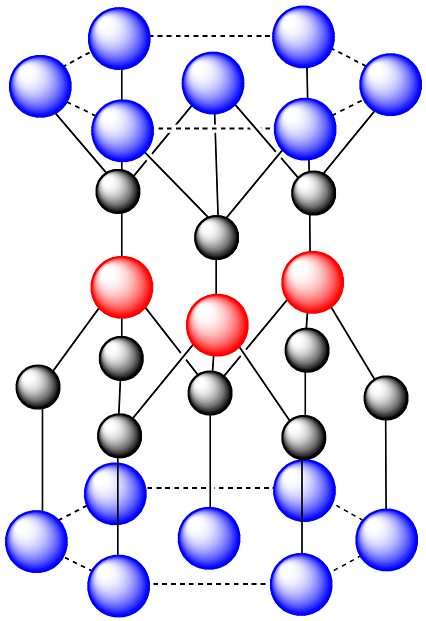
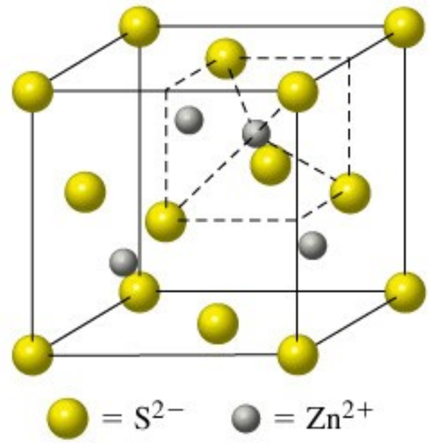
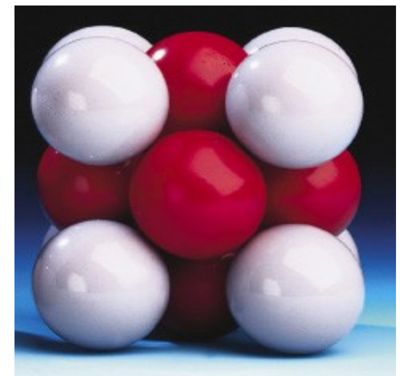
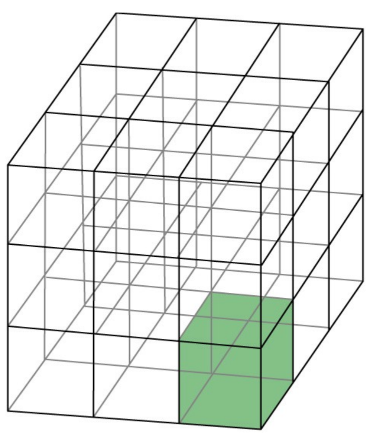
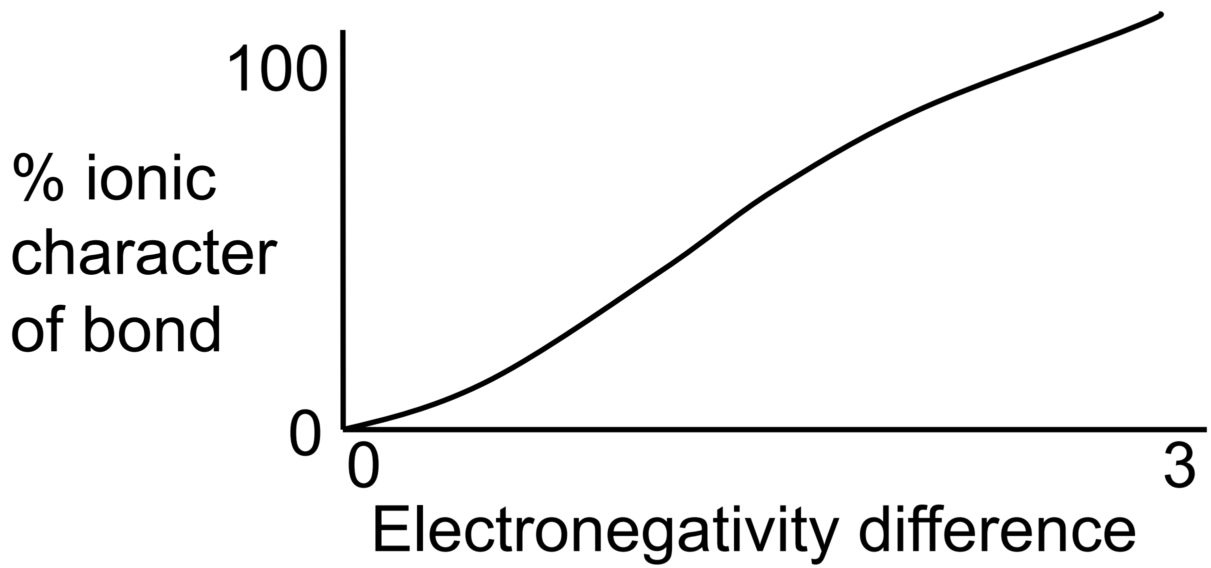






