Crystal Structure (metallic, ionic, and covalent)

Crystal Structure

Lattice ---→ Crystal

lattice points occupied by atoms, ions, or molecules

lattice points- all identical, collection of objects- must be identical

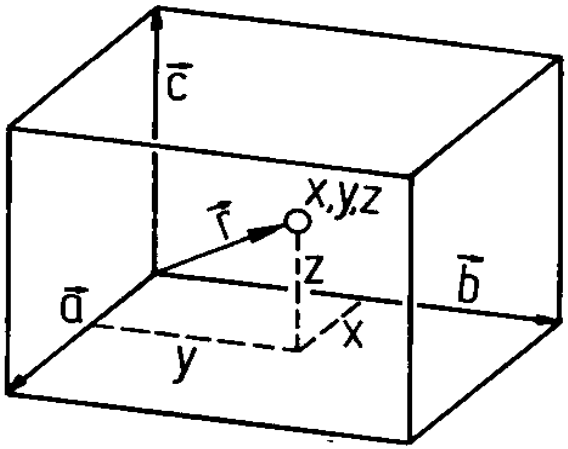
Ex) lattice rectangular unit cell

projected on a,b plane

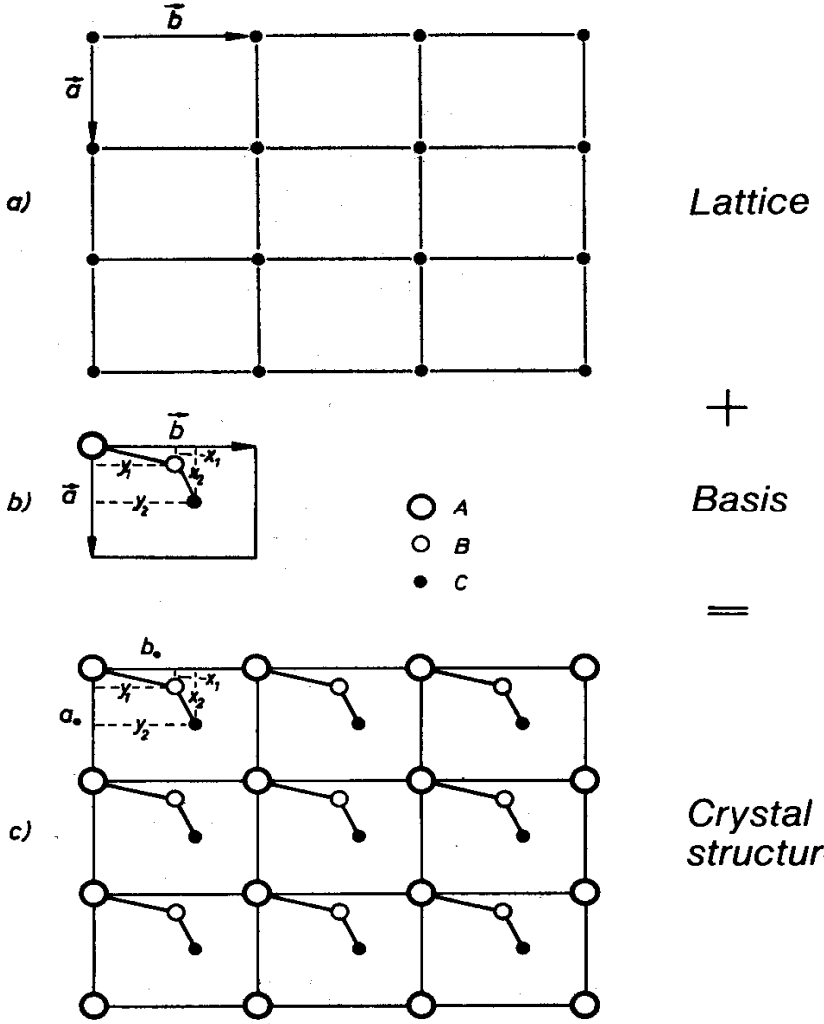
basis molecule ABC

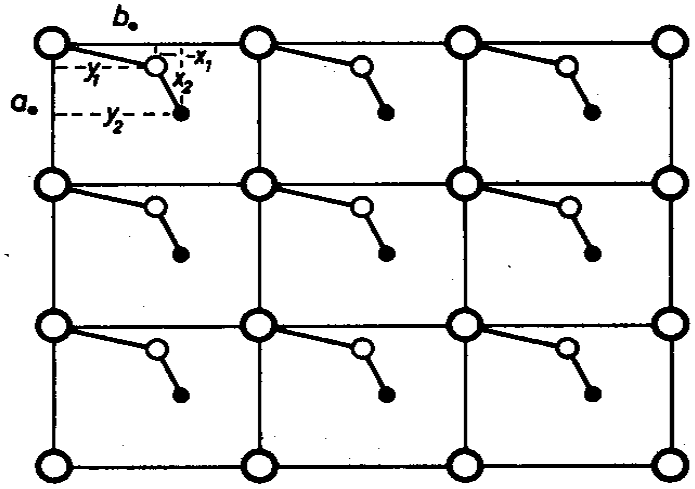
A: 0, 0, 0 B: x_1,y_1,z_1 C:x_2,y_2,z_2

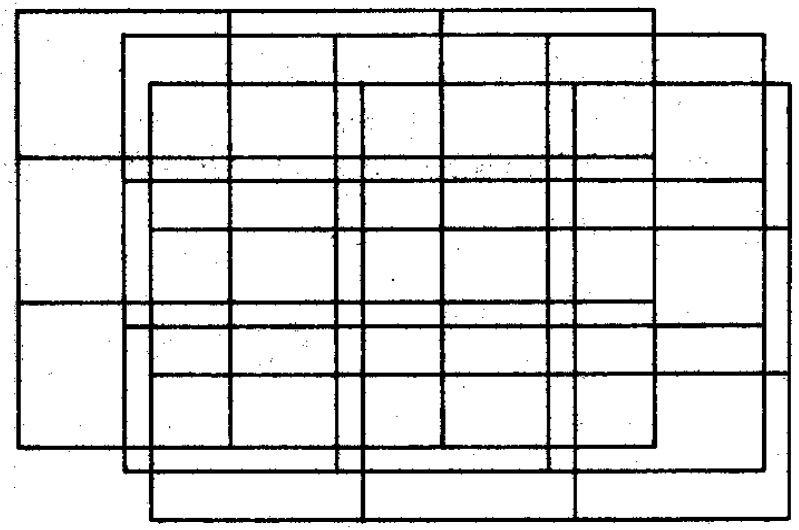
$$\vec{r} = x\vec{a} + y\vec{b} + z\vec{c}$$



$$0 \le x, y, z \le 1$$







Crystals are solid chemical substance with a three-dimensional periodic array of atoms, ions, or molecules.
This array is a called a **crystal structure.**

Contents

1. Simple metallic structure;

   FCC, HCP and BCC structure

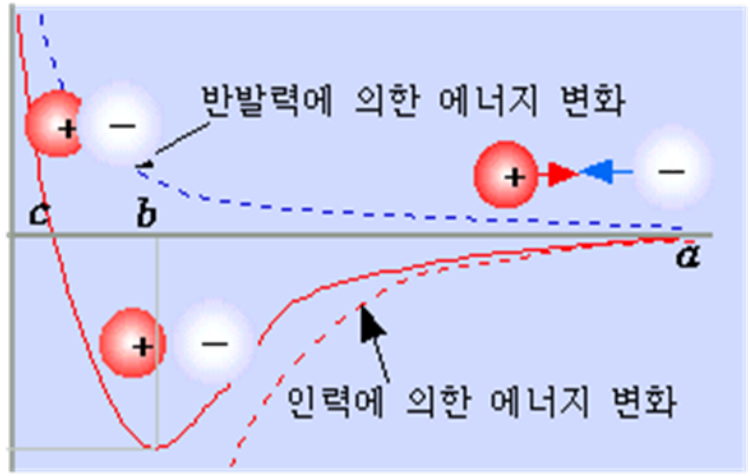
   Stacking sequence, [(110) projection structure]

   Interstitial sites

2. Complicate structure; Ionic and covalent structure

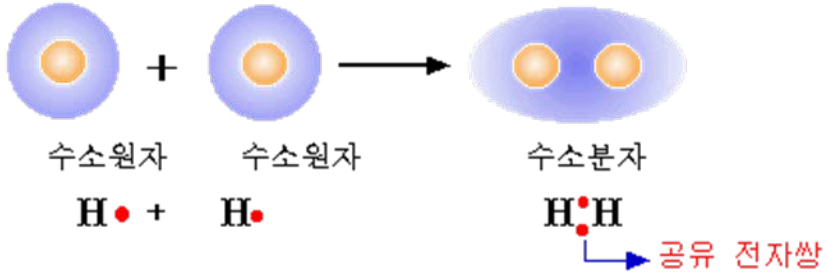
Chemical bonding :

