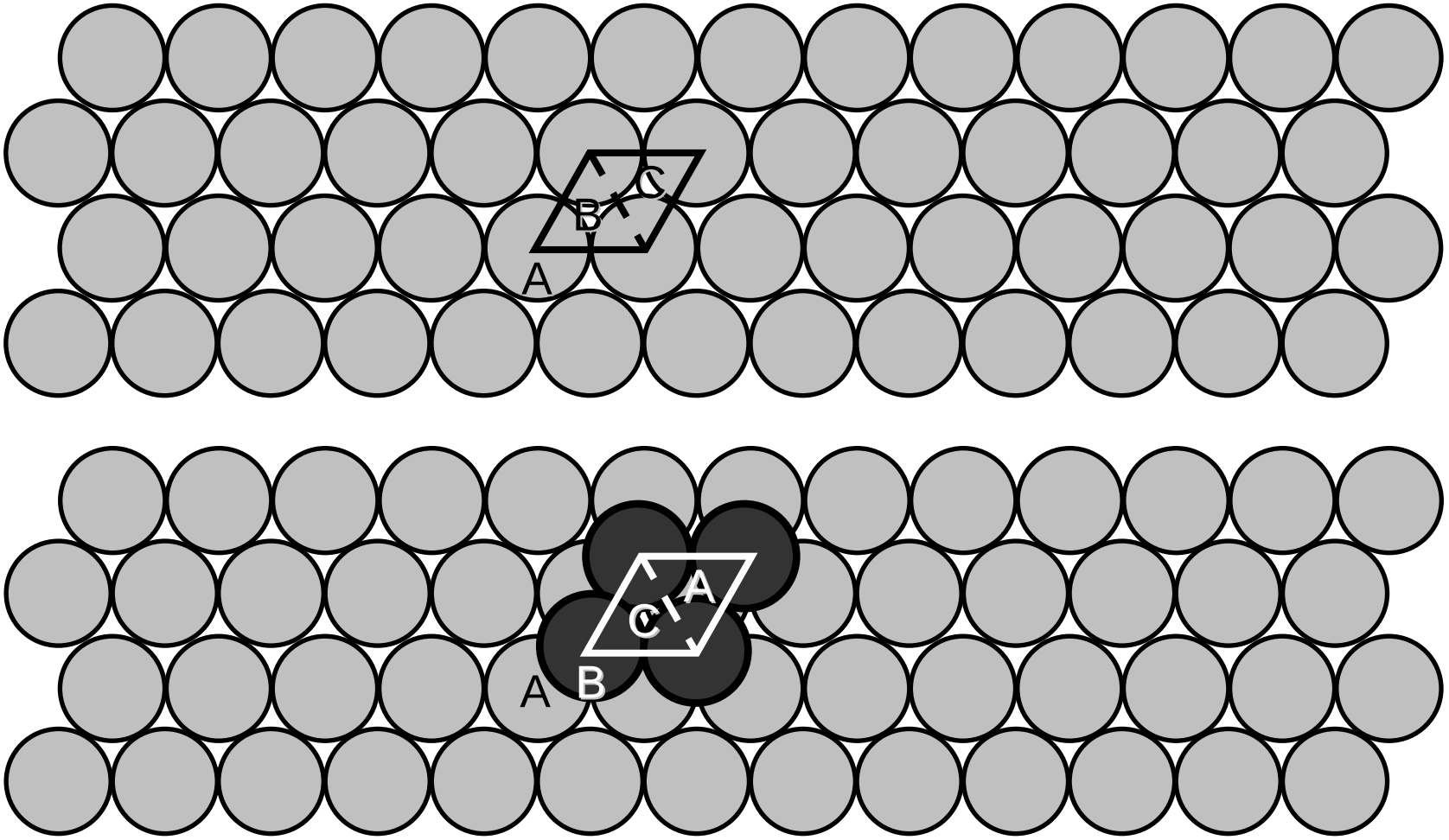
► Covalent bonding



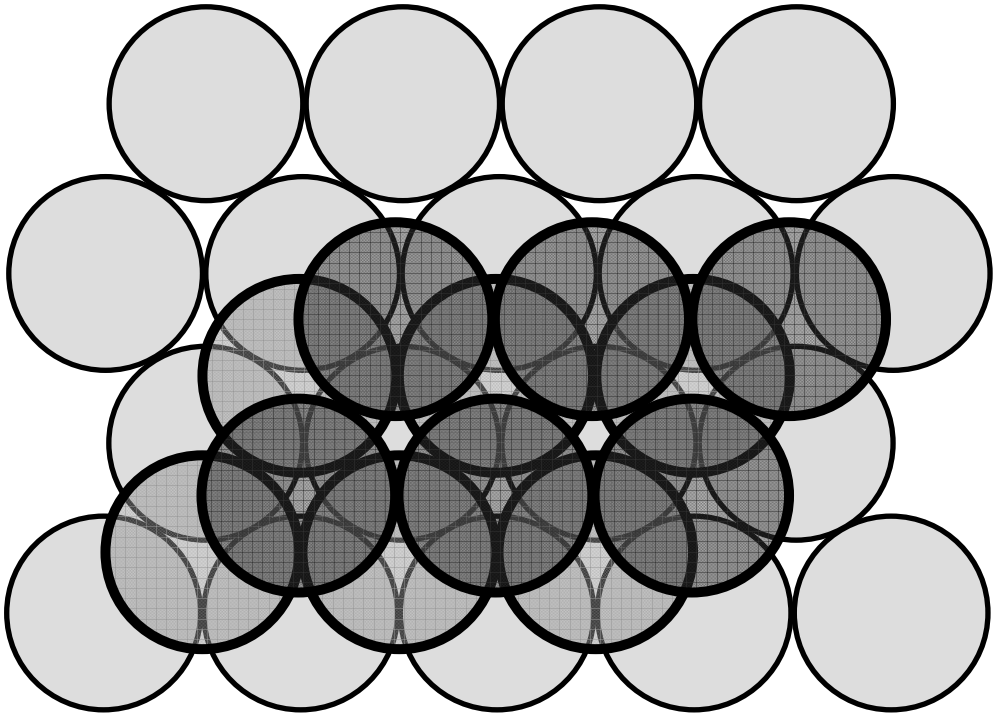
► Metallic bonding



Closed Packed Structures :



Closed Packed Structures :



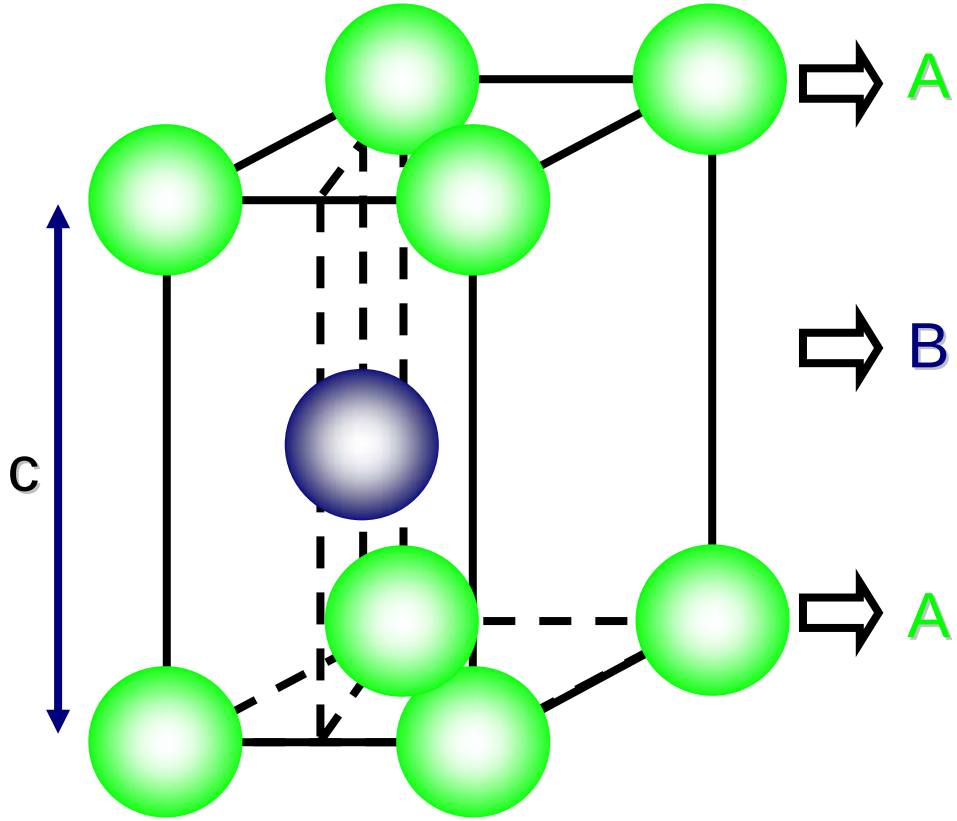
Stacking sequence

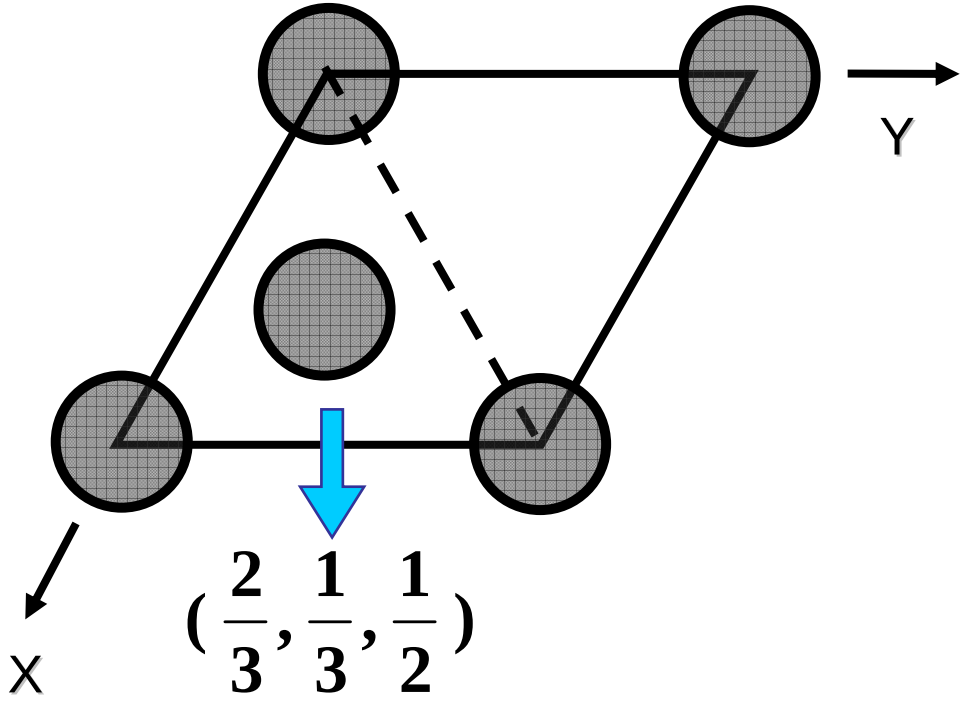
ABCABCABCABC (FCC)

ABABABABABAB (HCP)

APF → 74 %

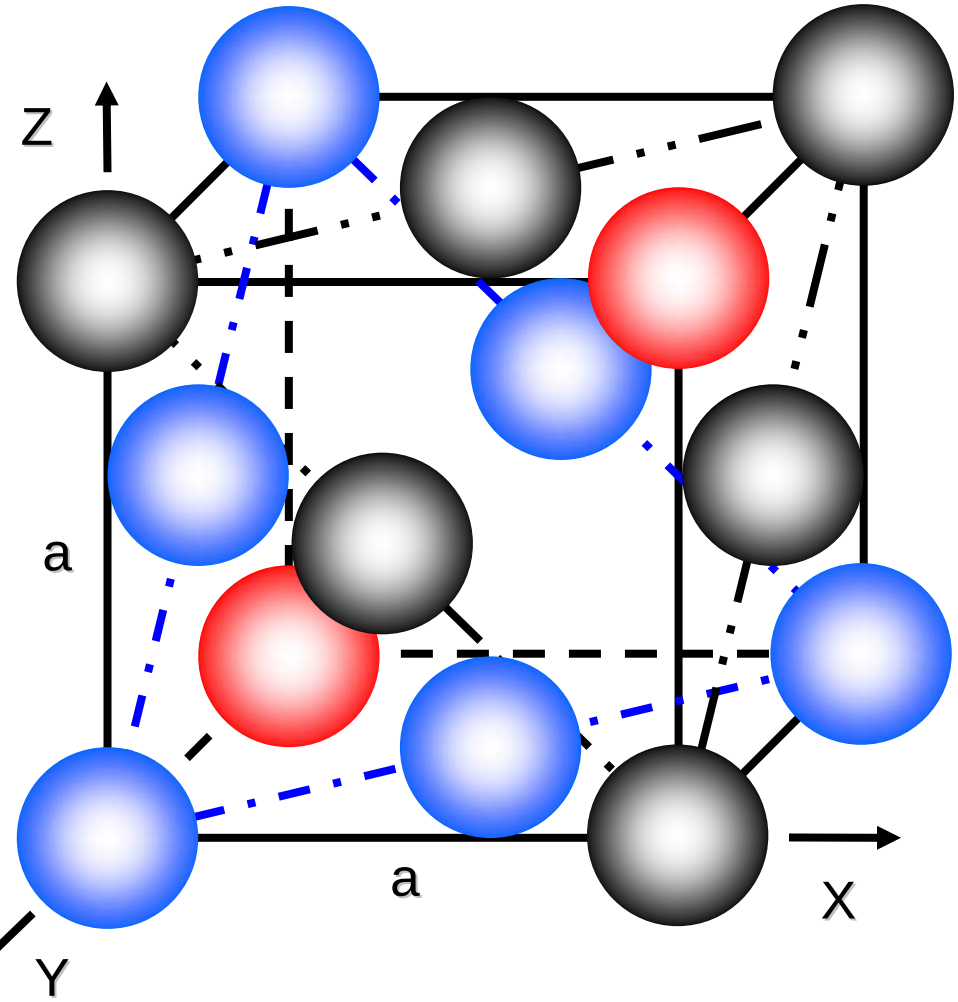
Unit cell of HCP :

