SUBJ: SOLID STATE PHYSICS
4TH YEAR LAZER BRANCH
YEAR 2008-2009
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DAWOOD FAISAL
References

1. Introduction to Solid State Phys. By: Kittel
2. Solid state Physics By: H.E. Hall
3. = = = = / J.S. Blackmore
4. = = = = / A.J. DEKKER

Phase diagram (Gas, Solid, Liquid)

SOLID CRYSTAL

This can be classified into two groups:

<table>
<thead>
<tr>
<th>Amorphous</th>
<th>Crystalline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Disorder</td>
<td>Order</td>
</tr>
<tr>
<td>(Non-crystalline)</td>
<td>Long range Order</td>
</tr>
</tbody>
</table>

Example:

- Glass
- Metals like: Fe, Cu, Al
- OR Semiconductors (Si, Ge)
Crystalline State of Solids

Introduction

Liquid State (plasma) - liquid state (gaseous state) - solid state (crystal)

Figure 1: Schematic illustration of the differences between a solid and a liquid phase. (Chen, S., & Zhou, T. (1990). Nature, 345, 40-44.)
Crystal structure:

Unit Cell:

Lattice:

The lattice model is fundamental in crystallography. It represents the arrangement of atoms in a crystal. The lattice model is used to describe the periodicity of the arrangement. The unit cell is the smallest repeating unit in a crystal lattice. It is a three-dimensional structure that contains all the information about the crystal's periodicity. The lattice points are the positions where the atoms are located. These points are connected by vectors that define the direction and distance between the atoms. The lattice model is used to predict the properties of a crystal, such as its hardness, electrical conductivity, and optical properties.
A B C D represent a unit cell.

Primitive unit cell; P.U.C

It is a volume which will fill space completely, without overlap, if shifted by each of lattice vectors. The P.U.C contains one Bravais lattice points and the atoms in it can be used as the basis to construct the crystal. The volume made up by primitive vector is a possible unit cell, but there are many other possibilities.
Bravais Lattices:

There are different types of lattices that make up the (14) Bravais lattice, that can be obtained by several fundamental translations of a primitive position by unit cell parameters. If we start with Pnma and assign this position by the coordinates 0 0 0, then the main translations are:

- for B.C. Cubic: 0 0 0 $\rightarrow \begin{array}{c} \frac{1}{2} \\ \frac{1}{2} \\ \frac{1}{2} \end{array}$
- for F.C. Cubic: 0 0 0 $\rightarrow 0, \frac{1}{2}, \frac{1}{2}, \frac{1}{2}$

A Bravais lattice is an infinite array of points determined by the lattice vectors ($\mathbf{b}$), where:

$\mathbf{b} = \mathbf{n}_1 \mathbf{a}_1 + \mathbf{n}_2 \mathbf{a}_2 + \mathbf{n}_3 \mathbf{a}_3$ called translating vector, $\mathbf{n}_1, \mathbf{n}_2, \mathbf{n}_3$ are vectors (non-zero).
### TABLE 3 Crystal Structures of the Elements

The data given are at room temperature for the most common form, or at the stated temperature in deg K. For further descriptions of the elements see Wyckoff, Vol. 1, Chap. 2. Structures labeled complex are described there. The notation ABAC refers to the sequence of close-packed planes.

<table>
<thead>
<tr>
<th>Element</th>
<th>Structure</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Crystal structure</th>
<th>a lattice parameter, in Å</th>
<th>c lattice parameter, in Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>hcp</td>
<td>3.491</td>
<td>2.57</td>
<td>3.59</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>hcp</td>
<td>3.20</td>
<td>3.21</td>
<td>4.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>hcp</td>
<td>3.64</td>
<td>3.64</td>
<td>5.68</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb</td>
<td>hcp</td>
<td>5.56</td>
<td>6.58</td>
<td>6.63</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cs</td>
<td>hcp</td>
<td>6.04</td>
<td>6.04</td>
<td>6.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fr</td>
<td>hcp</td>
<td>6.50</td>
<td>6.50</td>
<td>6.50</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Be</td>
<td>hcp</td>
<td>2.95</td>
<td>2.95</td>
<td>2.95</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>hcp</td>
<td>3.21</td>
<td>3.21</td>
<td>3.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>hcp</td>
<td>2.95</td>
<td>2.95</td>
<td>2.95</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>hcp</td>
<td>3.31</td>
<td>3.31</td>
<td>3.31</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>hcp</td>
<td>3.87</td>
<td>3.87</td>
<td>3.87</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>fcc</td>
<td>4.84</td>
<td>4.84</td>
<td>4.84</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>fcc</td>
<td>5.05</td>
<td>5.05</td>
<td>5.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
<td>fcc</td>
<td>5.31</td>
<td>5.31</td>
<td>5.31</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**
- ABAC refers to the sequence of close-packed planes.
3D-Δtial lattice

Unit Cell

lattice vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$

(a) Mathematical point lattice with a unit cell outlined; (b) unit cell with lattice vectors indicated.

