

# Tutorial 4

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*I wish to acknowledge this land on which the University of Toronto operates. For thousands of years it has been the traditional land of the Huron-Wendat, the Seneca, and most recently the Mississaugas of the Credit River. Today, this meeting place is still the home of many Indigenous people from across Turtle Island and we are grateful to have the opportunity to work on this land.*

- How is everyone?
- Therapy Dog Visit in the GB Lobby
  - When: **Wednesday, October 6** from 12:30 - 1:30 PM
  - Where: Galbraith Lobby (Drop-in)

- Quiz grades should be released by now
- **Problem Set 1 is due on October 7th**
- No tutorials next week since Thanksgiving is on the Monday

## ■ Simple Cubic

- $n_{SimpleCubic} = 1$

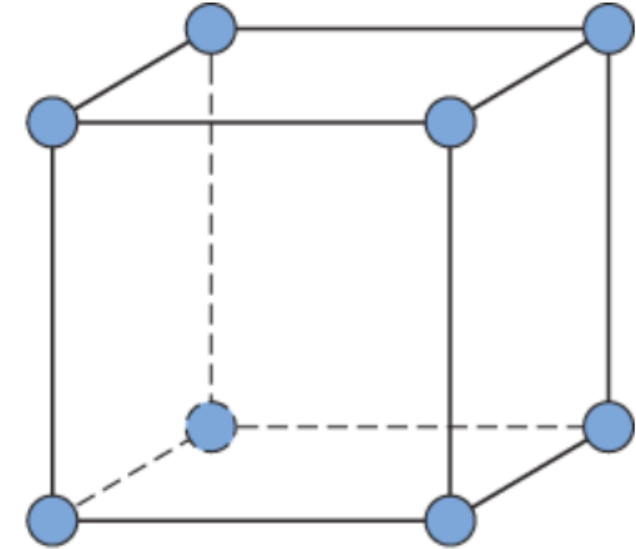
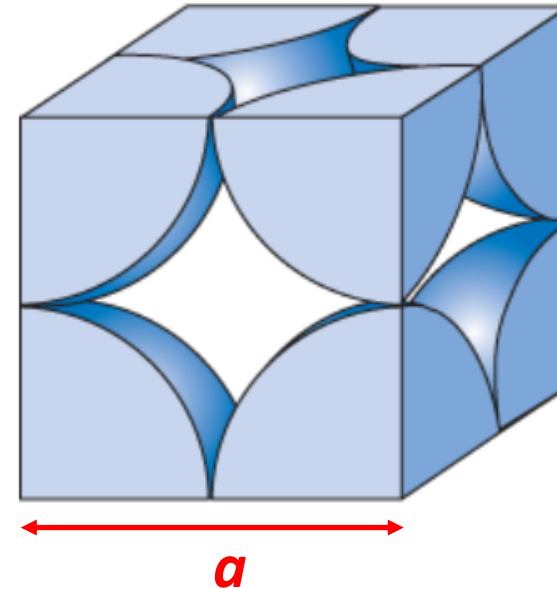
- $\rho = \frac{mass}{volume} = \frac{nA}{a^3 N_A}$

- $n$ : # atoms in unit cell

- $A$ : molar mass [g/mol]

- $a$ : lattice constant [m]

- $N_A$ : Avogadro's number [1/mol]



- $APF_{SimpleCubic} = \frac{volume\ of\ atoms}{volume\ of\ unit\ cell} = \frac{n \frac{4}{3} \pi R^3}{a^3} = 0.52$

- $R$ : atomic radius

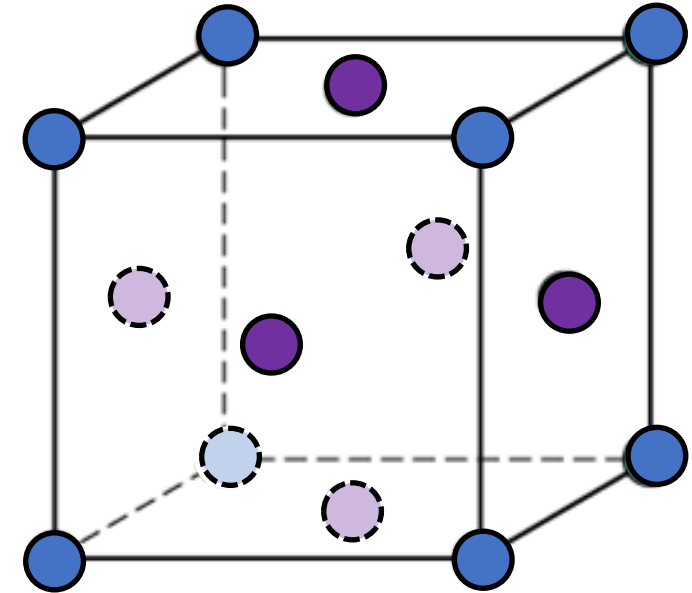
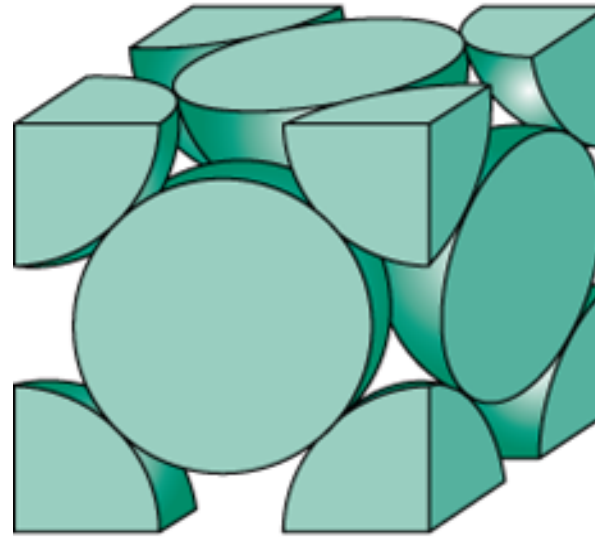
$$a = 2R$$

