3.1 Introduction

Solids are stable structures, and therefore there exist interactions holding atoms in a crystal together. For example, a sodium chloride crystal is more stable than a collection of free Na and Cl atoms. This implies that the Na and Cl atoms attract each other, i.e. there exist an attractive interatomic force. The amount of energy which is required to pull the crystal apart into a set of free atoms is called the cohesive energy of the crystal.

Cohesive energy = energy of free atoms – crystal energy

The magnitude of the cohesive energy varies for different solids from 1 to 10 eV/atom, except inert gases in which the cohesive energy is of the order of 0.1 eV/atom. The cohesive energy controls the melting temperature.

There are two basic types of bonds:

1- Primary bonds (chemical bond) with great energy.

2- Secondary bonds (physical bond) with low energy.

Primary bonding (ionic, covalent and metallic) is strong and the energies involved range from about 100 to 1000 kJ/mole. In contrast, secondary bonding is weak, involving energies ranging from about 0.1 to 10 kJ/mole.

3.2 Primary Bonds (with great energy)

3.2.1 Ionic Bonding in Solids

Many solids form by ionic bonding, which results from the electrostatic interaction of oppositely charged ions. The binding force of ionic crystals is due to coulomb attraction and is very high, giving rise to a high melting point. A prototypical example is the sodium chloride crystal. In the crystalline state, each (Na 11) atom loses its single valence electron to a neighboring (Cl 17) atom, producing Na^+ and Cl^- ions which have filled electronic shells. As a result, an ionic crystal is formed containing positive and negative ions coupled by a strong electrostatic interaction (Figure 3.1). Thus each Na+ ion is surrounded by 6 Cl- ions and vice versa.

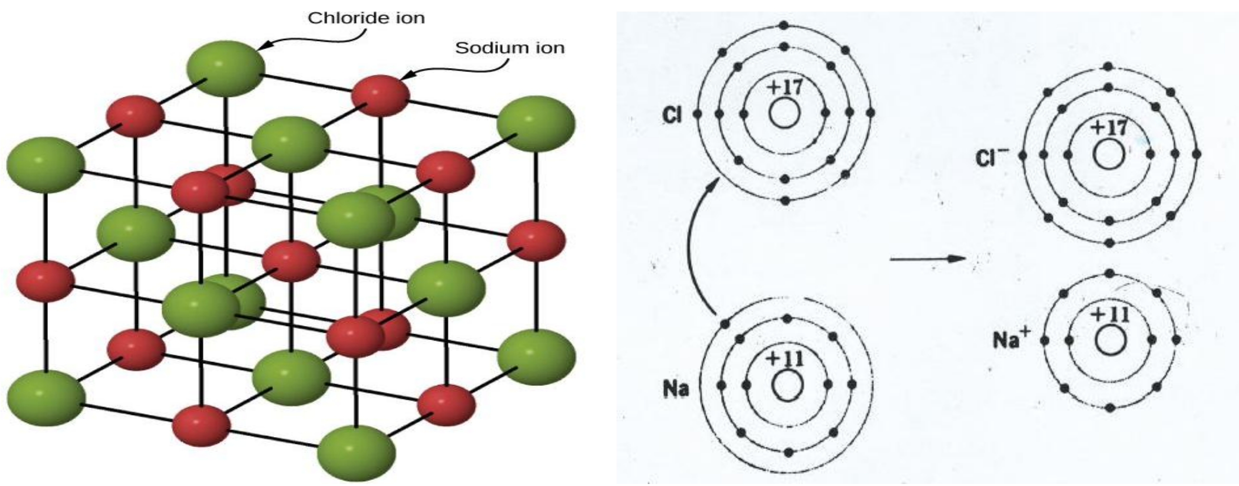


Figure 3.1: Structure of the sodium chloride crystal. The sodium and chloride ions are arranged in a face-centered cubic (FCC) structure.

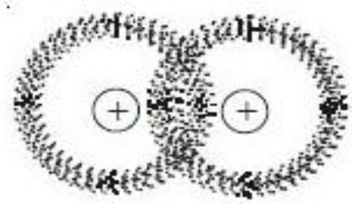
Because the ions in crystals are so tightly bound, ionic crystals have the following general characteristics:

1. They are hard and stable.
2. The ionic solids possess high melting points. They vaporize at relatively high temperatures (1000 to 2000 K).
3. They are transparent to visible radiation.
4. They are poor electrical conductors, because they contain effectively no free electrons.
5. Ionic compounds dissolve in polar solvents, which they are usually soluble in water.
6. The ionic compounds exhibit large band gaps. (insulators).
7. The resistivity of all ionic solids decreases with the rise of temperature. That is, they show negative temperature coefficient of resistivity.

3.2.2 Covalent Bonding in Solids

The covalent bond is another important type of bond which exits in many solids. wo atoms that are covalently bonded will each contribute at least one electron to the bond, and the shared electrons may be considered to belong to both atoms. The electrons forming the bond tend to be partly localized in the region between the two atoms joined by the bond. Hydrogen molecule is a good example of covalent bonding.

$$H_{\bullet} + H^{\bullet} \rightarrow H : H \text{ (Hydrogen molecule)}$$



electron pair covalent bond and interaction

Fig. Covalent bonding.

Covalently bonded crystals have the following general characteristics:

1- crystals are not as uniform as ionic crystals but are stable, reasonably hard.

2- High melting and boiling points.

3- poor electrical conductivity.

4- insoluble in water.

