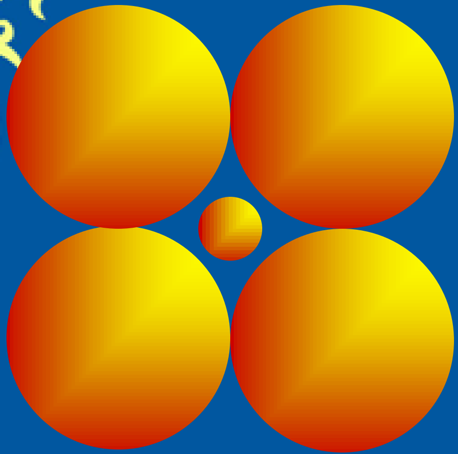
CATION-ANION CONFIGURATION

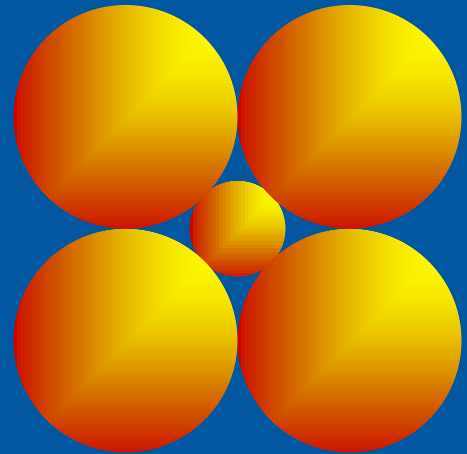
pranjoto utomo

Cation-anion configuration



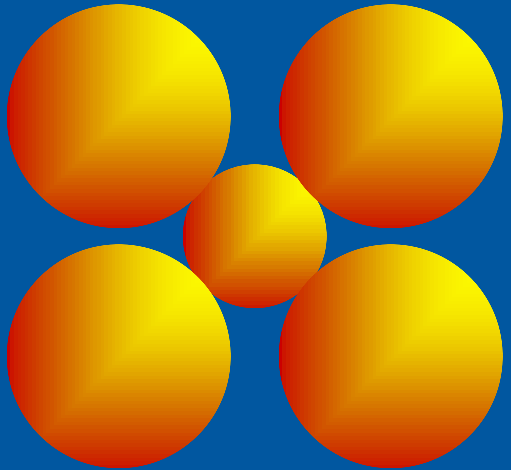
$$\frac{r_+}{r_-} < \text{ideal}$$

UNSTABLE



$$\frac{r_+}{r_-} = \text{ideal}$$

STABLE



$$\frac{r_+}{r_-} > \text{ideal}$$

STABLE

$$\frac{r_+}{r_-} = \text{ideal}$$

- Almost never occur

$$\frac{r_+}{r_-} > \text{ideal}$$

- Cation remain contact with anion
- Cation forces the anion apart

$$\frac{r_+}{r_-} < \text{ideal}$$

- Cation too small for the site
- Cation not in contact with anion

General principle of ionic lattice

1. Ions can be viewed as uncompressed and unpolaryzed hard sphere

2. Ions sorounded by opposite charge as much as possible

   Cations do not make the anions contact each others

3. Cation-anion ratio shows the chemical composition of the compound.

Hole types determination

- **Which sites are occupied by a given cation?**
  - **determined by the radius ratio (radius cation/radius anion)**

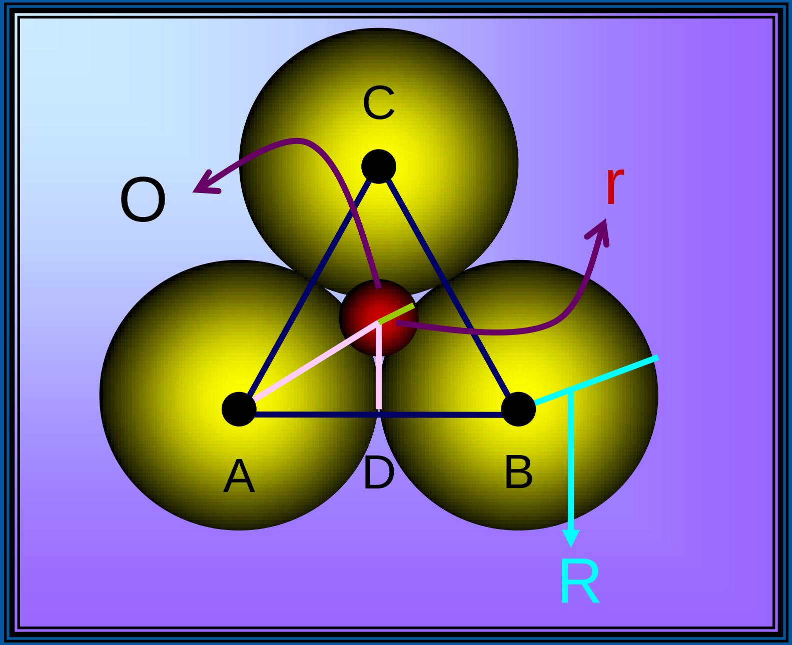
- **How many sites are occupied?**
  - **determined by the stoichiometry.**