► **Ionic bonding**

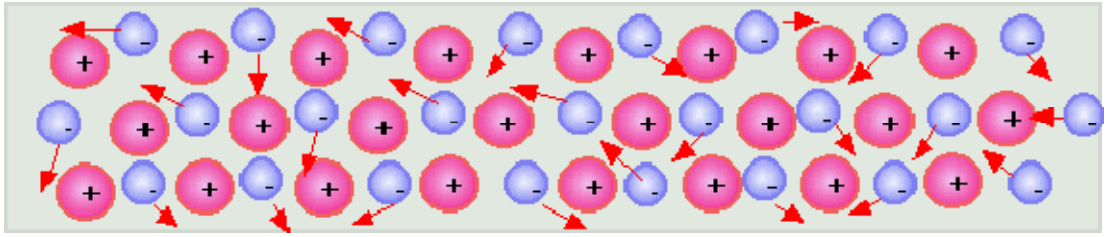


$$F = \frac{1}{\varepsilon} \cdot \frac{e_1 e_2}{r^2}$$

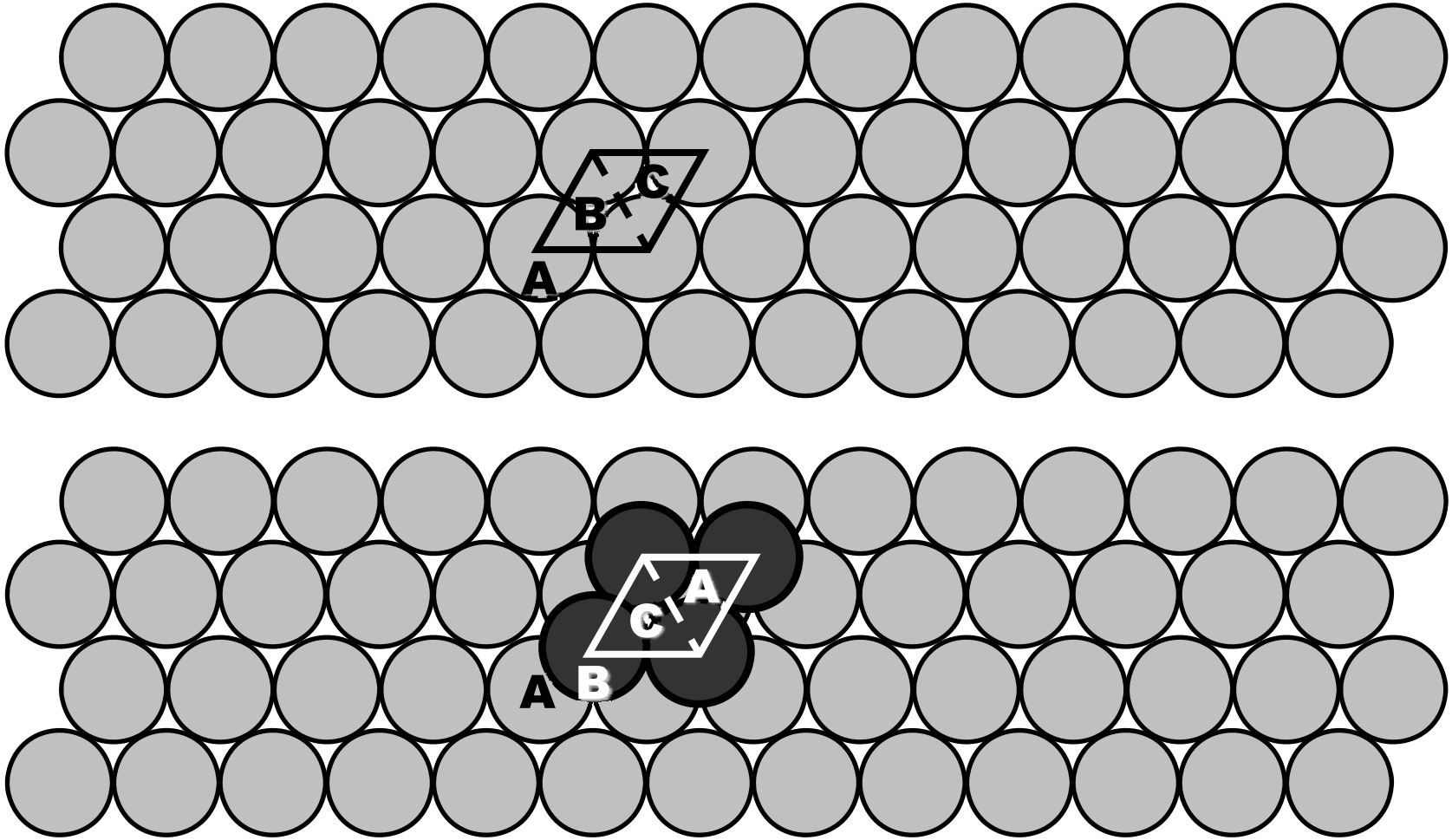
► **Covalent bonding**



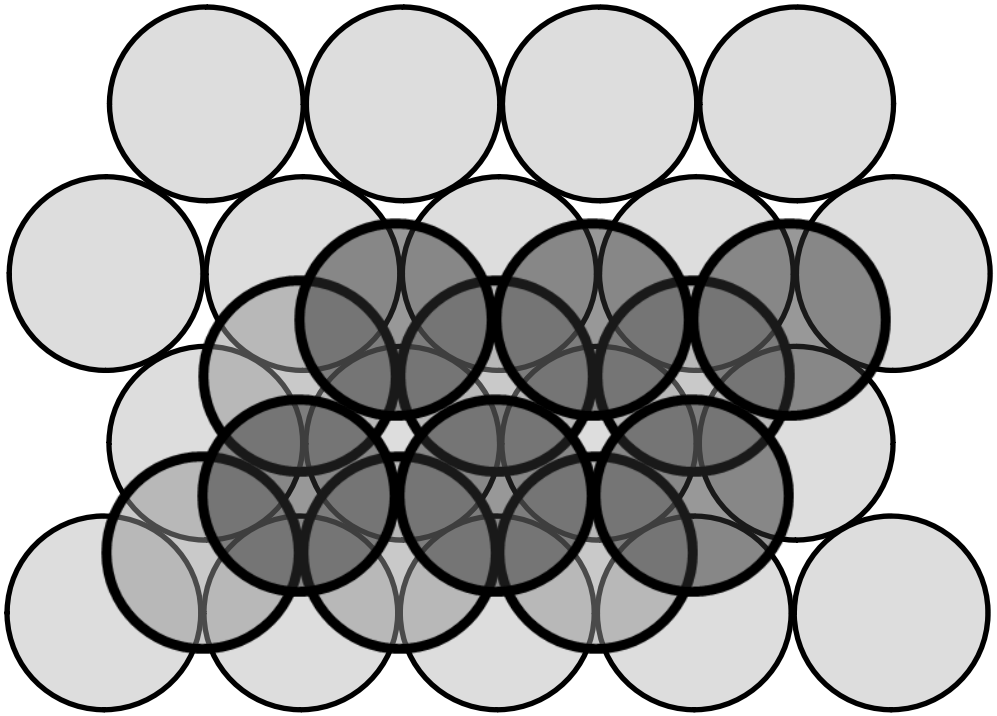
► **Metallic bonding**



Closed Packed Structures :



Closed Packed Structures :



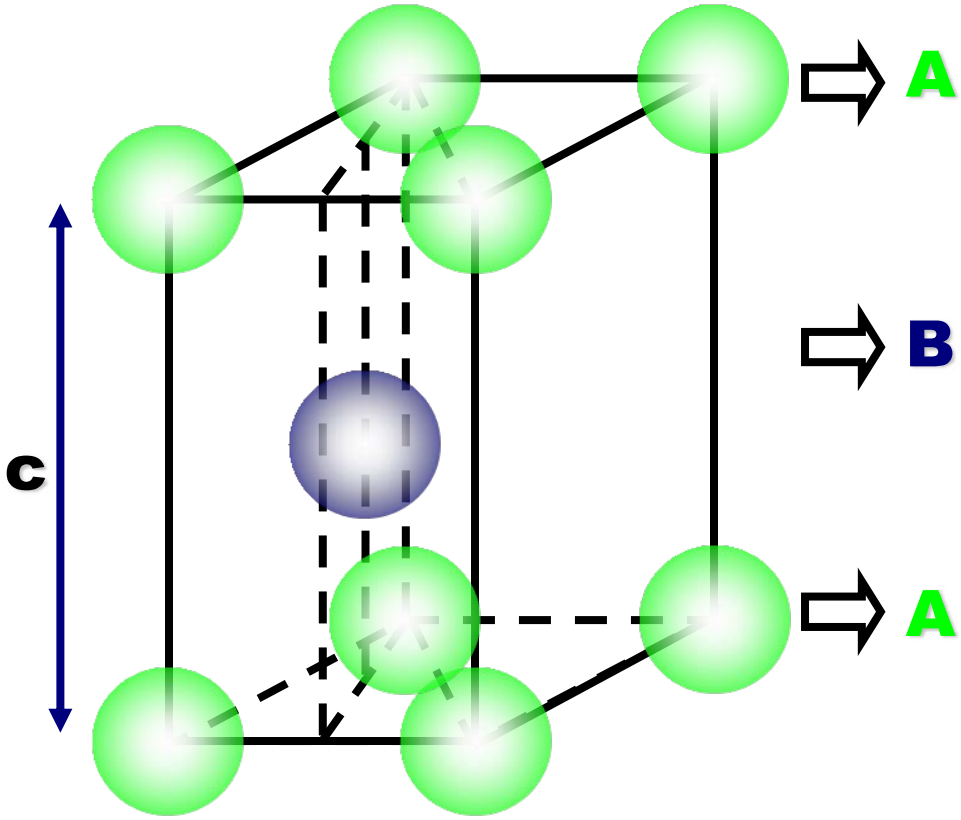
Stacking sequence

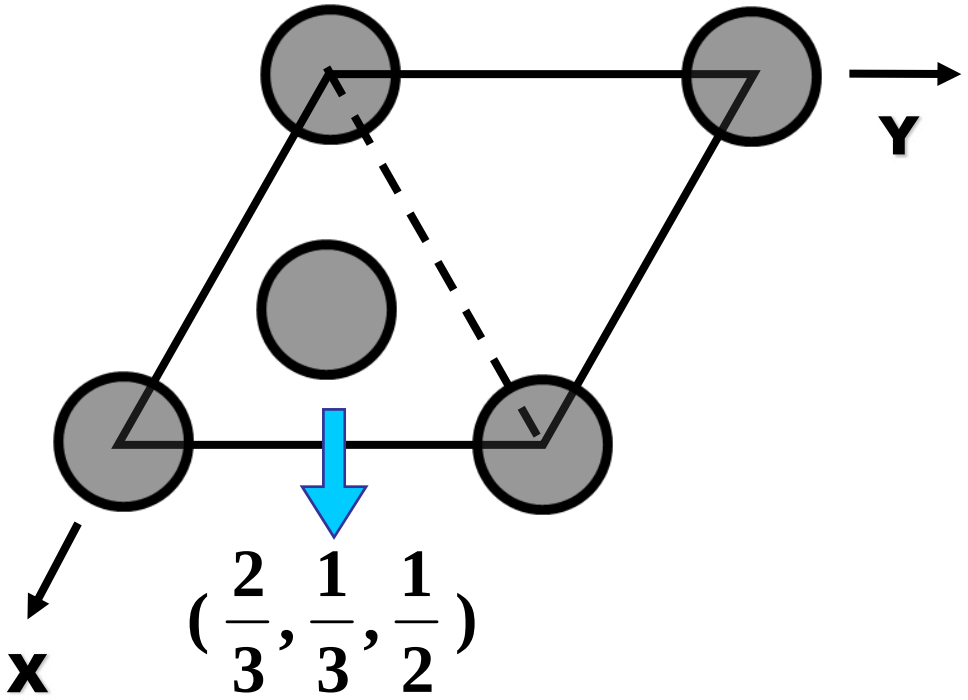
ABCABCABCABC (FCC)

ABABABABABAB (HCP)

APF → 74 %

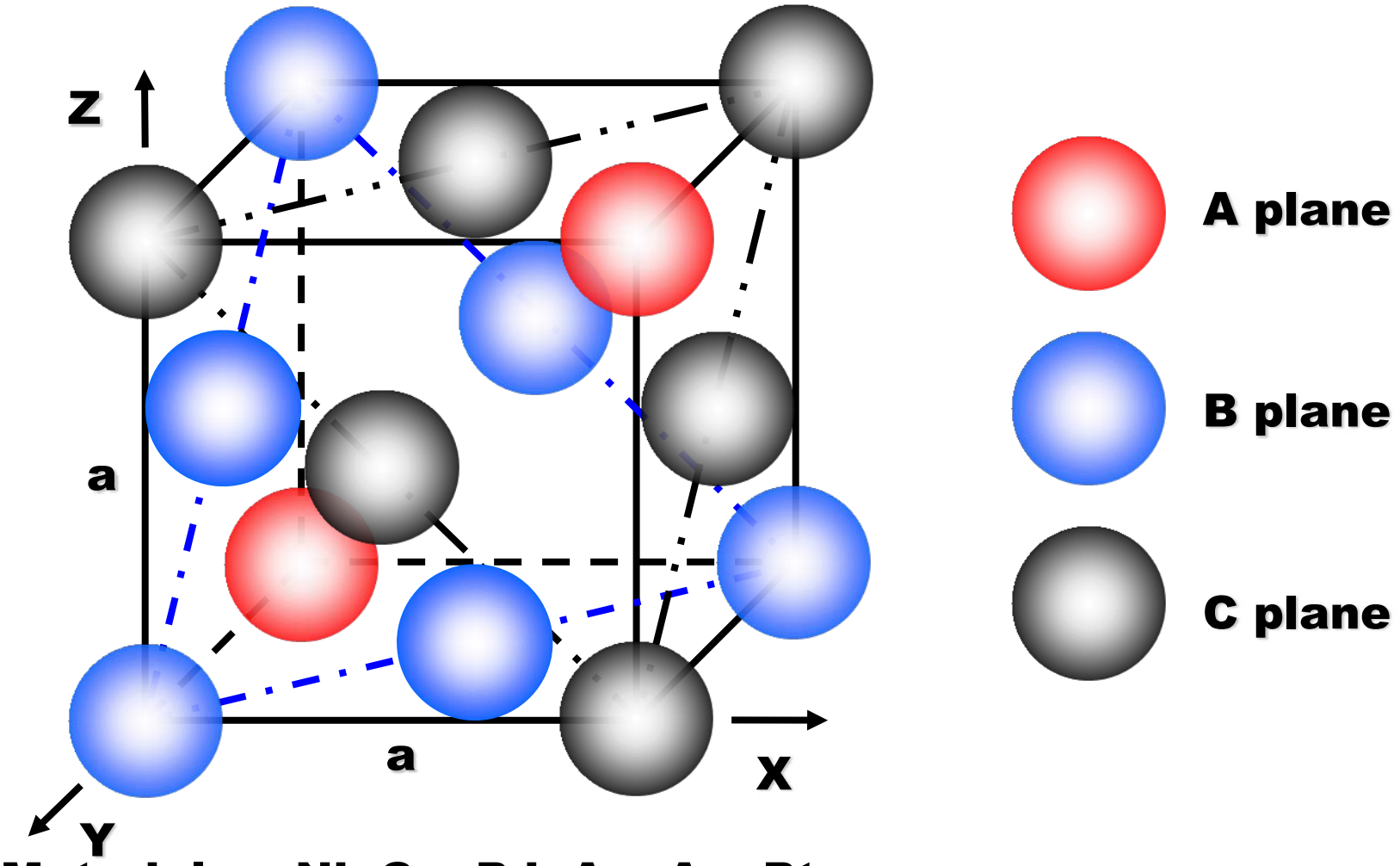
Unit cell of HCP :





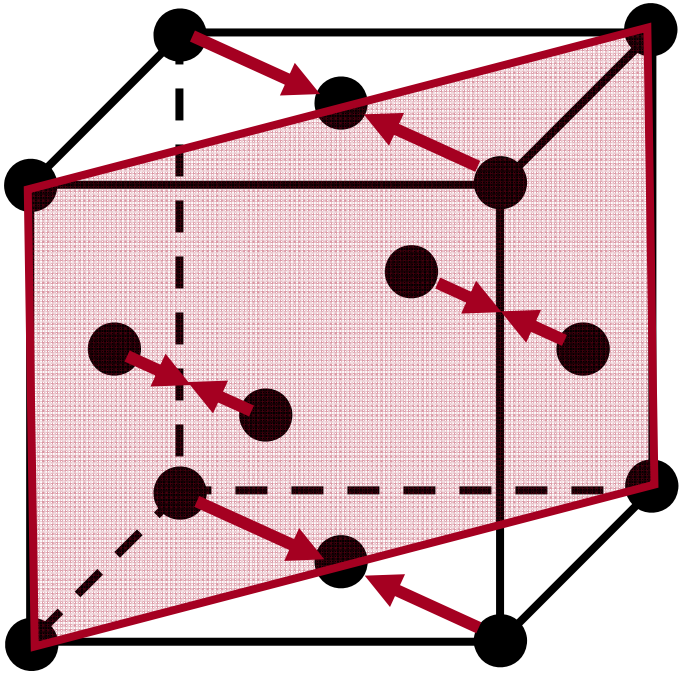
- **Materials : Mg, Ti, Co, Zn, Zr, ...**

