

Chapter 4

Ionic Solids

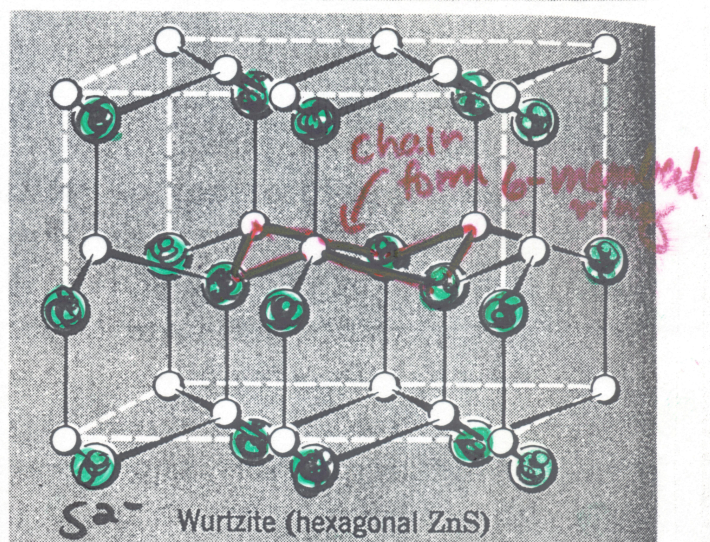
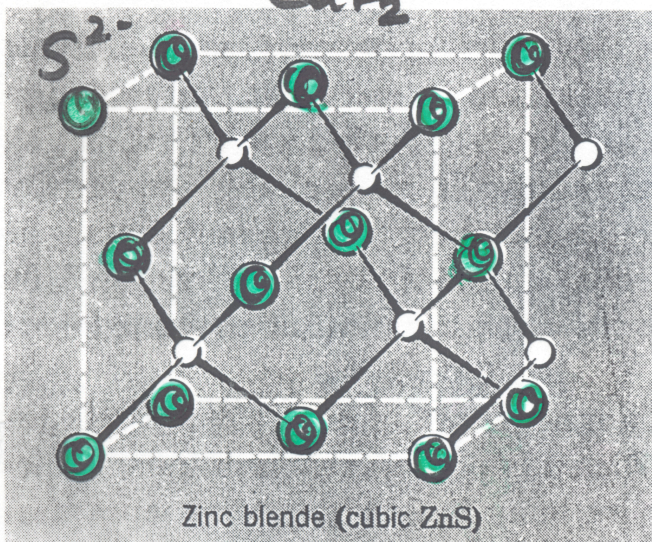
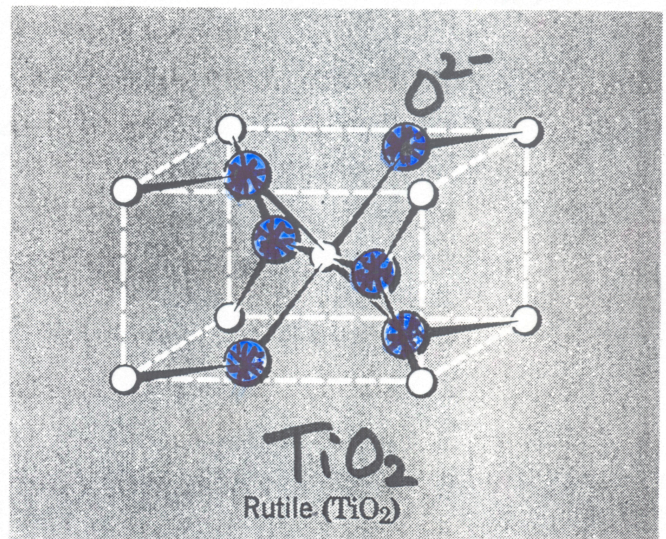
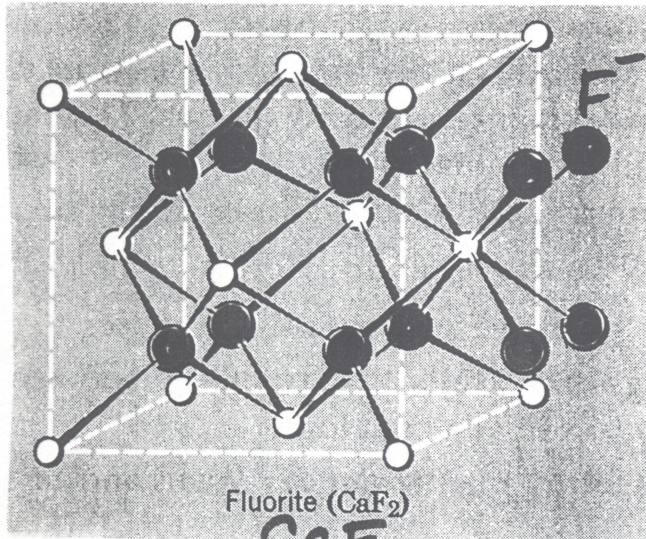
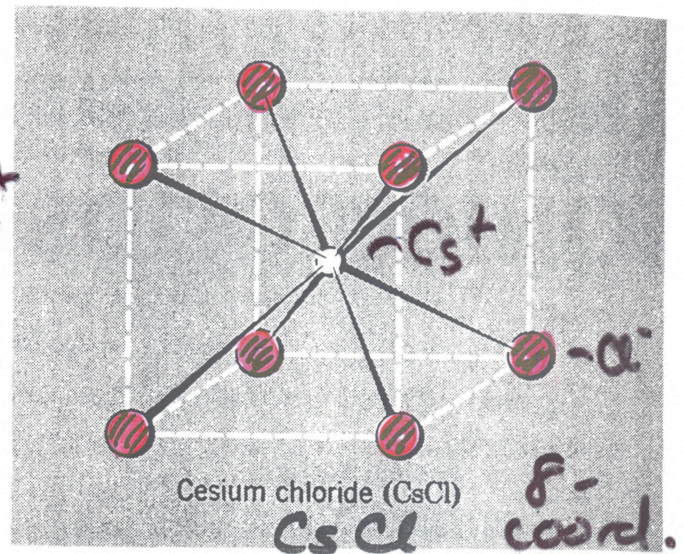
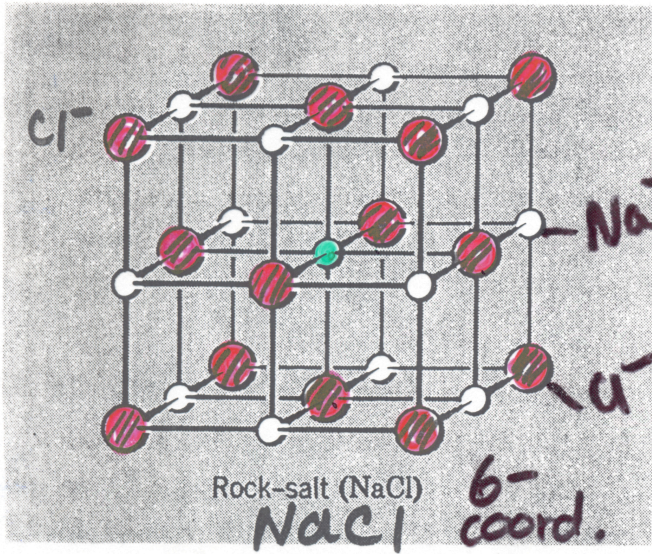
Energy of Arrays of Ions:

1. Coulombic (electrostatic) attractive and repulsive
+...+ +...-
 2. Additional repulsive energy from overlapping
outer electron density of adjacent ions
 3. minor terms, mainly van der Waals
- A. No covalency is taken into account in this model although it is certainly present to, at least, a small degree.
- B. The structures can be described as efficiently packed arrays of ions

As you will see, different sizes of ions pack in different ways. The ionic radii can explain this.

