- **Chapter 5: More Structures**

❖ **ROCK SALT:**

- ➢ Position our negative ions or anions at the cube corners
- ➢ Position our positive ions or cations between the anions
  - ■ This is because the anions are typically larger and it is easier for our human brains to visualize placing the large things first and then squeezing the small things in between the large ones.

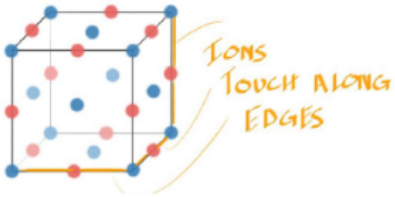


Figure 1: Anions represented as blue dots in the traditional FCC-type positions, with cations in the edge centre positions. Cations touch their nearest neighbour anions along the cube edges. Note: this is not yet Rock Salt - there is something missing.

- ➢ There must be a 1:1 ratio of anions to cations
- ➢ There are 4 anions within the unit cell, so there must also be 4 cations.
- ➢ The central cation touches each of the face centered anions, for a coordination number of 6.
- ➢ **a= 2(Ra +Rc), n=4**

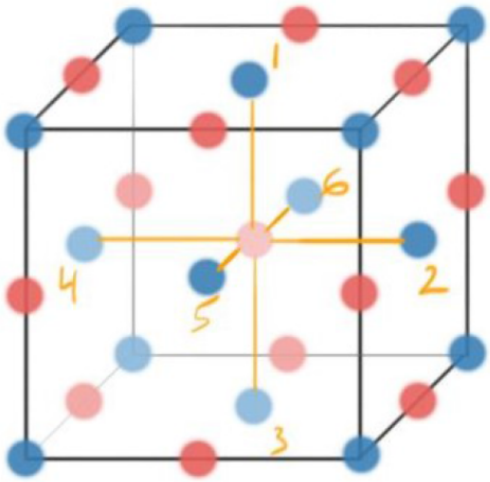


Figure 3: The rock salt ceramic crystal structure.

$$\text{Cation Coordination Number}_{RockSalt} = 6$$

- DENSITY FOR ROCK SALT:

$$\rho = \frac{n_C A_C + n_A A_A}{V_C N_A}$$

❖ **BODY CENTERED CUBIC CRYSTAL(BCC):**

- ➢ We start with atoms in each of the corner positions, again, each corner position only containing ⅛ of an atom within a unit cell
- ➢ Then we position a final atom exactly in the center of the unit cell
- ➢ This gives us a total of 2 atoms within the BCC unit cell
- ➢ **nBCC = 2**
- ➢ **a =4/sqrt*(3) R**
- ➢ **Coordination number = 8**
- ➢ The direction of contact between atoms is across the cube diagonals.

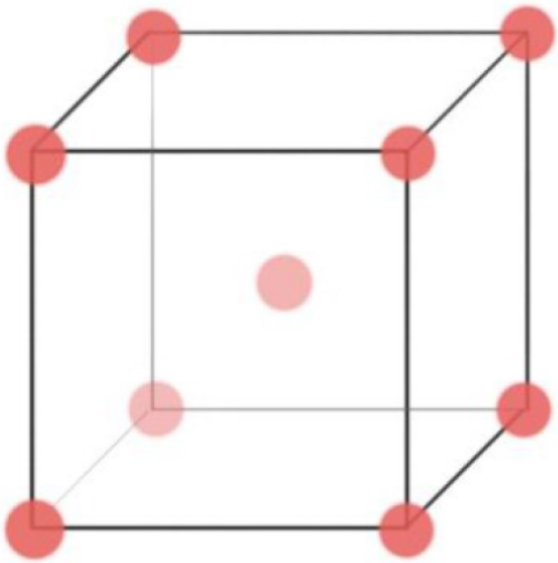


Figure 4: The body centred cubic crystal structure.

❖ APF BCC:

$$a^2 + a^2 + a^2 = (4R)^2$$
$$3a^2 = 16R^2$$

$$a_{\text{BCC}} = \frac{4}{\sqrt{3}}R$$

Which we can substitute back into our APF equation to give

$$\text{APF}_{\text{BCC}} = \frac{2\frac{4}{3}\pi R^3}{\left(\frac{4}{\sqrt{3}}R\right)^3}$$

$$\text{APF}_{\text{BCC}} = 0.68$$

$$APF_{BCC} = \frac{\text{Volume}_{\text{Spheres}}}{\text{Volume}_{\text{Unit Cell}}}$$

or,

$$\text{APF}_{\text{BCC}} = \frac{\text{n}\frac{4}{3}\pi R^3}{a^3}$$

and, specifically for BCC

$$\text{APF}_{\text{BCC}} = \frac{2\frac{4}{3}\pi R^3}{a^3}$$

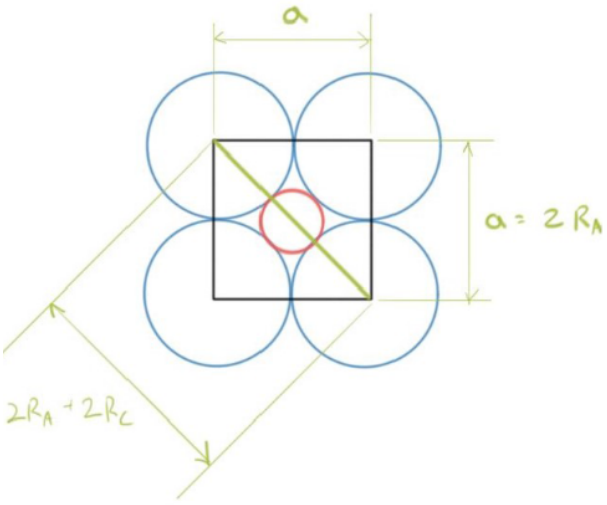
❖ INTERSTITIAL SITES:

