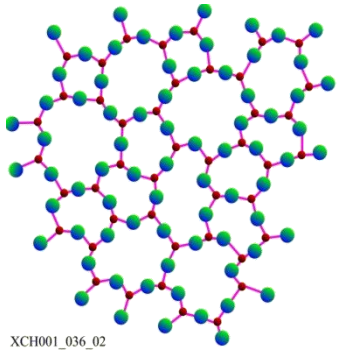
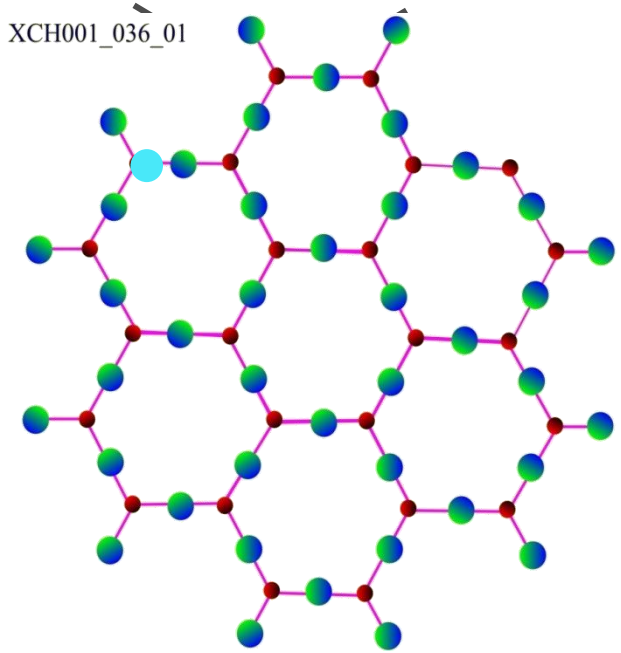
Chapter 1 Formation of crystal

· Basic concept

Amorphous (Non-crystalline) Solid
All atoms have order only within a few atomic or molecular dimensions. --- random arrangement in a bigger size



Crystal
All atoms or molecules in the solid have a regular geometric arrangement or periodicity. --- highly ordered

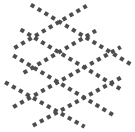
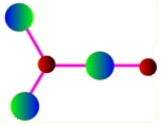


Periodicity
The quality of recurring at regular intervals.

Basis
Repeatable structure units.

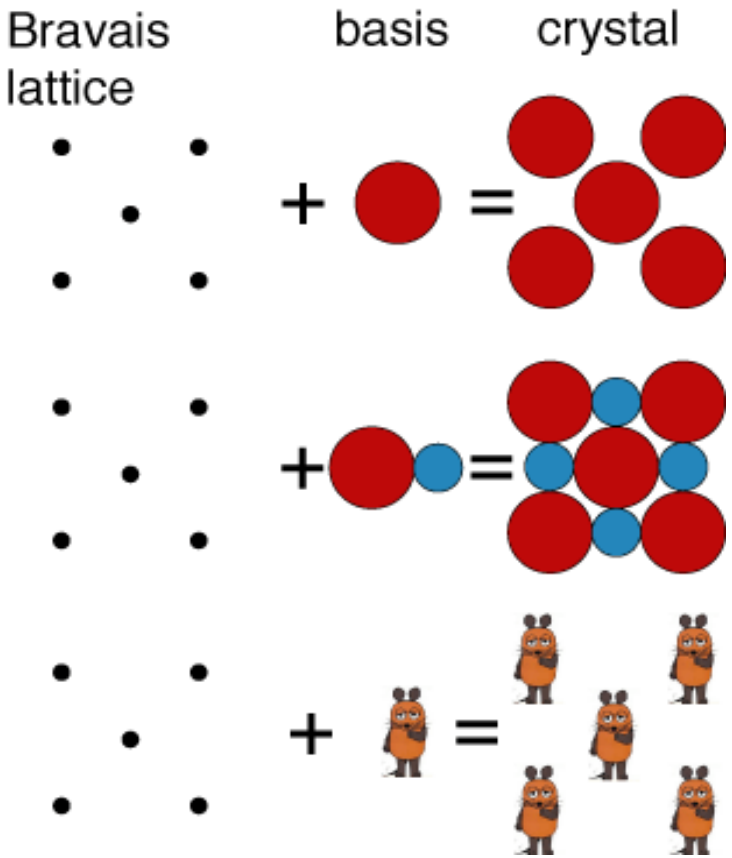
Lattice site
The dot representing a basis.

