
UNIT 5 CRYSTAL BONDING

Structure

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5.1 INTRODUCTION

In Block 1, you have learnt elementary (geometrical) aspects of crystal structure and various experimental techniques used to unfold the arrangement of atoms in a solid. You have also learnt that solids can be classified as crystalline or amorphous, depending on the range of order. Also, all solids can be classified into seven crystal systems based on their geometrical structure. The next logical question to ask is: What holds atoms in a crystal? In this unit you will learn about different ways in which atoms are bound in a solid.

We know that solids are aggregates of atoms. The arrangement of atoms in any material is determined by the nature and strength of the binding forces or by the nature of bonds between them. The nature of forces responsible for clinging atoms together is discussed in Sec. 5.2. You will learn that bonds are formed due to the presence of attractive and repulsive forces that hold the adjacent atoms at particular positions and maintain a perfect balance. The nature of bonding in a material determines its physical, chemical and electrical properties. It is, therefore, important for you to acquire a sound knowledge of different types of bondings. In Sec. 5.3, you will learn that the nature of bonding is determined by the electronic structure of constituent atoms. And based on the type of bonding, crystalline solids may be classified into five major types: ionic, covalent, metallic, hydrogen bonded and van der Waals bonded. However, this classification is somewhat arbitrary. Many solids fall into intermediate categories, that is, more than one type of bondings co-exist among their atoms. In Sec. 5.4, you will learn to derive expressions for cohesive energies for ionic crystals and van der Waals crystals.

Objectives

After studying this unit, you should be able to:

- explain how atoms cling together in a crystal;
- classify crystalline solids as ionic, covalent, metallic, hydrogen bonded and van der Waals bonded;
- correlate the characteristic properties of solids with the nature of bonding; and
- derive expressions for cohesive energies for ionic and van der Waals crystals.

5.2 HOW DO ATOMS CLING TOGETHER: COHESIVE ENERGY

We know that at STP (standard temperature and pressure), matter exists in three states: solid, liquid and gas. In solids, the atoms are closely packed. And according to Bohr's theory, an atom consists of a nucleus at the centre and electrons revolve around it in fixed orbits. Since nucleus carries almost the entire mass of the atom, it is considered to be at rest. This may lead you to consider that orbital electrons are responsible for most of the characteristic properties of a solid. If you think so, you may be on the right track. The properties of matter also depend on the way orbital electrons arrange themselves giving rise to bonding among atoms. And, all materials do not exhibit same type of bonding. Further, apart from the electronic configuration, the nature of bonding is determined by the energy of system; *all bound systems should have minimum energy in their stable form*. When some atoms combine to form a stable molecule, it is implied that it is a minimum energy state.

When two (identical or different) atoms, which form a molecule, approach each other, they first experience attraction upto a certain separation and at distances closer than that, they begin to repel. This is depicted in Fig. 5.1, which shows a plot of total energy U against the separation (r) between constituent atoms.

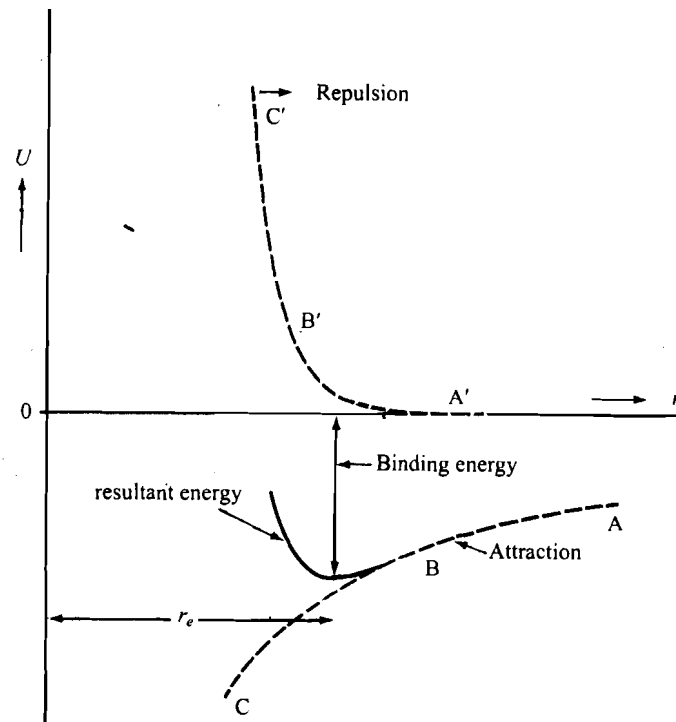


Fig. 5.1: Plot of energy of a system as a function of separation between constituent atoms

By convention, the energy of electrostatic interaction between two atoms placed infinite distance apart is taken as zero. The portion ABC of the dotted curve in Fig.5.1 signifies attractive force between them as they are brought closer. Note that repulsive force also comes into play when atoms are too close. This is to be expected from physical considerations for stability. Since the repulsive force gives rise to positive energy, it is shown by the portion $A'B'C'$ of the dotted curve. The resultant energy is shown by the solid curve.

To express it mathematically, let us assume that the energy due to attraction U_a varies as the m^{th} power of r and that due to repulsion, U_r , as the n^{th} power of r . Then we can write:

$$U_a \propto \frac{1}{r^m}$$

or

$$U_a = -\frac{A}{r^m},$$

and

$$U_r \propto \frac{1}{r^n}$$

or

$$U_r = \frac{B}{r^n},$$

where A and B are constants of proportionality. Can you combine these two expressions to express resultant energy mathematically? It is expressed as

$$U = U_a + U_r = -\frac{A}{r^m} + \frac{B}{r^n}.$$

Note that Fig. 5.1 exhibits a minimum at the equilibrium separation, r_e , between atoms. That is, at $r = r_e$, the energy has the least value and the bound system — the molecule in this case — is stable. It is called the cohesive or binding energy of the molecule. *The cohesive energy of a molecule is the energy required for formation of a molecule by bringing neutral atoms from infinity to the position of equilibrium separation. Alternatively, the cohesive energy of a molecule can also be defined as the energy required to separate its constituent atoms to infinity.*

While going through the above paragraphs, you may have wondered how neutral atoms could attract or repel each other! Bohr's model of atom provides a natural explanation. To illustrate it, let us consider how hydrogen molecule is formed.

