Tutorial 4

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Fall 2022

Land Acknowledgment

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I wish to acknoledge 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.

Health Resources

- How is everyone?

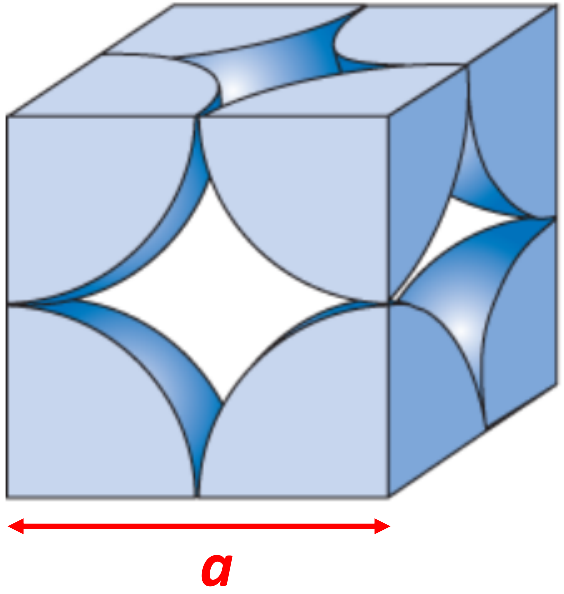
- Therapy Dog Visit in the GB Lobby
  - When: Wednesday, October 6 from 12:30 - 1:30 PM
  - Where: Galbraith Lobby (Drop-in)

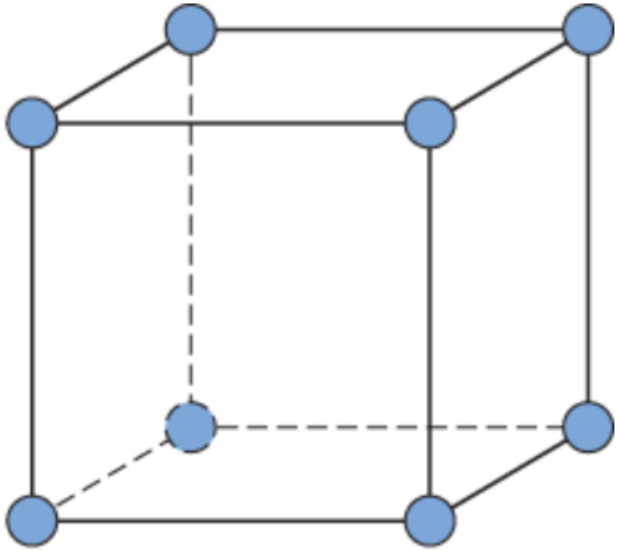
Anouncements

- 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

Theory Review

- 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]