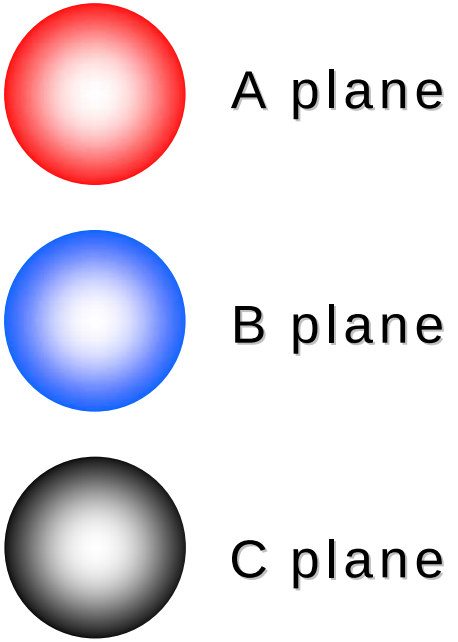




- Materials : Mg, Ti, Co, Zn, Zr, ...

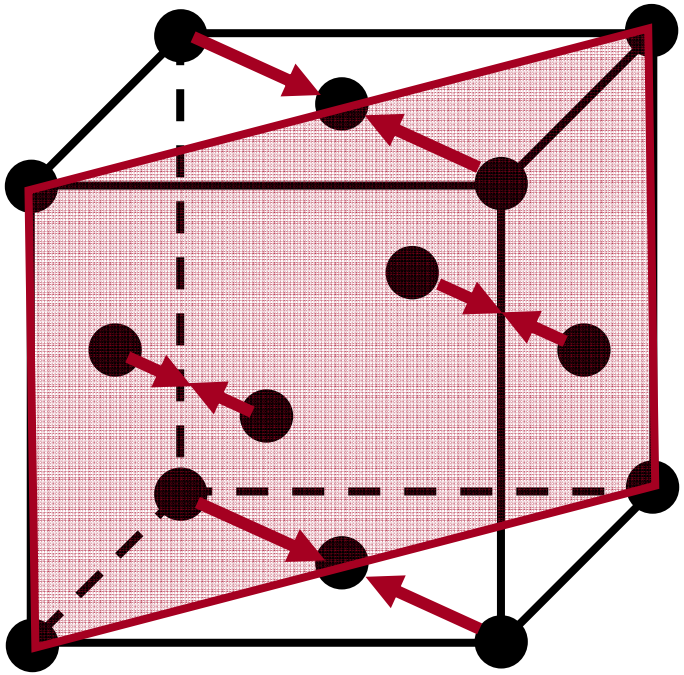
Unit cell of FCC :

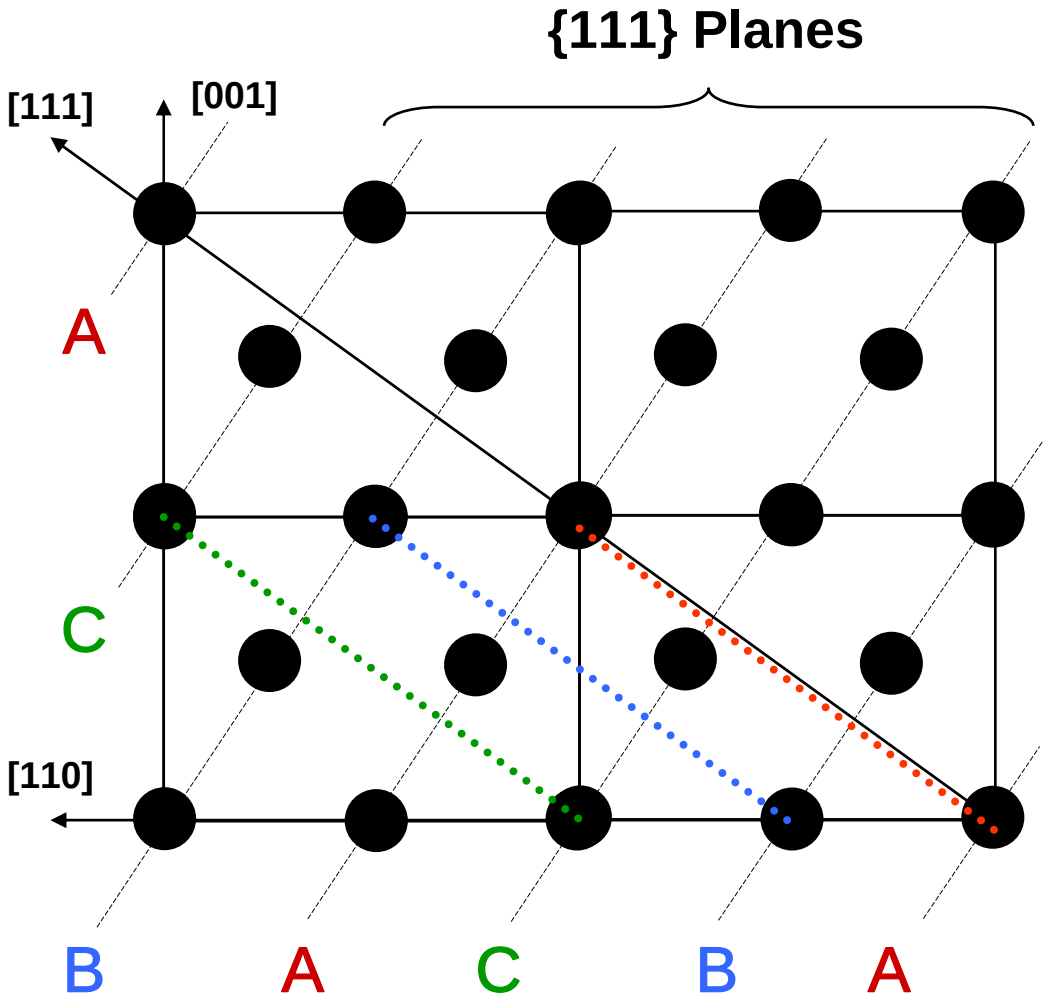




- Materials : Ni, Cu, Pd, Ag, Au, Pt, ...

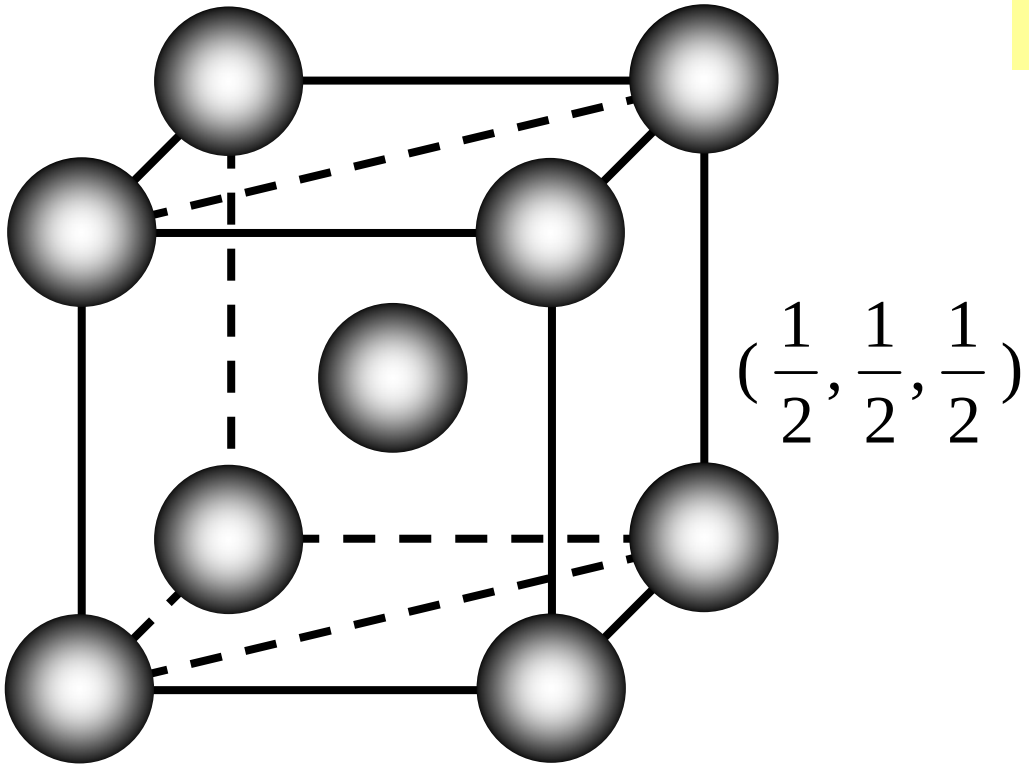
(110) plane projection of FCC :





→ Stacking sequence of FCC ; A B C A B C A B C .....

Unit cell of BCC :



$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$

APF → 68 %

Intrinsically unfilled structure

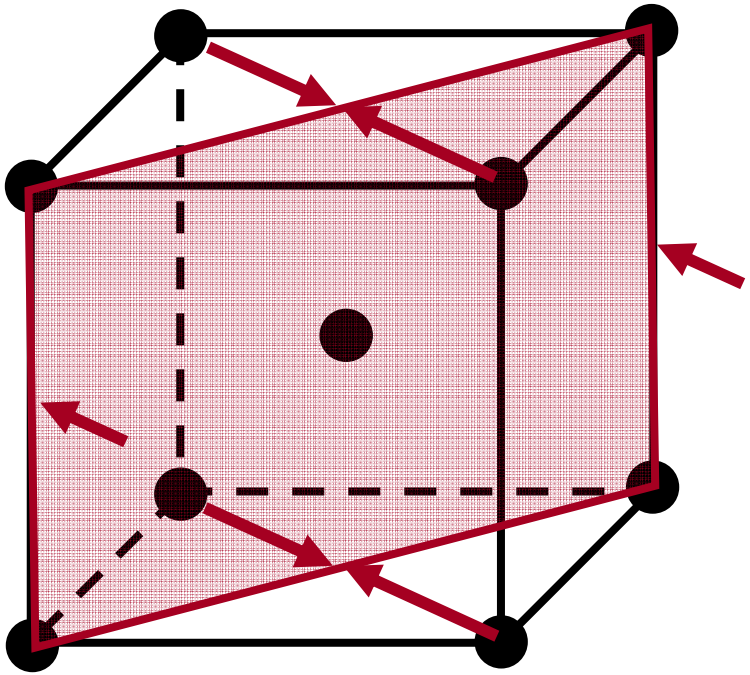
Bonding Directionality

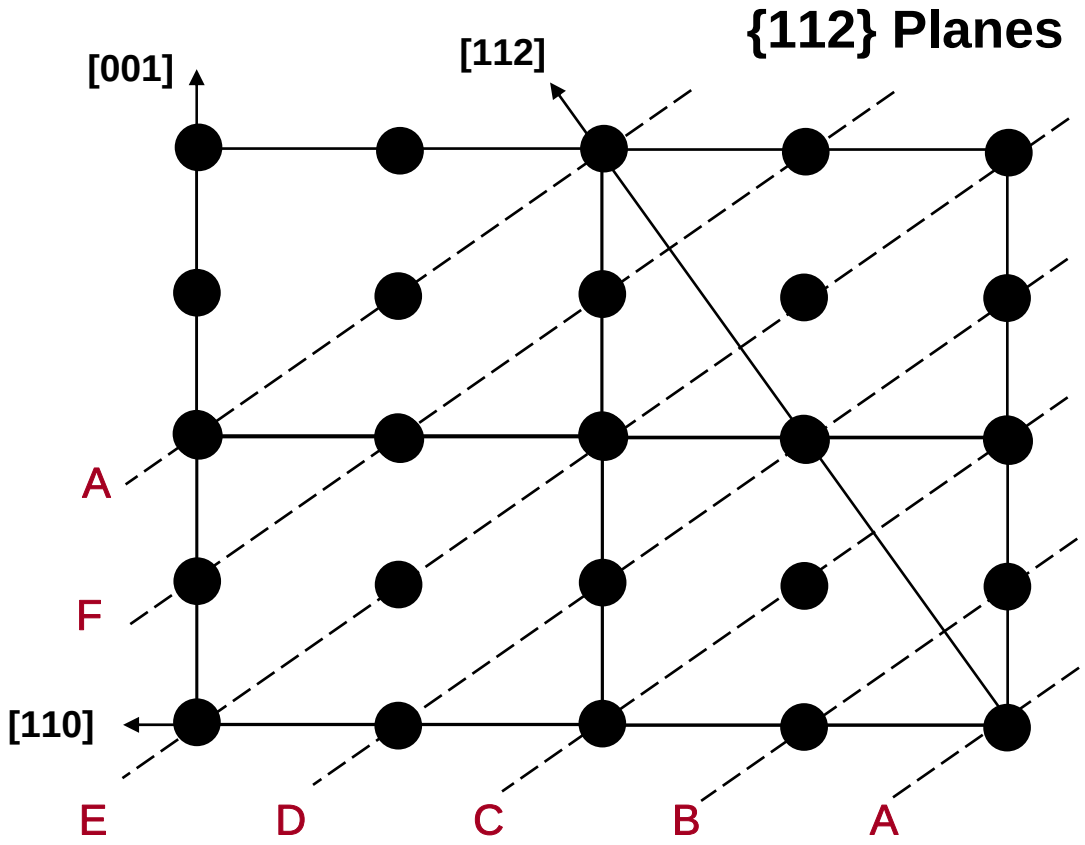
High E, T_m (?)