A hydrogen molecule has two electrons, one contributed by each of the two atoms. Refer to Fig. 5.2a which depicts H_2 molecule in terms of electron orbits. According to quantum mechanics, an electron may be thought of as being somewhere within a probability cloud; the denser the cloud, the greater the probability of locating the electron. Fig. 5.2b shows how electron probability clouds of two hydrogen atoms join to form the probability cloud of a hydrogen molecule. Since, on an average, the electrons are likely to spend more time near the protons than otherwise, there is effectively a net negative charge in-between the protons. The attractive force experienced by the protons due to this charge is more than enough to balance the repulsion between them. If the protons are too close, the repulsion between them dominates and refrains them from coming further closer. The attractive force balances repulsive force at a separation of 7.42×10^{-11} m, where the net energy of the H_2 molecule is -4.5 eV.

Before proceeding further, we would like you to answer the following SAQ.

SAQ 1

The binding energy of a hydrogen molecule is 4.5 eV, whereas that of a hydrogen atom is 13.6 eV. Which of these can be broken more easily.

*Spend
2 min.*

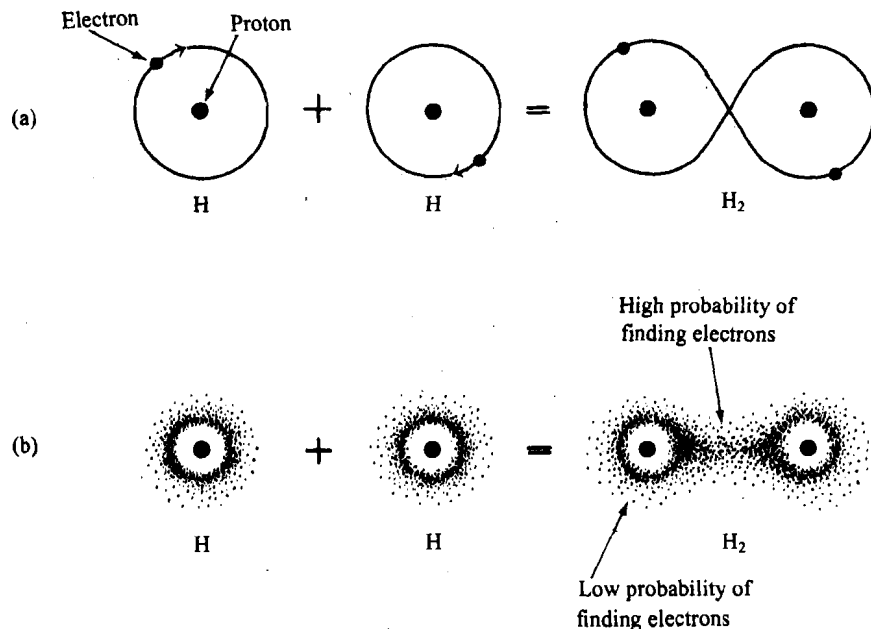
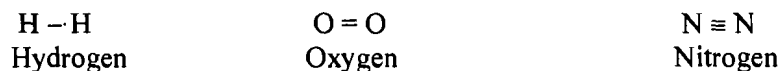
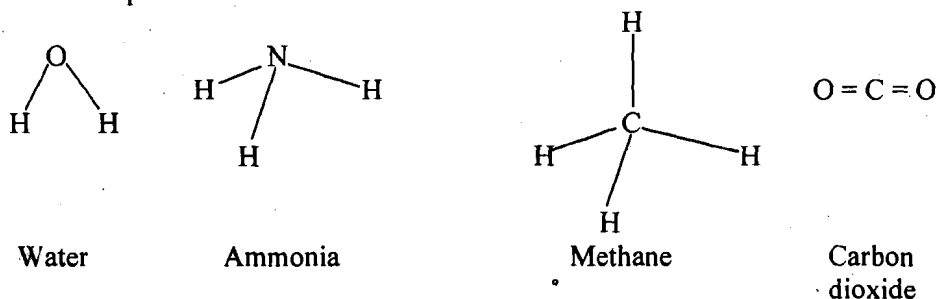


Fig. 5.2: a) Orbital model; and b) quantum mechanical model of hydrogen molecule

When electrons are shared by atoms and held together to form a molecule as in the case of H₂ molecule, we say that the molecule exhibits *covalent bonding*. It is quite convenient to think of the atoms as being held together by covalent bonds, with each shared pair of electrons making up a bond. More complex atoms than hydrogen also join together to form molecules by sharing electrons. Depending upon the electronic structure of atoms, there could be upto four shared pair of electrons giving rise to as many covalent bonds between the atoms. For example, in the oxygen molecule, there are two covalent bonds between O atoms, whereas in the nitrogen molecule there are three covalent bonds between the N atoms. These molecules are represented as



This discussion should not lead you to think that covalent bonds are formed between atoms of the same element only. Covalent bonds can also be formed between atoms of different elements. For example, in water molecule, H₂O, oxygen participates in two bonds with hydrogen and in ammonia molecule, NH₃, nitrogen forms three bonds with hydrogen. Similarly carbon atom forms four covalent bonds at the same time with other atoms to form molecules like methane and carbon dioxide. The bonding in these molecules is represented as follows:



In some molecules composed of different atoms, electrons show preference for a particular type of atom. For example in water molecule, oxygen atom has greater attraction for electrons than a hydrogen atom. Due to this, the molecule behaves as though it is positively charged at one end and negatively charged at the other end. A molecule of this kind is called *polar molecule*, whereas a molecule whose charge distribution is symmetric (uniformly distributed) is called a *non-polar molecule*.

You now know that a few covalent bonds can exist in a molecule. In a solid, there can simultaneously exist several covalent bonds. However, atoms in all solids are not bound only via covalent bonding. If it were so, the forms and varieties of solids and their properties would have been similar. In nature, we find such rich diversity, suggesting that other forms of bondings must also exist. Now you will learn about these.

5.3 BONDING: FORMS AND CHARACTERISTICS

In solids, five forms of bonding are known as of now:

- ionic bonding
- covalent bonding
- metallic bonding
- hydrogen bonding
- van der Waals bonding

Let us now understand the basic features of these bonding forms. We shall discuss these one by one. We begin by considering ionic bonding, which is the strongest form of bonding.

5.3.1 Ionic Bonding

Ionic bonding arises due to transfer of one or more electrons from one atom to another. This results in creation of positive and negative ions, which attract each other (Coulomb force). Note that ionic bonding is not possible between same type of atoms. That is, they have to be different. The electropositive atoms lose electrons because their ionisation energy is low. (The *ionisation energy* is defined as the energy that must be supplied in order to remove an electron from a neutral atom.) The electronegative atoms gain electrons and have high electron affinity. NaCl, whose crystals constitute ordinary table salt, is the best example of ionic bonding (Fig. 5.3).