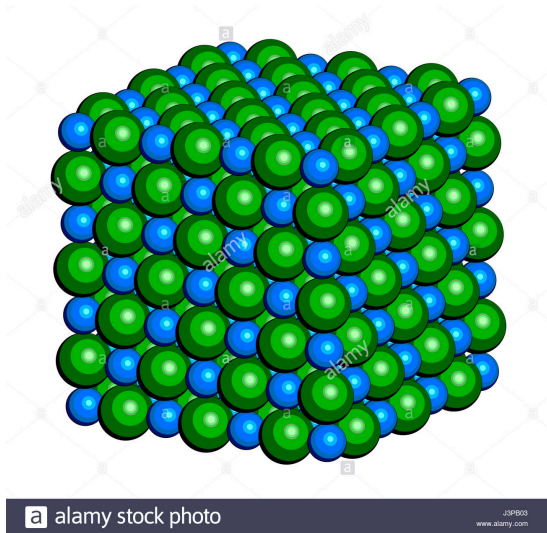
(NaCl, CsCl and CuCl have different structures)

Six basic types of ionic solids



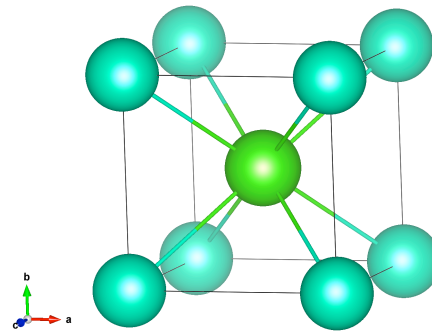
ZnS (cubic)
Zinc Blende

ZnS (hexagonal)
Wurtzite



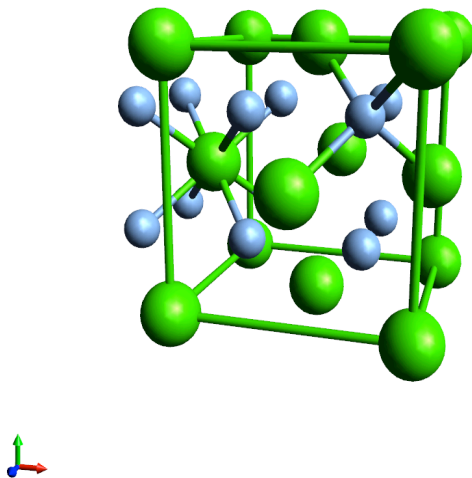
NaCl

face-centered cubic



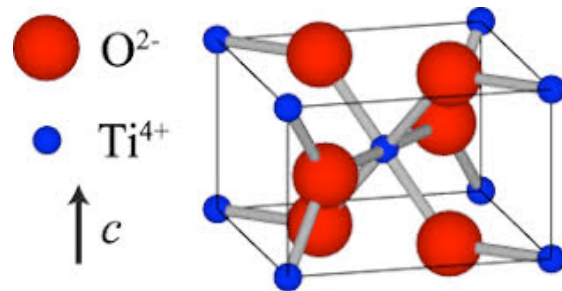
CsCl

body-centered cubic



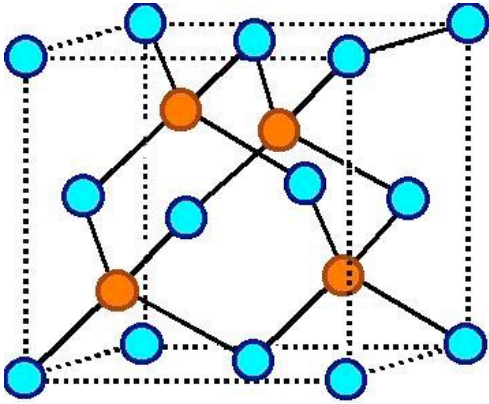
CaF₂ (fluorite)

Cubic

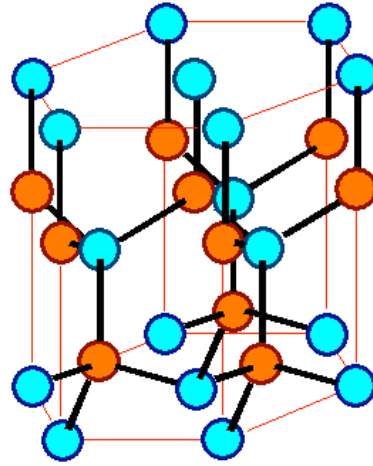


TiO₂ (rutile)

Rutile has a tetragonal unit cell (lower symmetry than cubic). The titanium cations have a coordination number of 6, meaning they are surrounded by an octahedron of 6 oxygen atoms. The oxygen anions have a coordination number of 3, resulting in a trigonal planar coordination.



ZnS (cubic zinc blende)



ZnS (hexagonal wurtzite)

Lattice Energy

Enthalpy (ΔH) of forming a solid ionic compound from gaseous ions. The **lattice** formation enthalpy is the enthalpy change when 1 mole of solid crystal is formed from its gaseous ions.

Lattice formation enthalpies are always **negative**.



Total lattice energy is a sum of attractive and repulsive terms.

This energy is called the **Madelung Energy which is a purely ionic model**

It is actually from the Born-Landé Equation

The **Born-Landé equation** is a means of calculating the **lattice energy** of a crystalline **ionic compound**. In 1918^[1] **Max Born** and **Alfred Landé** proposed that the lattice energy could be derived from the **electrostatic potential** of the ionic lattice and a repulsive potential energy term.

for NaCl type structures the equation is:

$$+ \quad U = \frac{N M_{NaCl} Z^2 e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n} \right)$$

- **M is Madelung constant** and it is the same for all structures that have the same packing geometry. It is a number that represents the sum total of the electrostatic interactions. The **Madelung constant** is used in determining the electrostatic potential of a single ion in a crystal by approximating the ions by point charges. It is named after Erwin **Madelung**, a German physicist.