Mostly transition metal

- Materials : Cr, Fe, Nb, Mo, Ta, W, ...

(110) plane projection of BCC :



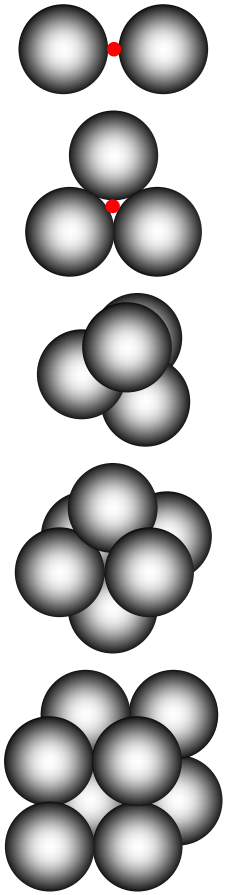


→ Stacking sequence of BCC ; A B C D E F A B C D E F .....

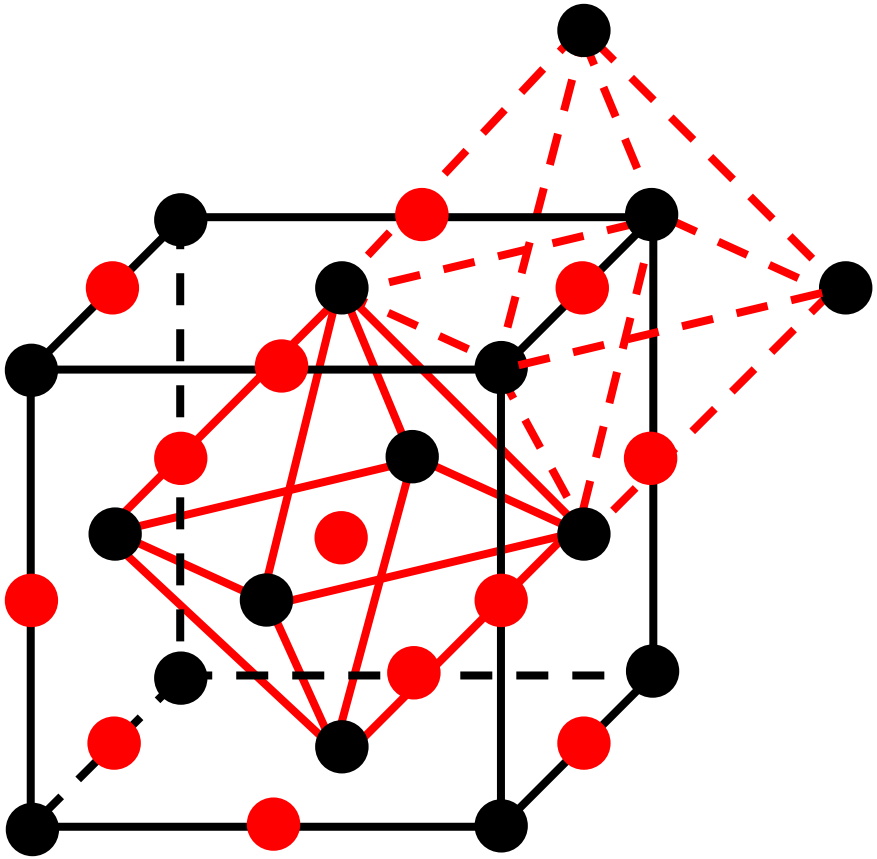
Interstitial Sites (Interstices)

Coordination #	Cation-Anion radius ration
2	< 0.155
3	0.155 - 0. 225
4	0. 225 - 0.414
6	0. 414 - 0. 732
8	0. 732 - 1. 0

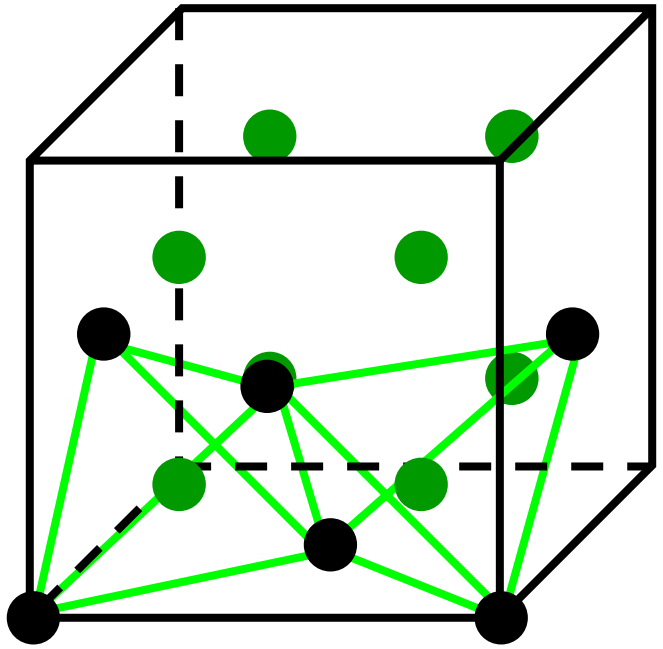
Geometry



Interstitial Sites ; FCC structure

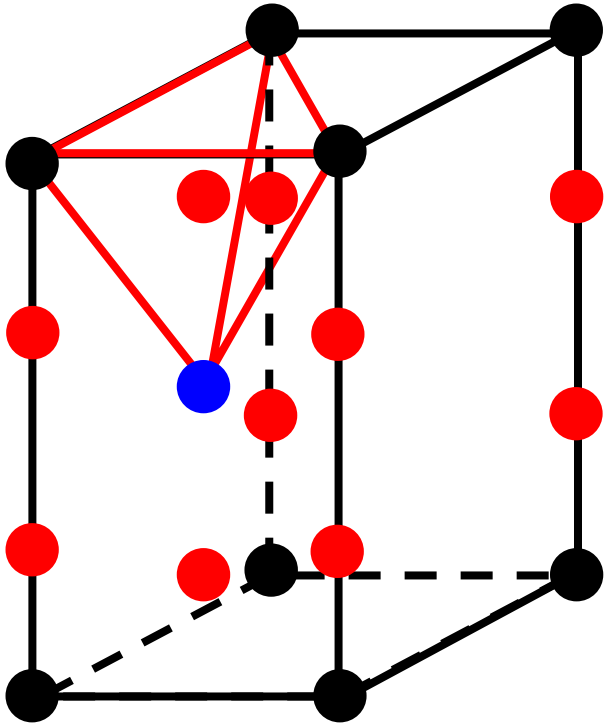


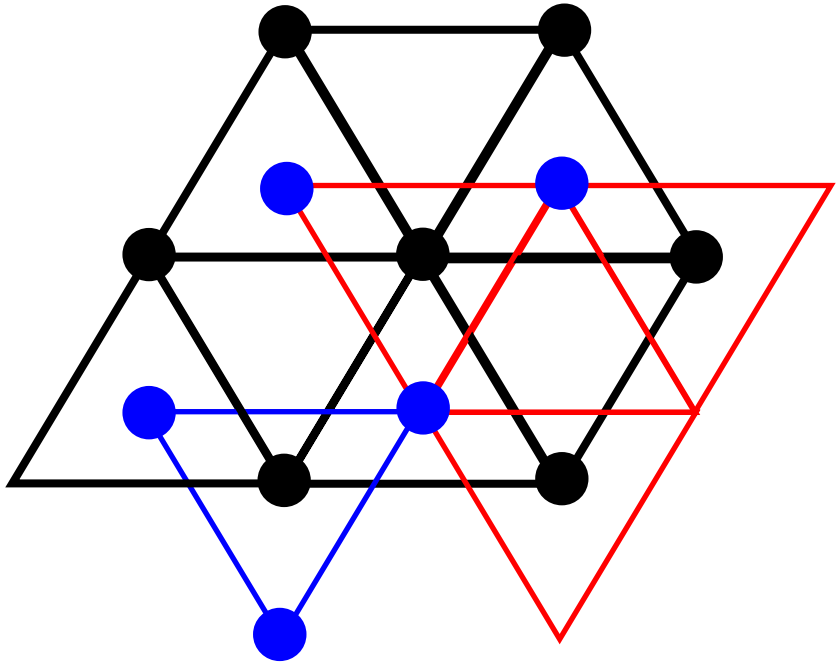
Octahedral sites ; 4



Tetrahedral sites ; 8

Interstitial Sites ; HCP

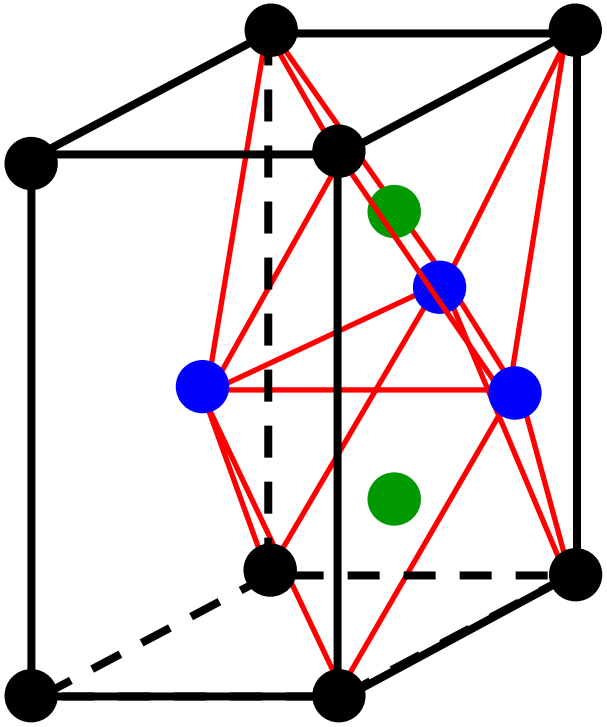


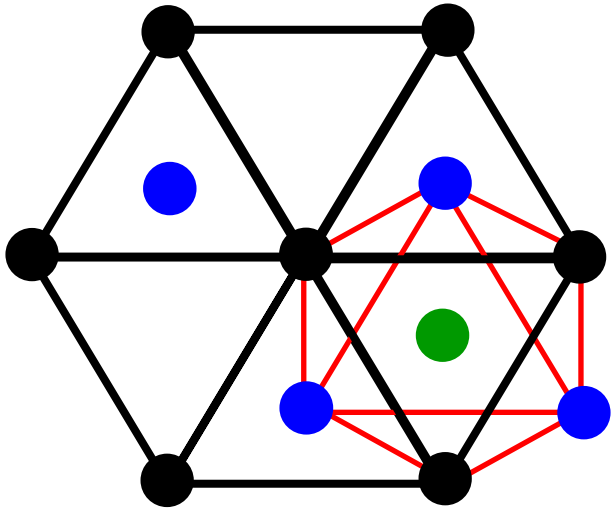


Tetrahedral sites ; 4

$$(0,0,\frac{3}{8}) \quad (0,0,\frac{5}{8}) \quad (\frac{1}{3},\frac{2}{3},\frac{1}{8}) \quad (\frac{1}{3},\frac{2}{3},\frac{7}{8})$$

