Chem 241

Lecture 21

UMas 🖞 🍐 🍐 🍐 🍐 🗁 🗗 ... 🛓 🖣 🕨 Initiative

Announcement

March 26 \rightarrow Second Exam

Recap

Calculation of space filling Counting atoms Alloys Ionic Solids Rock Salt CsCl



ZnS



- Sphalerite/ Zinc-blende
- Can be viewed as ccp in S²⁻ with Zn²⁺ in half the Td holes.
- Since all the Td holes are completely contained within a single unit cell, all 4 Zn ions count in the unit cell
- There are two types of S anions, those in faces, 6/2 = 3
- And those in corners, 8/8 = 1.
- The stoichiometry is 1:1; Z = 4







Fluorite Structure





- Can be viewed as ccp in one ion with the other in all the T_d holes. In the case of fluorite, this would be ccp in Ca²⁺ with F- in all the T_d holes. (Note anions not close packed, cations are.)
- Since there are twice as many Td holes in a close packed lattice (8) than there are spheres (4), the stoichiometry is 1:2.
- The formula unit is $CaF_2 Z = 4$.
- 8,4-coordination.



- In anti-fluorite, the positions of the cations and anions are reversed. *E.g.*, Li₂O. Here the lattice is ccp in O²⁻ with Li⁺ in all the Td holes.
- 4,8-coordination





Wurtzite

Wurtzite (another polymorph of ZnS)

- Can be viewed as hcp in S^{2-} with Zn^{2+} in $\frac{1}{2}$ the Td holes.
- Stoichiometry = 1:1
- Formula unit ZnS, Z = 2
- 4,4-coordination







(0,1)

 $\frac{7}{8}$

(b) 3 8

Nickel Arsenide



- Can be viewed as expanded hcp in $As^{2\text{-}}$ with $Ni^{2\text{+}}$ in O_h holes.
- Stoichiometry = 1:1
- Formula unit = NiAs, Z = 2
- 6,6-coordination
- As sites are trigonal prismatic, not Oh
- Often preferred by MX compounds with polarizable (soft) ions.
- The possible M-M bonding between atoms in adjacent layers, and is thus common for alloys where the metals interact.





Rutile





 (TiO_2)

- Can be viewed as expanded hcp in Ti⁴⁺ with O^{2-} in $\frac{1}{2}$ Oh holes
- Very distorted by tendancy of Ti(IV) to adopt Oh geometry.
- Each Ti⁴⁺ is 6-coordinate, thus each O²⁻ is 3coordinate, *i.e.*, 6,3-coordination.
- Stoichiometry is 1:2
- Formula unit is TiO_2 , Z = 2



Inorganic solids

| Table 3.4 The crystals s | | | | | |
|---|---|---|------------------|---|--|
| Crystal structure | Example [*] | | | | |
| Antifluorite | K20, K2S, Li20, Na20, Na2Se, Na2S | | | | |
| Caesium chloride | CsCl , CaS, TlSb, CsCN, CuZn | | | | |
| Fluorite | CaF ₂ , UO ₂ , BaCl ₂ , HgF ₂ , PbO ₂ | | | | |
| Nickel arsenide | NiAs, NiS, FeS, PtSn, CoS | | | | |
| Perovskite | CaTiO₃ , SrTiO ₃ , PbZrO ₃ , LaFeO ₃ , LiSrH ₃ , KM | InF ₃ | | | |
| Rock salt | NaCl , KBr, Rbl, AgCl, AgBr, MgO, CaO, TiO, FeO, NiO, SnAs, UC, ScN | | | | |
| Rutile | TiO ₂ , MnO ₂ , SnO ₂ , WO ₂ , MgF ₂ , NiF ₂ | | | | |
| Sphalerite (zinc blende) | ZnS, CuCl, CdS, HgS, GaP, InAs | Table 3.5 The relation of structure to the filling of holes | | | |
| Spinel | MgAl ₂ O ₄ , ZnFe ₂ O ₄ , ZnCr ₂ S ₄ | | | | |
| Wurtzite | ZnS , ZnO, BeO, MnS, AgI, AlN, SiC, NH_4F | Close-packing type | Hole filling | Structure type (exemplar) | |
| * The substance in bold type is the one that gives its name to the structure. | | Cubic (ccp) | All octahedral | Rock salt (NaCl) | |
| w.1.1. w. 2 | | | All tetrahedral | Fluorite (CaF ₂) | |
| | | | Half tetrahedral | Sphalerite (ZnS) | |
| | | Hexagonal (hcp) | All octahedral | Nickel arsenide (NiAs); with some distortion from perfect hcp | |
| | | | Half octahedral | Rutile (TiO ₂); with some distortion from perfect hcp | |
| | | | All tetrahedral | No structure exists: tetrahedral holes share faces | |
| | | | Half tetrahedral | Wurtzite (ZnS) | |