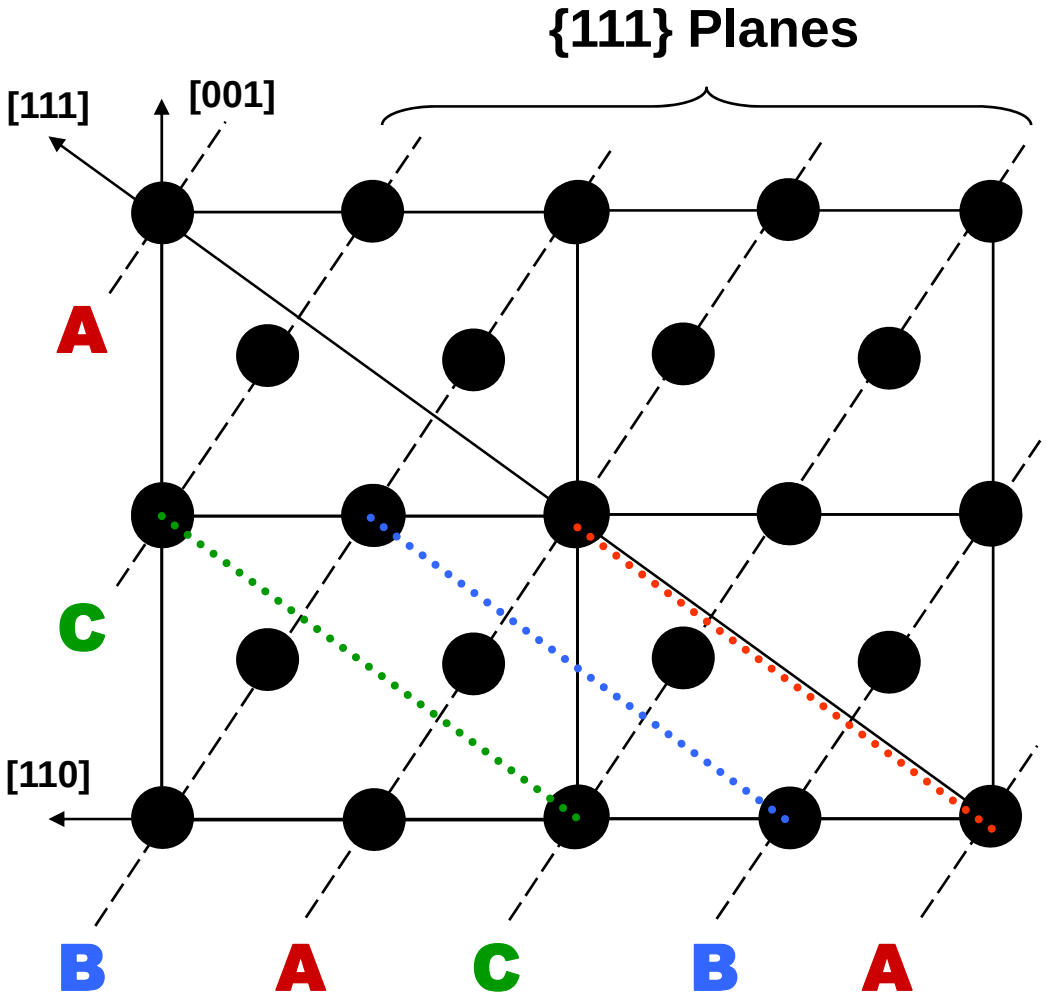
Unit cell of FCC :



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

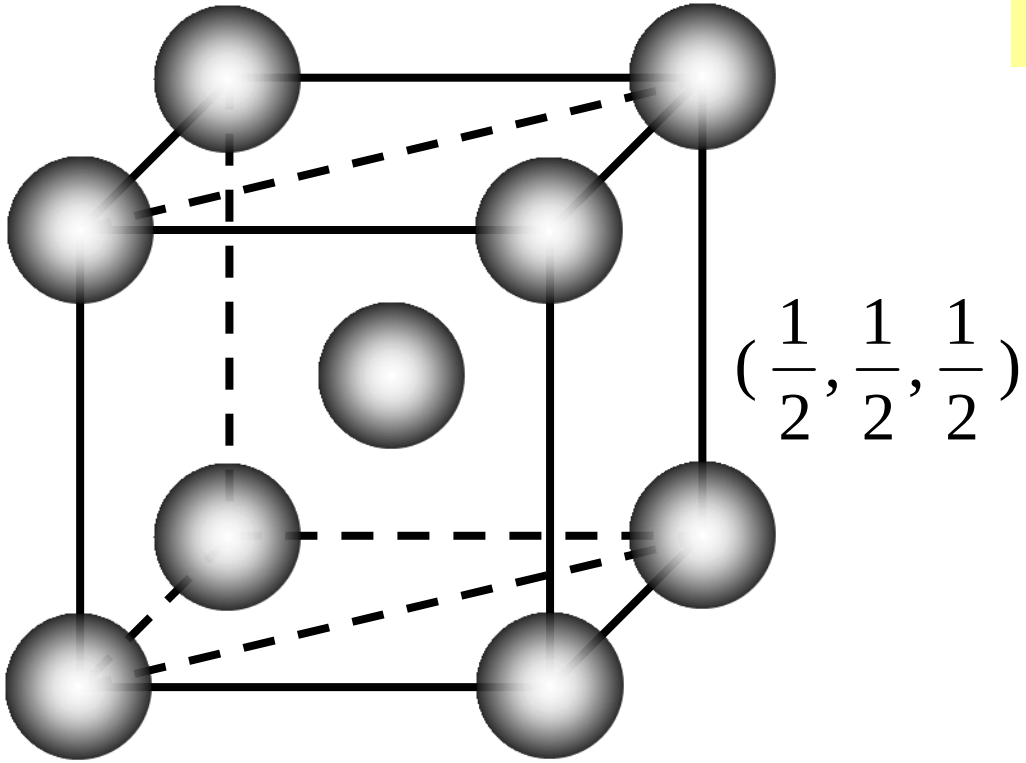
(110) plane projection of FCC :





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

Unit cell of BCC :



APF → 68 %

Intrinsically unfilled structure

↓

Bonding Directionality

↓

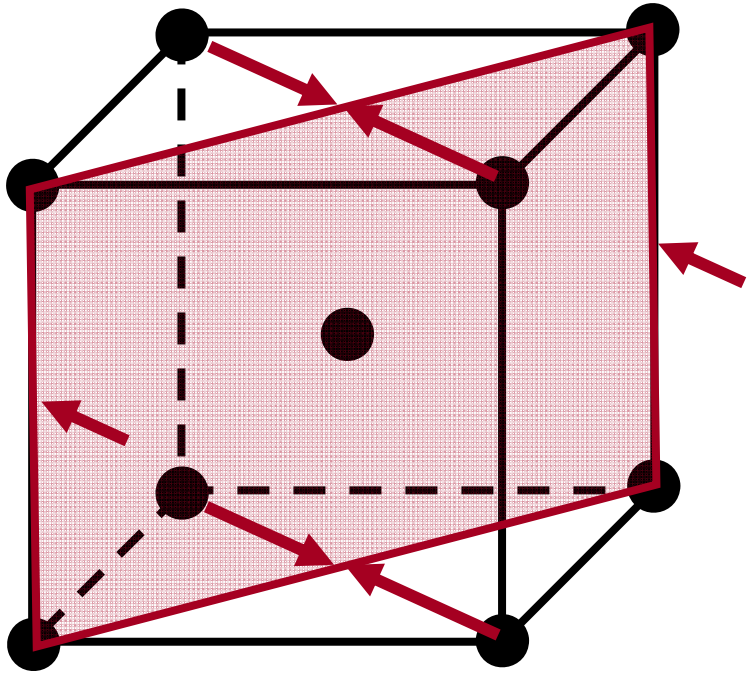
High E, T_m (?)

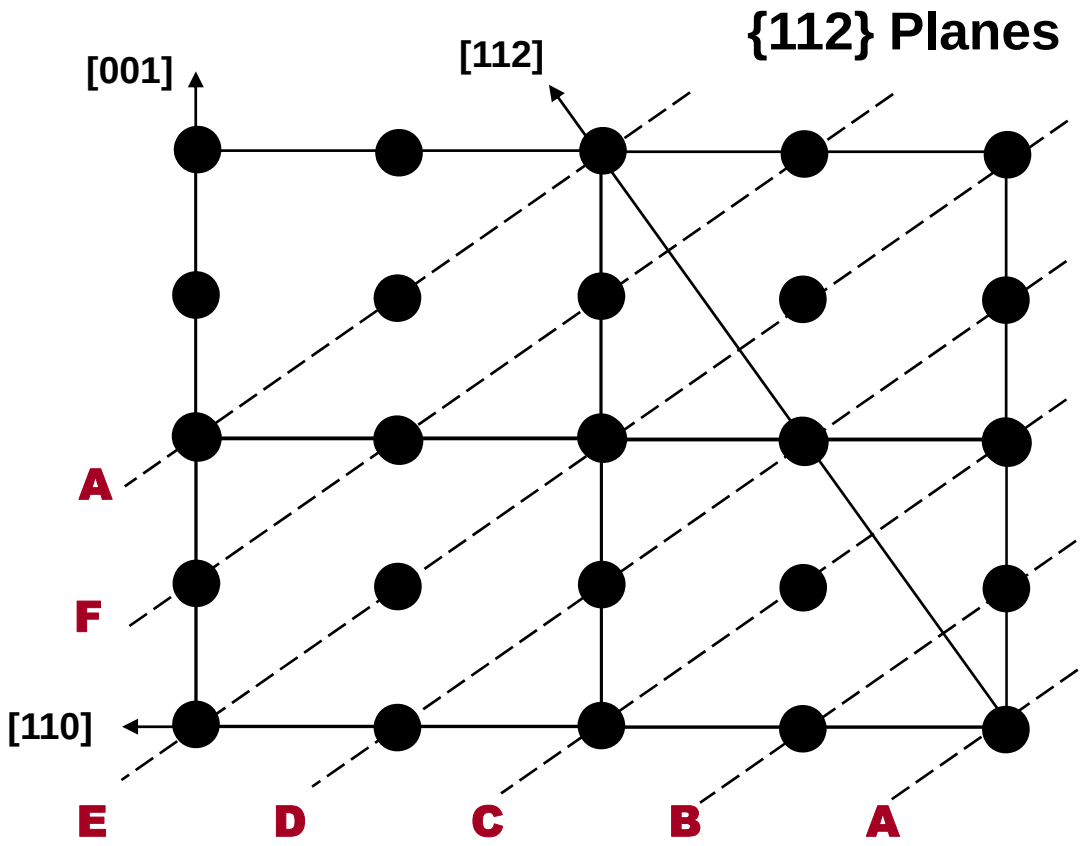
↓

Mostly transition metal

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

(110) plane projection of BCC :



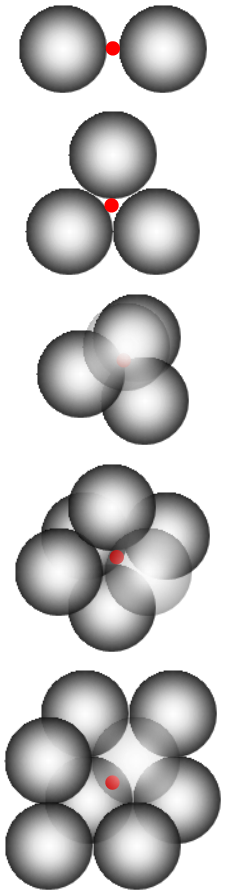


→ **Stacking sequence of BCC ; A B C D E F A B C D E F .....**

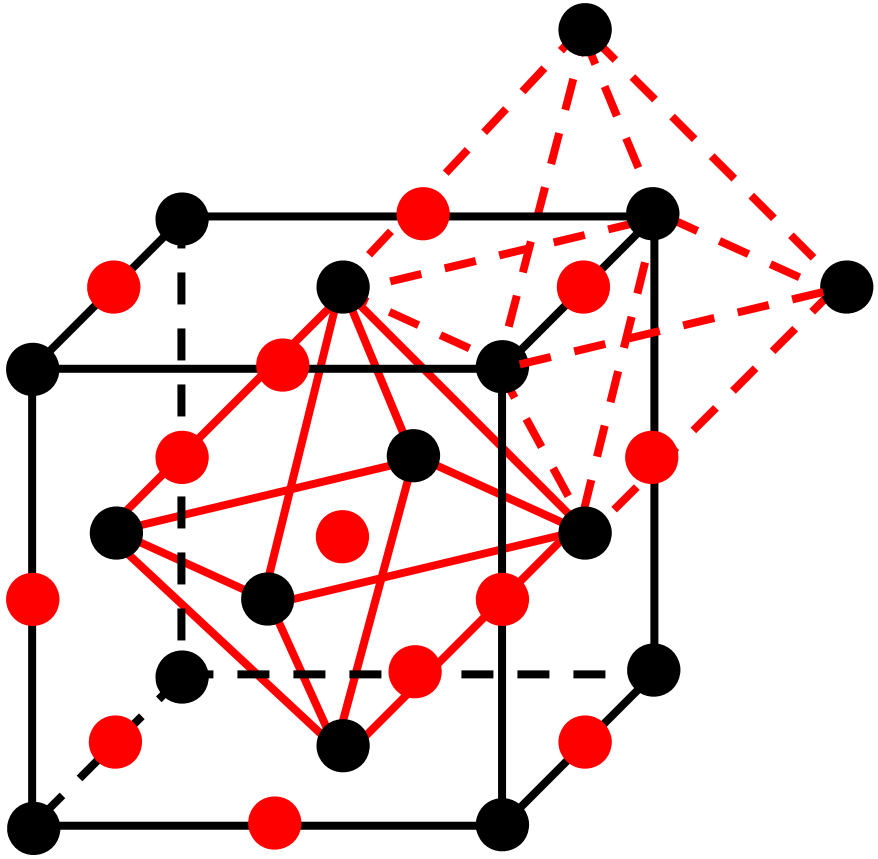
Interstitial Sites (Interstices)