Chapter 5:Ionic bonding

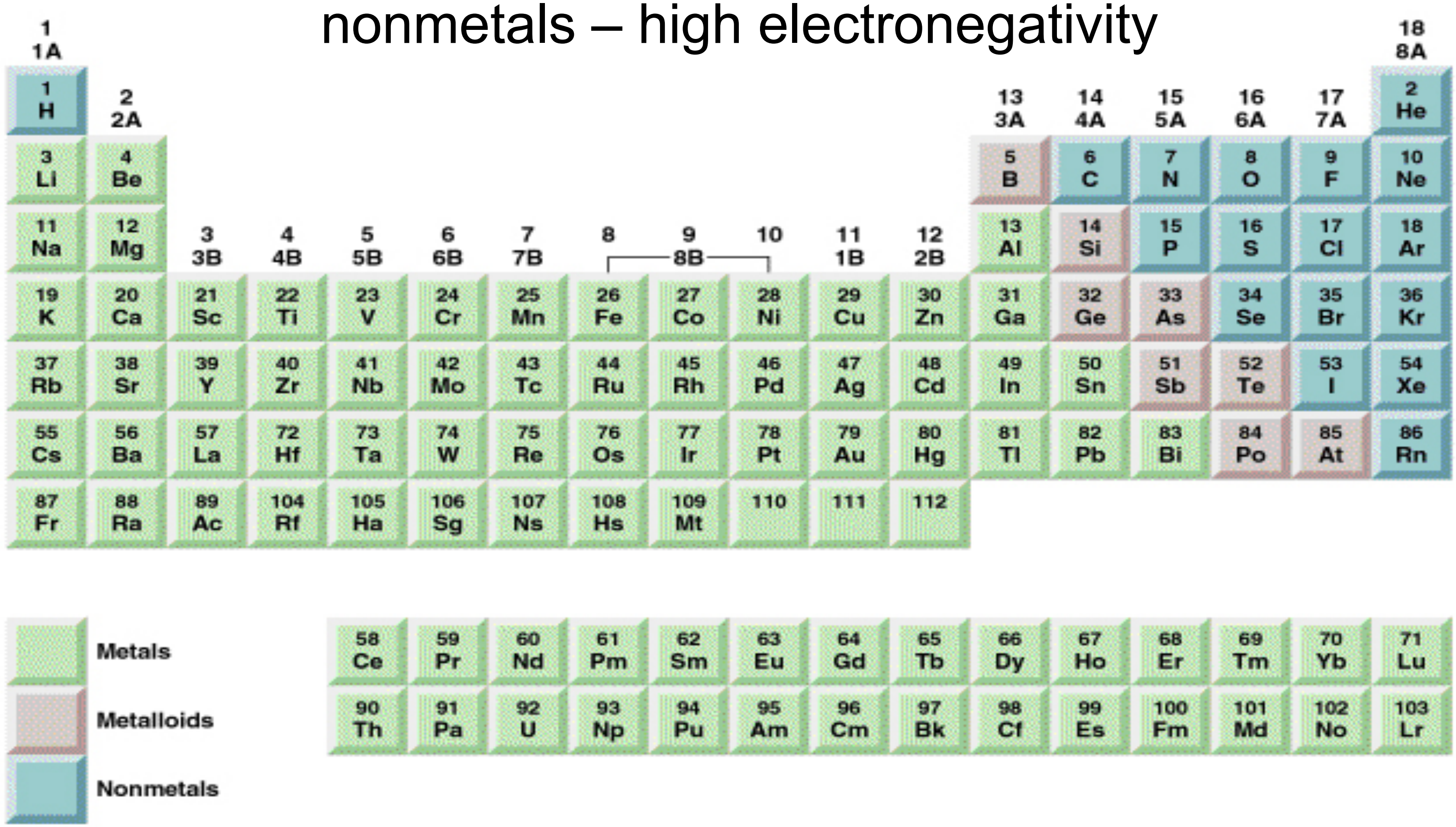




Ionic Bonding

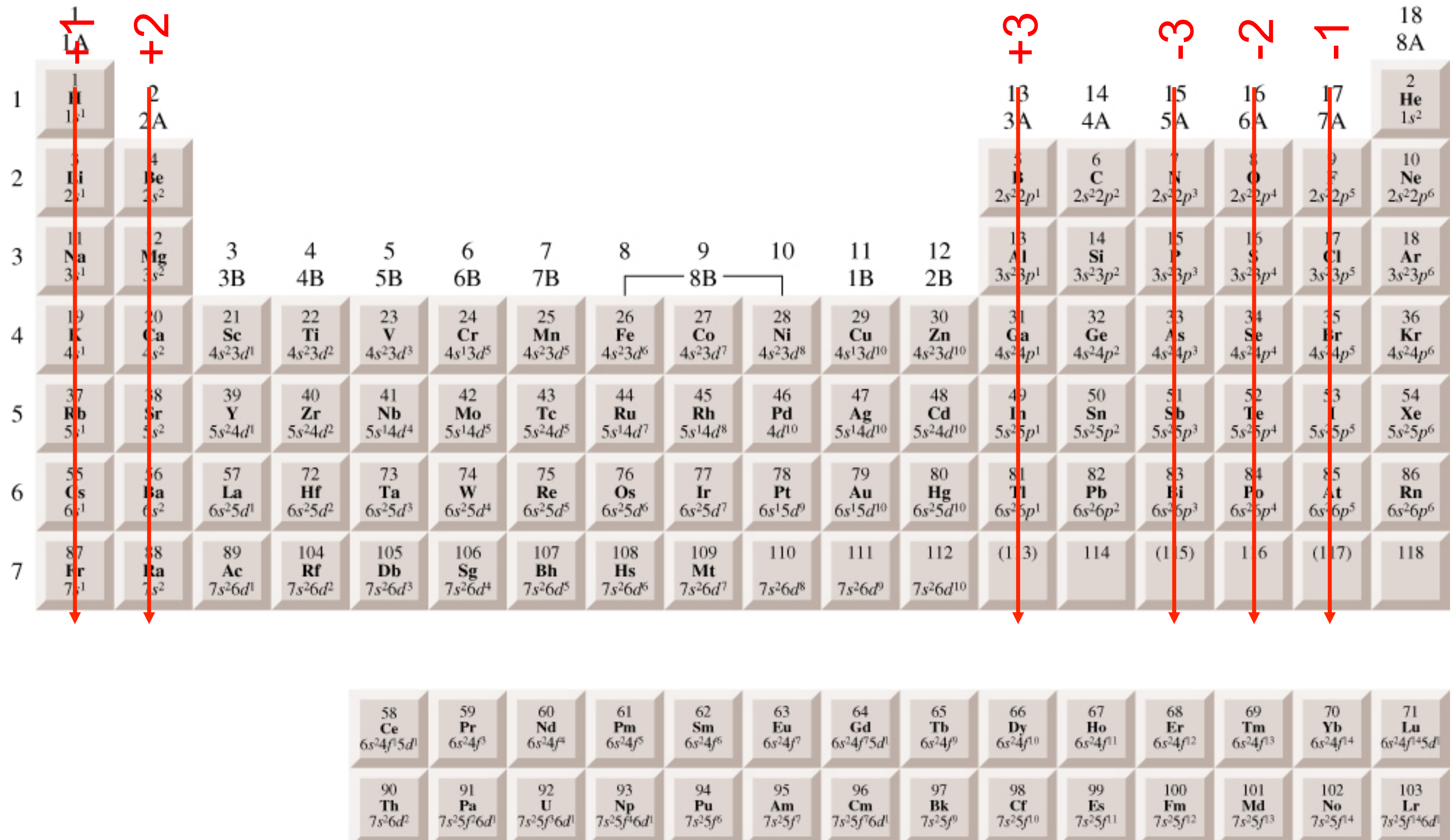
metals – low electronegativity

nonmetals – high electronegativity



Bonding between metals and nonmetals is ***usually*** ionic

Charge of Ions



Size of Ions

CATIONS have higher Z_{eff} (i.e. fewer shielding electrons) than neutral atoms, so have **SMALLER** size.