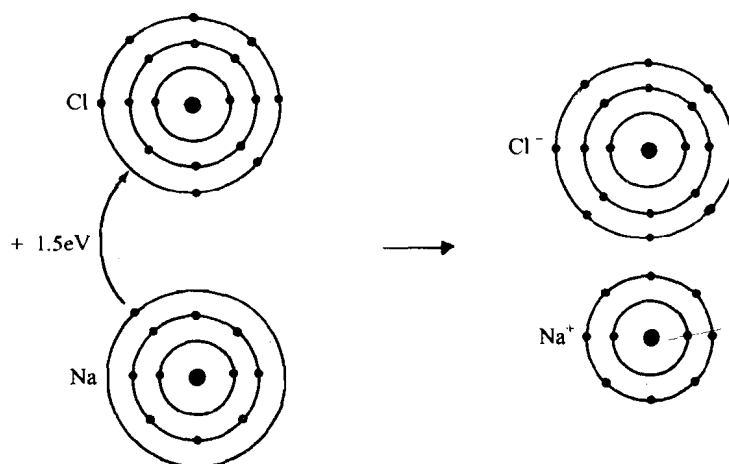


Fig.5.3: Electron transfer in a NaCl molecule; the electrostatic force binds the ions together

The ionisation energy of sodium atom is 5.1 eV, which means that this much energy would be required to remove the outermost electron from a Na atom, leaving it as Na^+ ion. The electron affinity, which signifies the gain in energy when an extra electron is added to a neutral atom, for chlorine atoms is 3.6 eV. Thus, when free electron from a sodium atom is added to a chlorine atom, 3.6 eV of energy is released and the chlorine atom becomes negatively charged. The net energy $(5.1 - 3.6) = 1.5$ eV is utilised in creating a positive sodium ion and a negative chlorine ion. The ions so formed bond strongly due to electrostatic force of attraction.

The structure of NaCl crystal is shown in Fig. 5.4. Each ion behaves like a point charge and tends to attract to itself as many oppositely charged ions as can fit around

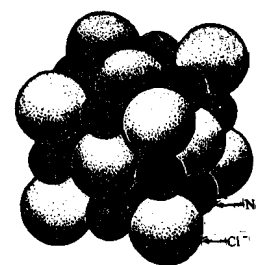


Fig. 5.4: Crystal structure of NaCl: each Na^+ and Cl^- ion is surrounded by six oppositely charged ions

it. By examining the figure, can you guess as to how many Cl^- ions surround each Na^+ ion and vice versa. If you counted the number as six, you were right! In crystals with other structures, the number of **nearest neighbours** of each ion could be different. Some other examples of ionic crystals are KCl , LiF , NaBr and ZnS . *Ionic bonds are usually very strong. For this reason, ionic crystals are hard and have high melting point.* The melting temperature of NaCl is 801°C , whereas the melting temperature for sodium is 97.8°C . What other unique characteristics of ionic crystals do you know? Look around and list these.

Before you proceed further, you may like to answer an SAQ.

Spend
2 min.

SAQ 2

Sodium melts at about 97.8°C , but melting temperature of NaCl is 801°C . How do you explain this?

5.3.2 Covalent Bonding

In Sec. 5.2, you have learnt that atoms in a H_2 molecule are held together by electron sharing. A shared pair of electrons constitutes a covalent bond. Note that such electron sharing is not peculiar to gases only. Covalent bonds also exist in certain crystalline solids. Fig. 5.5 shows an array of carbon atoms in a diamond crystal; each carbon atom shares electron pairs with four other carbon atoms adjacent to it forming a regular tetrahedron.

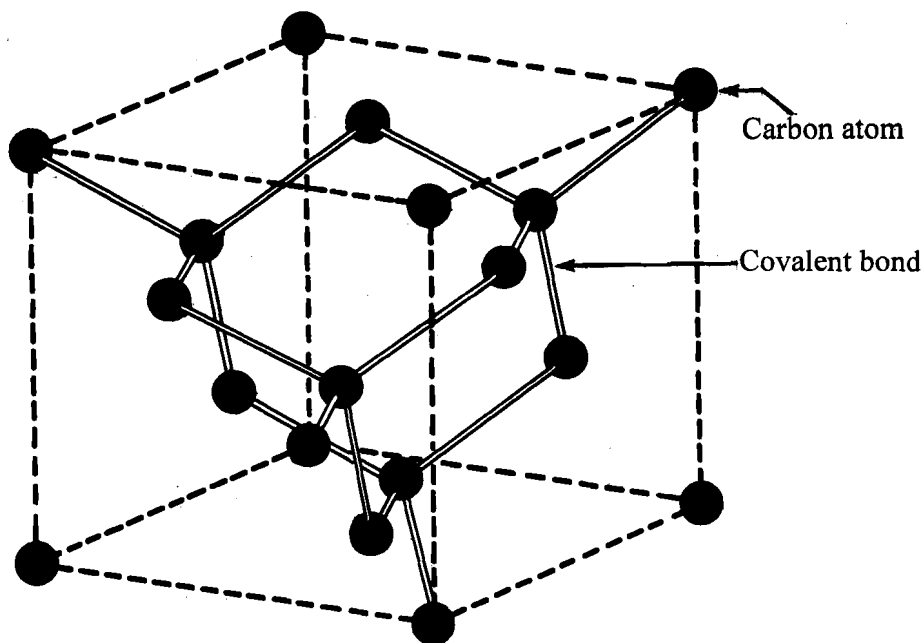


Fig.5.5: Structure of diamond; each carbon atom shares electrons with four other carbon atoms

Let us now understand why diamond crystals have a particular shape. You may recall that electronic configuration of carbon atom is $2s^2 2p_x^1, 2p_y^1$. Excitation of one electron from $2s$ orbital to the $2p_z$ orbital gives the configuration $2s^1, 2p_x^1, 2p_y^1, 2p_z^1$. One s and three p -orbitals hybridise to form sp^3 (hybrid) orbitals. These orbitals are directed to the corners of a tetrahedron. This explains why the diamond crystal has a regular tetrahedron structure. You will note that a covalent bond is a directional bond. Since all electrons in carbon atom participate in bonding, diamond is extremely hard; it melts at 3500°C . Apart from diamond, other materials which belong to this category are silicon, germanium and silicon carbide. Although ionic and covalent bondings explain some physical properties of solids, we cannot explain the high electrical conductivity of metallic crystals on the basis of these bondings.