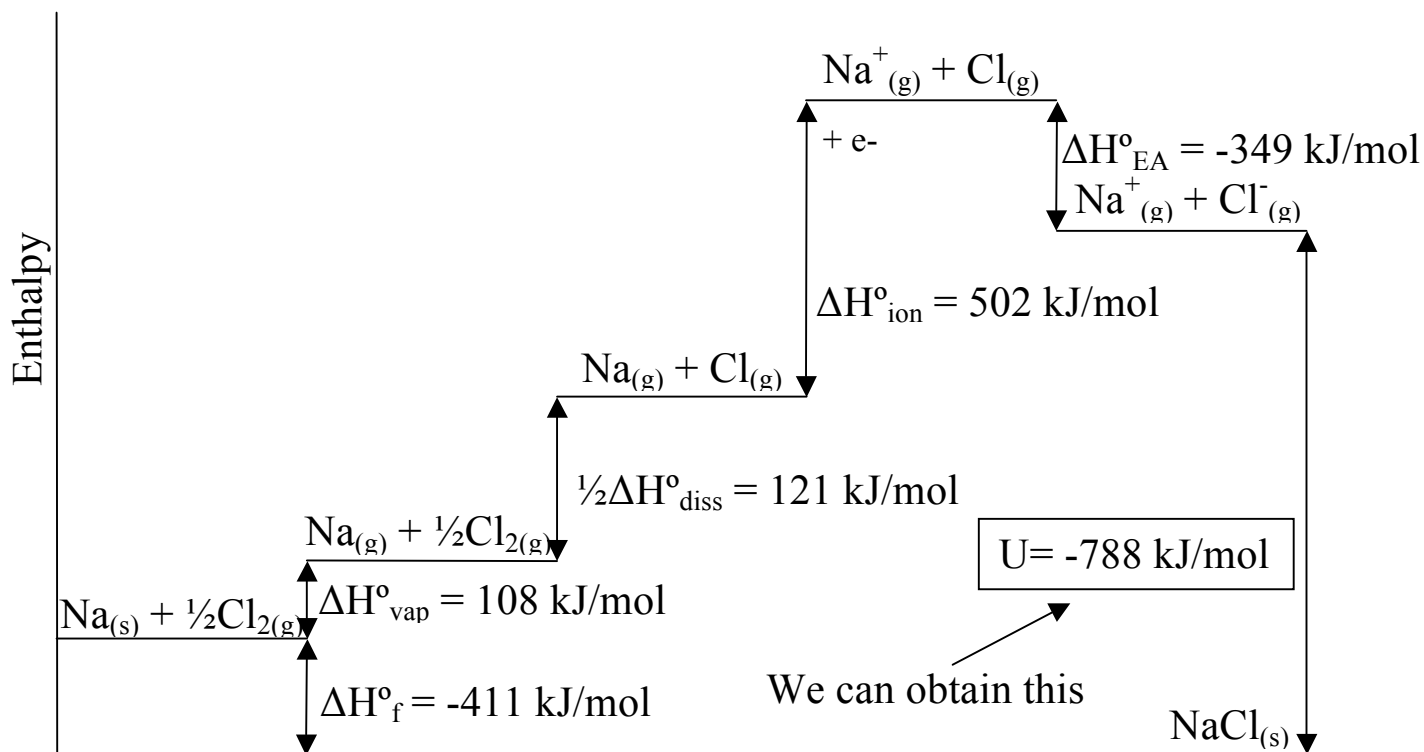
- **N = Avagadro's number**
- **Z = charges on ions ($Z^+ \times Z^- = Z^2$)**
- **r_0 = distance between cation and anion**
- **$e = e^-$ charge in coulombs**
- **ϵ_0 = dielectric constant of a vacuum**
- **n = factor for compressibility for the solid**

n = Born exponent, typically a number between 5 and 12, determined experimentally by measuring the compressibility of the solid, or derived theoretically

Q. BUT How does one obtain experimental Lattice Energies?

A. Use the Born – Haber cycle

One cannot directly measure the vaporization of NaCl(s) to $\text{Na}^+(\text{g})$ and $\text{Cl}^-(\text{g})$ or the reverse condensation process. NaCl(s) vaporizes to $\text{Na}^+\text{Cl}^-(\text{g})$ and eventually, at higher temps, they dissociate into atoms



Born – Haber Cycle for NaCl

This Born – Haber Cycle illustrates:



And that this reaction can be broken down into steps:

$$\Delta H_f^\circ = \Delta H_{\text{vap}}^\circ + \frac{1}{2} \Delta H_{\text{diss}}^\circ + \Delta H_{\text{EA}}^\circ + \Delta H_{\text{ion}}^\circ + U$$

From this we can solve for U:

$$U = \Delta H_f^\circ - \Delta H_{\text{vap}}^\circ - \frac{1}{2} \Delta H_{\text{diss}}^\circ - \Delta H_{\text{EA}}^\circ - \Delta H_{\text{ion}}^\circ$$

$$U = (-411) - (108) - (121) - (-349) - (-502)$$

$$U = -788 \text{ kJ/mol}$$

For NaCl, all the enthalpies except U have been experimentally measured so this value of U is easily obtained. The value obtained above compares very favorably with the Madelung Energy calculated from the Ionic model, which supports our hypothesis that the bonding is nearly perfectly ionic.

Ionic Radii

$$d = r^+ + r^-$$

distance between ions in an ionic crystal structure

radius of ions are substantially constant:

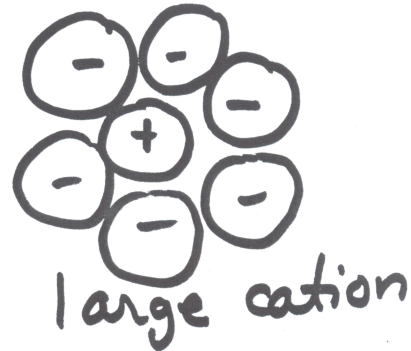
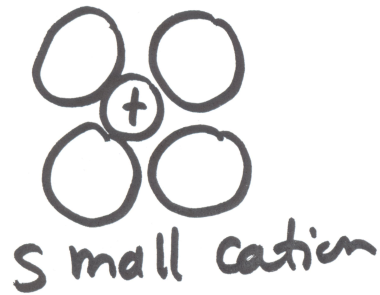
For example we can measure the **difference in the ionic radii of K^+ and Na^+**

$$\begin{aligned}
 r_{K^+} - r_{Na^+} &= d_{KF} - d_{NaF} = 0.3 \text{ \AA} \\
 &= d_{KCl} - d_{NaCl} = 0.33 \text{ \AA} \\
 &= d_{KBr} - d_{NaBr} = 0.32 \text{ \AA} \\
 &= d_{KI} - d_{NaI} = 0.30 \text{ \AA}
 \end{aligned}$$

Since the size difference of K^+ and Na^+ as determined in different salts is fairly constant as calculated, then the K^+ and Na^+ ions themselves must be staying fairly constant. (they are really ions and not engaging in different degrees of “bonding” as we would consider for interactions that involve a degree of orbital overlap and, therefore, covalency.

