

Unit - 06

States of Matter III: Solids

After reading this unit, the students will be able to:

- Describe simple properties of solids e.g., diffusion, compression, expansion of molecules, spaces between them, intermolecular forces and energy based on kinetic molecular theory. (Understanding)
- Differentiate between amorphous and crystalline solids. (Understanding)
- Describe properties of crystalline solids like geometrical shape, melting, cleavage planes, habit of a crystal, crystal growth, anisotropy, symmetry, isomorphism, polymorphism, allotropy and transition temperature. (Understanding)
- Use oxygen and sulphur to define allotropes. (Understanding)
- Explain the significance of the unit cell to the shape of the crystal using NaCl example. (Applying)
- Name three types of packing arrangements and draw or construct models of them. (Applying)
- Name three factors that affect the shape of an ionic crystal. (Understanding)
- Define lattice energy. (Remembering)
- Differentiate between ionic, covalent, molecular and metallic crystalline solids. (Applying)
- Explain the low density and high heat of fusion of ice. (Understanding)
- Define and explain molecular and metallic solids. (Understanding)

Teaching

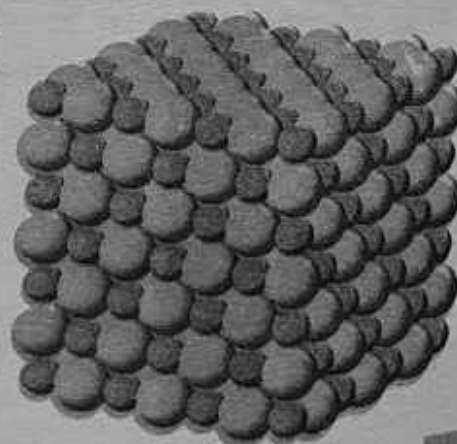
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Assessment

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Introduction

Solid is one of the physical states of matter, other being the gas, the liquid and the plasma states. The solid state of matter is characterized by its rigidity, hardness, definite shape, definite volume and mechanical strength. The forces of attraction between its structural units (atoms, ions, molecules) are quite strong and, therefore, they cannot move at random (as in the case of gases and liquids). Consequently, these units remain fixed to mean position to about which they vibrate and make solids rigid and have definite shape.

After studying this unit, you will be able to differentiate between amorphous and crystalline solids, describe the classification and properties of crystalline solids, crystal lattice and lattice energy.

Tidbit

The particles in the solid are separated by a distance of only a few Pico meters ($1\text{pm} = 1 \times 10^{-12}\text{m}$)

6.1 Kinetic molecular interpretation of solids

The Kinetic Molecular Interpretation of solids is as follows.

- i. Solids are composed of closely packed particles.
- ii. The particles of the solids are firmly held together by strong forces of attraction.
- iii. Solids are rigid in nature as the particles of solids are held in fixed positions and cannot move freely. They can only vibrate about a mean position.
- iv. In solids, particles are more ordered than liquids and gases.
- v. The particles in solids are arranged in regular configurations in three dimensions. Therefore, they adopt the definite geometrical shape called a lattice.
- vi. There is less empty space between particles in a solid than in a liquid.
- vii. Solids are almost incompressible and possess definite shape and volume.
- viii. As solids particles are closely packed, so they occupy minimum volume. The density is inversely proportional to volume; therefore, solids have high density.
- ix. In solids, the particles vibrate about a mean position, so there is no collision among the solid particles.
- x. The kinetic energy of the solids particles is due to vibration of particles, as there are no rotational and translational kinetic energy in solid particles.

6.1.1 Simple Properties of Solids Describing Vibration of Molecules Intermolecular Forces, Kinetic Energy

i. Diffusion

Solid particles do not diffuse readily into other solids. However, analysis of two blocks of different solids, such as copper and lead, which have been pressed together for a period of years show that each block contains some atoms of the other element. This demonstrates that solids do diffuse, but very slowly as shown in figure 6.1. The rate of diffusion is millions of times slower in solids than in liquids. The diffusion depends upon movement and velocity of particles. As in solids, the movement of the particles is very slow; therefore, the diffusion occurs to very small extent in very large time.

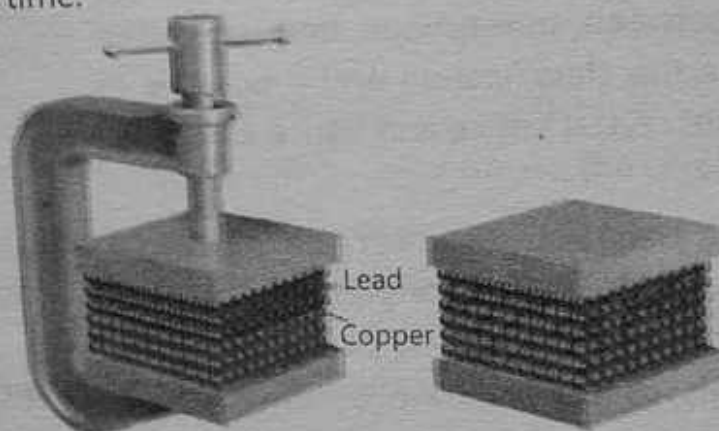


Figure 6.1: A Representation of Diffusion in Solids

ii. Compression (Effect of pressure)

Solids are generally less compressible than liquids. For practical purposes solids can be considered incompressible. Some solids, such as wood and cork may *seem* compressible, but they are not. They contain pores that are filled with air. When subjected to intense pressure, the pores are compressed, not the solid matter in the wood or cork itself.

iii. Expansion (Effect of Temperature)

The solids expand when temperature increases (heated) i.e. their volume increases. This is because the increase of temperature decreases the intermolecular attractive forces. As a result, the spaces between the molecules increase hence volume increases.

The expansions of solids are expressed in terms of co-efficient of expansion (α). It is defined as *the increase per unit volume when the temperature is increase by 1°C* . When a solid is heated, its geometric shape changes until at

certain temperature, it melts and changes into the liquid state. The temperature at which a solid changes into the liquid state is called melting point of the solids.

iv. Motion of Particles

In crystalline solids, the particles are strongly held with one another. The particles do not move freely as in liquid and in gases. There is no translational and rotational motion due to presence of strong intermolecular forces in the crystalline solid. The particles in the crystalline solids are closely packed together. However, the particles can vibrate about their mean positions and thus transfer the energy from one particle to another.

v. Spaces between Crystals

In crystalline solids, the particles are closely packed together, so there is less space between the particles. The intermolecular forces are maximum in between the particles. These maximum intermolecular forces and less space between the particles make them incompressible.

vi. Intermolecular Forces

In solids, there occur a number of intermolecular forces. These intermolecular forces are maximum in between the solid particles. These intermolecular forces held the solid particles together in fixed positions. They can vibrate only about their fixed positions and cannot move freely as in liquids and gases.

vii. Kinetic Energy Based on Kinetic Molecular Theory

According to kinetic molecular theory, the attractive forces between the solid particles are maximum. As the distance between the particles is minimum and attractive forces are maximum, therefore, particles of solids do not move from their fixed position. However, they can vibrate about their mean positions. Therefore, they possess only vibrational kinetic energy.

Reading Check

1. Define solid and kinetically interpret the solids.
2. What are the different properties of solids?

6.2 Types of Solids

Solids can be classified into two types on the basis of arrangement of constituent particles (atoms, ions or molecules).

- Amorphous solids
- Crystalline solids (True solids)

6.2.1 Amorphous Solids

Those solids in which particles are not arranged in three dimensional regular pattern are called amorphous solids. (Amorphous Greek word meaning 'without shape or geometry', 'no form or glassy'). An amorphous solid has atoms, molecules or ions arranged almost at random. It has disordered structure and

lacks the well-defined regular arrangement of basic units (atoms, molecules, or ions) found in a crystal.

Large classes of materials with highly variable mechanical and optical properties that solidify from the molten state without crystallization are called amorphous solids. It is typically made by silicates fusing with boric oxide, aluminum oxide or phosphorus pentoxide. It is generally hard, brittle, transparent or translucent and is considered to be super cooled liquid rather than true solids.

Unlike crystalline solids, amorphous solids do not have sharp melting points. It means, they melt gradually over a long range of temperatures. Also they do not have any characteristic heat of fusion. Because of their disorderly arrangement of particles, they behave like liquids. They are, therefore, sometimes called super cooled liquids. Examples are rubber, plastics, gemstone, coal tar, glass etc. Thus, glasses are to be regarded as super-cooled or highly viscous liquids.

Amorphous solids have been used in electronic devices, including solar cells, photocopiers, laser printers and flat panel displays for computer monitors and television screens.