2 D-Crystal lattice

Two-dimensional cubic lattice showing different low and high Miller index planes.
The 14 Bravais or space lattices. The cells shown are the conventional cells, which are not always the primitive cells.
<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Lattices</th>
</tr>
</thead>
<tbody>
<tr>
<td>triclinic</td>
<td><img src="image1" alt="Diagram" /></td>
</tr>
<tr>
<td>monoclinic</td>
<td>simple</td>
</tr>
<tr>
<td></td>
<td>$\alpha = 90^\circ$</td>
</tr>
<tr>
<td>orthorhombic</td>
<td>simple</td>
</tr>
<tr>
<td></td>
<td>$a \neq b \neq c$</td>
</tr>
<tr>
<td>hexagonal</td>
<td></td>
</tr>
<tr>
<td>rhombohedral</td>
<td>simple</td>
</tr>
<tr>
<td>(trigonal)</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>tetragonal</td>
<td>simple</td>
</tr>
<tr>
<td>cubic (isometric)</td>
<td>simple</td>
</tr>
</tbody>
</table>
Seven Crystal Systems

Table: The crystal systems

<table>
<thead>
<tr>
<th>No.</th>
<th>Name of system</th>
<th>Relation between primitives</th>
<th>Axial angles</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cubic</td>
<td>$a=b=c$</td>
<td>$a=β=γ=90°$</td>
<td>NaCl</td>
</tr>
<tr>
<td>2.</td>
<td>Tetragonal</td>
<td>$a=b$</td>
<td>$a=β=γ=90°$</td>
<td>SO₂</td>
</tr>
<tr>
<td>3.</td>
<td>Orthorhombic</td>
<td>$a≠b≠c$</td>
<td>$a=β=γ=90°$</td>
<td>KNO₃</td>
</tr>
<tr>
<td>4.</td>
<td>Monoclinic</td>
<td>$a≠b≠c$</td>
<td>$a=β=γ=90°$</td>
<td>Na₂SO₄</td>
</tr>
<tr>
<td>5.</td>
<td>Triclinic</td>
<td>$a≠b≠c$</td>
<td>$α≠β≠γ≠90°$</td>
<td>CaSO₄</td>
</tr>
<tr>
<td>6.</td>
<td>Rhombohedral</td>
<td>$a=b=c$</td>
<td>$α=β=γ=90°$</td>
<td>Calcite</td>
</tr>
<tr>
<td>7.</td>
<td>Hexagonal</td>
<td>$a=b≠c$</td>
<td>$α=β=90°, γ=120°$</td>
<td>ZnO</td>
</tr>
</tbody>
</table>

Table: Seven crystal systems in terms of minimum distinguishing symmetry elements

<table>
<thead>
<tr>
<th>Crystal System</th>
<th>Minimum Symmetry Elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>4 Threefold rotation axes</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>1 Fourfold rotation axis</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>3 Twofold rotation axes</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>1 Sixfold rotation axis</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>1 Twofold rotation axis</td>
</tr>
<tr>
<td>Triclinic</td>
<td>None</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>1 Twofold rotation axis</td>
</tr>
</tbody>
</table>
### The Two-dimensional Lattices

<table>
<thead>
<tr>
<th>Shape of unit cell</th>
<th>Lattice symbol</th>
<th>Conventional rule for choice of axes</th>
<th>Nature of axes and angles</th>
<th>Name of corresponding system</th>
</tr>
</thead>
<tbody>
<tr>
<td>General parallelogram rhomboid</td>
<td>R</td>
<td>None</td>
<td>$a \neq b$ (\gamma \neq 90^\circ)</td>
<td>Oblique</td>
</tr>
<tr>
<td>Rectangle</td>
<td>p/c</td>
<td>Two shortest, mutually perpendicular vectors</td>
<td>$a \neq b$ (\gamma = 90^\circ)</td>
<td>Rectangular</td>
</tr>
<tr>
<td>Square</td>
<td>p</td>
<td>Two shortest, mutually perpendicular vectors</td>
<td>$a = b$ (\gamma = 90^\circ)</td>
<td>Square</td>
</tr>
<tr>
<td>90°-angle rhombus</td>
<td>p</td>
<td>Two shortest vectors at 120° to each other</td>
<td>$a = b$ (\gamma = 120^\circ)</td>
<td>Hexagonal</td>
</tr>
</tbody>
</table>

### TABLE: The 14 Bravais Lattices and Conventional Unit Cells

<table>
<thead>
<tr>
<th>System</th>
<th>Number of lattices in system</th>
<th>Lattice symbols</th>
<th>Nature of unit-cell axes and angles</th>
<th>Lengths and angles to be specified</th>
<th>Symmetry of lattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>Triclinic</td>
<td>1</td>
<td>P</td>
<td>$a \neq b \neq c$ (a \neq b \neq c)</td>
<td>$a, b, c, a, b, c$</td>
<td>1</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>2</td>
<td>P</td>
<td>$a \neq b = c$</td>
<td>$a, b, c$</td>
<td>2/m</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>4</td>
<td>P</td>
<td>$a = b \neq c$ (a = b = c)</td>
<td>$a, b, c$</td>
<td>mm2</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>2</td>
<td>P</td>
<td>$a = b = c$ (a = b = c)</td>
<td>$a, c$</td>
<td>4/mmm</td>
</tr>
<tr>
<td>Cubic</td>
<td>3</td>
<td>P</td>
<td>$a = b = c$ (a = b = c)</td>
<td>$a$</td>
<td>m3m</td>
</tr>
<tr>
<td>Trigonal</td>
<td>1</td>
<td>P</td>
<td>$a = b = c$ (a = b = c)</td>
<td>$a$</td>
<td>3m</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>1</td>
<td>P</td>
<td>$a = b = c$ (a = b = c)</td>
<td>$a, c$</td>
<td>6/mmm</td>
</tr>
</tbody>
</table>
Miller Indices

accepted System for naming planes & Miller Indices

How to index HKL

Representations: plane ( )
family of planes [ ]
Direction [ ]
family of directions < >

Miller Index System: How to index planes.