ANIONS have lower Z_{eff} (I.e. more shielding electrons) than neutral atoms, so have **LARGER** size.

e.g. Size $Na^- > Na > Na^+$

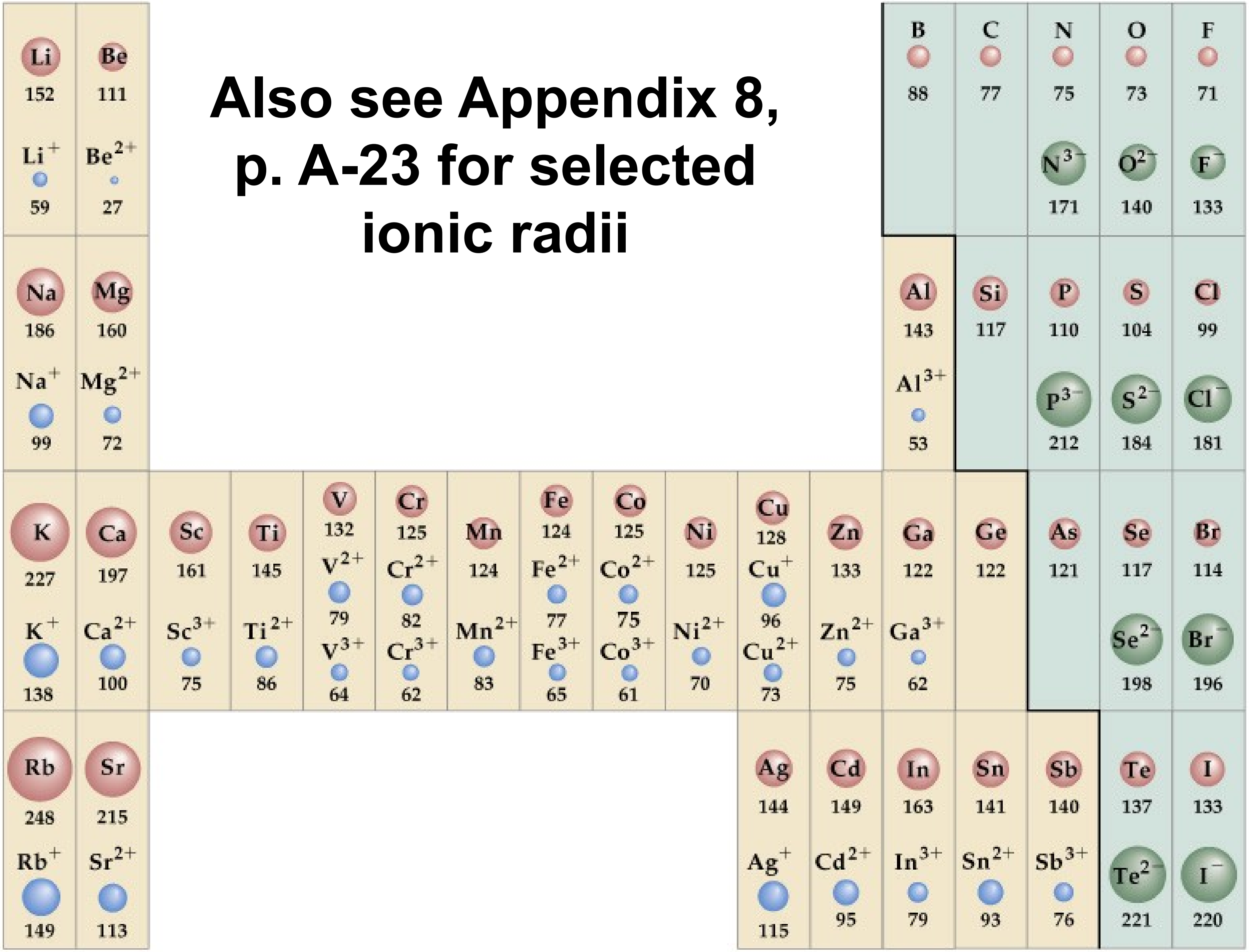
Size of Ions

Ion size in an isoelectronic series

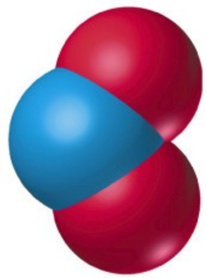
Ion	# electrons	# protons	ion radius (pm)
Na^{+}	10	11	116
Mg^{2+}	10	12	86
Al^{3+}	10	13	68
N^{3-}	10	7	132
O^{2-}	10	8	124
F^{-}	10	9	117

Increasing # protons increases Z_{eff} which decreases radius

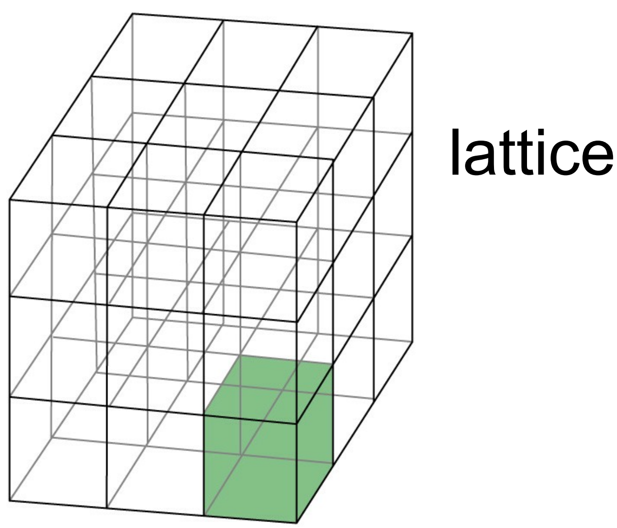
Also see Appendix 8, p. A-23 for selected ionic radii

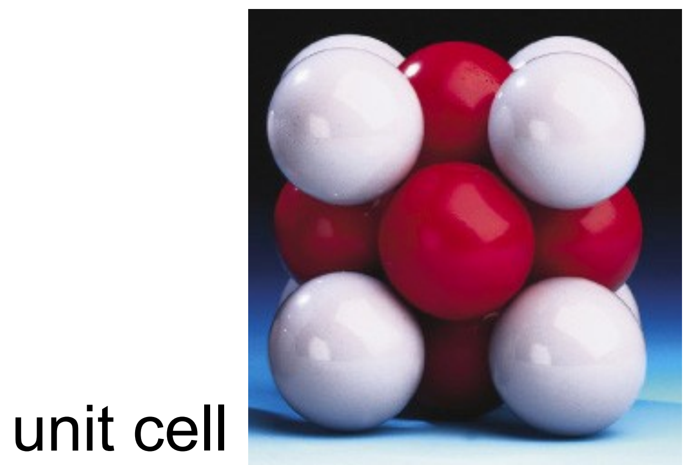


Covalent compounds – Atoms are combined to form **discrete molecular units**



Metals – Atoms are packed together in a **lattice**.





