

Lecture 16 – Classification of solids

Reading

Ashcroft & Mermin, Ch. 19 (374 - 392), Ch. 20 (398 - 399, 402 - 405)

Content

- Classification of insulators
- Ionic radii
- van der Waals force
- Hydrogen bonds
- Lennard-Jones potential
- Madelung constant

Central concepts

- **Classification of insulators**

The difference between metals and insulators is if there are partially filled energy bands (metals) or not (insulators).

Insulators can be divided into different categories:

1. Covalent crystals

The *covalent crystals* have not too localized electrons at the ion cores, but typically “bonds” in certain preferred directions. Diamond is an example. The covalent crystals are not always good insulators, but may be semiconductors.

2. Molecular crystals

The *molecular crystals* have very little electronic density between ion cores. All electrons are core electrons so that an actual band structure is not really present. Examples are Ne, Ar, Kr, and crystals of molecules such as N₂ or H₂.

3. Ionic crystals

Ionic crystals are composed of metallic and nonmetallic elements. They may be considered as molecular crystals, but with ions instead of atoms or molecules. Examples are sodium chloride with Na⁺ and Cl⁻ ions. The electrostatic forces between the ions determine the properties, which are quite different from those of molecular crystals.

- **Ionic radii**

For ionic crystals, the ions can be seen as hard spheres of a well-defined radius r , the *ionic radius*. The nearest neighbor distance is typically given by the sum of the two ionic radii. However, in case of very different sizes of the larger ion $r^>$ and smaller ion $r^<$, the larger ions may instead touch as next-nearest neighbors. This starts to happen at a critical ratio which depends on the crystal structure.

For metals, the ionic radii are typically not determining the lattice parameters. Instead, the compressibility is obtained mainly from the electron gas. However, in noble metals, the closed d -shells are important for

the metallic properties and the nearest-neighbor distances are not so different than the ionic radii in ionic crystals.

Generally, ionic size is determined by the d -shells.

- **van der Waals force**

The van der Waals force is a *fluctuating dipole* force. An instantaneous dipole moment p_1 of an atom gives rise to an electrical field $E \sim p_1/r^3$, which polarizes another atom to a dipole moment $p_2 = \alpha E$. The time-averaged net dipole moment vanishes, but there is an interaction energy of the order

$$\frac{p_1 p_2}{r^3} \sim \frac{1}{r^6}$$

- **Hydrogen bonds**

Hydrogen is unique in that H^+ is just a proton, a factor 10^5 times smaller than any other ion. Hydrogen also has a very high ionization potential, making it difficult to completely remove the electron from it.

- **Lennard-Jones potential**

The Lennard-Jones potential describes the balance between the repulsion between molecular crystal atoms and the van der Waals attraction. The potential is typically written as

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]$$

where ϵ and σ are parameters and the repulsive term exponent is chosen mainly for convenience and to exceed the attraction at short distances. In crystals, this gives an energy per particle u ,

$$u = 2\epsilon \left[A_{12} \left(\frac{\sigma}{r} \right)^{12} - A_6 \left(\frac{\sigma}{r} \right)^6 \right]$$

where the constants A_n depends on the crystal structure.

- **Madelung constant**

For ionic crystals, the coulomb interaction is strongly dominating over the van der Waals forces. The interaction energy scales as $1/r$ and thus falls off very slowly, so that summing must be done without introducing surface charges. Proper summing gives a coulomb energy per ion pair

$$u^{\text{coul}}(r) = -\alpha \frac{e^2}{r}$$

where α is known as the *Madelung constant*, which only depends on the crystal structure.