Lattice (Crystal lattice)
Geometric pattern of crystal structure

Crystal Structure = Lattice  **+ Basis** 

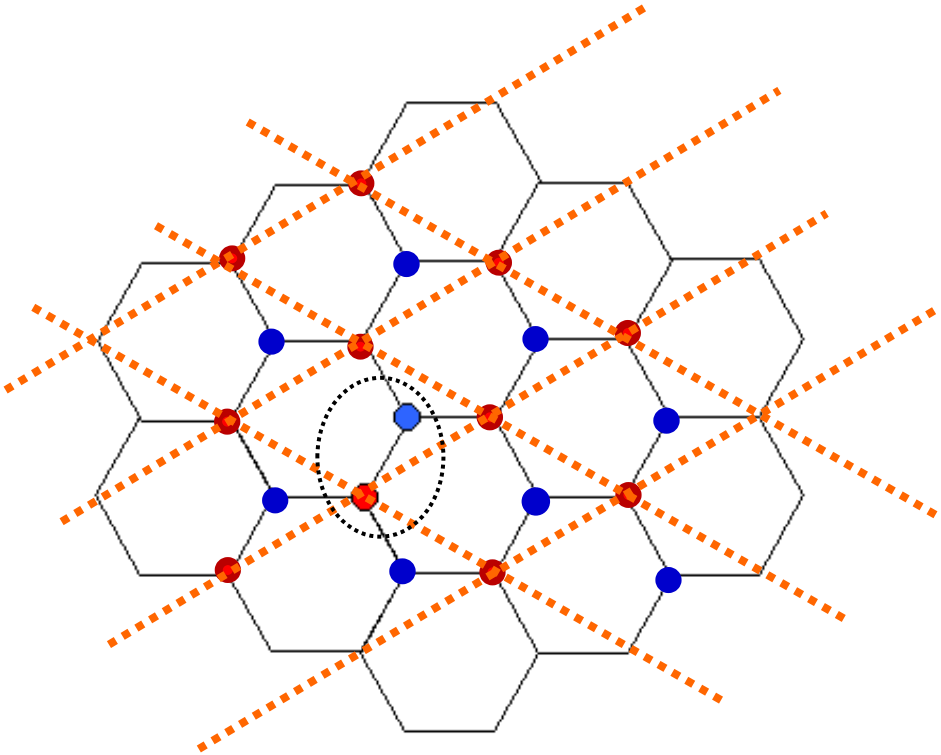
Barvais Lattice

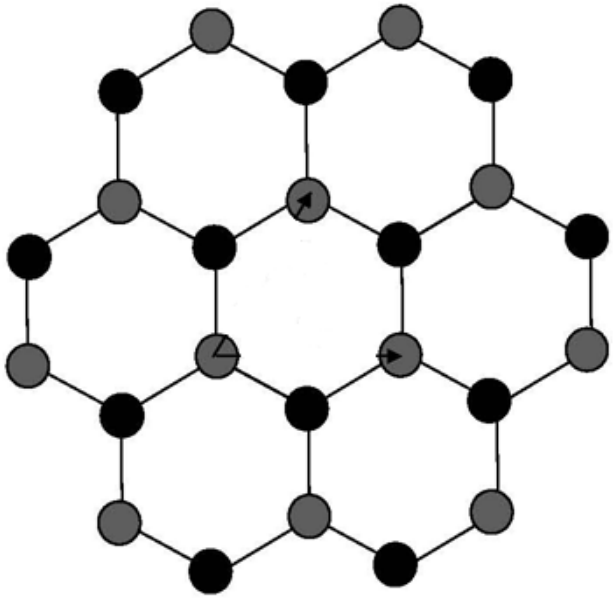
- **Barvais Lattice:** all points of the lattice is identical.
- For a crystal,
  - **Bravais lattice :** the geometric pattern of basis' arrangement.
  - **Lattice point:** the dot representing a basis.



- Bravais lattice only summarizes the geometry of crystals, regardless of what the actual units may be.
- The basis consists of the atoms, their spaces and bond angles.

How to analyze a honeycomb lattice ?





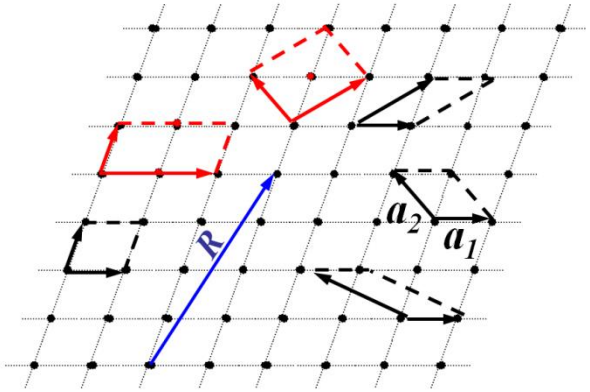
Honeycomb Lattice
(Graphite or BN layer)

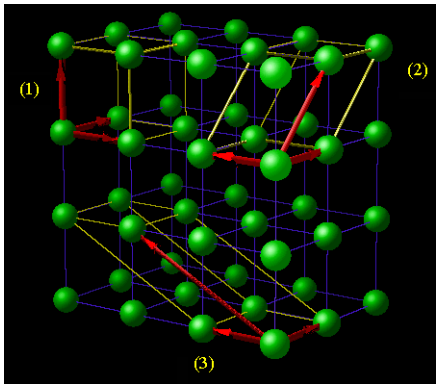
· Basic concept

Bravais lattice

The geometric pattern of basis' arrangement.
All points of the lattice is identical.

Primitive vectors 基矢, position vectors 格矢





$$\mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 \qquad \mathbf{R} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3$$

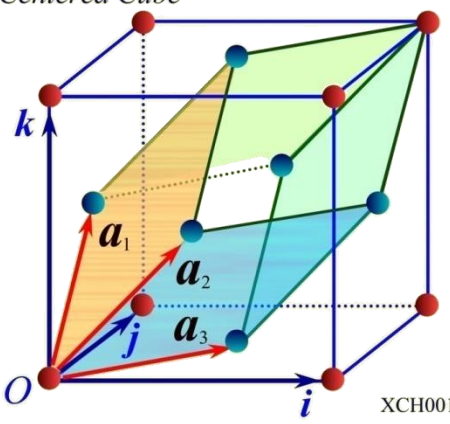
Primitive unit cell

A set of shortest vectors making the unit cell with a smallest volume

Conventional unit cell

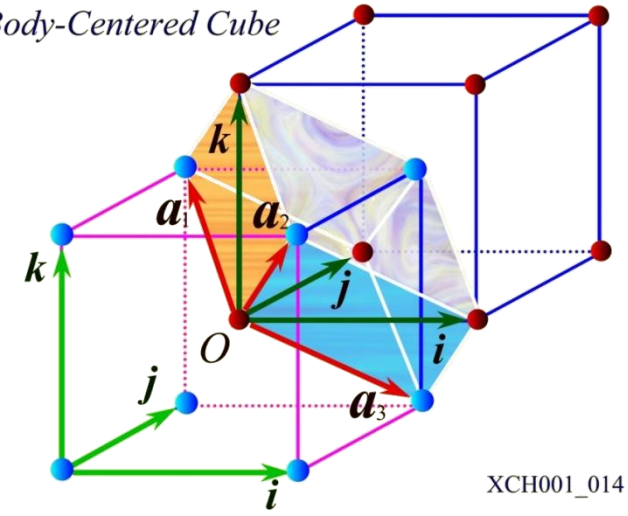
A set of vectors making the unit cell with a highest symmetry

Face-Centered Cube



$$\mathbf{a}_1 = \frac{1}{2}a(\mathbf{j}+\mathbf{k}), \mathbf{a}_2 = \frac{1}{2}a(\mathbf{k}+\mathbf{i}), \mathbf{a}_3 = \frac{1}{2}a(\mathbf{i}+\mathbf{j})$$