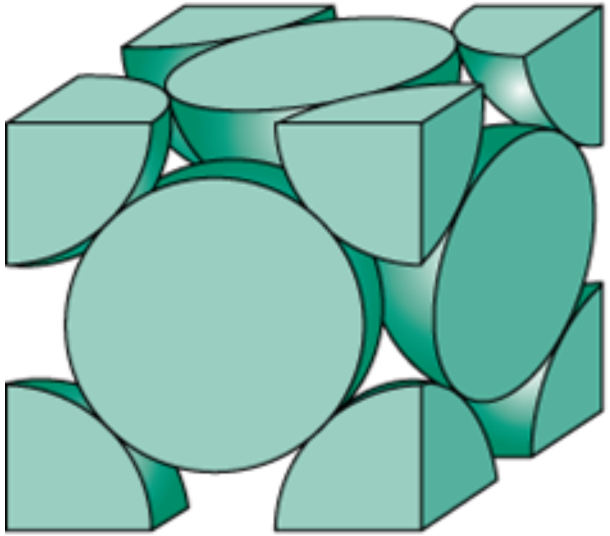


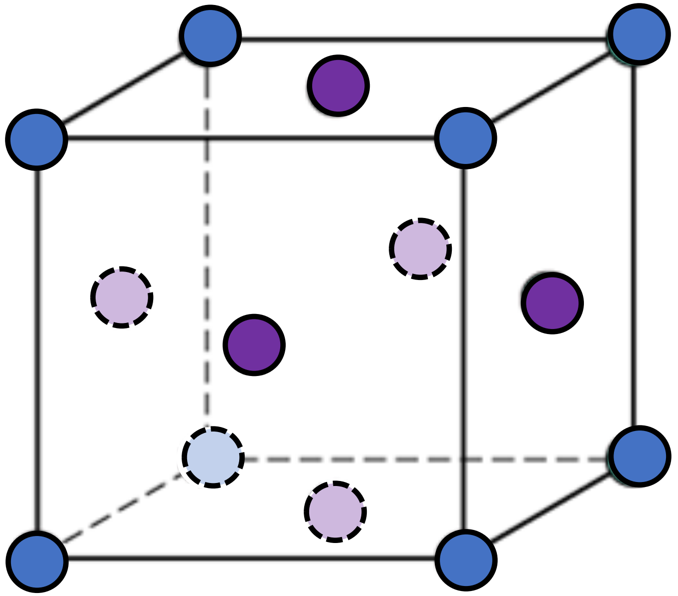


  - $APF_{SimpleCubic} = \frac{volume\ of\ atoms}{volume\ of\ unit\ cell} = \frac{n\frac{3}{4}\pi R^3}{a^3} = 0.52$ $\qquad a = 2R$
    - ***R:*** atomic radius
  - Coordination Number = 6

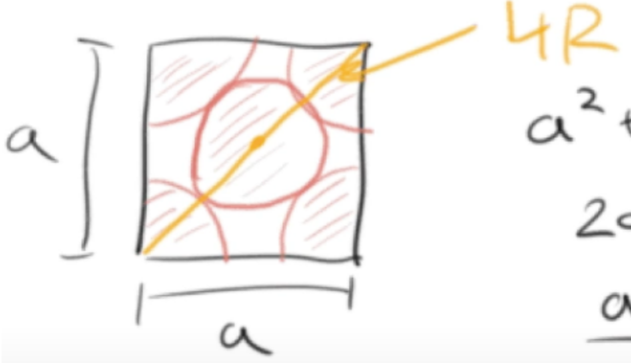
Theory Review

- Face-Centred Cubic (FCC)
  - $n_{FCC} = 8 * \frac{1}{8} + 6 * \frac{1}{2} = 4$
  - $\rho = \frac{mass}{volume} = \frac{nA}{a^3 N_A}$





  - $APF_{FCC} = \frac{volume\ of\ atoms}{volume\ of\ unit\ cell} = \frac{n \frac{3}{4}\pi R^3}{a^3} = 0.74$
  - Coordination Number = 12



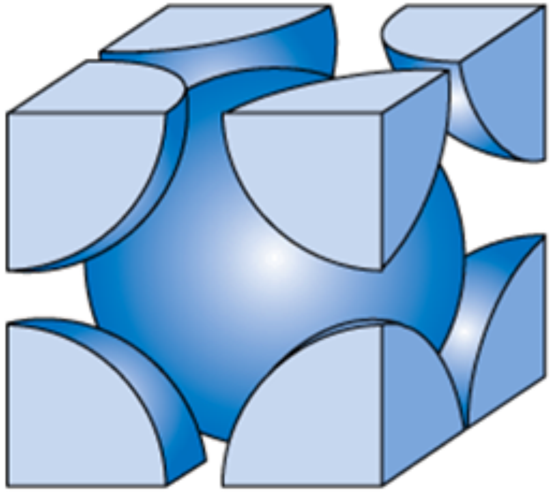
$a^2 + a^2 = (4R)^2$

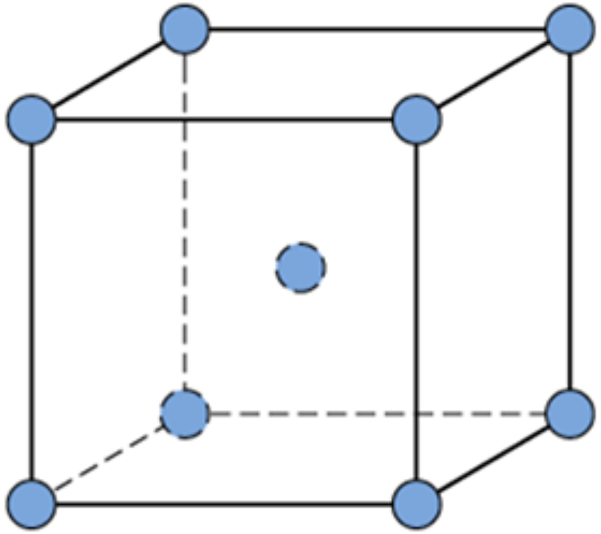
$2a^2 = 16R^2$

$a = 2\sqrt{2}R$

Theory Review

- Body-Centred Cubic (BCC)
  - $n_{BCC} = \mathbf{8} * \frac{\mathbf{1}}{\mathbf{8}} + \mathbf{1} = 2$
  - $\rho = \frac{mass}{volume} = \frac{nA}{a^3 N_A}$
  - $APF_{BCC} = \frac{volume\ of\ atoms}{volume\ of\ unit\ cell} = \frac{n\frac{3}{4}\pi R^3}{a^3} = 0.68$
  - Coordination Number = 8



