Solid State

1. Solid State

Solid state is the state of matter in which particles are closely packed and have fixed positions. They are mainly classified on the basis of incompressibility, rigidity and their mechanical strength. The molecules or atoms or ions that make a solid structure are closely packed and held together through strong cohesive forces. These particles are not allowed to move randomly. The molecular, ionic or atomic arrangements are well ordered in the solids.

Solids such as NaCl, Sulphur or Sugar have a proper geometric configurations and hence they are known as crystalline solids. The particles are arranged in well-defined pattern in a 3-D network. On the contrary, those solids (glass, rubber, plastics) which do not have regular arrangement of atom, molecules or ions are known as amorphous solids.

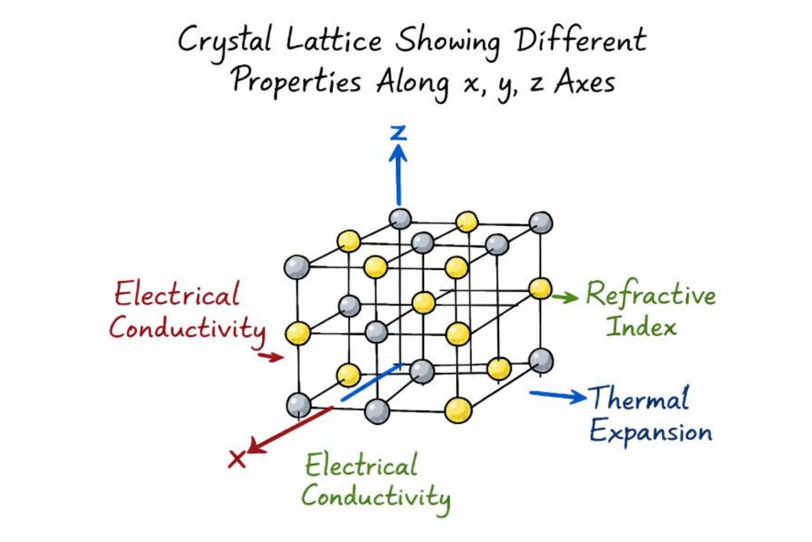
Key characteristics of solids include:

- **Definite shape and volume**
- **Strong intermolecular/interionic forces**
- **Low compressibility**
- **High density**

2. Types of Solids:

	Crystalline	**Amorphous**
Geometry	Definite and regular geometry due to definite & ordered arrangement in 3-D space. Have a long-range order.	Does not have any pattern of particle arrangement and no definite geometry. Have a short-range order
Melting Point	Sharp melting point. Abruptly changes into liquid state. Solid state conditions are mainly applied for crystalline.	Range of melting point. Slowly changes into liquid state. They are normally considered “liquid at all temperatures”.

Isotropy/Anisotropy	Shows varying electrical & thermal conductivity, mechanical strength and refractive index are in different direction. They are anisotropic in nature.	Shows electrical & thermal conductivity, mechanical strength and refractive index are same in every direction. They are isotropic in nature.



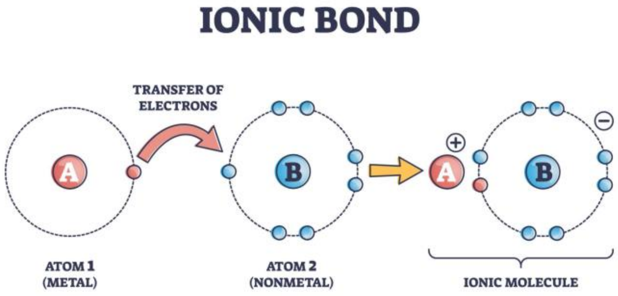
Quasicrystal was discovered in 1984 and they are formed when certain molten alloys are very rapidly cooled. Unlike amorphous solids, quasicrystals have both short-range and long-range order. But beside despite their long-range order, the symmetry of the Quasicrystal structure is incompatible with translational periodicity and so is of a type forbidden for ordinary crystals.