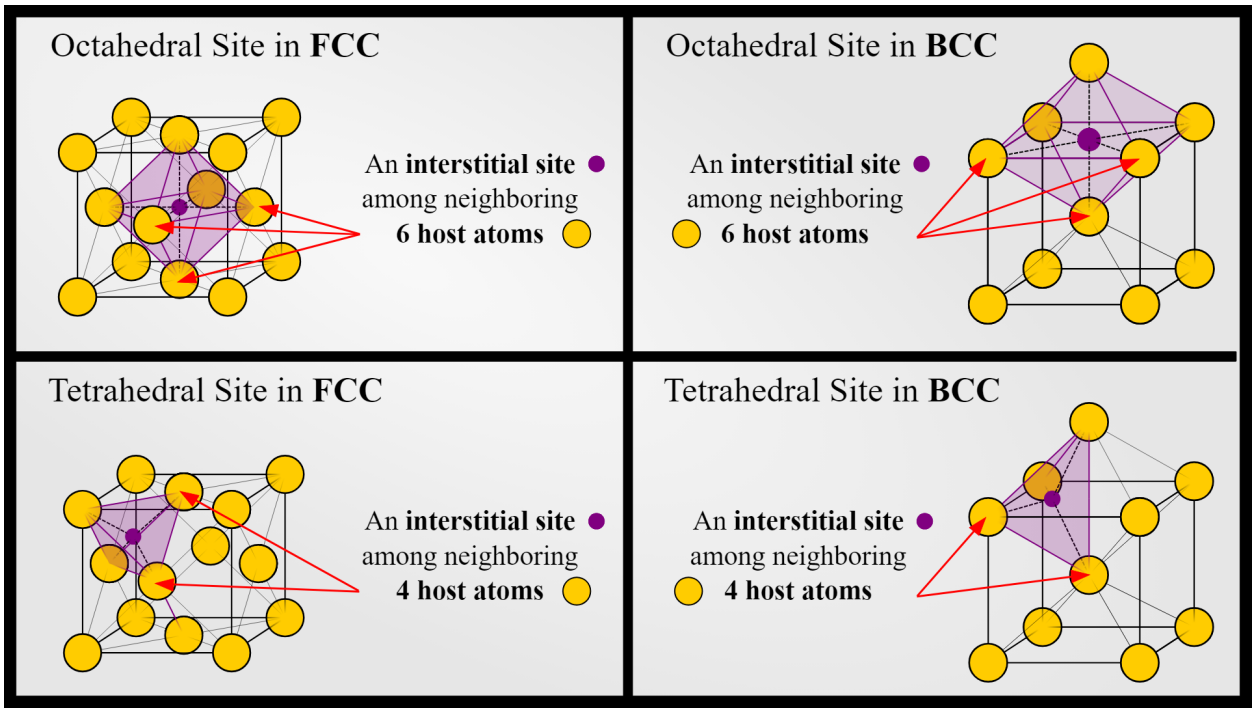
Space between atoms

- Coordination number simple cubic: 8
- SIZE OF INTERSTITIAL SITES

$$(2R_A + 2R_C)sin45 = 2R_A$$
$$2R_Asin45 + 2R_Csin45 = 2R_A$$
$$R_Asin45 + R_Csin45 = R_A$$
$$\frac{R_A}{R_A}sin45 + \frac{R_c}{R_A}sin45 = \frac{R_A}{R_A}$$
$$sin45 + \frac{R_C}{R_A}sin45 = 1$$
$$\frac{R_C}{R_A}\sin 45 = 1 - \sin 45$$
$$\frac{R_C}{R_A} = \frac{1 - \sin 45}{\sin 45}$$

$$\left(\frac{RC}{RA}\right)_{CN=6} = 0.414$$





❖ HEXAGONAL CLOSE PACKED (HCP)

- ➢ Metallic crystal structure with the same packing fraction as FCC - hexagonal close packed or HCP.
- ➢ APF for HCP must also be 0.74
- ➢ **A close-packed plane** is a layer of atoms that is placed together as closely as possible, in two-dimensions.
- ➢ You will notice that the top and bottom planes are exactly in line with each other vertically.
- ➢ Since these planes are close-packed this gives us the **ABABAB** stacking sequence for **HCP**.
- ➢ The stacking sequence of **FCC** and HCP as **ABCABCABC** and ABABABA respectively (close-packed planes)
- ➢ c/a ratio for HCP, as formed here is 1.633.
- ➢ **Coordination number = 12**