Interstitial Sites ; HCP

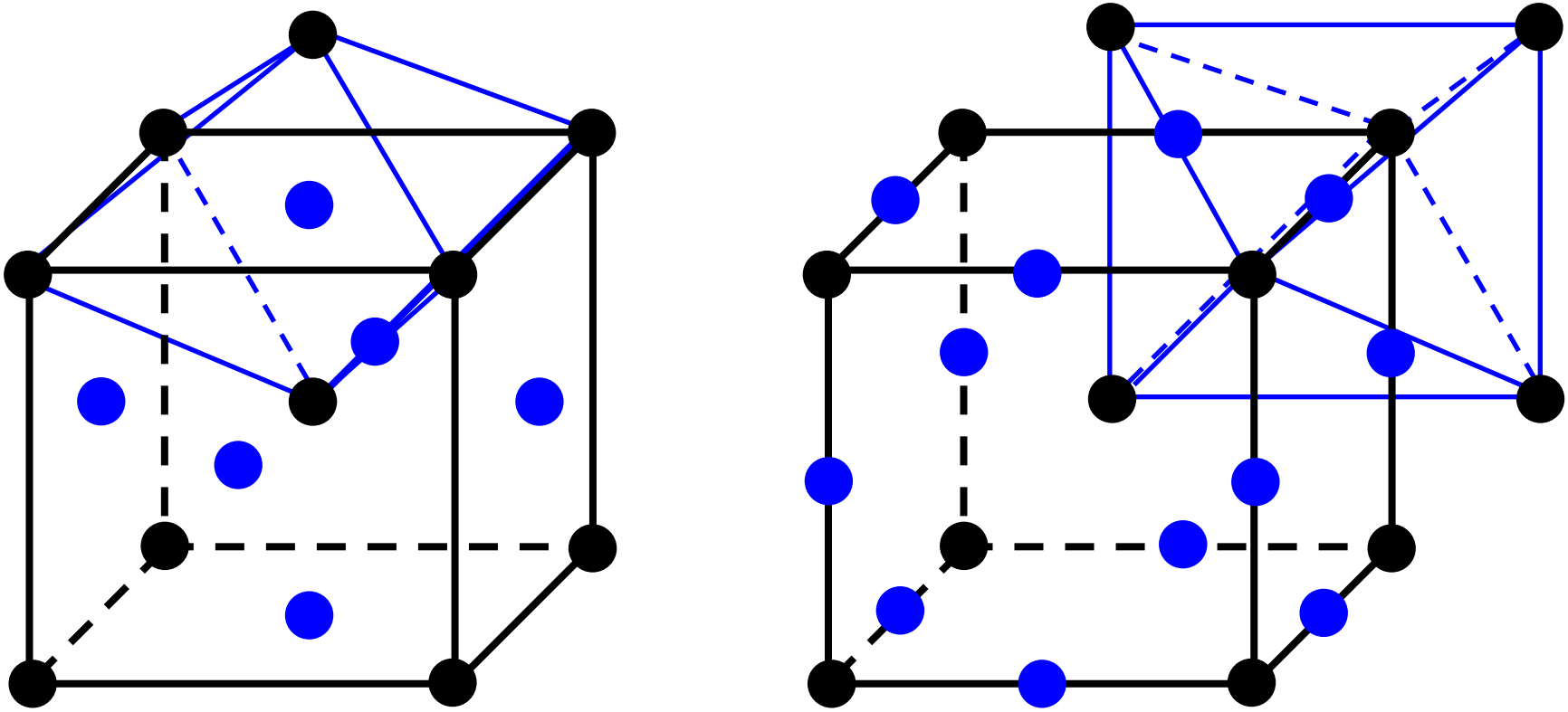




Octahedral sites ; 2

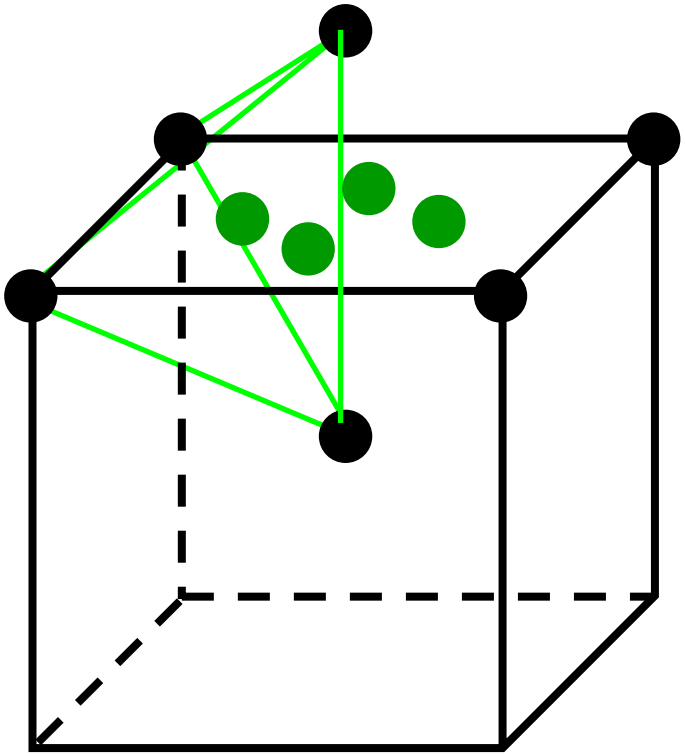
$$\left(\frac{2}{3},\frac{1}{3},\frac{1}{4}\right)\quad\left(\frac{2}{3},\frac{1}{3},\frac{3}{4}\right)$$

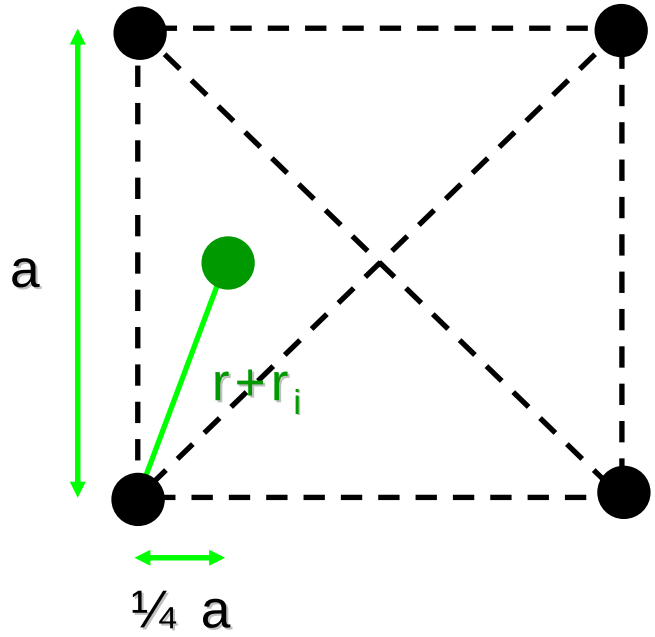
Interstitial Sites ; BCC



3 octa + 3 octa = 6 octa

Interstitial Sites ; BCC





4/2 tetra x 6 = 12 tetra

Interstitial Sites ; BCC

- Octahedral sites ;

$$\left.\frac{r_i}{r}\right|_{octsmall} = 0.155, \qquad \left.\frac{r_i}{r}\right|_{inplane} = 0.63$$

- Tetrahedral sites ;

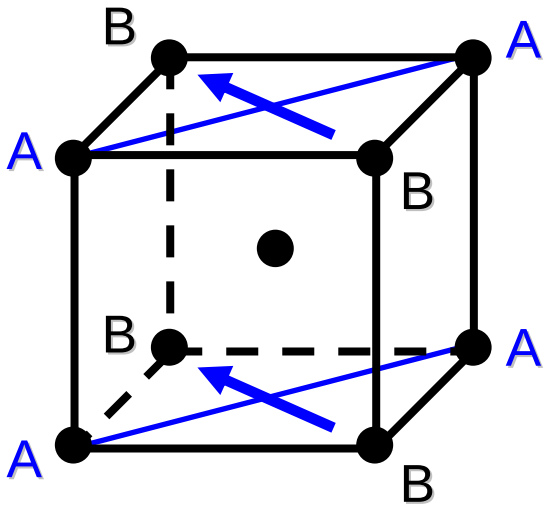
$$\left.\frac{r_i}{r}\right|_{tet} = 0.29$$

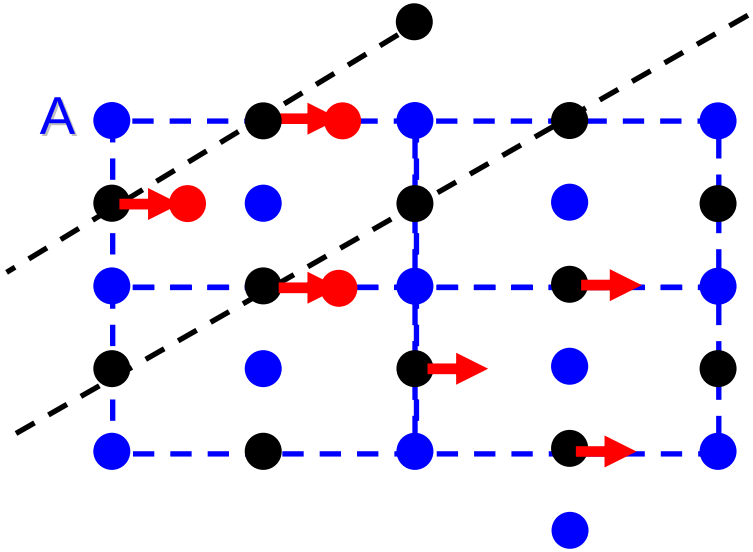
FCC		BCC
Octa	4 (0.414)	6 (0.155, 0.63)
Tetra	8 (0.225)	12 (0.29)

Phase transformation

FCC
HCP
→ Temp. →
BCC
→ Temp. →
Liquid

Exception ;
Fe : BCC → FCC → BCC→ liq.
Co : HCP → FCC → liq.
Ni : FCC → liq.

