

## Chapter 4

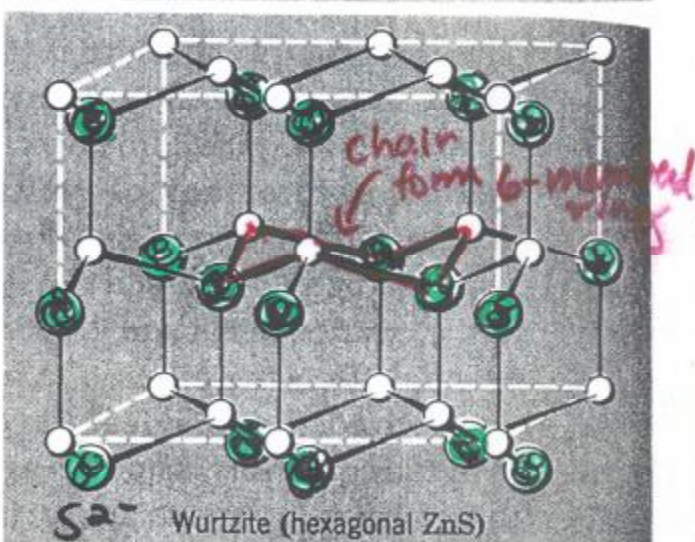
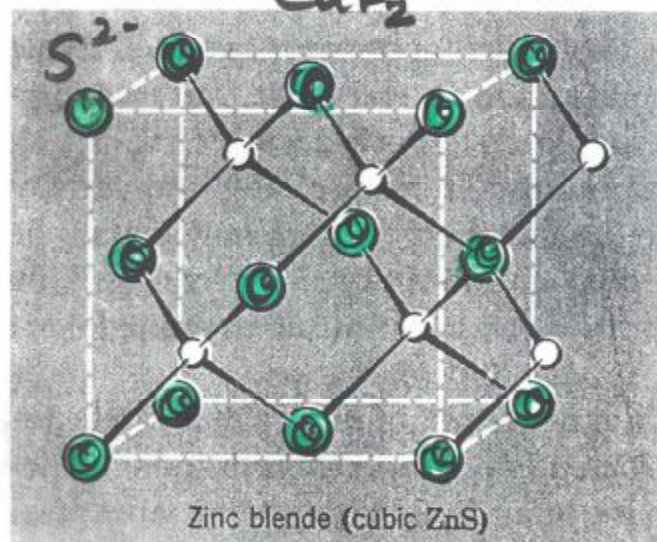
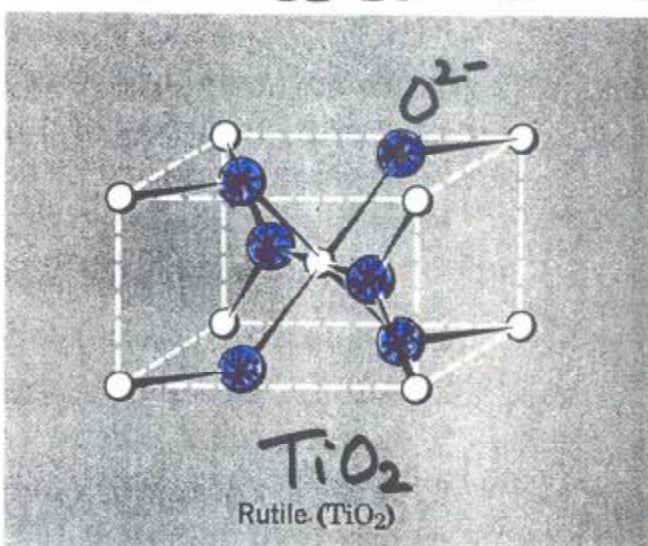
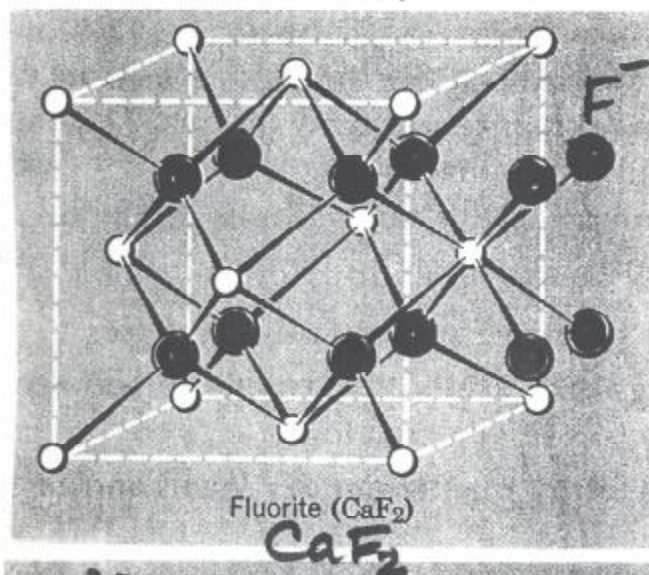
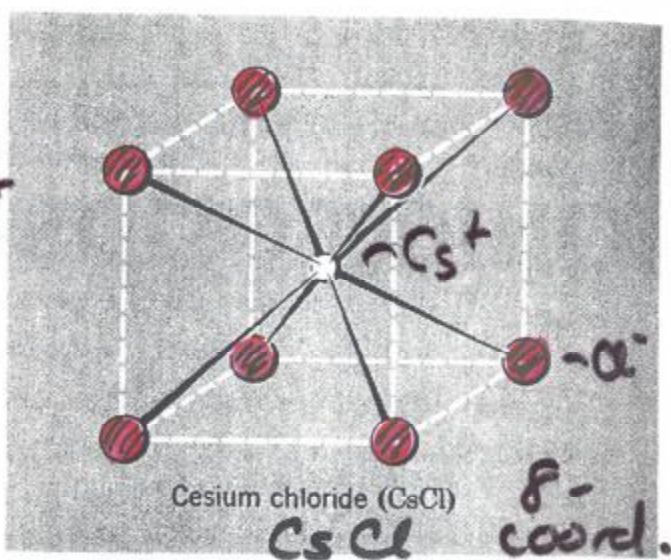
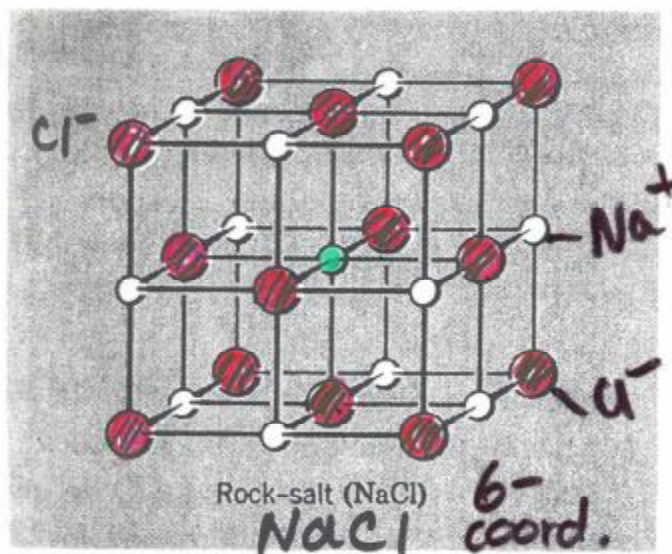
### Ionic Solids

