Solid State Physics (Lec-12)

B.Sc. Fourth Year

Reference Book: Kittel, C., Introduction to Solid State Physics, 8th ed., John Wiley & Sons Ltd, India (2005)

Types of Bonding

(1) Ionic Bond An ionic bond is formed by the actual transfer of electrons from one atom to the other so that each atom acwuires a stable electronic configuration similar to the nearest inert gas atoms. The crystals resulting from this type of bonding are called *ionic crystals*. Since after the transfer of electrons, the ions attain electronic configurations similar to inert gas atoms, the charge distribution on the ions is spherically symmetric. Hence an ion of one type tries to have as many neighbours of the opposite type as possible. The coordination number a cation is limited by the radius ration of cation to anion while that of an anion is limited by the condition that the charge neutrality of the crystal must be maintained. The cohesive energy of the ionic crystal is quite large; it is of the order 5 to $10 \ eV$.

A good example of ionic crystal is the crystal of NaCl. Each Na⁺ ion is surrounded by six Cl⁻ ions and, in turn, each Cl⁻ ion is surrounded by six Na⁺ ions to maintain the charge neutrality. Thus the coordination number of each ion is six. The binding energy per molecule of NaCl is 7.8eV

Since ionic crystals have large binding energy, these are, in general, hard and exhibit high melting and boiling points. At normal temperatures, these are poor conductors of electricity but the conductivity increases with increase in temperature owing to the increased mobility of ions. These crystals are generally transparent to visible light but exhibit characteristic absorption peaks in infrared region. These crystals are soluble in polar solvent such as water.

(2) Covalent Bond A covalent bond is formed by an equal sharing of electrons between two neighbouring atoms each having incomplete outermost shell. Unlike ionic bond, the atoms participating in the covalent bond have such electronic configurations that they cannot complete their octets by the actual transfer of electrons from one atom to the other. Hnece there is no charge associated with any atom of the crystal.

A covalent bond is formed between similar or dissimilar atoms each having a deficiency of an equal number of electrons. When two atoms, each having a deficiency of one electron, come so close that their electronic shell start overlapping, the original atomic charge distributions of the atoms are distorted and each atom transfers its unpaired electron to the common space between the atoms. Thus the common space contains a pair of electrons which belong equally to both the atoms and serves to complete the outermost shell of each atom. This is what is meant by 'sharing of electrons'. The sharing is effective if the shared electrons have opposite spins. In such a case the atoms attract each other and a covalent bond is formed. Since the participating atoms have the same valence state, this bond is also called the *valence bond*.

The number of covalent bonds an atom can form is determined by 8 - N rule, where N is the number of the column of the periodic table to which the atom belongs. Since oxygen belongs to VI group, it can form (8-6)=2 covalent bonds.

For the formation of stable covalent bond, there should be a net decrease in the potential energy of the system as a result of mutual sharing of electrons. This happens when the participating orbitals overlap effectively and also when the vacant electronic states are available in the outermost orbital of each atom. The overlap is more effective when the participating orbitals are directionally oriented rather than having spherical symmetry. Hence a covalent bond is always directional in character. Since p-orbitals are directional in nature, thery readily participate in the formation of covalent bonds.

The covalent bond is a strong bond. Thus the crystals having purely covalent bonding are generally very hard and brittle. These have high metling and boiling points. These exhibits low conductivity at ordinary temperatures which increases slightly with increase in temperature.

(3) Metallic Bond Metallic bond is formed by the partical sharing of valence electrons by the neighbouring atoms. Unlike the case of covalent bond, the sharing in metallic bond is not localized. Hence metallic bond may also be considered as delocalized or unsaturated covalent bond. The atoms in metals contribute their valence electrons to form a common pool of electrons which has freedon to move any-

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where in the framework of positive ion cores. This common pool of electrons is also known as the *free electron gas* and acts alike a mobile glue to bind all the ion cores together through electrostatic attraction. The bond so formed is called the *metallic bond*. In this type of bonding, the atoms can share the required number of electrons with their neighbours through the common pool to complete their octets. This sharing is not localized. The free nature of electron gas makes the bonding electrons resonate between different atoms and consequently the metallic sharing changes with time.

Due to delocalized nature of valence electrons, the metallic bond is much less directional than covalent bond. Hence metals prefer to form closed packed structures. The metallic bond is weaker than ionic or covalent bond. The binding energy ranges from 1 to 5eV per bond. The melting and boiling points of metallic solids are lower than the ionic or covalent solids. Also these solids have high ductility and malleability, hight electrical and thermal conductivities, and high optical reflection and absorption coefficients.

(4) Van der Waals' Bond This type of bonding exists in atoms or molecules which have their outermost shells completely filled and hence have no tendency to gain, lose or share valence electrons with other atoms or molecules in the solid. The cyrstal resulting from this type of bonding are called *molecular crystals*. The example of such solids are crystalline states of inert gases, and other gases like O₂, Cl₂, CO₂ etc. THis type of bonding arises due to dipolar interaction between the atoms or molecules of the crystal. This bond is also called *dispersion bond*. It is non directional in character.

The van der Waals' forces are very weak forces. At room temperature, the thermal energy acquired by atoms or molecules might get sufficient to make these forces ineffective. Molecular solids are characterized by very low melting and boiling points, low mechanical strength. These solids are also poor conductors of heat and electricity.

(5) Hydrogen Bond When a covalent bond is formed between a hydrogen atom and a highly electronegative atom, such as an atom of oxygen, fluorine, chlorine etc., the shared electron pair gets attracted more towards the electronegative atom than the hydrogen atom. Thus the electronegative atom acquires a slight negative charge and the hydrogen atom acquires an equal amount of positive charge. The molecule so formed is said to be polarized and behaves like a permanet dipolre. A number of such dipoles get attracted to one another due to the Coulombic force of attraction. This type of interaction between the oppositely charged end of permanently polarized molecules each containing a hydrogen atom is called hydrogen bond. In case the hydrogen atom does not participate in bond formation, the bond is called the *dipole bond*. A special significance is attached to hydrogen atom because it can be regarede simply as a proton fixed to one end of a covelent bond, the positive charge of whihe is not shielded by the surrounding electrons. This is not the case with other atoms participating in a covalent bond; their positive charges are shielded by the outer electrons which weaken the attraction of the positive nuclear charge with the negative ends of other polarized molecules. Thererofe, the positively charged hydrogen atom can interact more strongly with the negative ends of other moleules as compared to any other positively charged atom. Thus hydrogen bonds are stronger than dipole bonds. Materials exhibiting hydrogen bonding possess high melting and boiling points compared with molecular solids.

The hydrogen bond plays an important role in the formation of ice and water. Hydrogen bonding is responsible for the striking physical properties of water and ice. In the absence of hydrogen bonding, the boiling point of water at atmospheric pressure would have been $-80^{\circ}C$ instead of $100^{\circ}C$ and its viscosity mych lower than 0.01 Poise at room temperature. Since a hydrogen bond is formed between oppositely charged ends of two permanent dipoles, it is directional in character.