The intercepts are:

\[ \frac{3a}{2a} = \frac{3}{2} \]
\[ \frac{2b}{2b} = \frac{1}{2} \]
\[ \frac{2c}{2c} = \frac{1}{2} \]

Miller Indices (hkl):

\[ (2\ 3\ 3) \]

Figure: This plane intercepts the a, b, c axes at 3a, 2b, 2c. The reciprocals of these numbers are 1, 2, 3. The smallest three integers having the same ratio are 2, 3, 3, and thus the indices of the plane are (223).
For plane indices:

<table>
<thead>
<tr>
<th>Plane</th>
<th>Intercepts</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110)</td>
<td>$a = 1$, $b = 1$, $c = 0$</td>
</tr>
<tr>
<td>(321)</td>
<td>$a = 1$, $b = 1$, $c = 1$</td>
</tr>
<tr>
<td>(643)</td>
<td>$a = \frac{1}{3}$, $b = \frac{1}{2}$, $c = \frac{2}{3}$</td>
</tr>
<tr>
<td>(111)</td>
<td>$a = \frac{1}{3}$, $b = \frac{1}{3}$, $c = \frac{1}{3}$</td>
</tr>
<tr>
<td>(020)</td>
<td>$a = \infty$, $b = \frac{1}{2}$, $c = \frac{1}{2}$</td>
</tr>
</tbody>
</table>

Note:

$3 \cdot 2 \cdot \frac{3}{2} = 9$
A lattice contains a large number of planes of atoms. We name these planes using the **Miller indices** \((h, k, l)\).

Defined with the convention that the vectors:
\[
\mathbf{R} = n_x \mathbf{a}_1 + n_y \mathbf{a}_2 + n_z \mathbf{a}_3
\]

is a normal vector for the plane. \(\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3\) are basis vectors and \(n_x, n_y, n_z\) are integers.

**Hexagonal**: Indices with hexagonal are \((h \ k \ l)\).
There are various types of crystals classified into certain groups depending on their symmetry:

- **Symmetry**
  - External symmetry
  - Internal symmetry

2) Center of Symmetry: when it has a point such that all straight lines drawn through it will pass through a pair of similar points lying on opposite sides of the center of symmetry and at the same distance from it.

(iii) Axis of Symmetry:

- $n = 2, 3, 4, 6$
- Two fold, three fold, four fold,

- Fold axis

---

The center of symmetry is located at the center of the hexagonal system. The axis of symmetry is 6-fold. The angle between two adjacent axes is $60^\circ$. The hexagonal system is characterized by its 6-fold symmetry and the presence of a center of symmetry at the center of the crystal.
III) Plane of Symmetry:

When a plane passes through the center of a crystal, it divides the crystal into two mirror-image halves. This plane is called the plane of symmetry.

Internal Symmetry:

- Rotation: 2, 4, 6-fold axis of symmetry.
- Reflection: Operation produces the same effect as an inversion.
- Rotation, inversion, and glide plane.
- Screw axes: Rotation, glide plane.

@ Rotation: 2, 4, 6 fold axis of symmetry.
@ Reflection: Operation produces the same effect as an axis of symmetry.
@ Inversion Center: Every point located at a distance (r) relative to the center, there exists a similar point at -r and on the same line through this center.

@ Glide plane: exists in a crystal when it combines with a reflection plane with a translation parallel to this plane so that the symmetry structure is brought into self-coincidence by the movement and reflection across the specified plane.

@ Screw axis: combines rotation with translation parallel to the axis, like the working of a screw. The direction of rotation may be clockwise or anti-clockwise and existence of 2 fold, 3, 4, 6 rotation.
@ Rot. Inv.
Translating Vector

This is defined by the formula:

\[ \mathbf{T} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c} \]

For any type of lattice, there exist three fundamental transition vectors \( \mathbf{a}, \mathbf{b}, \mathbf{c} \); these are the shortest vectors, which satisfy the condition that, if we transverse any integer distances \( n_1 \mathbf{a}, n_2 \mathbf{b}, n_3 \mathbf{c} \) from a point in the crystal lattice, then we reach to a point which has identically the same environment as the original point.
2. Solid - liquid - gas - Plasma
3. Crystal Structure
4. Amorphous + Crystalline
5. Lattice, Lattice Point: Basis, Unit Cell, Primitive Unit Cell, Bravais Lattices 7 - 14.

5/1: Types of Crystals (Cubic) + Hex.
3. Lattice planes and Directions of Solid atoms. Cubic, Hexagonal.
4. 2D, 3D Cubic Structure.
   - Types of Cubic: Simple, Body Centered, Face Centered.
5. Periodic Table Shows the distribution of the Crystal Types.
7. Fraction of Volume occupied by the spheres (atoms) in the structure. (F)
8. How to calculate (F)
Number of Lattice points for unit cell:

To calculate N which is called the number of atoms/unit cell, for different types of unit cell (cubic):

\[
N = \frac{N_i}{1} + \frac{N_c}{8} + \frac{N_f}{2}
\]

- \(N_i\): number of atom inside the U.C.
- \(N_c\): = = at the corners of U.C.
- \(N_f\): = = at the faces of U.C.