#### 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



Zinc Blende

Wurtzite

## Lattice Energy

Enthalpy of forming a solid ionic compound from gaseous ions



Total lattice energy is a sum of attractive and repulsive terms. This energy is called the Madelung Energy

for NaCl type structures:

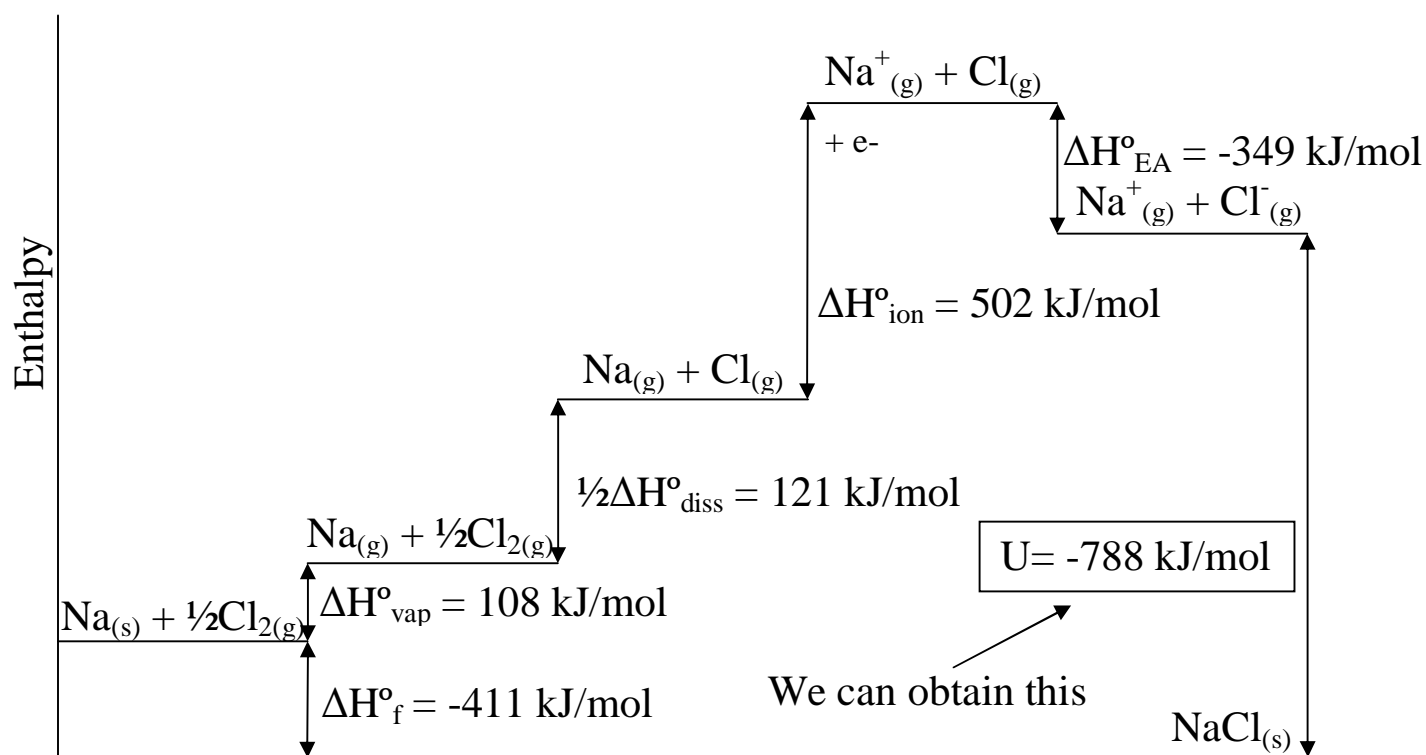
$$U = \frac{NM_{\text{NaCl}}Z^2e^2}{4\pi\epsilon_0r_o}\left(1 - \frac{1}{n}\right)$$

