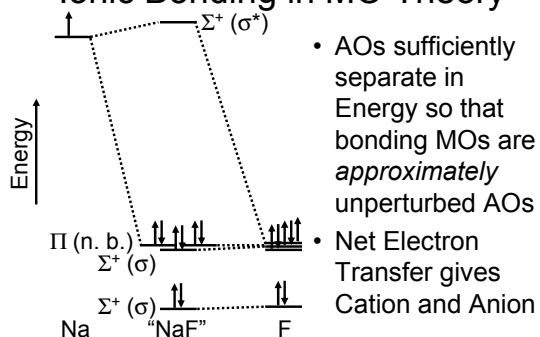


Chemistry 475

Ionic Bonding with Solid State Chemistry

Ionic Bonding in MO Theory



Ionic Bonding in MO Theory

- *Pure* Ionic Bond would have no overlap between AOs and would be Coulombic Interaction between charged Particles
 - All bonds are somewhere between covalent and ionic extremes
- $\Delta\chi$ between Elements in a Bond roughly related to Bond Character
 - Ionic bond: $\Delta\chi \geq 1.7$
 - Covalent bond: $\Delta\chi < 1.7$

Rules for Ionic Bonding

- Electron Gain/Loss controlled by IE and EA of Atom
- Leads to common Ionic Electronic Configurations
 - Noble-gas configuration, s^2p^6
 - Pseudo noble-gas configuration, $s^2p^6d^{10}$ (*18-electron rule*)
 - (18+2)-Electron configuration, $(n-1)s^2(n-1)p^6(n-1)d^{10}ns^2$ (*inert-pair effect*)

Ionic Bonding in Gaseous State

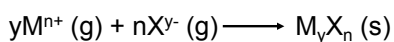
- In Limit of pure Ionic Bonding, Bond Energy given by Coulomb's Law between Ion Pairs

$$E_{ion\ pair} = C \frac{(n^+ e)(n^- e)}{d}$$

- Dependence on
 - Magnitude of charges (n^+ , n^-)
 - Distance (d)
 - Concentration

Ionic Bonding in Solid State

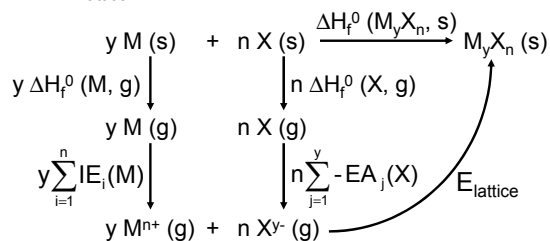
- Most Ionic Compounds are Solids
- In Solid State there are Interactions between adjacent and non-adjacent Ions
- Define *Lattice Energy* as Sum of all Coulombic Interactions in Solid Ionic Compound



$$\Delta H \equiv E_{lattice}$$

Born-Haber Cycle

- Application of Hess's Law to calculate E_{lattice} from Thermodynamic Quantities



Born-Haber Cycle

- EA and IE are not ΔH s, but Correction Factors cancel

$$\Delta H_{\text{ionization}} = \text{IE} + 5/2 \text{ RT}$$

$$\Delta H_{\text{electron gain}} = -\text{EA} - 5/2 \text{ RT}$$

- Following Equation describes Born-Haber Cycle

$$\Delta H_f^0 (\text{M}_y\text{X}_n, \text{s}) = y \Delta H_f^0 (\text{M, g}) + n \Delta H_f^0 (\text{X, g}) + y \sum_{i=1}^n \text{IE}_i (\text{M}) + n \sum_{j=1}^y -\text{EA}_j (\text{X}) + E_{\text{lattice}}$$

E_{lattice} and Stability

- More negative E_{lattice} *usually* gives a more negative ΔG_f^0 (more stable Compound)
 - Assuming $\Delta S_f^0 \approx 0$, so ΔH_f^0 dominates
- E_{lattice} depends on Size and Charge
 - Smaller cation/anion gives larger E_{lattice}
 - Higher charges give larger E_{lattice}
- Covalency perturbs general Trends and accounts for observed Properties
 - Example: CaCl_2 vs. NaCl

