

Faculty of Science.



Solid State Chemistry

A part of:

Physical Chemistry (III) (Chm 421) course.

for 4th year Science students, Chemistry group.

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Solid State Chemistry





The matter has three basic states, **Solid**, **Liquid** and **Gas** (**Plasma** or ionized gas is considered as a fourth state of matter.)

- Gases and liquids can flow and take up the shape of their container. Solids, on the other hand, are rigid and have a definite volume and shape.
- In both gases and liquids, atoms, ions and molecules translate randomly as well as rotate and vibrate which explains the ability of gases and liquids to flow. In solids, atoms, ions and molecules are held together by relatively strong chemical forces. So that, They do not translate or rotate and can only oscillate about their mean positions (vibration) which explains why solids are rigid and have definite

shape.

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Solid State is generally characterized by rigidity, mechanical strength, and incompressibility due to close packing of constituent particles of matter (atoms, molecules or ions). The atoms, molecules or ions are held together by strong forces which adhere them to occupy fixed positions (called lattice points) in a threedimensional structure called the solid lattice.



2- Types of solids

Broadly speaking, solids are of two types :

(a) Crystalline solids; also called true solids (b) Amorphous solids (amorphous = no form)

<u>A crystalline solid</u> exists as small crystals, each crystal having a characteristic geometrical shape. In a crystal, the atoms, molecules or ions are arranged in a regular, repeating three dimensional pattern called the crystal lattice. <u>An amorphous solid</u> has atoms, molecules or ions arranged in a random way without ordered crystalline lattice.

Examples





Two-dimensional representation of crystalline solid and an amorphous solid. Each substance has the formula A_2O_3 . *A* is shown by \bullet and *O* is shown by \bigcirc .



3- Isotropy and Anisotropy of solids

Isotropic material is that material in which the physical and mechanical properties are the same in all directions and **anisotropic** material is that material in which the physical and mechanical properties differ with orientation

Amorphous substances are said to be isotropic because they exhibit the same value of any property (e.g. Refractive index, Thermal and electrical conductivities, Coefficient of thermal expansion, etc) in all directions. This is due to the random arrangement of particles in the amorphous substances (as in liquids) which make all the directions to be equivalent and properties are independent of direction.

In the figure, When a property is measured along A and B directions, the value along A direction will be similar to that along B direction. This is so because there are two types of particles along the two directions.







Crystalline substances, on the other hand, are **anisotropic** and the magnitude of a physical property varies with directions. For example, in a crystal of silver iodide, the coefficient of thermal expansion is positive in one direction and negative in the other. Similarly, velocity of light in a crystal may vary with direction in which it is measured.



In the figure, When a property is measured along A and B axes, the value along A axis will be different from that along B axis. This is so because there is only one type of particles along A axis while there are two types of particles in alternate positions along B axis.

4- The habit of crystal and the interfacial angles

The external shape is called **the habit of the crystal**, the plane surfaces of the crystal are called **faces** and the angles between the faces are referred to as the **interfacial angles**.

The external appearance or size of crystals (Habit of the crystal) of a substance may be different depending on the conditions of crystal growth. For example, slow growth from a slightly super-saturated solution or a very slowly cooling solution gives large crystals. In addition, in the presence of certain impurities, different faces grow at different rates and give rise to many forms. However, the interfacial angles are always the same for a certain substance.



Interfacial angle



Interfacial angles are always the same.

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5- Symmetry of crystals

In addition to the angles, another important property of crystals is their symmetry. Symmetry in crystals may be due to a plane, a line or a point. Accordingly there are three types of symmetry elements associated with a crystal. These are called the Elements of Symmetry

1- Plane of Symmetry

A crystal is said to have a plane of symmetry if it can be divided by an imaginary plane into two equal parts, each of which is the exact mirror image of the other.



2- Axis of Symmetry

An axis of symmetry is an imaginary line drawn through the crystal such that during rotation of 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.



3- Centre of Symmetry (Point 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. The crystal may have a number of planes of symmetry or axes of symmetry but it can have only one centre of symmetry



Point of symmetry





6- Crystal structure

The particles (atoms, ions or molecules) in crystals are highly ordered as is evident from their 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**.

To describe the structure of a crystal it is convenient to view it as being made of a large number of basic units. The simple basic unit or the building block of the crystal lattice is called **the Unit cell**.