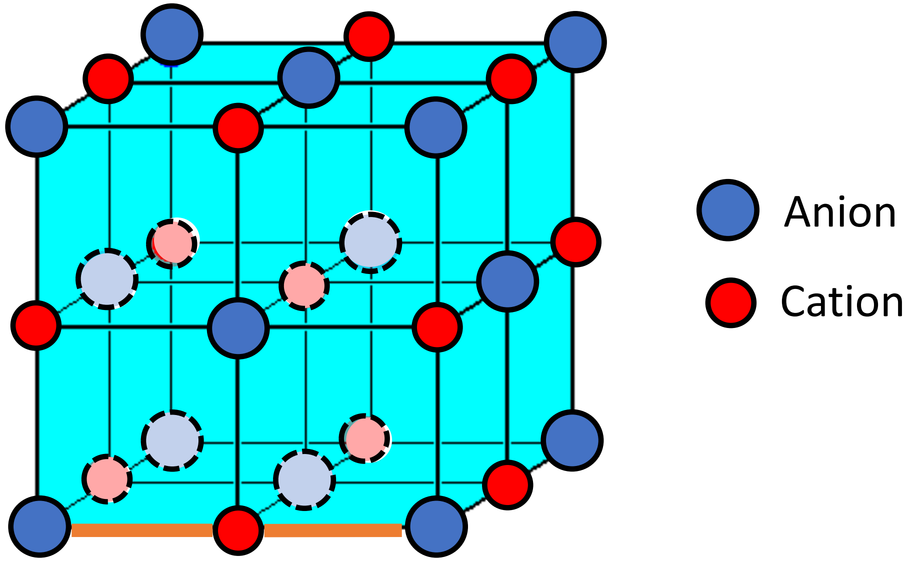


Atoms touch along the diagonal of the cube:

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

Theory Review

- Rock Salt
  - Number of cations: $n_c = 4$
  - Number of anions: $n_a = 4$
  - $\rho = \dfrac{n_c A_c + n_a A_a}{a^3 N_A}$
  - $APF = \dfrac{n_c \frac{3}{4}\pi R_c{}^3 + n_a \frac{3}{4}\pi R_a{}^3}{a^3}$
    - R_c: cation radius
    - R_a: anion radius
  - Coordination Number = 6