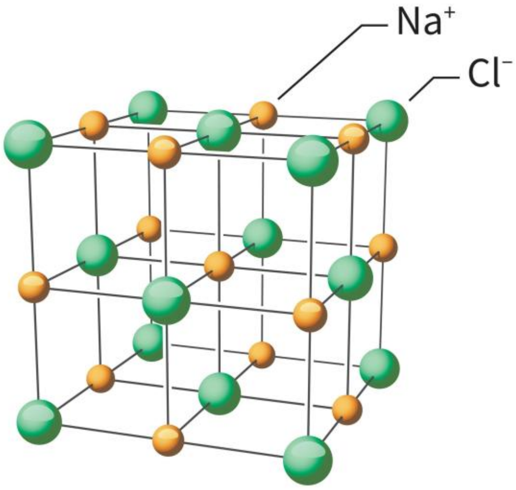
3. Chemical Bonding in Solids

Chemical bonding in solids refers to the forces that hold atoms, ions, or molecules together in a solid lattice. The type of bonding determines the structure, stability, and physical properties of solids. Broadly, solids are classified based on bonding into:

1. Ionic solids
2. Covalent (network) solids
3. Metallic solids
4. Molecular solids

a. Ionic Solids





These are made up of an array of positive and negative ions which are held together by the electrostatic attraction between oppositely charged ions.Ionic bonding arises due to electrostatic attraction between oppositely charged ions formed by electron transfer from one atom to another.

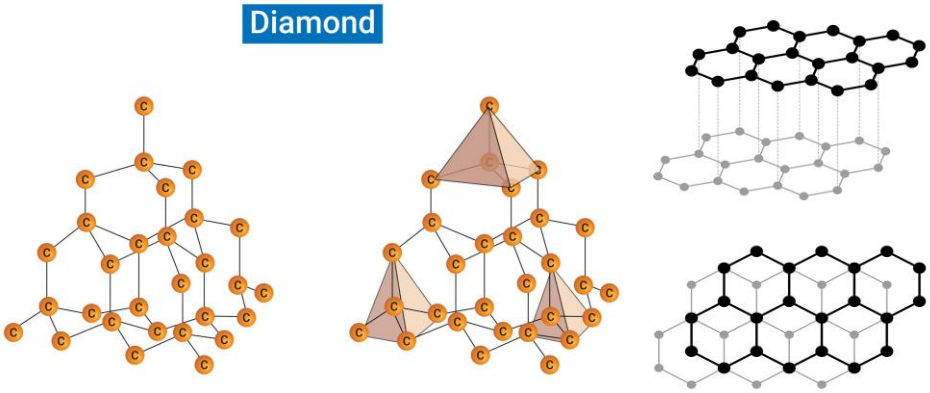
- Metal → loses electron → cation
- Non-metal → gains electron → anion

Example: NaCl, KBr, MgO

Characteristics of Ionic Solids

- Strong electrostatic forces
- Hard and brittle solids
- High melting and boiling points
- Soluble in polar solvents (water)
- Conduct electricity in molten or aqueous state

b. Covalent (Network) Bonding in Solids



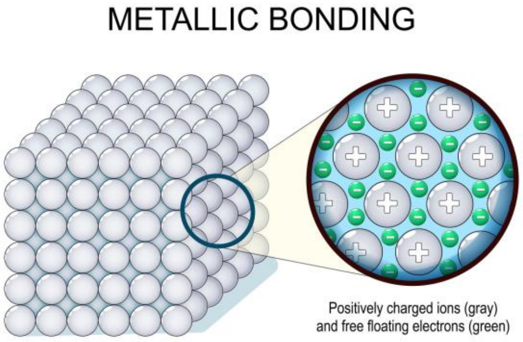
Covalent (or non-metallic network) crystals consist of an “infinite” network of atoms that are held together by polar or nonpolar covalent bonds with no individual molecules being present Atoms are linked by sharing of electrons, forming a continuous 3-D network.

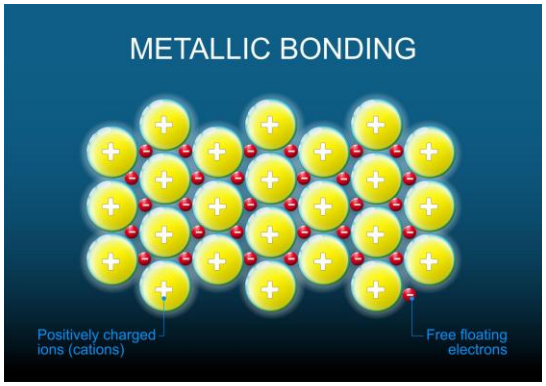
Characteristics

- Very hard solids
- Very high melting point
- Poor electrical conductivity (except graphite)
- Insoluble in most solvents

Important Examples: Diamond, Graphite, Silicon carbide (SiC), Quartz (SiO_2)

c. Metallic Bonding in Solids





They are mostly composed of bonded metal atoms; some of the valence electrons are delocalized over the entire metal and hold the crystal together. Positive metal ions arranged in lattice surrounded by a sea of delocalized electrons.