The number of lattice points for a unit cell \(N\) calculated by counting that bound \(\frac{1}{8}\) and are interior \(\frac{1}{2}\) to the cell and considering the sharing \(\frac{1}{2}\) of points by adjacent \(\frac{1}{2}\) cells.

Example

8 lattice points at corners in unit cell in e.g. Simple cubic, one each shared by 8 adjacent cells \((N_c)\); the points on the face of a cell shared by 2 cells \((N_f)\) and of course the interior points \(N_i\).
(21)

\[ N = \frac{N_i}{8} + \frac{N_k}{2} + \frac{N_c}{8} \]

Simple Cubic Structure (U.C)

Simple have 8 atoms at the corners.

Face centered atom in the Cubic = 6 atoms only

Face center Cubic (U.C)

Atom at the center of the Cube = 1. atom only

Body Centered Cubic (B.C.C) - two adjacent unit cells. Reverse sharing 1 atom at the face, gives half atom in each of the unit cell.
To calculate the density of unit cell, this depends on the type of the U.C. (B.C.C., S.C.), they have three different no. of atoms so they have different density.

\[
\text{Density } (\rho) = \frac{\text{Number of atoms per unit cell} \times M \text{ (g/mole)}}{\frac{1}{2} \times \text{Interatomic distance}^3 \times N_A} 
\]

\[
\text{X-ray Density}
\]

\[
\text{X-Ray and Electron Diffraction Techniques}
\]
CLOSE-PACKING-STRUCTURES

At each lattice position imagine a sphere of atoms or molecules at the basis of radius \( R \), (it is one or more atoms/molecules, called basis.)

For simplicity, consider all the spheres to be equivalent. Now imagine each of the cell dimensions shrinking uniformly (but not the radius of the spheres) until the spheres just touch, where \( R \): atomic radius.

\[ A_c: \text{Lattice parameter} \]

Atomic Packing Factor = \( f \), which is also called fractional volume factor.

\[ f = \text{Atomic packing factor} = \frac{N_{\text{atom}} \times V_{\text{atom}}}{V_{\text{crystal}}} \]

\[ V_{\text{atom}} = \frac{1}{2} \pi R^3 \]

\[ N_{\text{atom}} \Rightarrow \text{atoms per unit cell} \]

\[ V_{\text{crystal}} \Rightarrow \text{crystal volume} \]
How to calculate the total number of atoms per unit cell.

For simple cubic (SC), we have 8 corner atoms and each of these atoms is a member of 8 cells enclosing the corner, so there is $\frac{8}{8} = 1$ atom per unit cell.

The total number of atoms per unit cell $N_{\text{Tot}}$ can be represented by the formula:

$$N_{\text{T}} = \frac{N_i}{I} + \frac{N_e}{2} + \frac{N_c}{8}$$

@ for SC $\Rightarrow N_{\text{Tot}} = 1$ atom per U.C.

@ H-W for BCC $\Rightarrow N_{\text{Tot}} = 8$ atoms per U.C.

@ C for FCC $\Rightarrow N_{\text{Tot}} = 4$ atoms per U.C.

How to calculate the fractional volume of U.C.

Suppose $f$ is the fractional size of the unit cell.

So, for SC $\Rightarrow$

1. Calculate the total number of atoms per U.C.

(a) \[N_{\text{Tot}} \text{(S.C.)} = 1\]

2. Calculate the total volume of the atom

\[= \frac{4}{3} \pi R^3 = \frac{4}{3} \pi \left(\frac{a_o}{2}\right)^3 = \frac{\pi}{6} a_o^3\]
(25)

3. Calculate the total volume of the U.C. \( V = \frac{a_0^3}{6} \).

4. Calculate the fractional volume (f):

   \[ f = \frac{\pi}{6} \frac{a_0^3}{a_0^3} = \frac{\pi}{6} \]

   \( \text{H.W.} \)

   (b) The fractional volume for B.C. \( C = \frac{\pi \sqrt{3}}{8} \)

   \( \text{H.W.} \)

   (c) The f.v. for F.C. \( C = \frac{\pi}{6} \sqrt{2} \).
Calculate the lattice parameter (a₀) as a function of atomic radius (R).
For face center cubic:

\[(4r)^2 = a_o^2 + a_o^2 = 2a_o^2 \Rightarrow a_o = \frac{4r}{\sqrt{2}}\]

Example:
The radius of copper is 1.261276 Å, therefore,

\[a_o = \frac{4 \times 1.276 A^0}{\sqrt{2}} = 3.608 A^0\]

The distance \(a_o\) between the adjacent corners of the f.c. is thus 3.608 Å. This gives the lattice parameter or lattice constant.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Number of atoms per unit cell</th>
<th>Lattice parameter (a_o) (Å)</th>
<th>(\varphi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S.C.</td>
<td>1</td>
<td>(a_o = 2R)</td>
<td>(\frac{\pi}{6} = 52.5^0)</td>
</tr>
<tr>
<td>B.C.C.</td>
<td>2</td>
<td>(a_o = \frac{4R}{\sqrt{2}})</td>
<td>(\frac{\pi}{8} = 68^0)</td>
</tr>
<tr>
<td>F.C.C.</td>
<td>4</td>
<td>(a_o = \frac{4R}{\sqrt{3}})</td>
<td>(\frac{\pi^2}{6} = 74.5^0)</td>
</tr>
</tbody>
</table>
2.1. CRYSTAL BINDING OF SOLIDS

Types of bonds in Crystals:

- Crystals of inert gases
  - Van der Waals - London interaction
  - Repulsive interaction
  - Equilibrium lattice constants
  - Cohesive energy

- Ionic crystals

- Covalent crystals

- Metal crystals

- Hydrogen bonded crystals
TYPES OF BONDS IN CRYSTALS.