Fajans' Rules

- Covalent Character increases with decreasing Cation Size or increasing Cation Charge
- Covalent Character increases with increasing Anion Size or Charge
- Covalent Character is greater for Cations with 18- or (18+2)-Configurations than for Cations of same Size with Noble-Gas Configuration

E_{lattice} and Stability

- Primary Consideration for Stability of Ionic Compounds is E_{lattice}
- But ΔH_f^0 also depends on EA and IE
 - High EA and low IE give more negative ΔH_f^0
 - Low EA and high IE give less negative ΔH_f^0
 - EA and IE do not affect E_{lattice}

E_{lattice} and the Structure of Ionic Compounds

- Interactions between Ions depend on Three-Dimensional Structure
 - E_{lattice} and structure are intertwined
- Simplest Model of Ionic Solids assumes
 - Ions are hard spheres
 - No covalency
- With this Model can account for most Properties of Ionic Compounds

Review of Solid State

- *Unit Cell*: smallest Portion of the Lattice, which contains all Symmetry Properties of the Lattice, and which when repeated will reproduce the Lattice
 - For two dimensions, need two lengths and one angle to define unit cell
- For Escher Prints determine:
 - Unit cell (draw in)
 - “Chemical formula” of print
 - What symmetry elements are present?

Packing in Three Dimensions

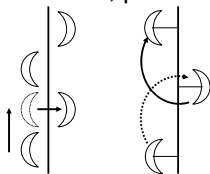
- In Two Dimensions there are 5 Unit Cells and 17 Ways to arrange Identical Objects in them (*Plane Groups*)
- In Three Dimensions there are 14 Unit Cells (*Bravais Lattices*) in 7 *Crystal Systems* (handout)
 - There are 230 distinct ways (*space groups*) to arrange identical objects in the Bravais lattices

Bravais Lattices

- Lattices can be
 - Primitive, P, positions only on corners
 - Body centered, I, corners and center of cell
 - Face centered, F, C, A, B, corners and center of two or more cell faces
- Lattice enforces Symmetry on each Position in Lattice
 - Molecules or ions can only crystallize in ways that are determined by symmetry
 - *Polymorphic, Polymorphs*

Space Groups

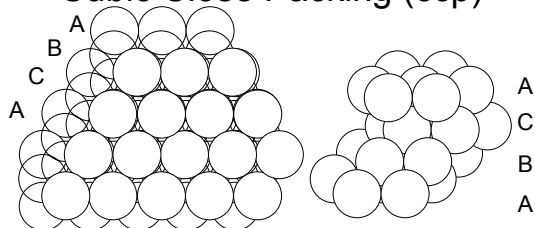
- Space Groups differ in Symmetry Elements present at each Lattice Point
 - Reflection, rotation, inversion
- Plus two Symmetry Elements, present only in Translation
 - Glide plane
 - Screw axis



Simplifications for Ionic Compounds and Metals

- Simplest Model of Ionic Compounds is hard Spheres without Electrons sharing
 - Metals can also be considered hard spheres, but with electron delocalization
- Can simplify Structure of Ionic Compounds to “Close-Pack” Structures
 - “How best to pack objects in space to minimize unused space?”