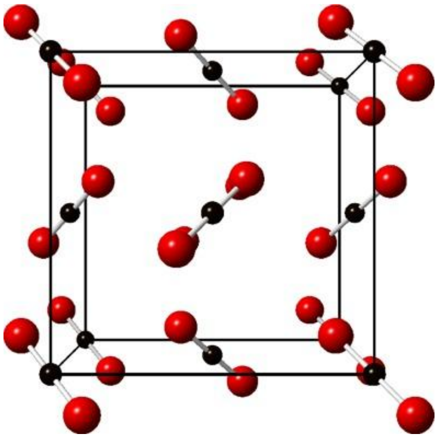
Characteristics

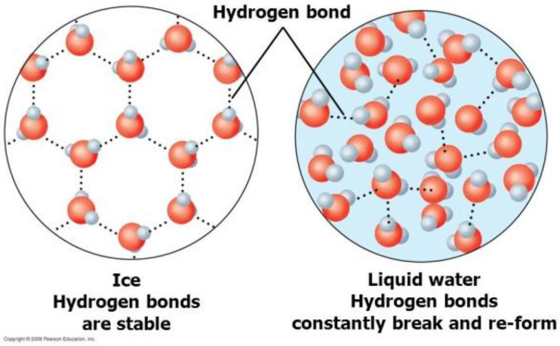
- Good electrical and thermal conductivity
- Malleable and ductile
- Shiny (metallic luster)
- Variable hardness

Strength of Metallic Bond Depends on Number of valence electrons, Charge on metal ions, and Size of metal atoms

Examples: Cu, Fe, Al, Na, Ag

d. Molecular Solids





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Mostly composed of individual molecules. The atoms within each molecule are held together by covalent bonds and relatively weak intermolecular forces (such as dipole-dipole or Hydrogen bonding) hold these molecules together in the crystalConstituent particles are molecules held together by intermolecular forces.

Types of Intermolecular Forces: Van der Waals forces, Dipole–dipole forces, Hydrogen bonding

Characteristics

- Soft solids
- Low melting points
- Poor electrical conductivity

Examples: Ice (H_2O), solid CO_2, iodine, naphthalene

4. Laws of Crystallography

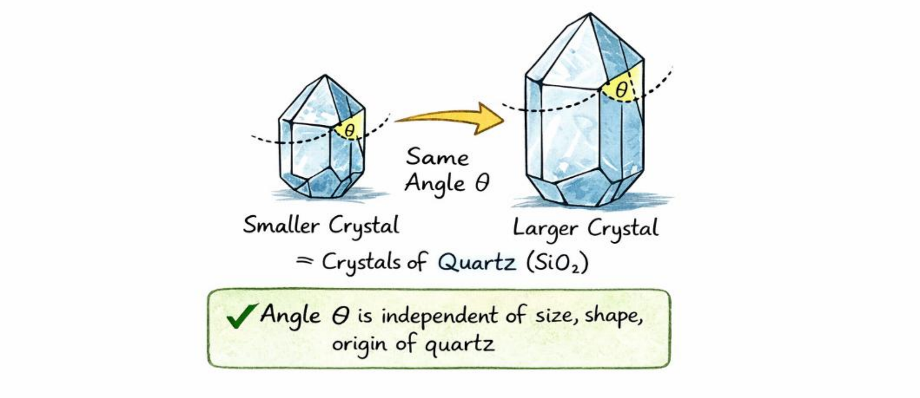
(a) Law of Constancy of Interfacial Angles: The law of constancy of interfacial angles states that the angle between any two corresponding faces of crystals of the same substance is always constant, irrespective of the size, shape, or origin of the crystal. Crystals of a substance may grow under different conditions such as temperature, pressure, or time. Due to this, their external shape and size may differ. However, the internal arrangement of atoms or ions is fixed and identical for a given substance. Since interfacial angles depend on the internal atomic structure, these angles do not change. Therefore, even though crystals look different externally, the angles between corresponding faces remain the same. This law proves that crystals have a regular and ordered internal structure.

A Classic Example Quartz (SiO_2):

- ➢ Quartz crystals are found in many shapes and sizes in nature.
- ➢ Some crystals are long and thin, while others are short and thick.
- ➢ Despite this difference, the angle between the same pair of faces in all quartz crystals is always the same.