6.2.2 Crystalline Solids (True solids)

Solids in which particles are arranged in a regular three-dimensional order are called crystalline solids. In crystalline solids, the structural unit is arranged in an orderly manner, which repeats itself in three dimensions. Hence, they have rigid and definite geometrical shapes. A crystalline solid exists as small crystals, each crystal having a characteristic geometrical shape. They are also called true solids. Most of the solids are crystalline in nature. Examples of such solids are diamond, graphite, sodium chloride (NaCl), calcium carbonate ($\text{CaCO}_3 \cdot x\text{H}_2\text{O}$), copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) etc.

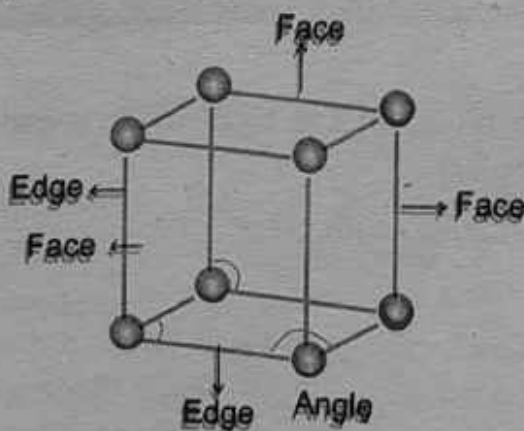


Figure 6.2 Faces, interfaced angle and edges of a typical solid

Tidbit

Crystal: Crystals are solid objects with a definite geometrical shape in which particles (atoms, molecules or ions) have a regular and repetitive three-dimensional arrangement.

6.3 Properties of Crystalline solids

Crystalline solids have a number of general properties, which distinguish them from amorphous solids. Some important properties of crystalline solids are,

6.3.1 Symmetry

Symmetry is the consistency or the repetition of something. A crystal possesses a number of surfaces, known as faces, edges and interfacial angles. Symmetry in crystals may be due to a plane, a line or a point. This repetition is called symmetry.

There are three types of symmetry elements associated with a crystal.

a. Plane of Symmetry

When a crystal is divided by an imaginary plane into two equal parts, each of which is the exact mirror image of the other than this plane is called plane of symmetry.

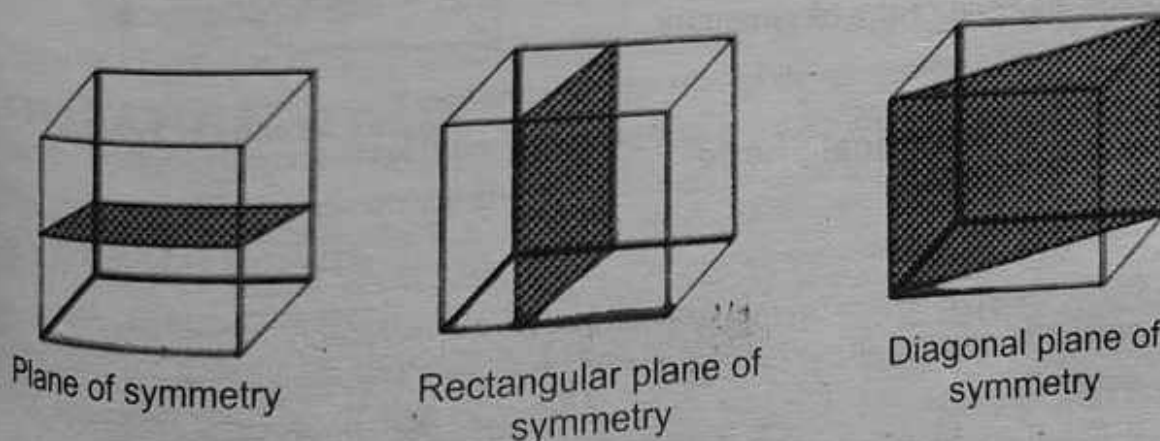


Figure 6.3 Plane of Symmetry

b. Axis of Symmetry

An axis of symmetry is an imaginary line drawn through the crystal such that rotating the crystal through 360° , the crystal presents exactly the same appearance more than once. If similar view appears twice, it is called an axis of two-fold symmetry or **diad axis**. If it appears thrice, it is an axis of three-fold symmetry or **triad axis**, and so on.

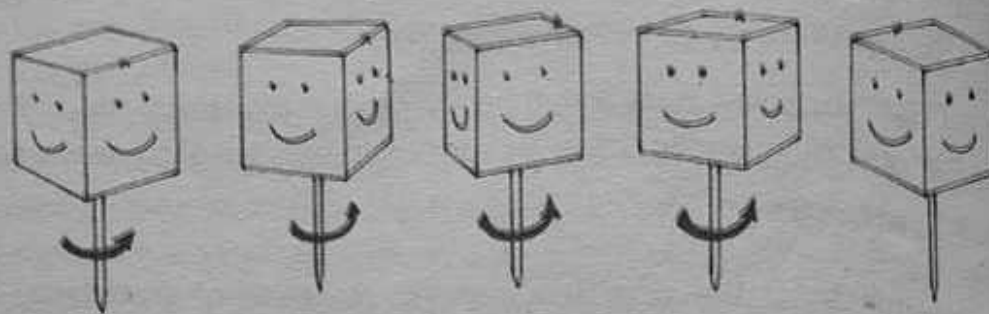


Figure 6.4 Axis of Symmetry

c. Centre of Symmetry

It is a point at the centre of the crystal so that any line drawn through it will meet the surface of the crystal at equal distances on either side.

Or It is a point at the centre of the crystal which is equidistant from opposite faces of a crystal.

It must be noted that a crystal may have a number of planes of symmetry or axis of symmetry but it can have only one centre of symmetry.

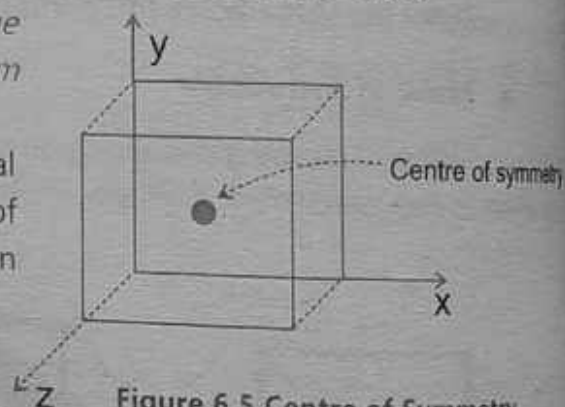


Figure 6.5 Centre of Symmetry

6.3.2 Geometrical Shape

Almost all the solids have a definite and orderly arrangement of the constituent particles (atoms, ions or molecules). These atoms, ions and molecules have fixed positions. They cannot move considerably. They give it definite geometry (shape). The arrangement of faces and interfacial angles are always the same for a given crystal, irrespective of the method and conditions of preparation. Moreover, the solids due to orderly arrangement of atoms, ions or molecules adopt the three-dimensional structure space e.g. NaCl is cubic in nature. Upon grinding to a very fine powder, the crystalline solids still retain their specific geometrical shapes.

6.3.3 Melting Point

Crystals being pure solids, have sharp melting points. As the crystals are orderly arranged so when a solid is heated, the atoms, ions or molecules present in a solid start vibrating and transfer their kinetic energy throughout the solid. At the melting point, their vibrational energies become so much that they leave their fixed positions simultaneously and become a liquid.

The temperature remain constant (even if heat is continuously being given), until all the particles become mobile

6.3.4 Cleavage Plane

When crystals break, they split along straight faces called cleavage planes, which are weak due to the atomic structure of the crystal.

Cleavage is the tendency of crystals to break along one or more sets of parallel plane. A crystal contains atoms, ions or molecules, which are closely packed to each other. When an external force (pressure) is applied to it, it breaks or splits into small crystals of the same shape as that of the original one.

Two adjacent cleavage planes intersect always at a definite angle. The magnitude of the interfacial angle, after cleavage has taken place, may differ from solid to solid and is a characteristic of a given solid.

6.3.5 Habit of Crystal

Habit refers to the way a crystal looks when it is found in its natural state.

The external shape is called the habit of the crystal. In other words, the shape of a crystal in which it usually grows is called habit of crystal. The habit of a crystal of a given compound depends on the rate of development of the different faces. Sodium chloride (NaCl) for example, has a cubic habit. It means NaCl will always have cubical geometrical shape whenever its crystals are formed.