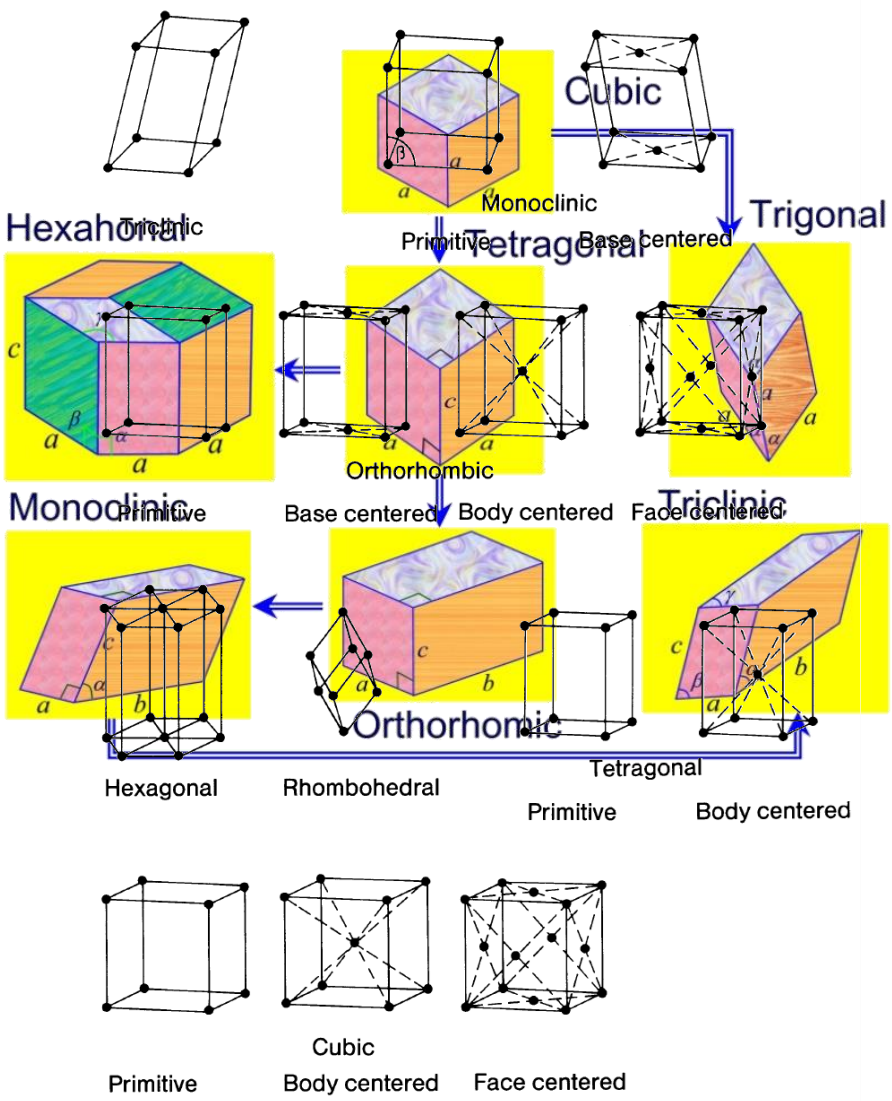
Body-Centered Cube



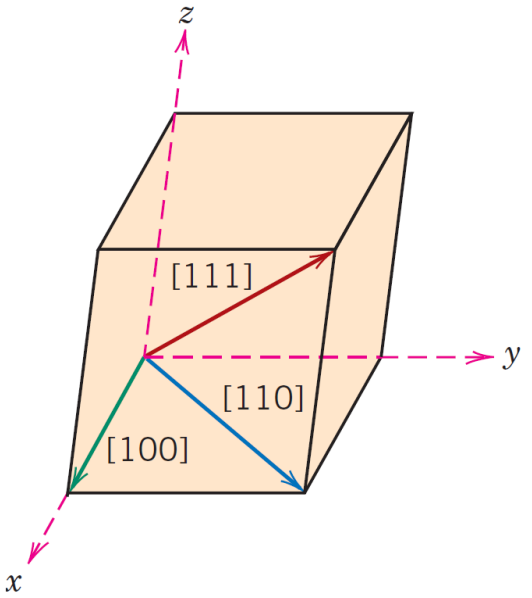
$$\mathbf{a}_1 = \frac{1}{2}a(\mathbf{j}+\mathbf{k}-\mathbf{i}), \mathbf{a}_2 = \frac{1}{2}a(\mathbf{k}+\mathbf{i}-\mathbf{j}), \mathbf{a}_3 = \frac{1}{2}a(\mathbf{i}+\mathbf{j}-)\mathbf{k}$$

