Crystal Theory

How the Crystals Look Like?
- Crystal Structure
- Crystal Systems
Classification of Materials based on Crystalline nature:

**AMORPHOUS STATE**

**CRYSTALLINE STATE**

**POLYCRYSTALLINE STATE**
Classification of Materials based on Crystalline nature:

- **Non-crystalline (Amorphous) materials**-
  - No periodic arrangement of atoms.
  - Occurs in complex structures.
  - Example: Glass, Coal.

- **Crystalline materials**-
  - Periodic arrangement of atoms in 3-Dimensions.
  - Example: metals, Semiconductors, and many other materials

- **PolyCrystalline materials**-
  - Multiple crystalline states exits.
What is a Crystal:

- A **crystal** or **crystalline solid** is a **solid material** made up of atoms or molecules or ions, that are arranged in a highly ordered microscopic structure.
- This ordered arrangement allows to choose a **crystal lattice** that can be extends in all directions to produce the crystal.
What is a Crystal:

• In other words, **crystal** is a combination of **lattice** and **basis**, where the basis is positioned at each lattice site.
• Basis – A group of atoms or molecules.
• Lattice – A periodic arrangement of lattice sites.
Bravais Lattice:

• A lattice that exhibit a discrete translational symmetry. When a whole lattice is translated by any translation vector $T_{mno}$ and the result is the same lattice. Then such lattice is called Bravais Lattice.

$$T_{mno} = ma_1 + na_2 + oa_3$$

- $m, n, c$ are integers.
- $a_1, a_2, a_3$ are real space vectors.

• There are 14 Bravais lattices, which are divided into 7 crystal systems.
Unit Cell and Primitive Cell:

• **Unit Cell** - A small volume of the crystal that can be repeated in all directions to produce the entire crystal.
  – Unit cell is not a unique entity. There can be multiple unit cells for a crystal.

• **Primitive Cell** – The **smallest possible unit cell** that can be repeated in all directions to produce the entire crystal.
Lattice Constant or Lattice Parameter:

- **Lattice constant** or **Lattice parameter** represents the physical dimensions of a unit cell in the crystal lattice.
- Full set of lattice parameters consist of the three lattice constants \((a,b,c)\) and the three angles \((\alpha,\beta,\gamma)\) between them.
## Types of Crystal Systems:

<table>
<thead>
<tr>
<th>System</th>
<th>Lattice constants and angles</th>
<th>Unit cell geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$a = b = c, \alpha = \beta = \gamma = 90^\circ$</td>
<td><img src="image" alt="Cube" /></td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$</td>
<td><img src="image" alt="Tetragonal" /></td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$</td>
<td><img src="image" alt="Orthorhombic" /></td>
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</tbody>
</table>
## Types of Crystal Systems:

<table>
<thead>
<tr>
<th>System</th>
<th>Axial lengths and angles</th>
<th>Unit cell geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhombohedral</td>
<td>$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$</td>
<td><img src="image" alt="Rhombohedral Unit Cell" /></td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$</td>
<td><img src="image" alt="Hexagonal Unit Cell" /></td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$a \neq b \neq c, \alpha = \gamma = 90^\circ, \neq \beta$</td>
<td><img src="image" alt="Monoclinic Unit Cell" /></td>
</tr>
<tr>
<td>Triclinic</td>
<td>$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$</td>
<td><img src="image" alt="Triclinic Unit Cell" /></td>
</tr>
</tbody>
</table>
Types of Unit cells: They help identify the bravais lattices.

**P:** Primitive (lattice points only at the corners of the unit cell)

**I:** Body-centred (lattice points at the corners + one lattice point at the centre of the unit cell)

**F:** Face-centred (lattice points at the corners + lattice points at centres of all faces of the unit cell)

**C:** End-centred or base-centred (lattice points at the corners + two lattice points at the centres of a pair of opposite faces)
### Types of Bravais lattices:

14 Bravais lattices are divided into 7 Crystal systems.

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Bravais lattices</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Cubic</td>
<td>P     I     F</td>
</tr>
<tr>
<td>2. Tetragonal</td>
<td>P     I</td>
</tr>
<tr>
<td>3. Orthorhombic</td>
<td>P     I     F   C</td>
</tr>
<tr>
<td>4. Hexagonal</td>
<td>P</td>
</tr>
<tr>
<td>5. Trigonal</td>
<td>P</td>
</tr>
<tr>
<td>6. Monoclinic</td>
<td>P</td>
</tr>
<tr>
<td>7. Triclinic</td>
<td>P</td>
</tr>
</tbody>
</table>

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Physics-I   ABV-IIITM Gwalior
## Cubic Crystal System - Attributes