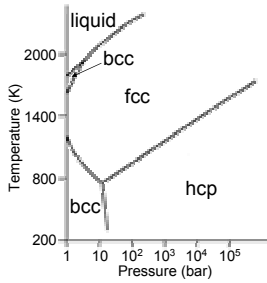
Cubic Close Packing (ccp)



- Note Colors only represent different Layers (All Objects are Identical)
- Pattern repeats every fourth Layer

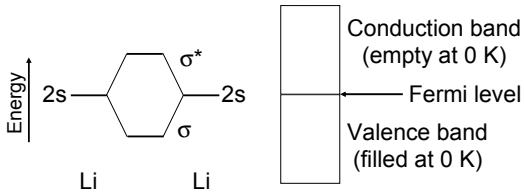
Pressure and Temperature Effects

- Unit Cell changes
 - Expands as T increases
 - Contracts as P increases
- For Cubic Cells, Density increases in order: $F > I > P$



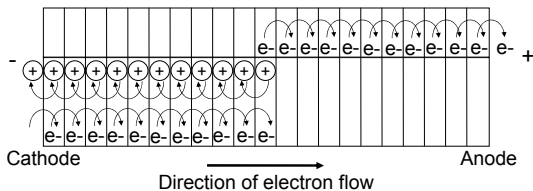
MO Model for Bonding in Metals

- Infinite Number of AOs gives an infinite Number of MOs
 - Quantized nature of energy levels lost



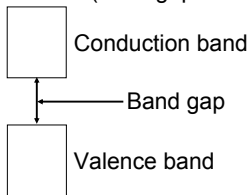
MO Model of Metallic Bonding

- At $T > 0$ K there is enough thermal energy to move electrons into conduction band
- Leaves a hole in valence band near Fermi level



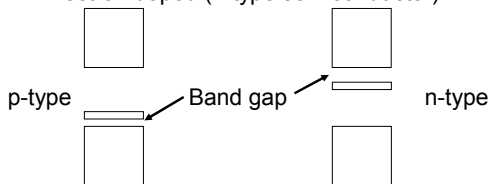
MO Model of Metallic Bonding

- For some Materials separation between Conduction and Valence Bands is not Zero
 - Insulators (band gap is large)
 - Semi-conductors (band gap is small)



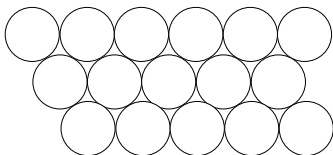
Doped Semi-Conductors

- Can make Insulators Semi-Conductors by adding Dopants
 - Hole doped (p-type semiconductor)
 - Electron doped (n-type semiconductor)

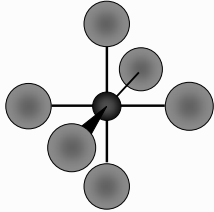


Close-Packing and Ionic Compounds

- Good for most Monatomic Ions and a few Polyatomic Ions
 - NH_4^+ , BF_4^- , PF_6^- , ClO_4^-
- Simple Close Packing does not Work
 - Repulsion
 - Cell holes



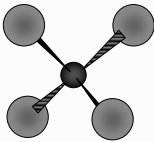
Octahedral Holes in ccp



Holes occur on edges half-way between ccp lattice points and in center of ccp lattice.

Each hole surrounded by 6 ccp lattice points and each ccp lattice point surrounded by 6 holes.

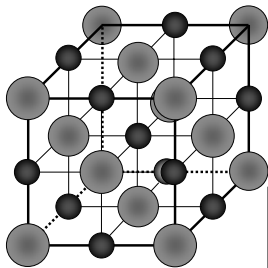
Tetrahedral Holes in ccp



Holes occur $\frac{1}{4}$ unit cell dimension from edges.

Each hole surrounded by 4 ccp lattice points and each ccp lattice point surrounded by 8 holes.