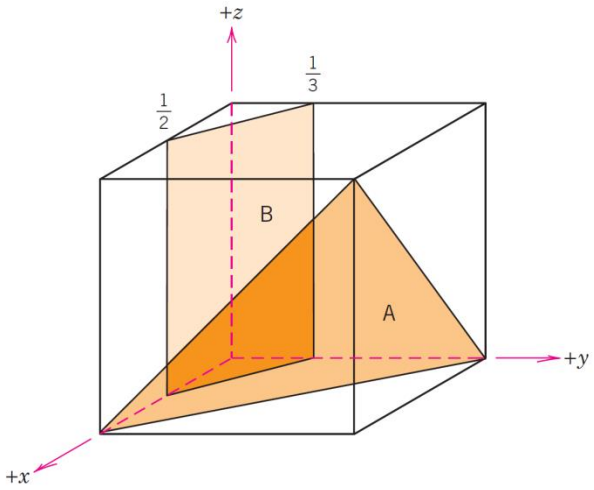
· Basic concept

Bravais lattice



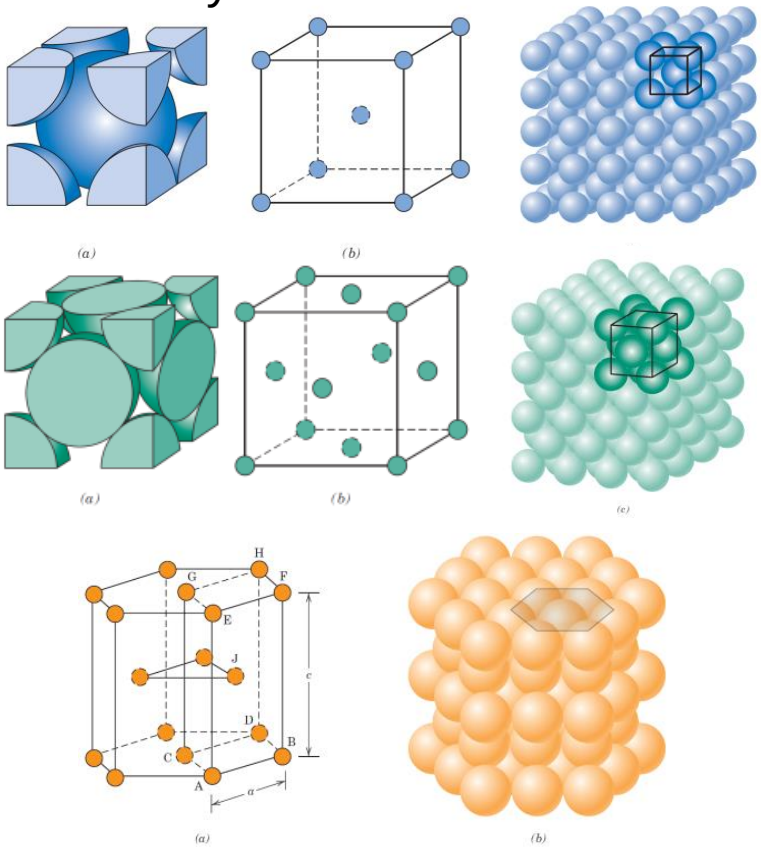
Crystal direction, crystal plane



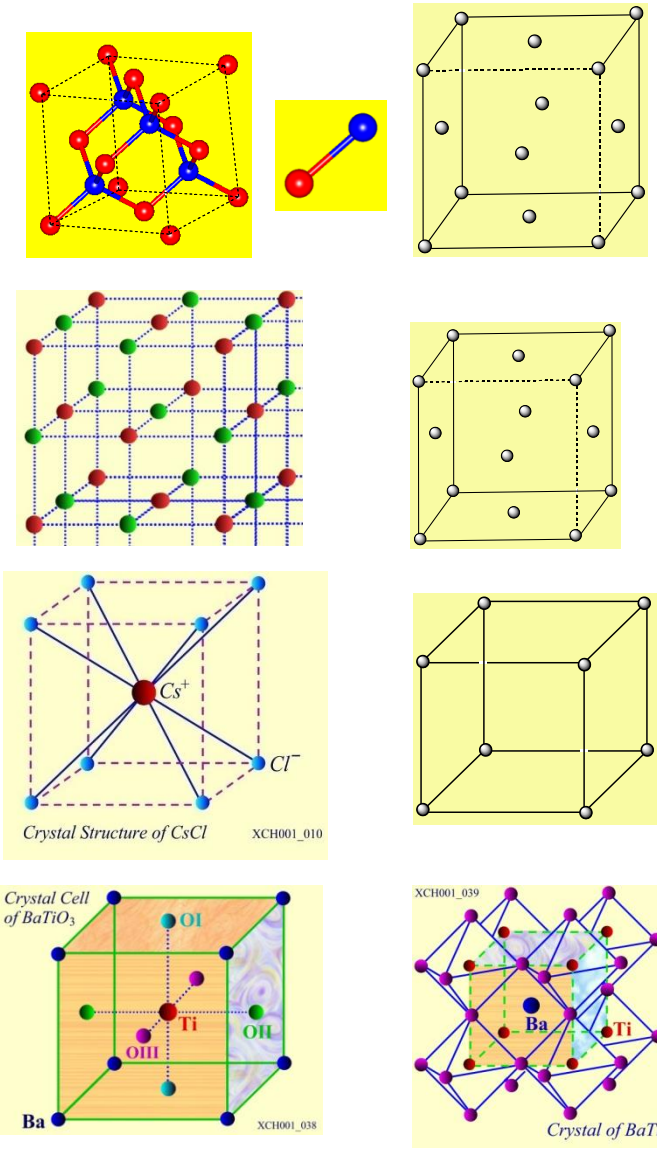


· Preface

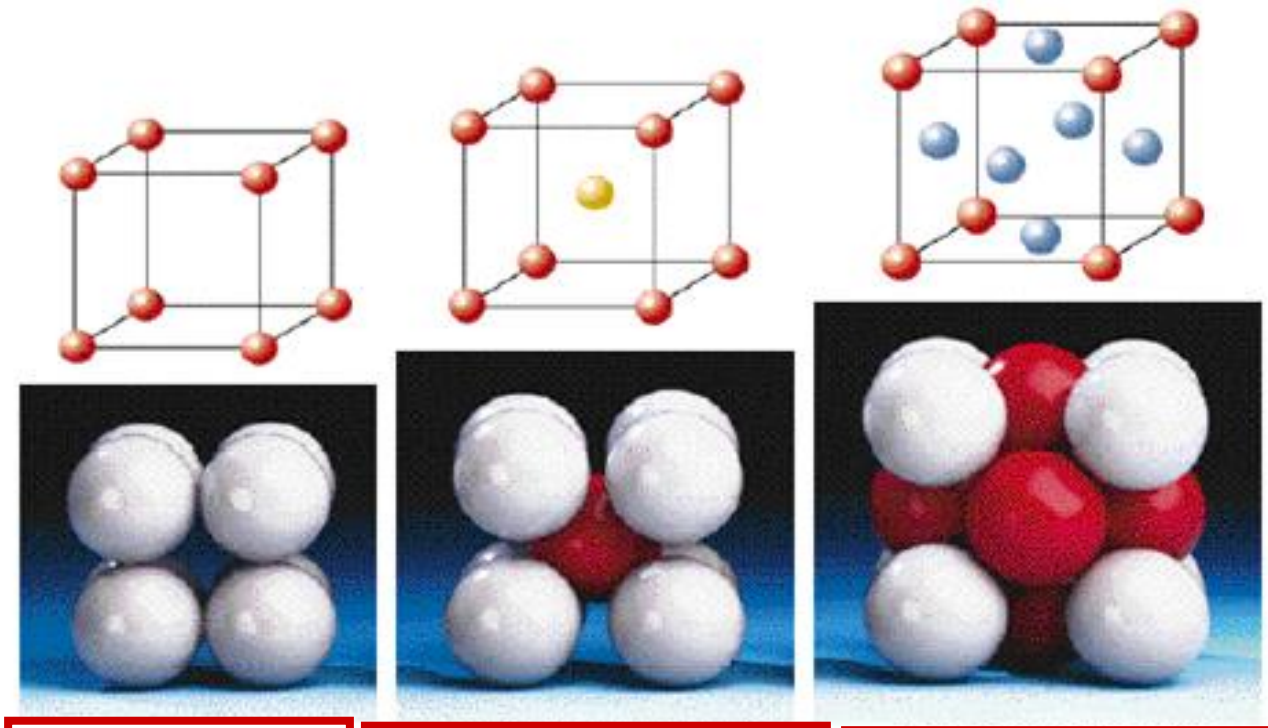
1 Element crystal



2 crystalline compounds



Three Typical Cubic Structures



lattice

Crystal structure

simple cubic

Body-centered cubic (BCC)

Face centered cubic (FCC)

Important Parameters in Crystal Structure

- **Number of atoms per unit cell (*n*): The number of atoms in a unit cell.**
- **The number of nearest neighbours, or Coordination Number (CN) : The number of atoms closest to a given atom.**
- **Atomic Packing Factor (APF): The fraction of the volume of a unit cell that is occupied by ‘‘hard sphere’’ atoms or ions.**

$$AFP = \frac{volume\ of\ atoms\ in\ unit\ cell}{volume\ of\ unit\ cell}$$

- **Atomic Radius: The radius of the “ hard sphere”.**

1. Body-centred Cube（BCC)

$$n=\frac{1}{8}\times 8+1=2$$

CN：8

Close-packed plane：{110};

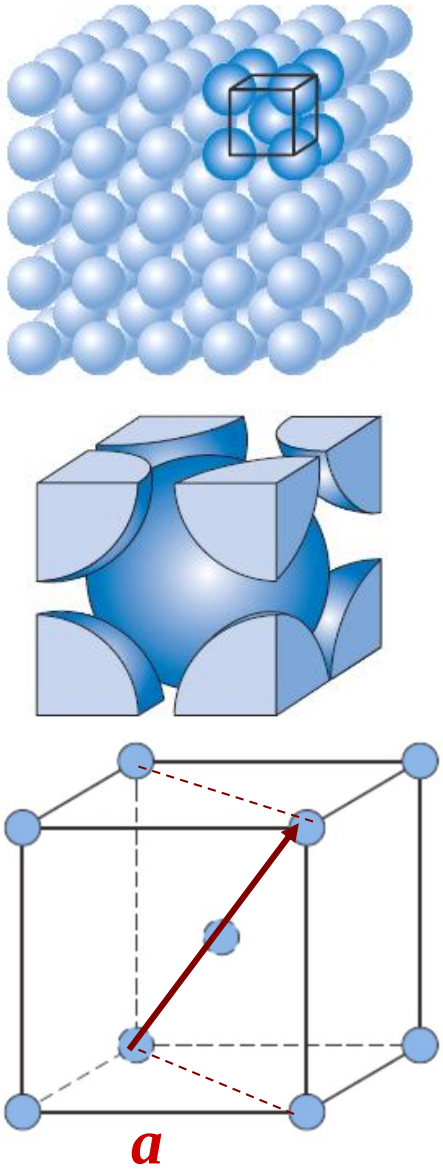
Close-packed direction： <111>

Atomic radius: $\frac{\sqrt{3}}{4}a$

APF:

$$K=\frac{nV_0}{V}=\frac{2\sqrt{3}\pi a^3}{16}\cdot\frac{1}{a^3}=\frac{\sqrt{3}\pi}{8}\approx 0.68$$