Introduction: Nature of bonding in matter

Types of binding interaction which causes the atoms and molecules to attract at relatively large distance, and which join atoms together to form molecules and other structures:

\[ \text{Bonds} \]

1. STRONG BONDS
   a. Covalent Bond
   b. Ionic Bond
   c. Metallic Bond

2. WEAK BONDS
   a. Vander Waals
   b. Hydrogen Bond

1. **STRONG BONDS**: These are results from the exchange or sharing of electrons and occur because the bonded system has a lower potential energy than the separate atoms.

A. **Covalent Bond**: Electrons are shared between different atoms. The bond energy is electrostatic in origin. In diamond, the individual atoms of carbons are linked by covalent bond to form a rigid crystal lattice.
b. Ionic bonds: Electrons are transferred from one neutral atom to another, and the resulting positive and negative ions attract each other by Coulomb Forces. Example: NaCl

C. Metallic bonds: Electrons have greater freedom of movement.

2. Weak bonds

a. Van der Waals: These are weak attractive forces acting over short distances outside a molecule and enable it to attract both polar and non-polar neighbours.

b. Hydrogen bonding: Are basically, electrostatic interactions between molecules. These bonds are particularly important in determining the properties of H2O molecule.
Van der Waals - London interaction

Consider two identical inert gas atoms at a separation \( R \) large in comparison with the radii of the atoms. The attractive interaction which varies as the minus sixth power of the separation of the two atoms oscillators. This is the Van der Waals interaction, known also as the London interaction.

\[
\Delta U = - \frac{A}{R^6}
\]
Repsulsive interaction

As the two atoms are brought together their charge distribution gradually overlap as shown in figure, thereby changing the electrostatic energy of the system. At sufficiently close separation the overlap energy is repulsive, in large part because of the "Pauli exclusion principle". It is usually to write the total potential energy of two atoms at separation \( R \) as:

\[
U(R) = 4\varepsilon \left[ \left( \frac{\sigma}{R} \right)^{12} - \left( \frac{\sigma}{R} \right)^{6} \right]
\]

where \( \sigma, \varepsilon \) are new parameters, with \( 4\varepsilon \sigma^{6} \equiv A \) and \( 4\varepsilon \sigma^{12} \equiv B \). This \( U(R) \) is called Lennard-Jones potential. The force between the two atoms is given by \(-\frac{dU}{dR}\).

(5)
Cohesive Energy:

The total energy of the two atoms separated by \( R \), is represented by:

\[
U(R) = 4\varepsilon \left[ \left( \frac{a}{R} \right)^{12} - \left( \frac{a}{R} \right)^{6} \right]
\]

where \( \varepsilon \) and \( a \) are parameters.

\[ A = 4\varepsilon a^6 \quad B = 4a^{12} \varepsilon \] in Lenard-Jones.

\[
\therefore U(R) = \left[ \left( \frac{B}{R^{12}} \right) - \left( \frac{A}{R^6} \right) \right]
\]

This is known as Lenard-Jones potential where the first term is called repulsive term and the second is the attractive term for interaction (also called the Van der Waals interaction \( \Rightarrow U(R) = AR^{-6} \)).

- To determine the equilibrium lattice constant of \( \text{Ar, Xe} \ldots \text{etc (inert gases)} \)?

The cohesive energy of an inert gas crystals at absolute zero and at zero pressure is:

\[
\frac{U(R)}{\text{Tot.}} = 2NE \left[ 12.13 \left( \frac{a}{R} \right)^{12} - 14.45 \left( \frac{a}{R} \right)^6 \right] = 0
\]

\[ a \Rightarrow R = R_0 \Rightarrow U(R) = -(2.15)(4NE) \]

the same for all inert gases.

(6)
Where $U(R_0)$ is the cohesive energy at $K.E. = 0$.

Potential Energy

$U(R) = \left[ \frac{B}{R^{12}} - \frac{A}{R^6} \right]$ 

at $R = R_0$

minimum P.E.

at equilibrium, we can determine $\frac{R_0}{\overline{R}} = 1.09$.
2.2: Crystal Diffraction of Solids and Reciprocal lattice.

- Incident beam
  - X-Ray
  - Neutron
  - Electron
  - Bragg's Law

- Experimental diffraction Methods
  - Laue method
  - Rotating crystal method
  - Powder method

- Reciprocal lattice
- Lattice geometry

(8)
To study crystal structure theory through diffraction of photons, neutrons, and electrons.

The diffraction depends on the crystal structure and on the wavelength (λ).

Where \( \lambda \ll \) lattice constant of the crystal.

- For Optical system \( \rightarrow \lambda \approx 5000 \AA \)
  - Large enough compared with any lattice parameter (constant) of the solid.
- X-Ray photons \( \epsilon \): The energy of X-Ray photons \( \epsilon = \hbar \nu = \frac{\hbar c}{\lambda} \)

Where \( \hbar = 6.62 \times 10^{-27} \text{erg} \cdot \text{s} = 6.62 \times 10^{-34} \text{J} \cdot \text{s} \) (Planck's Constant).

So, Energies needed for X-Ray photons \( \approx 10-50 \text{Kev range} \).