You may ask: Is the bonding mechanism in metals responsible for their high electrical conductivity? What bonding mechanism is responsible for holding atoms in metallic crystals? Let us try to find answers to such questions.

5.3.3 Metallic Bonding

In a metal, electrons in the outer most shell of its constituent atoms can be detached by supplying small amount of energy. According to the theory of *metallic bonding*, a metal consists of atoms that have given up their outer-most electrons to form an electron 'gas', which moves throughout the specimen. The electrical interaction between the positive ions at lattice sites and the negative electron gas holds the metal together, as shown in Fig. 5.6. (You will learn more about the free electron gas model in Unit 9, Block 3 of this course.)

Note that in metallic bonding, valence electrons are assumed to behave as a gas, whereas in ionic and covalent bonding, electrons are tightly bound to their parent atoms. For this reason, metallic bond is somewhat weaker than the ionic and covalent bonds. For instance, the melting point of sodium, 97.8°C is far from being negligible; yet it is significantly lower than the melting point of ionic and covalent solids. Metals are characterised by high electrical conductivity and they are highly ductile. High electrical conductivity arises due to the mobility of electron gas under the influence of an electric field, resulting in a net electrical current in the field direction. The high ductility is a consequence of non-directional nature of metallic bond. If an external bending torque is applied and the ions change positions to accommodate this torque, the electrons, being very small and highly mobile, readily adapt themselves to the new deformed situation.

There is yet another type of bonding, which occurs between certain molecules containing hydrogen atoms. This special bonding is known as *hydrogen bonding*. Let us learn about it now.

5.3.4 Hydrogen Bonding

In hydrogen bonded solids, hydrogen atoms take part in covalent bonding and the centres of the positive and negative charges do not coincide. Let us consider the example of H_2O molecule shown in Fig. 5.7a. Since electronegativity of oxygen atom is more than that of hydrogen atom, bonding electrons are actually pulled more strongly towards the oxygen atom, resulting in a net negative charge at the oxygen end and a net positive charge at the hydrogen end of the molecule, as shown in Fig. 5.7b. The opposite charges separated through a finite distance constitute an electric dipole in the water molecule. Such electric dipoles influence each other. Thus we find that water molecules are attracted to each other, forming a crystal (Fig. 5.7b).

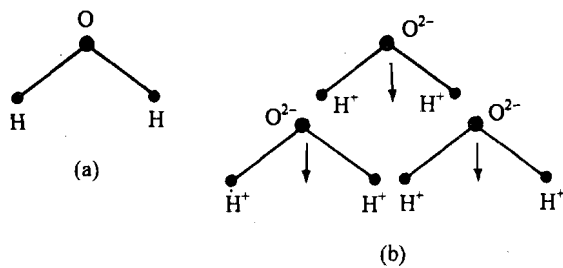


Fig. 5.7: a) A water molecule; and b) arrangement of water molecules as a result of hydrogen bonding. The arrows represent electric dipole moments of the molecules

The bond formed between water molecules due to attraction between the positively charged hydrogen end of a molecule and the negatively charged oxygen end of another molecule is called hydrogen bond. These bonds are weak.

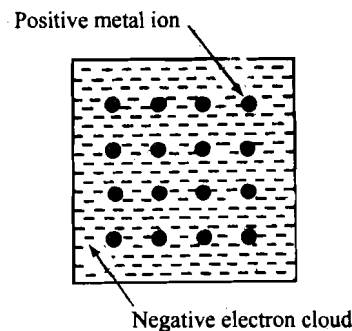


Fig.5.6: Metallic bonding

Metallic bonds do not vary with angle, i.e., they are non-directional, whereas covalent bonds have angular dependence i.e., they are directional.

The tendency of an atom to attract electrons to itself during the formation of bonds with other atoms is expressed by a parameter called *electronegativity* of that atom. This is not same as the *electron affinity*, which refers to the tendency of an atom to attract an isolated electron.

5.3.5 van der Waals Bonding

In some substances, particularly inert gases, the outer-most shells of constituent atoms are completely filled. Similarly, in molecules like methane, outer electrons are fully involved in the molecular bond itself. In such atoms or molecules, ionic or covalent or metallic bonding is ruled out. However, even these virtually non-interacting atoms or molecules are known to condense into solid state due to intermolecular forces, collectively known as *van der Waals forces*, which account for

- polar-polar interaction,
- polar-nonpolar interaction, and
- nonpolar-nonpolar interaction.

Polar-polar interaction

As you now know, polar molecules exhibit asymmetric charge distribution. That is, one end has excess positive charge and the other end has excess negative charge. When any such molecule comes close to other similar molecule, the ends of opposite polarity attract each other and hold the molecules together, as shown in Fig. 5.8a.

Polar-nonpolar interaction

When a polar molecule comes in the vicinity of a nonpolar molecule, the electric field of the polar molecule distorts the symmetric charge distribution of the nonpolar molecule. As a result, positive charges of non-polar molecule draw nearer the negative end of the polar molecule, as shown in Fig. 5.8b. Two such molecules begin to attract one another in the same way as any other pair of polar molecules.

Nonpolar-nonpolar interaction

The nonpolar-nonpolar interaction is also known as *London interaction* or *dispersion interaction*. To understand the origin of London interaction, let us recall that in a non-polar molecule, on an average, the electrons are distributed symmetrically. But at any point of time, one part of the molecule contains more electrons than the other part. It means that, at least momentarily, every molecule may behave as though it is polar. As a result, electrical attraction holds them together.

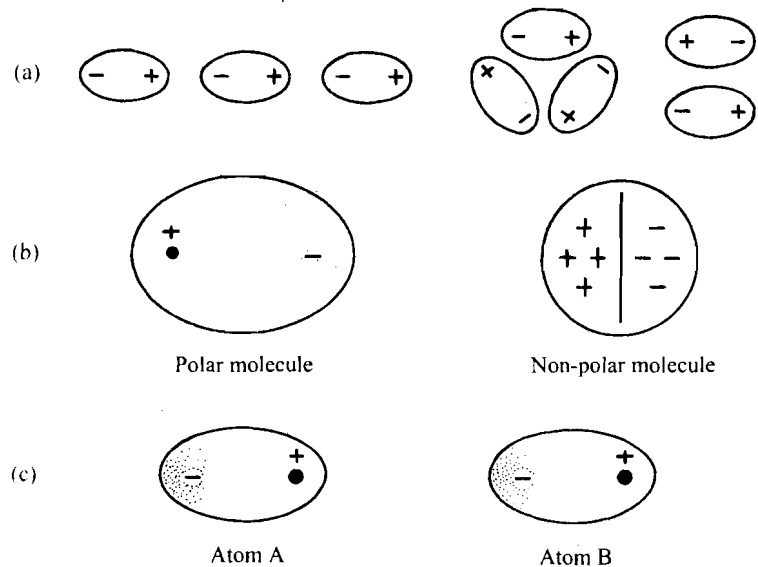


Fig. 5.8: van der Waals bonding: a) polar-polar interaction; b) polar-nonpolar interaction; and c) nonpolar-nonpolar interaction