Perovskite, A_aB_bX_n









CaTiO₃, ABX₃

- Idealized as a cube of B cations (1 per unit cell surrounding an A cation completely contained in the center of the unit cell, with X atoms located in the O_h holes on the cube edges (12/4 = 3).
- Usually A is large and has a small charge, B is small and has a large charge.
- The sum of the charges on the cations must = the sum of the charges on the anions, in this case 6.

e.g., for perovskite Ca(II) + Ti(IV). But could be (III) and (III), or even mixed, as in La(Ni_{0.5}Ir_{0.5})O₃.

Often have interesting electrical properties



Spinel

- MgAl₂O₄, AB₂X₄
 - Viewed as ccp array of O²⁻ ions with A occupying 1/8 of T_d holes and B occupying $\frac{1}{2}$ of O_h holes.
 - Normally B is smaller and more highly charged than A
 - Inverse spinels have B atoms in the occupied T_d holes and in ½ the occupied O_h holes. B[AB]O4, where brackets denote the ions in the O_h holes.
 - Sometimes A and B are the same element:
 - Fe(II)Fe(III)₂O₄







| Table 1.5 Ionic radii, r/pm* | | | | | | | |
|------------------------------|------------------|-------------------------|------------------|------------------|------------------------|------------------------|-----------------|
| Li ⁺ | Be ²⁺ | B ³⁺ | | | N ³⁻ | 0 ²⁻ | F ⁻ |
| 59(4) | 27(4) | 11(4) | | | 146 | 135(2) | 128(2) |
| 76(6) | | | | | | 138(4) | 131(4) |
| | | | | | | 140(6) | 133(6) |
| | | | | | | 142(8) | |
| Na ⁺ | Mg ²⁺ | Al ³⁺ | | | P ³⁻ | S ²⁻ | Cl- |
| 99(4) | 49(4) | 39(4) | | | 212 | 184(6) | 181(6) |
| 102(6) | 72(6) | 53(6) | | | | | |
| 118(8) | 89(8) | | | | | | |
| K+ | Ca ²⁺ | Ga ³⁺ | | | As ^{3–} | Se ²⁻ | Br ⁻ |
| 138(6) | 100(6) | 62(6) | | | 222 | 198(6) | 196(6) |
| 151(8) | 112(8) | | | | | | |
| 159(10) | 123(10) | | | | | | |
| 160(12) | 134(12) | | | | | | |
| Rb ⁺ | Sr ²⁺ | In ³⁺ | Sn ²⁺ | Sn ⁴⁺ | | Te ²⁻ | I- |
| 152(6) | 118(6) | 79(6) | 83(6) | 69(6) | | 221(6) | 220(6) |
| 160(8) | 125(8) | 92(8) | 93(8) | | | | |
| 173(12) | 144(12) | | | | | | |
| Cs ⁺ | Ba ²⁺ | Tl ³⁺ | | | | | |
| 167(6) | 149(6) | 88(6) | | | | | |
| 174(8) | 156(8) | Tl+ | | | | | |
| 188(12) | 175(12) | 164(6) | | | | | |

* Numbers in parentheses are the coordination number of the ion. For more values, see *Resource section* 1.