Example：α-Fe、Cr、W、Mo、V



2. Face-centred Cube (FCC)

n： 4

CN： 12

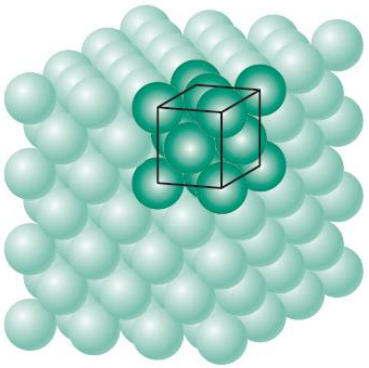
Close-packed plane： {111}

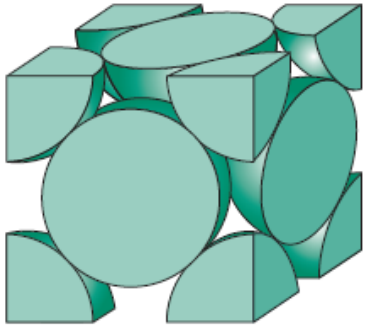
Close-packed direction： <110>

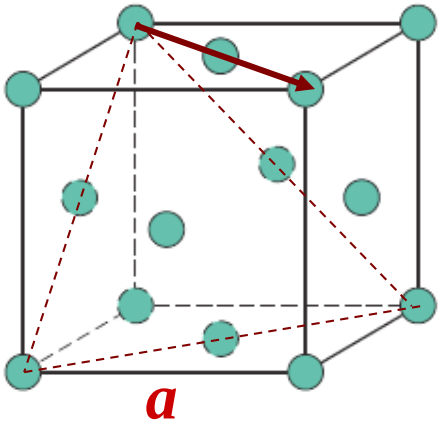
Atomic radius: $\frac{\sqrt{2}}{4}a$

APF:

$$K=\frac{4\times\frac{4}{3}\pi(\frac{\sqrt{2}}{4}a)^3}{a^3}=0.74$$

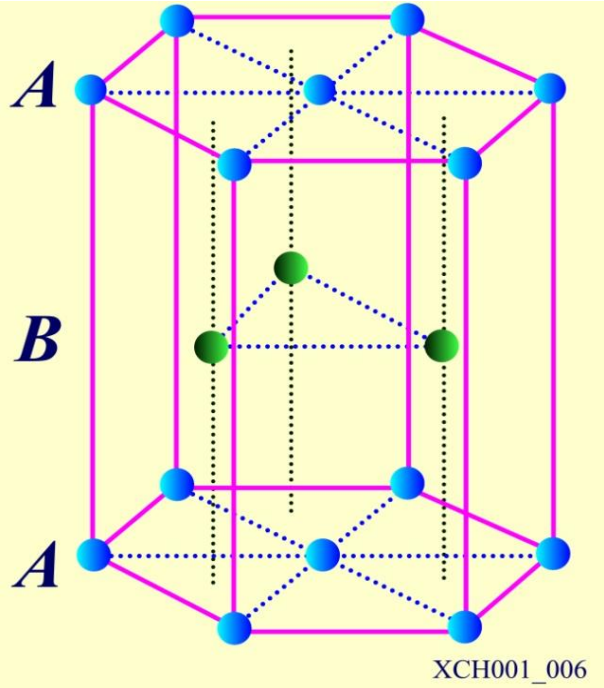


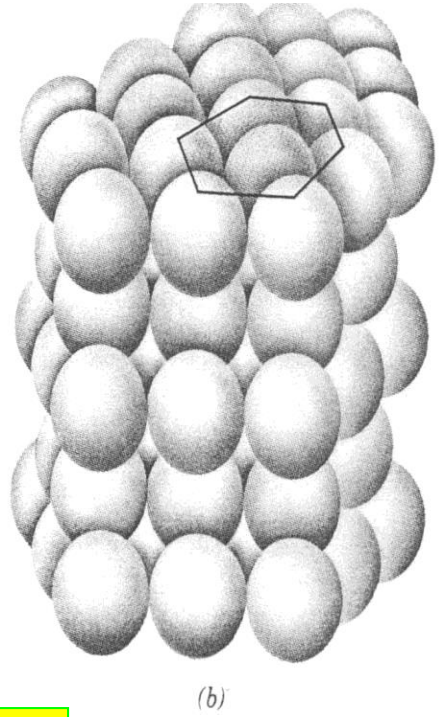


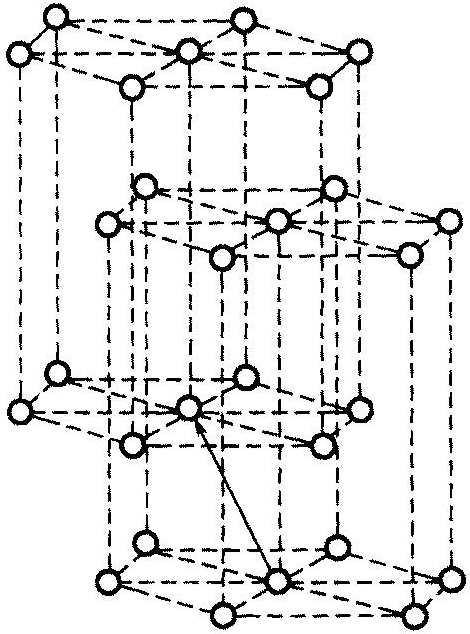


Example： γ-Fe、*Cu* 、*Al* 、*Ag*、*Au*、*Pb*、*Ni*

3. Hexagonal Close-Packed Structure (HCP)







a=b, α=120, c=1.633a

Example: ***He, Be, Mg, Ti, Zn, Cd, Co, Y, Zr, Gd, Re…***

n, CN, APF, lattice type?

SUMMARY

Structure	*a* vs. *r*	n	CN	APF	Examples
SC	$a = 2r$	1	6	0.52	*P,α-Mn*
BCC	$a = \frac{4}{\sqrt{3}} r$	2	8	0.68	*α-Fe, Ti, W, Mo, Nb, K, Na, V, Zr, Cr*
FCC	$a = \frac{4}{\sqrt{2}} r$	4	12	0.74	*γ-Fe, Cu, Au, Pt, Ag, Pb,Ni*
HCP	$a = 2r$ $c / a \approx 1.633$	6	12	0.74	*Mg, Zn, Be, Co, Zr, Cd*