Coordination Number

- number of nearest neighbors
- determined mainly by ion size (especially ions which are very large)

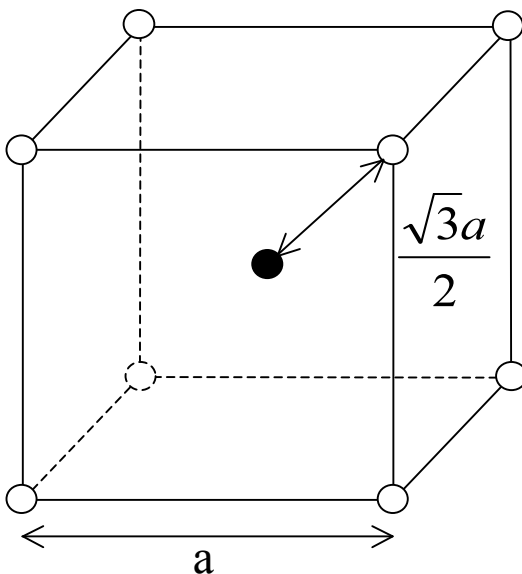


Radius ratio

$$\frac{r^-}{r^+}$$

defined for “perfect packing”

Which means that the anions are just touching each other while making contact with the cation at the same time



● Cation, Cs^+

○ Anion, Cl^-

Perfect body-centered

Cation-Anion touch at:

$$r^+ + r^- = \frac{\sqrt{3}a}{2}$$

Anion-Anion touch at:

$$2r^- = a \quad (\text{cube edge})$$

Based on this one Geometry (Body-Centered Cubic),
 One can come up with the “ideal” ratio of anion to
 cation size $\rightarrow \frac{r^-}{r^+}$

For BCC, these EQ'S Apply:

1. $r^+ + r^- = \frac{\sqrt{3}a}{2}$ (cation + anion distance)
2. $2r^- = a$ ($r^- = a/2$) (anion + anion distance)

Solve for r^+ and r^- in terms of a :

$$r^+ + r^- = \frac{\sqrt{3}a}{2}$$

$$r^- = \frac{a}{2}$$

$$r^+ + \frac{a}{2} = \frac{\sqrt{3}a}{2}$$

$$r^+ = \frac{\sqrt{3}a}{2} - \frac{a}{2} = \frac{\sqrt{3}-1}{2}(a)$$

$$r^- = \frac{a}{2}$$

$$\frac{r^-}{r^+} = \frac{\frac{a}{2}}{\frac{\sqrt{3}-1}{2}(a)} = \frac{a}{2} \times \frac{2}{(\sqrt{3}-1)a} = \frac{1}{\sqrt{3}-1} = \frac{1}{1.73-1} = \frac{1}{0.73} = 1.37$$

for cubic CsCl type structures

Geometries of Crystal Lattices

Let us go back to the diagrams of the six basic types of ionic solids

AB 4 types
rock salt (NaCl)
cesium chloride (CsCl)
zincblende (ZnS, Cubic)
Wurtzite (ZnS hexagonal)

AB₂ 2 types
Fluorite (CaF₂)
Rutile (TiO₂)

AB types

Six coordinate NaCl

Eight coordinate CsCl

Four coordinate ZnS (both types)

What this translates to is that when the anion/cation ratio is ~ 1.3 , the CsCl structure will be adopted.

If one uses the same geometrical arguments for NaCl and ZnS structures (which are 6 and 8 coordination numbers respectively)

The Radius Ratios are:
(rules work best for oxides, halides, sulfides)

| | | | coord.# |
|-----------|------|------|---------|
| r^-/r^+ | NaCl | 2.44 | 6 |
| r^-/r^+ | ZnS | 4.44 | 4 |
| r^-/r^+ | CsCl | 1.37 | 8 |

* Important to stress that these are only guidelines, as there are other factors besides ion size that affect packing \rightarrow covalency in some salts versus as opposed to the more purely ionic halides, oxides, sulfides.

Small Cations with Large Anions

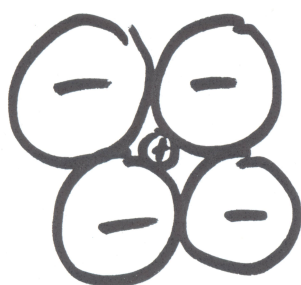
Other problems exist when the cation is very small.

For example Li^+ , Be^{2+} , Al^{3+} , Mg^{2+}

and the anions are large such as:

Cl^- , Br^- , I^- , ClO_4^- , CO_3^{2-} , NO_3^-

In these situations, the anions do not contact the cations very well, even when they are very close to each other:

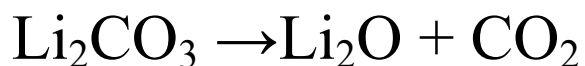


Here, the cation \oplus -
anion \ominus interactions
are not optimized.

What are the consequences of small cation/large anion combinations?

1. The anhydrous salts are not stable – they prefer to have the cation surrounded by water. This means they are very water soluble compared to salts with bigger cations (consider Li^+ vs Na^+ solubilities)

2. They can be thermally unstable. The anion can decompose to a smaller one.



So, we have just seen that **both structures and properties can be predicted** with some accuracy by knowing the **sizes of ions**.

Table 4-2 lists Pauling Ionic Radii deduced from effective nuclear charge arguments – one can use these to make predictions.

Closest Packing of Anions

Besides AB and AB₂ crystal lattice geometries, there are others, with very small cations, that are based only on the closest packing of spheres (anions)

Two main types:

- 1) **Hexagonal Closest Packed**

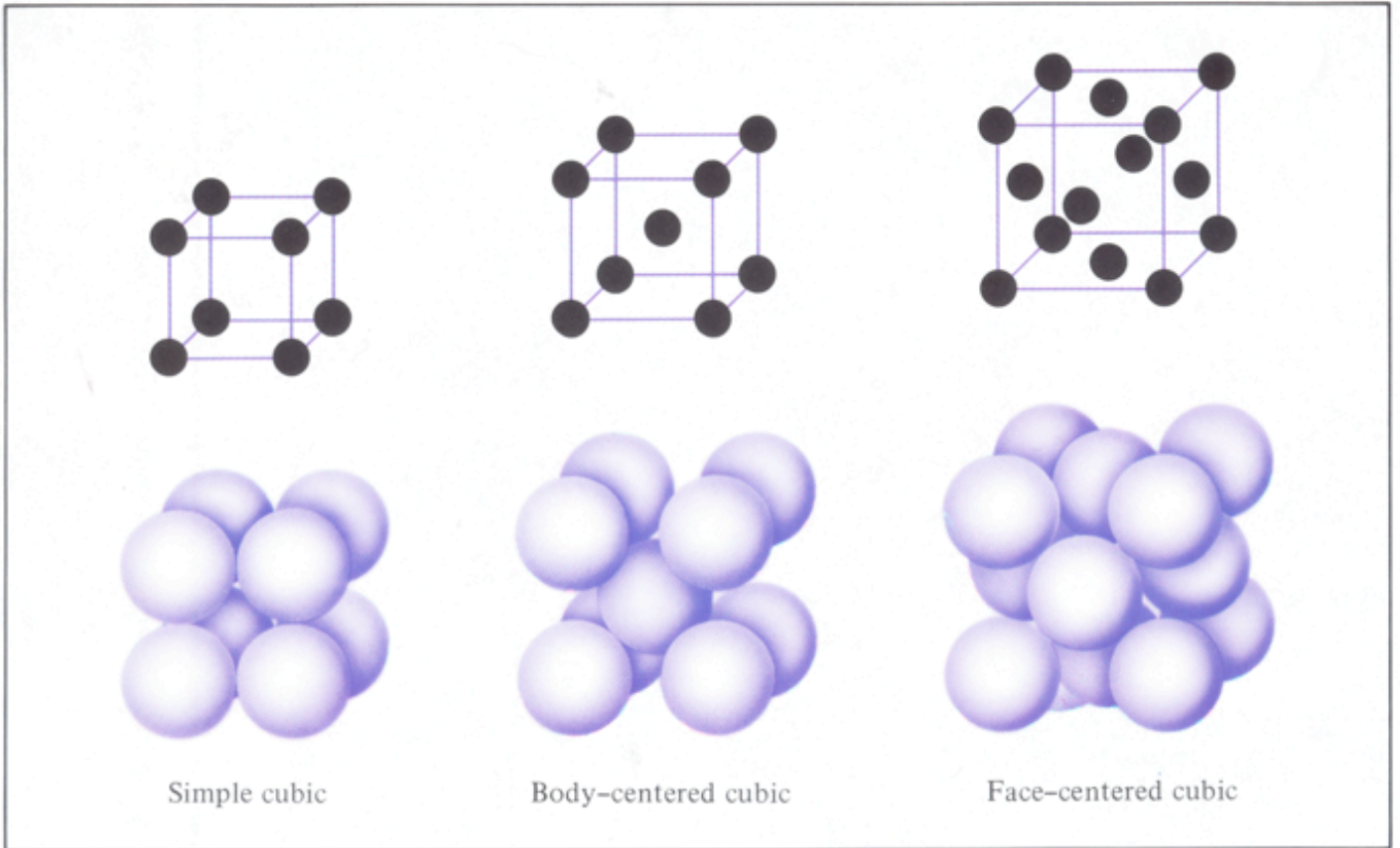
ABABAB....alternating A & B layers

- 2) **Cubic Closest Packed**

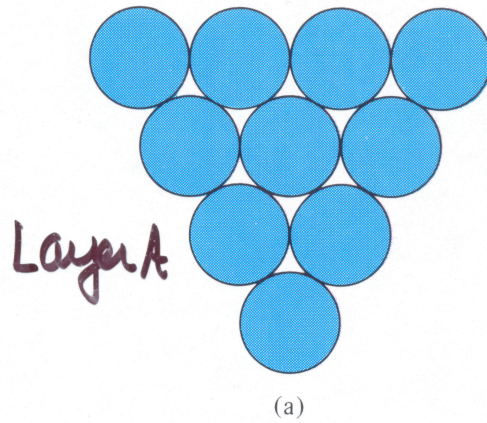
ABCABCABC...alternating A, B, C layers

The differences are in the holes that are created by the arrangements of the spheres → holes where the cations will reside

Three types of Cubic Cells

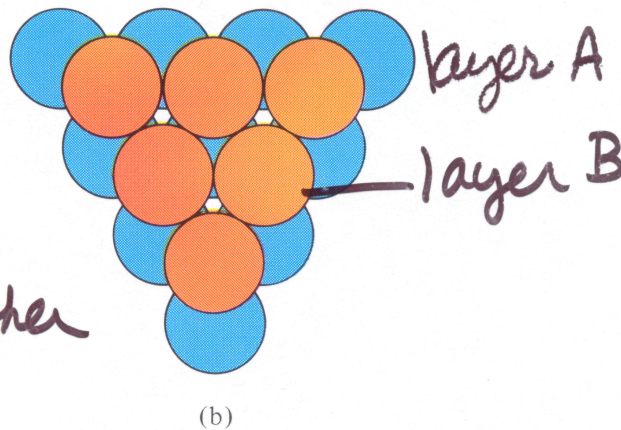


Closed-Packed Layers

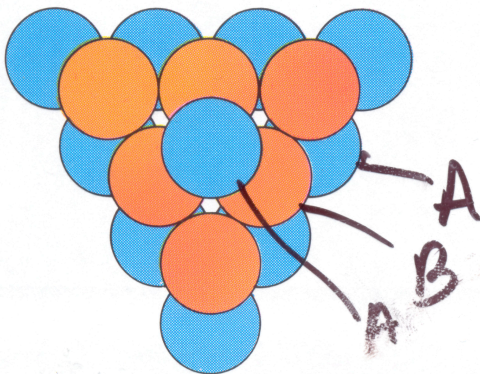


each atom is in contact with six others in the same layer

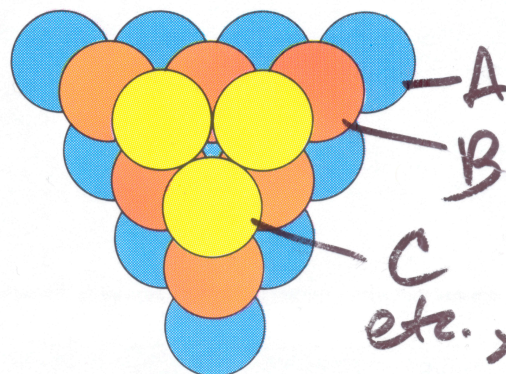
each atom in the next layer fits into the holes or (depressions) left by the other layer