Ionic Compounds – ***Cations and anions*** **are packed together in a lattice.**

Ionic Lattice vs. Metallic Lattice

Ionic and metallic lattices are ***very similar***. There are two main differences:

1. In an ionic lattice, some "spheres" are positively charged and others are negatively charged.

2. The cations and anions in the ionic lattice have different sizes.

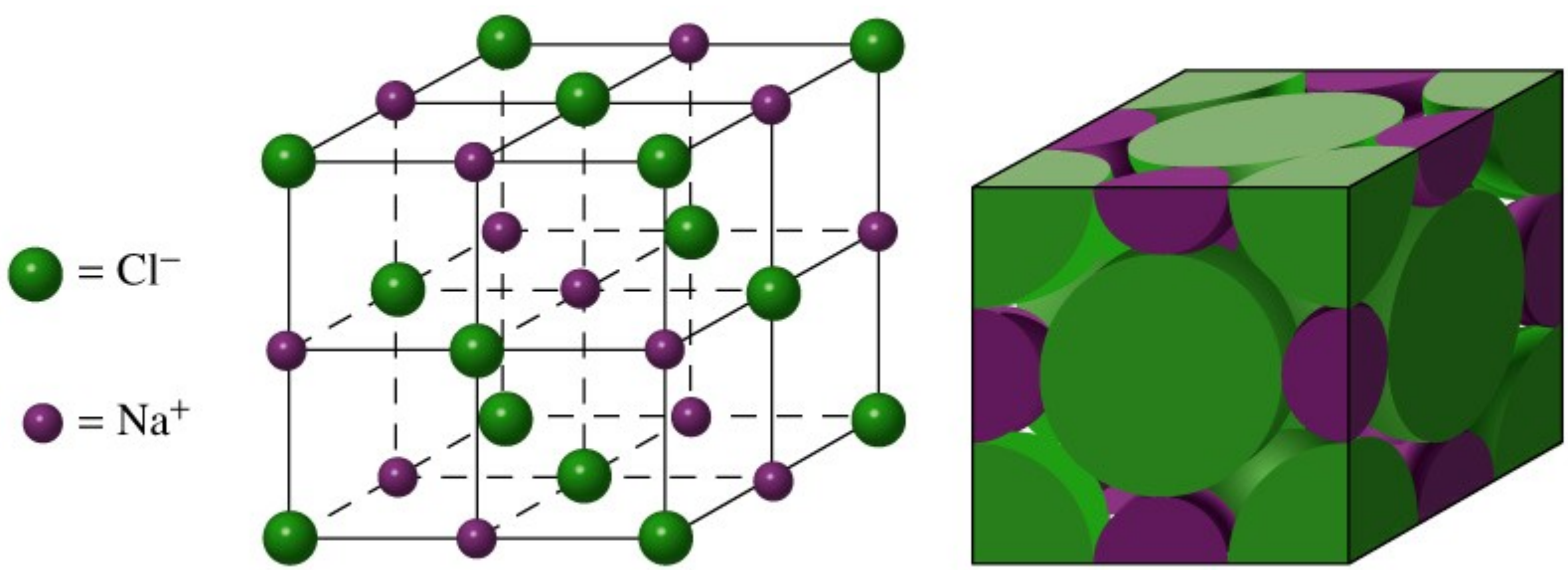
Thus, the type of ionic lattice formed will depend on the ***charge*** and the ***size*** of the ions involved.

Ion Crystal Packing

Anions are larger than the cations, so they form the lattice framework.

Cations are smaller, so they fit into vacant holes in the lattice.

e.g. Sodium Chloride (NaCl) (Cl in fcc (cubic closest packed) positions)



Ion Size and Lattice Structure

The most energetically favorable packing arrangement is one in which:

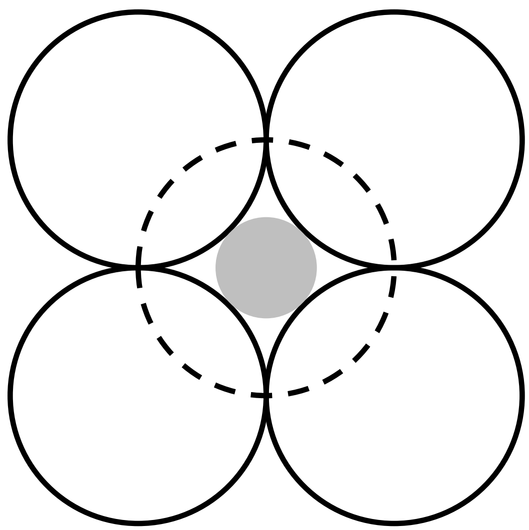
- like-charged ions ***do not*** touch one another
- oppositely charged ions ***do*** touch one another

This is best accomplished when cations occupy “holes” of the anionic lattice that are *slightly smaller* than the size of the cation. This

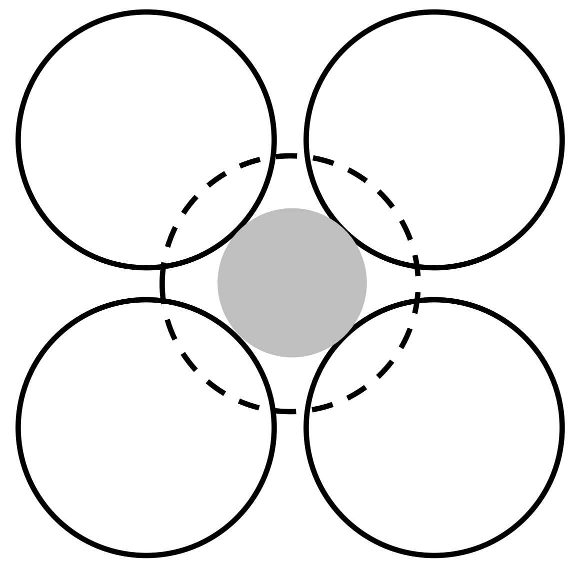
- pushes anions apart, minimizing their repulsions
- insures contact between the cation and anion, maximizing their attractions

Ion Size and Lattice Structure

Example:



cation (grey) just fills the hole left by the larger anions



cation is large enough to keep anions from touching each other.

(better!)

Ion Size and Lattice Structure

The most stable packing arrangement depends on the ratio of cation to anion radii (r_+/r_-)

$r_+/r-$	anion packing	cation location
> 0.73	simple cubic	cubic hole
0.41 to 0.73	ccp	octahedral holes
0.23 to 0.41	ccp or hcp	tetrahedral holes