6.3.6 Crystal Growth

A crystal commonly grows in the typical shape. Crystal are usually prepared (or grown) by slow cooling of a substance in liquid state or cooling a hot saturated solution of the substance concerned. The apparent shape of the crystal depends on the method and conditions of preparation. Slow growth from a slightly super-saturated solution or a very slowly cooling solution gives large crystals. Different crystals of the same substance may not look alike. In the presence of certain impurities, different faces grow at different rates and give rise to many forms. For example, if sodium chloride is crystallized from its supersaturated solution, it forms cubic crystals. However, if 10% urea is present as impurity in its solution, it gives needle like crystals. As already stated, the external appearance or size of crystals of a substance may be different. It depends upon the conditions under which it is prepared. However, the interfacial angles are always the same. This is illustrated diagrammatically in figure 6.6.

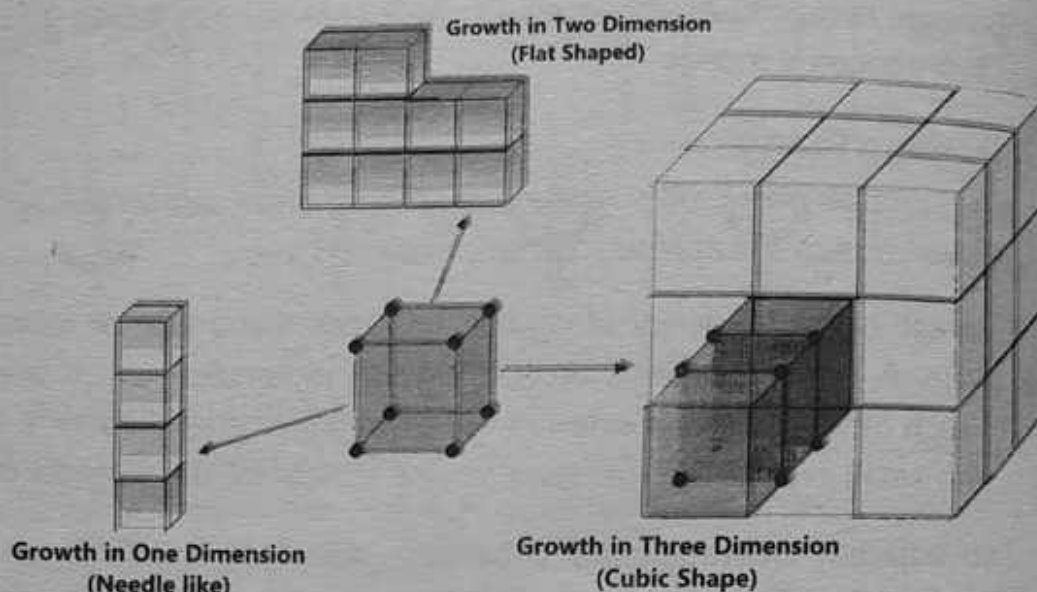


Figure 6.6 Crystal Growth in Different Shapes

For example, sodium chloride (NaCl) with cubic crystal habit may grow into a cubic (three-dimensional), a flat shaped (two dimensional) or a long needle like structure (one – dimensional) depending upon the conditions under which it is crystallized.

6.3.7 Anisotropy

The property of substance, which shows different intensities (magnitudes) of physical properties in different directions, is called anisotropy. The substances, which show this property, are called anisotropics and such properties are called anisotropic properties.

Crystalline substances are anisotropic and the magnitude of a physical property varies with directions, because of regular and well-ordered arrangement of the constituent particles. For example, in a crystal of silver iodide, the coefficient of thermal expansion is positive in one direction and negative in the other. Similarly, electrical conductivity of graphite is greater in one direction than in another. Actually, electrons in graphite are mobile for electrical conduction parallel to the layers

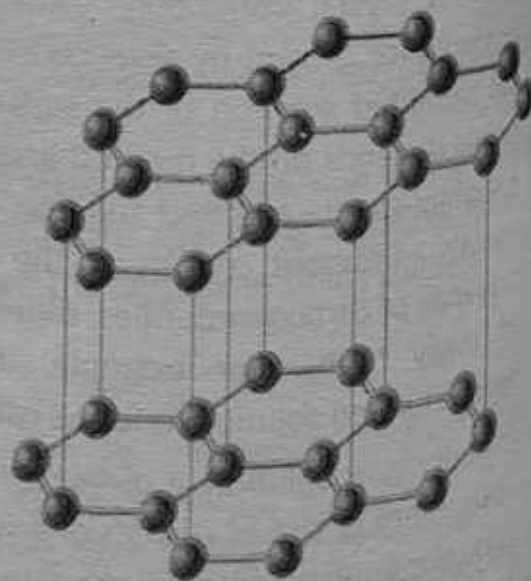


Figure 6.7 Structure of Graphite

only. Therefore, its conductivity in this direction is far better than perpendicular to the layers. Similarly, cleavage itself as an anisotropic behaviour.

6.3.8 Isomorphism

There are certain substances, which are similar in shape. Two or more different crystalline substances having the same crystalline shapes are called isomorphs of each other, and this phenomenon is called isomorphism.

The formula units of different isomorphs have usually the same atomic ratio. The example of some isomorphs is given in the table 6.1.

Table 6.1 Examples of Isomorphous Compounds

Isomorphs	Atomic ratio	Crystalline form
NaF and MgO	1:1	Cubic
KNO ₃ and NaNO ₃	1:1:3	Rhombohedral
ZnO and CdS	1:1	Hexagonal

It is to be noted that the physical and chemical properties of isomorphs are quite different from each other as they are totally different compounds of different nature.

6.3.9 Polymorphism

The occurrence of the same crystalline substance in more than one crystalline forms under different conditions is known as Polymorphism.

The substance showing polymorphism is said to be polymorphic and the different crystalline forms are called polymorphs of each other. Polymorphs have the same chemical properties but different physical properties due to different arrangement of particles in their structure. Examples of polymorphs are given in table 6.2.

Table 6.2 Examples of Polymorphic forms

Substance	Crystalline Forms
AgNO ₃	Rhombohedral and Orthorhombic
CaCO ₃	Trigonal and Orthorhombic
KNO ₃	Rhombohedral and Orthorhombic

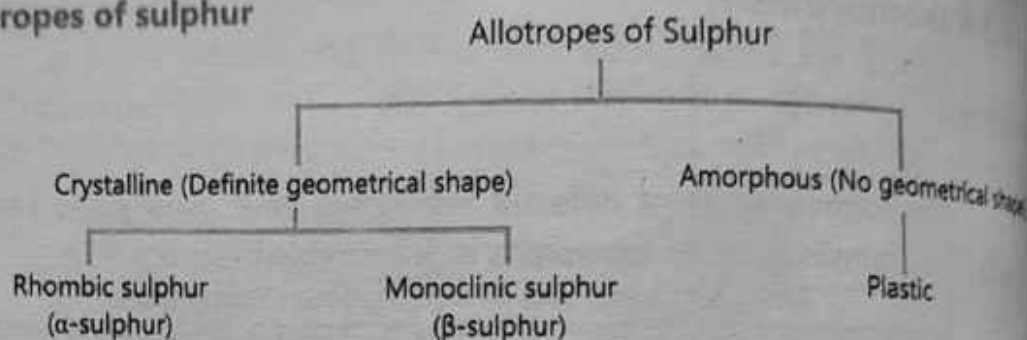
The different crystalline forms are inter-convertible into each other under different conditions of temperature.

6.3.10 Allotropy

The occurrence of an element in different forms is called allotropy. These various physical forms are called allotropes or allotropic forms. For example, sulphur is found in orthorhombic and monoclinic form and plastic (amorphous) forms and

Oxygen occurs in the form of oxygen (dioxygen, O_2) and ozone (O_3). The allotropes of sulphur and oxygen are discussed in detail.

Allotropes of sulphur



Allotropes of oxygen

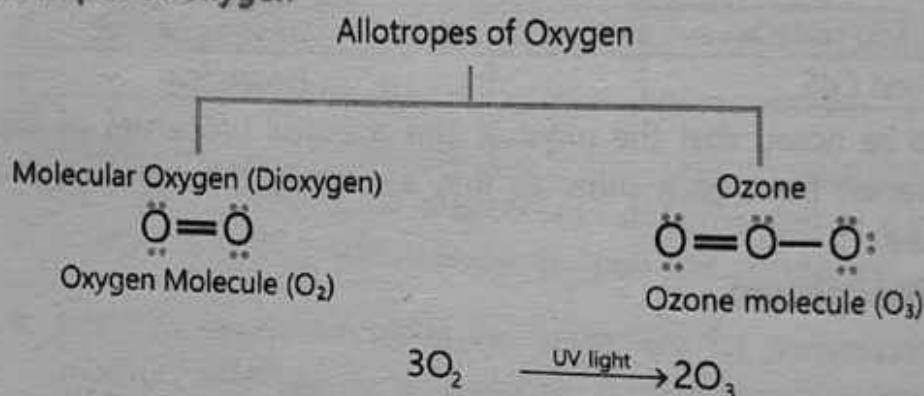


Figure 6.8 Allotropic of Sulphur and Oxygen

6.3.11 Transition Temperature

The temperature at which one crystalline form of a substance changes to another crystalline form is called transition temperature. In other words, the temperature at which more than one crystalline forms of a given substance can exist in equilibrium with each other is called transition temperature.