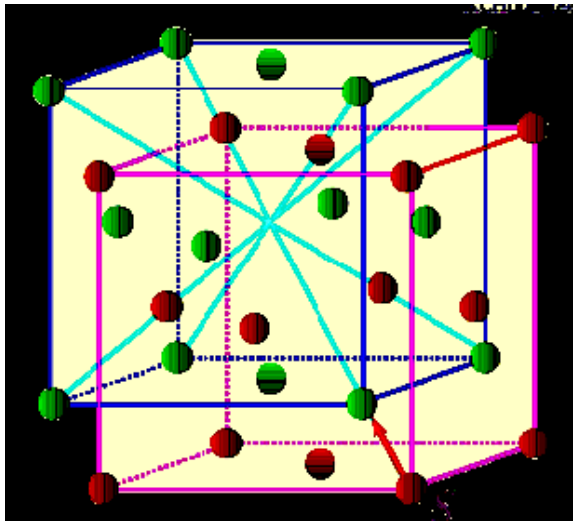
Semiconductor's structure

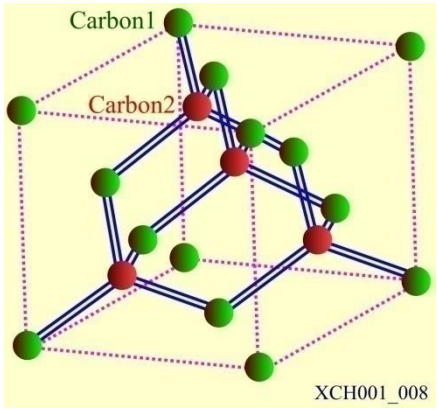
1. Diamond Structure

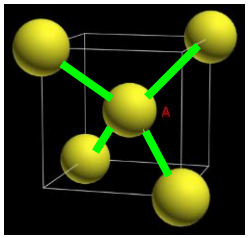
The diamond lattice (formed by the carbon atoms) consists of two interpenetrating face-centered cubic Bravais lattices, displaced along the body diagonal of the cubic cell by one quarter the length of the diagonal.

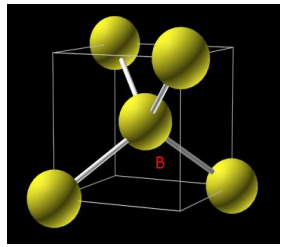
Basis: two identical atoms at

$$000;\ \frac{1}{4}\frac{1}{4}\frac{1}{4}$$





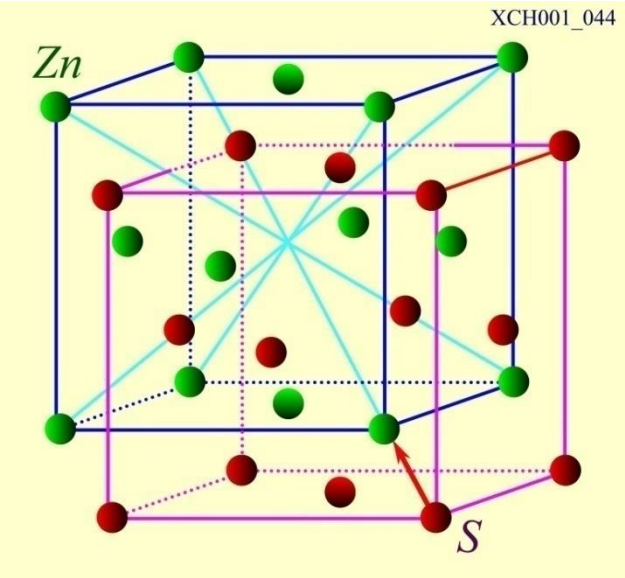


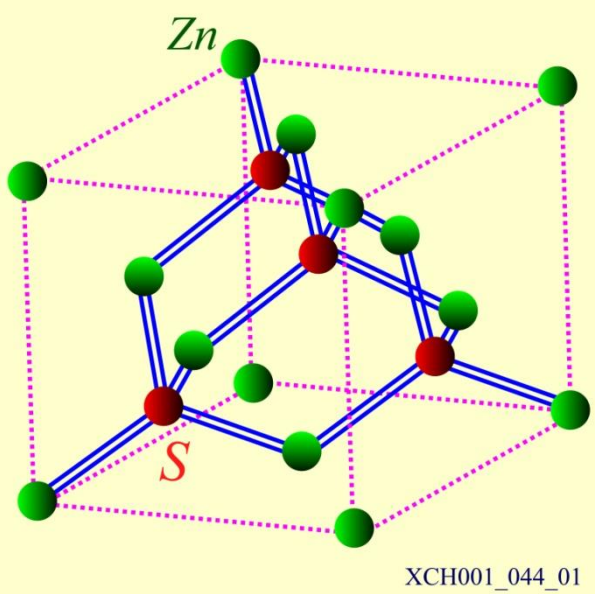


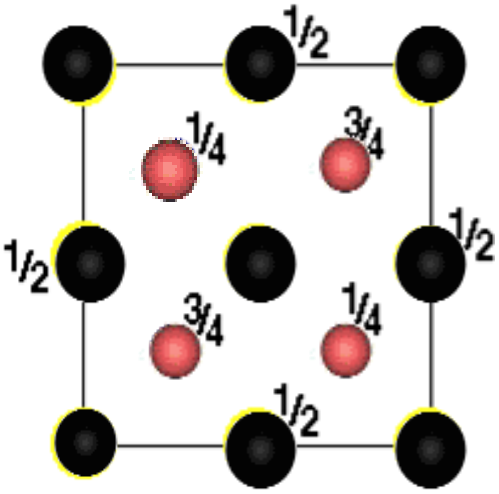
Lattice type and basis?

2.Zinc Blende Structure (ZnS)

Zinc Blende has equal numbers of zinc and sulfur ions distribute on a diamond lattice or is the FCC arrays of S and Zn interpenetrating eatch other.