How to Represent Crystal Lattice and Units Cells ?

The overall shape and structure of a crystal system is governed by that of the unit cell of which it is composed. The unit cell of any crystal lattice of a substance is depicted by showing the position of particles in space. These positions are represented by bold dots (or circles) and are referred to as **lattice points or lattice sites**.

The **simple or primitive unit cell** has one atom or ion at each corner. Also, there may be atoms or ions in faces and interior of the cell. A cell with points at its faces is called **face-centered unit cell** and a cell with an interior point is called **body-centered unit cell**.







Primitive unit cell

Face-centered unit cell

Body-centered unit cell

Parameters of the Unit Cells

The unit cells may be characterized by the following two parameters :

1- Relative lengths of the edges along the three axes (a, b, c).

2- The three angles between the edges (α , β , γ).

According to these parameters, there are seven types of primitive unit cells are known

Crystal system	Relative axial length	Angles
Cubic (isometric)	a = b = c	$\alpha = \beta = \gamma = 90^{\circ}$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^{\circ}$
Rhombohedral (trigonal)	a = b = c	$\alpha = \beta = \gamma \neq 90^{\circ}$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^{\circ}, \gamma = 120$
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^{\circ}, \gamma \neq 90^{\circ}$
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^{\circ}$

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7- Cubic unit cell

These are the simplest unit cells that are particularly important for two reasons. **<u>First</u>**, a number of ionic solids and metals have crystal lattices comprising cubic unit cells. <u>**Second**</u>, it is relatively easy to make calculations with these cells because in them all the sides are equal and the cell angles are all 90^o.

Three types of Cubic Unit Cells

1- Simple cubic unit cell

Is one in which the atoms or ions are occupying only the corners of the cube.

2- Body-centred cubic unit cell

Is one which has one particle at the centre of the cube in addition to the particles at the







corners.

3- Face-centred cubic unit cell

Is one which has one particle at each of the six faces of the cube apart from the particles at the corners.





How to compute atoms or points in a unit cell ?

In counting the number of atoms (or points) per unit cell, we must keep in mind that atoms on corners of faces are shared with adjoining cells. Therefore the number of atoms in a cubic unit cell may be computed as follows.

1- Eight unit cells share each corner atom.

At each corner we have $\rightarrow 1/8$ atom At 8 corners we have $\rightarrow 1/8 \times 8 = 1$ atom

Therefore, the simple cubic unit cell contains the equivalent of one atom.



2- Each face-centred atom is shared by two unit cells.

8 corners = 1 atom 6 face-centred sites = $6 \times 1/2 = 3$ atoms Total equivalent atoms = 1 + 3 = 4



Therefore, the face-centred unit cell contains the equivalent of four atoms.

3- Each body centred unit cell contains a central unshared atom

8 corners = 1 atom central unshared atom 1 x 1 = 1 atom Total equivalent atoms = 1 + 1 = 2



Therefore, A body centred unit cell contains the equivalent of two atoms.

Calculation of mass of the unit cell

Mass of the unit cell can be calculated from the number of atoms in the unit cell by multiply the mass of one atom by the number of atoms in the unit cell

the mass of one atom = $\frac{\text{molar mass of the substance}}{\text{Avogadro's number}}$

<u>Solved Problem 1</u>: The unit cell of metallic gold is face-centred cubic

- (a) How many atoms occupy the gold unit cell?
- (b) What is the mass of a gold unit cell ?

Solution

Eight corners at 1/8 atom each = 1 atom Six faces at 1/2 atom each = 3 atoms

 \therefore 4 atoms occupy the gold unit cell.

Mass of gold atom = $\frac{\text{molar mass}}{\text{Avogadro's number}} \implies \frac{197 \text{ g/mol}}{6.022 \times 10^{23} \text{ Au atoms/mol}} = 32.71 \times 10^{-23} \text{ g}$

the mass of a gold unit cell = $4 \times 32.71 = 130.9 \times 10^{-23} \text{ g}$

8- Classification of crystals on the basis of bonds

Crystals can also be classified on the basis of the bonds that hold the ions, molecules or atoms together in the crystal lattice. So that, there are four type of crystals:

A- Ionic crystals

B-Molecular crystals

C- Network covalent crystals

D-Metallic crystals

9- Ionic crystals

In an ionic crystal the lattice is made of positive and negative ions held together by ionic bonds. The positive and negative ions attract one another and pack together in an arrangement so that the attractive forces maximize. Each ion is surrounded by neighbors of opposite charge and there are no separate molecules. Since the ions are fixed in their lattice sites, typical ionic solids are hard and rigid with high melting

points.