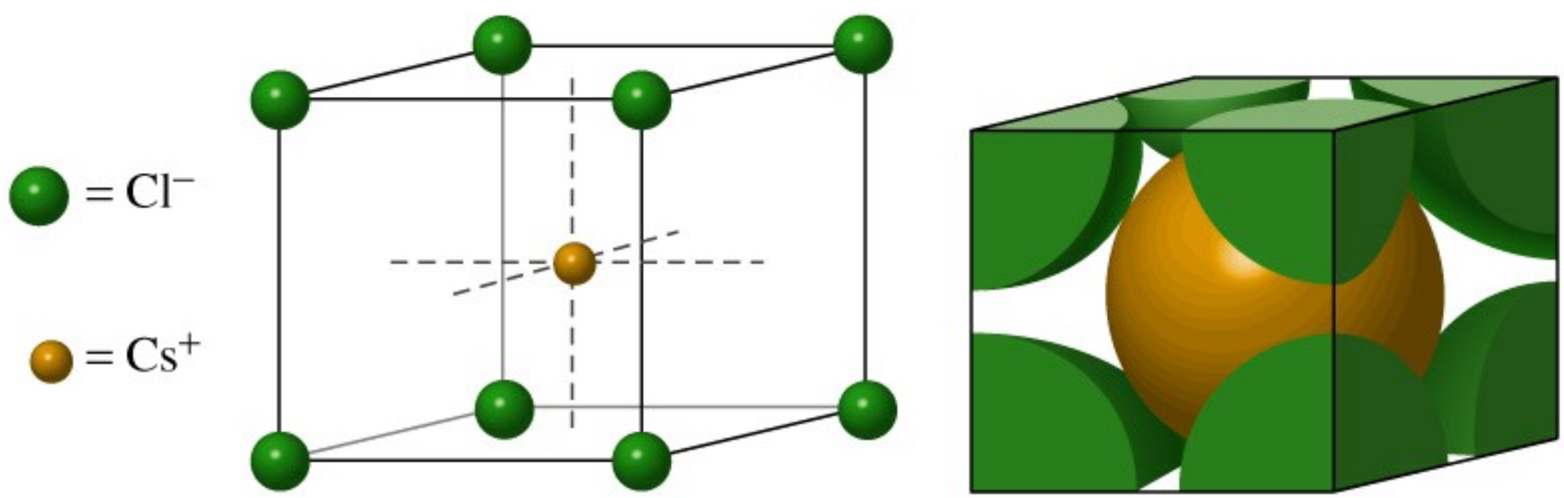
(There are exceptions!)

The unit cell must be one that is consistent with the formula of the compound!

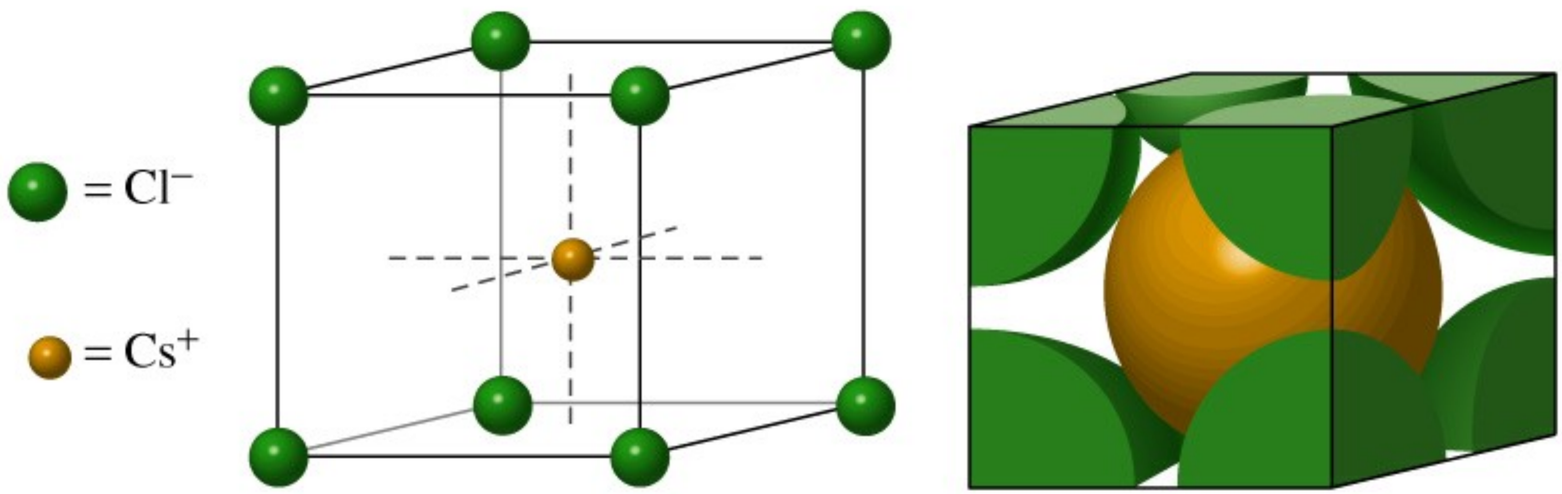
Simple Cubic Lattice
(When $r_+/r_- > 0.73$)

When anions form a simple cubic lattice, there is only 1 possible location for the cation: in the middle of the cubic unit cell.

e.g. CsCl



Chemical Formula of Cesium Chloride Structure



Each unit cell contains 8 corners (1/8 Cl^- ion each) = **1 Cl^-**
1 whole Cs^+ ion

This gives a 1:1 ratio of cation to anion: CsCl

This is called the ***cesium chloride structure***

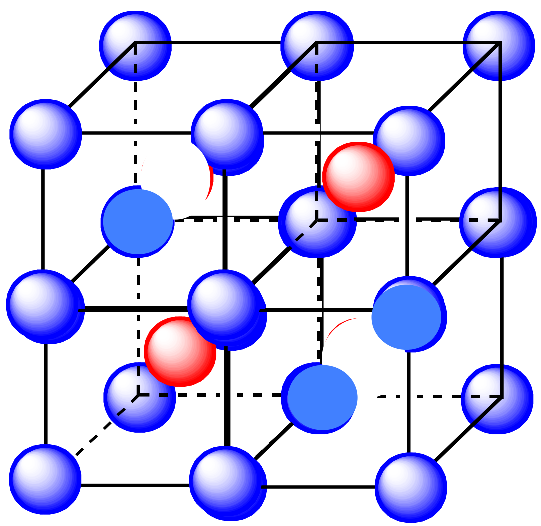
Fluorite Structure

What happens if $r_+/r_- > 0.73$ BUT the cation to anion ratio is 1:2??? e.g. CaF_2

$r_+/r_- > 0.73$ requires a cubic unit cell for the anions

If every unit cell contain a cation, the cation to anion ratio is 1:1

To obtain a 1:2 ratio, only ½ of the cubic unit cells contain a cation!



(4 interconnected cubic unit cells)

This is called the ***fluorite structure***

Summary of Simple Cubic Structures

Occur if $r_+/r_- > 0.73$

1. Cesium Chloride Structure

- occurs if cation:anion ratio is 1:1
- every cubic unit cell contains a cation

2. ***Fluorite Structure***

- occurs if cation:anion ratio is 1:2
- ½ of the cubic unit cells contains a cation