<table>
<thead>
<tr>
<th>Lattice type</th>
<th>Number of lattice points/atoms per unit cell</th>
<th>Maximum packing density</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simple cubic</td>
<td>1</td>
<td>( \frac{\pi}{6} = 52% )</td>
<td>Phosphor</td>
</tr>
<tr>
<td>Body centered cubic</td>
<td>2</td>
<td>( \frac{\pi\sqrt{3}}{8} = 68% )</td>
<td>Tungsten</td>
</tr>
<tr>
<td>Face centered cubic</td>
<td>4</td>
<td>( \frac{\pi\sqrt{2}}{3} = 74% )</td>
<td>Aluminum</td>
</tr>
</tbody>
</table>
Simple Cubic:
Calculating the number of atoms per unit cell and the atomic Packing Density or Atomic Packing Fraction (APF).

$$\text{APF} = \frac{\text{Volume of atoms}^* \text{ in unit cell}}{\text{Volume of unit cell}}$$

*assume hard spheres

Close-packed direction:
$$a = 2R$$

There are 8 of 1/8 atoms.  1 atom/unit cell

$$\text{APF} = \frac{1 \cdot \frac{4}{3} \pi (0.5a)^3}{a^3} = 0.52$$
Body Centered Cubic:
Calculating the number of atoms per unit cell and the atomic Packing Density or Atomic Packing Fraction (APF).

Number of atoms in the unit cell = \( \frac{1}{8} \times 8 + 1 = 2 \)

Close-packed directions:
length = \( 4R = \sqrt{3} a \)

\[ \text{APF} = \frac{2 \times \frac{4}{3} \pi (\sqrt{3}a/4)^3}{a^3} \]
\[ = 0.68 \]
Face Centered Cubic:
Calculating the number of atoms per unit cell and the atomic Packing Density or Atomic Packing Fraction (APF).

Unit cell contains:
\[ 6 \times \frac{1}{2} + 8 \times \frac{1}{8} = 4 \text{ atoms/unit cell} \]

Close-packed directions:
length = 4R
\[ = \sqrt{2} a \]

\[
\text{APF} = \frac{4 \times \left(\frac{\pi}{\sqrt{3}}\right) \left(\frac{\sqrt{2}a}{4}\right)^3}{\frac{4}{3} \pi (\sqrt{2}a/4)^3}
\]
\[ = \frac{\pi}{(3\sqrt{2})} = 0.74 \]
Coordination Number

- Coordination number is the number of nearest neighbor to a particular atom in the crystal.

- For example, Coordination number for different unit cells are:
  - Simple cubic – 6
  - Body centered – 8
  - Face centered --12
How were the Crystals Classified?

- Based on Symmetry
Symmetry

After applying some sort of transformation on an object in space, if the object regains its initial state, then the object is said to have symmetry.

Types of Basic Transformations:

- Transformation about a vector (Translation Symmetry)
- Transformation about an axis (Rotation symmetry)
- Transformation about a plane (Reflection or mirror symmetry)
- Transformation about a center (Inversion Symmetry)
Symmetry Groups

Using symmetry operations the lattice points can be arranged in several unique ways in 3D-space.

• All possible lattice arrangements of lattice points using **Translational symmetry operation** are called **Translational Groups**.

✓ All possible lattice arrangements of lattice points using **Non-Translational symmetry operations (Rotation, Reflection)** are called **Point Groups**. (Total 32 Point Groups exist)

✓ All possible lattice arrangements of lattice points using **Translational and Non-Translational symmetry operations** are called **Space Groups**. (Total 230 Space Groups exist)
Crystal Systems and Bravais Lattices

32 Point Groups

Classified into 7 Categories

7 Crystal Systems

230 Space Groups

Classified into 14 Categories

14 Bravais Lattices
7 Crystal Systems and the 14 Bravais Lattices
Symmetry Operations

symmetry operations:

- **Translation Symmetry** (performed about a vector)
- **Rotation** symmetry (performed about an axis)
- **Reflection** or mirror symmetry (Performed about a plane)
- **Inversion** Symmetry (Performed about an inversion center)

Joint Symmetry Operations:

- **Screw axis Symmetry** (Rotation + Translation)
- **Glide reflection Symmetry** (Reflection+ Translation)
Translation Symmetry:

The first point is repeated at equal distances along a line by a translation \( uT \), where \( T \) is the translation vector and \( u \) is an integer.

- **Translational symmetry** is when an object has undergone a movement or a shift or a slide, in a specified direction by a specified distance without any rotation or reflection.
Rotation Symmetry:

- An object is said to have **Rotation symmetry**, if it obtains its initial state when rotated $360^0$ in certain orientation.
- **Degree of rotational symmetry** is given by the number of orientations and the number of times it obtains symmetry in each orientation.

Ex: Four 3-fold Symmetry.

![Diagram of different rotation symmetries](image-url)
Rotation Symmetry: What about 5, 7, 8 fold Rotations?

Is it possible to have 5, 7 or 8-fold rotation symmetry?

Objects with 5, 7 and 8 or higher order symmetry do exist in nature, e.g. star fish (5-fold), flowers with 5 or 8-fold symmetry.