Above and below transition temperature only one polymorph or allotrope can exist. The transition temperatures of some substances are shown below.

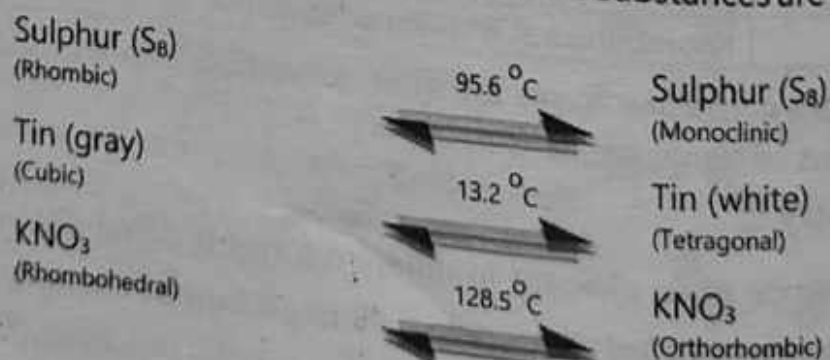


Table 6.3 Differences between Amorphous Solids and Crystalline Solids

Property	Amorphous Solids	Crystalline Solids
Shape	They do not have definite geometrical shape.	They have characteristic geometrical shape.
Melting point	Amorphous solids do not have particular melting point. They melt over a wide range of temperature.	They have sharp melting point.
Anisotropy	Physical properties of amorphous solids are same in different direction, i.e. amorphous solids are isotropic.	Physical properties of crystalline solids are different in different directions. This phenomenon is known as Anisotropy.
Symmetry	Amorphous solids are unsymmetrical	Crystalline solids are symmetrical
Cleavage plane	Amorphous solids do not break at fixed cleavage planes.	Crystalline solids break along particular direction at fixed cleavage planes.

Self-Assessment

1. Differentiate between amorphous solids and crystalline solids.
2. Define symmetry. What are elements of symmetry?
3. Explain the terms polymorphism and allotropy.
4. Differentiate between habit of crystal and crystal growth, isotropy and anisotropy.
5. Define allotropy. Use oxygen and sulphur as an example.

Science, Technology and Society

Crystalline and amorphous solids have specific uses in daily life. Examples of crystalline solids are table salt (sodium chloride), sugar, gemstones including quartz and diamond. Some of the uses of crystals are,

- Diamond is used in jewelry.
- Sodium chloride (NaCl) has been used to flavor and preserve foods for thousands of years. Doctors use an intravenous sodium chloride solution to supply water and salt to patients to decrease dehydration.
- Sodium fluoride (NaF) is used in toothpastes to prevent cavities. It makes teeth stronger.
- Sugar (sucrose) is used in daily life for sweet taste.

- Salts of iodine are used for treatment of goiter.

Examples of amorphous solids are plastic, glass, rubber, coal, fiberglass, cellophane, teflon, polyurethane, polyvinylchloride (PVC). Some of the uses of amorphous solids are,

- Plastics are used in the construction, industry, electrical and electronic applications. It is also used in packaging goods, including containers, bottles, drums, trays, boxes, cups and baby products etc.
- Rubber is used in vehicles tyres, airbags, flooring, natural rubber gloves, erasers, adhesives and coatings, rubber gloves etc.
- Fiberglass is durable, safe and offers high thermal insulation. Fiberglass is widely used in industries such as beverage industry, chemical industry, communication towers, fountains and aquariums, etc.
- Glass is used in making drinking vessels, barometer, windows panes, optical instruments etc.

6.4 Crystal Lattice

The regular three-dimensional array of atoms, ions, or molecules in a crystal is expressed in terms of points is called the **lattice** that identifies the locations of the individual species.

The crystal lattice of a substance is represented by showing the positions of particles (**structural units**) in space.

The location of particles in a crystalline solid can be represented by points on a framework called crystal lattice.

The particles (atoms, ions or molecules) in crystals are highly ordered in a three dimensional pattern. It is the property of the crystal, which is responsible for their specific geometrical shapes, smooth surfaces and specific interfacial angles. The particles in crystals are arranged in regular patterns that extend in all directions. The overall arrangement of particles in a crystal is called the **crystal lattice, Space lattice or simply lattice**. These positions of the constituent particles in a crystal are represented by bold dots (or circles) and are referred to as **lattice points** or **lattice sites** irrespective of the size and nature of the particles. Each point in the lattice is occupied by a particle of the substance.

To describe the structure of a crystal it is convenient to view it as made of a large number of basic units called the **Unit cell** as shown in Fig.

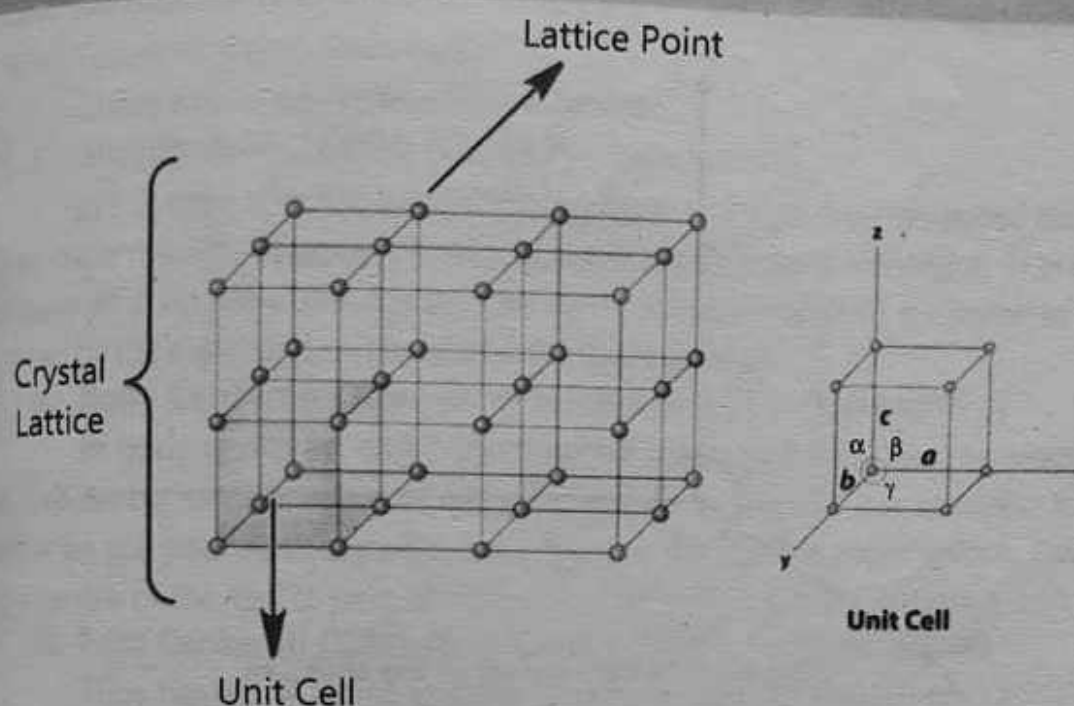


Figure 6.9 Crystal Lattice and Unit Cell

6.4.1 Unit cell

You can divide a crystal lattice into boxlike cells or unit cells. The **unit cell** of a crystal is the smallest boxlike unit (each box having faces that are parallelograms) from which you can imagine constructing a crystal by stacking the units in three dimensions.

The smallest portion of a crystal lattice that shows the three-dimensional pattern of the entire lattice is called a unit cell. On the other hand, you can say that the basic repeating structural unit of a crystalline solid is a unit cell. A unit cell being the structural unit carries complete information about the given crystal.

A unit cell has the smallest arrangement of atoms in a crystal lattice that has the same symmetry as the whole crystal. A unit cell is small, representative part of a larger whole. The unit cell can be thought of as a building block whose shape determines the shape of the crystal.