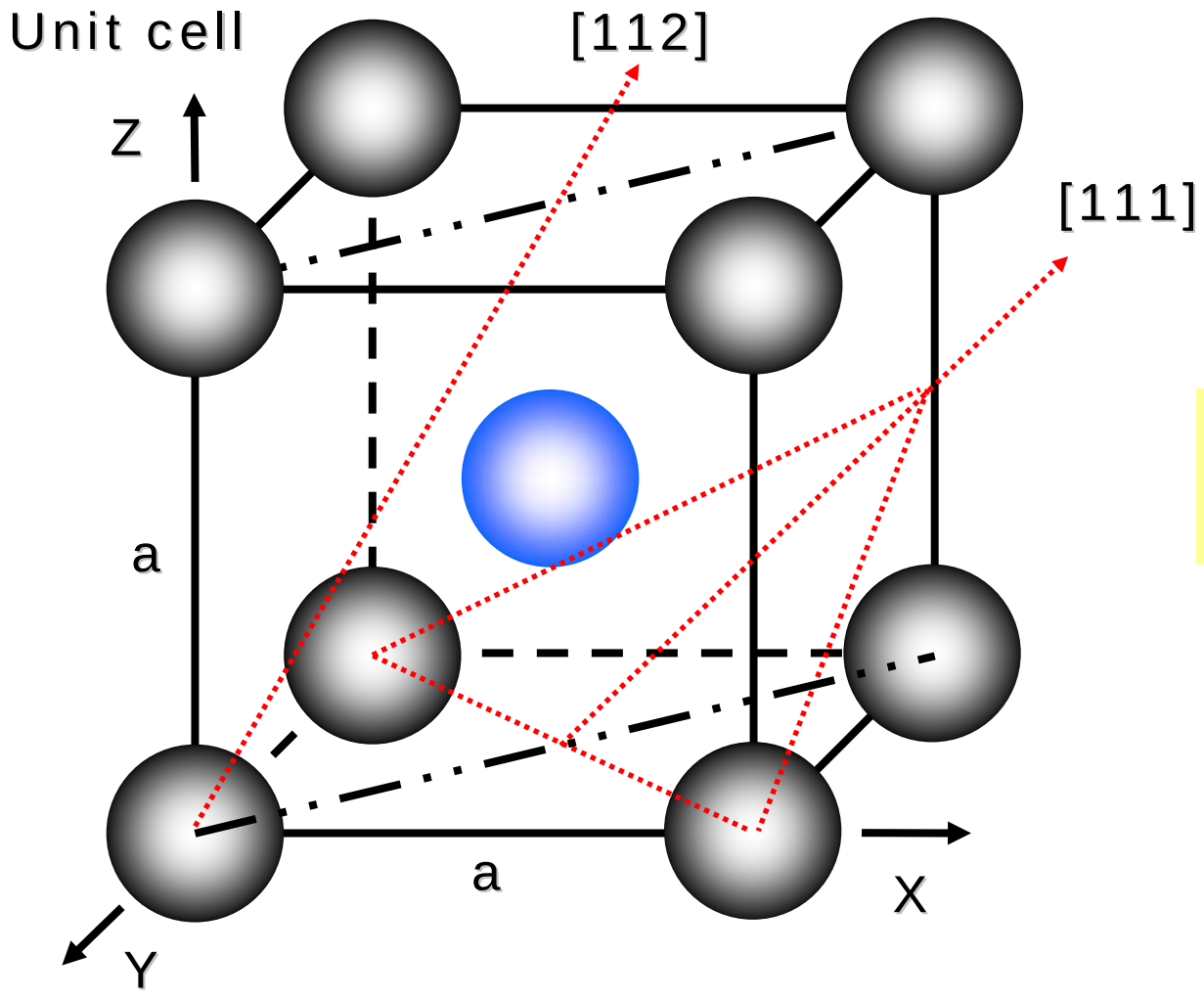




(110) projection
: ABABAB

- Phase trans. From BCC to HCP ; **somewhat deformation**

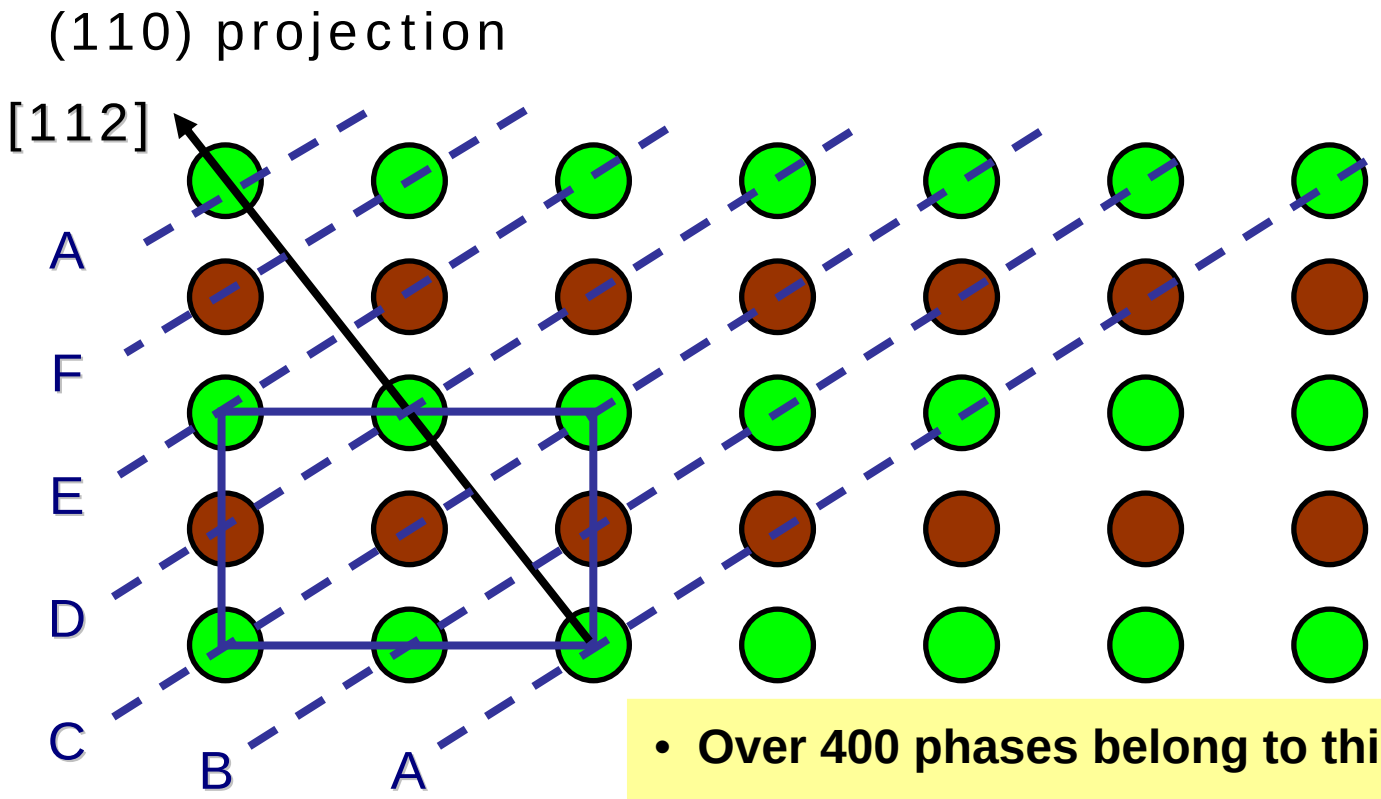
1. CsCl structure



Cs^+, Cl^- cubic interstitial

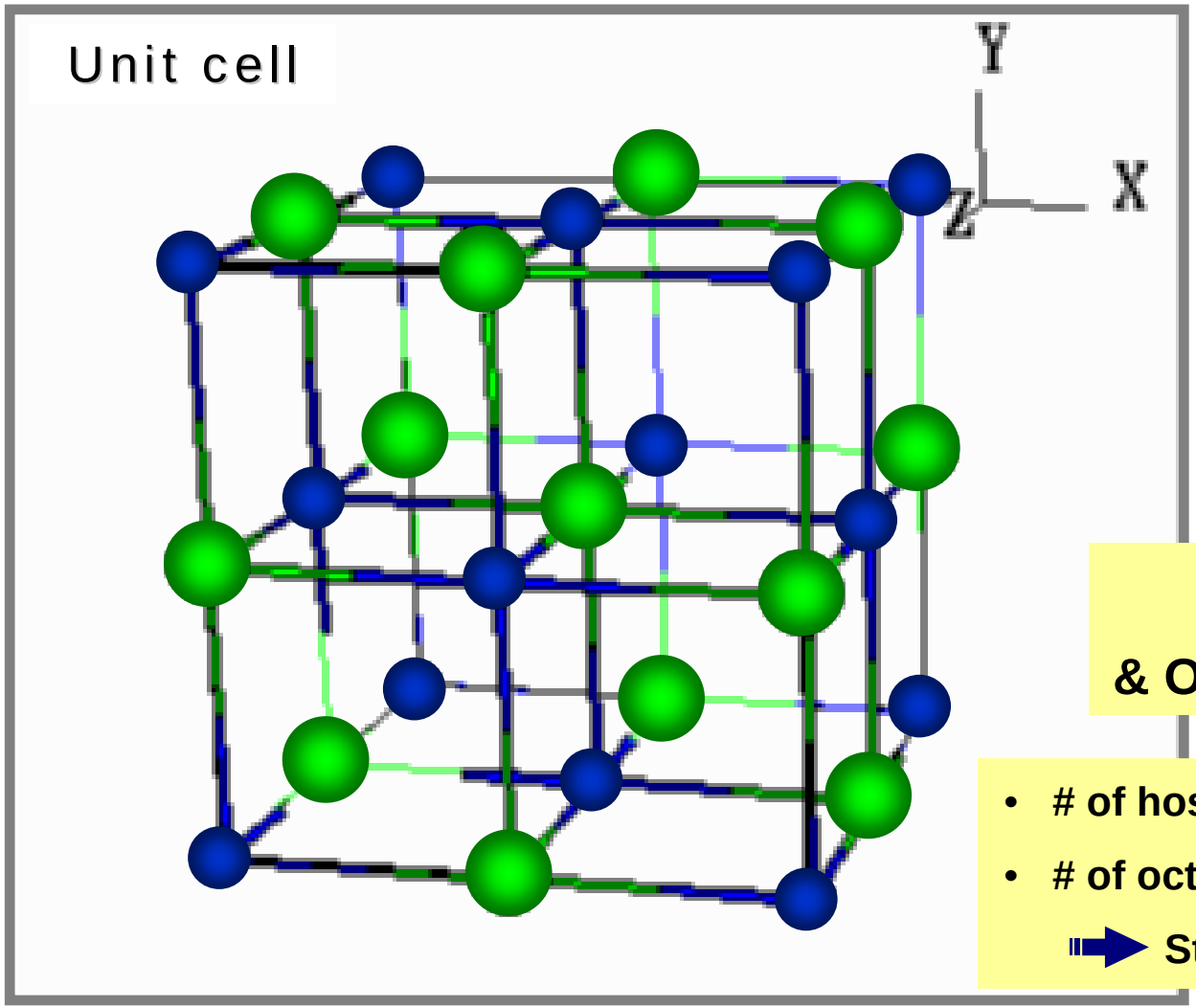
$r^+ / r^- \approx 0.732 \sim 1$

1. CsCl structure



- **Over 400 phases belong to this type**
- **Not a BCC structure**
- **$P_{2,}$ $P_{m\bar{3}m}$**
- **Stacking sequence : <u>A B C D E F</u> A B C E D F …**

2. NaCl structure (rock-salt structure)



FCC array of anions

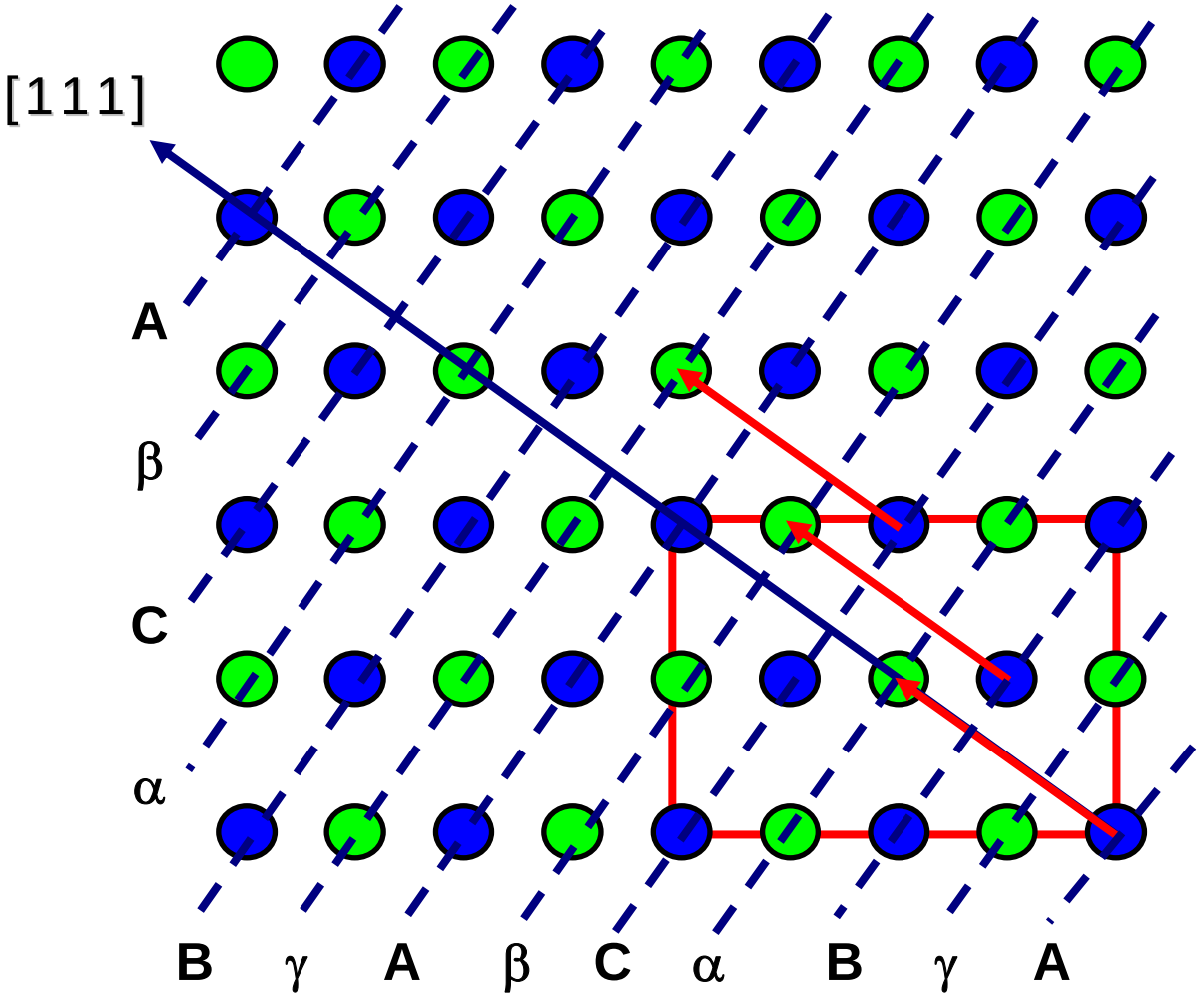
& Octahedral sites of cations

- **# of host atoms in an unit cell → 4**
- **# of octahedral sites in an unit cell → 4**

Stoichiometry 1 : 1

Y

2. NaCl structure (rock-salt structure)

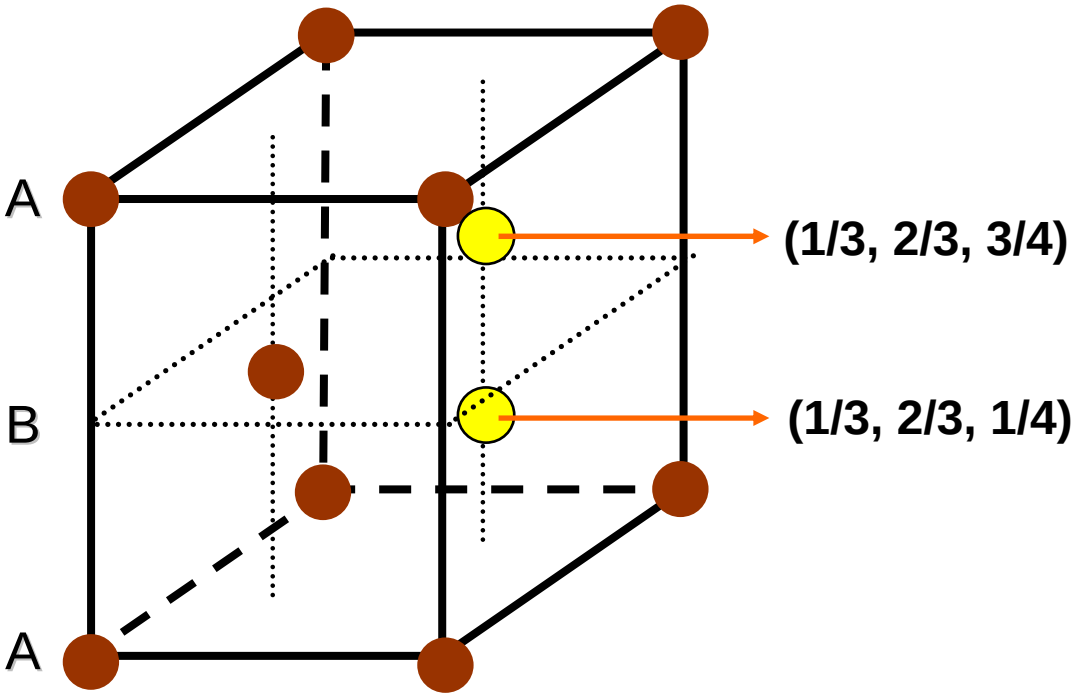


Stacking sequence :