Types of hole

- Linear
- Triangular
- Tetrahedron
- Octahedron
- Cubic

Triangular hole

In Δ DAO



$$\cos 30^\circ = \frac{AD}{AO}$$

$$\frac{1}{2}\sqrt{3} = \frac{R}{R+r}$$

$$0{,}866(R+r) = R$$

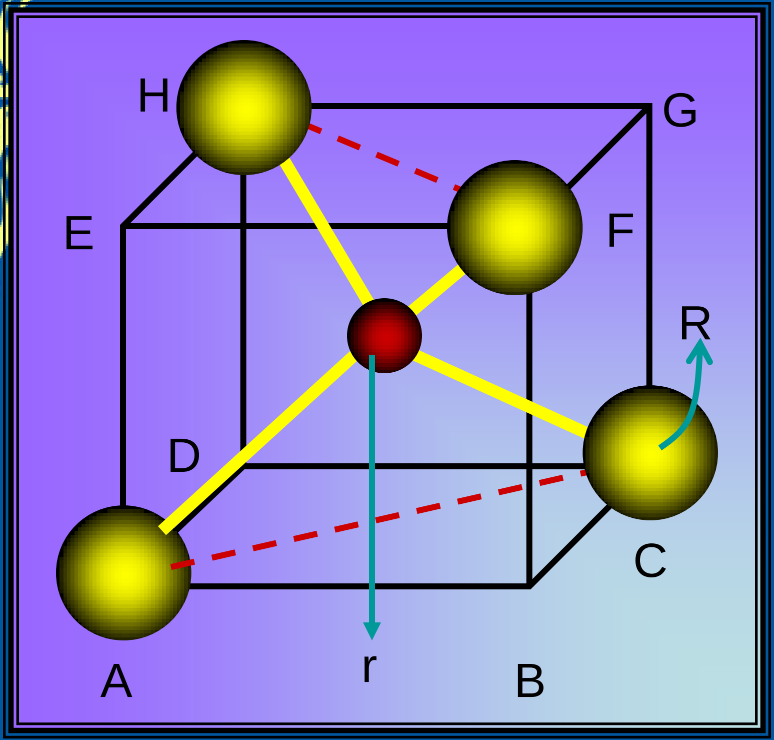
$$r = \frac{(1-0.866)R}{0.866}$$

$$r = 0.155R$$

$$\frac{r}{R} = 0.155$$

$$\frac{r_+}{r_-} = 0.155$$

Tetrahedron hole



$$\text{face diagonal} = a\sqrt{2} = 2R$$

$$a = R\sqrt{2} \text{ ....(1)}$$

$$\text{1/2 body diagonal} = 1/2\, a\sqrt{3} = R + r \text{ ...(2)}$$

from (1) and (2):

$$1/2\, R\sqrt{2}\,.\,\sqrt{3} = R + r$$

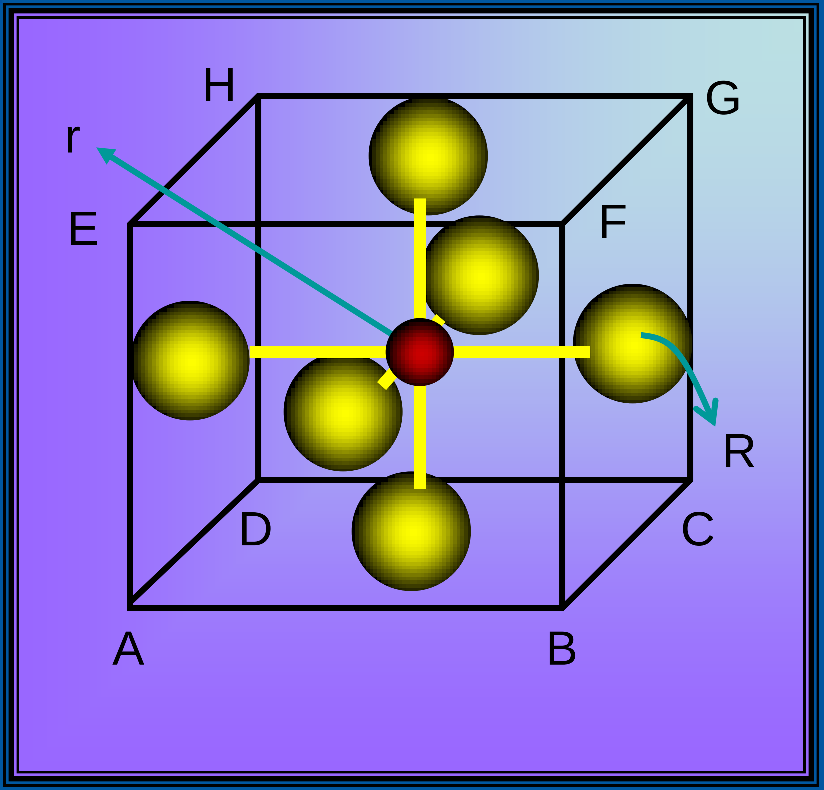
$$1.225\, R = R + r$$

$$r = 0.225\, R$$

$$\frac{r}{R} = 0.225$$

$$\frac{r_+}{r_-} = 0.225$$

Octahedron hole



$$\text{face diagonal} = a\sqrt{2} = 2R$$

$$a = R\sqrt{2} \;.......(1)$$

$$a = R + r \;......(2)$$

from (1) and (2):