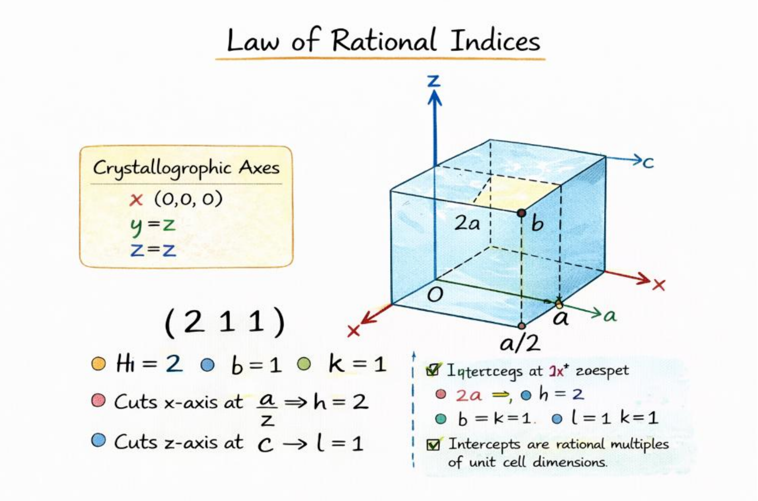
Applications:

- ➢ Helps in identification of minerals
- ➢ Confirms the crystalline nature of solids
- ➢ Forms the basis of crystallography



(b) Law of Rational Indices: The Law of Rational Indices states that the intercepts made by the faces of a crystal on the crystallographic axes are either equal to the unit cell dimensions or simple whole-number multiples of them. In other words, the intercepts of a crystal face on the x, y, and z axes are always in simple rational ratios such as 1, 1/2, 2, 3, etc., and never irrational values. In crystalline solids, atoms or ions are arranged in a regular and periodic three-dimensional lattice. Due to this regular arrangement, crystal faces intersect the crystallographic axes at fixed and orderly positions. These positions correspond to simple fractions or multiples of the unit cell lengths (a, b, c). As a result, the intercepts of any crystal face can be expressed as rational numbers. This law explains why crystal planes can be represented mathematically and forms the foundation of the Miller indices system.

The intercepts made by crystal faces on crystallographic axes are simple whole-number ratios of the unit cell dimensions.



Basis of Miller indices

Miller indices are a set of three integers (h k l) used to represent the orientation of crystal planes in a crystal lattice. The basis of Miller indices lies in the fact that crystal faces intersect the crystallographic axes at rational distances, as explained by the Law of Rational Indices.

5. Miller Indices (h k l)

Miller indices are a set of three integers (h k l) used to describe the orientation of crystal planes and directions in a crystal lattice. They provide a concise and universal way to specify lattice geometry. In general, Miller indices (h k l) are the **reciprocals of the intercepts** made by a crystal plane with crystallographic axes, reduced to the smallest integers.

They are extensively used in:

- X-ray diffraction
- Crystal structure determination
- Materials science & solid-state physics

Importance of Miller Indices

- Indexing X-ray diffraction peaks
- Identifying crystal orientation
- Explaining anisotropic properties
- Predicting slip systems in metal

Steps to Determine (h k l)

a. Find intercepts of the plane on x, y, z axes in terms of lattice constants (a, b, c).
b. Take reciprocals of intercepts.
c. Clear fractions to obtain smallest integers.
d. Enclose in parentheses: (h k l)

Example:

1. Intercepts: a, b, ∞ → Reciprocals: 1, 1, 0 → Miller indices = (110)

2. Plane cuts axes at: x = a, y = 2b, z = 3c

Intercepts → (1, 2, 3)
Reciprocals → (1, 1/2, 1/3)
Multiply by 6 → (6, 3, 2)