- 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
- N = Avagadro's number
- Z = charges on ions
- R<sub>0</sub> = distance between cation and anion
- e = e<sup>-</sup> charge in coulombs
- ε<sub>0</sub> = dielectric constant of a vacuum
- n = factor for compressibility

Q. How does one obtain experimental Lattice Energies?

A. Use the Born – Haber cycle

One cannot directly measure the vaporization of  $\text{NaCl(s)}$  to  $\text{Na}^+(\text{g})$  and  $\text{Cl}^-(\text{g})$  or the reverse condensation process.  $\text{NaCl(s)}$  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:



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

r ions are substantially constant:

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

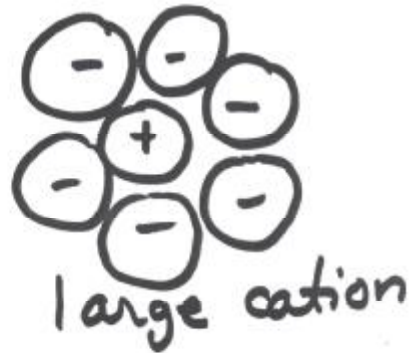
$$\begin{aligned} r_{K^+} - r_{Na^+} &= d_{KF} - d_{NaF} = 0.3 \text{ \AA} \\ &= d_{KCl} - d_{NaCl} = 0.33 \text{ \AA} \\ &= d_{KBr} - d_{NaBr} = 0.32 \text{ \AA} \\ &= d_{KI} - d_{NaI} = 0.30 \text{ \AA} \end{aligned}$$

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)

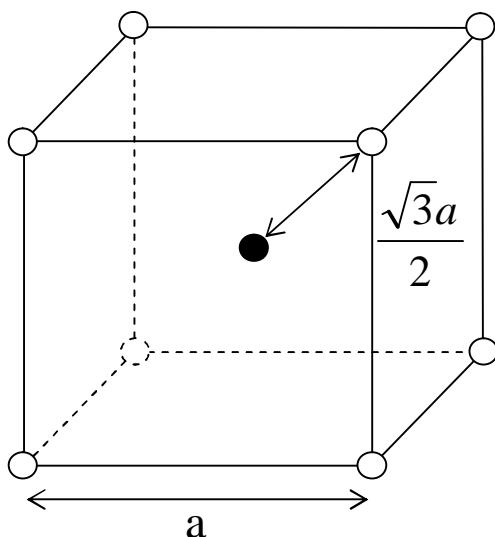


## Radius ratio

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

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, e.g.  $\text{Cs}^+$  in cubic

○ Anion, e.g.  $\text{Cl}^-$

Perfect packing requires:

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 on 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  $a$ :

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

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

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

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

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

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

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  
zincblende (ZnS, Cubic)  
Wurtzite (ZnS hexagonal)

AB<sub>2</sub>    2 types  
Fluorite (CaF<sub>2</sub>)  
Rutile (TiO<sub>2</sub>)

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  $\sim 1.3$ , 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  $\text{Li}^+$ ,  $\text{Be}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$

and the anions are large such as:

$\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{ClO}_4^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_3^-$

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



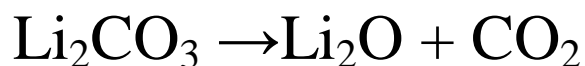
Here, the cation  $\oplus$  -  
anion  $\ominus$  interactions  
are not optimized.

## 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  $\text{Li}^+$  vs  $\text{Na}^+$  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 AB<sub>2</sub> 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