Ion Size and Lattice Structure

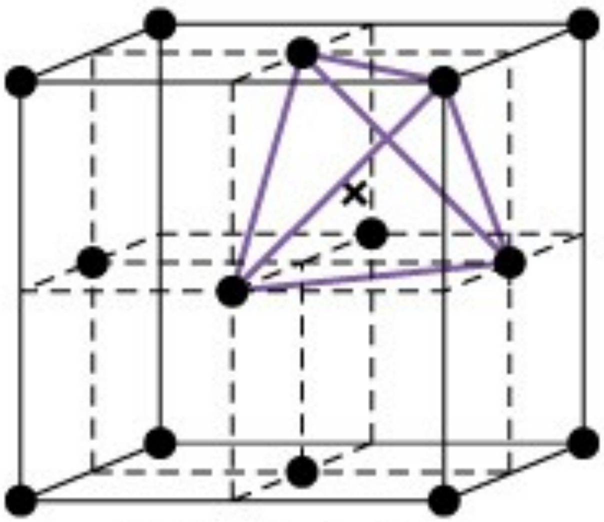
The most stable packing arrangement depends on the ratio of cation to anion radii (r_+/r_-)

r_+/r_-	anion packing	cation location
> 0.73	simple cubic	cubic hole
0.41 to 0.73	ccp	octahedral holes
0.23 to 0.41	ccp or hcp	tetrahedral holes

We will now look at ccp structures

Cubic Closest Packed Structures

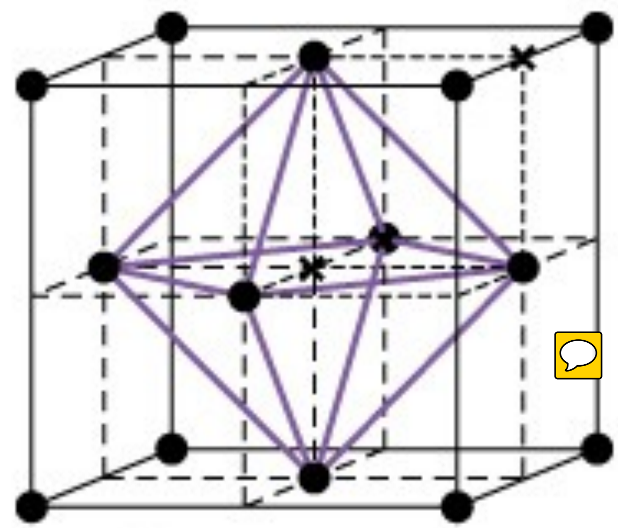
When anions form face-centered cubic unit cells (cubic-closest packed lattice), there are 2 common locations for the cation:



(b) Tetrahedral hole

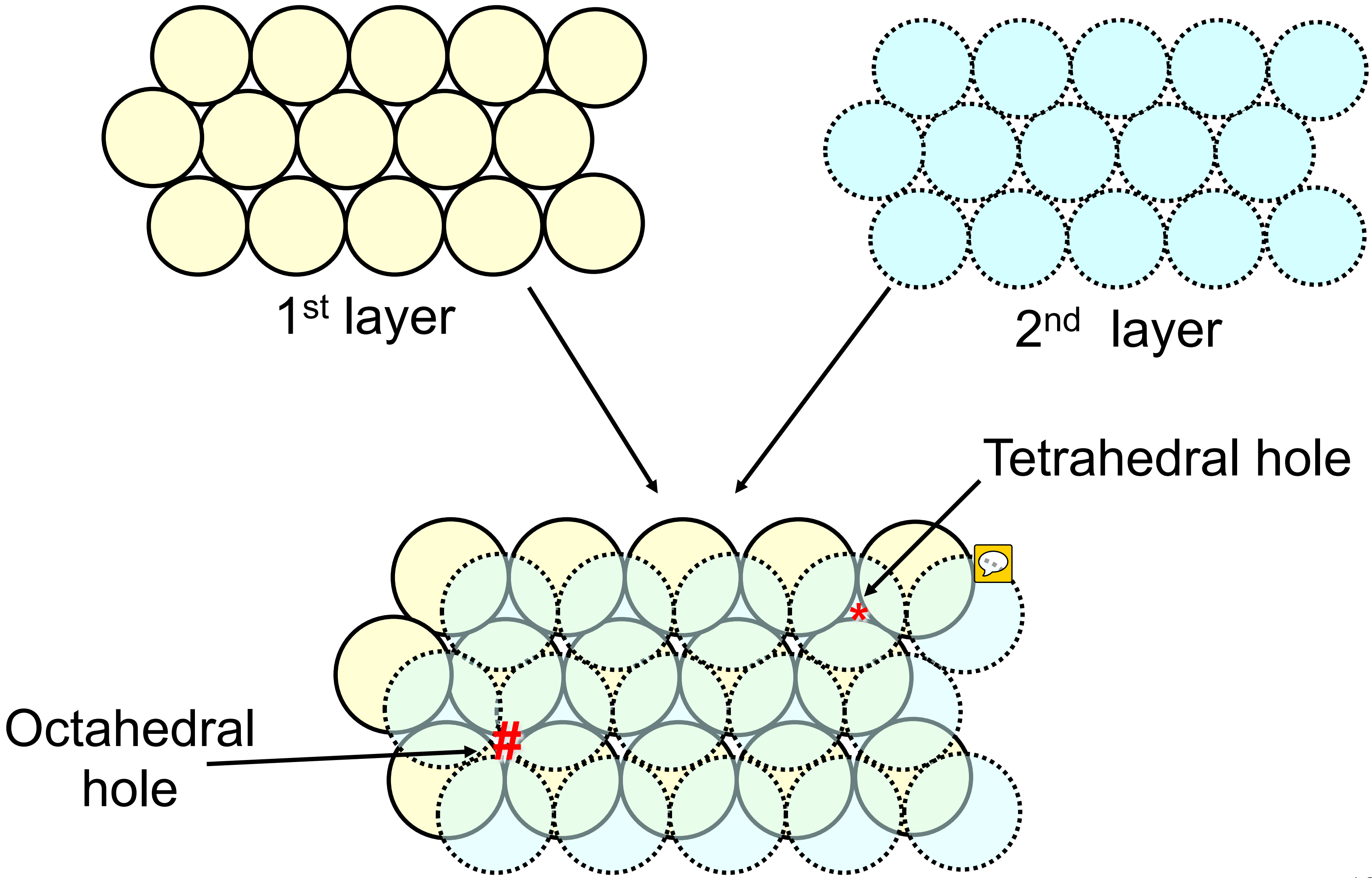
Tetrahedral hole:
Formed by 3 face-centered spheres and one corner sphere