A γ B α C β A γ B α C β …

(110) projection

3. NiAs structure



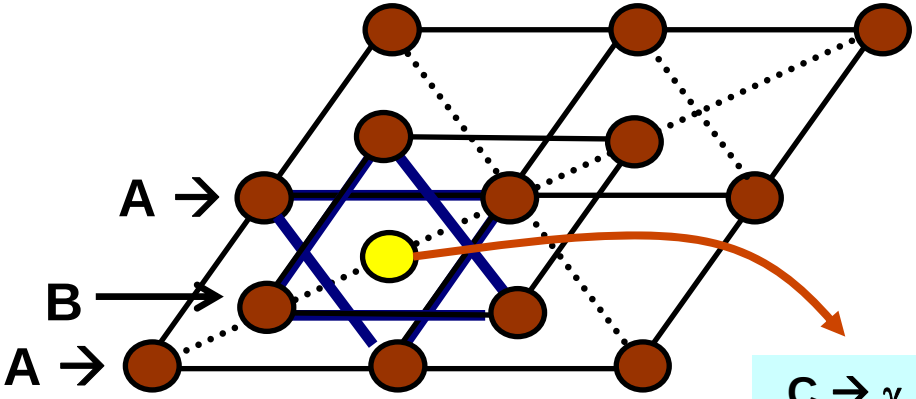
HCP array of Ni &

As occupying 2 octahedral sites

- **# of host atoms in HCP → 2**
- **# of octahedral sites in HCP → 2**

  ⇒ **stoichiometry 1 : 1**

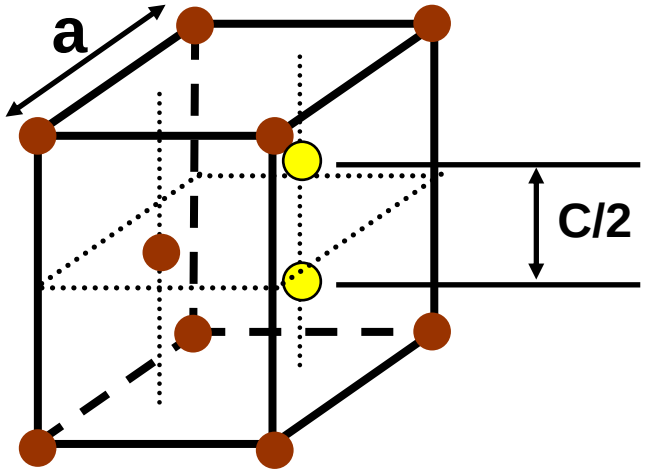
3. NiAs structure



Stacking sequence :

A γ B γ A γ B γ A γ B γ…

C → γ ; Octahedral position

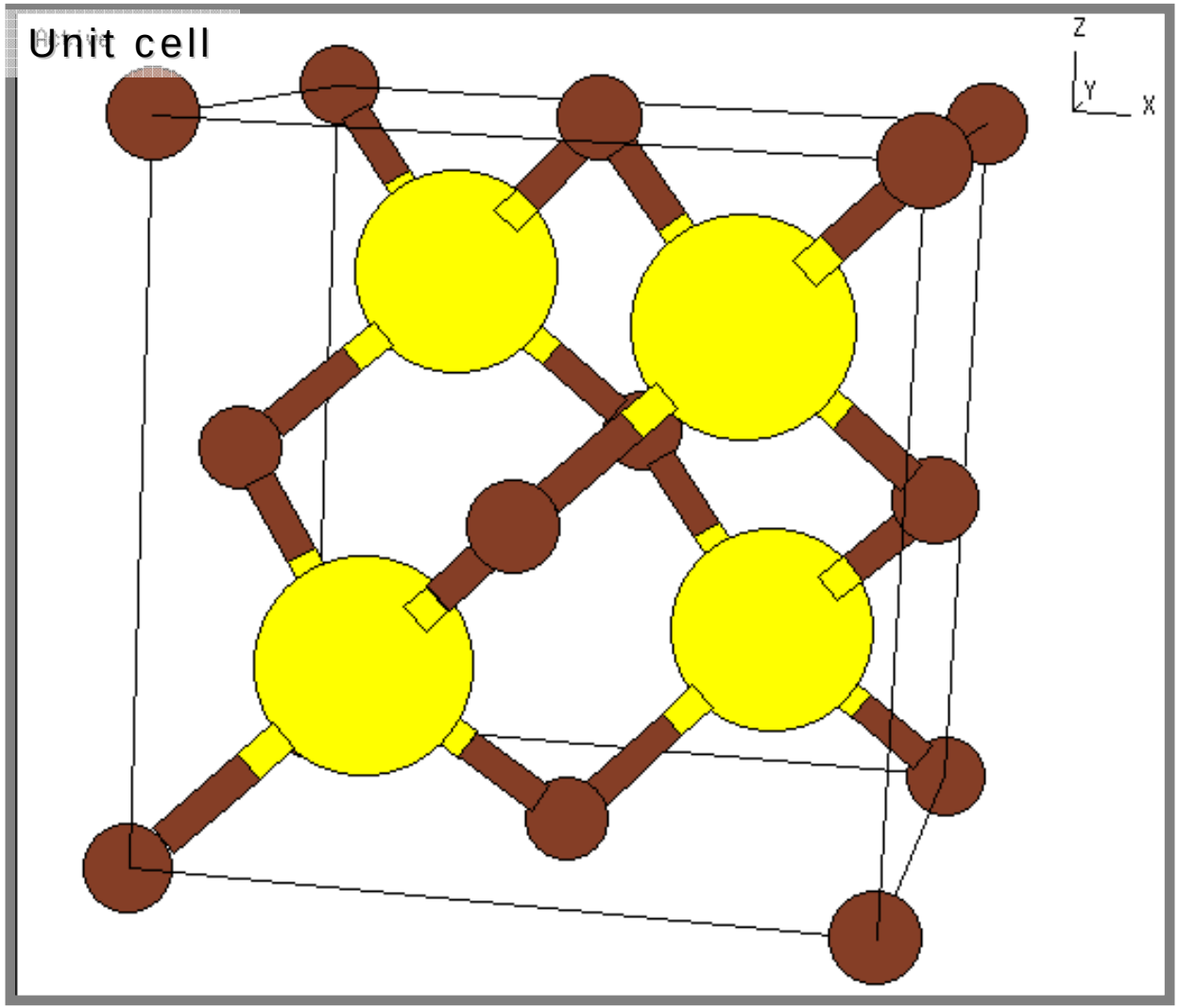


Distance between 2 cations :

internal compression effect between 2 metallic atoms

→ c/a ratio is generally smaller than that of HCP

4. Zinc Blende structure (Sphalerite)



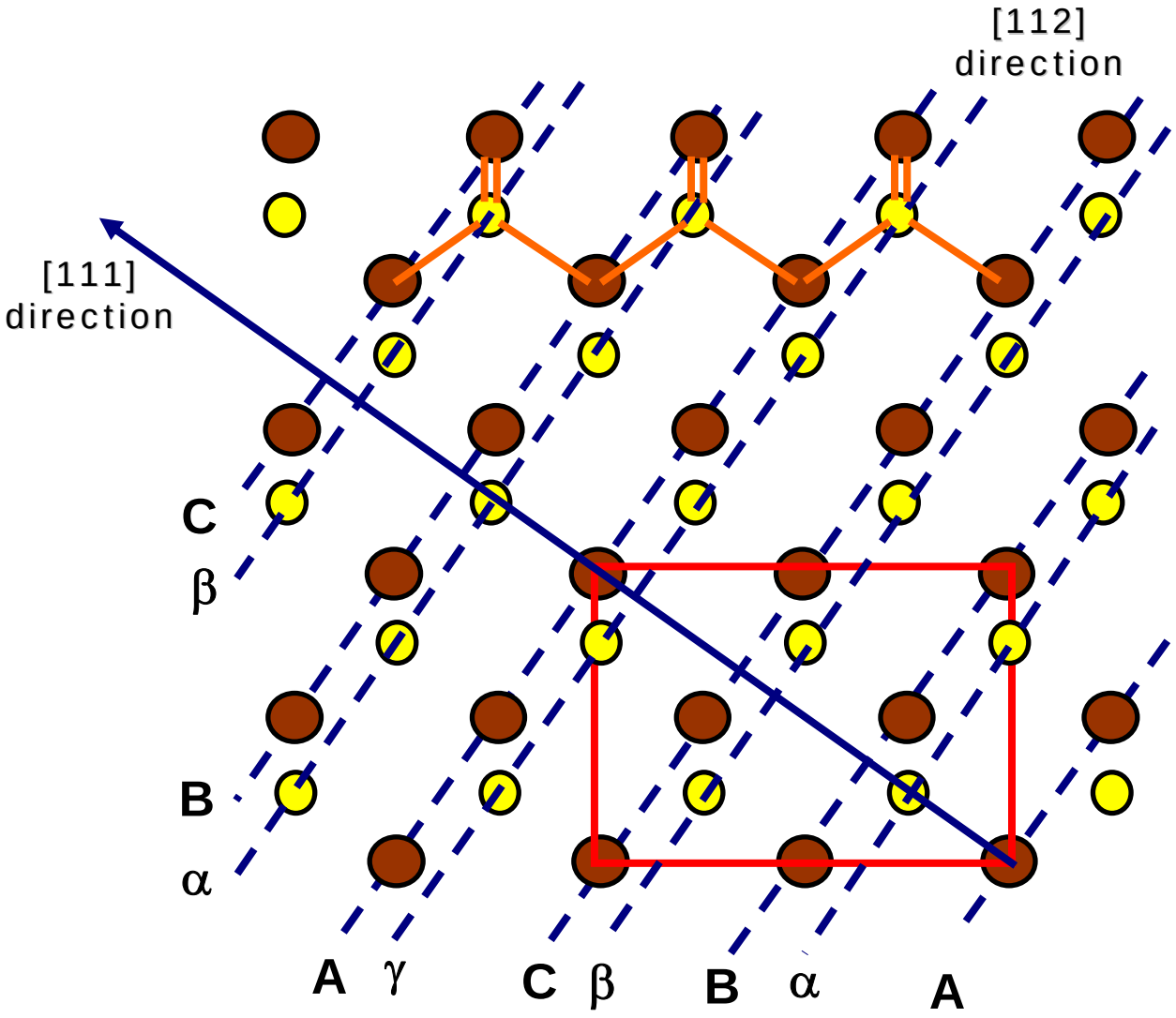
FCC array of S &
Zn occupying of
½ tetrahedral sites

Lattice sites

$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	$(0, 0, 0)$
$(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$	$(\frac{1}{2}, \frac{1}{2}, 0)$
$(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$	$(\frac{1}{2}, 0, \frac{1}{2})$
$(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$	$(0, \frac{1}{2}, \frac{1}{2})$

< in FCC >
4 upright tetrahedral sites
4 inverted tetrahedral sites
→ Take 2 in each cases