3.2.3 Metallic Bonding in Solids

Metallic bonding, the final primary bonding type, is found in metals and their alloys. A relatively simple model has been proposed that very nearly approximates the bonding scheme. Metallic materials have one, two, or at most, three valence electrons. With this model, these valence electrons are not bound to any particular atom in the solid and are more or less free to drift throughout the entire metal.

They may be thought of as belonging to the metal as a whole, or forming a (sea of electrons) or an (electron cloud) The remaining nonvalence electrons and atomic nuclei form what are called ion cores, which possess a net positive charge equal in magnitude to the total valence electron charge per atom.

The free electrons shield the positively charged ion cores from mutually repulsive electrostatic forces, which they would otherwise exert upon one another; consequently, the metallic bond is nondirectional in character. In addition, these free electrons act as a glue to hold the ion cores together. Metallic bonds are weaker than ionic or covalent bonds, with dissociation energies in the range 1−3eV. For instance, the melting temperature of metallic sodium is about 400^o which is smaller than 1100^o in NaCl and about 4000^o in diamond. Nevertheless, this type of bond should be regarded as strong.

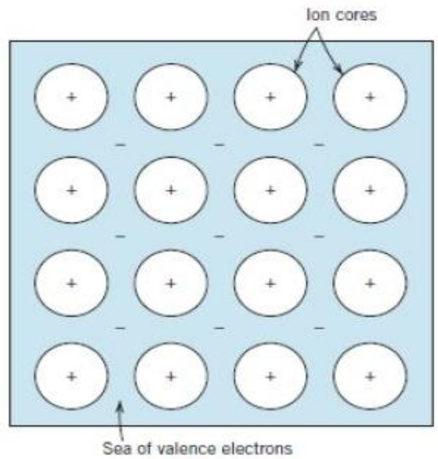


Figure Schematic illustration of metallic bonding.

Metals, such as copper and aluminum, are held together by bonds that are very different from those of molecules. Rather than sharing and exchanging electrons, a metal is essentially held together by a system of free electrons that wander throughout the solid. The simplest model of a metal is the free electron model. This model views electrons as a gas.

Metallic bonded crystals have the following general characteristics:

1- Weaker than ionic and covalent bonding.

2- Possess high thermal and electrical conductivities. This is because of the free electron movement in the lattice.

3- Exhibit ductility. They are brittle below a certain temperature. Many metals like tungsten are tough. But some metal like pure silver, aluminum, and gold are soft and malleable.

4- Their melting points vary from 64 ^{0} C (Potassium) to 2000 ^{0}C, Titanium (1812 ^{0} C).

5- Metals are opaque to light and they reflect light energy very efficiently.

3.3 Secondary Bonds (with low energy)

3.3.1 Van der Waals (molecular) bonding

van der Waals, or physical bonds are weak in comparison to the primary or chemical ones; bonding energies are typically on the order of only 10 kJ/mol (0.1 eV/atom). Secondary bonding exists between virtually all atoms or molecules, but its presence may be obscured if any of the three primary bonding types is present. Secondary bonding is evidenced for the inert gases, which have stable electron structures, and, in addition, between molecules in molecular structures that are covalently bonded.

Secondary bonding forces arise from atomic or molecular dipoles. In essence, an electric dipole exists whenever there is some separation of positive and negative portions of an atom or molecule. The bonding results from the coulombic attraction between the positive end of one dipole and the negative region of an adjacent one, as indicated in Figure 4. Dipole interactions occur between induced dipoles, between induced dipoles and polar molecules (which have permanent dipoles), and between polar molecules.

3.3.2 Hydrogen bonding

Hydrogen bonding, a special type of secondary bonding, is found to exist between some molecules that have hydrogen as one of the constituents. It is stronger than the van der Waals bond, and is a special case of polar molecular bonds.

When hydrogen combines with a highly electronegative non-metallic element (Cl, F, O, N), a distinct covalent bond with high polarity is produced in which the electron pair tends to the electronegative element, which makes the (H) atom closer to being a proton capable of attracting the negative end of one of the molecules adjacent to it, which leads to the formation of what is called a (hydrogen) bond.

One of the conditions for hydrogen bonding is the size of electronegative atoms or molecule should be small. The weaker the hydrogen bond, the shorter the lifetime of the complex it forms.

Hydrogen atom acts as a bridge between two atoms, holding one atom by a covalent bond and the other atom by a hydrogen bond. The hydrogen bond is represented by dotted line (….), while covalent bond is represented by the solid line (—).

$$\ldots\ H^{\delta+} - A^{\delta-} \ldots\ldots\ldots\ldots\ H^{\delta+} - A^{\delta-} \ldots\ldots\ldots\ldots\ H^{\delta+} - A^{\delta-}$$

Hydrogen fluoride (HF), the hydrogen atom while remaining bonded with fluorine atom, forms another weak bond with fluorine atom of adjacent bonding molecule. Hence, the formation of a hydrogen bonding results in the formation of a cluster of hydrogen fluoride (HF) molecules as (HF)n, as shown below.

…...HF……HF…. HF…. HF…. HF…

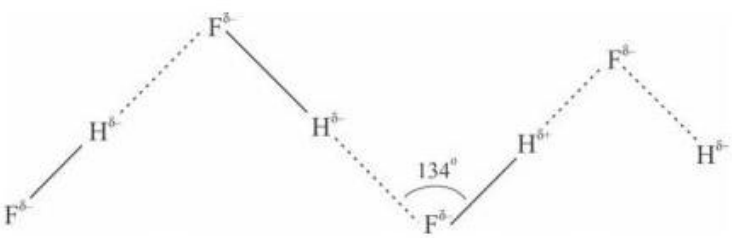


Fig. Hydrogen bonding $(HF)_n$ in HF solid state.