- Coordination Number = 6

- Face-Centred Cubic (FCC)

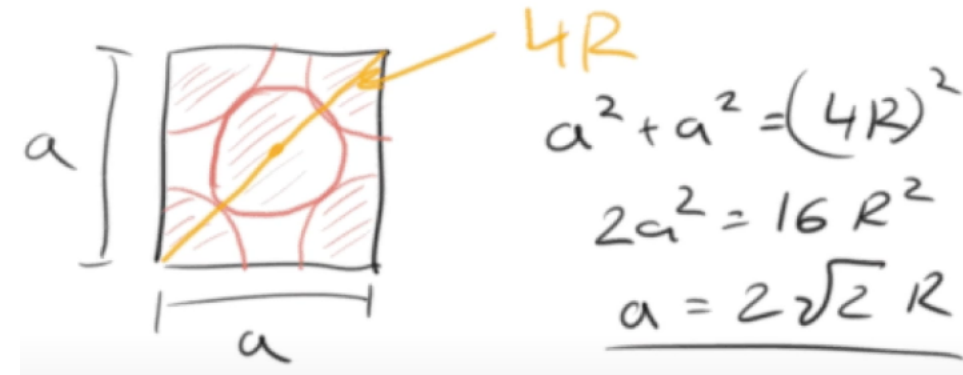
- $n_{FCC} = 8 * \frac{1}{8} + 6 * \frac{1}{2} = 4$

- $\rho = \frac{mass}{volume} = \frac{nA}{a^3 N_A}$



- $APF_{FCC} = \frac{volume\ of\ atoms}{volume\ of\ unit\ cell} = \frac{n \frac{4}{3} \pi R^3}{a^3} = 0.74$

- Coordination Number = 12



Handwritten diagram and equations for the FCC unit cell. The diagram shows a square face of the unit cell with side length 'a'. A diagonal line is drawn across the square, and a circle is inscribed within it, representing the face-centered atom. The diagonal is labeled '4R'. The equations shown are:

$$a^2 + a^2 = (4R)^2$$
$$2a^2 = 16R^2$$
$$a = 2\sqrt{2}R$$

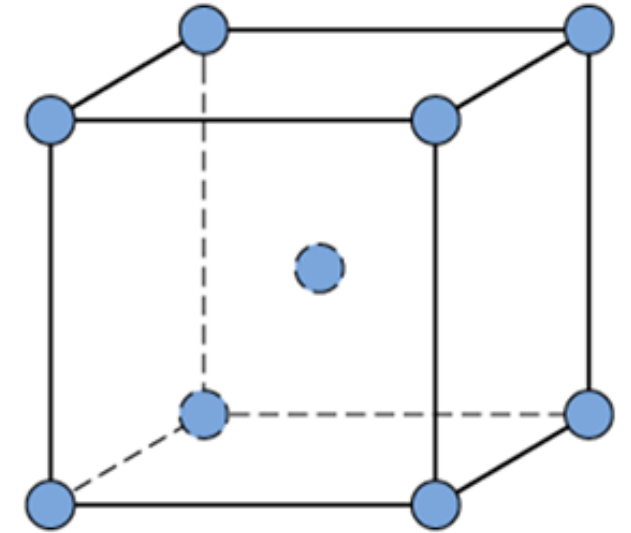
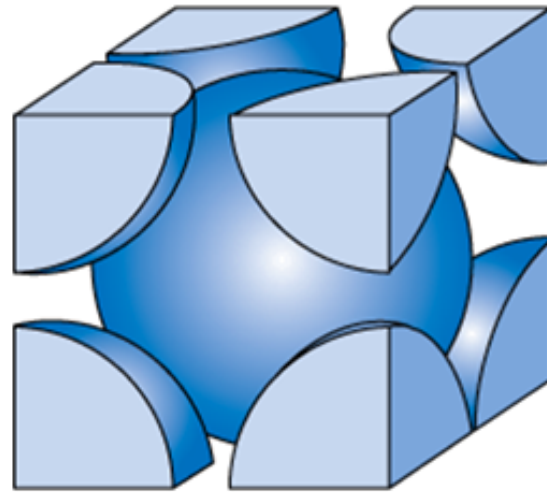
- Body-Centred Cubic (BCC)