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

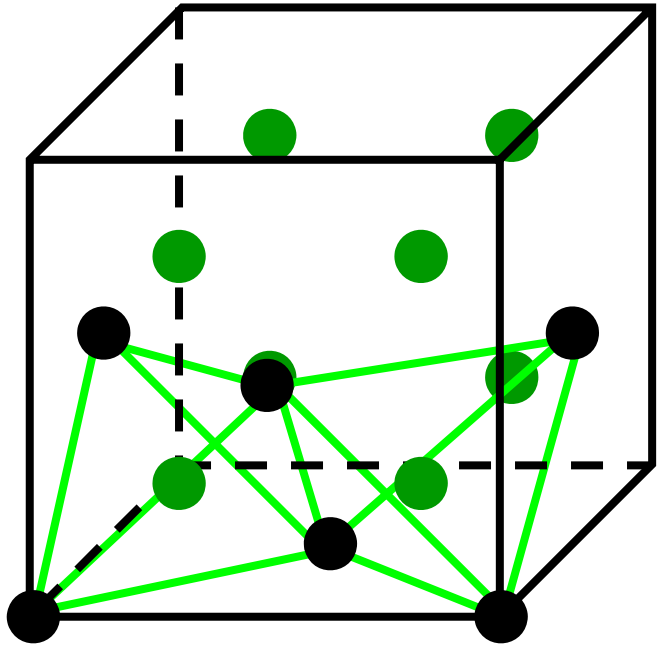
Geometry



Interstitial Sites ; FCC structure

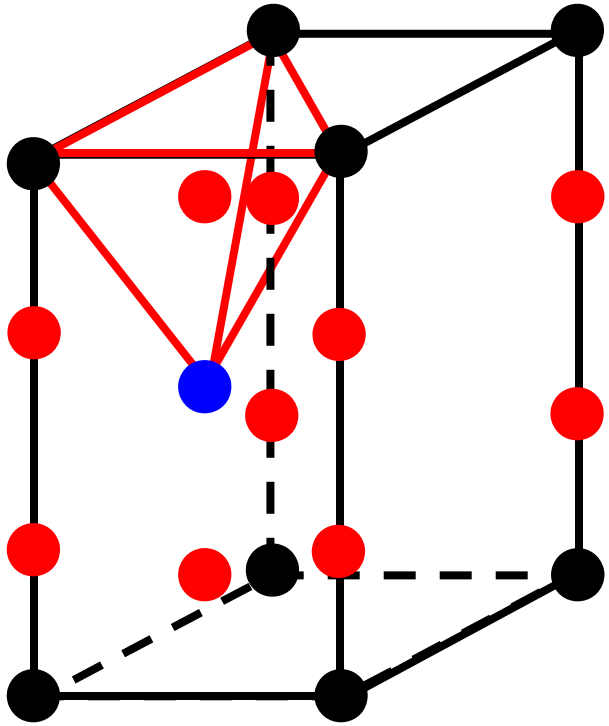


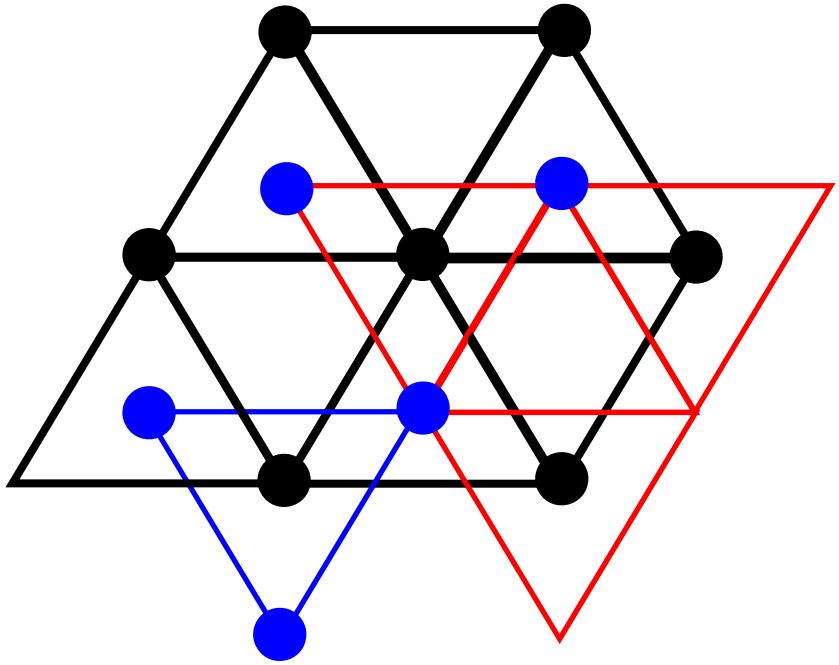
Octahedral sites ; 4



Tetrahedral sites ; 8

Interstitial Sites ; HCP

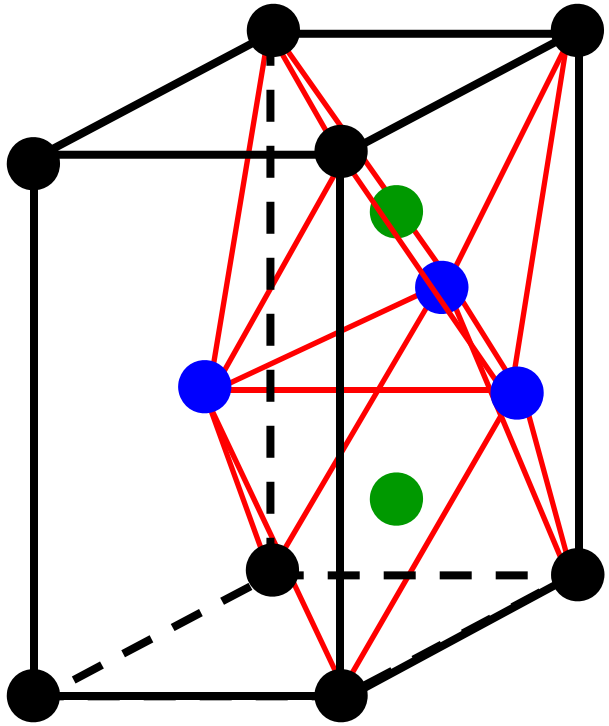


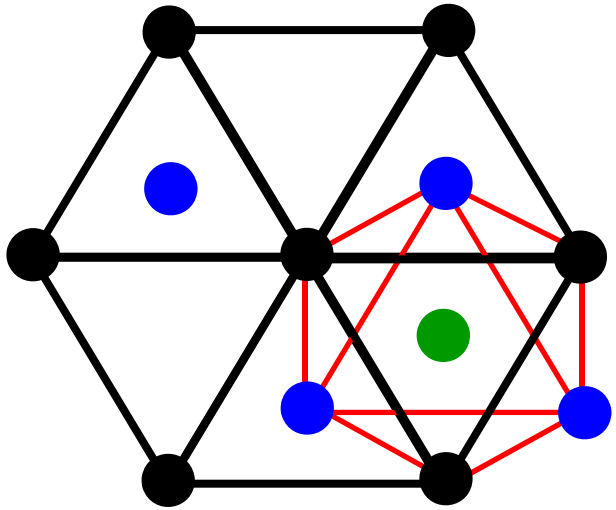


Tetrahedral sites ; 4

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

Interstitial Sites ; HCP

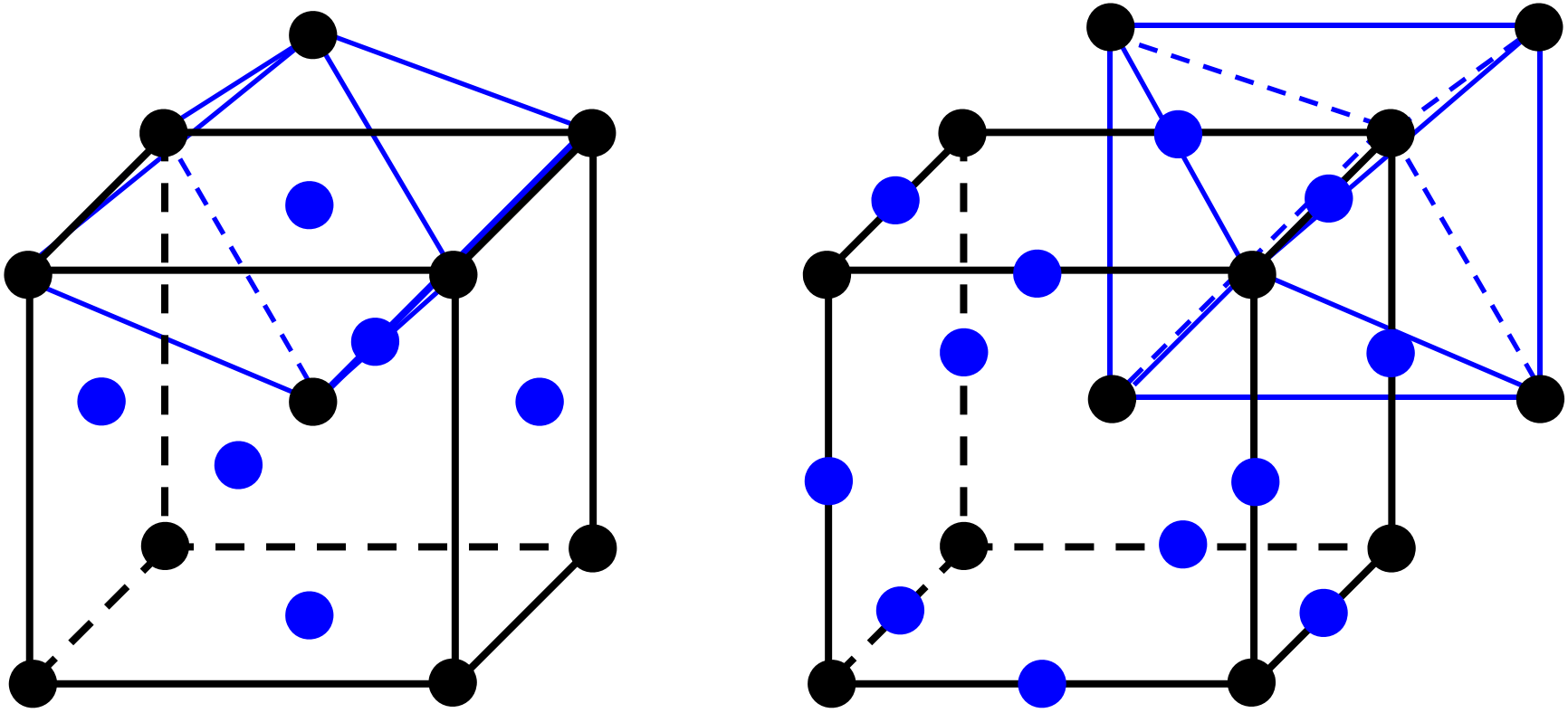




Octahedral sites ; 2

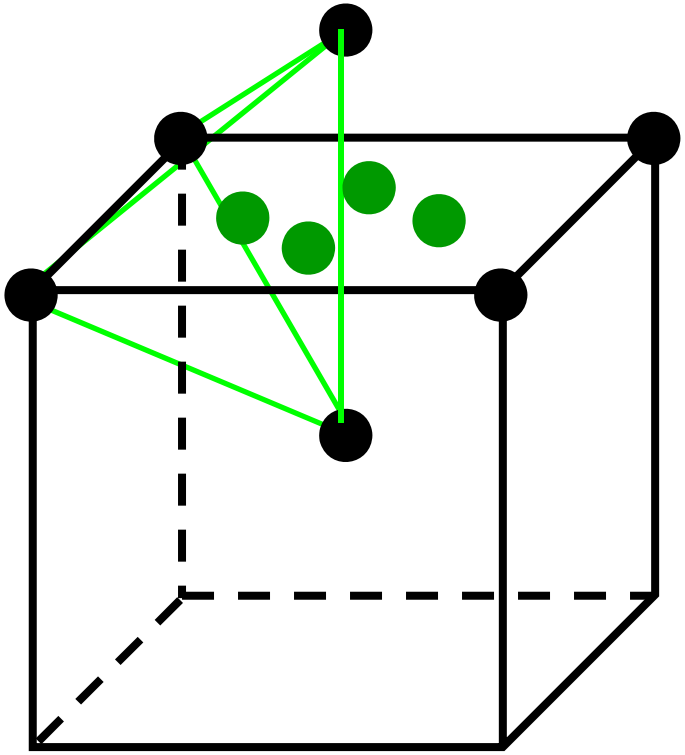
$$(\frac{2}{3},\frac{1}{3},\frac{1}{4}) \quad (\frac{2}{3},\frac{1}{3},\frac{3}{4})$$