| Table 3.6 The correlation of structural type with radius ratio | | | | | |
|--|--|-----------------------------|--|--|--|
| Radius ratio (p) | Coordination numbers for 1:1 and 1:2 stoichiometries | Binary AB structure type | Binary AB ₂ structure type | | |
| 1 | 12 | None known | None known | | |
| 0.732-1 | 8:8 and 8:4 | CsCl | CaF ₂ | | |
| 0.414-0.732 | 6:6 and 6:3 | NaCl (ccp), NiAs (hcp) | TiO ₂ | | |
| 0.225-0. 414 | 4:4 | ZnS (ccp and hcp) | | | |



Lattice Energy

 $MX(s) \rightarrow M^+(g) + X^-(g) \Delta H_L^{o}$

| Na+(g) | Na ⁺ (g) + Cl (g) | | | | | | |
|-------------------------|------------------------------|--------------------------|-----------------------|--|--|--|--|
| ∆H ^e dise | 1/2 x 242 | ΔH^{θ}_{ea} | -364 | | | | |
| Na ⁺ (g) | + ½Cl ₂ (g) | Na+ (g) + | - Cl ⁻ (g) | | | | |
| ΔH_i^{θ} | +494 | | | | | | |
| Na (g) | + ½Cl₂(g) | | | | | | |
| ΔH^{θ}_{a} | +109 | | - ΔH ^θ L | | | | |
| Na (s) | + ½Cl2(g) | | | | | | |
| ΔH_{f}^{θ} | -411 NaCl | (s) | | | | | |



Born-Mayer Equation

$$\Delta H_L = \frac{N_A |z_A z_B| e^2}{4\pi\varepsilon_0 d_0} \left(1 - \frac{d}{d_0}\right) A$$

$$\Delta H_L \propto \frac{|z_A z_B|}{d_0}$$

| Table 3.8 Madelu constants | ing |
|---|---|
| Structural type | \mathcal{A} |
| Caesium chloride Fluorite Rock salt Rutile Sphalerite | 1.763 2.519 1.748 2.408 1.638 |
| Wurtzite | 1.641 |



Thermal Stability

| Table 3.11 Decomposition data for carbonates* | | | | | | |
|---|---------------------|-------------------|-------------------|-------------------|-------------------|--|
| | | MgCO ₃ | CaCO ₃ | SrCO ₃ | BaCO ₃ | |
| $\Delta G^{ ightarrow}$ / (kJ mo | l ⁻¹) | +48.3 | +130.4 | +183.8 | +218.1 | |
| $\Delta H^{ m e}/({ m kJmo}$ | l ⁻¹) | +100.6 | +178.3 | +234.6 | +269.3 | |
| $\Delta S^{ ightarrow}/(m JK^{-1}$ | mol ⁻¹) | +175.0 | +160.6 | +171.0 | +172.1 | |
| $\theta_{\rm decomp}/^{\circ}{\rm C}$ | | 300 | 840 | 1100 | 1300 | |

* Data are for the reaction $MCO_3(s) \rightarrow MO(s) + CO_2(g)$ at 298 K. θ is the temperature required to reach $p(CO_2) = 1$ bar and has been estimated from the thermodynamic data at 298 K.

$\Delta \mathsf{H}^{0} = \Delta \mathsf{H}(\mathsf{CO}_{3}^{2-} \rightarrow \mathsf{O}^{2-}/\mathsf{CO}_{2}) + \Delta \mathsf{H}_{\mathsf{L}}(\mathsf{MCO}_{3}) - \Delta \mathsf{H}_{\mathsf{L}}(\mathsf{MO})$



Counter Ions





Solubility



 $MX(s) \rightarrow M^+(aq) + X^-(aq)$





Electronic Structure

MOT of small molecules can be extended to solids, which consist of an almost infinite number of atoms, ions, etc.

- 1. Particularly useful in explaining the electrical conductivities of materials.
- 2. Types of conductors
 - a. metallic conductor: electrical conductivity decreases with increasing temperature
 - b. semiconductor: electrical conductivity increases with increasing temperature.
 - c. an insulator has very low electrical conductivity
 - d. a superconductor has zero electrical resistance below a critical temperature.