- Neutron: \( \lambda = \frac{\text{c}}{\epsilon} \) (eV)

- Electrons: \( \lambda_{\text{ele}} = \frac{12}{\epsilon} \) (eV)^{-1/2}

Where

\[
\epsilon = \frac{\hbar^2}{2m\lambda^2}
\] (9)
Solved Problems

1. To calculate the wavelength $\lambda$ for X-rays:

- The energy of an X-ray photon is related to its $\lambda$ by:
  \[ E = h \nu = \frac{hc}{\lambda} \]
  where $\nu = \frac{c}{\lambda}$.

- $h = 6.62 \times 10^{-34}$ Js, $c = 3 \times 10^8$ ms, $1$ eV = $1.602 \times 10^{-19}$ J.

  In lab. unit: $\lambda (\text{Å}) = \frac{12.4}{E \text{(Kev)}}$

\[ \lambda = \frac{6.62 \times 10^{-34} \text{Js}}{E} \times \frac{1}{1.6 \times 10^{-19} \text{J}} \times 3 \times 10^8 \text{m/s} \]

\[ \lambda \times E = 124 \times 10^{-10} \text{m.Kev} \text{ or } \lambda \times E = 6.62 \times 10^{-34} \times 1.6 \times 10^{-19} \]

\[ = 12.4 \times 10^{-7} \times \frac{10^3}{10^{-2}} \text{eV.m} \text{m} \times 3 \times 10^3 \text{Kev} \]

\[ \lambda (\text{Å}) = \frac{12.4}{E \text{(Kev)}} \]

at 30 Kev X-ray energy: $\lambda = 0.4 \text{Å}$

50 Kev $\lambda = 0.248 \text{Å}$.

2. To derive and calculate $\lambda$ for electrons:

\[ \lambda = \frac{h}{p} = \frac{h}{mv} \]

\[ \frac{m^2v^2}{m} = \frac{h^2}{m^2} = m \times v^2 \]

\[ \frac{1}{2}mv^2 = E \text{(eV)} \text{ electric potential.} \]
\[
\frac{1}{2} \left( \frac{\hbar^2}{m_e \lambda^2} \right) = E
\]

\[
\lambda = \sqrt{\frac{\hbar^2}{2 meE}} = \frac{\hbar}{\sqrt{2 meE}}
\]

\[
\lambda = \frac{(6.63 \times 10^{-34} \text{ J s})}{\sqrt{2 \times 0.911 \times 10^{-27} \text{ J} \cdot \text{s} \cdot \text{E (eV)}}} \approx \frac{12}{\sqrt{E (\text{eV})}}
\]

\[
\theta R = \frac{150}{V_{\text{volt}}}
\]

Examples: 
\[V = 100 \text{ KV}\] electron energy is 1 
so, \[\lambda_e = 0.038 \text{ Å}.\]

\[V = 1000 \text{ KV} = 1 \text{ MV} = 10^6 \text{ V}\] 
so, \[\lambda = 0.01 \text{ Å}.\]

So, we can obtain any small \(\lambda_e\) for crystal diffraction of solids with a comparable lattice constant.
Bragg's Law

To derive and satisfy Bragg's law, suppose an incident beam on a plane of solids (arrangement of atomic layers) as shown below.

\[ d \sin \theta + d \sin \phi = 2d \sin \theta \]

where \( \sin \theta = \frac{BC}{d} \) \( \Rightarrow \) \( BC = BD = d \sin \theta \).

Total path difference = \( d \sin \theta + d \sin \phi = 2d \sin \theta \)

Constructive interference of the radiation from successive planes occurs when the path difference is an integral number \( (n \lambda = 2d \sin \theta) \) \( n = 1, 2, \ldots \).

This is called Bragg's law used in a diffraction of crystals with X-rays and electrons.
Experimental Diffraction Methods:

- Lane method: A diffraction technique used with single crystal samples. This is typically used to determine the orientation of a specific face of a crystal relative to the incident beam. This technique uses many λ's.

- Rotating crystal method: This is used for determining the entire crystal structure, in particular, the shape and size of unit cells and atom positions. The technique uses monochromatic X-rays and requires a single crystal of materials.

- Powder method: Uses monochromatic X-rays, but in this method, the sample is finely grounded.
LATTICE GEOMETRY

Planner Spacing Formula for d - interplaner spacing
(The distance between atomic planes).

\[
\frac{1}{d^2_{hkl}} = \frac{h^2 + k^2 + l^2}{a_0^2}
\]

For Cubic Lattice

When \( d_{hkl} \) is perpendicular to the plane of atoms shaded, as shown in the Geometry below:

Then: \( a_0 \): is the atomic distance called atomic constant.

\( d \): is the distance between parallel planes.
The fractional intercepts that the $l$ makes with the coordinate system, are:

$$\frac{a}{h}, \frac{b}{k}, \frac{c}{l}$$

for the axes $a, b, c$.

**NOTE:** $a_0$ is the full lattice vector length $a_0 = 1$; $\frac{1}{h}$ is fractional intercepts.

From figure, one can define the following:

- $\alpha_1$: angle between $\vec{d}$ and $\vec{a}$.
- $\alpha_2$: $\vec{d}$ and $\vec{b}$.
- $\alpha_3$: $\vec{d}$ and $\vec{c}$.