Parameters of the Unit Cell

The structures of all crystals can be classified according to the symmetry of the unit cells. There are in total seven groups, collectively called, crystal system. These are triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal and cubic. The unit cells are characterized by the following parameters:

- Relative lengths of the edges along the three axes (a , b , c),
- The three angles between the edges (α , β , γ).

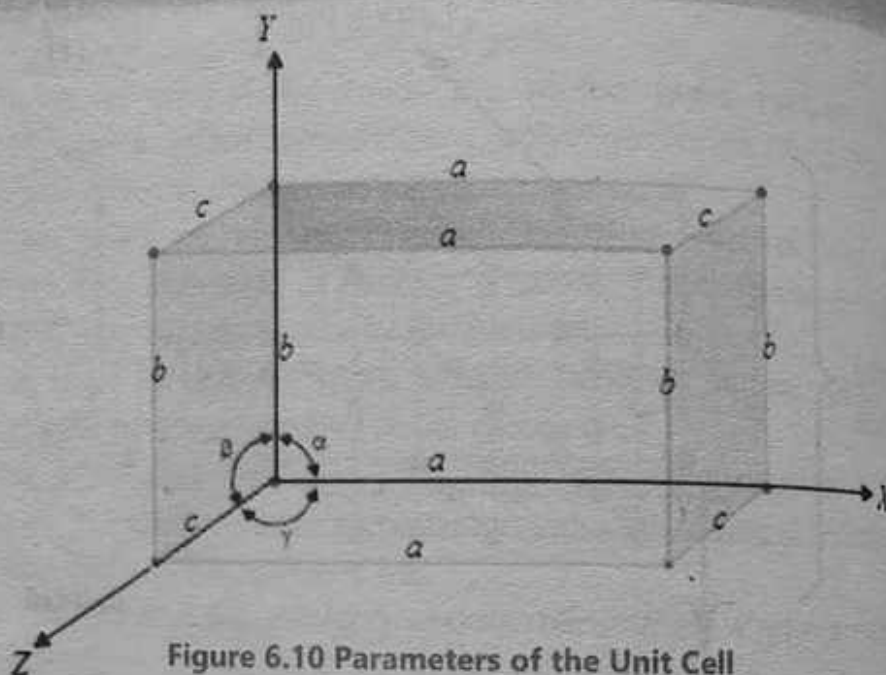


Figure 6.10 Parameters of the Unit Cell

The six parameters of a unit cell, 3 edges (a , b , and c) and 3 angles (α , β , and γ) are called unit cell dimensions or crystallographic elements. These parameters can be illustrated as in figure 6.10. Parameters of the seven Bravais unit cells are listed in Table 6.4.

Table 6.4 The Seven Crystal Systems

Crystal system	Edge length	Angles	Example
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, Cu
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	TiO ₂ (rutile), Sn (white tin)
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	CaCO ₃ (aragonite), BaSO ₄
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ, \gamma \neq 90^\circ$	PbCrO ₄
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ, \gamma = 120^\circ$	C (graphite), ZnO
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	CaCO ₃ (calcite), HgS (cinnabar)
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	K ₂ Cr ₂ O ₇ , CuSO ₄ ·5H ₂ O

Cubic Unit Cells

These are the simplest unit cells. These unit cells are particularly important for two reasons.

First, a number of ionic solids and metals have crystal lattices composed of cubic unit cells. Second, it is relatively easy to make calculations with these because in them all the sides are equal (i.e. $a=b=c$) and the cell angles are all 90° (i.e. $\alpha = \beta = \gamma = 90^\circ$).

Three Types of Cubic Unit Cells

There are three types of cubic lattices.

i. **Simple Cubic Lattice (Cubic P – type lattice)**

In this type of cubic lattice, the points are only at the corners of each unit cell. They have maximum vacant space and are rarely found in nature. There are eight corners in a simple cubic system and each point occupying a corner of the cell is shared by the eight unit cell as shown in figure 6.11(a).

ii. **Body Centered Cubic (bcc) Lattice (Cubic I – type lattice)**

In body centered cubic (bcc) lattice, each unit cell has one point (particle) at the center of the cube in addition to the points at the corners. In this case particles are packed more efficiently than in the simple cubic lattice. Each point in the centre of the cell is part of only one unit cell as shown in figure 6.11 (b).

iii. **Face Centered Cubic (fcc) Lattice (Cubic F – type lattice)**

They have one point at each of the six faces of the cube, in addition to the points at the corners. Maximum space is occupied by the particles in this case. Here each point at the corner is shared by eight unit cells and the point at the centre of each face is shared by two unit cells figure 6.11 (c).

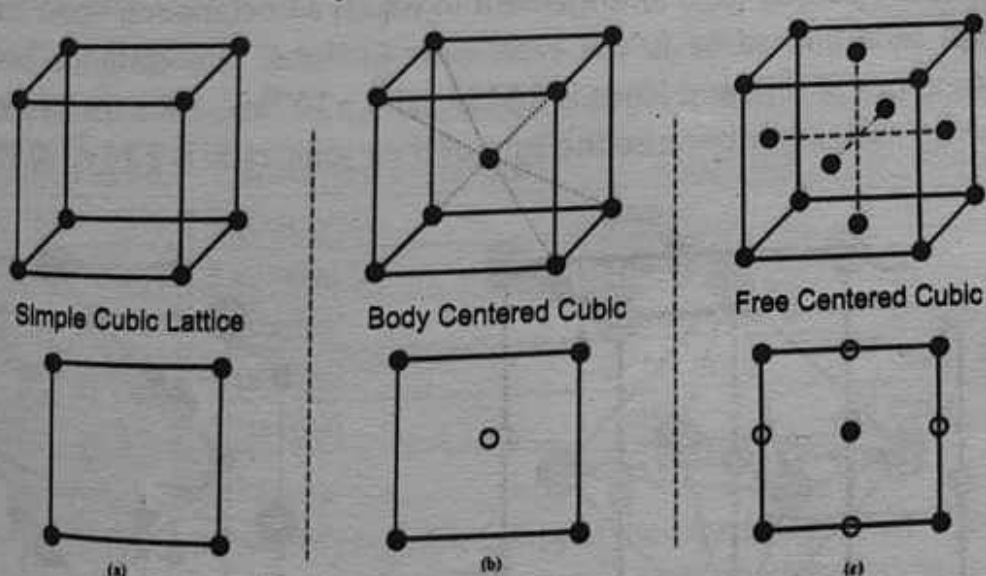
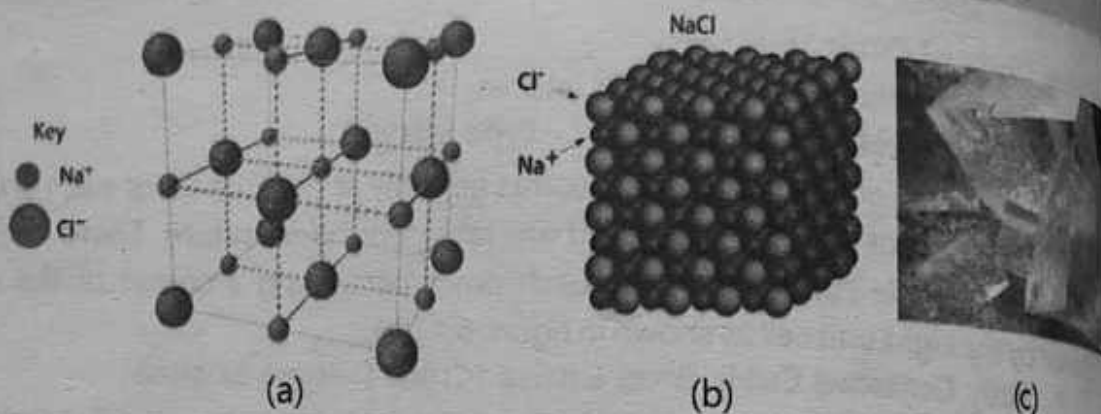


Figure 6.11 (a), (b), (c) Three Cubic Units Cells

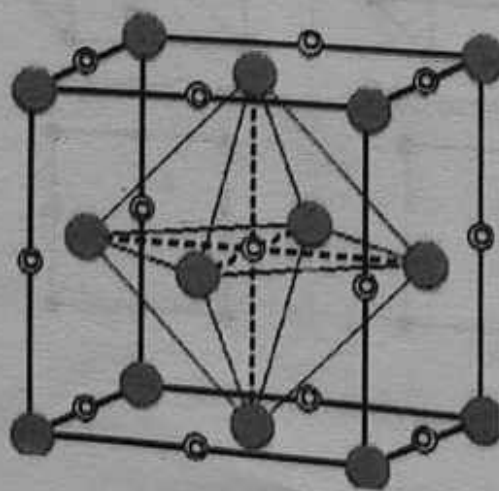
6.4.2 Sodium Chloride (NaCl) Crystal

Sodium chloride (NaCl) is a typical example of face centered cubic arrangement (system) and it consists of equal numbers of Na^+ and Cl^- ions arranged in a three-dimensional network as shown in figure 6.12. In such a compound, there is a 1:1 ratio of cations to anions so that the compound is electrically neutral.