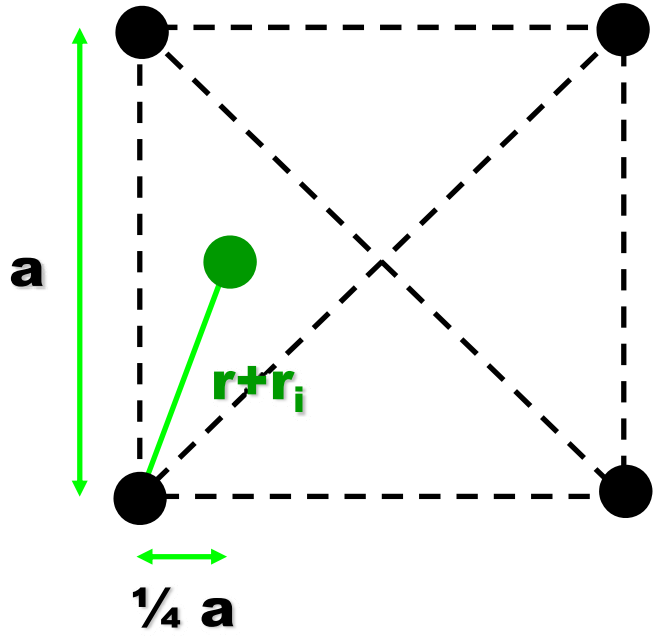
Interstitial Sites ; BCC



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

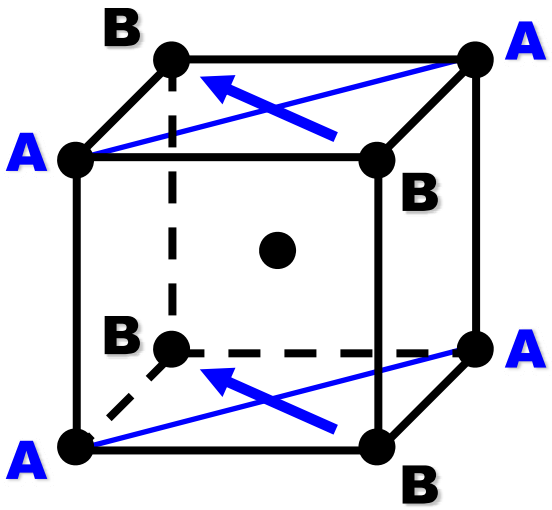
Temp. →

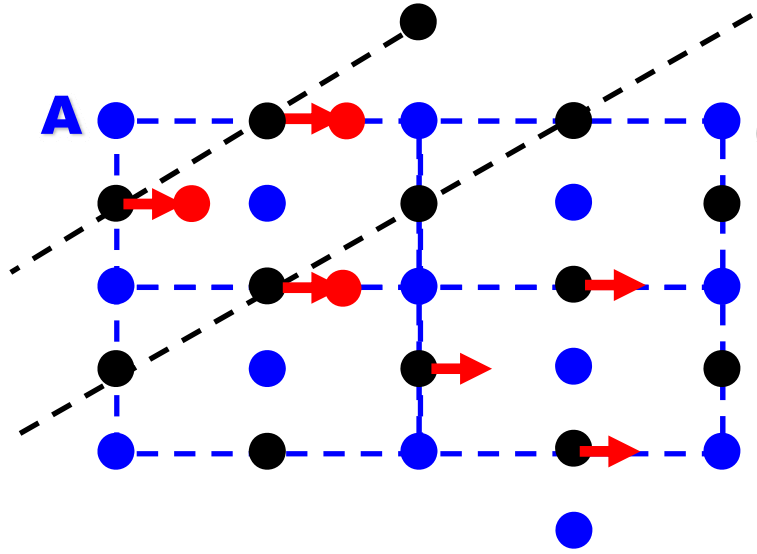
BCC

Temp. →

Liquid

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

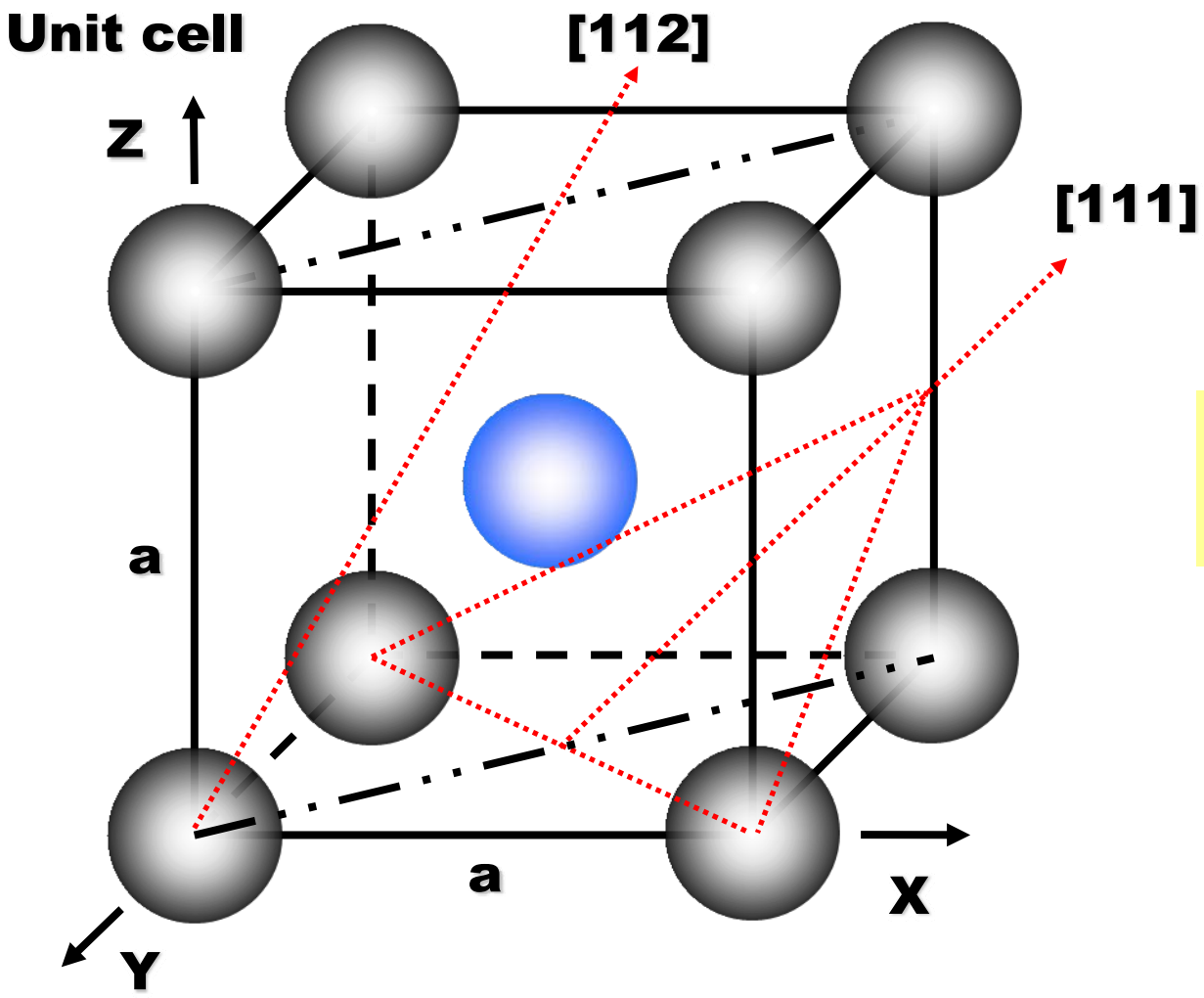




(110) projection
: ABABAB

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

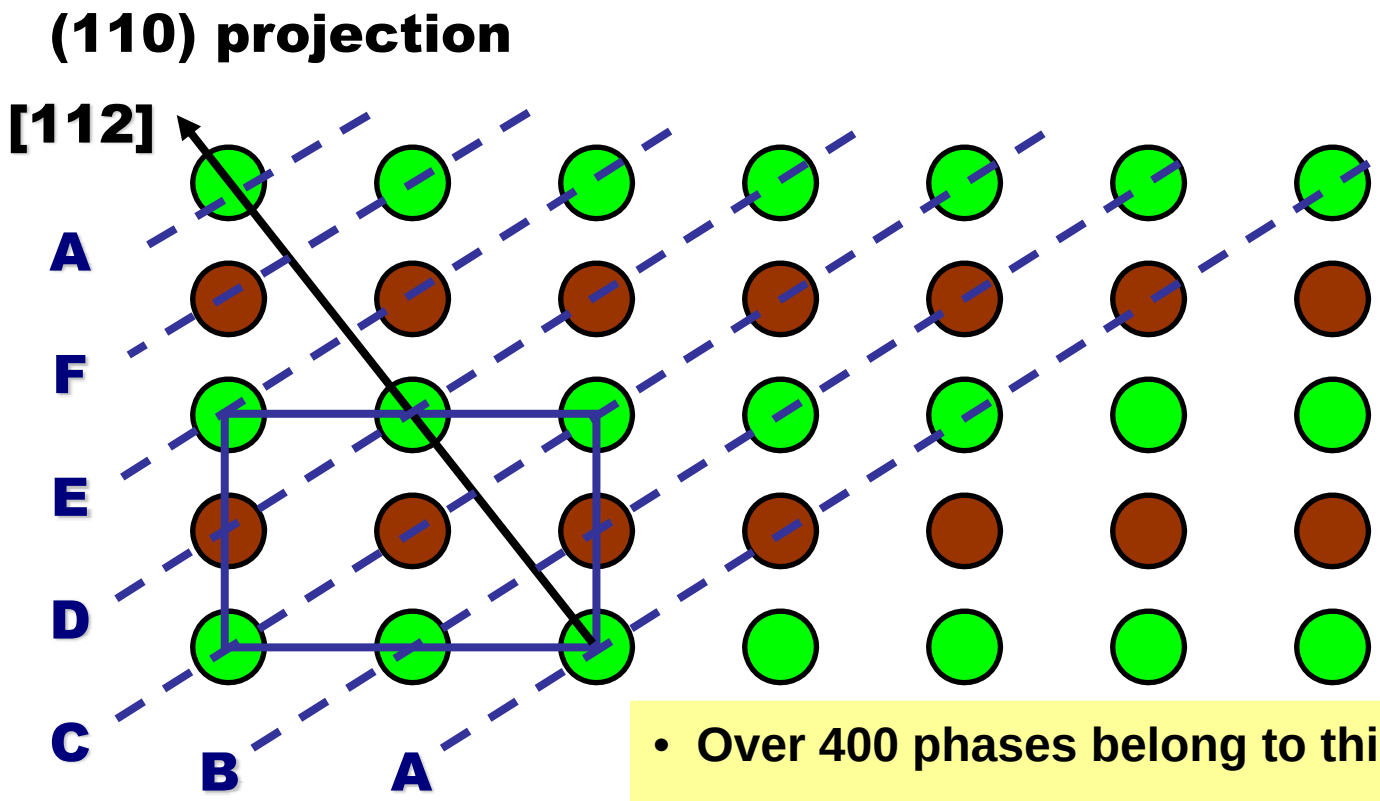
1. CsCl structure



Cs^+, Cl^- cubic interstitial

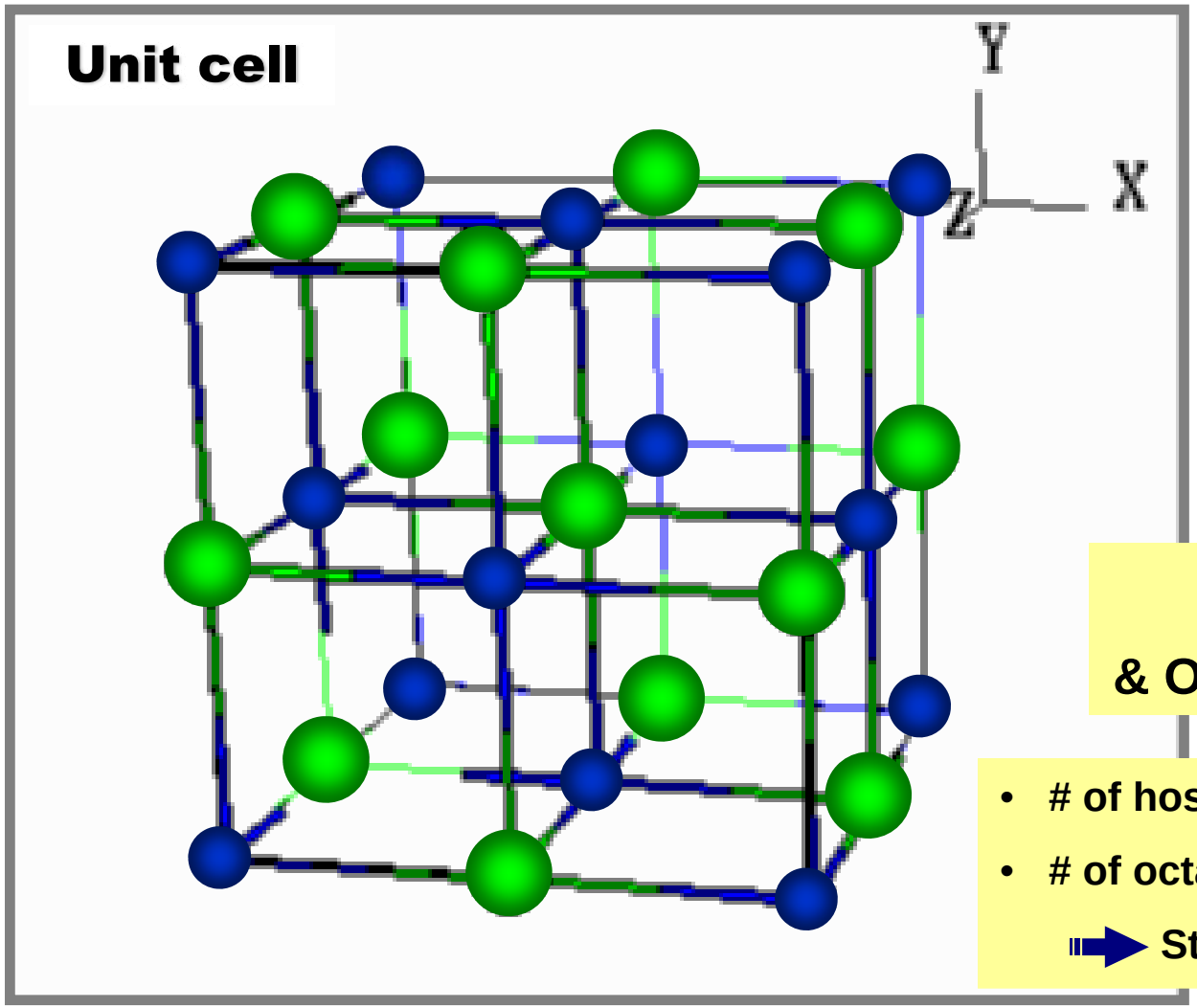
$r^+ / r^- \approx 0.732 \sim 1$

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

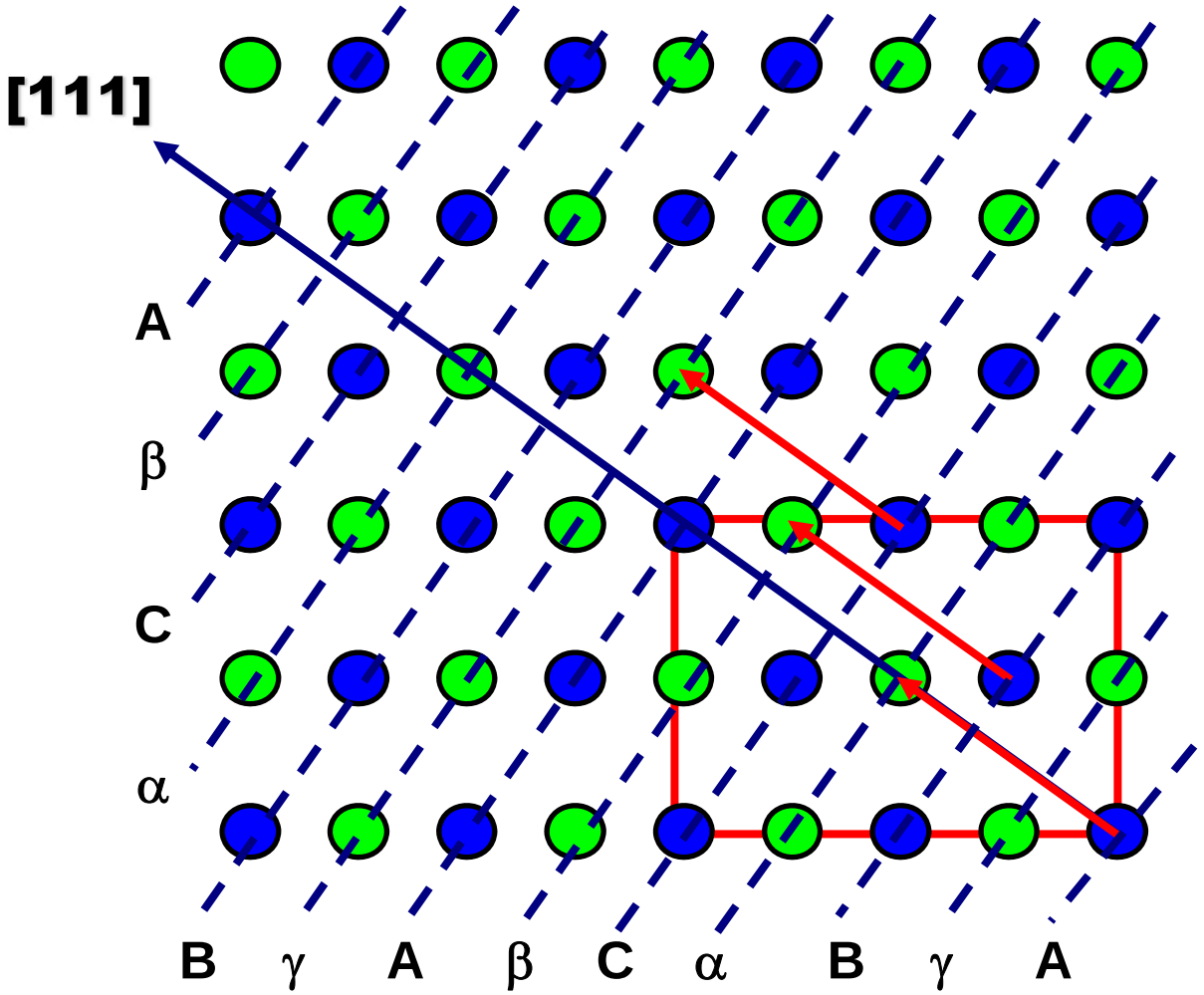
& Octahedral sites of cations

- **# 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)