Basic Ionic Lattices



Rock Salt Structure

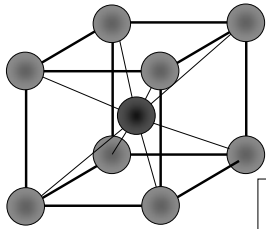
ccp of A^- with C^+ in all octahedral holes

Formula: CA

Coordination number of both A^- and C^+ is 6

Examples: NaCl, NaF, NaBr, NaI, NaH, halides of Li, K, Rb; AgF, AgCl, MgO, CaO, SrO, BaO, MnO, CoO, NiO, MgS, CaS, SrS, BaS

Basic Ionic Lattices



CsCl Structure

Cubic lattice of A^-
with C^+ in center

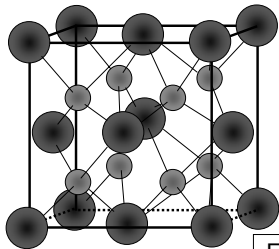
Formula: CA

Coordination number
of C^+ and A^- is 8

Examples: CsCl, CsBr, CsI,
TlCl, TlBr, NH_4Cl^* , NH_4Br^*

*Undergo phase change to
NaCl lattice (at 457 K for
 NH_4Cl and 411K for NH_4Br).

Basic Ionic Lattices



Fluorite Structure

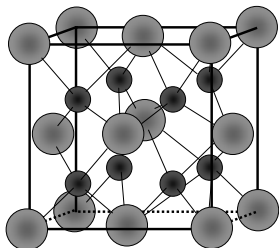
ccp lattice of C^{2+}
with A^- in all
tetrahedral holes

Formula: CA_2

Coordination number
of C^{2+} is 8 and A^- is 4

Examples: group 2 fluorides
(e. g. CaF_2), $BaCl_2$ and
dioxides of f-block metals

Basic Ionic Lattices



Antifluorite Structure

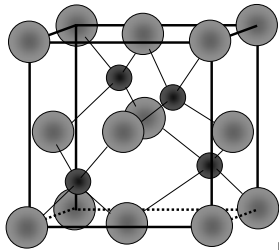
ccp lattice of A^{2-}
with C^+ in all
tetrahedral holes

Formula: C_2A

Coordination number of
 A^{2-} is 8 and C^+ is 4

Examples: group 1
oxides (except Cs_2O)

Basic Ionic Lattices



Zincblende (β -ZnS) Structure

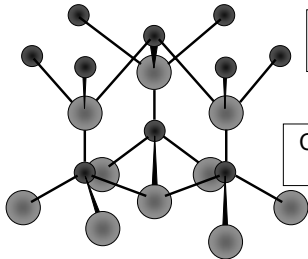
ccp lattice of A^{2-} with C^{2+} in half of tetrahedral holes

Formula: CA

Coordination number of A^{2-} is 4 and C^{2+} is 4

Examples: ZnS, Si, Ge, Sn (α form), C (diamond)

Basic Ionic Lattices



Wurtzite (α -ZnS) Structure

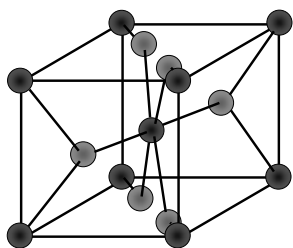
Hexagonal lattice of A^{2-} and C^{2+}

Formula: CA

Coordination number of A^{2-} is 4 and C^{2+} is 4

Examples: ZnS

Basic Ionic Lattices



Rutile Structure

Tetragonal Body-centered Cell of C^{4+} two A^{2-} in cell, four on faces

Formula: CA_2

Coordination number of A^{2-} is 3 and C^{4+} is 6

Examples: TiO_2 , SnO_2 , MnO_2 , PbO_2

Radius Ratio

- Geometric Limitation on Size of Hole in Close-Pack Structures
 - Useful for predicting structures of salts that have one of the common structures
 - Limited applicability outside these salts
- Size of Ion depends on Hole in the Lattice
 - Ionic radii are not constant, depend on *coordination number*

Radius Ratio

C. N.	Geometry	Limiting Ratio	Possible Lattices
4	tetrahedral	0.414; 2.42	wurtzite, zinblende
6	octahedral	0.732; 1.37	NaCl, rutile
8	cubic	1.00	CsCl, fluorite, antiferite
12	dodecahedral		No simple ionic lattice