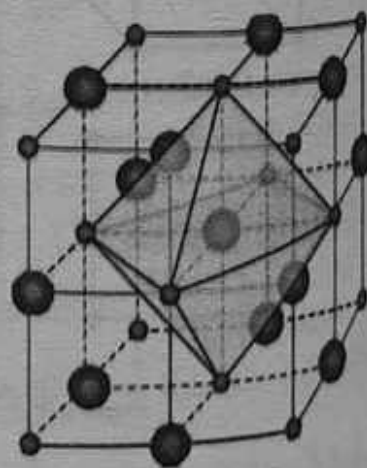


As you can see in figure 6.12, one Na^+ ion in NaCl is associated with just one particular Cl^- ion. In fact, each Na^+ ion is equally held by six surrounding Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions. Thus co-ordination number of each ion is six.

NaCl has a face centered cubic arrangement and in the octahedral structure, shown in figure 6.13 (a) and (b), Cl^- ions may be regarded as having a cubic closed packed (ccp) arrangement in which all octahedral holes are occupied by Na^+ ions and same is the case with Cl^- ions. The distance between two adjacent ions of different kinds is $2.815 \text{ \AA}$ ($1 \text{ \AA} = 10^{-10} \text{ m}$). Thus the two ions are not touching each other because the sum of their ionic radii is $2.76 \text{ \AA}$ ($0.95 + 1.81$).



Octahedral Arrangement of 6Cl^- ions around Na^+ ion
(a)



Octahedral Arrangement of 6Na^+ ions around Cl^- ion
(b)

Figure 6.13

Factors that Affect the Shape of an Ionic Solid

There are some factors which effect the shape of an ionic crystal. Few of them are given below.

i. Electrostatic Force of Attraction

Ionic crystals are formed between cations and anions which are strongly held together due to electrostatic forces. The strength with which these ions are held together is known as lattice energy. Due to high lattice energy ions are strongly held together and a crystal acquires a definite shape.

ii. Radius Ratio

In ionic crystals cations are surrounded by anions. Generally, cations are smaller in size than anions. The anions around the cations are located in such a way that they are at a suitable distance from each other to avoid repulsion between anions. Thus, around a given cations only a certain number of anions can be accommodated, this number is called Coordination number. The coordination number is related with relative size of cation and anion, called as radius ratio which is the ratio of size of cation to that of anion. For example, for NaCl the radius ratio of Na^+ to Cl^- is 0.54 which has coordination number of 6 and acquire an octahedral crystal structure.

Some examples of radius ratio and crystal structure are given in table 6.5.

Table 6.5 The structure and limiting radius ratio of certain crystalline substance

Radius ratio	Coordination number	Structure	Example
<0.155	2 (unstable)	Linear	----
$0.155 - 0.225$	3 (unstable)	Triangular planer	Non
$0.225 - 0.414$	4 (stable)	Tetrahedral	ZnS, CuCl_2
$0.414 - 0.732$	6 (stable)	Octahedral	NaCl, MgO
$0.732 - 1$	8 (stable)	Cubic	CsCl

iii. Effect of Temperature

A perfect crystal would require cooling of the liquid phase at a very slow rate so as to allow ions or particles to find their proper position in the lattice. In this way, proper temperature has significant impact upon the crystal formation.

iv. Effect of impurity

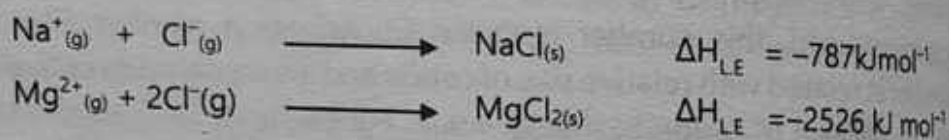
If there are impurities in solution from which the crystallization of a substance is to be carried out, the resulting crystal will have defects, called crystal defect. These impurity particles will fit into the holes of the crystal lattice causing a defect in the crystal structure.

6.4.3 Lattice Energy

When ions combine to form an ionic solid there is a huge release of energy. The reaction is highly exothermic. The energy given out when ions of opposite charges come together to form a crystalline lattice is called the lattice energy, ΔH_{LE} .

Lattice energy can be defined as *the amount of energy released when one mole of an ionic crystal is formed from gaseous ions of opposite charges.* It is expressed in kJ.mol^{-1} . For example,

Equations describing the lattice energy of sodium chloride and magnesium chloride are shown here.



The large exothermic value of the lattice energy shows that the ionic lattice is very stable with respect to its gaseous ions. Higher the lattice energy, the stronger the ionic bonding in the lattice.

It is impossible to determine the lattice energy of a compound by a single direct experiment. We can, however, calculate a value for ΔH_{LE} using several experimental values and an energy cycle called a Born-Haber cycle.

Lattice energy increases with increase in charge and decrease in size of ions. Lattice energy of some ionic crystal is given in table 6.6.

Table 6.6 Lattice Energies of some Ionic Compounds

Compound	Lattice energy (kJ/mol)
NaF	895
LiCl	833
NaCl	787
NaBr	728
NaI	690
KBr	665
KI	630

6.4.4 Low Density and High Heat of Fusion of Ice

Liquid water is readily convertible under conditions to the solid and gaseous forms. Water has several unusual properties that make it to distinguish from other substances. For example, its solid phase, ice is less dense than liquid water.

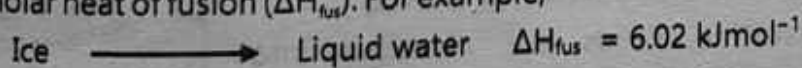
i. Low density of Ice

The most striking property of water is that its solid form is less dense than its liquid form that is why ice floats on the surface of liquid water. The density of almost all other substances is greater in the solid state than in the liquid state as shown in figure 6.14.

The unusual properties of water are largely linked to its ability to form hydrogen bonds. For example, ice is less dense than liquid water because of hydrogen bonding. When the temperature is decreased, the molecules come close to each other. Each oxygen atom in ice is surrounded tetrahedrally by four hydrogen atoms, two by covalent bonds and two by hydrogen bonds. The tetrahedral angles give rise to a three-dimensional structure that contains open space. As a result, about 9% more space than liquid water is produced. As we have $d = m/v$, that is, density is inversely proportional to volume, the increase in volume decreases the density of ice. That is why ice floats over water.

ii. High Heat of Fusion of Ice

The energy (usually in kJ) required to melt 1 mole of a solid at its melting point is called the molar heat of fusion (ΔH_{fus}). For example,



As Table 6.7 shows, ice has a high heat of fusion. This is consistent with the fact that molecules in a liquid are fairly closely packed together, so that high energy is needed to bring about the rearrangement from solid to liquid.

Tidbit

Ice structure extends in three dimensions due to tetrahedral arrangement. Because of empty spaces in its structure, ice has smaller density than liquid water and float on the surface of water.



Figure 6.14 Water and Benzene

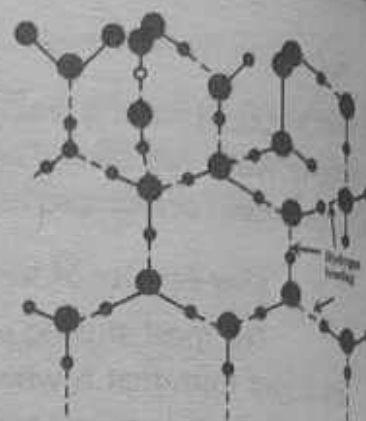


Fig. 6.15 Structure of Ice

Table 6.7 Molar Heats of Fusion for Selected Substances

Substance	Melting Point(°C)	H_{fus} (kJ/mol)
Argon (Ar)	-190	1.3
Benzene (C_6H_6)	5.5	10.9
Diethyl ether ($\text{C}_2\text{H}_5\text{OC}_2\text{H}_5$)	-116.2	6.90
Ethanol ($\text{C}_2\text{H}_5\text{OH}$)	-117.3	7.61
Mercury (Hg)	-39	23.4
Methane (CH_4)	-183	0.84
Water (H_2O)	0	6.02

6.5 Types of Crystalline solids

Crystalline solids are classified into categories according to the types of particles in the crystal and the bonding or interactions among them. The four categories are (1) ionic solids, (2) covalent solids (3) metallic solids, and (4) molecular solids.