$$R\sqrt{2} = R + r$$

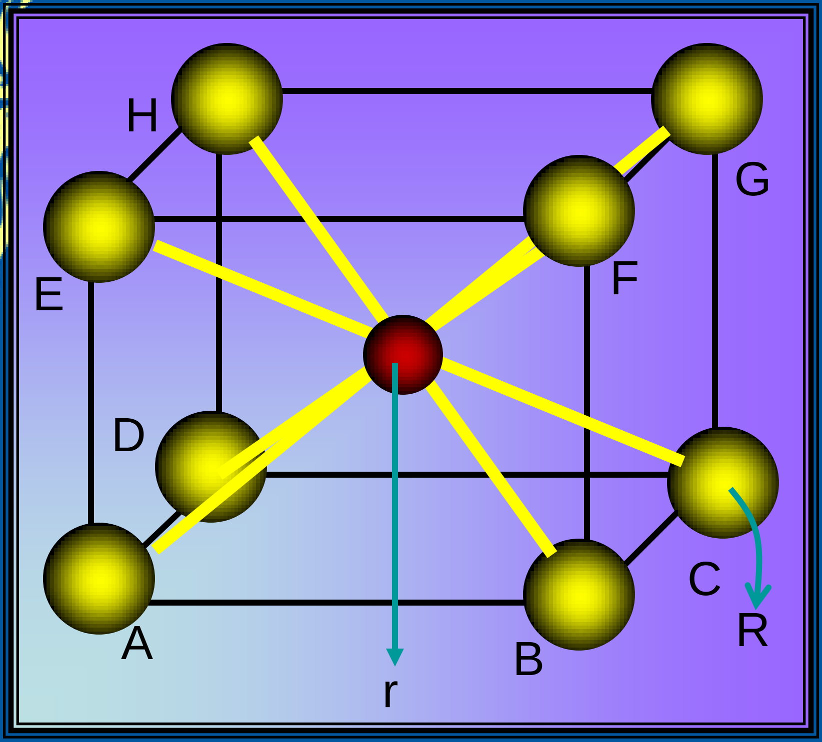
$$1.414\,R = R + r$$

$$r = 0.414\,R$$

$$\frac{r}{R} = 0.414$$

$$\frac{r_+}{r_-} = 0.414$$

Cubic hole



$$\text{body diagonal} = a\sqrt{3} = 2(R + r) \ldots (1)$$

$$a = 2R \;\ldots\ldots\ldots (2)$$

from (1) and (2):

$$2R\sqrt{3} = 2(R + r)$$

$$1.732\,R = R + r$$

$$r = 0.732\,R$$

$$\frac{r}{R} = 0.732$$

$$\frac{r_+}{r_-} = 0.732$$

Types of hole

Coordination Geometry

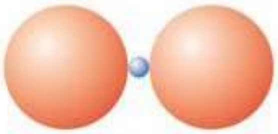
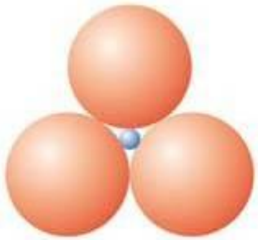
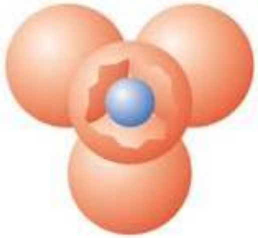
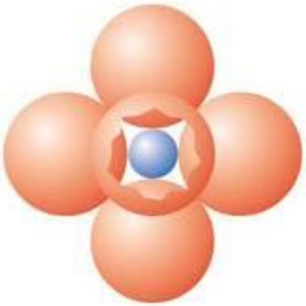
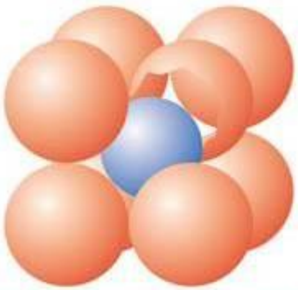
linear