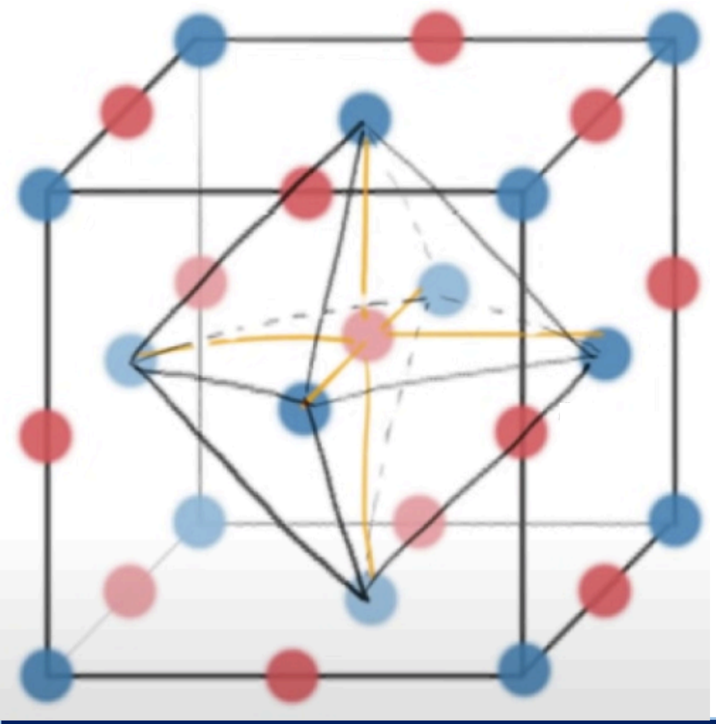


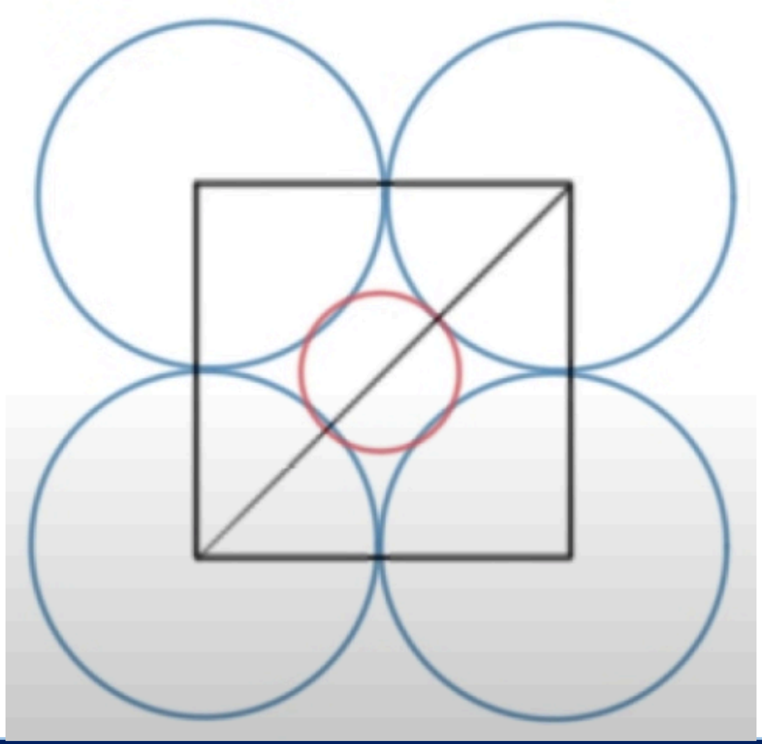
Ions touch along the edges:

$a = 2R_a + 2R_c$

Theory Review

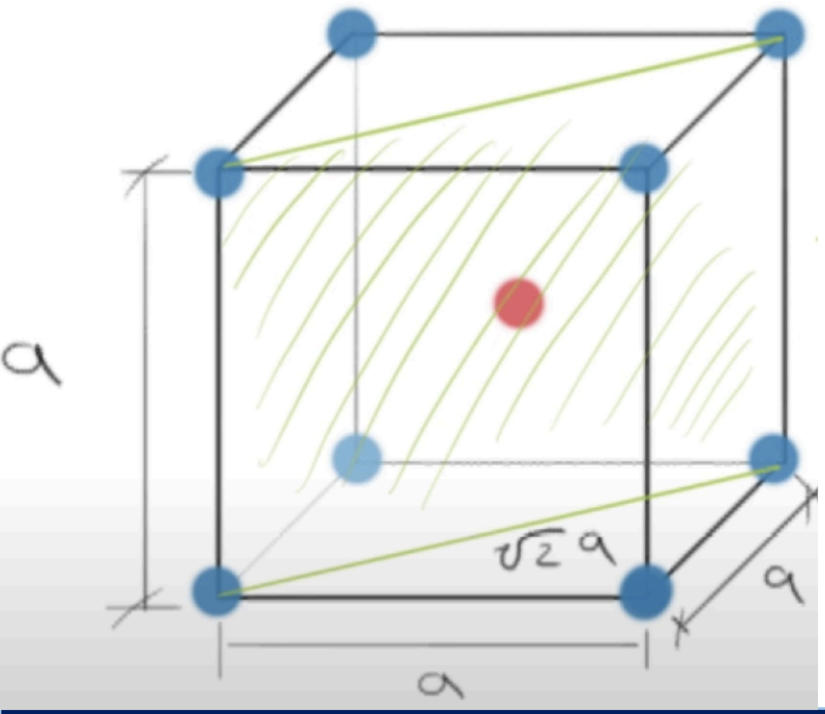
- Octahedral Interstitial Site
  - What is the best ratio R_c / R_a ?
    - R_c / R_a = 0.414