2 choices



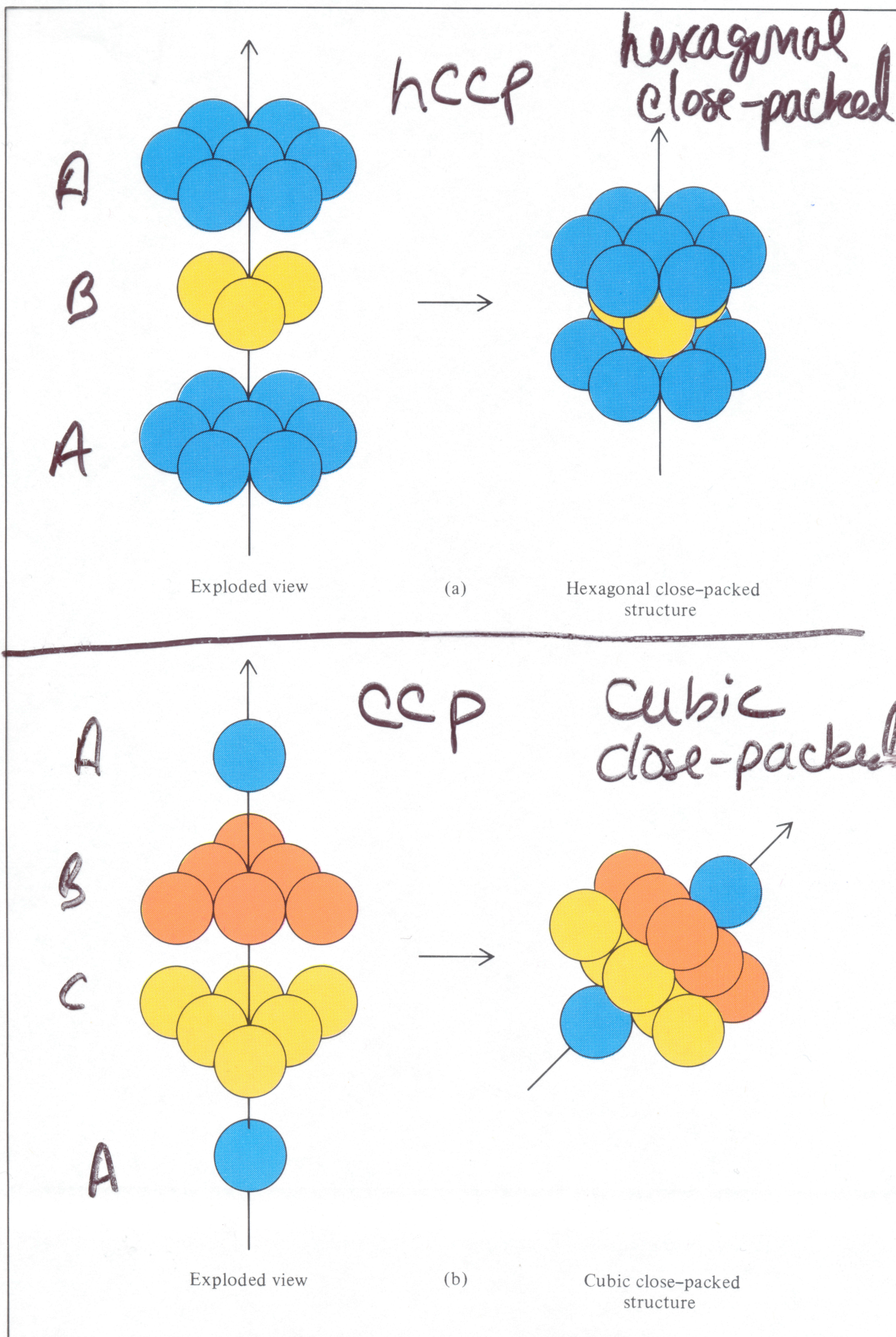
hexagonal close-packed
hcp



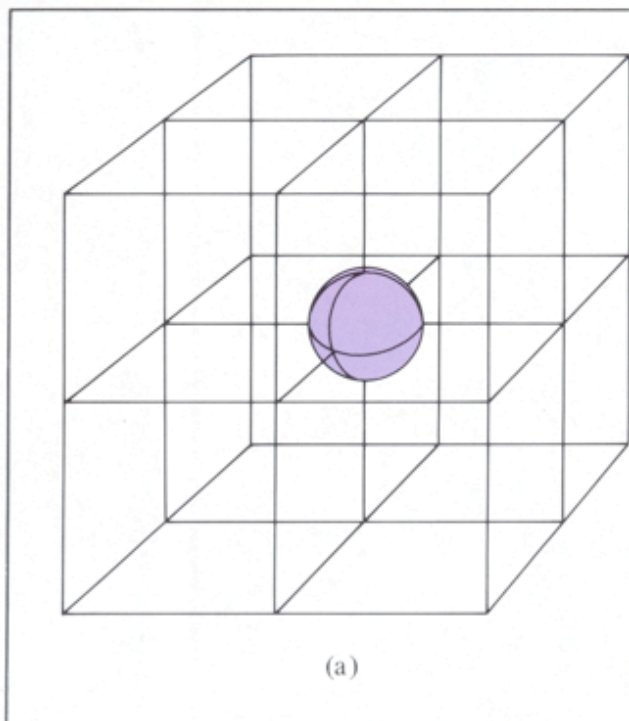
cubic-close packed
ccp

Exploded views of

Figure 11.22

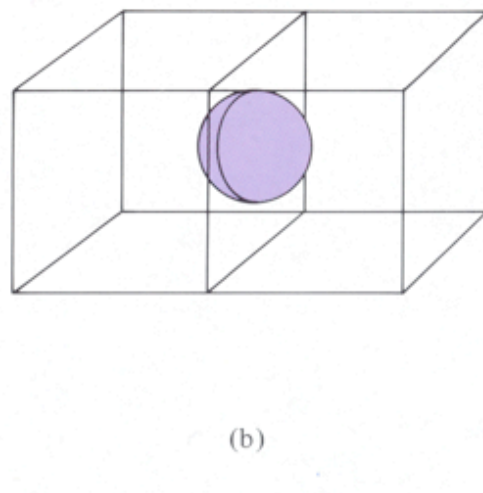


A corner atom

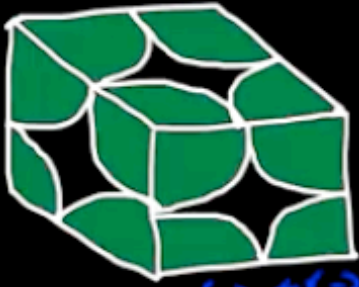


shared by 8 unit cells
contributes $\frac{1}{8}$ to each unit cell

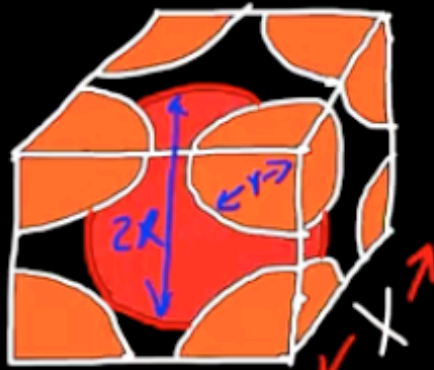
a face-centered atom



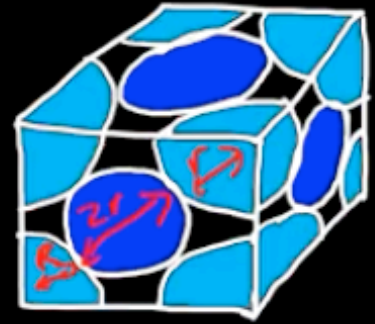
shared by 2 unit cells
contributes $\frac{1}{2}$ to each unit cell