- $n_{BCC} = 8 * \frac{1}{8} + 1 = 2$

- $\rho = \frac{\text{mass}}{\text{volume}} = \frac{nA}{a^3 N_A}$

- $APF_{BCC} = \frac{\text{volume of atoms}}{\text{volume of unit cell}} = \frac{n \frac{4}{3} \pi R^3}{a^3} = 0.68$

- Coordination Number = 8



Atoms touch along the diagonal of the cube:

$$a = \frac{4}{\sqrt{3}} R$$

## ■ Rock Salt

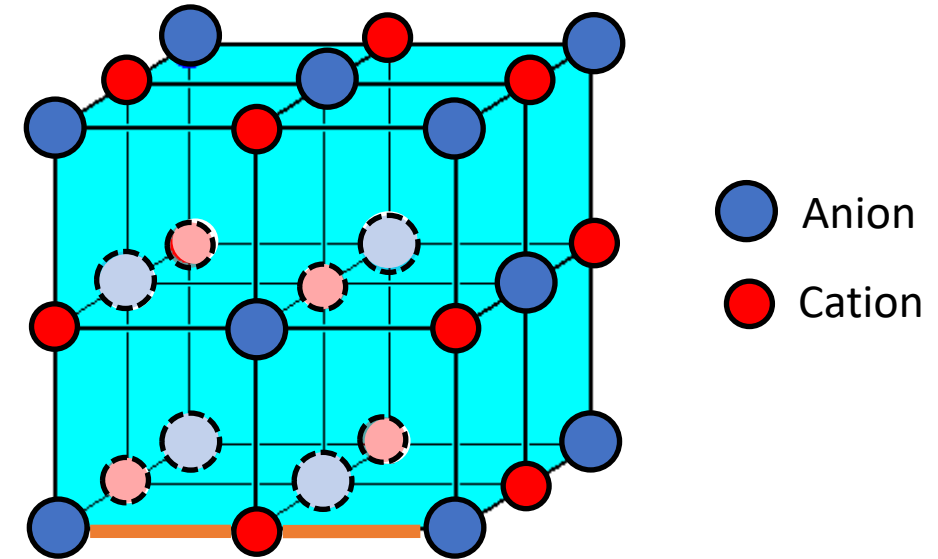
- Number of cations:  $n_c = 4$
- Number of anions:  $n_a = 4$