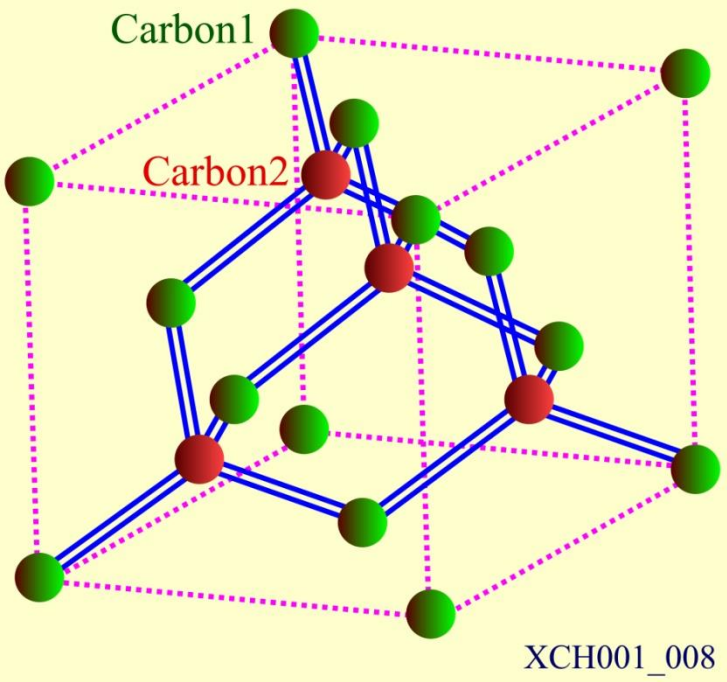




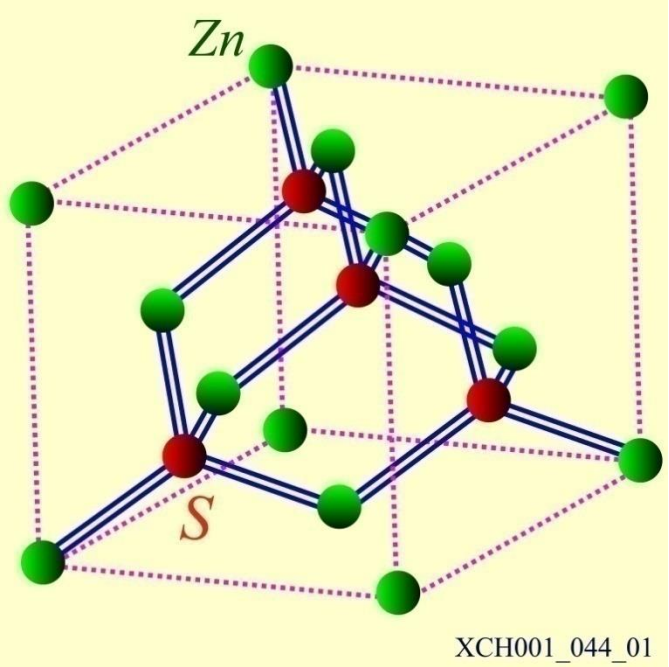


lattice? Basis?

3.Comparison Between Diamond and ZnS



Diamond



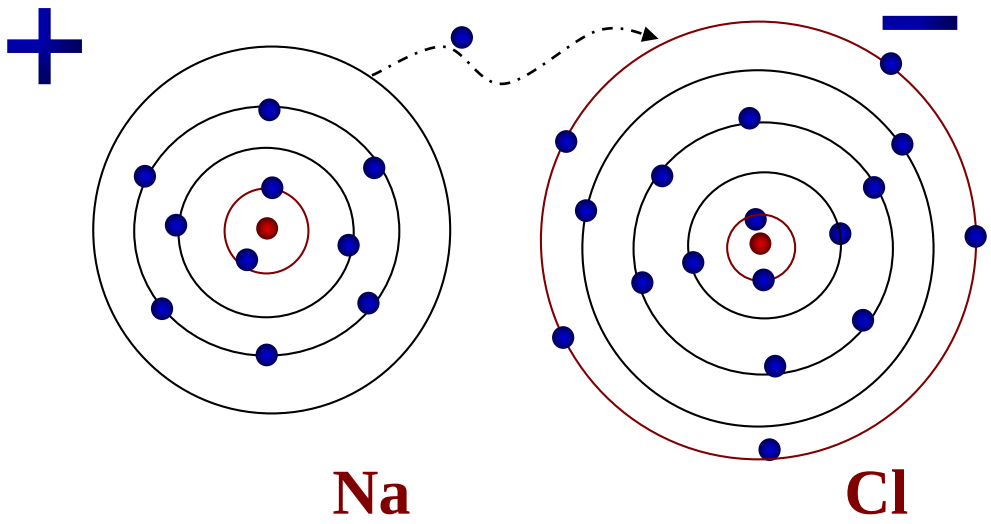
Zinc Blende
(Cubic Zinc Sulfide)

Summary

Crystal Structure	CN	Atoms/per unit cell	APF	Examples
Diamond	4	8	0.34	Diamond, Ge, Si,α-Sn
Zinc blende	4	8	0.34	ZnS, GaAs, GaSb, InAs, InSb

Ionic Crystals' Structure

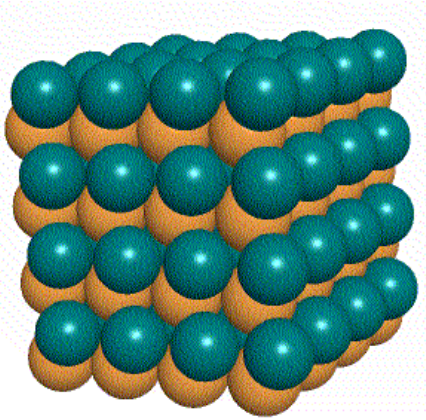
- **In an ionic crystal , the cations and anions are held together by electrostatic forces, thus forming an ionic bond.**
- **The ions has a full shell structure, thus tend to close-packed.**

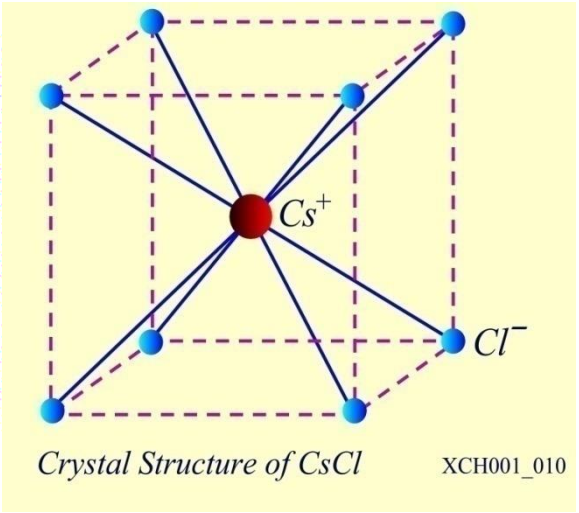


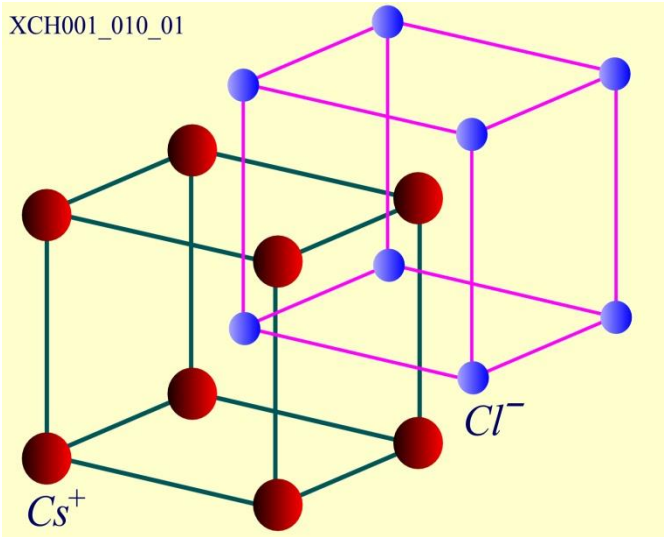
Transfer electrons!

1.Cesium Chloride Structure (CsCl)

A simple cubic Bravias lattice with a basis consisting of a cesium and a chlorine ion at the points of corners and body centered cubic lattice respectively.