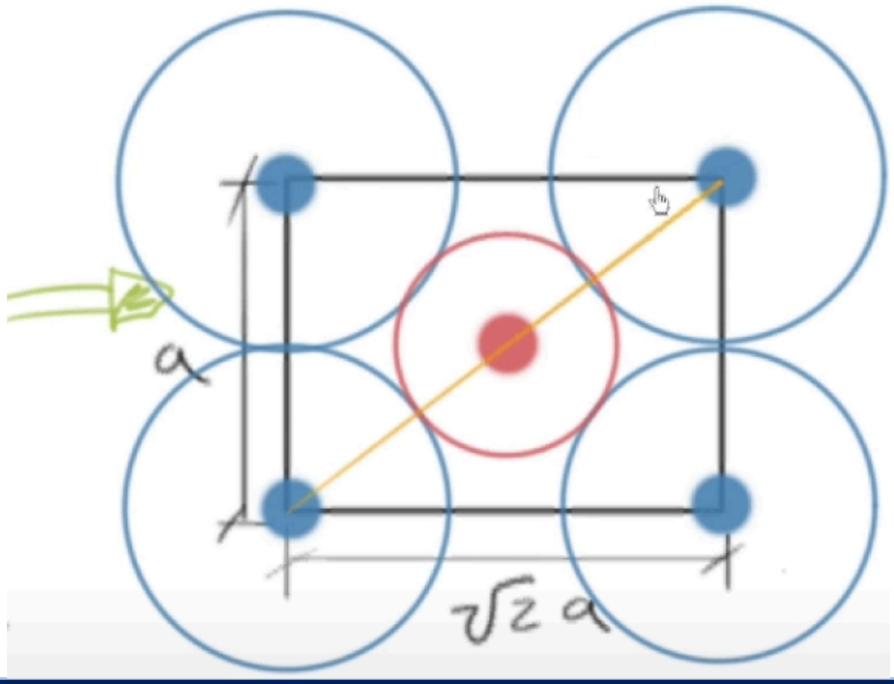




Theory Review

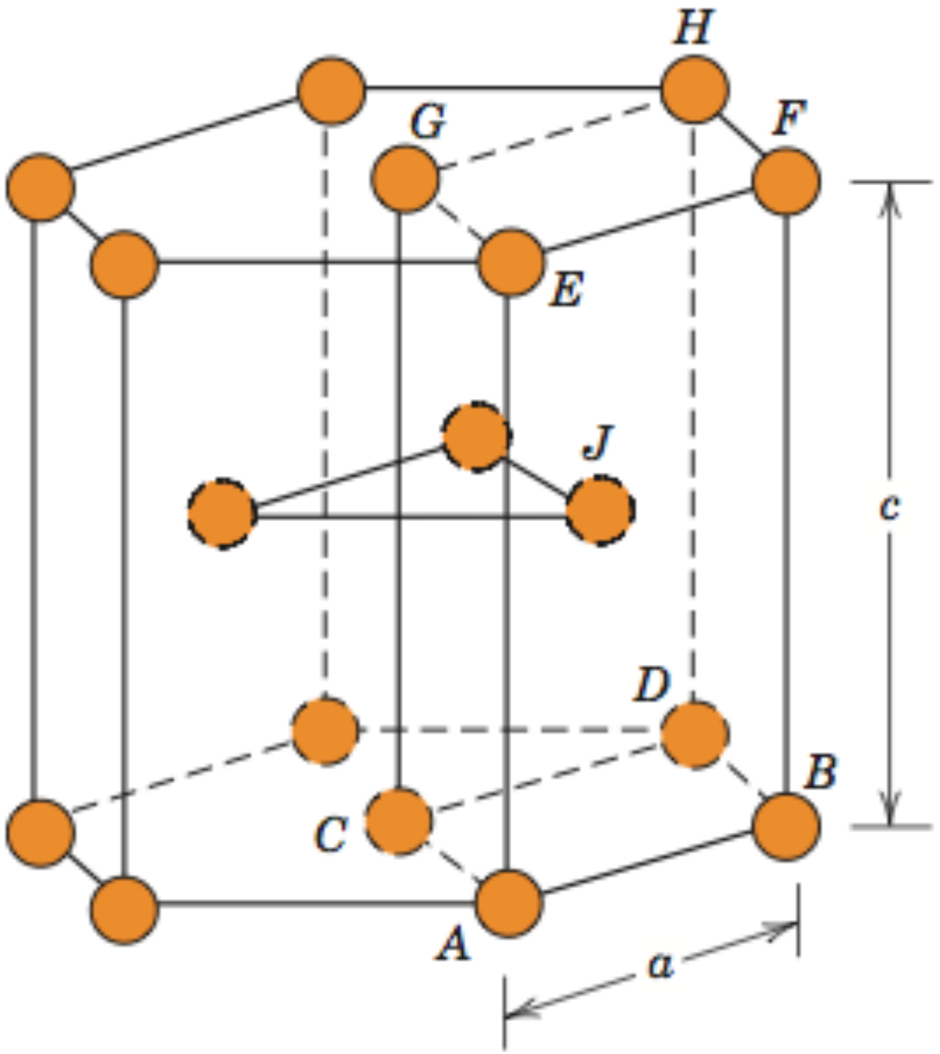
- Cubic Interstitial Site
  - What is the best ratio R_c / R_a ?
    - R_c / R_a = 0.732