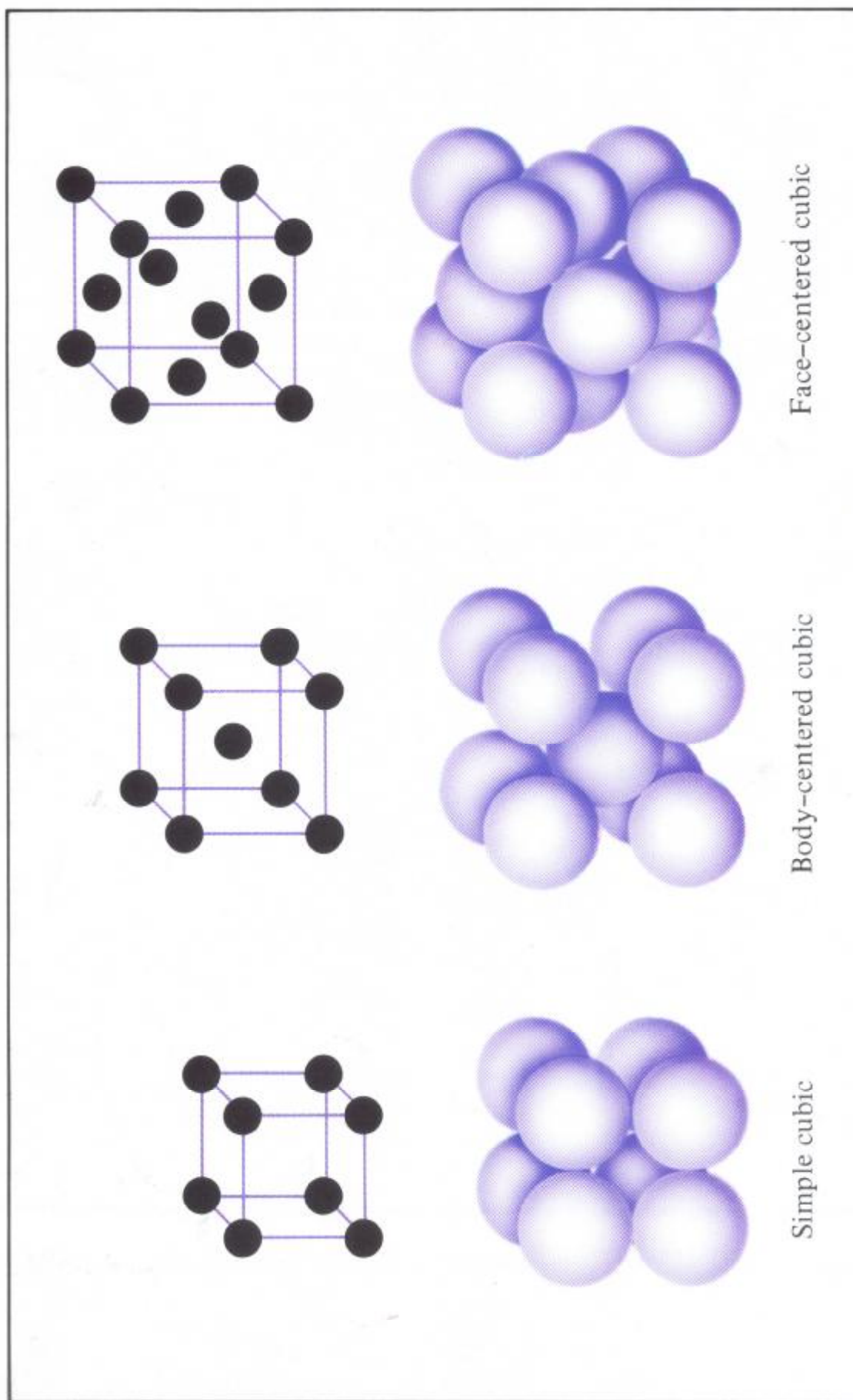
ABABAB.....alternating A & B layers

- 2) Cubic Closest Packed

ABCABCABC...alternating A, B, C layers