Inorganic solids

Treat solid like a very large molecule that has a nearly infinite number of atoms, and thus a nearly infinite number of bonding MOs and antibonding MOs. (Tight binding approximation).



a. Atomic orbitals of the same type, say the valence s orbitals, give rise to a large number of molecular orbitals that are very similar in energy. This is a **band** of energy levels, the example would be an s-band.

b. The bands are separated from each other by **band gaps**, which are ranges of energies that contain no MOs.

c. Building up bands (# of atoms = # of orbitals)



Inorganic solids



d. The result of carrying this out for a large number of atoms, is a large number of orbitals

e. The upper and lower energy of the band is constrained by the energy of the most bonding and most antibonding level. Most antibonding

f. since the energy range is finite, Number of atoms, N Figure 3-0 Shirver & Athins Inorganic Chemistry, Fourth Edition * 2006 by D.F. Shirver, RW. Atkins, T.L. Overton, J. P. Rourke, M.T. Weller, and f the band consists of a nearcontinuum of energy levels.

Intermediate orbitals Most bonding

Eigure 3.40



Bands

- We can do the same for p-orbitals, d-orbitals, etc. to form p- and d-bands.
 - a. since atomic p-orbitals are higher in energy that sorbitals, the p-band will lie above the s-band in energy by an amount that is determined by the difference in energy of the atomic orbitals.
 - b. the width (in energy) of a band is determined by the strength of the interaction between the orbitals. If the interaction is strong, the band will be wide. Sometimes the width of the band is sufficient for bands to overlap.



Filling them up



Now we need to put electrons into the bands.

a. The highest level occupied in a band at T = 0 K is the Fermi level. In a case where the diatomic would fill the bonding, but not the antibonding, the Fermi level is in the middle of the band.

b. Conduction band explains metallic conductors.



- c. The ability of the electrons to move in the solid is dependent on the uniformity of the material (purity of the material all atoms the same.
- d. the number of energy levels in a given energy range is the density of states, ρ, and is high in the middle of a band, and low at the edges. (0 in a band gap)



Semimetals

In some cases the highest energy level of a filled band is the same as the lowest energy of an empty band (there is no band gap), but since the density of states at the top edge of the lower band and the lower edge of the upper band is very low. Such solids are semimetals (*e.g.*, graphite).



 $[\]begin{tabular}{|c|c|c|c|} \hline \begin{tabular}{|c|c|c|} \hline \begin{tabular}{|c|c|c|} \hline \begin{tabular}{|c|c|} \hline \begin{tab$

Insulators

•Insulators are materials where a filled band is separated in energy from an empty band by a large band gap.

•Semiconductors are materials that have small band gaps, where empty bands can be populated thermal excitation of electrons from the filled band to the empty band.

Thus, insulators are just semiconductors with large band gaps.



Intrinsic semiconductors

Bands in the pure material are close enough in energy to be thermally populated.

- The promotion of electrons from the filled band into the empty band, introduces electrons into the empty band, and holes in the filled band.

- The population of the upper band has Boltzmann-like temperature dependence, and thus the conductivity shows an exponential dependence with temperature.

 $\sigma = \sigma_0 e^{-E_{gap}/2kT}$

-This predicts an activation energy equal to ¹/₂ the band gap.



Extrinsic Semiconductors

Acceptor band

p band

Donor band

s band

Shriver & Atkins Inorganic Chemistry, Fourth Edition © 2006 by D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong

(b)

₳

Energy –

(a)

These are compounds where the semiconductor properties are the result of introducing impurities that produce either occupied donor bands (n-type) or empty acceptor bands (p-type) in the band gap of the pure material.

-the process is called doping

-very low levels of dopant (one atom per 10⁹) are required.

- Ex1. If you dope a Si crystal ([Ne]3s²3p²) with As ([Ar]4s²4p³), you introduce one additional valence e- per As. **n-type**

- Ex2. If you dope a Si crystal ([Ne]3s²3p²) with Ga ([Ar]4s²4p¹), you introduce one additional valence e- per As. **p-type**



Homework

Chapter 3: Exercises: 2, 4, 7,9, 16, 17