However, these are not possible in crystallography as they cannot fill the space completely.
Reflection or Mirror Symmetry:

• A type of symmetry where one half of object is the **reflection** of the other half.
Inversion Symmetry:

- If an inverted object w.r.t a center of inversion appears same as the original object then, it has inversion symmetry.
Mirror image and Inversion image are not same
**Screw axis Symmetry:** (Rotation + Translation)

Involves Rotation operation and Translation operation
Glide reflection Symmetry: (Reflection + Translation)
Involves reflection and translation operation
Symmetry operations on a Cube

• Total Symmetry elements in Cube = 23
  Inversion Symmetry = 1
  Rotational Symmetry = 3+4+6 = 13
  Reflection Symmetry = 3 + 6 = 9

Inversion Symmetry
Symmetry operations on a Cube: Rotational

Three 4-fold Symmetry
- The axes have 4-fold rotational symmetry. Each is formed by joining the centres of 2 opposite faces.

Four 3-fold Symmetry
- The axes have 3-fold rotational symmetry. Each is a diagonal of the cube.

Six 2-fold Symmetry
- The axes have 2-fold rotational symmetry. Each is formed by joining the mid-points of 2 opposite edges.
Symmetry operations on a Cube: Reflection
## Characteristic Symmetry of Crystal Systems

<table>
<thead>
<tr>
<th>System</th>
<th>Unit-cell dimensions</th>
<th>Unit-cell angles (°)</th>
<th>Characteristic symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>$a \neq b \neq c$</td>
<td>$\alpha \neq \beta \neq \gamma \neq 90$</td>
<td>Only inversion center possible</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$a \neq b \neq c$</td>
<td>$\alpha = \gamma = 90$, $\beta \neq 90$</td>
<td>Single twofold axis or/and mirror</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$a \neq b \neq c$</td>
<td>$\alpha = \beta = \gamma = 90$</td>
<td>Three perpendicular twofold axes or/and mirrors</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$a = b \neq c$</td>
<td>$\alpha = \beta = \gamma = 90$</td>
<td>One fourfold axis</td>
</tr>
<tr>
<td>Trigonal</td>
<td>$a = b \neq c$</td>
<td>$\alpha = \beta = 90$, $\gamma = 120$</td>
<td>One threefold axis</td>
</tr>
<tr>
<td></td>
<td>$a = b = c$</td>
<td>$\alpha = \beta = \gamma \neq 90$</td>
<td></td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$a = b \neq c$</td>
<td>$\alpha = \beta = 90$, $\gamma = 120$</td>
<td>One sixfold axis</td>
</tr>
<tr>
<td>Cubic</td>
<td>$a = b = c$</td>
<td>$\alpha = \beta = \gamma = 90$</td>
<td>Four threefold axes</td>
</tr>
</tbody>
</table>
Reciprocal Space and Brillouin zone
Reciprocal Space

• The images of 7 crystal systems and 14 bravais lattices in earlier slides are represented in **real space**.

• However, there is another space called **Reciprocal Space**, which is not-real and purely fictional.

• This space is created by the scientists, since not all the concepts of materials science can be explained in real space.

• For instance, **X-ray Diffraction** phenomenon is visualized in the reciprocal space.
What is Reciprocal Space?

- Mathematically, it is the Fourier Transform of real space.
Reciprocal Lattice:

• **Reciprocal Lattice** is the reciprocal of real space Lattice.

\[
\text{reciprocalLattice} = \frac{1}{\text{BravaisLattice}}
\]

• **Reciprocal Lattice Parameters** are reciprocal of real space Lattice Parameters. If \( a, b, c \) are real space lattice constants then the reciprocal lattice constants will be \( 1/a, 1/b, 1/c \).

\[
\text{reciprocalLatticeParameters} = \frac{1}{\text{realSpaceLatticeParameters}}
\]

• **Volume of reciprocal unit cell** is the reciprocal of volume of real space unit cell.

\[
\text{reciprocalUnitCellVolume} = \frac{1}{\text{realSpaceUnitCellVolume}}
\]
Real and Reciprocal cells:

[Diagrams of real and reciprocal space cells]
Real and Reciprocal cells:

Real Space

Volume: 1

Reciprocal Space

Volume: 1

Real Space

Volume: 0.494

Reciprocal Space

Volume: 2.02429
Brillouin Zone:

- Brillouin zone is the **Primitive cell** of the crystal in the reciprocal space.
- Introduced by French Physicist Leon Brillouin.

The First Brillouin zone is also called Irreducible Brillouin zone.
Bonding and Material Properties
**Atomic Structure**

- **Mass** of electron: $9.1 \times 10^{-31}$ Kg  
  Mass of Proton and Neutron: $1.67 \times 10^{-27}$ Kg
- **Charge** of electron: $-1.6 \times 10^{-19}$ Coulombs  
  Charge of Proton: $+1.6 \times 10^{-19}$ Coulombs  
  Charge of Neutron: 0
- **Atomic Number**: No. of Protons (or) No. of electrons in neutrals state of atom.
Atomic Mass and Atomic Weight

- **Atomic Mass**: No. of Protons + Number of Neutrons. (it is specific to each isotope.)
- **Atomic Weight**: It is the weighted average of all the naturally occurring isotopes of an element. Calculated by multiplying the atomic mass of each isotope with its natural abundance and summing the results.
  