- $$\rho = \frac{n_c A_c + n_a A_a}{a^3 N_A}$$

- $$APF = \frac{n_c \frac{4}{3}\pi R_c^3 + n_a \frac{4}{3}\pi R_a^3}{a^3}$$

- $R_c$ : cation radius
- $R_a$ : anion radius

- Coordination Number = 6

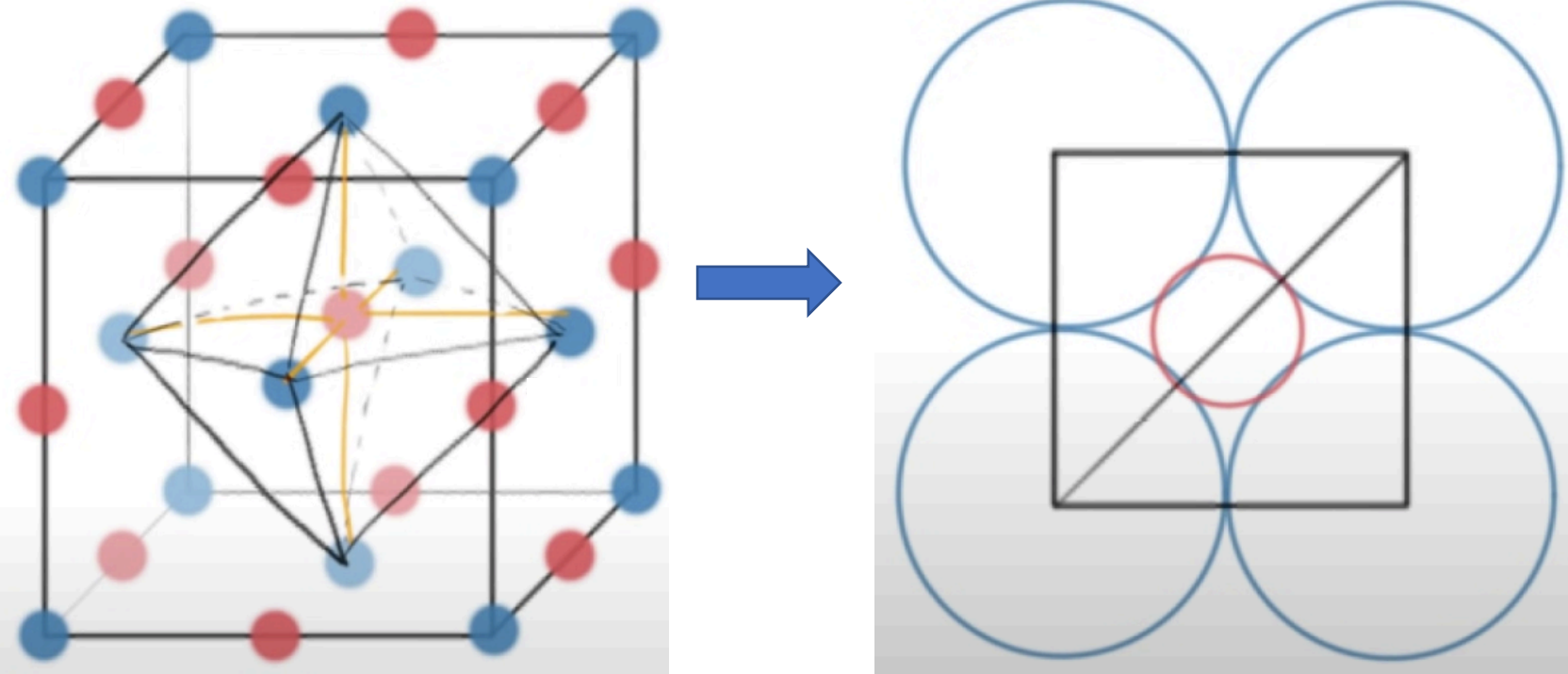


Ions touch along the **edges**:

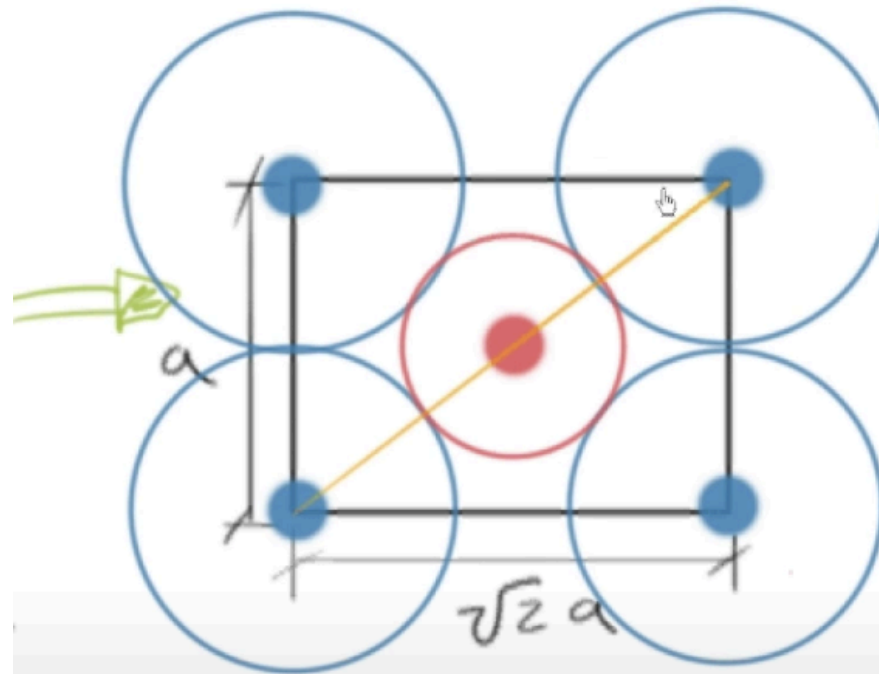
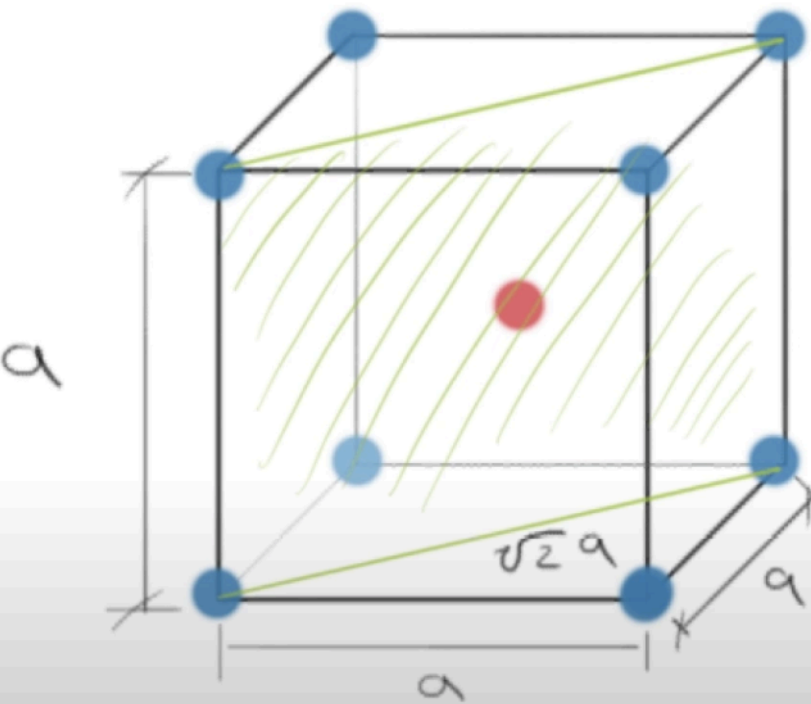
$$a = 2R_a + 2R_c$$



- Octahedral Interstitial Site
  - What is the best ratio  $R_c / R_a$  ?
    - $R_c / R_a = 0.414$



- Cubic Interstitial Site
  - What is the best ratio  $R_c / R_a$  ?
    - $R_c / R_a = 0.732$