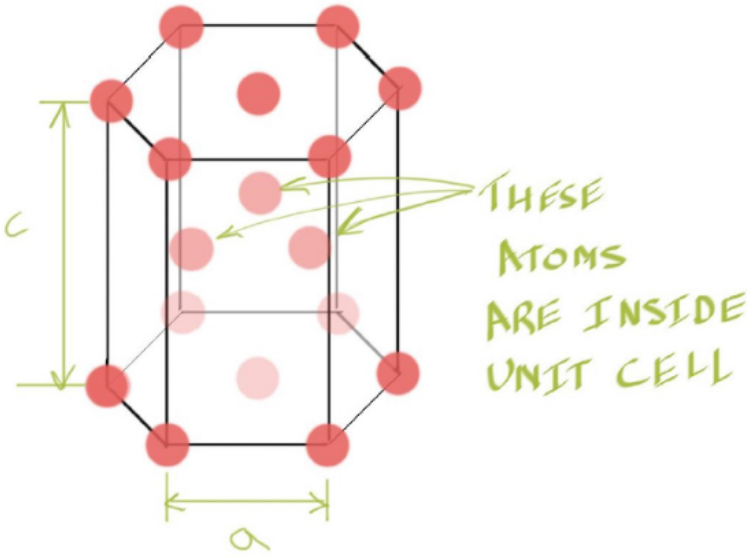
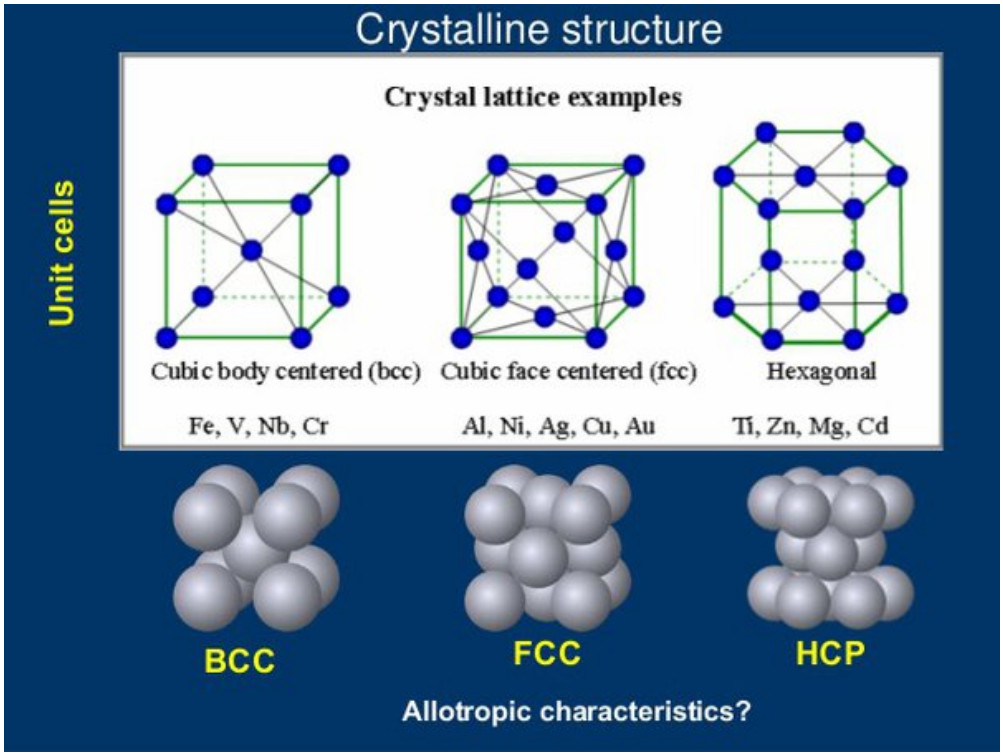


Figure 11: A hexagonal close packed unit cell. Note that the three atoms in the middle are inside the unit cell and are part of a close packed plane that is identical to the top and bottom planes.

COMPARISON FCC, HCP, BCC & ROCK SALT:

	FCC	**HCP**	**BCC**	**Rock Salt**	**Simple cubic**
Coordination Number	12	12	8	6	
Number of atoms in unit cell	4	4 OR 6	2	4	1
a	$2\sqrt{2}$ R	$2\sqrt{2}$ R OR 2R and h=1.633a	4/√3 R	2(Ra +Rc)	2R
Volume(a^3)	$(2\sqrt{2}$ R)^3	$(2\sqrt{2}$ R)^3 OR (3*sqrt(3))/2* h*a^2	(4/√3 R)^3	(2(Ra +Rc))^3	
APF	0.74	0.74	0.68	Calculate: n*Volume of sphere/ volume unit cell	


Crystalline structure
Unit cells
Crystal lattice examples
Cubic body centered (bcc)
Cubic face centered (fcc)
Hexagonal
Fe, V, Nb, Cr
Al, Ni, Ag, Cu, Au
Ti, Zn, Mg, Cd
BCC
FCC
HCP
Allotropic characteristics?