  **Example**: Atomic mass of $^{12}$C: 12 u  
  Atomic weight of C: 12.011 u

- **Atomic Mass Unit** (a.u or u): It is $1/12$ of the mass of an atom of $^{12}$C. ($1.67 \cdot 10^{-27}$ kg)

  - **Calculate Atomic Weight of Carbon ?**
  
  **Step-1**: Identify its natural isotopes, their abundance and mass.

<table>
<thead>
<tr>
<th>Isotopes of Carbon</th>
<th>Abundance</th>
<th>Mass (experimentally observed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{12}$C</td>
<td>98.89 %</td>
<td>12.00 u</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>1.11 %</td>
<td>13.0034 u</td>
</tr>
</tbody>
</table>

  **Step-2**: Multiply the atomic mass of each isotope with its natural abundance and sum the results.

  Atomic Weight of C = 0.9889*12 + 0.0111*13.0034  
  = 12.0111 = 12.01 u
<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
<th>Atomic Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>1.008</td>
</tr>
<tr>
<td>He</td>
<td>2</td>
<td>4.0026</td>
</tr>
<tr>
<td>Li</td>
<td>3</td>
<td>6.94</td>
</tr>
<tr>
<td>Be</td>
<td>4</td>
<td>9.0122</td>
</tr>
<tr>
<td>Na</td>
<td>11</td>
<td>22.990</td>
</tr>
<tr>
<td>Mg</td>
<td>12</td>
<td>24.305</td>
</tr>
<tr>
<td>Al</td>
<td>13</td>
<td>26.982</td>
</tr>
<tr>
<td>Si</td>
<td>14</td>
<td>28.085</td>
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<tr>
<td>P</td>
<td>15</td>
<td>30.974</td>
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<tr>
<td>S</td>
<td>16</td>
<td>32.06</td>
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<tr>
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<td>17</td>
<td>35.45</td>
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<tr>
<td>Ar</td>
<td>18</td>
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<tr>
<td>K</td>
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<td>V</td>
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<td>Ni</td>
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<td>Cu</td>
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<td>As</td>
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</tr>
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<td>Se</td>
<td>34</td>
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<tr>
<td>Br</td>
<td>35</td>
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<tr>
<td>Kr</td>
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<td>Rb</td>
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<tr>
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<tr>
<td>Y</td>
<td>39</td>
<td>88.906</td>
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<tr>
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<td>(98)</td>
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<tr>
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<td>Mc</td>
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<tr>
<td>Lr</td>
<td>103</td>
<td>262</td>
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</table>

* Lanthanide series

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>57</td>
</tr>
<tr>
<td>Ce</td>
<td>58</td>
</tr>
<tr>
<td>Pr</td>
<td>59</td>
</tr>
<tr>
<td>Nd</td>
<td>60</td>
</tr>
<tr>
<td>Pm</td>
<td>61</td>
</tr>
<tr>
<td>Sm</td>
<td>62</td>
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<td>Eu</td>
<td>63</td>
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<td>Gd</td>
<td>64</td>
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<tr>
<td>Tb</td>
<td>65</td>
</tr>
<tr>
<td>Dy</td>
<td>66</td>
</tr>
<tr>
<td>Ho</td>
<td>67</td>
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<tr>
<td>Er</td>
<td>68</td>
</tr>
<tr>
<td>Tm</td>
<td>69</td>
</tr>
<tr>
<td>Yb</td>
<td>70</td>
</tr>
<tr>
<td>Lu</td>
<td>71</td>
</tr>
</tbody>
</table>

# Actinide series

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Number</th>
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<tbody>
<tr>
<td>Ac</td>
<td>89</td>
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<tr>
<td>Th</td>
<td>90</td>
</tr>
<tr>
<td>Pa</td>
<td>91</td>
</tr>
<tr>
<td>U</td>
<td>92</td>
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<td>Np</td>
<td>93</td>
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<tr>
<td>Pu</td>
<td>94</td>
</tr>
<tr>
<td>Am</td>
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<td>Cm</td>
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<td>Bk</td>
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<td>Cf</td>
<td>98</td>
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<td>Es</td>
<td>99</td>
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<tr>
<td>Fm</td>
<td>100</td>
</tr>
<tr>
<td>Md</td>
<td>101</td>
</tr>
<tr>
<td>No</td>
<td>102</td>
</tr>
<tr>
<td>Lr</td>
<td>103</td>
</tr>
</tbody>
</table>
Bonding

• **What is bonding:** Bonding is the result of the balance of the force of attraction and the force of repulsion due to electric nature between atoms (ions), when they brought closer.
  
  Net Force on the bonded atoms separated by equilibrium distance is Zero (Force of Attraction = Force of Repulsion).

• **Why Atoms participate in bonding:** To gain stability (To gain the electron number as of a noble gas)

• **Who participate in Bonding:** The Valence electrons of an atom.