Even though the ionic solids are hard, they are brittle. They shatter easily by hammering. By hammering, a layer of ions slips away from their oppositely charged neighbors to be closer to ions of the same charge which increases the electrostatic repulsions along the displaced plane causes the crystal to break. 20

Lattice energy of an lonic crystal

The positive and negative ions in the ionic crystal are held together by electrostatic forces. The bond energy is expressed in terms of the lattice energy which may be defined as : The change in enthalpy (heat change) when 1 mole of a solid crystalline substance is formed from its gaseous ions.

Determination of lattice energy

The lattice energy of an ionic crystal can be found by applying Hess's law. The formation of an ionic solid from its elements can expressed as occurring directly in one step or indirectly as the sum of the series of steps. Let us illustrate by taking example of NaCl.



A Born-Haber cycle for the formation of NaCl crystal from its elements. Enthalpy change for direct formation. The enthalpy change for the direct formation of sodium chloride from sodium metal and chlorine is -411 kJ.

$$Na(s) + \frac{1}{2}(Cl_2) \longrightarrow NaCl(s)$$
 $\Delta H^{\circ} = -411 \text{ kJ}$

Enthalpy change by indirect steps. The direct enthalpy change of NaCl stated above is equal to enthalpy changes of five steps by which the formation of NaCl can be accomplished.

Step 1. Conversion of sodium metal to gaseous atoms (sublimation).

$$Na(s) \longrightarrow Na(g) \qquad \Delta H_1^{o} = +108 \, kJ$$

Step 2. Dissociation of chlorine molecules to chlorine atoms. The enthalpy of dissociation is 121 kJ per mole of chlorine.

$$\frac{1}{2}\text{Cl}_2 \longrightarrow \text{Cl}(g) \qquad \qquad \Delta \text{H}_2^{o} = +121 \text{ kJ}$$

Step 3. Conversion of gaseous sodium to sodium ions by losing electrons. The enthalpy of ionisation is the ionisation energy, 495 kJ/per mole of sodium atoms.

$$Na(g) \longrightarrow Na^+(g) + e^- \Delta H_3^o = +495 \text{ kJ}$$

Step 4. Chlorine atoms gain an electrons to form chloride ions. The energy released is the electron affinity of chlorine –348 kJ.

$$Cl + e^- \longrightarrow Cl^-(g)$$
 $\Delta H_a^o = -348 \text{ kJ}$

Step 5. Sodium and chloride ions get together and form the crystal lattice. The energy released in this process is the negative of lattice energy.

$$Na^+(g) + Cl^-(g) \longrightarrow NaCl(s)$$
 $\Delta H_5^{o} = -$ (lattice energy)

The lattice energy can be calculated by equating the enthalpy of formation of NaCl, -411 kJ, to the sum of the enthalpy changes for the five steps.

 $\Delta H^{o}_{1} + \Delta H^{o}_{2} + \Delta H^{o}_{3} + \Delta H^{o}_{4} + \Delta H^{o}_{5} = -411 \text{ kJ}$ 108 kJ + 121 kJ + 495 kJ - 348 kJ - lattice energy = -411 kJ By solving this equation we get

Lattice energy = $+787 \text{ kJ mol}^{-1}$

10- Molecular crystals

In molecular crystals, molecules are the structural units and are held together by van der Waals' forces to form a tightly packed pattern. When this type of crystal melts, it is only the weak van der Waals forces that must be overcome. Therefore molecular solids have low melting points. Most organic substances are molecular

solids.



Arrangement of CO molecules in the crystal lattice

Crystal lattice of dry CO_2 (**Dry ice, or frozen carbon dioxide**) is the best example of a molecular solid. The van der Waals' forces holding the CO_2 molecules together are weak enough so that dry ice passes from solid state to gaseous state at -78°C.