Note that van der Waals bonding involves attractive interactions. These account for cohesive forces. van der Waals bonds are probably the weakest. Two main reasons for

the weak strength of the van der Waals bonds are: (i) the fluctuating atomic dipoles are small, and (ii) the atomic dipoles are not synchronised, a fact which tends to cancel their attractive effects.

van der Waals bonding is present universally between closely spaced atoms, but becomes dominant only when the conditions for the existence of stronger bonding mechanisms do not prevail. The inert gas solids are the best examples of solids bound solely by van der Waals forces. (The close shell configurations of such atoms exclude the possibility of other stronger bonding mechanisms.)

Before proceeding further, you may like to answer the following SAQ.

SAQ 3

Spend
5 min.

Fig. 5.9 shows different types of crystal bondings. Identify them and justify your answer.

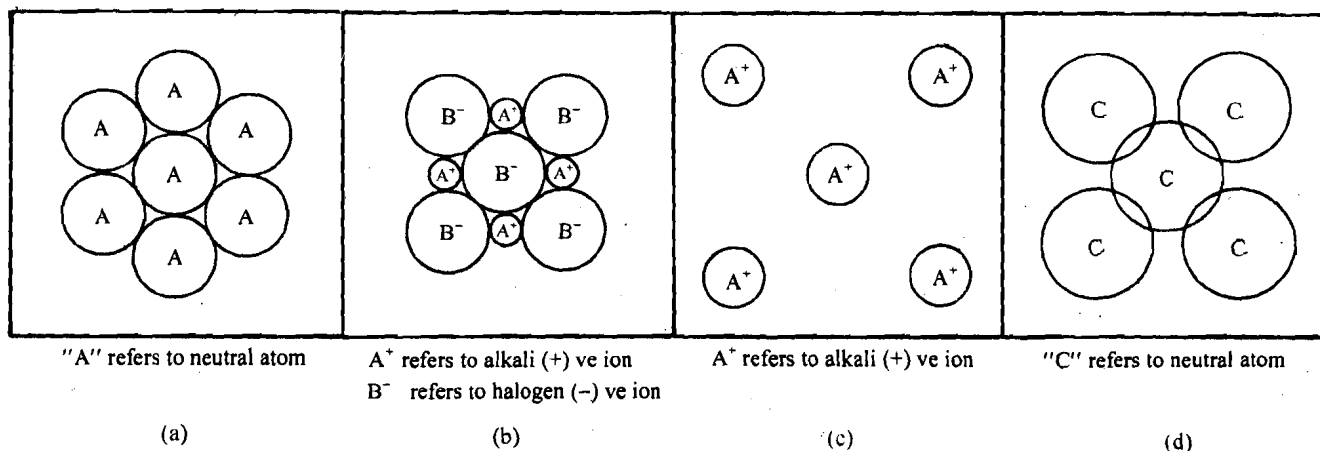


Fig. 5.9: Different types of crystal bonding

5.4 COHESIVE ENERGY FOR IONIC AND van der WAALS CRYSTALS

In sec. 5.2 you have learnt the concept of cohesive energy of solids. *The cohesive energy of an ionic crystal is the energy liberated on the formation of a crystal from individual neutral atoms.* Cohesive energy is expressed in eV per atom, or eV per molecule or in kJ per kmol.

We know that ionic crystals are made up of positive and negative ions. Refer to Fig. 5.10. It shows Na⁺ and Cl⁻ ions in a NaCl crystal. The question is: Which physical quantities do we need to know to derive an expression for cohesive energy? The calculation of cohesive energy of an ionic crystal requires information about forces acting between the constituent atoms. Let us first consider the interaction between two neighbouring ions. Being oppositely charged, these ions attract one another due to Coulomb force, which gives rise to attractive potential energy. Mathematically, we can write it as

$$U_a = -\frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r}, \quad (5.1)$$

where $Z_1 e$ is the charge, say on the positive ion, $Z_2 e$ is the charge on the negative ion and r is the separation between them. The factor $\frac{1}{4\pi\epsilon_0}$ signifies the proportionality constant.

In literature, you may come across the term *lattice energy*. You should not confuse it with cohesive energy. Lattice energy is the energy evolved when a crystal is formed from individual ions, rather than from individual atoms.

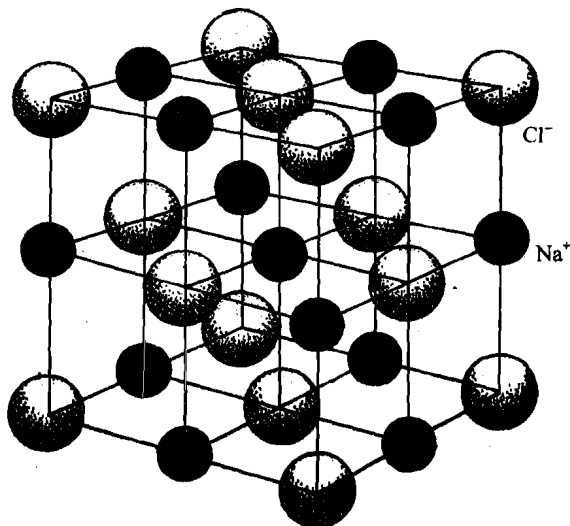


Fig.5.10: NaCl Crystal

As discussed earlier, if oppositely charged ions come very close, their electron orbitals begin to overlap, that is, some electrons try to occupy orbits which are already occupied. But, this is forbidden by Pauli exclusion principle, as outermost shells of both the ions are completely filled. Thus, when the two ions come very close together, Pauli exclusion principle leads to repulsive force which increases rapidly with decreasing distance. The repulsive potential energy is given by

$$U_r = \frac{B}{r^n}, \quad (5.2)$$

where B and n are constants. Note that the sign of the repulsive energy term U_r is positive. Thus, the resultant expression for lattice energy of two ions is obtained by combining expressions given in Eqs. (5.1) and (5.2):

$$\begin{aligned} U &= U_a + U_r \\ &= -\frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r} + \frac{B}{r^n}. \end{aligned} \quad (5.3)$$

To obtain expression for the lattice energy of the entire crystal, the attractive potential energy term of any one ion must also include the term which arises due to the presence of all other ions in the crystal. Thus, for the entire crystal, we can express net attractive potential energy as

$$U_a = -\frac{\alpha e^2}{4\pi\epsilon_0 r}. \quad (5.4)$$

The constant α is known as *Madelung constant*. Its value is same for all crystals having similar structure. For NaCl type crystals, $\alpha = 1.748$, for CsCl type crystals, $\alpha = 1.763$ and for ZnS type crystals, $\alpha = 1.638$.