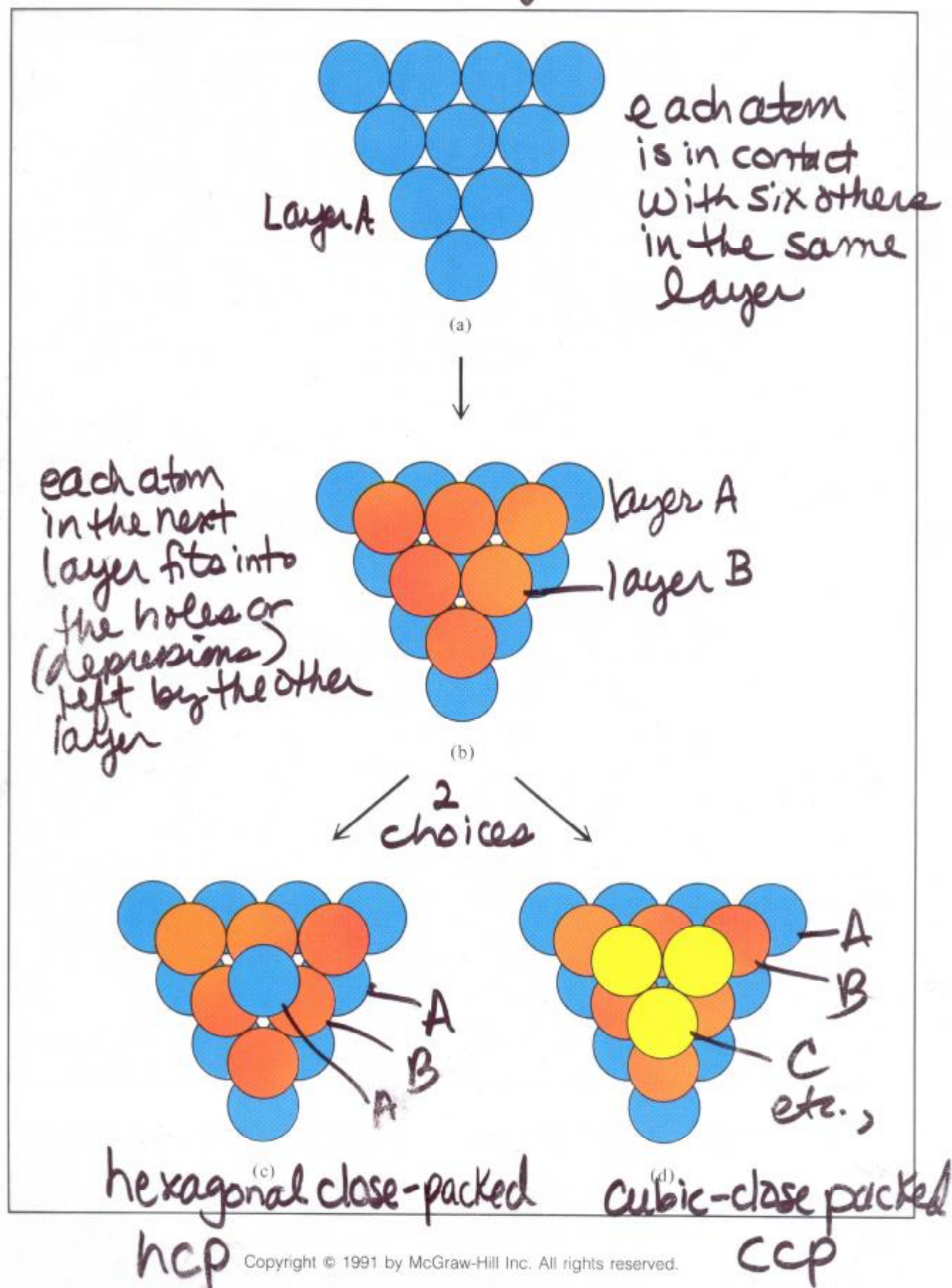
**The differences are in the holes that are created by the arrangements of the spheres → holes where the cations will reside**