• **Why is bonding important:** It determine the chemical, electrical, thermal and optical properties of the matter.
Bonding

- What are the types of bonding:

  **Primary bonding:**
  - Ionic (transfer of valence electrons)
  - Covalent (sharing of valence electrons, directional)
  - Metallic (delocalization of valence electrons)

  **Secondary or van der Waals Bonding:**
  - (Common, but weaker than primary bonding)
    - Dipole-dipole
    - H-bonds
    - Polar molecule-induced dipole
    - Fluctuating dipole (weakest)
Ionic bonding:

• Involves **Transfer of electrons.** Takes place between elements with high electro-negativity difference.
  
  Example: NaCl, CsCl, ZnS etc.
Covalent bonding:

- Involves **Sharing of electrons**. Takes place between elements with no/low electro-negativity difference.
  
  Example: Si, Ge, Graphite, diamond etc.

![Diagram of covalent bonding](image)
Metallic bonding:

- Arises from the **electrostatic attraction force** between conducting electrons (in the form of an electron cloud or sea of delocalized electrons) and the positively charged metal ions.
  
  Example: Au, Ag, Fe, Cu etc.
Secondary bonding:

Arises from interaction between “electric” dipoles

- Fluctuating dipoles
  - Asymmetric electron clouds

- Permanent dipoles - molecule induced
  - General case:
  - Example: liquid HCl
  - Example: polymer
Remember, for a stronger bond, $E_0$ (the energy difference) should be large, but Energy ($E$) at $r_0$ should be smaller (since $E$ is a negative quantity).
Potential Energy Curve:

- Properties of material depend on the bonding type, shape of the Potential Energy curve, values of curves: they vary for different materials.
- **Bonding energy** (minimum on curve) is the energy that would be required to separate the two atoms to an infinite separation.
Melting Temperature $T_m$ prediction based on Potential Energy Curve:

$T_m$ is larger if $E_0$ is larger.
Elasticity Modulus (E) prediction based on Potential Energy Curve:

\[
\frac{F}{A_0} = E \frac{\Delta L}{L_0}
\]

E is large if \( E_0 \) is large
Coefficient of Thermal Expansion ($\alpha$) prediction based on Potential Energy Curve:

$$\text{Coef. thermal expansion} \quad \frac{\Delta L}{L_0} = \alpha (T_2 - T_1)$$

$\alpha$ is Large if $E_0$ is Smaller
<table>
<thead>
<tr>
<th>Type</th>
<th>Bond Energy</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic</td>
<td>Large!</td>
<td>Nondirectional (ceramics)</td>
</tr>
<tr>
<td>Covalent</td>
<td>Variable</td>
<td>Directional</td>
</tr>
<tr>
<td></td>
<td>large-Diamond</td>
<td>(semiconductors, ceramics</td>
</tr>
<tr>
<td></td>
<td>small-Bismuth</td>
<td>polymer chains)</td>
</tr>
<tr>
<td>Metallic</td>
<td>Variable</td>
<td>Nondirectional (metals)</td>
</tr>
<tr>
<td></td>
<td>large-Tungsten</td>
<td></td>
</tr>
<tr>
<td></td>
<td>small-Mercury</td>
<td></td>
</tr>
<tr>
<td>Secondary</td>
<td>smallest</td>
<td>Directional</td>
</tr>
<tr>
<td></td>
<td></td>
<td>inter-chain (polymer)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>inter-molecular</td>
</tr>
<tr>
<td>Bond</td>
<td>Melting point</td>
<td>Hardness (Ductility)</td>
</tr>
<tr>
<td>------------------</td>
<td>---------------</td>
<td>----------------------</td>
</tr>
<tr>
<td>Covalent</td>
<td>High</td>
<td>Hard (poor)</td>
</tr>
<tr>
<td>Ionic</td>
<td>High</td>
<td>Hard (poor)</td>
</tr>
<tr>
<td>Metallic</td>
<td>Varies</td>
<td>Varies</td>
</tr>
<tr>
<td>Van der Waals</td>
<td>Low</td>
<td>Soft (poor)</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>Low</td>
<td>Soft (poor)</td>
</tr>
</tbody>
</table>
Ceramics
(Ionic & covalent bonding):

Large bond energy
large $T_m$
large $E$
small $\alpha$

Metals
(Metallic bonding):

Variable bond energy
moderate $T_m$
moderate $E$
moderate $\alpha$

Polymers
(Covalent & Secondary):

Directional Properties
Secondary bonding dominates
small $T$
small $E$
large $\alpha$
Material Classification Based on Band Theory

- Metals (Conductors)
- Semi-Conductors
- Insulators
Material Classification:

- **Metals (Conductors):** The valence and conduction bands overlap. Possess low resistance which allows electrical current flow.

- **Semi-conductors:** The valence and conduction bands are separated by a band gap of zero to 4.
  - **Narrow bandgap** semiconductors: 0-2 eV band gap
  - **Wide bandgap** semiconductors: 2-4 eV band gap
  - **Direct bandgap** semiconductors: Valence band upper edge and Conduction band lower edge are located at same value of electron momentum.
  - **Indirect bandgap** semiconductors: Valence band upper edge and Conduction band lower edge are located at different values of electron momentum.