The direction cosines are:

$$\cos \alpha_1 = \frac{\vec{d} \cdot \vec{a}}{|\vec{d}| |\vec{a}|} = \frac{\vec{d} \cdot \vec{a}}{a_0},$$

$$\cos \alpha_2 = \frac{\vec{d} \cdot \vec{b}}{|\vec{d}| |\vec{b}|} = \frac{\vec{d} \cdot \vec{b}}{a_0},$$

$$\cos \alpha_3 = \frac{\vec{d} \cdot \vec{c}}{|\vec{d}| |\vec{c}|} = \frac{\vec{d} \cdot \vec{c}}{a_0}.$$

For cubic system: $|\vec{a}| = |\vec{b}| = |\vec{c}| = a_0$ and $d = |\vec{d}|$.

Then, $\cos^2 \alpha_1 + \cos^2 \alpha_2 + \cos^2 \alpha_3 = 1$.

$$1 = \frac{a_0^2 (h^2 + k^2 + l^2)}{a_0^2},$$

Then, $\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a_0^2}$.

OR $d^2 = \frac{a_0^2}{h^2 + k^2 + l^2}$ and $|d| = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$. 

(15)
Home Work: Prove that

\[ \frac{1}{\rho^2} = \frac{k^2 + k'^2}{a^2} + \frac{l^2}{c^2} \quad \text{for Tetragonal}. \]

Where: \( a = b \neq c \) and \( \alpha = \alpha_2 = \alpha_3 = 90^\circ \)

\[ \left( \frac{d}{a} \right)^2 = \left( \frac{d}{b} \right)^2 = \left( \frac{d}{c} \right)^2 \]

For tetragonal: \( |\vec{a}| = |\vec{b}| = a \) and \( |\vec{c}| = c \)

Substitute for \( \cos \alpha_1, \cos \alpha_2, \cos \alpha_3 \) in \((1)\)

\[ \frac{d^2}{a^2} + \frac{d^2}{b^2} = \frac{d^2}{c^2} = 1 \]

\[ d^2 \left( \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \right) = 1 \]

\[ \frac{1}{\rho^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad \text{This formula for } \rho \text{ of tetragonal}. \]

\((16)\)
Reciprocal distances are the appropriate unit to use to connect the diffraction phenomena.

The fundamental relationship uniting crystal indexes, planar spacings, and the measured diffraction angles is Bragg's law:

\[ 2d \sin \theta_{hkl} = n \lambda \]

The measured Bragg angles are proportional to \( \frac{1}{d} \), as follows:

\[ \sin^2(\theta_{hkl}) = n \lambda \cdot \frac{1}{2d_{hkl}} \]

For cubic structure \( \frac{1}{d} \), is proportional to

\[ \sin^2(\theta_{hkl}) = \frac{\alpha}{2} \left( \frac{h^2 + l^2 + k^2}{a^2} \right) \]

Thus the measured Bragg angles \( \theta \) are proportional to reciprocal distances in the lattice.

\[(17)\]
Reciprocal lattice (R.L.)

The reciprocal lattice of a crystal lattice is a mathematical tool used in crystallography to represent the crystal's symmetry and its diffraction properties. It is constructed by taking a lattice and generating a new lattice of points, called the reciprocal lattice, according to specific mathematical rules.

Diffraction pattern from selected area represents:

- Diffraction pattern of the crystal gives the structure of it.

Image of sample from electron micrograph represent:

- Real crystal structure.

\[ \mathbf{A} = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \]
\[ \mathbf{B} = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \]
\[ \mathbf{C} = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} \]

Where \( \mathbf{A}, \mathbf{B}, \mathbf{C} \) are vectors of the reciprocal lattice.

(18)
If $\mathbf{a}, \mathbf{b}, \mathbf{c}$ are primitive vectors of the crystal lattice, then $\mathbf{A}, \mathbf{B}, \mathbf{C}$ are primitive vectors of the (R.L). Each vectors of $\mathbf{A}, \mathbf{B}, \mathbf{C}$ are Orthogonal to two of the axis vectors of the crystal lattice. Thus, $\mathbf{A}, \mathbf{B}, \mathbf{C}$ have the property:

\[
\begin{align*}
\mathbf{A} \cdot \mathbf{a} &= 2\pi \\
\mathbf{B} \cdot \mathbf{a} &= 0 \\
\mathbf{C} \cdot \mathbf{a} &= 0 \\
\mathbf{A} \cdot \mathbf{b} &= 0 \\
\mathbf{B} \cdot \mathbf{b} &= 2\pi \\
\mathbf{C} \cdot \mathbf{b} &= 0 \\
\mathbf{A} \cdot \mathbf{c} &= 0 \\
\mathbf{B} \cdot \mathbf{c} &= 0 \\
\mathbf{C} \cdot \mathbf{c} &= 2\pi
\end{align*}
\]

Any arbitrary set of primitive vectors $\mathbf{A}, \mathbf{B}, \mathbf{C}$ of a given crystal lattice leads to the same set of (R.L) points.

\[
\mathbf{G} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C} \quad h,k,l = \text{integer}
\]

Any vectors $\mathbf{G}$ of this form is called 

"(Reciprocal Lattice Vectors - R.L.V)"

R.L. to S.C. lattice.

The primitive translation vectors of a simple cubic may be taken as the set:

\[
\mathbf{a} = a\mathbf{x} \quad \mathbf{b} = a\mathbf{y} \quad \mathbf{c} = a\mathbf{z}.
\]

$\mathbf{x}, \mathbf{y}, \mathbf{z}$ are unit vectors.

The volume of the cell is $\mathbf{a} \cdot \mathbf{b} \times \mathbf{c} = a^3$.  