Simple Cubic

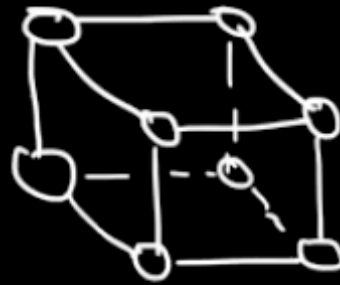
1 atom
 $C = 6$
 52% Volume
 $X = 2R$

Body Centered Cubic

2 atoms
 $C = 8$
 68% Volume
 $X = \frac{4}{\sqrt{3}} R$

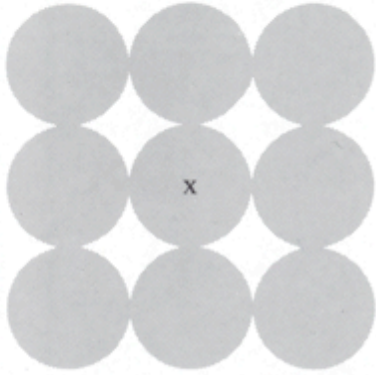
Face Centered Cubic

4 atoms
 $C = 12$
 74% Volume
 $X = \sqrt{8} R$

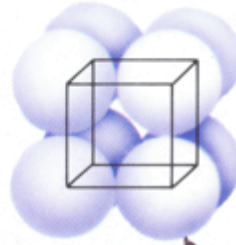
Simple Cubic

$$\frac{1}{8}(8) = 1$$

Arrangement of identical spheres in a simple cubic cell.



(a) Top view of a layer of atoms



(b)

each corner contributes only $\frac{1}{8}$ th so total atoms in unit cell (c) = $\frac{1}{8} \times 8 = 1$

Simple Cubic



52% volume

Coordination = 6

$$V = lwh$$

$$V = (X)(X)(X) \quad \boxed{V = X^3}$$

$$\boxed{X = 2R}$$

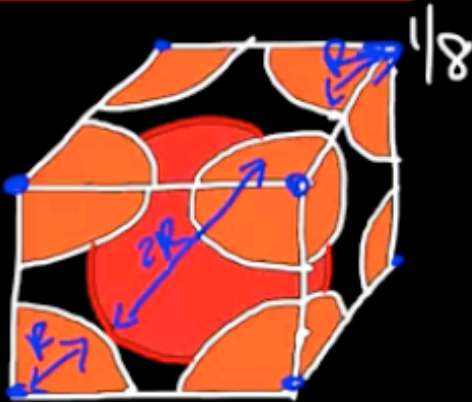
$$\frac{V_{\text{atoms}}}{V_{\text{cube}}} = \frac{1 \left(\frac{4}{3} \pi R^3 \right)}{X^3}$$

$$\frac{4.1888}{8} \frac{\frac{4}{3} \pi R^3}{(2R)^3} = \frac{\frac{4}{3} \pi R^3}{8 R^3}$$

$$= 0.5236$$

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Body Centered Cubic



$$d = 4R$$

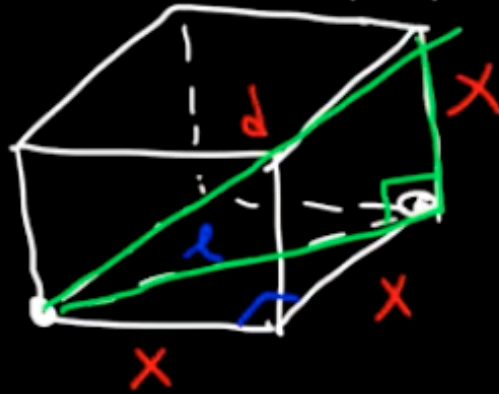
$$X = \frac{4}{\sqrt{3}} R$$

Coord. = 8

$$\frac{1}{8} (8) + 1 = \boxed{2}$$

$$d^2 = X^2 + X^2 + X^2$$

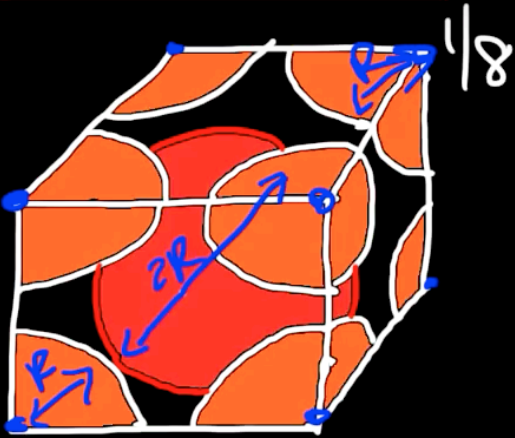
$$d^2 = X^2 + X^2 + X^2 = d^2$$



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Unit Cell - Simple Cubic, Body Centered Cubic, Face Centered Cubic Crystal Lattice Struct...

Body Centered Cubic



$$d = 4R$$

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

$$\text{Coord.} = 8$$

$$\frac{1}{8}(8) + 1 = \boxed{2}$$

$$r^2 = x^2 + x^2$$

$$(r^2) + x^2 = d^2$$

$$x^2 + x^2 + x^2 = d^2$$

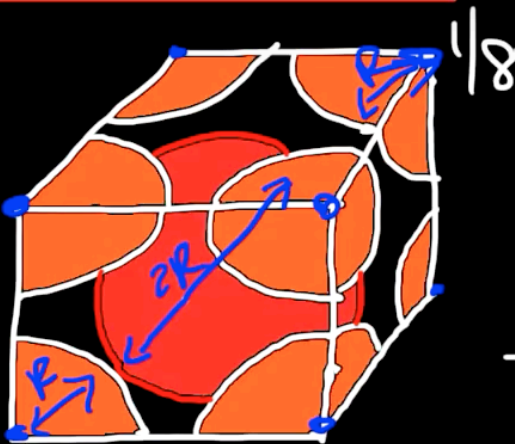
$$\sqrt{3x^2} = \sqrt{d^2}$$

$$\sqrt{3}(x) = d$$

$$\sqrt{3}X = 4R$$

Unit Cell - Simple Cubic, Body Centered Cubic, Face Centered Cubic Crystal Lattice Struct...

