Structures of Solids

- Many dense solids are described in terms of “packing” of atoms or ions.
- Although these geometric descriptions are often used and can appear as though solids are assembled from “atomic marbles”, the forces and physical laws that govern solid state structure and molecular structure are exactly the same.
- These are just useful ways to visualize and classify structures.
- See the class web site for longer animations. Also useful: http://www.dur.ac.uk/john.evans/

Unit Cells - Not(?)

- Text describes the shaded areas as unit cells. Are either of them really unit cells?
- Can you offer a “better” choice?
Graphite - Unit Cell Concepts

See class web site for this animation

Hexagonal Close Packing - Unit Cell

- All crystals are built up from units that are repeated throughout their structures, known as the "unit cell".
- How many atoms are in the unit cell of an hcp element?

Cubic Close Packing = Face-Centered Cubic

- The …ABC… stacking sequence generates packing of atoms with cubic symmetry.
- When viewed from the perspective of the cube, the cube is seen to have an atom in every face (face-centered cubic).
The third common dense metal structure is body-centered cubic (bcc).
This is not a close packing, but is nearly as dense. Each atom has 8 nearest neighbors and 6 only ~15% further away.

Close-packed arrays possess an equal number of octahedral “holes” and twice as many tetrahedral “holes”.

See class web site for this animation
Rocksalt (NaCl) type: ccc stacked Cl; all octahedral holes filled

Zinc-Blende (sphalerite, ZnS) Type
- ZnS (zinc-blende) is described as fcc arrays of S²⁻ ions with half the tetrahedral holes filled with Zn²⁺ cations.
- “antistructures” have cation and anion positions (and compositions) swapped. ZnS is its own antistructure.

Zinc-Blende = “heteroatomic diamond”
Flourite (CaF₂) Type

- CaF₂ (fluorite) is described as an fcc array of Ca²⁺ ions with all tetrahedral holes filled with F⁻ anions.
- "antistructures" have cation and anion positions (and compositions) swapped. Li₂O has an antifluorite structure.

CdI₂-type: hcp stacked I; half-filled

CdCl₂-type: ccp stacked Cl; half-filled

BiI₃-type: hcp stacked I; 1/3rd-filled
**BiI₃-type: ball & stick view**

**Interpreting Polyhedral Pictures**

**MoS₂-type: Trigonal prismatic Mo**
**MoS_2-type: A Lamellar Structure!**

Molybdenite

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**ReO_3 and Perovskite Structures**

Perovskite, \( \text{ABO}_3 = \text{ABO}_{\frac{3}{2}} \); Examples: \( \text{BaTiO}_3, \text{KNbO}_3 \)

\( \text{ReO}_3 = \square \text{BO}_3 \)

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**Perovskite with a Shifted Origin**

Perovskite, \( \text{ABO}_3 = \text{ABO}_{\frac{3}{2}} \); Examples: \( \text{BaTiO}_3, \text{KNbO}_3 \)

\( \text{ReO}_3 = \square \text{BO}_3 \)
BaTiO$_3$ is a ferroelectric with spontaneous polarization (cooperative alignment of dipoles throughout the crystal).

**Ionic Bonding; Lattice Energies**

Lattice Energies - Details

\[ V = V_{\text{Coulomb}} + V_{\text{repulsion}} + V_{\text{ion - ion Coulomb interactions}} \]

\[ V_{\text{Coulomb}} = \sum N_A \left( \frac{e^2}{r} \right) \left[ Z^+ \cdot Z^- \right] \]

\[ V_{\text{min}} = N_A \left( \frac{e^2}{r_{\text{min}}} \right) \left[ Z^+ \cdot Z^- \right] (1 - r_{\text{min}}) \]

The Madelung constant is a geometrical parameter that is the same for all compounds of a given structure type.

**Ion core — Ion core repulsions**

- \[ V_{\text{repulsion}} = + \frac{N_A C e^2}{r} \exp\{-C(r/r^*)\} \]
- \[ V_{\text{min}} = \frac{N_A e^2}{r_{\text{min}}} \left[ Z^+ \cdot Z^- \right] (1 - r_{\text{min}}) A \]

He 5
Ne 7
Ar 9
Kr 10
Xe 12

Alternative:

\[ V_{\text{rep}} = + \frac{N_A e^2}{r} \]

ion core

\[ \text{He} \]

\[ \text{Ne} \]

\[ \text{Ar} \]

\[ \text{Kr} \]

\[ \text{Xe} \]
Thermochemical (Born-Haber) Cycle

\[ \begin{align*}
\text{M(g) + X(g) &\xrightarrow{I(M) - E_x} M^+(g) + X^-(g)} \\
S_M + \left(\frac{1}{2}\right)D_{X_2} &\xrightarrow{} M(s) + \left(\frac{1}{2}\right)X_2(g) \quad \Delta H_L \quad \text{MX(s)}
\end{align*} \]

Values for NaCl (kJ/mol)

\[ 
S_M : \text{sublimation Enthalpy of Metal (298 K)} \quad 108 \\
D_{X_2} : \text{dissociation Energy of } X_2 \text{ bond (298 K)} \quad 242 \\
I(M) : \text{Ionization Enthalpy of Metal M} \quad 496 \\
E_x : \text{electron attachment Enthalpy of X atom} \quad 349 \\
\Delta H_L : \text{Enthalpy for separation of salt to ions theory}
\]

Consequences of Lattice Enthalpies

- Electrostatic component stabilizing ionic solids gives us
  \[ \text{Lattice energy} = \frac{[Z_A \cdot Z_B]}{d} \]

- Thermal stabilities: “Large Cations stabilize large Anions”. 

Experiment (Born-Haber cycle):

\[ \Delta H_f = S_M + \left(\frac{1}{2}\right)D_{X_2} + I(M) - \Delta H_L \]

for NaCl, measured value of \( \Delta H_f \) is -411 kJ/mol

\[ -411 = 108 + \left(\frac{242}{2}\right) + 496 - 349 - \Delta H_L \]

\[ \Rightarrow \Delta H_L = 787 (-2 \text{ for } C_p \text{ correction}) = 785 \text{ kJ/mol} \]
# Effects of charge and size on lattice energies (m.p.s)

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<tr>
<th></th>
<th>melting points (°C)</th>
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<tbody>
<tr>
<td>NaF</td>
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<tr>
<td>CaF₂</td>
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<tr>
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<tr>
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<td>1275 (subl)</td>
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<tr>
<td>BaO</td>
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