triangular

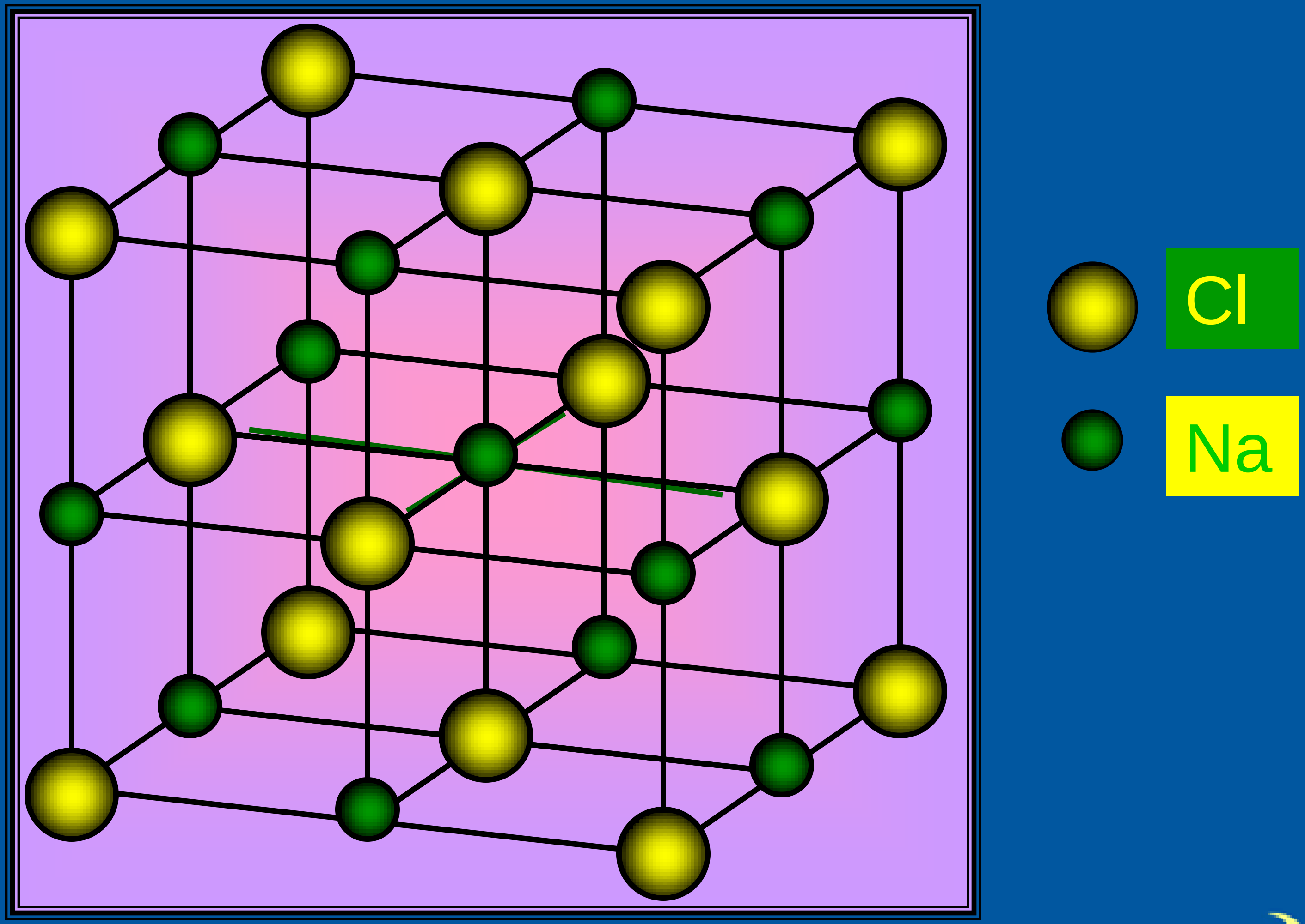
tetrahedron

octahedron

cubic

Coordination Number	*Cation–Anion Radius Ratio*	*Coordination Geometry*
2	<0.155	
3	0.155–0.225	
4	0.225–0.414	
6	0.414–0.732	
8	0.732–1.0	

Sodium chloride (NaCl)



Sodium chloride (NaCl)

- fcc
- 1 unit cell contains:

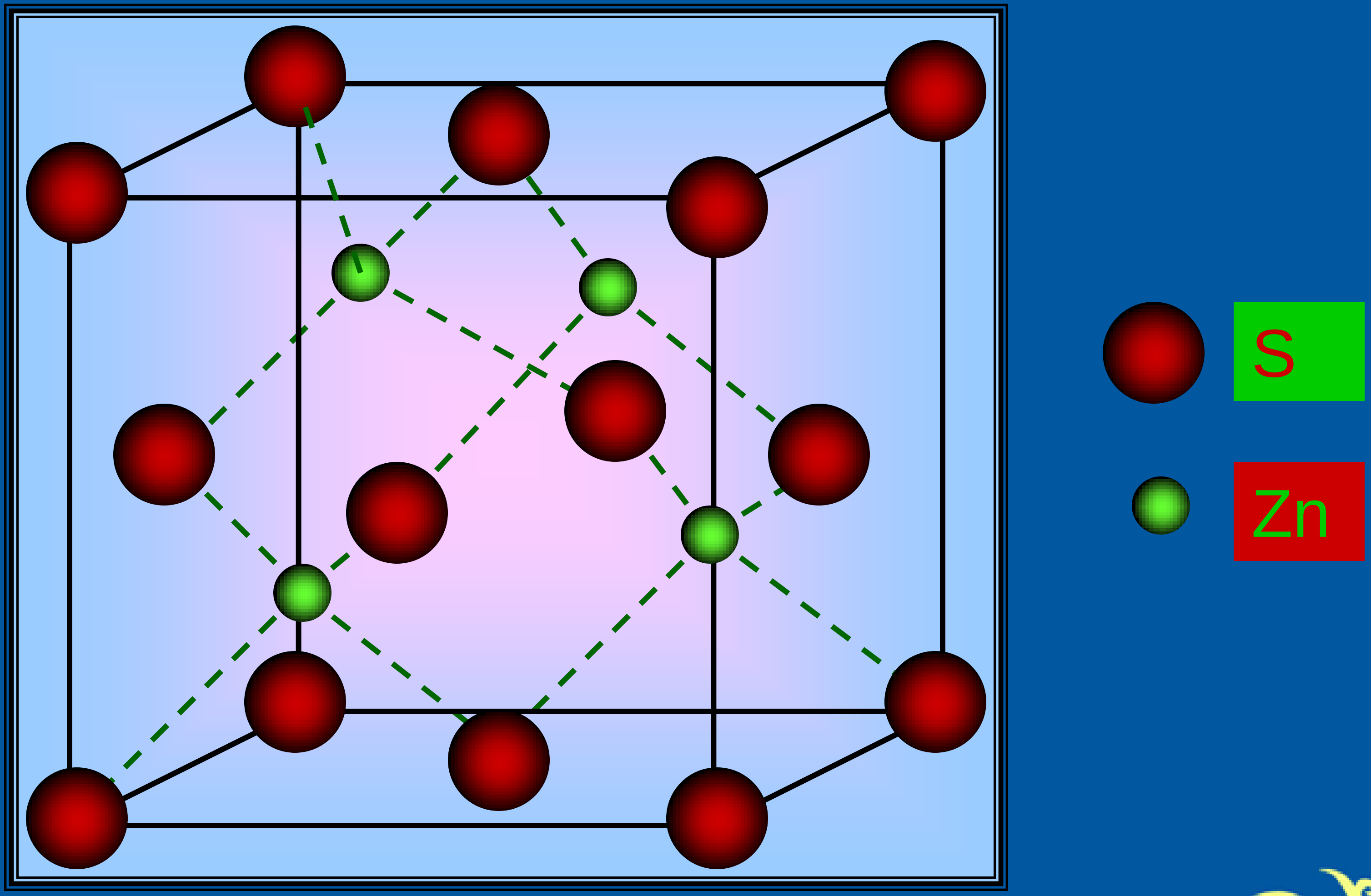
    4 atoms Na [(1/4 x 12 site atoms) + (1 interior atom)]

    4 atoms Cl [(1/8 x 8 corner atoms) + (1/2 x 6 face atoms)]

Sodium chloride (NaCl)

- r Na^+ = 102 pm, r Cl^- = 181 pm
- r_+/r_- = 0.564 → octahedron hole (CN max = 6)
- CN of Na = 6, Cl = 6
- CN of NaCl = (6,6)
- Stoichiometry Na:Cl = 1:1

Zinc blende (ZnS)



Zinc blende (ZnS)

- fcc
- 1 unit cell contains:

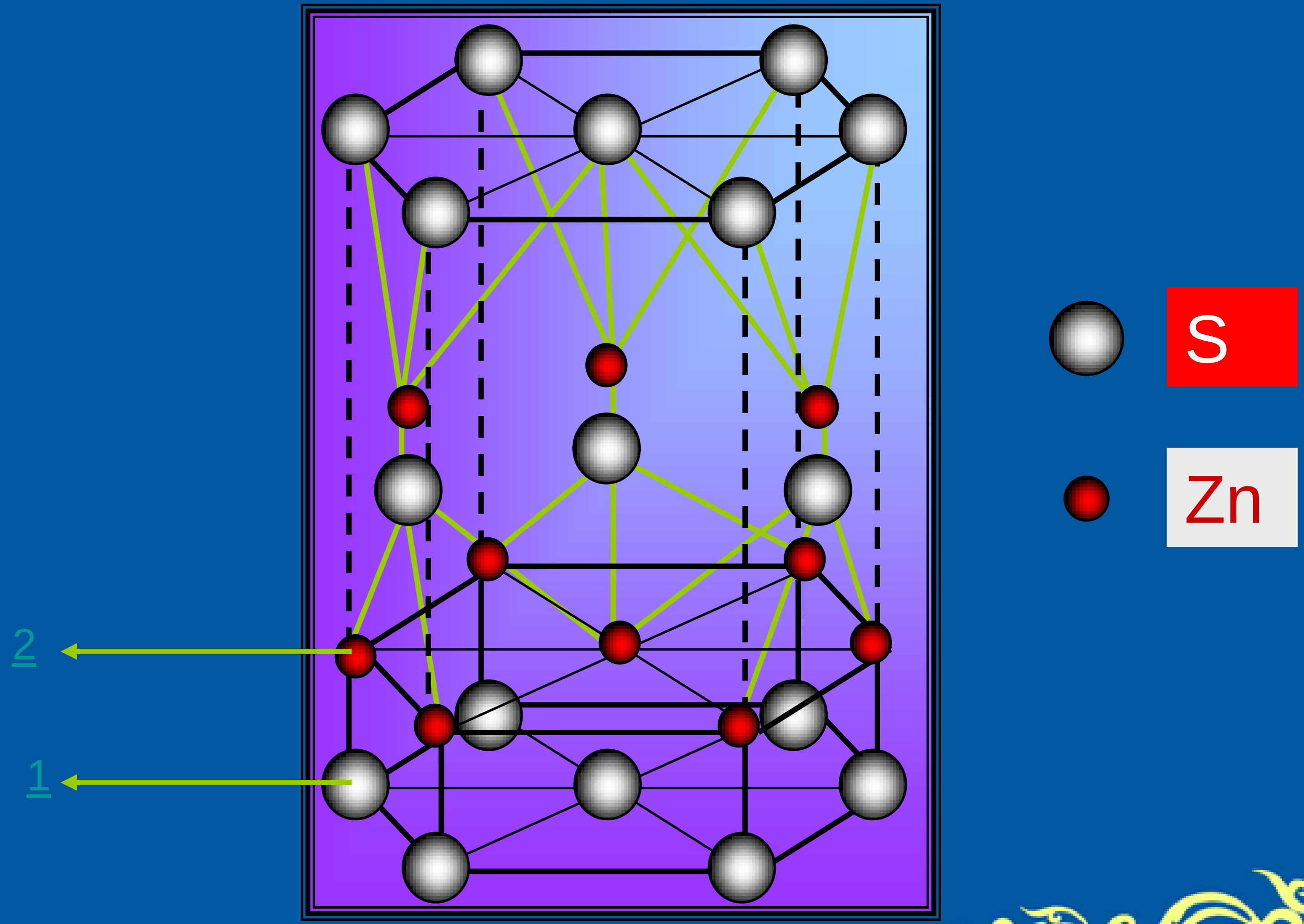
    4 atoms Zn (4 interior atoms)