Reading Check

- What is Crystal Lattice?
- Define unit cell. What are the different parameters of the unit cell?

6.5.1 Ionic Solids

In an ionic crystal, the lattice is made of positive and negative ions. These are held together by ionic bonds. Ionic bonds are strong electrostatic attractions between oppositely charged ions. As a result, the cations and anions attract one another in such a manner so that the attractive forces maximize. The structure of an

ionic crystal depends on the charges on the cation and anion and on their radii. Examples of ionic solids are NaCl, MgO, NaBr etc. In sodium chloride lattice, each ion is surrounded by opposite charge and there are no separate molecules as shown in figure 6.16.

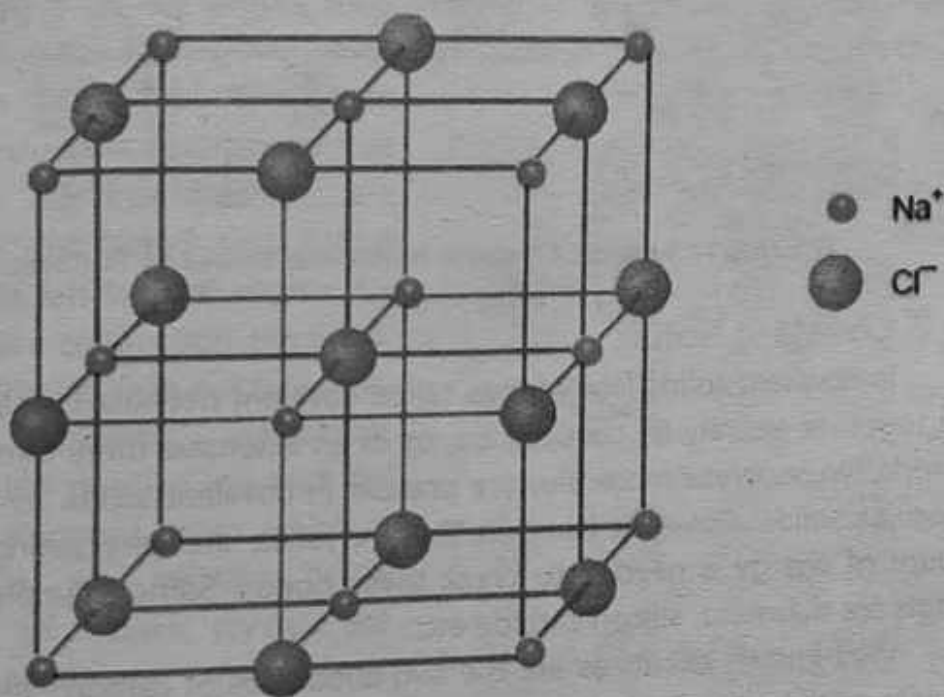


Figure 6.16 Sodium Chloride Crystal Lattice

Properties of Ionic Solids

Some of the properties of Ionic solids are,

1. In ionic solids, the cations and anions are closely packed into a compact specific geometrical shape and have strong ionic bond.
2. They are solid and usually very hard at room temperature. They never exist in liquid or gaseous form at ordinary temperature and pressure.
3. Ionic solids are brittle. They shatter easily by hammering as shown in figure 6.17.
4. Ionic solids have high melting points and heats of fusion (ΔH_{fus}).
5. These solids do not conduct heat and electricity because the ions can vibrate only about their fixed positions. However, in the molten state (that is, when melted) or dissolved in water, they conduct electricity.
6. They are soluble in polar solvent like water.

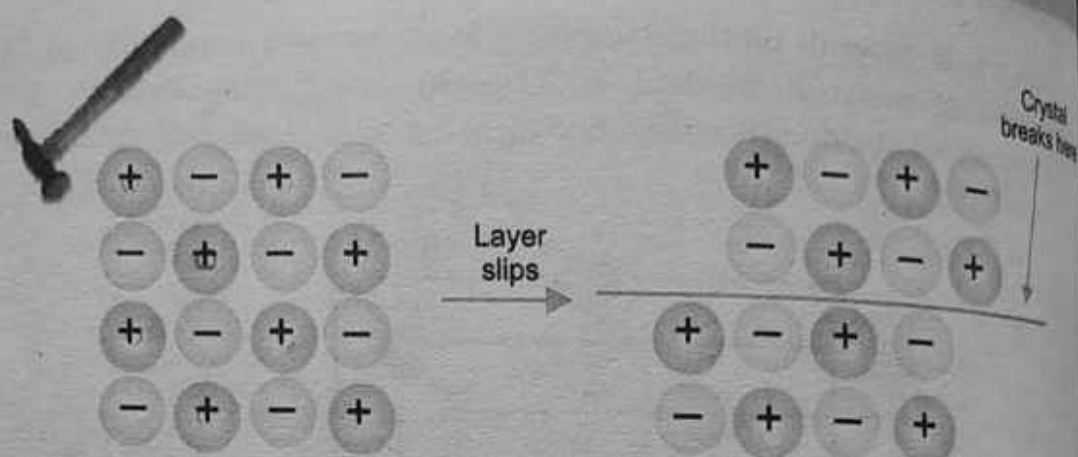


Figure 6.17 An Ionic Crystal is Brittle and Breaks by Hammering

6.5.2 Covalent Solids

In covalent solids (sometimes called covalent network crystals), atoms are held together entirely by covalent bonds in an extensive three-dimensional rigid network. No separate molecules are present in covalent solids, as in the case of molecular solids. Covalent bonds in these crystals are very strong and a huge amount of energy is needed to break these bonds. Some examples of covalent crystals are diamond, silicon carbide etc.

Well-known examples are the two allotropes of carbon: diamond and graphite as shown in figure 6.18.

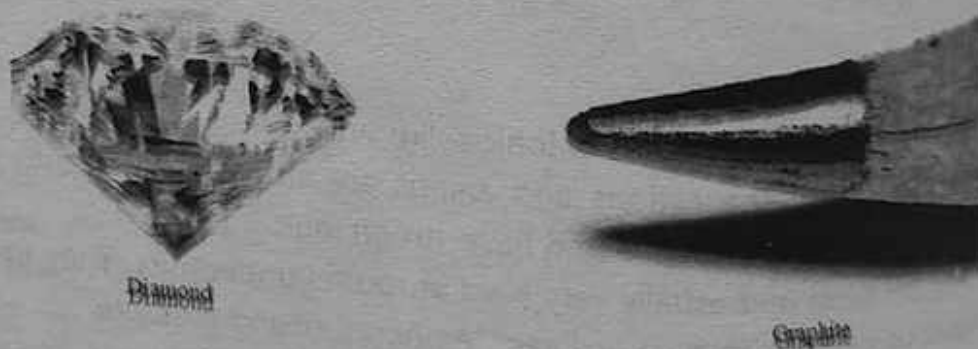


Figure 6.18 Diamond and Graphite

Properties of Covalent Solids

Properties of covalent solids are,

1. Covalent solids are also very hard and cannot be broken easily.
2. They have high melting point and heat of fusion.
3. They are poor conductor of heat and electricity except graphite.
4. They are usually insoluble in polar solvents.

6.5.3 Metallic Solids

In metallic solids, the metal atoms are held together by a special type of bonding, called metallic bond, which is totally different from ionic or covalent bond.

In metals, the electrons in the outer most orbital of the atoms are generally very loosely bound. Thus, they have high mobility and can move freely from one place to another inside the metallic crystals lattice, much like the molecules in a gas. These are called conduction electrons, or free electrons. The free electrons are uniformly distributed throughout the metals lattice. The metals, by losing these conduction electrons, are transformed into positive ions. Thus a columbic interaction between the positive ion and the negative electrons arises which is termed as the metallic bond. Examples of metallic crystals are copper, aluminum, silver, iron, sodium etc.