Body Centered Cubic



$$d = 4R$$

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

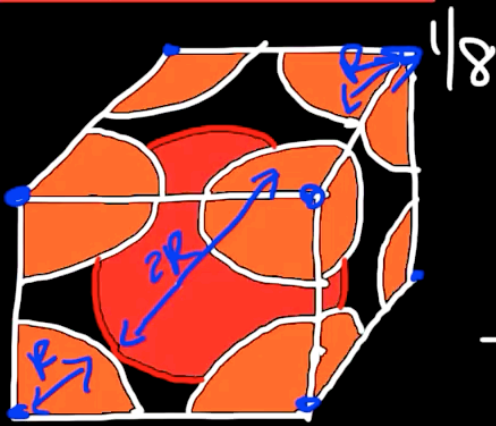
$$\text{Coord.} = 8$$

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

$$\frac{V_{\text{atoms}}}{V_{\text{cube}}} = \frac{2 \left(\frac{4}{3} \pi R^3 \right)}{\left(\frac{4}{\sqrt{3}} R \right)^3}$$

Pause (k)

Body Centered Cubic



$$d = 4R$$

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

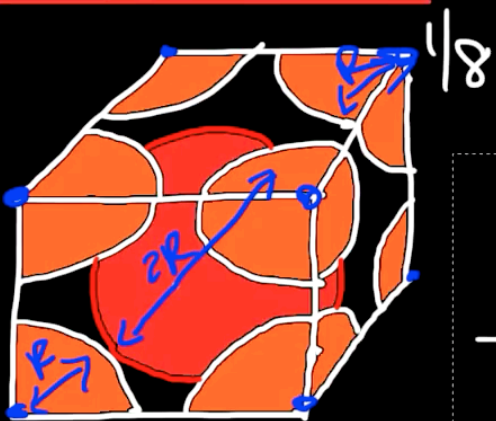
$$\text{Coord.} = 8$$

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

$$\frac{V_{\text{atoms}}}{V_{\text{cube}}} = \frac{2 \left(\frac{4}{3} \pi R^3 \right)}{\left(\frac{4}{\sqrt{3}} R \right)^3}$$

$$= \frac{2(4) \left(\frac{1}{3} \right) \pi R^3}{\frac{4 \cdot 4 \cdot 4}{3\sqrt{3}} R^3}$$

Body Centered Cubic



$$d = 4R$$

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

$$\text{Coord.} = 8$$

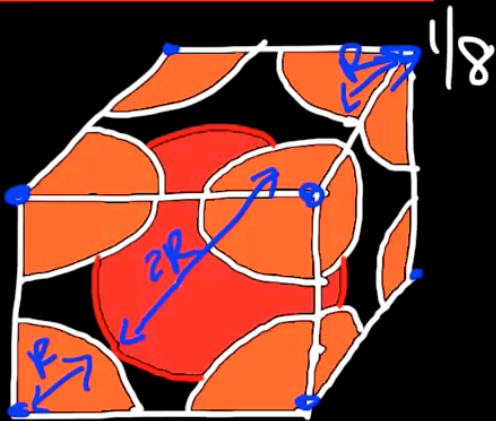
$$X = \frac{4}{\sqrt{3}} R$$

$$\frac{2\pi(\sqrt{3})}{16}$$

$$\frac{V_{\text{atoms}}}{V_{\text{cube}}} = \frac{2 \left(\frac{4}{3} \pi R^3 \right)}{\left(\frac{4}{\sqrt{3}} R \right)^3}$$

$$= \frac{2(4) \left(\frac{1}{3} \right) \pi R^3}{\frac{4 \cdot 4 \cdot 4}{3\sqrt{3}} R^3} = \frac{2\pi\sqrt{3}}{\frac{16}{\sqrt{3}}}$$

Body Centered Cubic



$$d = 4R$$

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

$$\text{Coord.} = 8$$

$$x = \frac{4}{\sqrt{3}} R \quad \frac{2\pi(\sqrt{3})}{16}$$

$$= 0.6802$$

$$\approx 68\%$$

Crystal structures of various metals

Figure 11.31

| 1A | 2A | | | | | | | | | | | 3A | 4A | 5A | 6A | 7A | 8A | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|--|
| Li | Be | | | | | | | | | | | | | | | | | |
| Na | Mg | | | | | | | | | | | Al | | | | | | |
| 3B | 4B | 5B | 6B | 7B | 8B | | 1B | 2B | | | | | | | | | | |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | | | | | | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | | | | | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | | | | | |

| | |
|----------------------------------|---|
| HCP Hexagonal close-packed | BCC Body-centered cubic |
| fcc Face-centered cubic | others Other structures (see caption) |

Many ionic solids can be described by the closest packing argument

Table 4-4 lists different stoichiometries which are a **consequence of different occupancies of cations in either hcp or ccp lattices.**

Table 4-4 A Description of the Structures of Ionic Substances
Using the Concept of Close Packing of Anions

| Formula | Structure of the Anions | Location of the Cations |
|-------------------------|-------------------------|--|
| CdI_2 | hcp | Cations occupy octahedral holes in every other layer |
| CdCl_2 | ccp | Cations occupy octahedral holes in every other layer |
| NaCl | ccp | Cations occupy all octahedral holes in every layer |
| BI_3 | ccp | Cations occupy two-thirds of the octahedral holes in every other layer |
| Al_2O_3 | hcp | Cations occupy two-thirds of the octahedral holes in every layer |
| CaTiO_3 | hcp | Fe^{2+} and Ti^{4+} ions jointly occupy two-thirds of the octahedral holes |
| Na_2S | ccp | Cations occupy all of the tetrahedral holes ^a |

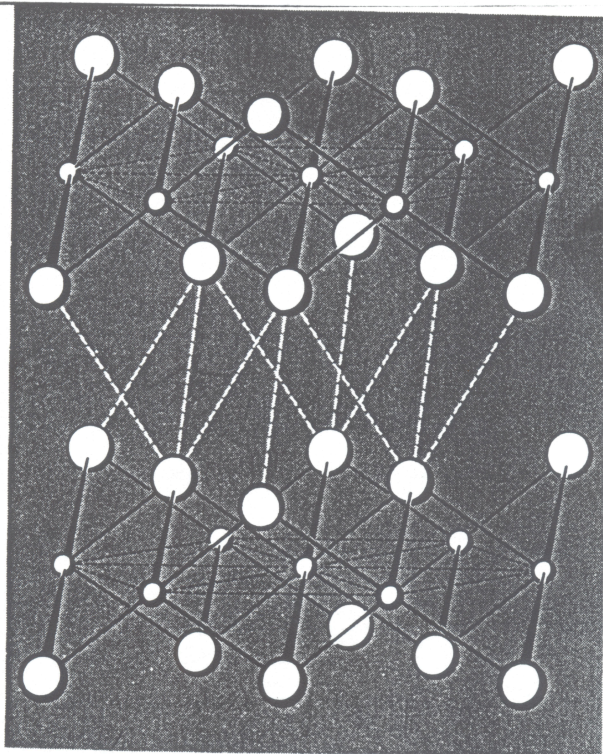


Figure 4-7 A portion of the CdI_2 structure. Small spheres represent metal cations.