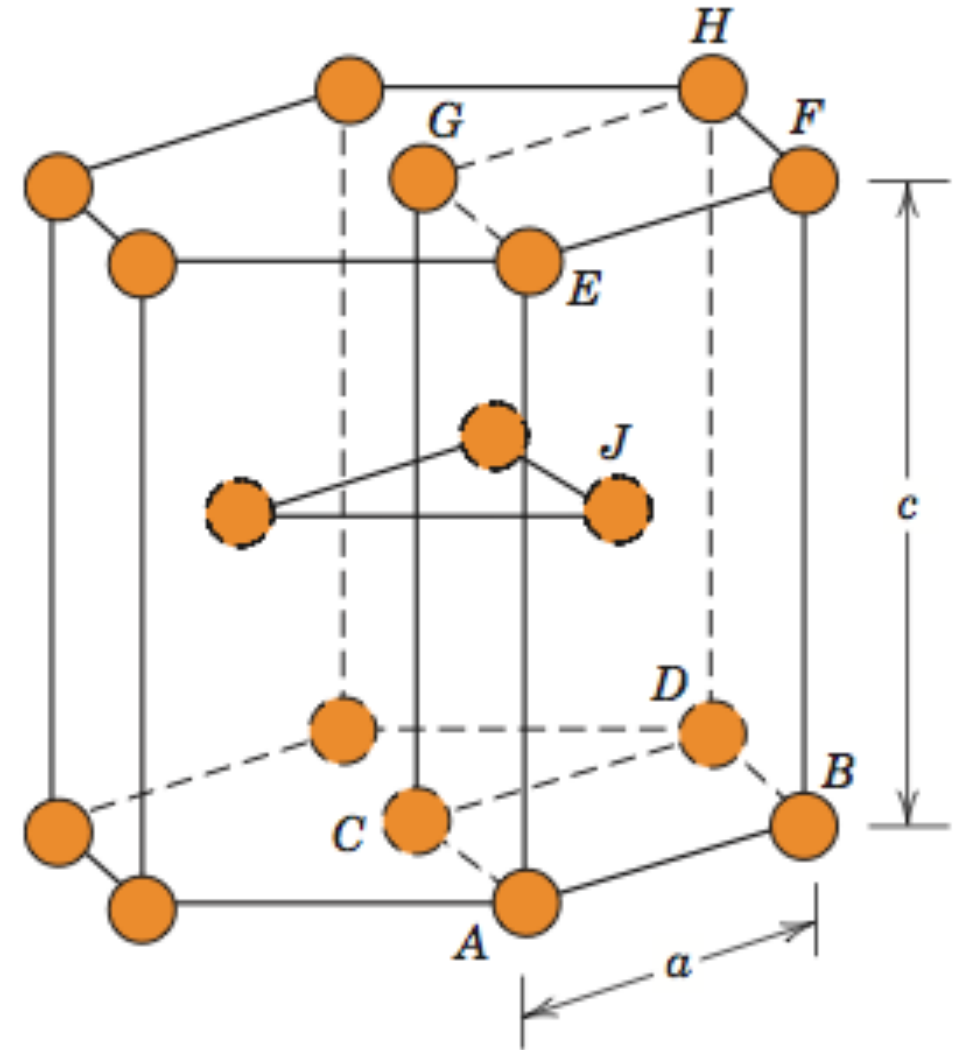
- Hexagonal Close Packed (HCP)