# Three types of Cubic Cells



# Closed-Packed Layers

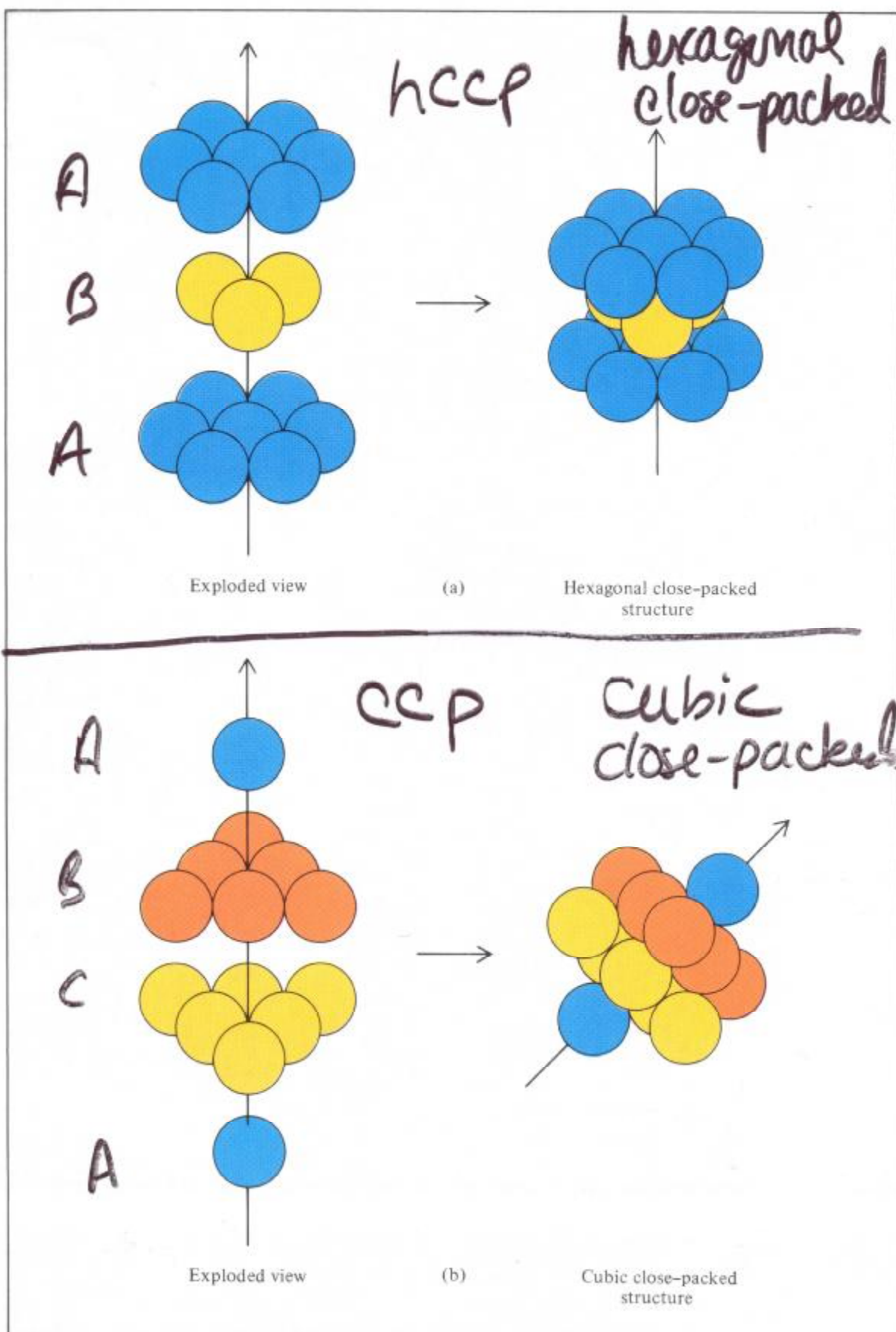
Figure 11.21





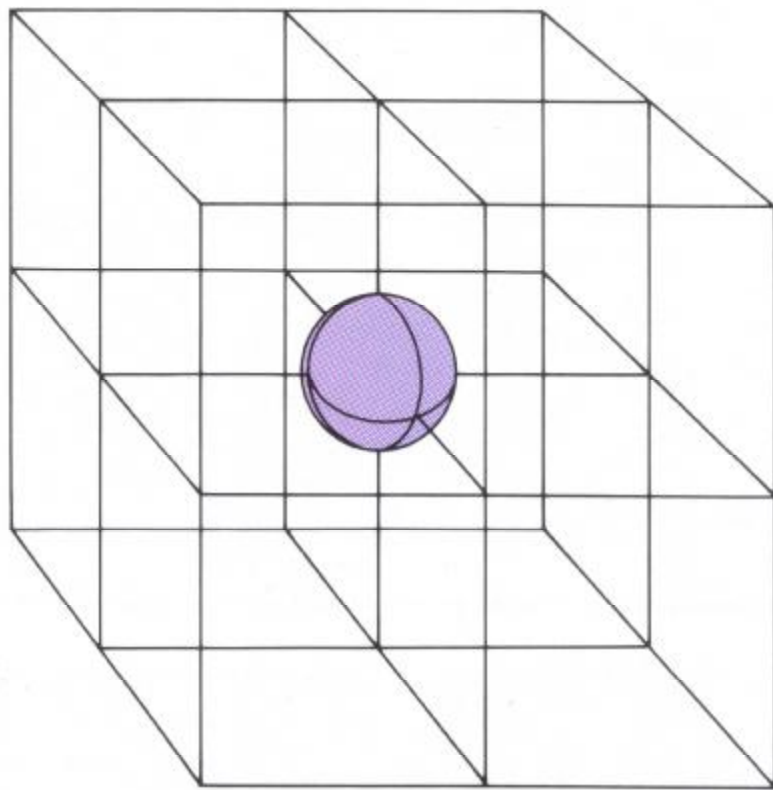
## Exploded views of

Figure 11.22





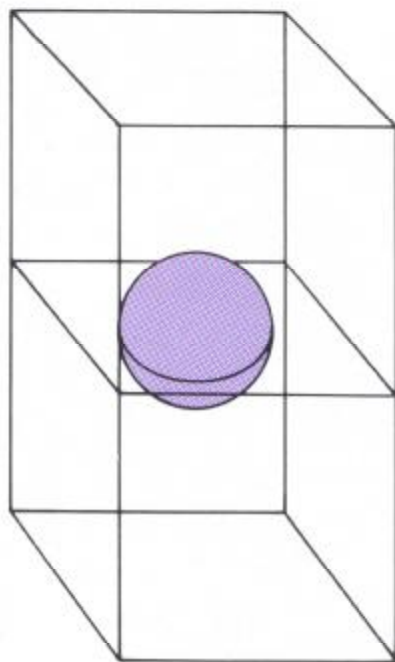
A corner atom



(a)