Radius Ratio

- Example: strontium fluoride

Determine formula, if not given. SrF_2

From ionic radii, determine radius ratio for both cation and anion.

$$\frac{r_{\text{Sr}^{2+}}}{r_{\text{F}^-}} = \frac{132 \text{ pm}}{119 \text{ pm}} = 1.11$$

$$\frac{r_{\text{F}^-}}{r_{\text{Sr}^{2+}}} = \frac{119 \text{ pm}}{132 \text{ pm}} = 0.902$$

Radius Ratio

- Radius Ratio for $\text{Sr}^{2+}/\text{F}^-$ between Limiting Values for Cubic and Octahedral
 - Maximum C. N. for Sr^{2+} is 8
- Radius Ratio for $\text{F}^-/\text{Sr}^{2+}$ between Limiting Values for Cubic and Octahedral
 - Maximum C. N. for F^- is 8
- Possibilities: CsCl, fluorite, antiferite
 - Stoichiometry

Radius Ratio

- Radius Ratio should be used with Caution!
- Fails with increasing Covalent Character in the primarily Ionic Bond
- Example: ZnS

$$\frac{r_{\text{Zn}^{2+}}}{r_{\text{S}^{2-}}} = \frac{88 \text{ pm}}{170 \text{ pm}} = 0.52$$

Predicts rock salt or CsCl lattice structure.

Structure and Bonding in Ionic Compounds

- From Knowledge of Structure and Charges can predict E_{lattice}
 - Each ion-ion interaction determined by geometry
 - Energy of interaction is a converging infinite series
 - Each lattice converges to a different value (*Madelung constant*)

Born-Landé Equation

- Gives approximate E_{lattice} at 0 K
- Accounts for
 - All Ion-Ion Interactions (Madelung constant)
 - Finite Size of Ions (*Born exponent*)
 - Electron-electron and nucleus-nucleus interactions (*Born exponent*)
- Does not account for Covalency
 - Difference between Born-Landé and experimental E_{lattice} measure of covalency

Born-Landé Equation

$$E_{\text{lattice}} \text{ (J/mole)} \approx -\frac{NA|z_+||z_-|e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right)$$

$$N = 6.022 \times 10^{23} \text{ mole}^{-1} \quad e = 1.602 \times 10^{-19} \text{ C}$$

$$\epsilon_0 = 8.854 \times 10^{-12} \text{ F}\cdot\text{m}^{-1} \quad r_0 = \text{sum of ionic radii (m)}$$

$$A = \text{Madelung constant} \quad n = \text{Born exponent}$$

$$|z_+|, |z_-| = \text{charge on cation and anion, respectively}$$

Madelung Constants

Lattice type	A (no units)
Sodium chloride	1.7476
Cesium chloride	1.7627
Wurtzite	1.6413
Zincblende	1.6381
Fluorite	2.5194
Rutile	2.408

Born Exponents

Ion's electronic configuration	n (no units)
[He]	5
[Ne]	7
[Ar] or [3d ¹⁰][Ar]	9
[Kr] or [4d ¹⁰][Kr]	10
[Xe] or [5d ¹⁰][Xe]	12

For a compound average the n values for the ions.
Example: BaO, Ba²⁺ = [Xe] n = 12, O²⁻ = [Ne] n = 7,
for BaO n = (12 + 7)/2 = 9.5

Defect Structures

- Schottky Defects
 - Equal number of cations and anions missing from lattice
- Frenkel Defects
 - Ion in interstitial site (normal position empty)
- Solid Electrolytes
 - High molar conductivity caused by movement of ions in lattice
- F-Centers
 - Free electron occupies lattice site

Intercalation Compounds

- Guest Molecules trapped within (*intercalated*) a Host Lattice
 - MC₈ and M(C₁₂)_n (M = K, Rb, Cs; n = 2, 3, 4, 5)
 - Organic molecules in zeolites
- Have novel Properties and novel Reactivities
 - Organics trapped in zeolites react differently than if free