4. Zinc Blende structure (Sphalerite)

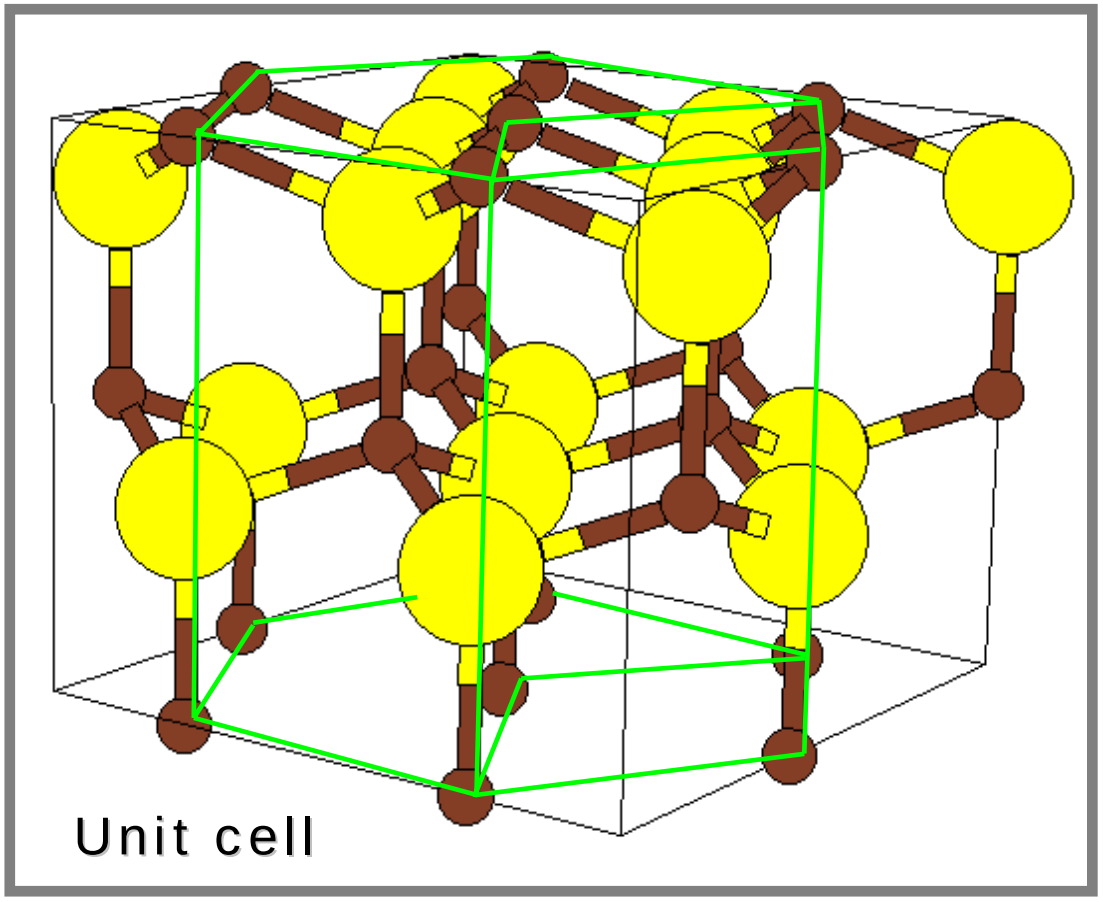


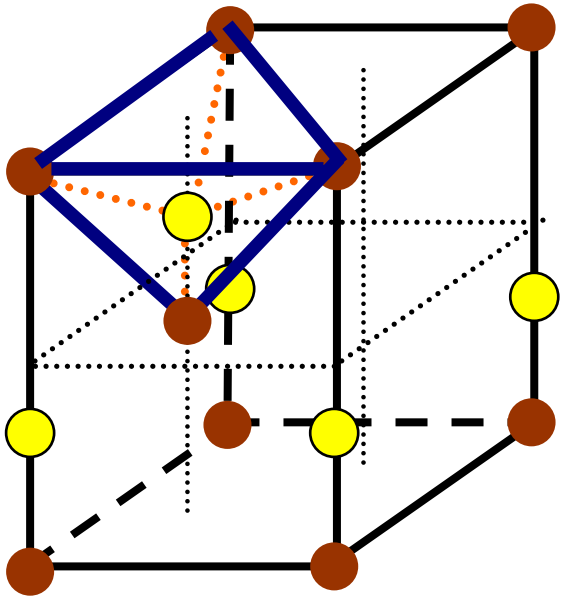
(110) projection

Stacking sequence :

A α B β C γ A α B β C γ …

5. Wurzite structure





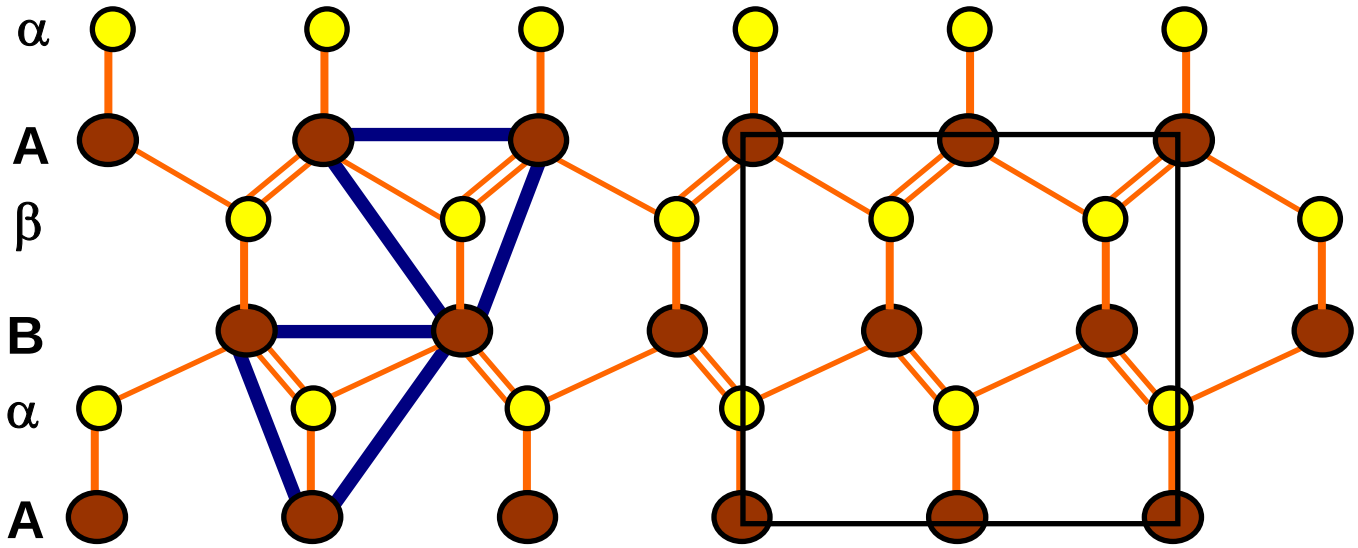
HCP array of S &

Zn occupying of ½ tetrahedral sites

# of tetrahedral sites : 4

Upright 2 ; (2/3,1/3,1/8) (0,0,5/8) or
Inverted 2 ; (2/3,1/3,7/8) (0,0,3/8)

5. Wurzite structure



Stacking sequence :