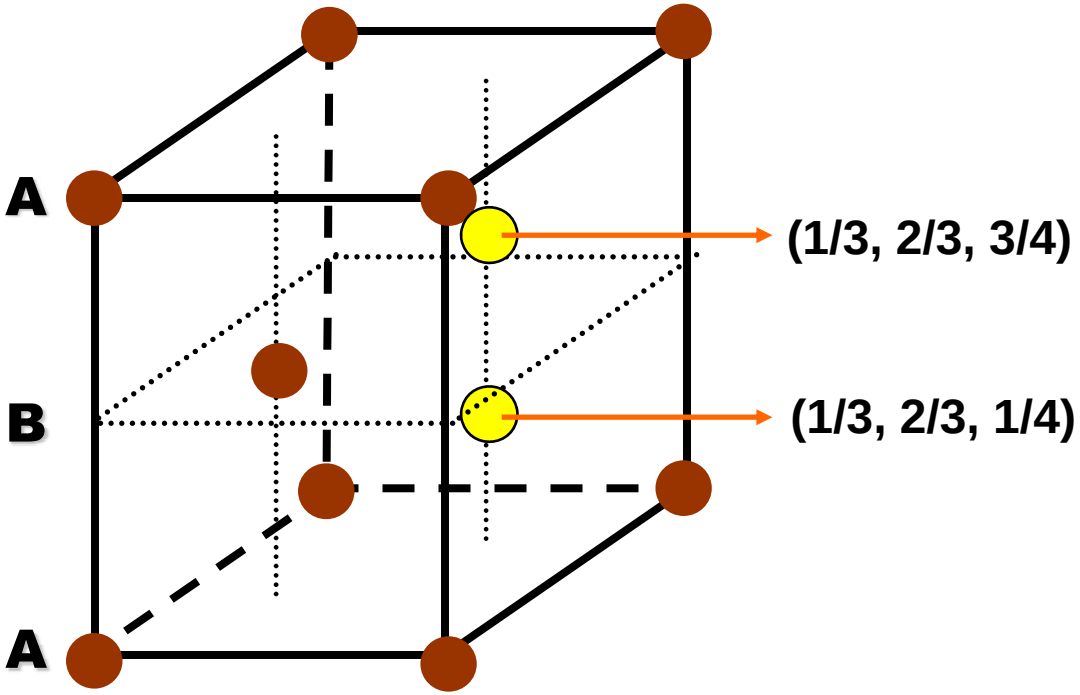


Stacking sequence :

A γ B α C β A γ B α C β …

(110) projection

3. NiAs structure



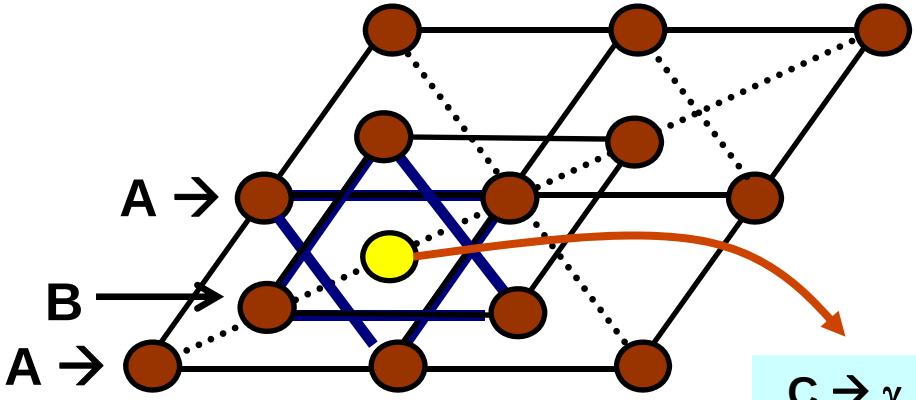
HCP array of Ni &

As occupying 2 octahedral sites

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

  ⇒ stoichiometry 1 : 1

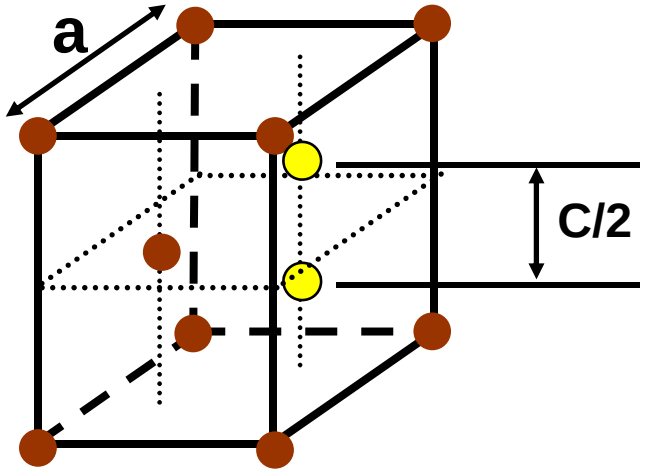
3. NiAs structure



Stacking sequence :

A γ B γ A γ B γ A γ B γ…

C → γ ; Octahedral position

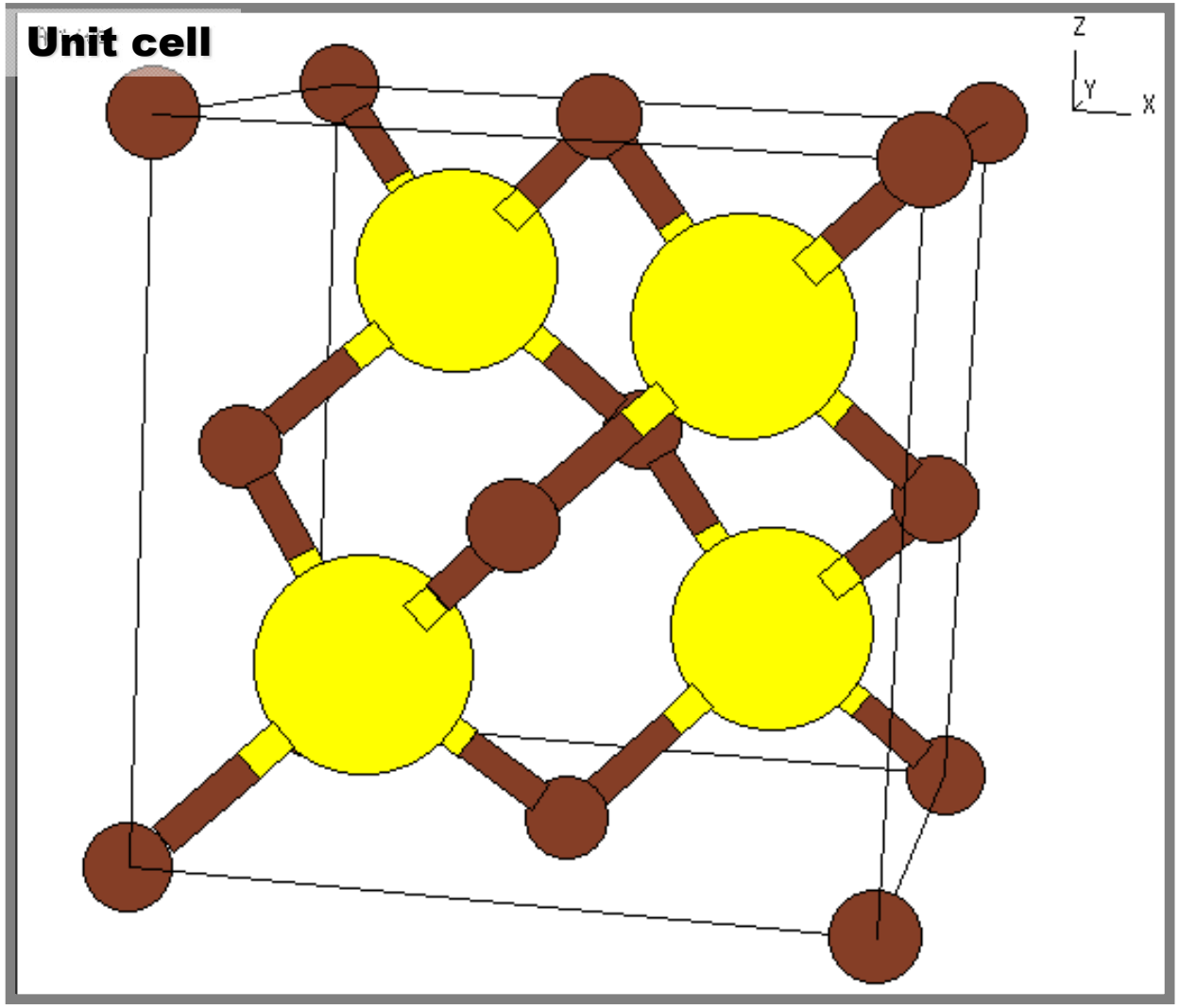


Distance between 2 cations :

internal compression effect between 2 metallic atoms

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

4. Zinc Blende structure (Sphalerite)

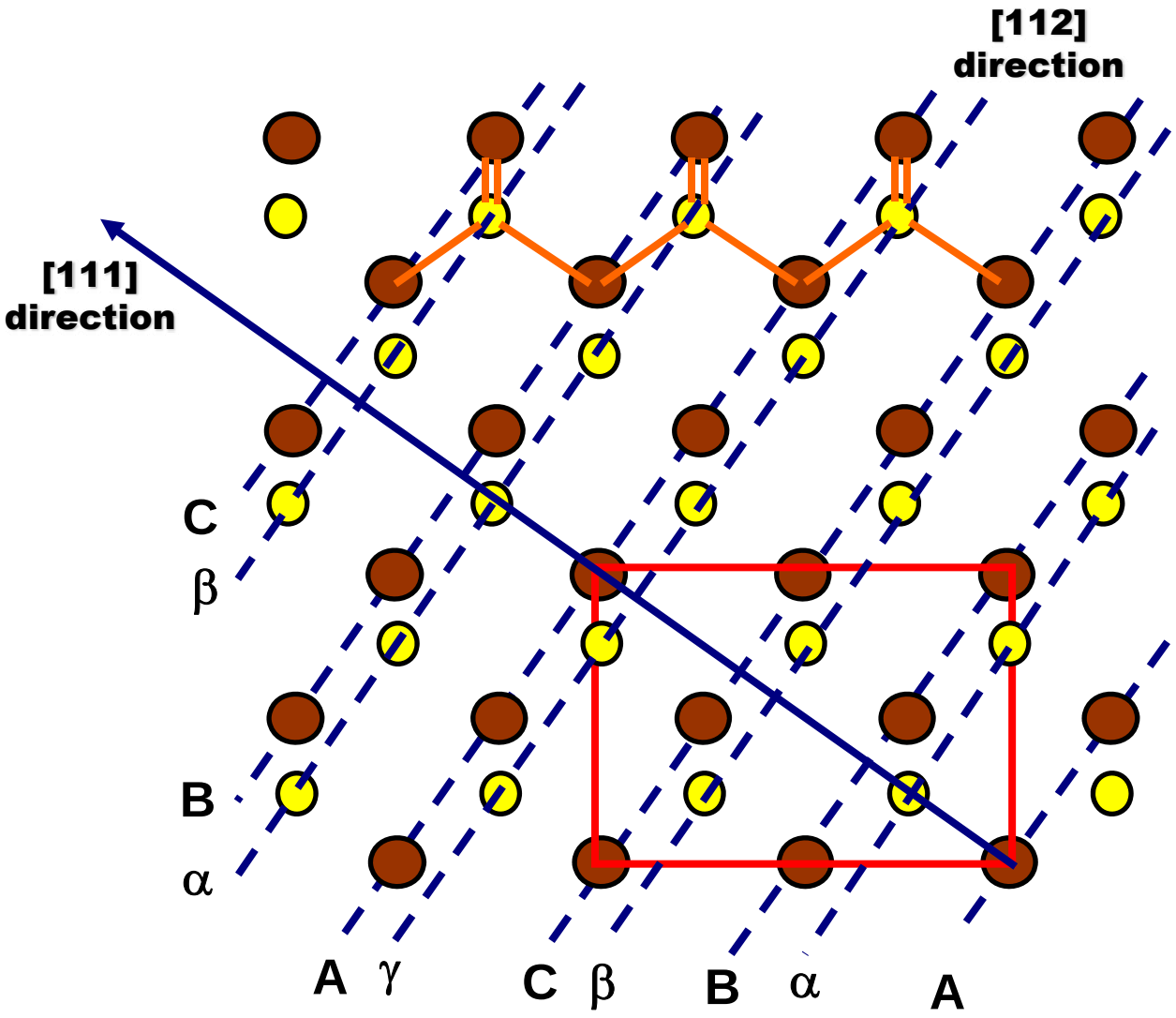


FCC array of S &
Zn occupying of
½ tetrahedral sites

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)