- $n_{HCP} = 6$

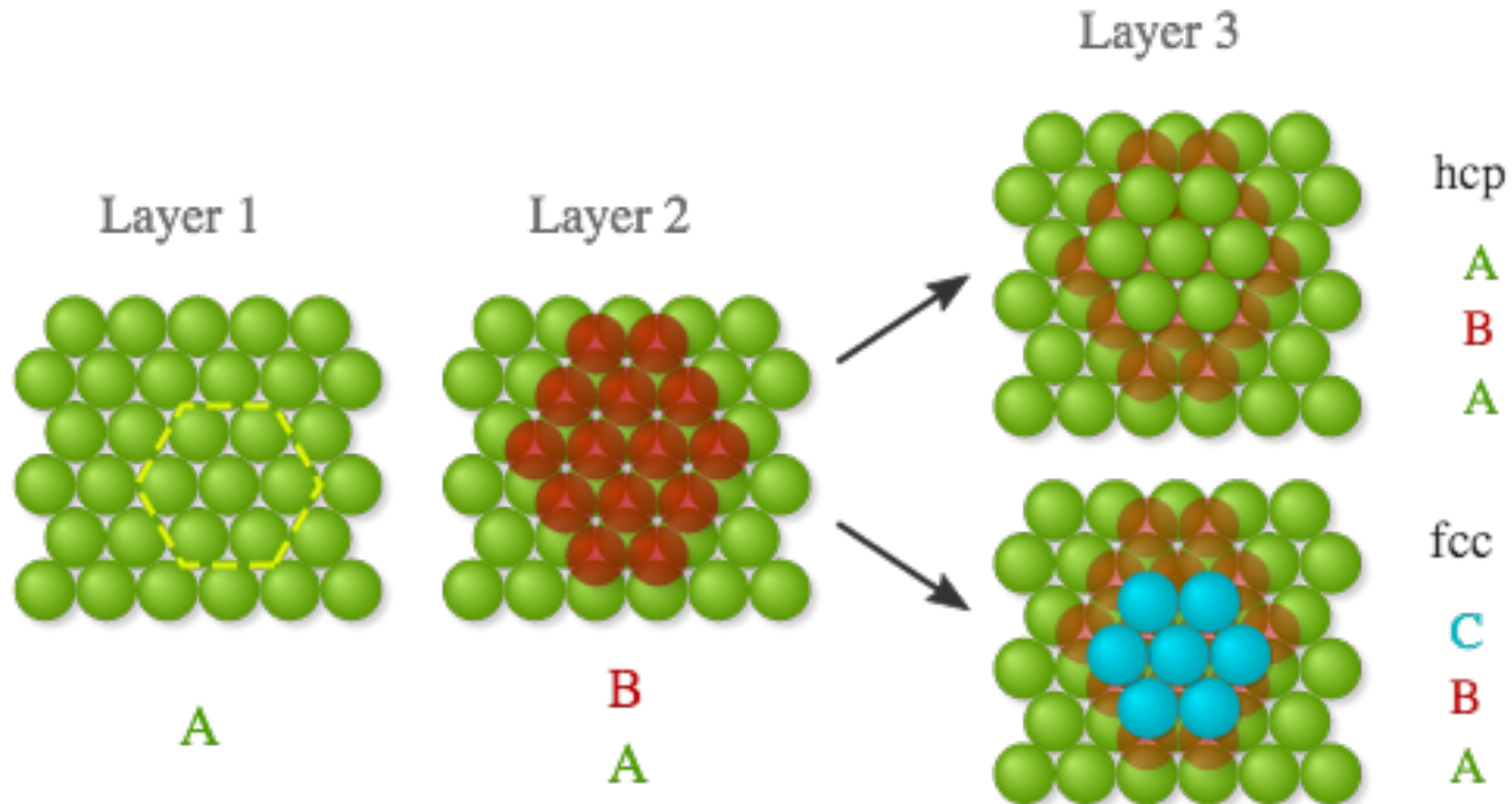
- $\rho = \frac{\text{mass}}{\text{volume}} = \frac{nA}{VN_A}$ 
    - $A_{\text{hexagon}} = \frac{3\sqrt{3}}{2}a^2$
    - $V = cA_{\text{hexagon}}$

- $APF_{HCP} = 0.74$

- Coordination Number = 12



## ■ Close Packed Planes



# Sample Problems

1. Below are listed the atomic weight, density, and atomic radius for three hypothetical alloys. For each determine whether its crystal structure is FCC, BCC, or simple cubic and justify why.

| Alloy | Atomic Weight (g/mol) | Density (g/cm <sup>3</sup> ) | Atomic Radius (nm) |
|-------|-----------------------|------------------------------|--------------------|
| A     | 43.1                  | 6.40                         | 0.122              |
| B     | 184.4                 | 12.30                        | 0.146              |
| C     | 91.6                  | 9.60                         | 0.137              |

Method → Assume random crystal structures & calculate density to compare.

# Sample Problems

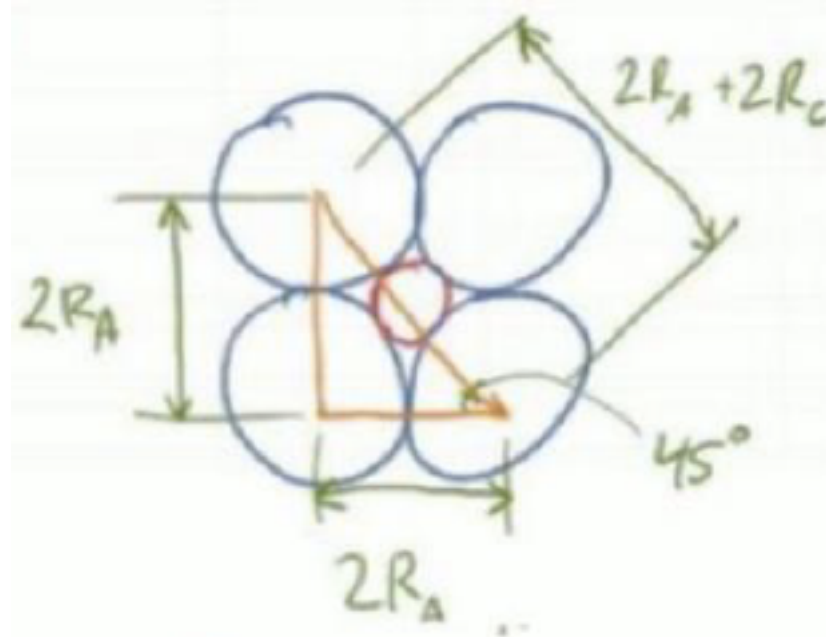
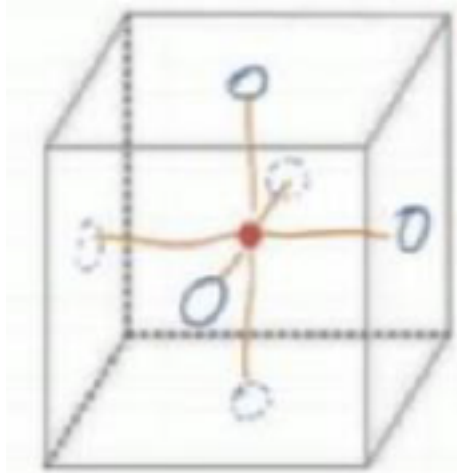
$$\textcircled{A} \text{ Assume BCC } \rightarrow \rho = \frac{n \cdot A_a}{\left(\frac{4R}{\sqrt{3}}\right)^3 N_a} = \frac{(2 \cdot 43.1)}{\left(\frac{4 \cdot 1.22 \times 10^{-8} \text{ cm}}{\sqrt{3}}\right)^3 \cdot N_a} \\ = 6.40$$