The expression for total lattice energy of one ion due to the presence of all other ions in the crystal can now be written as:

$$U = -\frac{\alpha e^2}{4\pi\epsilon_0 r} + \frac{B}{r^n}. \quad (5.5)$$

If the crystal is composed of N positive ions and N negative ions, we have

$$U = N \left[\frac{B}{r^n} - \frac{\alpha e^2}{4\pi\epsilon_0 r} \right]. \quad (5.6)$$

To put this expression in a more meaningful form, we express the constant B in terms of α . For this, we invoke the condition that potential energy must be minimum at equilibrium separation, i.e.

$$\left[\frac{dU}{dr} \right]_{r=r_e} = 0,$$

where r_e is equilibrium separation. Thus, by differentiating the expression for U given in Eq. (5.6) with respect to r and equating the resultant expression to zero at $r = r_e$, we get

$$\left[\frac{dU}{dr} \right]_{r=r_e} = N \left[\frac{\alpha e^2}{4\pi\epsilon_0 r_e^2} - \frac{Bn}{r_e^{n+1}} \right] = 0.$$

Since N is finite, the term within the parenthesis must vanish:

$$\frac{\alpha e^2}{4\pi\epsilon_0 r_e^2} = \frac{Bn}{r_e^{n+1}}$$

On rearrangement, we obtain

$$B = \frac{\alpha e^2 r_e^{n-1}}{4\pi\epsilon_0 n}. \quad (5.7)$$

Substituting this value of B in Eq. (5.6) and putting $r = r_e$, we get

$$\begin{aligned} U &= \frac{N\alpha e^2 r_e^{n-1}}{4\pi\epsilon_0 n r_e^n} - \frac{N\alpha e^2}{4\pi\epsilon_0 r_e} \\ &= -\frac{N\alpha e^2}{4\pi\epsilon_0 r_e} \left[1 - \frac{1}{n} \right] \\ &= -\left[\frac{N\alpha e^2}{4\pi\epsilon_0 r_e} \right] \left[\frac{n-1}{n} \right]. \end{aligned} \quad (5.8)$$

Let us pause for a while and ask: What have we achieved? What does Eq. (5.8) signify? You will note that in arriving at Eq. (5.8), we have considered the interactions between ions. If you recall (see margin remark on page 13) the definitions of cohesive energy and lattice energy, you will conclude that Eq. (5.8) represents lattice energy. To obtain an expression for cohesive energy, we must take into account the energy needed to transfer an electron from electro-positive atom to an electro-negative atom. If we denote this energy by U_i , the cohesive energy U_c can be expressed as

$$U_c = U + U_i. \quad (5.9)$$

You must have noted from Eqs. (5.8) and (5.9) that the expression for cohesive energy involves two unknown parameters, the Madelung constant, α and repulsive exponent n . You will now learn to determine Madelung constant.

Determination of Madelung constant

The Madelung constant is a measure of the influence of geometrical arrangement of ions on the electrostatic potential energy of the crystal. It is a structural property of the crystal and depends on lattice parameters. To obtain the value of Madelung constant, refer to Fig. 5.11. It shows an infinite linear chain of equally spaced but oppositely charged ions. Note that consecutive positions are occupied by oppositely charged ions.

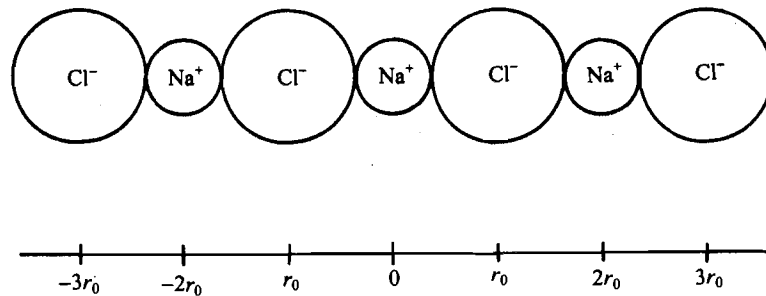


Fig. 5.11: A hypothetical one-dimensional NaCl lattice

Let us choose a Na ion as the reference position. We denote the distance between adjacent ions by r_0 . Since the reference ion has two oppositely charged nearest neighbours, the energy due to attraction (attractive Coulomb energy) is given by

$$-\frac{e^2}{4\pi\epsilon_0 r_0} + \left[-\frac{e^2}{4\pi\epsilon_0 r_0} \right] = -\frac{2e^2}{4\pi\epsilon_0 r_0}$$

Similarly, the repulsive Coulomb energy due to the two positive ions at a distance of $2r_0$ from the reference ion is $\frac{2e^2}{4\pi\epsilon_0 (2r_0)}$. The attractive Coulomb energy due to the subsequent two neighbours at a distance $3r_0$ on either side of the reference ion is $-\frac{2e^2}{4\pi\epsilon_0 (3r_0)}$ and so on. Thus net energy of the 1-D infinite linear array is given by

$$U = -\frac{2e^2}{4\pi\epsilon_0 r_0} + \frac{2e^2}{4\pi\epsilon_0 (2r_0)} - \frac{2e^2}{4\pi\epsilon_0 (3r_0)} + \dots$$

$$= -\frac{e^2}{4\pi\epsilon_0 r_0} \left[2 \left(1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots \right) \right]$$

Using the expansion $\ln(1+x) = x - \frac{x^2}{2} + \frac{x^3}{3} - \frac{x^4}{4} + \dots$, you can easily see that the expression for energy simplifies to:

$$U = -\frac{e^2}{4\pi\epsilon_0 r_0} [2 \ln 2]. \quad (5.10)$$

The factor $(2 \ln 2)$ may be identified with Madelung constant. You may note that an elementary calculation of Madelung constant for 1-D infinite linear chain leads to a numerical value of about 1.38, which is of the same order as the observed value. For real crystals, we should consider three-dimensional lattice. But the calculations become involved and we shall not go into these details here.