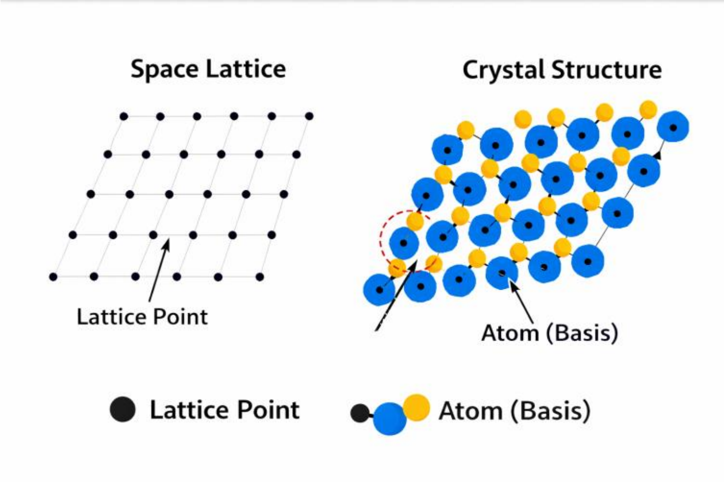
Miller indices = (6 3 2)

6. Crystal structures

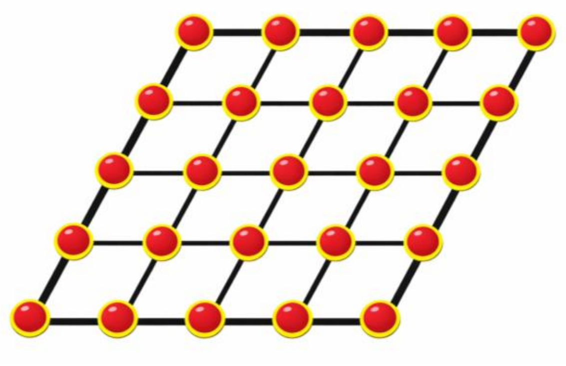
A crystal consists of structural unit which called the basis or the motif which repeat themselves in three dimensions to generate the crystal structure. The environment of each repeated unit is same throughout the crystal except some of the surface deformities. These may be atom or molecules or ions or group of them. The entire repeated basis groups possess the same structure, same spatial orientation and same stoichiometric composition as every other basis group in the crystal. For example in NaCl, the basis consists of one Na+ ion and one Cl- ion (ionic crystal), in Cu the basis is a single Cu atom (metallic crystal), in diamond the basis is two C atoms which are surrounded tetrahedrally by four carbons, but the four bonds at one basis atom differ in orientation from those at the other atom (covalent crystal) and in CO_2, the basis is four CO_2 molecules (molecular crystals).

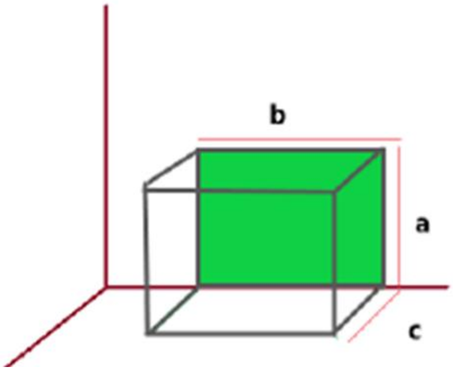
7. Space Lattice

On placing the single point at the same location in each repeated basis group, a set of points are obtained that forms the (space) lattice of the crystal. Each point of the space lattice has the same environment and it is not same as crystal structure. However, the crystal structures are generated by placing an identical structural group (the basis) at each lattice point. The space lattice is primarily a geometrical abstraction and it shows a two-dimensional lattice (which is mainly a hypothetical two-dimensional crystal structure that is formed by joining each lattice point a basis as shown in the image below in which the crystal structure is generated by associating a basis group with each lattice point.



The Unit Cell: The space lattices of any crystal are mainly divided into similar or identical parallelepipeds by joining the lattice points with straight lines. Parallelepipeds are six-sided geometrical solid whose faces are all parallelograms. A unit cell is a kind of parallelepipeds and a lattice is broken up into unit cells is not unique.





The angles between the edges a, b and c represented by α, β and γ, some of the arrangements are been shown. Bravais (1848) showed that there are 14 kinds of lattices that are arranged in three dimensions. These unit cells of the 14 Bravais lattices are tabulated as below and they are classified into seven crystal systems on the basis of their unit-cell symmetry.

- There are 14 types of crystal systems divided into seven Bravias lattices.
- Unit cells that have lattice points only at their corners are called primitive (or simple) unit cells.

- A body-centered lattice (I which is derived from the German *innenzentrierte*) consists of lattice point within the unit cell as well as at each corner of the unit cell.
- A face-centered (F) lattice has a lattice point on each of the six unit-cell faces as well as at the corners.
- End-centered lattice (C) with a lattice point on each of the two faces bounded by edges of lengths a and b.