- **Insulators:** The valence and conduction bands are separated by large band gaps (usually larger than 4 eV).
  - Possess high resistance which suppresses electrical current flow.
Material Classification:

- **Metals**
  - Empty
  - Overlap
  - Filled

- **Semiconductors**
  - Empty
  - Small gap
  - Filled

- **Insulator**
  - Empty
  - Large gap
  - Filled

Energy vs. Momentum plots:
- **Direct band gap**
- **Indirect band gap**
Resistivity \((\rho = RA/L)\) and Conductivity \((\sigma = 1/\rho)\) for various materials at 293 K

<table>
<thead>
<tr>
<th>Material</th>
<th>Resistivity ((\Omega \cdot m))</th>
<th>Conductivity ((\Omega^{-1} \cdot m^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Metals</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silver</td>
<td>(1.59 \times 10^{-8})</td>
<td>(6.29 \times 10^{7})</td>
</tr>
<tr>
<td>Copper</td>
<td>(1.72 \times 10^{-8})</td>
<td>(5.81 \times 10^{7})</td>
</tr>
<tr>
<td>Gold</td>
<td>(2.44 \times 10^{-8})</td>
<td>(4.10 \times 10^{7})</td>
</tr>
<tr>
<td>Aluminum</td>
<td>(2.82 \times 10^{-8})</td>
<td>(3.55 \times 10^{7})</td>
</tr>
<tr>
<td>Tungsten</td>
<td>(5.6 \times 10^{-8})</td>
<td>(1.8 \times 10^{7})</td>
</tr>
<tr>
<td>Platinum</td>
<td>(1.1 \times 10^{-7})</td>
<td>(9.1 \times 10^{6})</td>
</tr>
<tr>
<td>Lead</td>
<td>(2.2 \times 10^{-7})</td>
<td>(4.5 \times 10^{6})</td>
</tr>
<tr>
<td><strong>Alloys</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Constantan</td>
<td>(4.9 \times 10^{-7})</td>
<td>(2.0 \times 10^{6})</td>
</tr>
<tr>
<td>Nichrome</td>
<td>(1.5 \times 10^{-6})</td>
<td>(6.7 \times 10^{5})</td>
</tr>
<tr>
<td><strong>Semiconductors</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>(3.5 \times 10^{-5})</td>
<td>(2.9 \times 10^{4})</td>
</tr>
<tr>
<td>Germanium</td>
<td>(0.46)</td>
<td>(2.2)</td>
</tr>
<tr>
<td>Silicon</td>
<td>(640)</td>
<td>(1.6 \times 10^{-3})</td>
</tr>
<tr>
<td><strong>Insulators</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wood</td>
<td>(10^8)–(10^{11})</td>
<td>(10^{-8})(–10^{-11})</td>
</tr>
<tr>
<td>Rubber</td>
<td>(10^{13})</td>
<td>(10^{-13})</td>
</tr>
<tr>
<td>Amber</td>
<td>(5 \times 10^{14})</td>
<td>(2 \times 10^{-15})</td>
</tr>
<tr>
<td>Glass</td>
<td>(10^{10})–(10^{14})</td>
<td>(10^{-10})(–10^{-14})</td>
</tr>
<tr>
<td>Quartz (fused)</td>
<td>(7.5 \times 10^{17})</td>
<td>(1.3 \times 10^{-18})</td>
</tr>
</tbody>
</table>
 Resistivity vs. Temperature

**Figure** : (a) Resistivity versus temperature for a typical conductor. Notice the linear rise in resistivity with increasing temperature at all but very low temperatures. (b) Resistivity versus temperature for a typical conductor at very low temperatures. Notice that the curve flattens and approaches a nonzero resistance as $T \to 0$. (c) Resistivity versus temperature for a typical semiconductor. The resistivity increases dramatically as $T \to 0$. 
Intrinsic, ExtrinsicSemiconductors, and Fermi level concept:

- When an Intrinsic (Pure) semi-conductor is doped with donor or acceptor dopants then the resultant is an extrinsic semiconductor.
- **Fermi level** is the maximum occupancy energy level.
- Position of Fermi level of extrinsic semi-conductor varies with the doping concentration and temperature.
- Detailed explanation (with figures) of Fermi level movement in semiconductors w.r.t to doping concentration and temperature are explained on board.
Effective Mass of Electron ($m_e^*$)

- Rest mass of electron $m_e = 9.1 \times 10^{-31}$ Kg
- Effective mass of electron ($m_e^*$) is the mass experienced by the electron that is interacting with other particles and atoms of the matter.
- Effective mass is always expressed as a value of the rest mass.
  
  $$m_e^* = (0.01 \text{ to } 10) \ m_e$$

- Effective mass can either be smaller or higher than the rest mass.
Phonons

- **Phonon** is the lattice vibrational energy of a solid.
- Atoms vibrate as a result of their thermal energy. The higher the thermal energy, the greater the vibrational energy. Atomic vibrations of solid causes the crystal lattice to vibrate. This vibrational energy is considered as phonon.
- Phonon is a quasiparticle.
Fermi-Dirac distribution Function