$$\textcircled{B} \text{ Assume simple cubic } \rho = \frac{n \cdot A_B}{(2R)^3 N_a} = \frac{(1 \cdot 184.4)}{(2 \cdot 1.46 \times 10^{-8})^3 \cdot N_a} \\ = 12.3 \text{ g/cm}^3$$

$$\textcircled{C} \text{ BCC } \rho = \frac{n A_c}{\left(\frac{4R}{\sqrt{3}}\right)^3 N_a} = \frac{(2 \cdot 91.6)}{\left(\frac{4 \cdot 1.37 \times 10^{-8}}{\sqrt{3}}\right)^3 \cdot N_a} \\ = 9.6 \text{ g/cm}^3$$



2. Demonstrate that the ideal cation-to-anion ratio ( $R_c/R_a$ ) for a cation that just fits into the octahedral interstitial site, without pushing the anions apart is 0.414. Begin with a sketch of one octahedral site within the unit cell below, clearly showing the coordination number.



$$\sin 45^\circ = \frac{2R_A}{2R_A + 2R_c}$$

# Sample Problems

$$\sin 45 = \frac{2R_A}{2R_A + 2R_C}$$

$$R_A \sin 45 + R_C \sin 45 = R_A$$

$$\frac{R_A}{R_A} \sin 45 = \frac{R_C}{R_A} \sin 45 = \frac{R_A}{R_A}$$

$$\frac{R_C}{R_A} = \frac{1 - \sin 45}{\sin 45} = 0.414$$



# Quizz (not graded)

1. In an FCC unit cell, how many complete atoms are contributed to the unit cell from the atoms in the corners of the cell?
  - a. 8
  - b. 4
  - c. 1
  - d. 2
2. Which of the following is equal to the radius of atoms forming a BCC unit cell in terms of its lattice parameter ( $a$ )?
  - a.  $1.732a$
  - b.  $0.57735a$
  - c.  $0.433a$
  - d.  $0.353a$
3. A lump of solid gold having a mass of 38g is placed into a cylinder of water that is already full to the top. How much water spills out of the cylinder? Gold has the FCC crystal structure and you can assume that the atomic radius of gold is 0.146 nm.  $A_{\text{Au}} = 196.67 \text{ g/mol}$

# Quizz (not graded)

4. Data has been obtained for some elements or compounds and is shown in the table below. Using the data given, calculate the missing data (bold numbers)

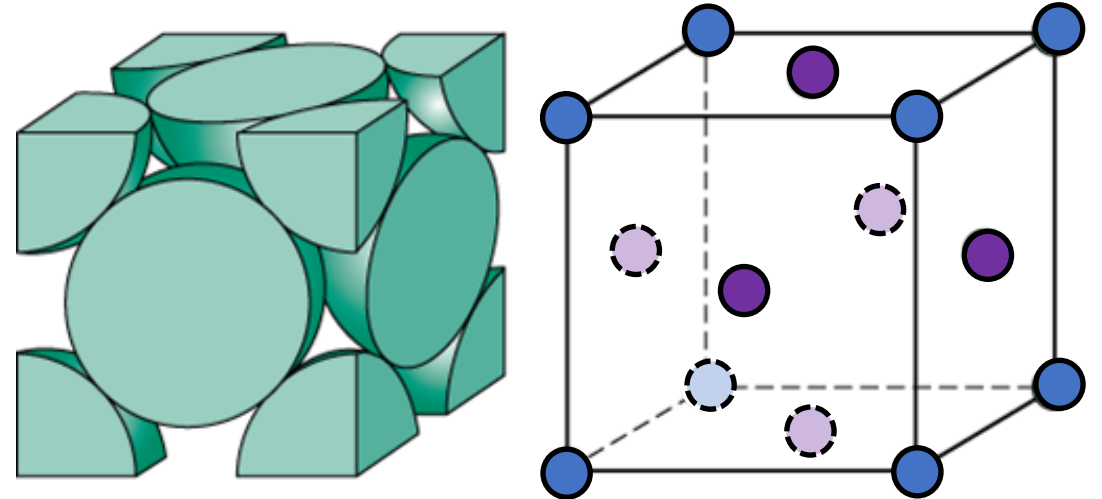
| Element/Compound | Radius (pm)   | Crystal Structure | Molar mass (g/mol)         | Density (g/cm <sup>3</sup> ) |
|------------------|---|-------------------|----------------------------|------------------------------|
| Copper           | <b>1</b>  | FCC               | 63.546                     | 8.96                         |
| Cobalt           | 200   | HCP               | 58.933                     | <b>4</b>                     |
| Polonium         | 168   | Simple Cubic      | <b>3</b>                   | 9.196                        |
| Scandium         | 162   | HCP               | 44.955                     | <b>5</b>                     |
| Silver Chloride  | $R_{\text{Ag}} = 144$<br>$R_{\text{Cl}} = ?$ <b>(2)</b> | Rock Salt         | Ag – 107.87<br>Cl – 35.453 | 5.56                         |

# Quizz (not graded) – Solutions

1. In an FCC unit cell, how many complete atoms are contributed to the unit cell from the atoms in the corners of the cell?