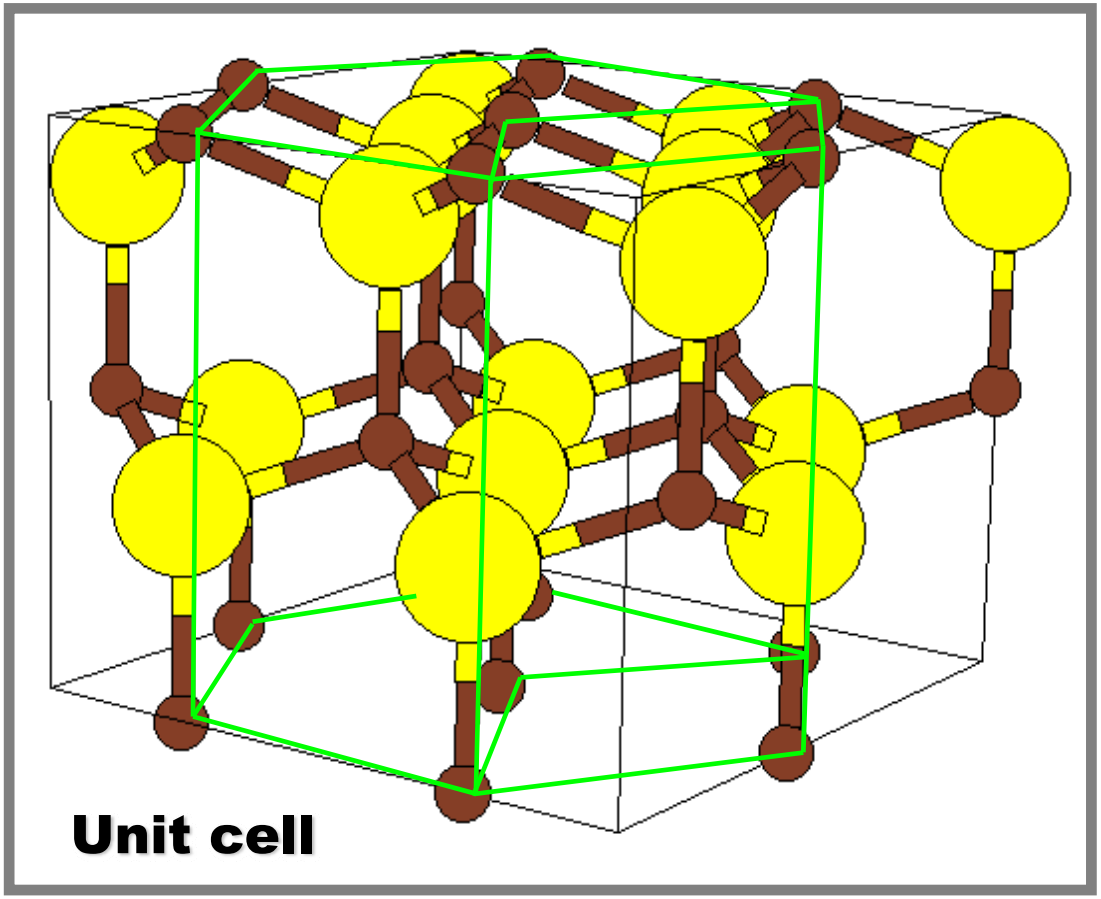


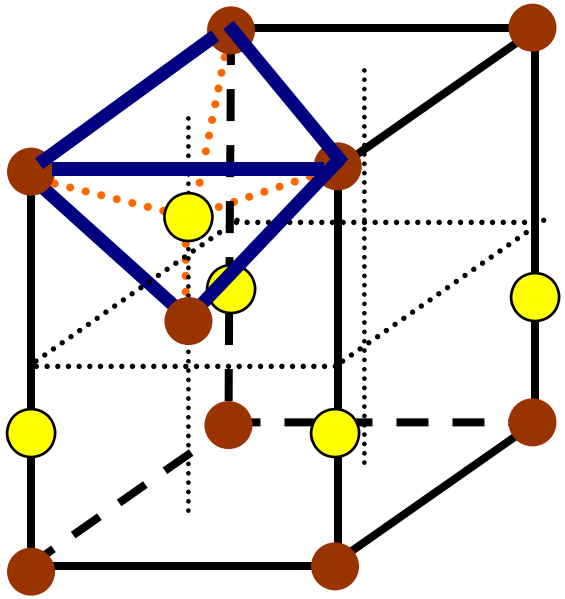
(110) projection

Stacking sequence :

A α B β C γ A α B β C γ …

5. Wurzite structure





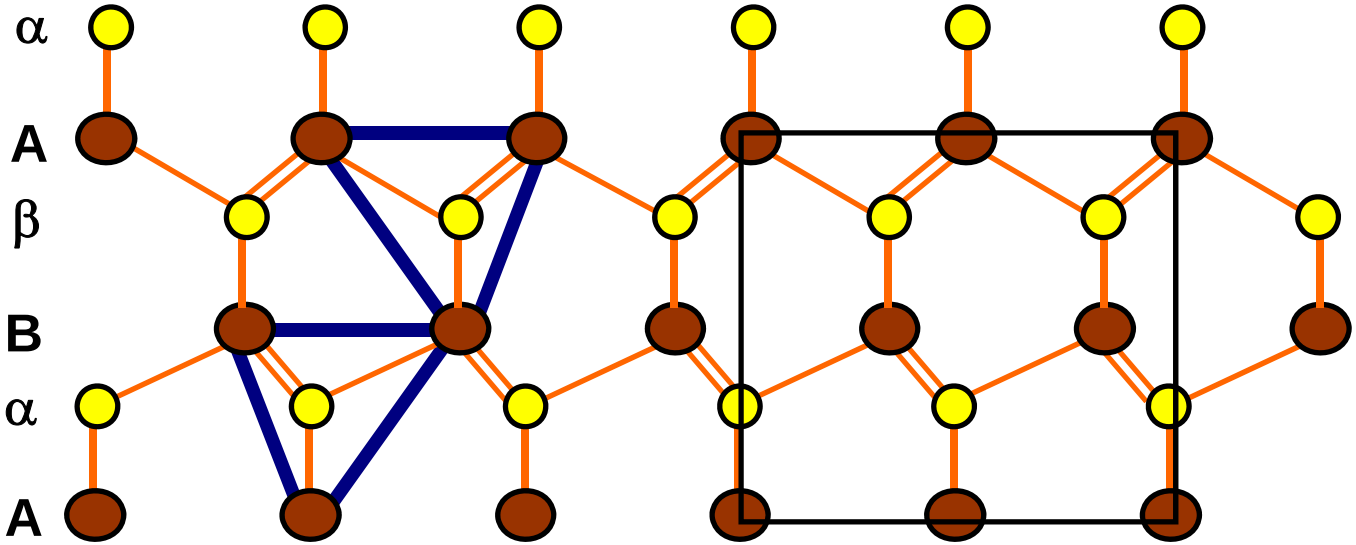
HCP array of S &

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



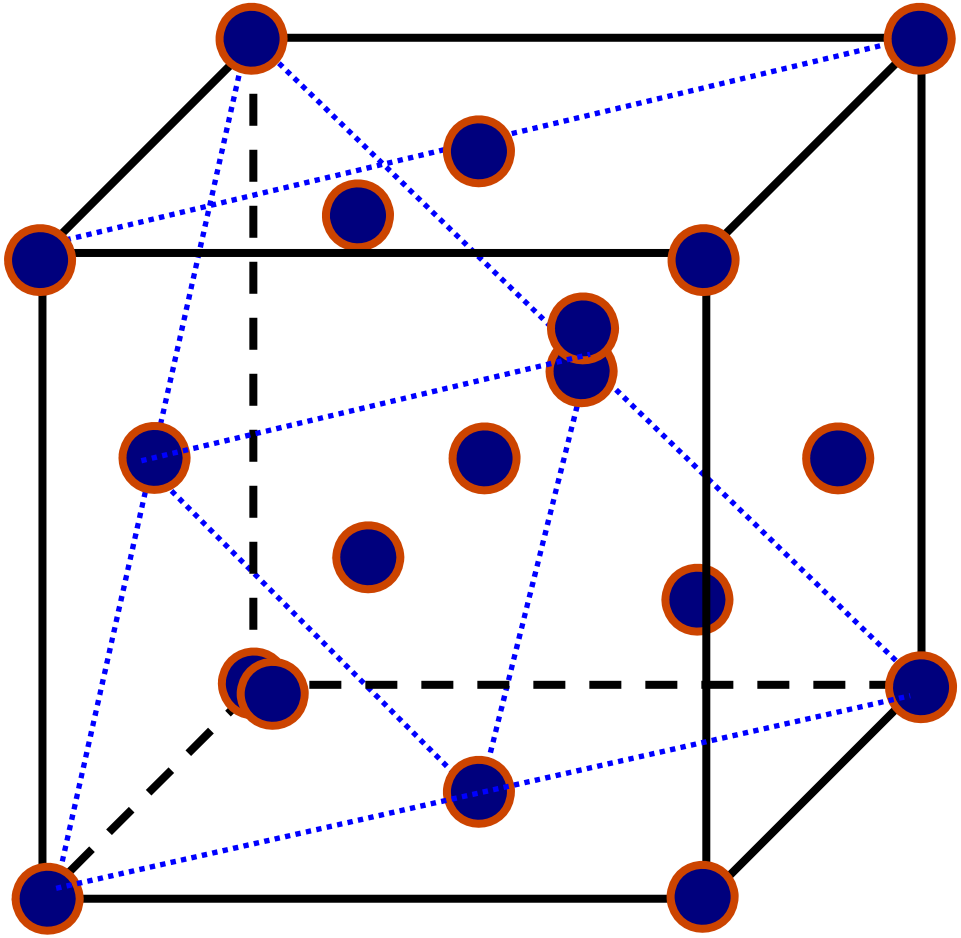
Stacking sequence :