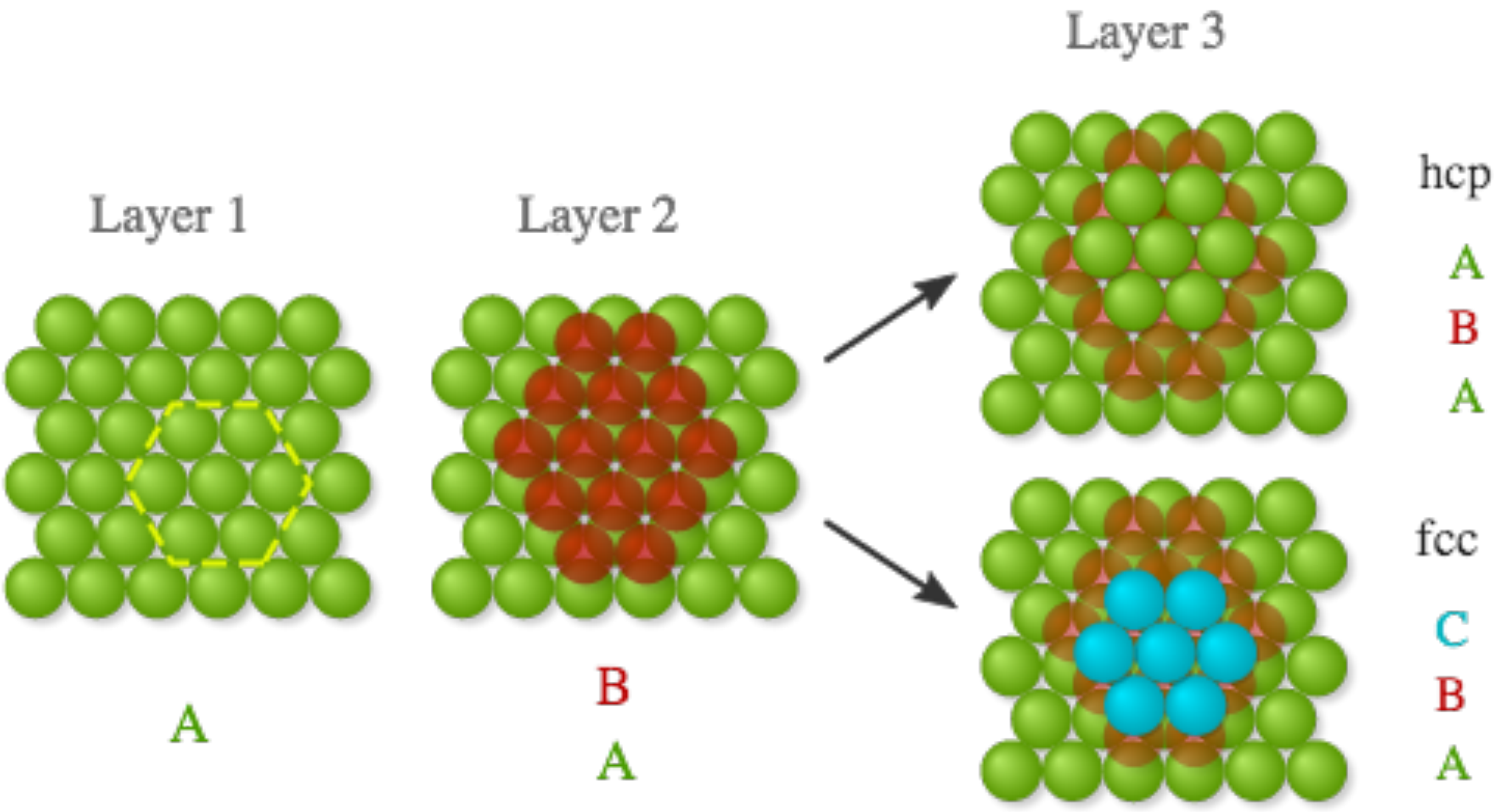
Theory Review

- Hexagonal Close Packed (HCP)
  - $n_{HCP} = 6$
  - $\rho = \frac{mass}{volume} = \frac{nA}{VN_A}$
    - $A_{hexagon} = \frac{3\sqrt{3}}{2}a^2$
    - $V = cA_{hexagon}$
  - $APF_{HCP} = 0.74$
  - Coordination Number = 12