Octahedral hole:
Formed by all 6 face-centered spheres in the cube



(c) Octahedral hole

Tetrahedral and Octahedral Holes



"Holes" in a Face-Centered Cubic Unit Cell

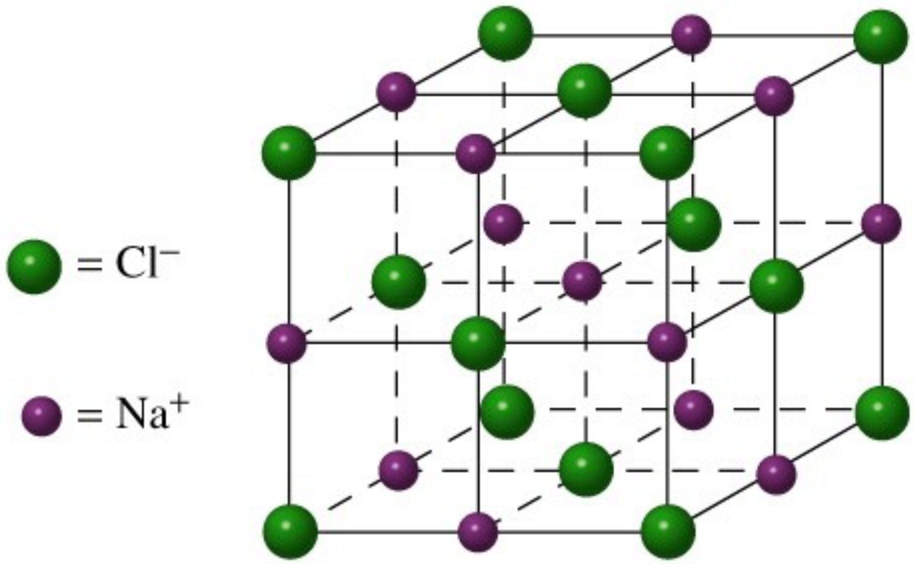
The size of each "hole" depends on the size of the anions, and can be calculated from rules of geometry:

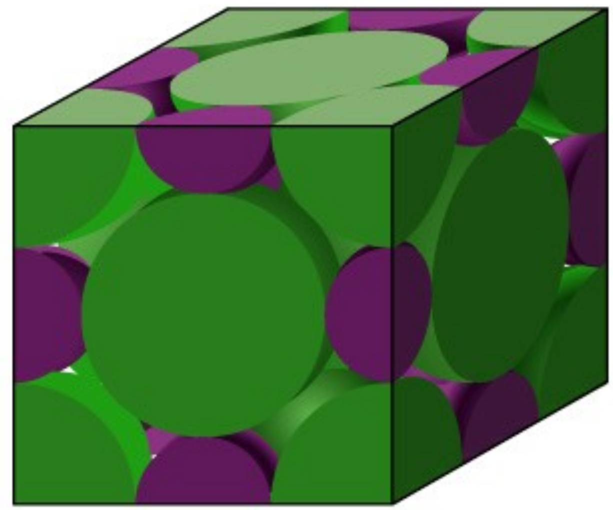
tetrahedral hole:	$r_+ = 0.155\ r_-$
octahedral hole:	$r_+ = 0.414\ r_-$

r_+ = radius of a cation that would just fit into the hole
r_- = radius of the anion

$r_+/r-$	cation location
0.41 to 0.73	octahedral holes
0.23 to 0.41	tetrahedral holes

Octahedral Lattice $0.41 < r_+/r_- < 0.73$



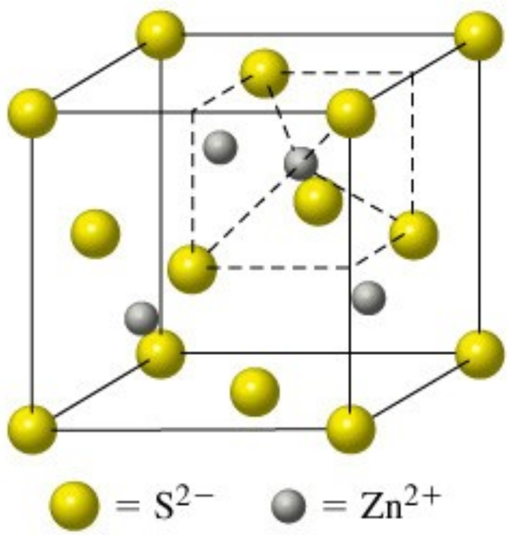


Each unit cell contains:
1 central Na^+
12 Na^+ on the edges (1/4 each)
6 Cl^- on the faces (1/2 each)
8 Cl^- on the corners (1/8 each)

This is called the ***sodium chloride structure***

Total = 4 Na and 4 Cl
Unit cell contains one formula unit: NaCl

Tetrahedral Lattice $0.23 < r_+/r_- < 0.41$



There are 8 tetrahedral holes in a face-centered cubic unit cell.

Only ½ of the tetrahedral holes are filled

Each unit cell contains
8 corners (1/8 S^{2-} ion each) = **1 S^{2-}**
6 face-centered atoms (1/2 S^{2-} ion each) = **3 S^{2-}**
4 whole Zn^{2+} ions

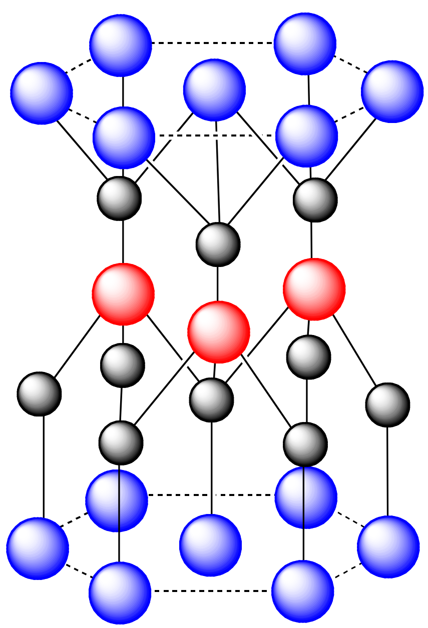
Total: 4 S^{2-} and 4 Zn^{2+} Chemical Formula = ZnS

This is called the ***zinc sulfide or sphalerite structure***

Tetrahedral Lattice with HCP

When anions pack with ***hexagonal closest packing***, there are also tetrahedral holes.

Cations fill ½ of the tetrahedral holes to form the ***wurtzite structure:***



ZnS can also pack in the wurtzite structure

Summary of Ion Crystal Packing

Simple Cubic Lattice (r_+/r_- is > 0.73)

Cesium Chloride Structure

Fluorite Structure

Octahedral Lattice (r_+/r_- is 0.41 to 0.73)

Sodium Chloride Structure

Tetrahedral Lattice (r_+/r_- is 0.23 to 0.41)

Sphalerite structure

Wurtzite structure

Polyatomic Ions in Crystal Structures

e.g. $CaCO_3$ CO_3^{2-} occupies the anion sites

Size mismatch in ions can cause thermal instability of the ionic compound

If $r_- >> r_+$ the cation can be hydrated to help fill the cation cavity and add stability to the crystal structure.

e.g. $MgSO_4$ (a common drying agent in organic chemistry)

$$MgSO_4 \xrightarrow{H_2O} MgSO_4 \cdot 7H_2O$$

Small, highly charged cations are often hydrated (surrounded by water molecules) in the crystal lattice

Melting Points of Ionic Compounds

For melting to occur, ions must overcome attractions to near-by oppositely charged ions.