To obtain an expression for the cohesive energy of a van der Waals crystal, we note that if the charge distributions on the atoms making the crystal were symmetric at all times, the interaction between atoms would be zero. Do you know why? This is because the electrostatic potential of a spherical distribution of electronic charges equals the electrostatic potential of the charge on the nucleus. As a result, the inert gas atoms should show no cohesion. But in practice, the atoms induce dipole moments in each other and the induced moments cause an attractive interaction. Therefore, atoms tend to oscillate. In fact, they act as coupled oscillators and you may recall from your PHE-02 course that their motion can be analysed in terms of normal modes. We advise you to go through Unit 5 of PHE-02 course on Oscillations and Waves.

We will not go into mathematical details and just quote the result for the frequencies of these oscillators:

$$\omega \cong \omega_0 \left[1 \pm \frac{1}{2} \left(\frac{2e^2}{KR^3} \right) - \frac{1}{8} \left(\frac{2e^2}{KR^3} \right)^2 + \dots \right], \quad (5.11)$$

where $\omega_0 = \sqrt{K/m}$; K is force constant and R is the separation between oscillators.

For a two-oscillator non-interacting system, the zero point energy is equal to $\hbar\omega_0$.

For the coupled system, the zero point energy is $\frac{1}{2}\hbar(\omega_s + \omega_a)$ where subscripts s and a correspond to symmetric and anti-symmetric modes of oscillation. It means that due to interaction between the two harmonic oscillators, the energy changes as

$$\Delta U = \frac{1}{2}\hbar(\omega_s + \omega_a) - \hbar\omega_0 = -\hbar\omega_0 \cdot \frac{1}{8} \left(\frac{2e^2}{KR^3} \right)^2 = -\frac{A}{R^6}. \quad (5.12)$$

What do you conclude from this result? It shows that interaction between the oscillators is attractive and it is inversely proportional to the sixth power of the separation between the oscillators. Note that existence of van der Waals interaction does not depend on any overlap of the charge densities of the two atoms.

Now you may like to answer an SAQ.

SAQ 4

The van der Waals potential varies as $\frac{1}{R^6}$. Obtain spatial dependence of ionic potential.

Let us now summarise what you have studied in this unit.

5.5 SUMMARY

- The energy U of a system of two atoms varies as a function of distance r between them as

$$U(r) = -\frac{A}{r^m} + \frac{B}{r^n},$$

where m and n are positive numbers, and constants A and B determine the strength of attractive force and repulsive force, respectively.

Zero point energy of the atoms refers to kinetic energy at absolute zero.

From Eq. (5.11), we can write

$$\omega_s = \omega_0 \left[1 + \frac{e^2}{KR^3} - \frac{1}{2} \left(\frac{e^2}{KR^3} \right)^2 + \dots \right]$$

and

$$\omega_a = \omega_0 \left[1 - \frac{e^2}{KR^3} - \frac{1}{2} \left(\frac{e^2}{KR^3} \right)^2 + \dots \right]$$

so that

$$\omega_s + \omega_a = \omega_0 \left[2 - \left(\frac{e^2}{KR^3} \right)^2 + \dots \right]$$

and

$$\frac{\hbar}{2}(\omega_s + \omega_a) = \hbar\omega_0 \left[1 - \frac{1}{2} \left(\frac{e^2}{KR^3} \right)^2 + \dots \right]$$

$$\therefore \Delta U = \hbar\omega_0 \left[1 - \frac{1}{2} \left(\frac{e^2}{KR^3} \right)^2 + \dots - 1 \right]$$

$$= -\frac{\hbar\omega_0}{2} \frac{e^4}{K^2 R^6}$$

$$= -\frac{A}{R^6}$$

Spend
1 min.

- Cohesive energy of a solid is the energy liberated in the formation of a crystal from neutral atoms situated at infinity.
- In an ionic bond, electrons are transferred from one atom to another, and the resulting ions attract each other through Coulomb force.
- Sharing of electrons between neighbouring atoms results in a covalent bond.
- Metallic bond is characteristic of the elements having a few loosely held valence electrons. This bond exists due to electrostatic force of attraction between the electron 'gas' constituted by valence electrons and positive ions of the same metallic element.
- The hydrogen bond is formed only between the atoms of most electronegative elements like F, O and N. Since hydrogen has only one electron, it can form a covalent bond with only one atom of another element. But when a hydrogen atom is covalently bonded to F, or O or N, a permanent dipole is set up. As a result of dipole attraction, hydrogen atom is attracted to two atoms of F, or O or N thus forming a hydrogen bond between them.
- van der Waals bonding arises due to asymmetric charge distribution around atoms. This results in fluctuating electric dipole on each of the atoms which tend to attract each other.
- For ionic crystals, the equilibrium lattice energy is given by

$$U = -\frac{N\alpha e^2}{4\pi\epsilon_0 r_e} \left(1 - \frac{1}{n}\right),$$

where r_e is equilibrium interatomic distance, N is the number of positive-negative ion pairs, n is a constant and α is **Madelung Constant**.

- The energy due to van der Waals interaction varies as $1/R^6$ where R is the interatomic distance.

5.6 TERMINAL QUESTIONS

Spend 25 min.

1. If the potential energy function is expressed as

$$U(r) = -\frac{\alpha}{r^6} + \frac{\beta}{r^{12}}$$

- Show that the inter-molecular distance r_e for which the potential energy is minimum is given by $\left(\frac{2\beta}{\alpha}\right)^{1/6}$
- Show that the inter-nuclear distance r'_e for which the potential energy is zero is given by $r_e \times (2)^{-1/6}$.
- Show that the minimum potential energy is given by, $U_{\min} = -\frac{\alpha^2}{4\beta}$.