Theory Review

- 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^3)	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

(A) Assume BCC $\rightarrow$ $\rho = \dfrac{n \cdot A_a}{\left(\frac{4R}{\sqrt{3}}\right)^3 N_a} = \dfrac{(2 \cdot 43.1)}{\left(\frac{4 \cdot 1.22\times10^{-8}cm}{\sqrt{3}}\right)^3 \cdot N_a}$

$= 6.40$

(B) assume simple cubic $\rho = \dfrac{n \cdot A_B}{(2R)^3 N_a} = \dfrac{(1\times184.4)}{(2\times1.46\times10^{-8})^3 \cdot N_a}$

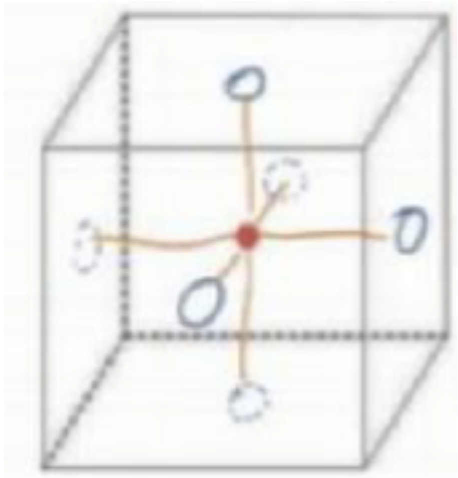
$= 12.3 g/cm^3$

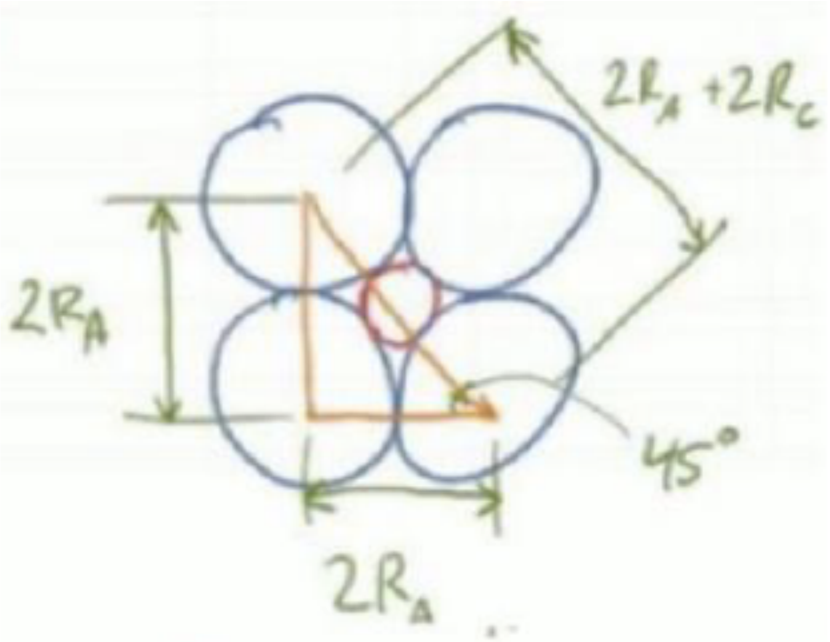
(C) BCC $\rho = \dfrac{n A_c}{\left(\frac{4R}{\sqrt{3}}\right)^3 N_a} = \dfrac{(2\times91.6)}{\left(\frac{4\cdot1.37\times10^{-8}}{\sqrt{3}}\right)^3 \cdot N_a}$

$= 9.6 g/cm^3$

Sample Problems

2. Demonstrate that the ideal cation-to-anion ratio (Rc/Ra) for a cation that just fits into the octahedral interstital 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.