11- Network covalent crystals

In this type of crystals, atoms occupy the lattice sites and are bonded to one another by covalent bonds. The atoms interlocked by a network of covalent bonds to produce a crystal which is considered to be a single giant molecule. Such a solid is called a network covalent solid or covalent solid. Due to the strong covalent bonds, these crystals are very hard and have very high melting points.

Diamond offers the best example of a network covalent solid. It consists of carbon atoms bonded to one another in a threedimensional pattern to form the crystal. However, each carbon is sp³ hybridized and is bonded to four neighbouring carbon atoms towards the arranged corners of а tetrahedron.



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The crystal structure of a diamond is a face-centered cubic and as the diamond crystal made of carbon atoms joined by a network of strong covalent bonds, it is considered as the hardest substance known and has an extremely high melting point (3550°C).

Diamond and graphite as two allotropes of carbon

Allotropes are different structural forms of the same element and can exhibit quite different physical properties and chemical behaviors.

Diamond and graphite are two allotropes of carbon are covalent network solids which differ in the bonding geometry of the carbon atoms. Diamond has the tetrahedral geometry, while in graphite the carbons bond with each other in the trigonal planar arrangement.



Face-centered cubic unit cell



Diamond



Graphite

In graphite, each atom of carbon forms three covalent bonds, leaving one delocalized electron in each outer orbital to create multiple "free electrons" within each plane of carbon which grants graphite electrical conductivity. Its melting point is high, due to the large amount of energy required to rearrange the covalent bonds. However, the layers in graphite can be easily displaced, so the substance is malleable which explains the use of graphite in pencils.





12- Metallic crystals

The crystals of metals consist of atoms present at the lattice sites and held together by a metallic bond. The valence electrons of the metal atoms are considered to be delocalized leaving positive metal ions and move throughout the vacant spaces between the ions. The electrostatic attractions between the metal ions and the electron cloud constitute the metallic bond. So that, a metal crystal may be described as having positive ions at the lattice positions surrounded by mobile electrons throughout the crystal.



The electron sea model explains well the properties of metals. The mobile electrons in the crystal structure make metals excellent conductors of heat and electricity. On application of force, say with a hammer, metals can be deformed without breaking as the metal ions in the crystal change positions while the attractive force between ions and the electron cloud remains the same. On application of force, positive ions can be moved within the sea of electrons without materially changing the environments. That is why metals can be worked into sheets or foils without cracking.





Structure of metal crystals

The individual atoms in a metallic crystal lattice can be thought of as hard spheres. The spherical atoms are packed together in the lattice very efficiently in geometrical arrangements so as to leave minimum interspaces. A layer of uniform spheres can be arranged either as in (a) or (b). Clearly the second pattern uses space more efficiently. The metallic crystals are of the second type i.e., close packing.



The three dimensional metallic crystals consist of closely packed layers stacked one over the other. The spheres forming the second layer fill the holes or voids in the first layer and the spheres of the third layer fill the voids in the second layer. Depending upon the geometrical arrangements of spheres in the three layers, the close-packed metallic crystals are of two types :

(a) Hexagonal close-packed (hcp)

In the hexagonal close-packed structure, the bottom layer (A) and the top layer (A) have three spheres in similar orientation. The middle layer (B) consists of six spherical atoms. The three spheres in the top and the bottom layer fit into the same voids on either side of the middle layer. Each sphere in this structure is in contact with 12 neighboring spheres, six in its own layer, three in the layer above and three in the layer below. So, the coordination number of the closepacked structure is 12. In the overall close-packed structure, the layers repeat in the manner ABABAB. The examples of metals having hexagonal close-packed structures are Ba, Co, Mg and Zn.



(b) Cubic close-packed (ccp)

In the cubic close-packed (ccp) pattern the top layer (C) and the bottom layer (A) are oriented in opposite directions. Therefore, the three spheres in the top layer do not lie exactly on the spheres in the bottom layers and the coordination number is 12 as in the hcp structure. In ccp structure, the layers are repeated in the order ABCABCABC. By turning the whole crystal you can see that the ccp structure is just the facecentred cubic structure. Many metals including Ag, Au, Ca, Ni, have the ccp structure.



13- Crystal defects

So far in our discussion of crystalline substances, we have assumed them to be perfect crystals. A perfect crystal is one in which all the atoms or ions are lined up in a precise geometric pattern. But crystals are never actually perfect. The real crystals that we find in nature or prepare in the laboratory always contain imperfections in the formation of the crystal lattice. These crystal defects can affect the physical and chemical properties of a solid.