Strength of attraction between ions is related to:

- distance between ions
- charge of ions

Smaller ions → shorter interionic distance → stronger electrostatic attraction → higher melting point

Ion	ion radius (pm)	mp of potassium salt (^{o}C)
F^-	117	857 (KF)
Cl^-	167	772 (KCl)
Br^-	182	735 (KBr)
I^-	206	685 (KI)

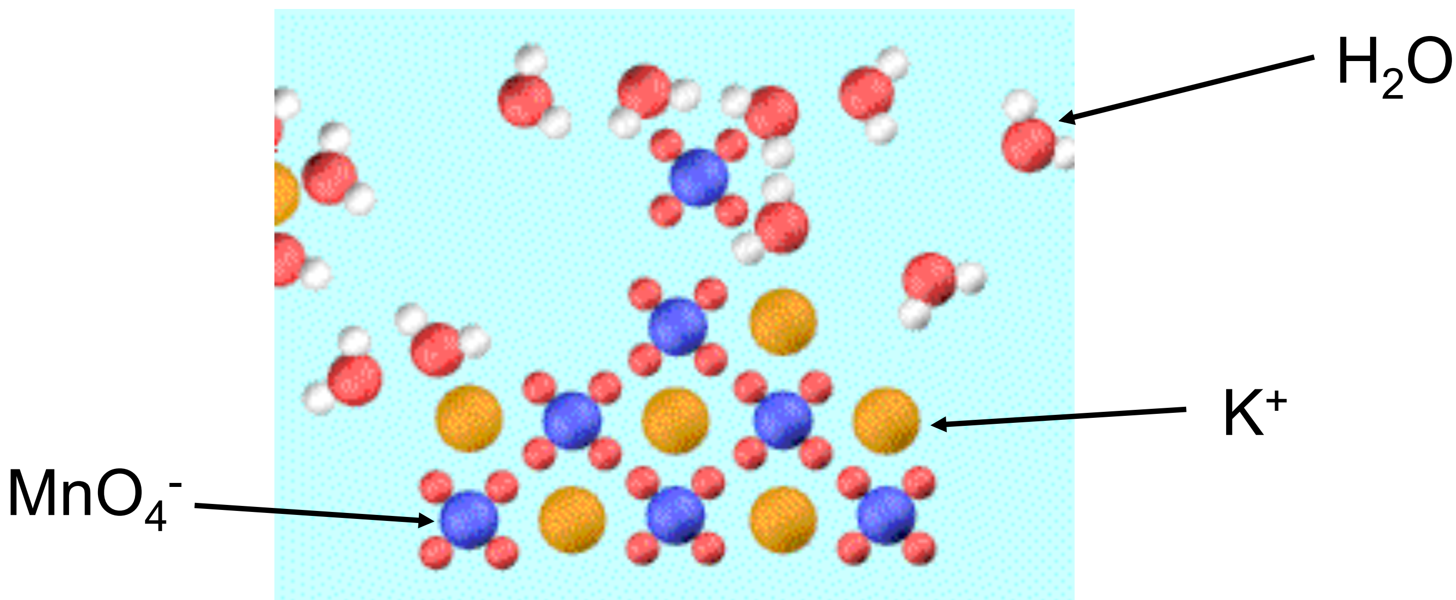
Ionic compounds have ***high melting points***

Solvation of Ions

Attractions of ions to solvent (ion-dipole attraction) must be stronger than cation-anion attractions for solvation to occur.

Solvents must be **POLAR** to dissolve ions

$$KMnO_4(s) \rightarrow K^+(aq) + MnO_4^-(aq)$$

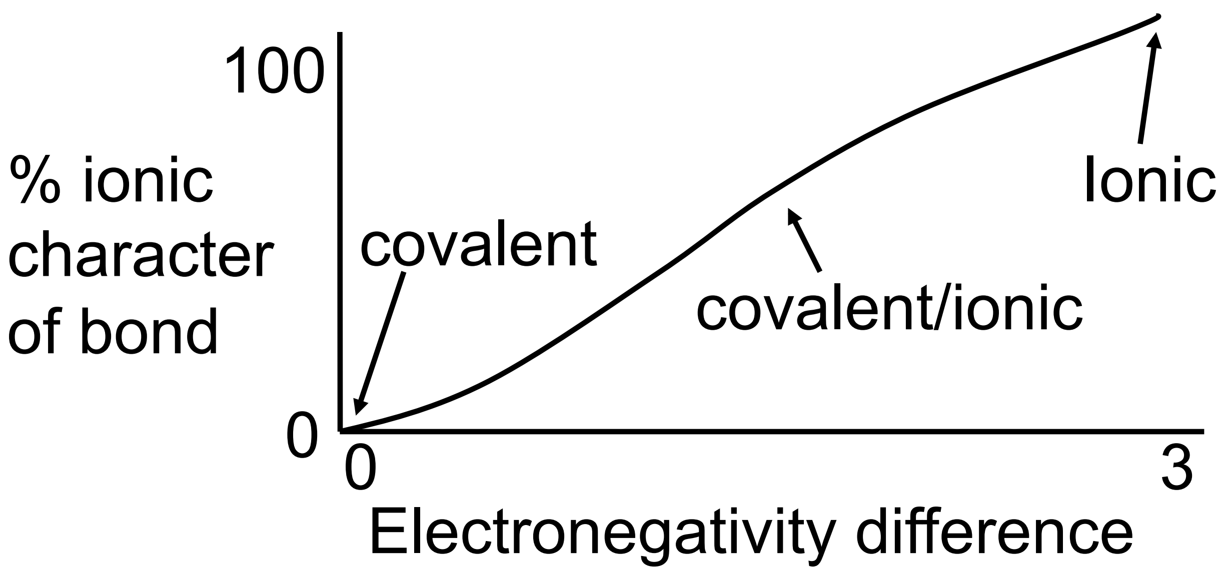


The Ionic - Covalent Continuum

Covalent bond – electrons are shared among atoms in a molecule

As the electronegativity difference between bonded atoms increases, the bond becomes more polar. Eventually, the electrons are no longer "shared."

Ionic bond – an electrostatic attraction between a cation and an anion



Pauling's Electronegativity scale:
F has en=4
Li has en = 1

Polarization and Covalency

Bonding between metals and nonmetals is usually **ionic**, BUT sometimes has ***covalent*** character!

When?

Polarization of electron density from the anion to the cation can cause covalent character in an ionic bond.

Polarization (and thus covalent character) is favored by:

1. small, highly charged cations
2. large, highly charged anions

Cation Charge Density

$$\text{Cation charge density} = \frac{\text{Ion charge}}{\text{Ion volume}}$$

Charge density is larger when:

1. Ion charge is larger (e.g. +3 or +4)
2. Ion size is smaller (e.g. top of the periodic table)

Polarization and Charge Density

A **higher cation charge density** leads to greater polarization of anion's electrons toward the cation, thus **more covalent character** in the bond.

Cation charge	ionic/covalent character
+1, +2	ionic
+3	mostly covalent (except fluorides)
+4	covalent

Larger anions are more polarizable, giving **more covalent character**

e.g. AlF_3 ionic
AlI_3 covalent