    4 atoms S [(1/8 x 8 corner atoms) + (1/2 x 6   face atoms)]

Zinc blende (ZnS)

- r Zn^{2+} = 74 pm, r S^{2-} = 184 pm
- r_+/r_- = 0.402 → tetrahedron hole (CN max = 4)
- CN of Zn = 4, S = 4
- CN of ZnS = (4,4)
- Stoichiometry Zn:S = 1:1

Wurtzite (ZnS)



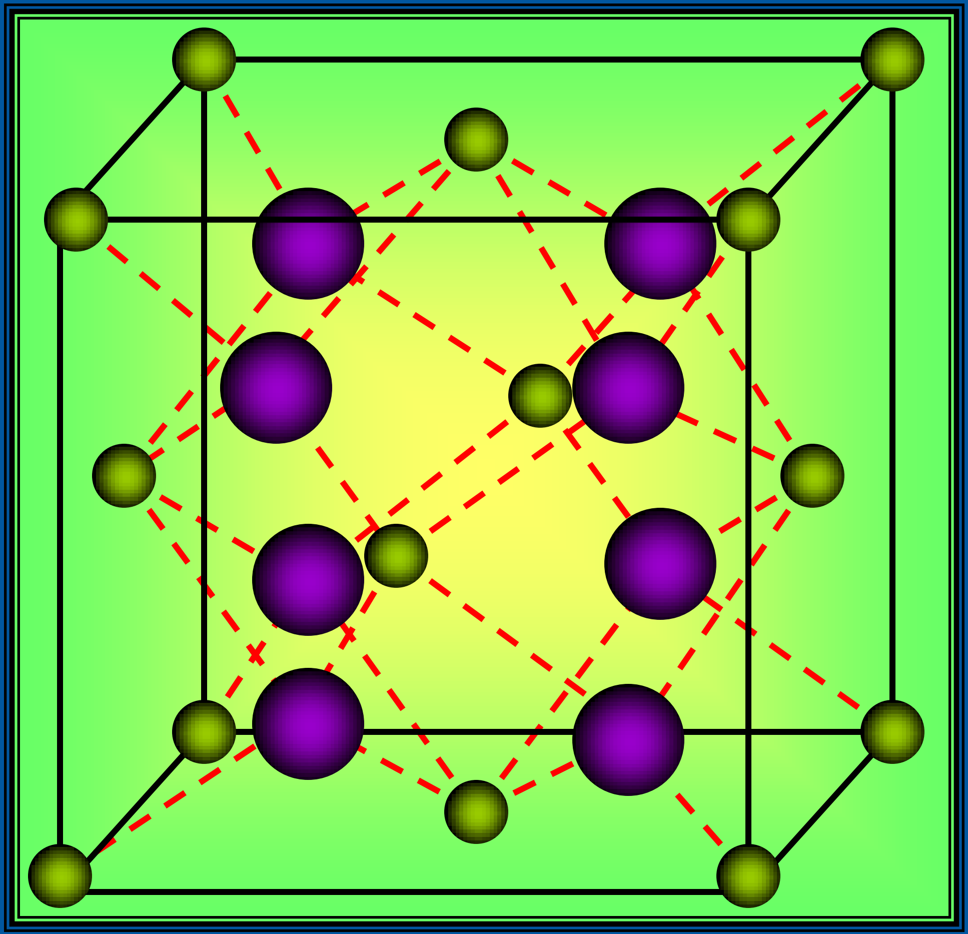
Wurtzite (ZnS)