The common crystal defects are :

- (a) Vacancy defects
- (b) Interstitial defects
- (c) Impurity defects

(a) Vacancy defects

When a crystal site is rendered vacant by removal of a structural unit in the lattice, the defect is referred to as the vacancy defect. In an ionic crystal, a cation and anion may leave the lattice to cause two vacancies. Such a defect which involves a cation and an anion vacancy in the crystal lattice is called a Schottky defect. This defect is found in the crystals of sodium chloride and cesium chloride (CsCl).



(b) Interstitial defects

Here, an ion leaves its regular site to occupy a position in the space between the lattice sites (interstitial position). This causes a defect known as Interstitial defect or Frenkel defect. As shown in the figure, ordinarily the cation moves as it is smaller than the anion and can easily fit into the vacant spaces in the lattice. Thus in AgCl crystal, Ag+ ion occupies an interstitial position leaving a vacancy (or hole) at the original site



Ag Cl Ag Cl Ag Cl Ag Cl Ag Cl Ag Cl Ag Ag Cl Cl Ag Ag Cl Ag Cl Ag Cl Ag (a)



(c) Impurity defects

These defects arise due to the corporation of foreign atoms or ions in regular lattice sites or interstitial sites. When foreign particles are substituted for normal lattice particles, it is called **substitution impurity**. When foreign particles are trapped in vacant interstitial spaces, it is called **interstitial impurity**. Both types of impurities can affect the properties of solids.



14- Metal alloys

Other elements can be introduced into a metallic crystal to produce substances called alloys. Alloys are of two types.

(1) Substitutional alloy in which the host metal atoms are replaced by other metal atoms of similar size. For example, in brass (an alloy of copper and zinc) about one-third of the copper atoms have been substituted by zinc atoms.



(2) Interstitial alloy in which some of the holes in close-packed metal structure are occupied by small atoms. For example, steel is an alloy of iron and carbon. It contains carbon atoms in the holes of an iron crystal.

presence of interstitial The atoms changes the properties of the host metal. Thus pure iron is relatively soft and malleable. The introduction of the carbon atoms forms the directional carbon-iron bonds (C–Fe). This makes the relative movement of spherical iron atoms rather difficult and the resulting steel is harder and stronger compared to pure iron.



15- Semiconductors

Metals are good conductors of electricity while elements like silicon and germanium are nonconductors at ordinary temperature. However, they exhibit appreciable conductivity by addition of impurities as arsenic and boron. The resulting materials are called semiconductors.

In silicon and germanium crystals, each atom is covalently bonded to four neighbors so that all its four valence electrons are tied down, so that they are nonconductors. Suppose an atom of As is introduced in place of silicon or germanium in the crystal lattice. As has five valence electrons, four of which will be utilized in the formation of covalent bonds and the remaining electron is free to move through the lattice which enhance conductivity 39



Semiconductors which exhibit conductivity due to the flow of excess negative electrons, are called n-type semiconductors (n for negative).

If boron atom be introduced in place of silicon atom in the crystal lattice. A boron atom has only three valence electrons and can form only three of the four bonds required for a perfect lattice. Thus it is surrounded by seven electrons only. As a result, an electron vacancy or a 'positive hole' is formed in the lattice. Another electron from the bond of the adjacent Si atom moves into this hole, completing the four bonds on the B atom. This electron also leaves a hole at its original site. In this way electrons move from atom to atom through the crystal structure and the holes move in the opposite direction. Which improve the conductivity.

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Semiconductors which exhibit conductivity due to the positive holes, are called p-type semiconductors (p for positive).

Solar cells as an application of semiconductors

It is a device to convert light energy into electrical energy. It is made of a thin wafer of silicon containing a tiny amount of arsenic (ntype semiconductor). A thin layer of silicon containing a trace of boron is placed on the surface of the wafer. Thus a junction, called the p-n junction, exists between the p-type silicon and n-type silicon. When the cell is exposed to sunlight, energy from sunlight excites electrons from n-type silicon to the holes of the p-type silicon. From the p-type silicon, the electrons flow through the external circuit as an electric

n-Type silicon Sunlight p-Type silicon

current.

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