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 &

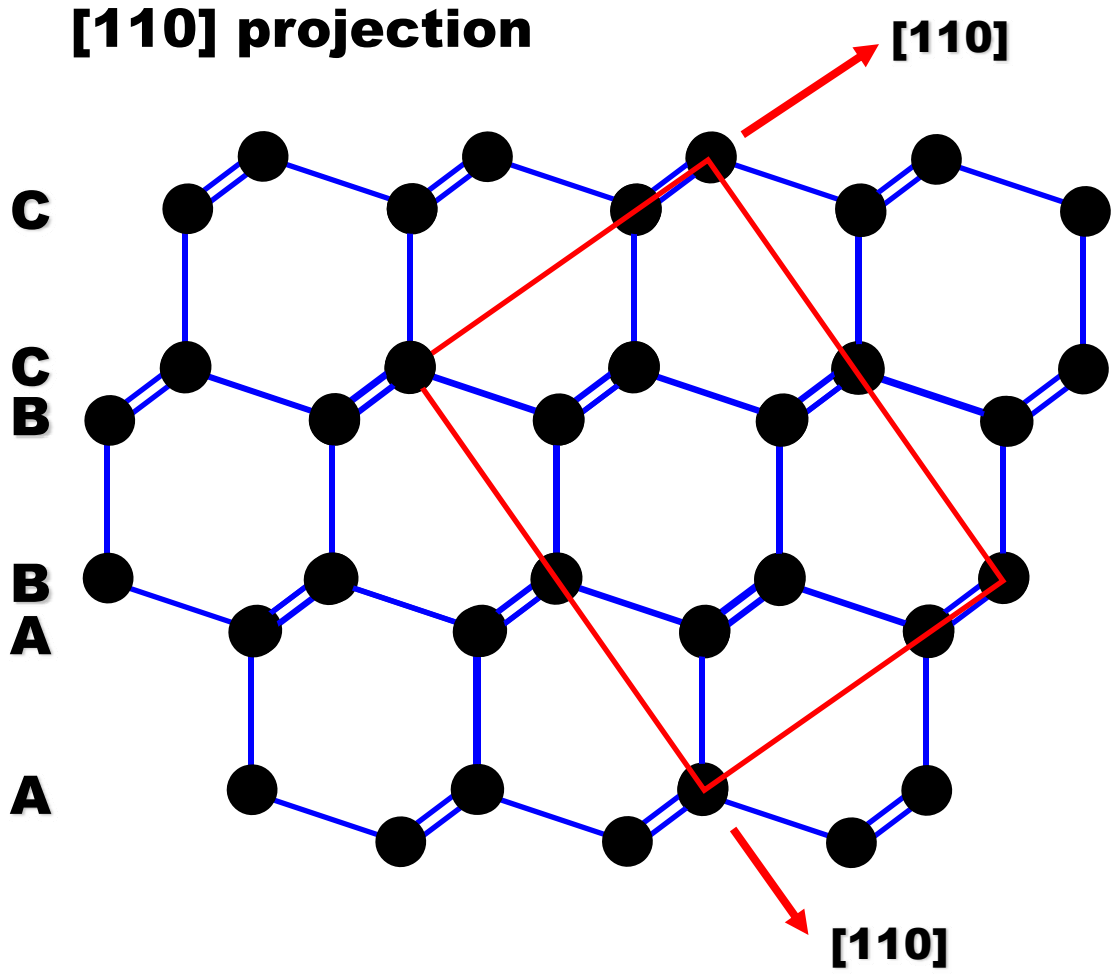
- ½ tetrahedral sites

Similar to Zinc blende

except that the same element

occupies tetrahedral sites

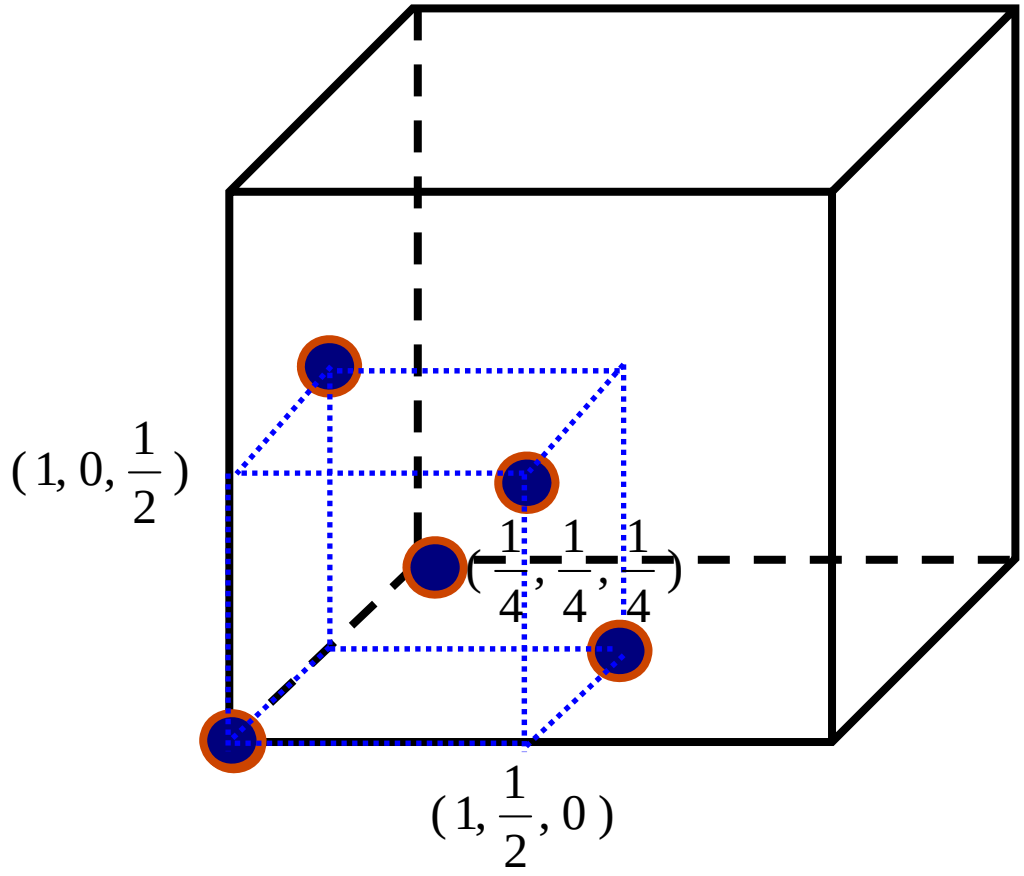
6. Diamond structure



Stacking sequence :

AABBCC AABBCC…

6. Diamond structure

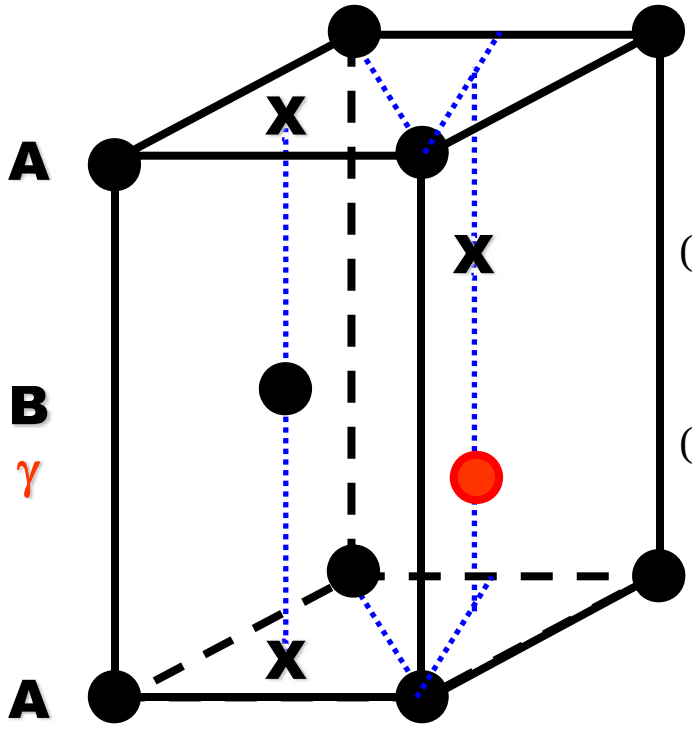


Coordination number : 4

Atomic Packing Factor : 34 %

→ ½ of BCC (why?)

7. CaI_2 structure



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

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

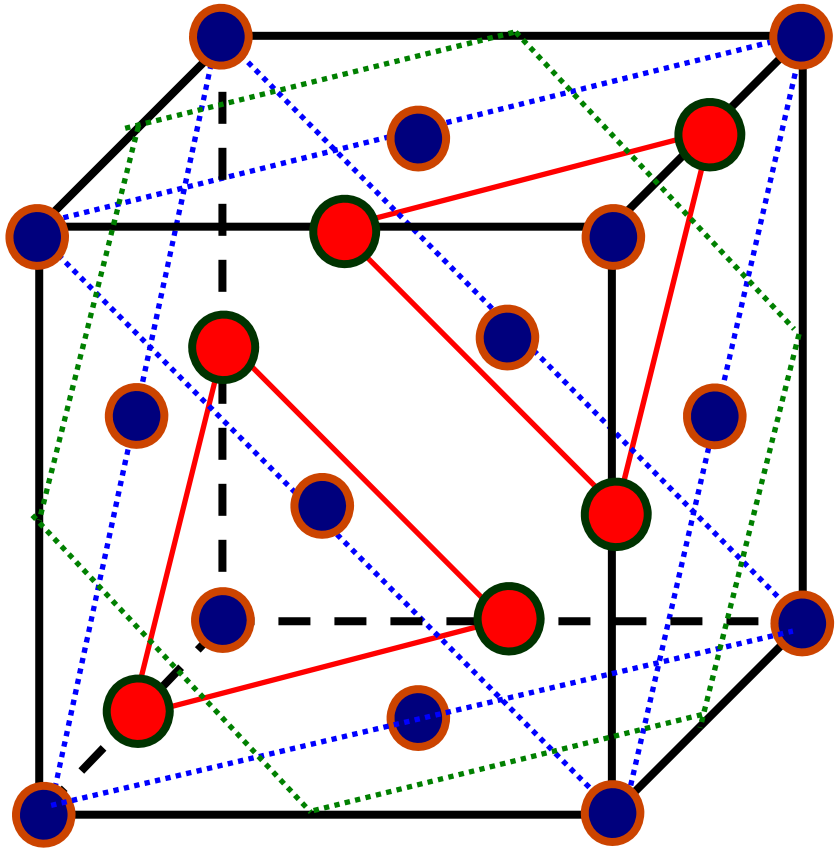
- HCP array of I
- Alternating layers of octahedral sites ; Ca

Stacking sequence :

A γ B A γ B A γ B ...

missing missing

8. $CdCl_2$ structure



- **FCC array of Cl**$^{-}$
- **Alternating Cd layers in octahedral position ; Ca**

Stacking sequence :

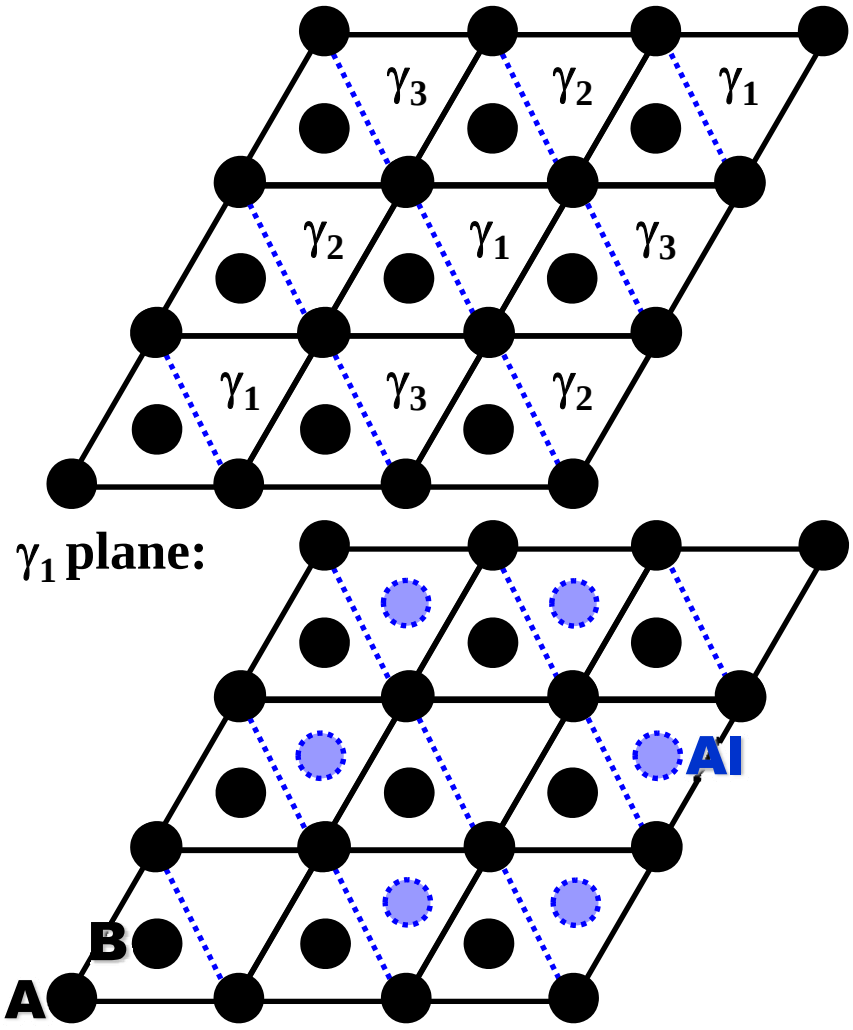
A γ B α C β A γ B α C β A γ B α C β A γ B α C

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)



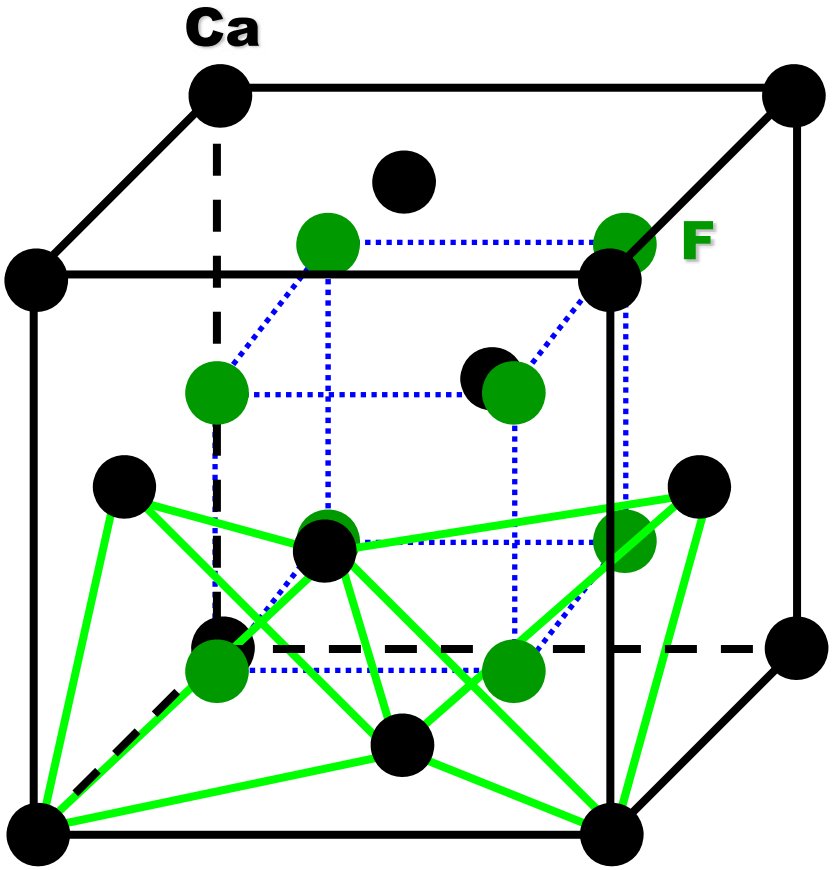
- **HCP array of oxygen ions**
- **Al^{+++} : 2/3 of available octahedral sites**

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