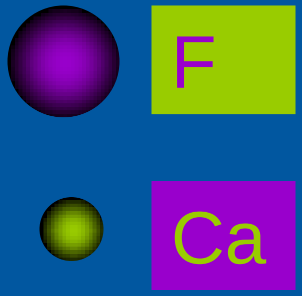
- fcc
- 1 unit cell contains:
  - 6 atoms Zn [1/3 x 6 site atoms) + (4 interior atoms)
  - 6 atoms S [(1/6 x 12 corner atoms) + (1/2 x 2 face atoms) + (3 interior atoms)]

Wurtzite (ZnS)

- r Zn^{2+} = 74 pm, r S^{2-} = 184 pm
- r_+/r_- = 0.402 → tetrahedron hole (CN max = 4)
- CN of Zn = 6, S = 6
- CN of ZnS = (6,6)
- Stoichiometry Zn:S = 1:1

Calcium fluoride (CaF_2)





Calcium fluoride (CaF_2)

- fcc
- 1 unit cell contains:

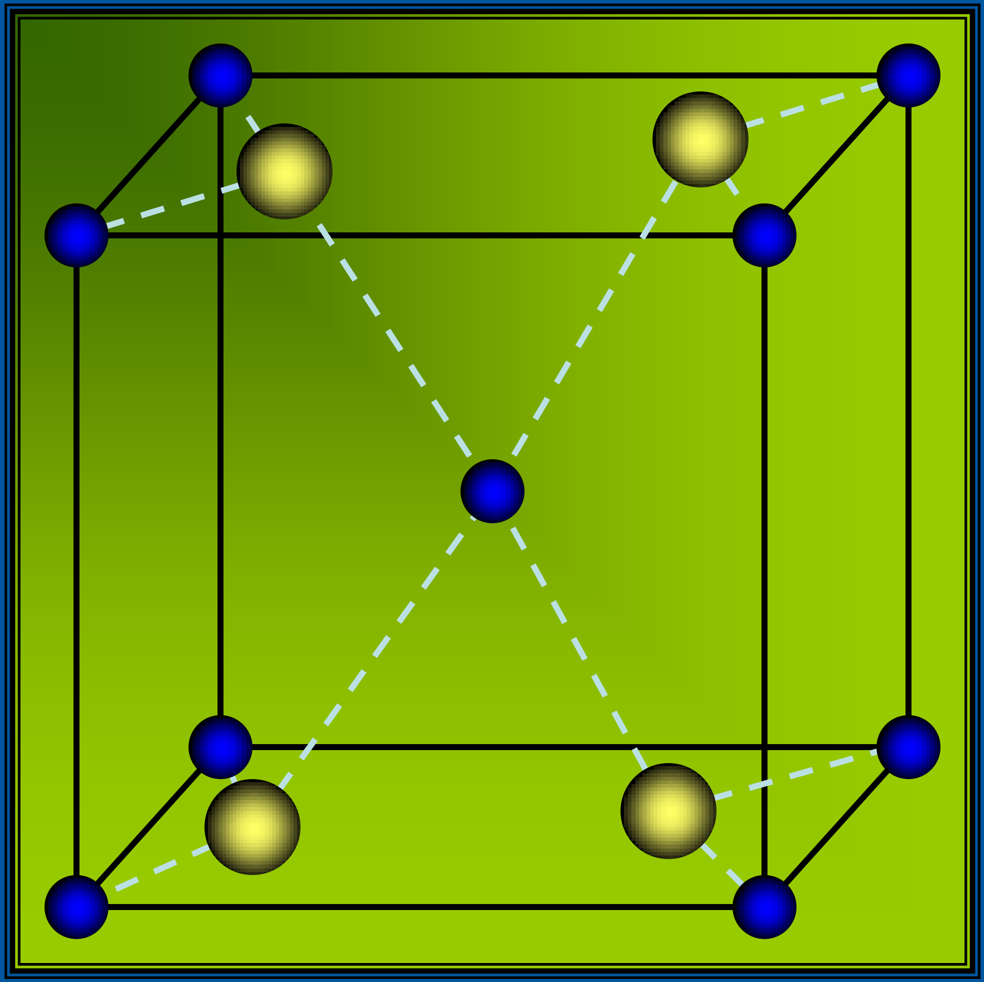
    4 atoms Ca [1/8 x 8 corner atoms) + (1/2 x 6 face atoms)

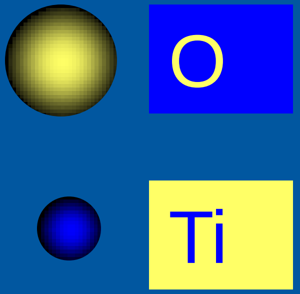
    8 atoms F (8 interior atoms)

Calcium fluoride (CaF_2)

- r Ca^{2+} = 112 pm, r F^- = 131 pm
- r_+/r_- = 0.855 → cubic hole (CN max = 8)
- CN of Ca = 8, F = 4
- CN of calcium fluoride = (8,4)
- Stoichiometry Ca:F = 1:2

Rutile (TiO_2)