Types of bond	Bonding force	Strength of the bond	Character of bond	Melting point	Electrical conductivity	Examples
Ionic Bond	Electrostatic attraction of oppositely charged ions	These bonds are generally stronger than Metallic bond	Non-directional	Intermediate	-----	NaCl, CsCl
Covalent Bond	-----	These bonds are generally less stronger than ionic bonds	-----	-----	Low	Diamond, Germanium
Metallic Bond	Attraction between the ion cores and valence electron gas	These bonds are generally less stronger than covalent bonds	Non-directional	Intermediate	-----	Al, Cu, Na
Hydrogen Bond	Permanent dipoles between similar molecules	These bonds are stronger than van der Waal bonds	Directional	Low	Low	----- -----
van der Waals Bond	Electrostatic force due to oscillating dipoles	-----	Directional for polar-polar interaction; Non-directional for polar-nonpolar interaction and nonpolar-nonpolar interaction	Very low	Low	Argon,

3. Bragg has shown that the Madelung constant for NaCl can be calculated as follows: Start with any atom in NaCl crystal. It is surrounded by six nearest neighbours of opposite sign at a distance r , twelve next nearest neighbours of like sign at a distance $\sqrt{2}r$, eight next-next-nearest neighbours of unlike sign at $\sqrt{3}r$, six next-next-next nearest neighbour of like sign at $2r$ etc. Following this method, compute the Madelung constant.

5.7 SOLUTIONS AND ANSWERS

Self-Assessment Questions (SAQs)

1. Binding energy of hydrogen molecule is 4.5 eV. Because $13.6 \text{ eV} > 4.5 \text{ eV}$, it is easier to break the molecule.
2. NaCl is an ionic crystal and each Na^+ ion is tightly bound to six Cl^- ions. The strength of bonding leads to rise in melting temperature.
3. In (a), neutral atoms with closed electron shells are weakly bound to each other by the van der Waals forces associated with fluctuations in the charge distributions. In (b), electrons are transferred from the alkali atoms to the halogen atoms, and the resulting ions are held together by ionic bonds due to attractive electrostatic forces between the positive and negative ions. In (c), the valence electrons are taken away from each alkali atom to form an electron gas in which the positive ions are dispersed. Thus, the bonding is metallic. In (d), the overlapping electron orbitals of constituent atoms shows that sharing of electrons takes place which gives rise to covalent bonding.
4. From Eq. (5.8), it is obvious that the ionic potential varies as $\frac{1}{R}$.

Terminal Questions (TQs)

1. (a) The condition for the potential energy to be minimum is

$$\left(\frac{dU}{dr}\right)_{r=r_e} = 0$$

Therefore, for the given system

$$\left(\frac{dU}{dr}\right)_{r=r_e} = \left[\frac{6\alpha}{r^7} - \frac{12\beta}{r^{13}}\right]_{r=r_e} = 0$$

or

$$\frac{6\alpha}{r_e^7} = \frac{12\beta}{r_e^{13}}$$

or

$$r_e = \left(\frac{2\beta}{\alpha}\right)^{1/6}$$

- b) The inter-nuclear distance r'_e for which the potential energy is zero is given by:

$$\left[-\frac{\alpha}{r_e'^6} + \frac{\beta}{r_e'^{12}}\right] = 0$$

or

$$(r'_e)^6 = \frac{\beta}{\alpha}$$

From the result of (a) above, we use $r_e = \left(\frac{2\beta}{\alpha}\right)^{1/6}$

$$\therefore (r'_e)^6 = \frac{r_e^6}{2}$$

$$r'_e = r_e (2)^{-1/6}$$

- c) The potential energy is minimum at $r = r_e$, thus,

$$\begin{aligned} U_{\min} &= \left[-\frac{\alpha}{r_e^6} + \frac{\beta}{r_e^{12}}\right] \\ &= -\frac{\alpha}{r_e^6} \left[1 - \frac{\beta}{\alpha} \cdot \frac{1}{r_e^6}\right] \end{aligned}$$

Substituting the value for r_e^6 from (a), we obtain

$$U_{\min} = -\frac{\alpha}{\left(\frac{2\beta}{\alpha}\right)} \left[1 - \frac{\beta}{\alpha} \cdot \frac{\alpha}{2\beta} \right]$$

$$U_{\min} = -\frac{\alpha^2}{2\beta} \left[1 - \frac{1}{2} \right] = -\frac{\alpha^2}{4\beta}$$

$$\therefore U_{\min} = -\frac{\alpha^2}{4\beta}$$

2. Following is the complete table.

Types of Bond	Bonding force	Strength of the bond	Character of Bond	Melting point	Electrical Conductivity	Examples
Ionic Bond	Electrostatic attraction of oppositely charged ions	These bonds are generally stronger than Metallic bond	Non-directional	Intermediate	Low	Na, CsCl
Covalent Bond	Mutual sharing of valence electrons between atoms	These bonds are generally less stronger than ionic bonds	Directional	High	Low	Diamond, Germanium
Metallic Bond	Attraction between the ion cores and valence electron gas	These bonds are generally less stronger than covalent bonds	Non-directional	Intermediate	High	Al, Cu, Na
Hydrogen Bond	Permanent dipoles between similar molecules	These bonds are stronger than van der Waal bonds	Directional	Low	Low	H ₂ O, NH ₃
van der Waals Bond	Electrostatic force due to oscillating dipoles	These bonds are weakest of all bonds	Directional for polar-polar interaction; Non-directional for polar-nonpolar interaction and nonpolar-nonpolar interaction	Low	Low	Argon

3. To calculate the total Coulomb potential energy, it is necessary to sum up all the attractive and repulsive energies between all the ions of NaCl crystal. Suppose Na⁺ ion is surrounded by six nearest neighbours of opposite sign (Cl⁻ ions) each situated at a distance r . These six chlorine ion contribute an attractive potential

energy of $\frac{6e^2}{4\pi\epsilon_0 r}$. There are twelve Na⁺ ions each at $\sqrt{2}r$ distance and they

contribute the repulsive energy $\frac{12e^2}{4\pi\epsilon_0 \sqrt{2}r}$. There are eight Cl⁻ ions at

$\sqrt{3}r$ distance, 6 Na⁺ ions at $2r$ distance etc. Therefore, the Coulomb energy of this Na⁺ ion due to all other ions is:

$$U = -\frac{6e^2}{4\pi\epsilon_0 r} + \frac{12e^2}{4\pi\epsilon_0 \sqrt{2} r} - \frac{8e^2}{4\pi\epsilon_0 \sqrt{3} r} + \frac{6e^2}{4\pi\epsilon_0 2r}$$

or

$$U = -\frac{e^2}{4\pi\epsilon_0 r} \left[6 - \frac{12}{\sqrt{2}} - \frac{8}{\sqrt{3}} + \frac{6}{\sqrt{4}} \right]$$

Thus Madelung constant

$$\begin{aligned} \alpha &= \frac{6}{\sqrt{1}} - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \dots \\ &= 6.000 - 8.485 + 4.620 - 3.000 + \dots \\ &\approx 1.7475. \end{aligned}$$