- a. 8
- b. 4
- c. 1
- d. 2

*Only the blue ones!*



2. Which of the following is equal to the radius of atoms forming a BCC unit cell in terms of its lattice parameter (a)?

- a.  $1.732a$
- b.  $0.57735a$
- c.  $0.433a$
- d.  $0.353a$

$$a = \frac{4}{\sqrt{3}} R$$

# Quizz (not graded) – Solutions

3.

$$\rho = \frac{nA}{V_c N_A} \quad \left| \quad \begin{array}{l} n = 4 \\ A = 196.67 \text{ g/mol} \\ N_A = 6.023 \times 10^{23} \end{array} \right.$$

$$V_c = a^3 \quad \text{with } a = 2\sqrt{2} R$$

$$\rho = \frac{\text{mass}}{\text{volume}} \rightarrow \text{volume} = \frac{m}{\rho}$$

$$V = \frac{m \cdot (2\sqrt{2} R)^3 \cdot N_A}{nA} = \frac{38 \cdot (2\sqrt{2} \cdot 0.146 \times 10^{-9})^3 \cdot N_A}{4 \cdot 196.67}$$

$$= 2.05 \times 10^{-6} \text{ m}^3$$

$$= 2 \text{ cm}^3 = 2 \text{ cc} = 2 \text{ mL}$$

# Quizz (not graded) – Solutions

4.

① for FCC Copper

$$\hookrightarrow \rho = \frac{n \cdot A}{a^3 \cdot N_A} \quad \left| \quad a = 2\sqrt{2}R \right.$$

$$\therefore \rho = \frac{n \cdot A}{(2\sqrt{2}R)^3 \cdot N_A} \Rightarrow R = \left( \frac{nA}{\rho N_A} \right)^{1/3} \cdot \frac{1}{2\sqrt{2}}$$

$$R = \left( \frac{4 \cdot 63.546}{8.96 \times 10^6 \cdot N_A} \right) \cdot \frac{1}{2\sqrt{2}} = 127 \text{ pm}$$

# Quizz (not graded) – Solutions

4.

④ Cobalt (HCP) (using FCC shortcut).

$$\rho = \frac{n \cdot A}{V_c \cdot N_A} \quad \left| \begin{array}{l} n=4 \\ A=58.933 \end{array} \right| \quad \left| \begin{array}{l} V_c = (2\sqrt{2}R)^3 \\ R=200 \times 10^{-12} \text{ m} \end{array} \right.$$
$$\rho = \frac{4 \cdot 58.933}{(2\sqrt{2} \cdot 200 \times 10^{-12})^3 \cdot N_A} = 2.2 \text{ g/cm}^3$$

$$V_c = \frac{3\sqrt{3}}{2} a^2 \cdot h \quad \left| \begin{array}{l} h=1.633a \\ a=2r \end{array} \right.$$

$$\rho = (6 \cdot 58.933) / \left( \frac{3\sqrt{3}}{2} \cdot 1.633 (2 \times 200 \times 10^{-12})^3 \cdot N_A \right)$$
$$= 2.2 \text{ g/cm}^3$$

# Quizz (not graded) – Solutions

4.

$$\textcircled{3} \quad c = \frac{n \cdot A}{V_c \cdot N_a} \rightarrow A = \frac{c \cdot V_c \cdot N_a}{n}$$

$$A = \frac{9.196 \times 10^6 \cdot (2 \times 10^{-12})^3 \cdot N_a}{1}$$

$$= 210.07 \text{ g/mol.}$$

# Quizz (not graded) – Solutions

4.

$$\textcircled{2} \ell = \frac{n_a A_a + n_c A_c}{V_c \cdot N_a}$$

$$= \frac{n_a A_a + n_c A_c}{(2R_a + 2R_c)^3 \cdot N_a}$$

$$(2R_a + 2R_c) = \left( \frac{n_a A_a + n_c A_c}{\ell \cdot N_a} \right)^{1/3}$$

$$R_a = \left[ \left( \frac{n_a A_a + n_c A_c}{\ell \cdot N_a} \right)^{1/3} - 2R_c \right] \cdot \frac{1}{2}$$

$$= \left( \left[ \frac{(4 \times 35.453 + 4 \times 107.87)}{5.56 \times 10^6 \cdot N_a} \right]^{1/3} - 2.144 \times 10^{-12} \right)$$

$$\cdot \frac{1}{2}$$

$$= 133 \text{ pm}$$