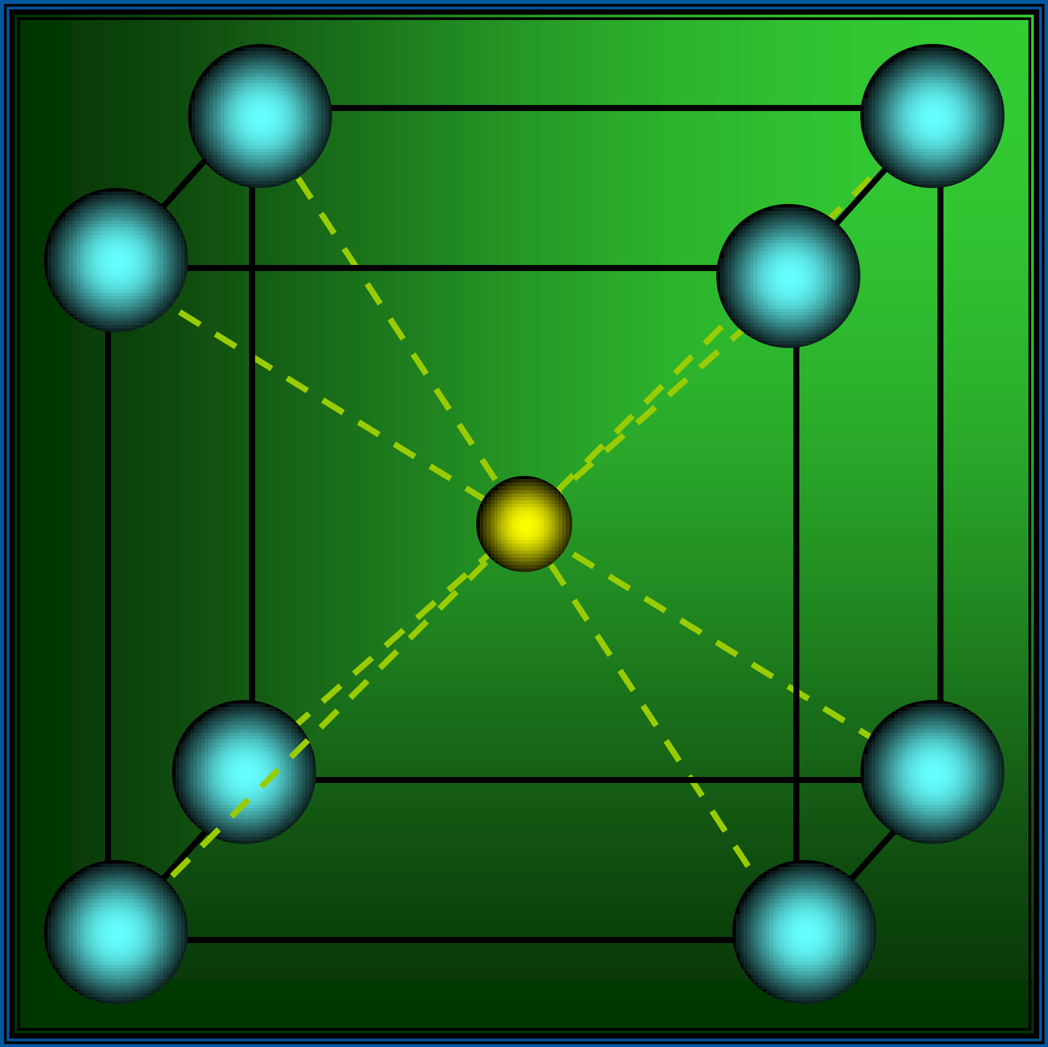
Rutile (TiO_2)

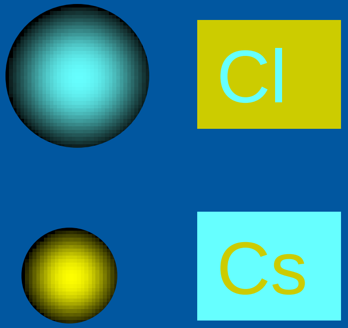
- bcc
- 1 unit cell contains:
  - 2 atoms Ti [1/8 x 8 corner atoms) + (1 interior atom)]
  - 4 atoms O [(1/2 x 4 face atoms) + (2 interior atoms)]

Rutile (TiO_2)

- r Ti^{4+} = 61 pm, r O^{2-} = 140 pm
- r_+/r_- = 0.436 → octahedron hole (CN max = 6)
- CN of Ti = 6, O = 3
- CN of titanium oxide = (6,3)
- Stoichiometry Ti:O = 1:2

Cesium chloride (CsCl)





Cesium chloride (CsCl)

- sc
- 1 unit cell contains:
  - 1 atom Cs (1 interior atom)
  - 1 atom Cl [(1/8 x 8 corner atoms)]

Cesium chloride (CsCl)

- r Cs^+ = 170 pm, r Cl^- = 181 pm
- r_+/r_- = 0.939 → cubic hole (CN max = 8)
- CN of Cs = 8, Cl = 8
- CN of CsCl = (8,8)
- Stoichiometry Cs:Cl = 1:1