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

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_{Au} = 196.67 g/mol

Quizz (not graded)

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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)

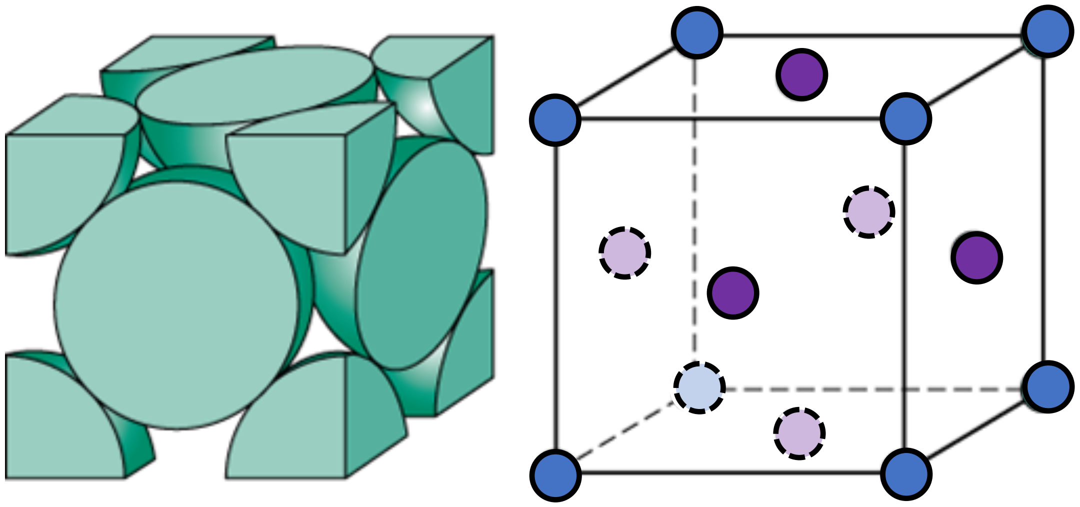
Element/Compound	Radius (pm)	Crystal Structure	Molar mass (g/mol)	Density (g/cm^3)
Copper	**1**	FCC	63.546	8.96
Cobalt	200	HCP	58.933	**4**
Polonium	168	Simple Cubic	**3**	9.196
Scandium	162	HCP	44.955	**5**
Silver Chloride	R_{Ag} = 144 R_{Cl} = ? **(2)**	Rock Salt	Ag – 107.87 Cl – 35.453	5.56

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.

$$\rho = \frac{nA}{V_c N_a} \quad \Bigg| \quad \begin{aligned} n &= 4 \\ A &= 196.67\ g/mol \\ N_a &= 6.023 \times 10^{23} \end{aligned}$$

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

$\rho =$ mass/volume $\rightarrow$ volume $= m/\rho$

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

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

$$= 2 cm^3 = 2 cc = 2 mL$$

Quizz (not graded) – Solutions

4.

① for FCC Copper

$\hookrightarrow \rho = \dfrac{n \cdot A}{a^3 \cdot N_a}$ | $a = 2\sqrt{2}R$

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

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

Quizz (not graded) – Solutions

4.

④ Cobalt (HCP) (using FCC shortcut).

$$\rho = \frac{n \cdot A}{V_c \cdot N_A} \quad \Big| \quad n = 4, \quad A = 58.933 \quad \Big| \quad V_c = (2\sqrt{2}R)^3, \quad R = 200\times10^{-12}\,m$$

$$\rho = \frac{4 \cdot 58.933}{(2\sqrt{2} \cdot 200\times10^{-12})^3 \cdot N_A} = 2.2\,g/cm^3$$

$$V_c = \frac{3\sqrt{3}}{2} a^2 \cdot h \quad \Big| \quad h = 1.633a, \quad a = 2r$$

$$\rho = (6 \cdot 58.933) \Big/ \left(\frac{3\sqrt{3}}{2} \cdot 1.633 (2\times200\times10^{-12})^3 \cdot N_A \right)$$

$$= 2.2\,g/cm^3$$

Quizz (not graded) – Solutions

4.

③ $\rho = \dfrac{n \cdot A}{V_c \cdot N_a} \rightarrow A = \dfrac{\rho \cdot V_c \cdot N_a}{n}$

$$A = \frac{9.196 \times 10^6 \cdot (2 \times 168 \times 10^{-12})^3 \cdot N_a}{1}$$

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

Quizz (not graded) – Solutions

4.

(2) $$\rho = \frac{n_a A_a + n_c A_c}{V_c \cdot N_a}$$

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

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

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

$$= \left(\left[\frac{(4 \times 35.453 + 4 \times 107.87)}{5.56 \times 10^6 \cdot N_a}\right]^{1/3} - 2.144 \times 10^{-12}\right) \cdot \frac{1}{2}$$

$$= 133\,pm$$