

CHEM 3420: Physical Chemistry II — Spring 2009

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Lecture 30: Introduction to the solid state

### References

1. Levine, *Physical Chemistry*, Chapter 23
2. Solid state handout

### Key Concepts

- Typically, solids fall into one of two groups (although that is not always true):
  - Structurally ordered — often referred to as crystalline solids
  - Structurally disordered — or amorphous solids

This grouping is not exclusive and there are some materials that fall in-between.

- One of the simplest solid types to understand are ionic solids due to the electrostatic nature of the interactions. This type of interaction is very strong and non-directional. Ionic crystals are typically very hard and have high melting points.
- If we consider a pair of ions, the total interaction energy is the sum of the attractive (positive attracted to negative) energy and the repulsive (two electrons clouds repulsing one another) energy.

$$E_{pair} = -\frac{e^2}{4\pi\epsilon_0 r} + \frac{b}{r^n}$$

where  $n$  is the Born exponent and is usually between 6 and 12.

- At the equilibrium separation,  $r_o$ , the energy can be written as:

$$E_{pair} = -\frac{e^2}{4\pi\epsilon_0 r_o} \left(1 - \frac{1}{n}\right)$$

- When we consider a 1-D array of ions instead of single pairs, the energy is further reduced by a geometric term, defined as the Madelung constant ( $M$ ). For a 1-D array,  $M = 1.386$  and for the 3-D structure of NaCl,  $M = 1.748$ .
- Therefore the crystalline, solid structure is stabilized, i.e. it has a lower energy than single pairs of ions.
- Different geometric arrangements of ions (different crystal structures) have different Madelung constants.