Shared by 8 unit cells  
Contributes  $\frac{1}{8}$  to each unit cell

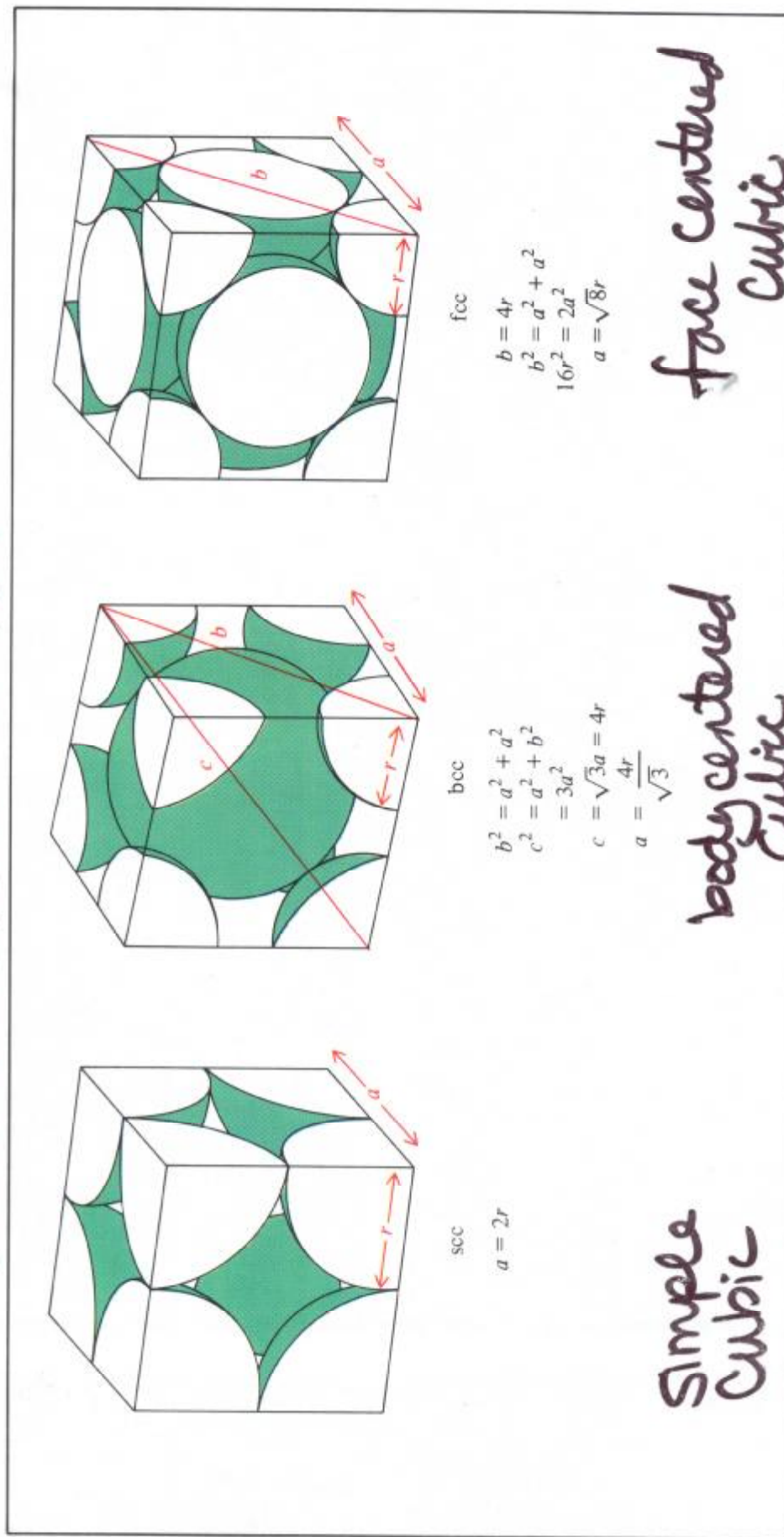
a face-centered atom



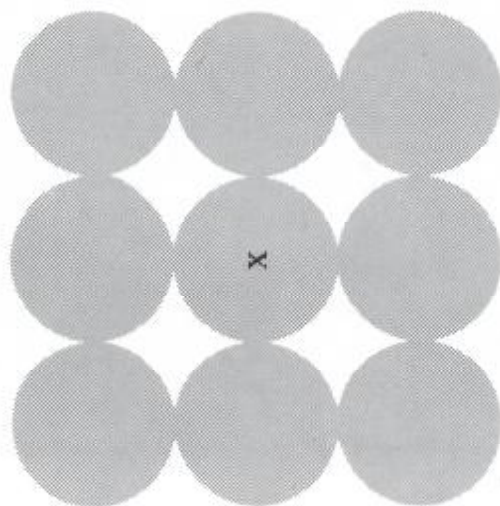
(b)

Shared by 2 unit cells  
Contributes  $\frac{1}{2}$  to each unit cell

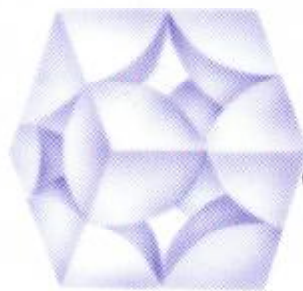
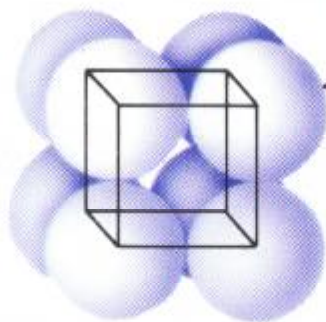
Relationship between edge length  
and radius of atoms for:



Arrangement of identical spheres in a simple cubic cell.