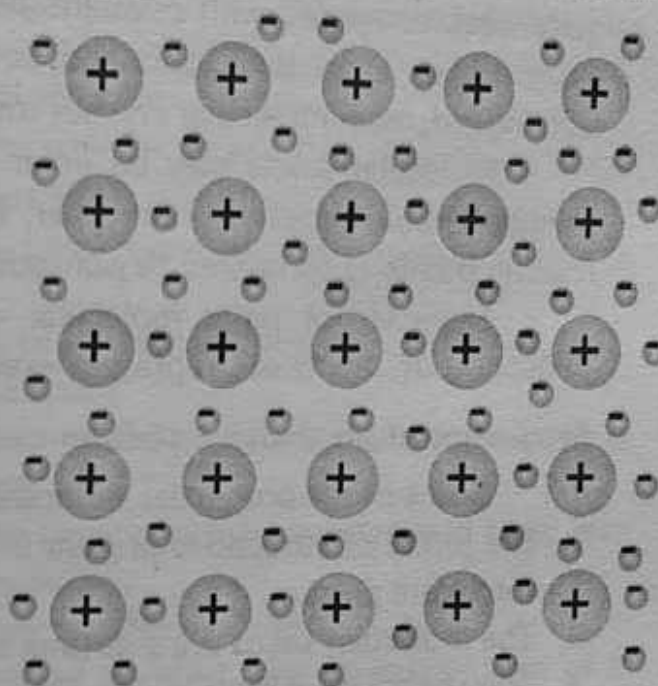


Figure 6.19 Internal Structure of Metallic Solids

Properties of Metallic Solids

Some of the properties of metallic solids are,

1. Metallic solids have usually compact structure and the atoms are closely packed together.
2. They are hard and have high melting point (A few of them are very soft and can be cut with a knife, e.g. sodium).
3. These crystals have metallic luster.
4. The free conduction electrons make the metallic solids good conductors of heat and electricity.
5. They are malleable (could be transformed into sheets) and ductile (could be drawn into wires).

6.5.4 Molecular Solids

Molecular solids consist of atoms or molecules held together by Van der Waal's forces.

Examples of molecular solids are I_2 , P_4 and S_8 . In general, except in ice, molecules in molecular solids are packed together as closely as their size and shape allow. Because Van der Waals forces and hydrogen bonding are generally quite weak compared with covalent and ionic bonds, molecular solids are more easily broken apart than ionic and covalent crystals. These solids are relatively soft. Indeed, most molecular crystals melt below 200°C .

Molecular solids may be polar or non-polar. For example, the atoms in solidified noble gases are non-polar. Polar molecular crystals have usually higher melting points as compared to non-polar molecular crystals.

Examples of polar molecular crystal are ice and sugar while sulphur, phosphorous, iodine etc. represent example of non-polar molecular crystals.

Properties of Molecular Solids

Some of the properties of molecular solids are,

1. The forces of attractions present in these solids are very weak; Van der Waal's forces are present.
2. The molecular solids are soft (due to the presence of Van der Waal's forces).
3. They have low melting points.
4. Polar molecular solids are soluble in polar solvents and non-polar molecular solids are soluble in non-polar solvents.

Self-Assessment

1. Explain the significance of the unit cell to the shape of the crystal using NaCl as an example.
2. Name three types of packing arrangements and draw or construct models of them.
3. Name three factors that affect the shape of an ionic crystal.
4. Differentiate between ionic, covalent, molecular and metallic crystalline solids.
5. Explain the low density and high heat of fusion of ice.
6. Define and explain molecular and metallic solids.

Solid is the physical state of matter with definite shape and volume.

Particles in solids are closely packed and cannot move freely. They, however, vibrate about their mean position.

Kinetic energy in solid exists in the form of vibrational kinetic energy.

In solids, particles are closely packed so they have minimum empty spaces and rigid structure. This accounts for negligible diffusion and compressibility of the particles into each other.

Solids are classified into crystalline and amorphous solids.

Crystalline solids have definite geometrical shape with repetitive three-dimensional structure, while amorphous solids do not have.

Crystalline solids possess symmetry, have sharp melting points and specific cleavage planes.

The habit of crystal refers to the shape of a crystal in which it usually grows.

Anisotropy is the property of crystalline solids.

Polymorphism is the term used when two or more different crystalline substances having the same crystalline shapes exist.

Polymorphism is the occurrence of the same crystalline substance in more than one crystalline form under different conditions.

Allotropy is the occurrence of an element in different forms.

Transition temperature is the temperature at which one crystalline form of a substance changes to another form.

Crystal lattice is the location of particles in a crystalline solid which can be represented as points on a framework.

Unit cell is the smallest portion of a crystal lattice that shows the three-dimensional pattern of the entire lattice.

Unit cells have six parameters 3 edges (a , b , and c) and 3 angles (α , β , γ) and are called unit cell dimensions or crystallographic elements.

Coordination number is the number of atoms (or ions) surrounding an atom (or ion) in a crystal lattice.

Lattice energy is the amount of energy released when one mole of an ionic crystal is formed from gaseous ions of opposite charges.

Crystalline solids are classified into four categories. These are (i) Ionic solids, (ii) Covalent solids (iii) Metallic solids and (iv) Molecular solids, depending upon the forces present among the particles of the crystal.

Ionic, covalent and metallic solids are hard and have high melting point, while molecular solids are soft and have low melting points.

EXERCISE

Choose the Correct Option.

1. The crystal of ice is an example of
 - a. Metallic solid
 - b. Molecular solid
 - c. Covalent solid
 - d. Ionic solid
2. KNO_3 and NaNO_3 both have the atomic ratio of 1:1:3 in their crystals. The property is
 - a. Isotropy
 - b. Anisotropy
 - c. Isomorphism
 - d. Polymorphism
3. The number of centers of symmetry of a cubic crystal is/are
 - a. One
 - b. Two
 - c. Three
 - d. Six
4. A pair of compounds, which are isomorphous in nature is,
 - a. NaCl and KNO_3
 - b. MgO and ZnO
 - c. NaNO_3 and CdS
 - d. NaF and CaCO_3
5. Crystals show variation in physical properties depending upon the direction. The property is called
 - a. Isomorphism
 - b. Polymorphism
 - c. Anisotropy
 - d. Isotropy
6. The parameters of unit cell are
 - a. 4
 - b. 5
 - c. 6
 - d. 7
7. Sodium chloride (NaCl) on crystallization forms the
 - a. Face centered cubic lattice
 - b. Orthorhombic lattice
 - c. Body centered cubic lattice
 - d. Simple cubic lattice
8. The molecules of CO_2 in dry ice form the
 - a. Ionic crystals
 - b. Covalent crystals
 - c. Molecular crystals
 - d. Metallic crystal
9. The nature of bonds between atoms in graphite is
 - a. Ionic
 - b. Covalent
 - c. Molecular
 - d. Metallic
10. The example of metallic solid is
 - a. C
 - b. B
 - c. Si
 - d. Cu
11. In solid state, the crystals which are good conductors of heat and electricity are
 - a. Covalent
 - b. Ionic
 - c. Molecular
 - d. Metallic

2. When a crystalline substance conducts current in one direction but not through other directions of the crystal, this property is
- Anisotropy
 - Isotropy
 - Allotropy
 - Isomorphism
3. Crystals of the same substance can co-exist in equilibrium with each other at its
- Boiling point
 - Melting point
 - Transition temperature
 - Heat of fusion
4. Crystal lattice is an arrangement of particles in
- Four dimensions
 - Three dimensions
 - Two dimensions
 - One dimension

Short Questions

- Briefly explain the term unit cell and crystal lattice.
- Why are crystalline solids anisotropic?
- Give the reason that metallic crystals are good conductors of electricity but ionic crystals are not.
- Differentiate between crystalline and amorphous solids.
- Justify that crystalline solids have sharp melting points.
- What is transition temperature? Give examples.
- Explain that isomorphous substances have usually the same atomic ratio.
- Give the reason that covalent crystals are hard while molecular crystals are soft.
- Define lattice energy and give examples.
- Differentiate between polymorphism and isomorphism.

Descriptive Questions

- Explain the kinetic molecular interpretation of solids.
- Discuss in detail the following properties, keeping in view the Kinetic Molecular Theory.
 - Diffusion
 - Compression
 - Expansion
 - Motion of molecules
- Discuss in detail a sodium chloride lattice.
 - Describe the following properties of crystalline solids:
 - Habit of a crystal
 - Cleavage planes
 - Crystal growth
 - Anisotropy
 - Symmetry.

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3. Differentiate between the following pairs:
 - (i) Ionic solid and molecular solid
 - (ii) Lattice energy and crystal lattice
 - (iii) Plane of symmetry and axis of symmetry
4. (a) Define allotropy. Use oxygen and sulphur as an example to illustrate allotropes.
(b) Explain the low density and high heat of fusion of ice.
5. (a) Define and explain molecular and metallic solids
(b) What are the features of three types of packing arrangements in a crystal system and construct models of them?
6. (a) Write down the three factors that affect the shape of an ionic crystal.
(b) What is meant by unit cell of crystal? Sketch the unit cell of NaCl .

Project

- Collect the different household items and classify them as amorphous or crystalline substances.

Table salt	Sugar	Washing soda
Baking soda	Ice	Glass