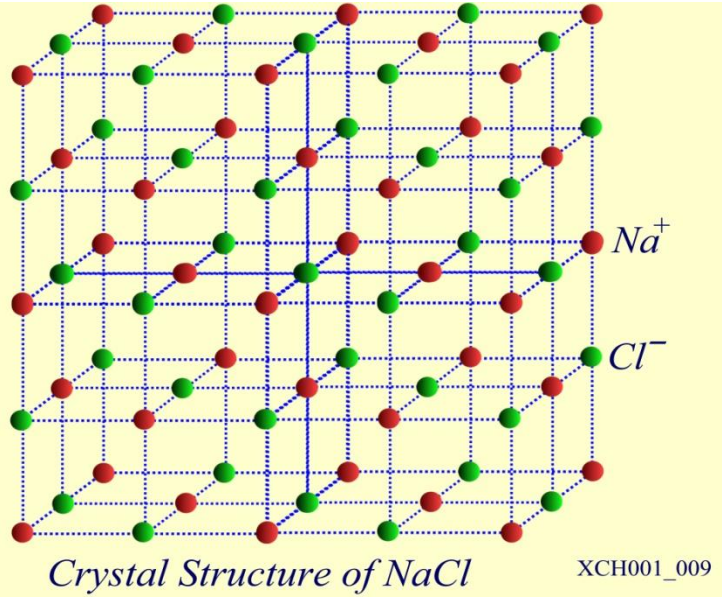


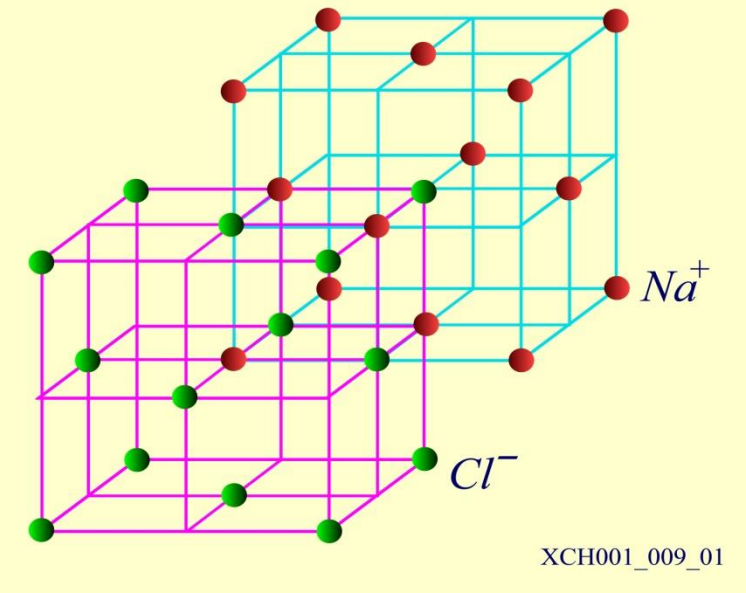


Number of atoms per unit cell?

Rock Salt Structure (NaCl)

A face-centered-cubic Bravais lattice with a basis consisting of a sodium ion at 000 and chlorine ion at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

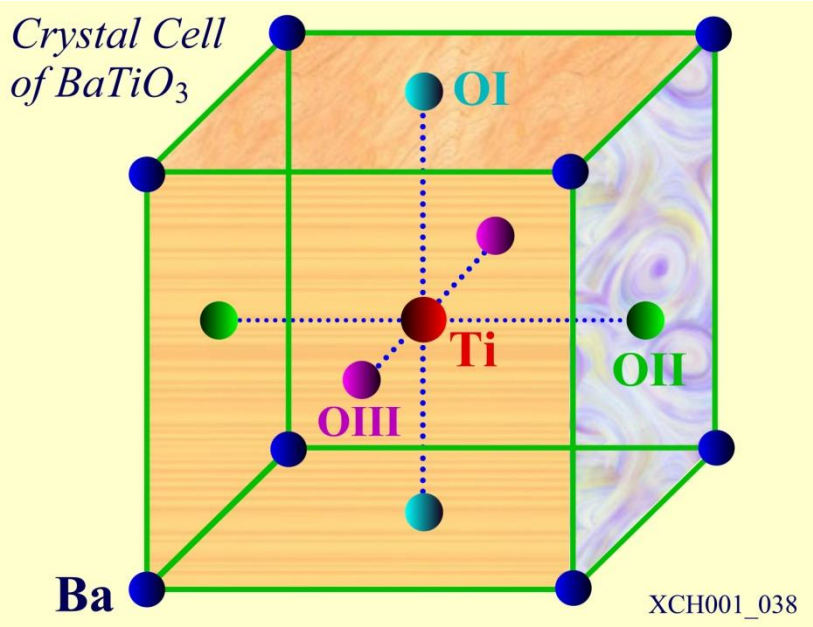


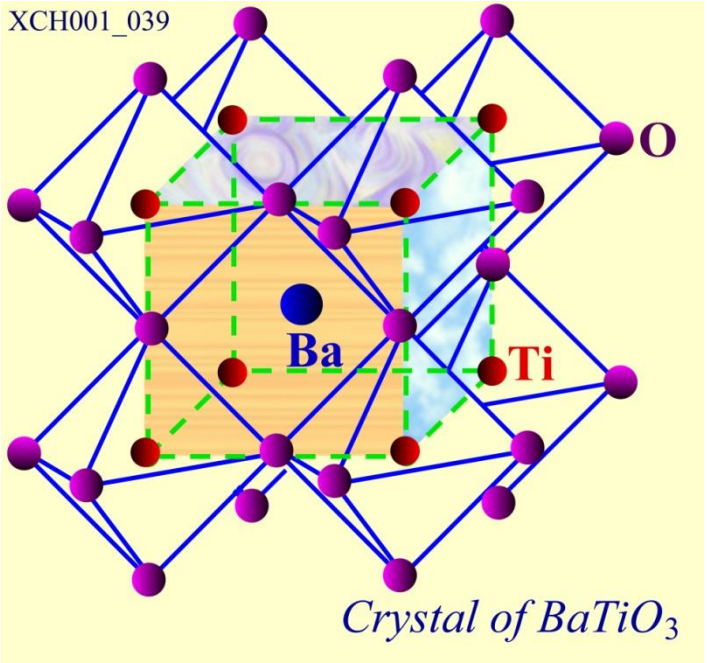


CN？number of atoms per unit cell?

Perovskite Structure ($CaTiO_3$)

Perovskite structure is composed by five simple cubes of Ba, Ti, O_I, O_{II} and O_{III}.





Typical materials: *$BaTiO_3$, $PbZrO_3$, $LiNbO_3$, $LiTaO_3$...*

Summary of Some Common Ionic Crystal Structures

Structure name	Structure type	Lattice	CN Cation anion	Examples
Rock salt (NaCl)	AX	FCC	6 6	NaCl, MgO, FeO
Cesium chloride	AX	Simple cubic	8 8	CeCl
Zinc blende	AX	FCC	4 4	ZnS, SiC
Perovskite	ABX_3	Simple cubic	12(A)6(B), 6	$BaTiO_3$, $SrZrO_3$
Spinel	AB_2X_4	FCC	4(A)6(B), 4	$MgAl_2O_4$, $FeAl_2O_4$

Metals

- Cubic （SC, FCC, BCC)
- Hexagonal Closed-Packed Structure (HCP)

Semiconductor

- Diamond Structure (Si, C, Ge)
- Zinc Blende (ZnS)

Ceramics

- Cesium Chloride Structure (CsCl)
- Sodium Chloride Structure (NaCl)—rock salt structure
- Perovskite Structure ($CaTiO_3$)