A α B β A α B β …

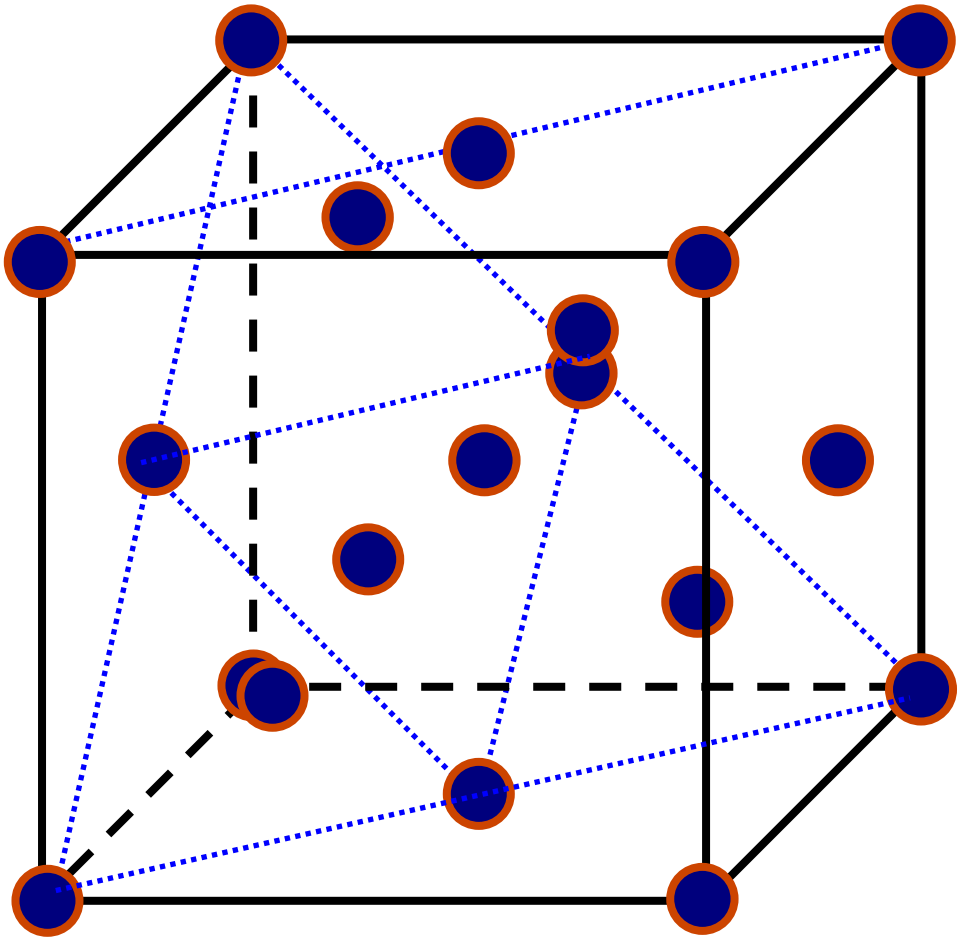
A γ B
B α C
C β A

Octahedral coordination

A α B
B β C
C γ A

Tetrahedral coordination

6. Diamond structure



Host atom

- FCC array &

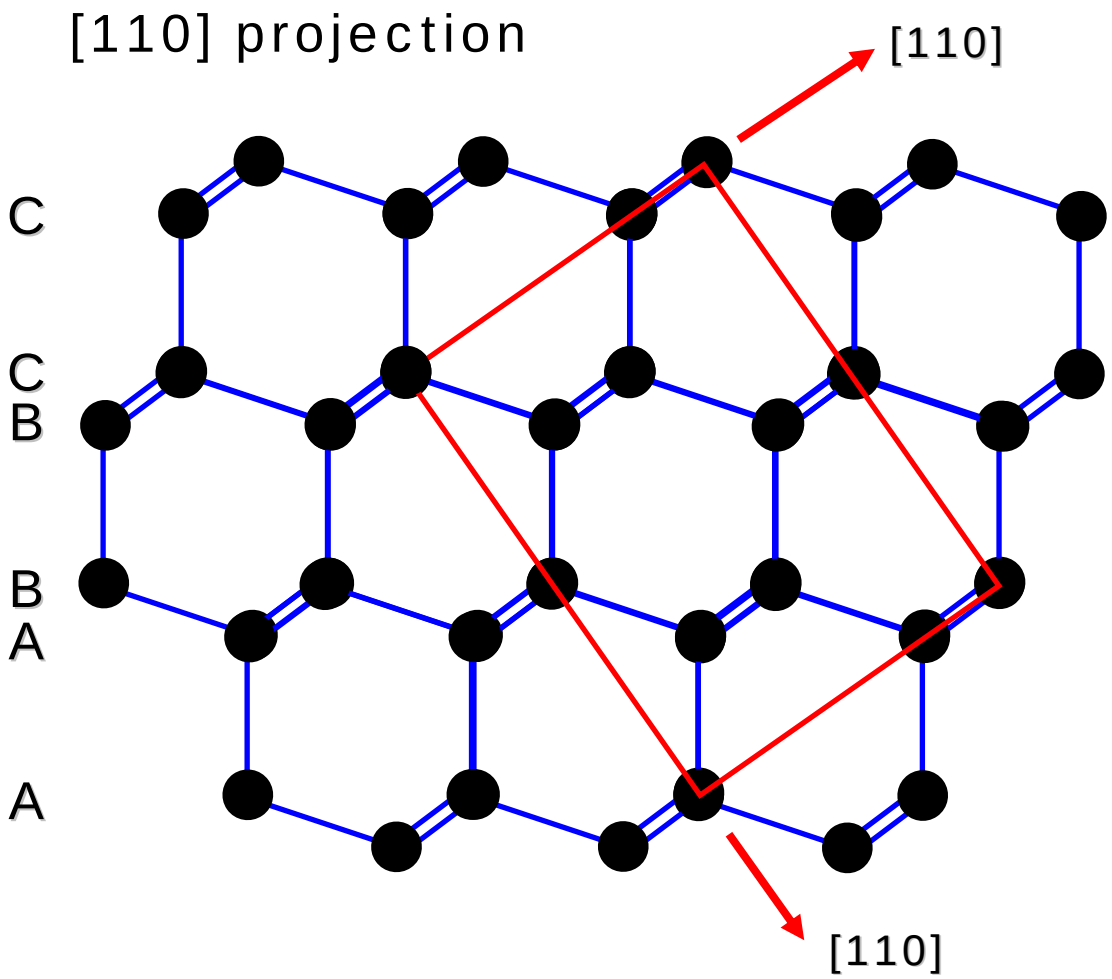
- ½ tetrahedral sites

Similar to Zinc blende

except that the same element

occupies tetrahedral sites

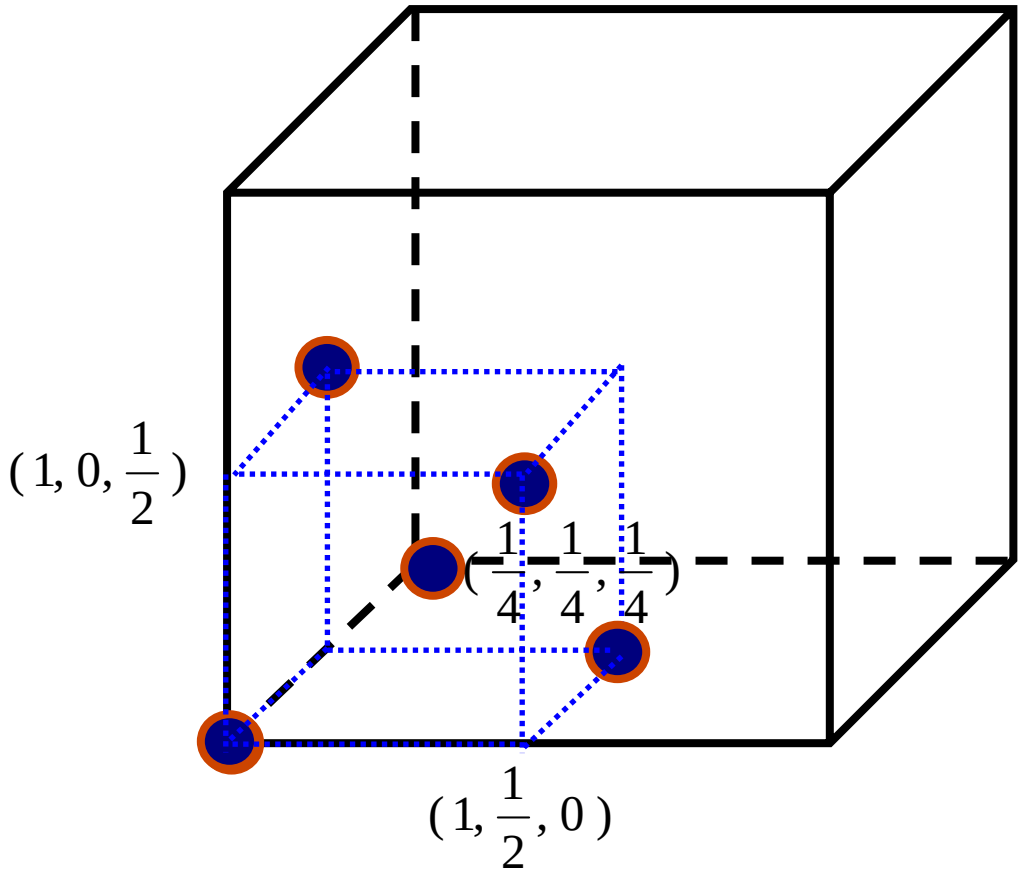
6. Diamond structure



Stacking sequence :

AABBCC AABBCC…

6. Diamond structure

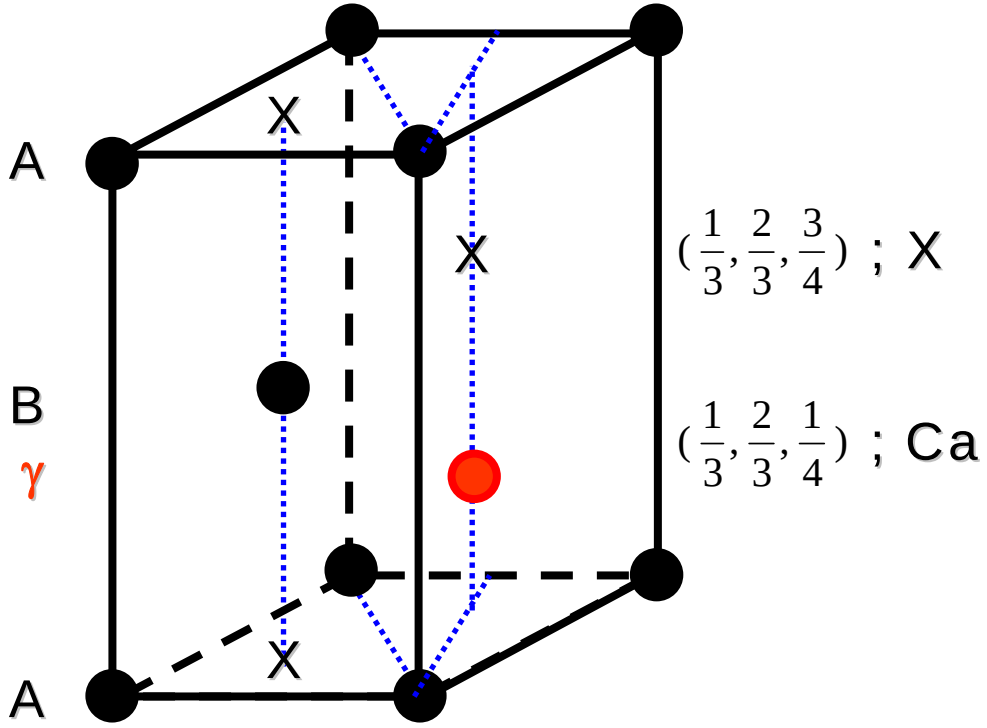


Coordination number : 4

Atomic Packing Factor : 34 %

→ ½ of BCC (why?)

7. CaI_2 structure



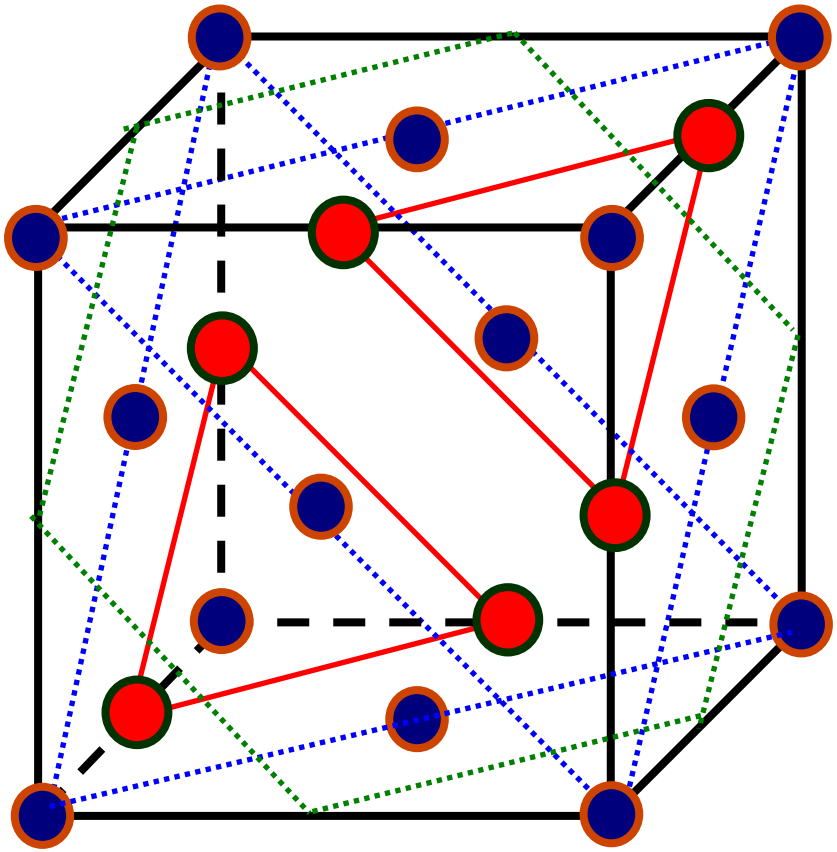
- HCP array of I
- Alternating layers of octahedral sites ; Ca

Stacking sequence :

A γ B A γ B A γ B ...

missing missing

8. $CdCl_2$ structure



- FCC array of ClI
- Alternating Cd layers in octahedral position ; Ca

Stacking sequence :

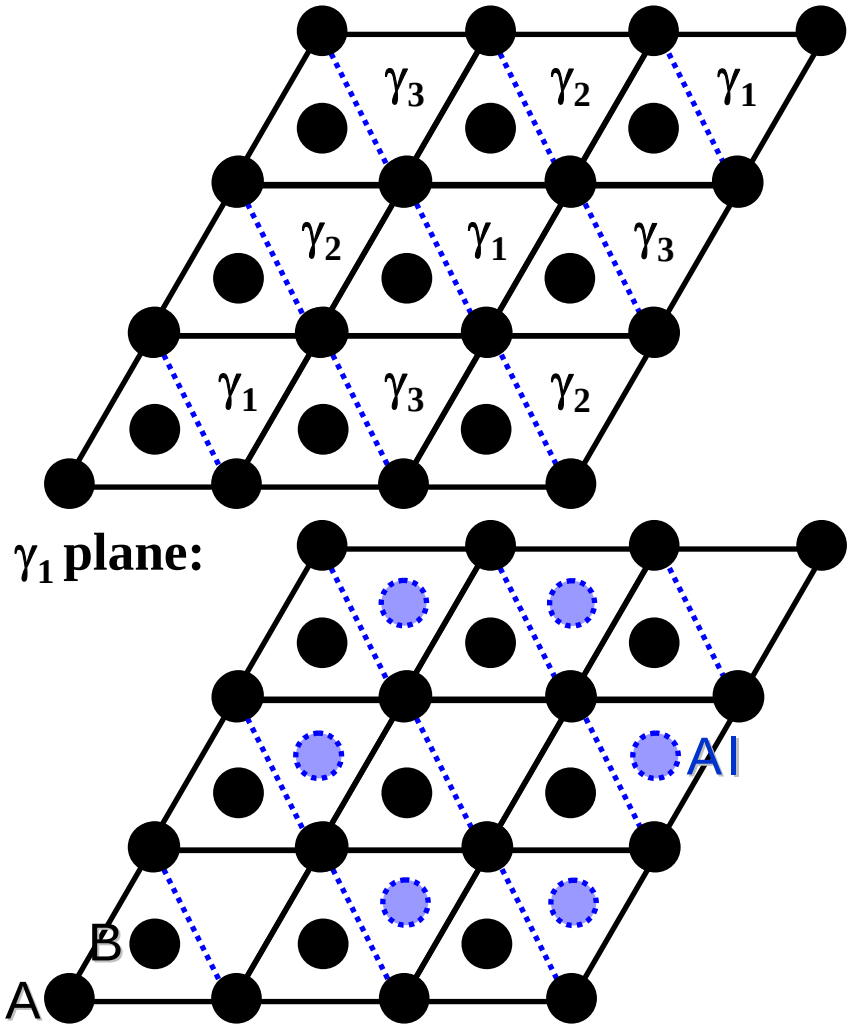
A γ B α C β A γ B α C β A γ B α C β A γ B α C

missing missing missing missing missing

unit cell of the structure :

A γ B C β A B α C A γ B C β A B α C

9. Al_2O_3 (sapphire structure)



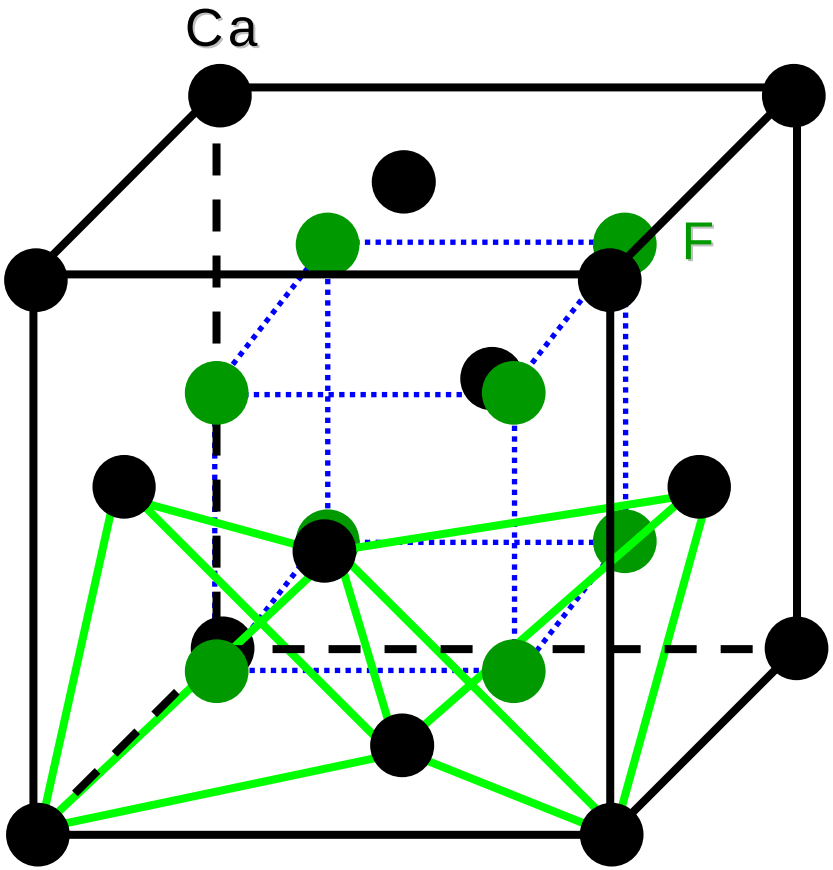
- HCP array of oxygen ions
- Al^{+++} : 2/3 of available octahedral sites

Stacking sequence :

A γ_1 B γ_2 A γ_3 B γ_1 A γ_2 B γ_3 A γ_1 B

Unit cell of Al_2O_3

10. CaF_2 (Calcium difluoride) structure



- FCC array of Ca
- F : in all tetrahedral sites

- Every Ca^{++} ion is surrounded by F^- ions by every ½ cube sites

- F^- ions form a cubic array with ½ cubic interstitials is occupied by Ca^{++}

Stacking sequence :

A β α B γ β C α γ A β α B γ β C α γ