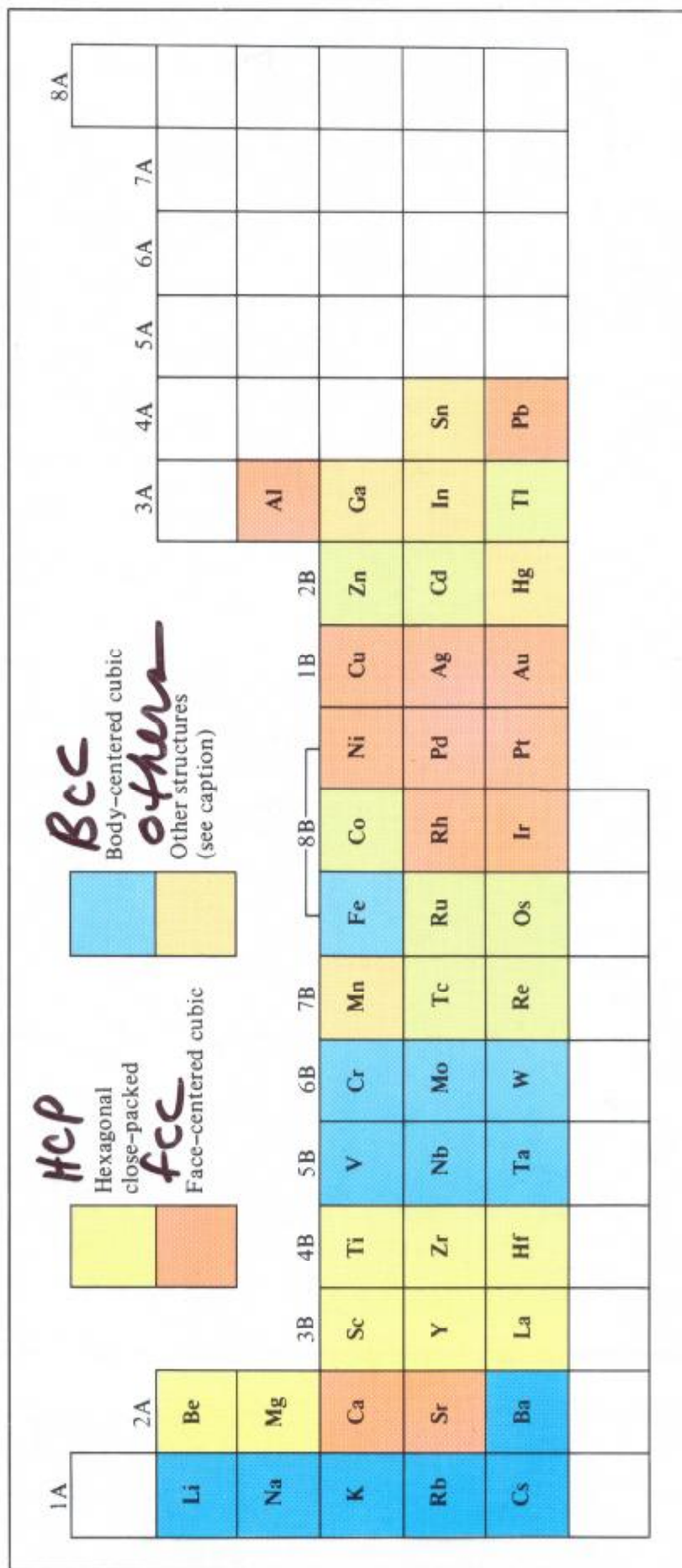
Top view of a layer of atoms <sup>(a)</sup>



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

(b)

Crystal structures of various metals



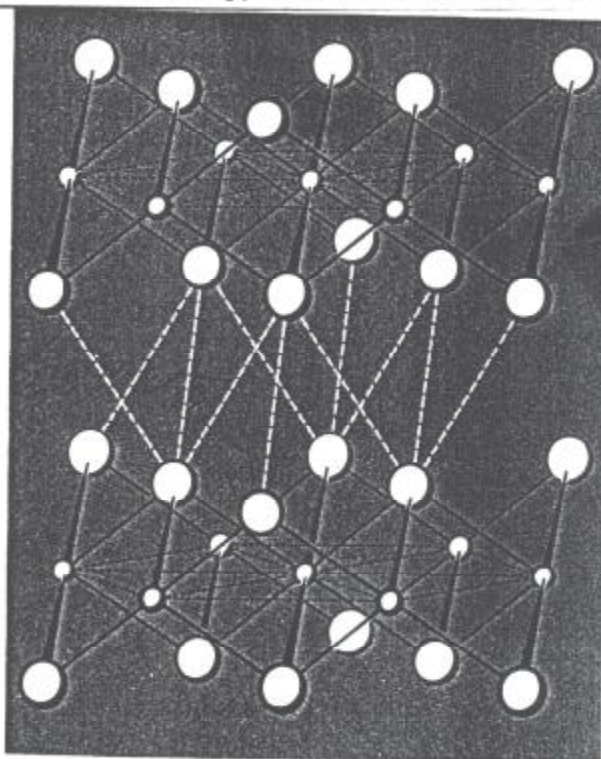


Many ionic solids can be described by the closest packing argument

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
$\text{CdI}_2$	hcp	Cations occupy octahedral holes in every other layer
$\text{CdCl}_2$	ccp	Cations occupy octahedral holes in every other layer
$\text{NaCl}$	ccp	Cations occupy all octahedral holes in every layer
$\text{BI}_3$	ccp	Cations occupy two-thirds of the octahedral holes in every other layer
$\text{Al}_2\text{O}_3$	hcp	Cations occupy two-thirds of the octahedral holes in every layer
$\text{CaTiO}_3$	hcp	$\text{Fe}^{2+}$ and $\text{Ti}^{4+}$ ions jointly occupy two-thirds of the octahedral holes
$\text{Na}_2\text{S}$	ccp	Cations occupy all of the tetrahedral holes <sup>a</sup>



**Figure 4-7** A portion of the  $\text{CdI}_2$  structure.  
Small spheres represent metal cations.