- It describes the distribution of Fermions over energy states in a system.
- **Fermions**: Particles having half integer spin (1/2, 1.5, 2.5, ...). They obey Pauli’s exclusion principle (Only one fermion allowed per energy state). **Example**: Electrons, Neutrons, Protons, etc.
- **Bosons**: Particles having integer spin (1, 2, 3, ...). Doesn’t obey Pauli’s exclusion principle (Multiple bosons can occupy a single energy state). **Example**: Photons, Mesons, etc.
- The Fermi-Dirac distribution Function \( f(E) \) is given by,

\[
f(E) = \frac{1}{1 + (e^{(E-E_F)/KT})}
\]

![Graph showing Fermi-Dirac distribution function](image-url)
What is Nano?

Nano:
From the Greek *nanos* - meaning "dwarf", this prefix is used in the metric system to mean $10^{-9}$ or $1/1,000,000,000,000$. 

![Diagram showing structure size with labels: Macro, Micro, Nano, 0.1 mm, 0.1 μm, 0.1 nm.](image)
How Small is Nano?

- Earth: 1.27 × 10^7 m
- Soccer ball: 0.22 m
- Fullerenes C_{60}: 0.7 × 10^{-9} m

10 millions times smaller
1 billion times smaller
Nano is Different: Size Matters

Bulk Gold = Yellow

Nano Gold = Red

Quantum Dots for Imaging and Diagnostics

Optical properties change with size. Depending on their size, CdSe particles can appear green or red in colour.

Quantum dot size can be controlled during their synthesis.

nanocrystals absorb all energies higher than their band gap, they can also be used as color converters. Sizes of biological molecules are also on the order of a few nanometers.
Carbon Nano-Materials

- Fullerenes (0-D Material)
- Carbon Nanotube (1-D Material)
- Graphene (2-D Material)
- Graphite (3-D Materials)
8 Carbon Allotropes

a) diamond
b) graphite
c) lonsdaleite
d) C60
e) C540
f) C70
g) amorphous carbon
h) SW-CNT.

Carbon nanotubes (CNTs) were discovered by Ijima in Japan in 1991.

- CNTs can be thought as rolled up sheets of graphene.
- Electrical properties depend on chirality or the direction of this distortion.
- CNTs can be metallic or semiconducting depending on the chirality.

Fig. 1: Strip of graphene sheet rolled up into tube
Carbon NanoTube

- Hamada Indices \((n, m)\) are used to represent the size or type of CNT.
- Given the Hamada Indices the diameter and chiral angle of CNT can be calculated.

If \(n=m\) structure is armchair

If \(n\) or \(m=0\) structure is zigzag

Nanotube diameter and chiral angles are given as

\[
d_t = \frac{\sqrt{3a_{c-c}}\sqrt{m^2 + mn + n^2}}{\pi}
\]

\[
\theta = \tan^{-1}\left(\frac{\sqrt{3n}}{2m + n}\right)
\]

Physics-I ABV-IIITM Gwalior
Graphene – An allotrope of Carbon

http://upload.wikimedia.org/wikipedia/commons/thumb/9/9e/Graphen.jpg/750px-Graphen.jpg
Graphene – Why is it a wonder material?

• Properties-
  – Strongest material on earth (but Brittle, not Harder)
    • 40 times stronger than Diamond
    • 300 times stronger than A36 structured Steel
  – Light and flexible
  – Very High conductivity
    • Electron and hole mobility > 15,000 cm$^2$V$^{-1}$s$^{-1}$.  
      (Electron mobility of Si ≤ 1,400 cm$^2$V$^{-1}$s$^{-1}$)
  – Ballistic Transport
  – High thermal conductivity
  – Zero band gap semiconductor
  – Special chemical reactivity – Every atom available for reaction from two sides.
Graphene – Characterization

- Graphite + -ene (functional group) → Graphene.
- Isolated and characterized by Andre Geim and Konstantin Novoselov at the University of Manchester (UK) in 2004 → Received Nobel Prize in Physics in 2010.
- A single layer of graphite with honeycomb structure.
- Not directly available in nature – Extracted from graphite (example - pencil lead).

http://phelafel.technion.ac.il/~tzipora/graphite_graphene.png
Graphene – Structure

• Graphene has Hexagonal lattice, C-C bond length 1.42 Ang.
Graphene – Strength & Weight

40 times stronger than

300 times stronger than

**Tensile strength**

- Graphene: 130 G Pascals
- A36 structural steel: 0.4 G Pascals

1000 times less heavier than a paper

< 1 gram is enough
Graphene – why so strong?

Graphene, Graphite and diamond, all three are made of carbon, then what makes Graphene strongest of the three?

--- less Bond length (Strong bond) than Diamond.
--- Lack of Van der waals forces unlike in graphite.

---

\[
\begin{array}{c}
\text{C-C} \\
\text{Graphene} & 1.42 \text{ Å} \\
\text{Graphite} & 1.42 \text{ Å} \\
\text{Diamond} & 1.54 \text{ Å}
\end{array}
\]

When you write using pencil, the letters are actually tiny layers of graphene that slides on the paper due to their weak Van der waals interaction.

# Graphene - Conductivity

<table>
<thead>
<tr>
<th>Material</th>
<th>Electrical Conductivity (S/m)</th>
<th>Thermal Conductivity (W/m-k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>1.00×10^8</td>
<td>~5000</td>
</tr>
<tr>
<td>Graphite</td>
<td>2.00×10^5 To 3.00×10^5 //basal plane 3.30×10^2 ⊥basal plane</td>
<td>25 To 470</td>
</tr>
<tr>
<td>Diamond</td>
<td>~10^{-13}</td>
<td>2,200</td>
</tr>
<tr>
<td>Silver</td>
<td>6.30×10^7</td>
<td>~420</td>
</tr>
<tr>
<td>Copper</td>
<td>5.96×10^7</td>
<td>~380</td>
</tr>
<tr>
<td>Gold</td>
<td>4.10×10^7</td>
<td>~350</td>
</tr>
<tr>
<td>Aluminium</td>
<td>3.50×10^7</td>
<td>~230</td>
</tr>
<tr>
<td>Stainless Steel</td>
<td>1.45×10^6</td>
<td>~18</td>
</tr>
</tbody>
</table>
Graphene – Reasons for superior conductivity

- Zero Band gap
- Relativistic velocity ($v=c$) of Electrons and holes
- Delocalization of Pi-cloud
Zero band gap

Zero band gap is observed in graphene at Dirac point (k-point), Where the upper edge of valance band and lower edge of conduction band meet.

The cones are called Dirac Cones.

Zero band gap of Graphene Visualized from a computational DFT result
Relativistic Velocity of carriers

• In graphene, electrons and holes have zero effective mass and feel no inertia.
• Hence travel with velocity equal to velocity of light (v=c), called relativistic velocity.
• Carriers in graphene are called Dirac fermions. Since the above property is observed at Dirac point where valence and conduction bands meet.
• The Zero effective mass of carriers is due to the linear energy–momentum relation (the spectrum for excitations) at low energies at Dirac points.
  – For massive particles— (Not in graphene)
    \[ E = \sqrt{(mc^2)^2 + (cp)^2} \]
    ----(1)
    m=rest mass
    p= momentum
    c= velocity of light
For non-relativistic velocity ($v \ll c$), the above equation becomes:

$$E = mc^2 \sqrt{1 + \frac{p^2}{m^2 c^2}}$$

Solving,

$$E = mc^2 + \frac{p^2}{2m}$$

(neglecting higher order terms)
For **relativistic velocity** (in graphene),

where \( m=0 \) and \( v=c \),

Eq-1 becomes,

\[
E = \sqrt{(mc^2)^2 + (cp)^2}
\]

substitute \( m=0 \)

\[
E = c \ |p|
\]
Delocalized Pi- electron cloud

- Carbon electronic configuration,
  \[ C(6) = 1s^2 \ 2s^2 \ 2p^2 \]

In graphene, every carbon is bonded to 3 surrounding carbon atoms; To acquire stability, it has to share the 4 valance electrons with 3 carbon atoms.

Needs to form a double bond, hence the carbon undergoes \( sp^2 \) hybridization.
Delocalized Pi-electron cloud

Each carbon forms 3 sigma bonds (using 3- sp² hybrid orbitals) and 1 pi-bond (using p-orbital)

The Pi-cloud got resonance problem (Resonance Effect)

The resultant is delocalization of Pi-electron cloud and Aromaticity in graphene.

Each honeycomb is aromatic with 2 Pi-electrons
Sheet Vs Ribbon

Infinitely long in 2-directions (2-D)

Infinitely long in one direction
And confined in other directions (1D)

Zig-Zag Nanoribbon (3,3)

Arm-chair Nanoribbon (3,0)
Graphene Nanoribbon (GNR) Vs CNT

<table>
<thead>
<tr>
<th>Hamada Indices (n,m)</th>
<th>GNR</th>
<th>CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>n=m</td>
<td>Zig-Zag</td>
<td>Arm-Chair</td>
</tr>
<tr>
<td>m=0</td>
<td>Arm-Chair</td>
<td>Zig-Zag</td>
</tr>
</tbody>
</table>

Reason for this variation → Shape of scattering region
Graphene — Applications

- A massive research is going on and researchers predicting that graphene will change the face of many technologies.
- Applications-
  - Electronics (Transistors, Interconnects, Devices, Flexible electronics, displays...)
  - Sensors (Gas, Biomedical, Chemical...)
  - Energy (Batteries, Supercapacitors, Solar cells, Photovoltaics...)
  - Filtration membranes (water, gas, chemical...)
  - Radiation isotope filters
  - Superconductor [latest discovery]
  - Miscellaneous - Armour design, Badminton racket throat,...
  - And many others...