(19)
The primitive translation vectors of the R.L. are found from the standard prescription:

\[ \mathbf{A} = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} = \frac{2\pi}{a} \hat{\mathbf{x}}; \]

\[ \mathbf{B} = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} = \frac{2\pi}{a} \hat{\mathbf{y}}; \]

\[ \mathbf{C} = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot \mathbf{b} \times \mathbf{c}} = \frac{2\pi}{a} \hat{\mathbf{z}}. \]

Thus, the R.L. is itself a simple cubic lattice of constant \( \left( \frac{2\pi}{a} \right) \).

\[ \text{كَانَ نَاَهُ المُسْبِلُ الحَرُوبُ لَدَّهُ سَبَّةُ لِلْمَضْلُوكَ} \]

والرَّجُلُ المُصْرِفُ بالشَّوَابِ (\( \frac{2\pi}{a} \)).
Crystal lattice $\rightarrow$ Crystal in solids are either crystalline or amorphous as previously described in Ch. 1. We are talking about the crystalline solids which have a crystal lattice of atoms in an ordered system. This system reveals asymmetry $\rightarrow$ Lattice vibrational modes $\rightarrow$ which is either longitudinal mode or transverse mode $\rightarrow$ These vibrations are responsible to transfer an energy.

The theories describe these energies of vibrations are started from these points.

If vibrational Energy of N-atoms arranged in a linear chain as follows:

\[ 1D \quad O-\cdots-O \text{-atom} \]

So, it can be expressed as a one-dimensional system. In 1D $\rightarrow$ energy of N-harmonic oscillator $\rightarrow$ In 3D $\rightarrow$ Extending to 3D case. This leads to vibrational energy of crystal (Atal) with N-atoms is equal to the Energy of a system of 3D - H DO (harmonic Osc ili.)
Lattice Vibration

Crystal lattice of atoms

A \quad \downarrow \quad \rightarrow \quad B

Classical Theory
(Dulong and Petit theory)

Quantum Theory
(Quantized)

\( \text{1) Debye} \)
\( \text{2) Einstein} \)

A) Classical Theory: The total energy for a single 3D isotropic Harmonic Oscillator:

\[
E_{\text{tot}} = E = K.E + P.E. = \frac{P^2}{2m} + V(r)
\]

\[
V(r) = \frac{1}{2} m \omega_o^2 (x^2 + y^2 + z^2) = \frac{1}{2} m \omega_o^2 r^2
\]

where \( m \): mass of atom; \( \omega_o \): frequency of oscillators of atom.

Now: According to Maxwell functions of the energy:

\[
f(\varepsilon) = A e^{-\frac{\varepsilon}{kT}} - \frac{P^2}{2m kT}
\]

for certain energy

\[
f(\varepsilon) = A e^{-\frac{m \omega_o^2 r^2}{2kT}} = f(P, r)
\]

where \( A \) is constant.

So, the average energy \( \langle \varepsilon \rangle = \ldots \)

We have chosen to use spherical coordinates \( (r, \theta, \phi) \) in coordinate space.

So,

\[
\langle \varepsilon \rangle = \langle \varepsilon_k \rangle + \langle \varepsilon_p \rangle
\]

(2)
Evaluating the integrals, so one find

\[ \langle \varepsilon \rangle = \langle \varepsilon_p \rangle + \langle \varepsilon_k \rangle = 3kT \]

\[ \frac{3}{2}kT \quad \frac{3}{2}kT \]

Where \( \langle \varepsilon_k \rangle = \langle \varepsilon_p \rangle = \frac{3}{2}kT \).

For an assembly of \( N \)-independent oscillators, so the total internal energy \( U \) is equal to:

\[ U_{\text{tot}} = N \langle \varepsilon \rangle = 3NkT \]

And the specific heat capacity for a gram (or for unit volume),

\[ C_v = \left( \frac{\partial U}{\partial T} \right)_V = 3NK \]

\( C_v \rightarrow \text{constant volume} \)

\( C_v \rightarrow \text{constant value, independent on temperature as shown} \)

\[ \boxed{C_v = 3NK} \]

So, for mole of any substance of \( N \) atoms, is equal to Avogadro's number \( (N_A) \) and the molar heat capacity \( (C_v_m) \) is a function of \( T \rightarrow \)

\[ C_v = f(T) \text{ for typical solid substance} \]

(3)
This is known as Dulong and Petit's law of Dulong and Petit. The law fairly well with experimental results for most substances at and above room $T_r$. But the breaks at low $T$. At low $T$-range, $C_v$ for all substances $\approx$ Zero. $C_v = \alpha T^3$ as $T$ approaches to Zero as shown in the above curve for $C_v$.

According to the classical theory, each atom vibrates independently.

B) Quantum Theory

1. Einstein Theory of $(C_v)$ in 1911, in this theory, Einstein considered as independent harmonic oscillators with single natural vibrational frequency $(\omega_0)$, but they are regarded as Quantum harmonic oscillator, which may have
only discrete energy values such as:
\[ \varepsilon_n = (n + \frac{1}{2}) \hbar \omega = \]
\[ \hbar \omega_0, \quad n = 0, 1, 2, \ldots \]

The oscillators may still be regarded as having the (Maxwell Boltzmann distribution) of energies:
\[ f(\varepsilon) = \frac{\varepsilon}{e^{\frac{-\varepsilon}{kT}}} \]

The oscillators are distributed in energy according to Boltzmann's law:
\[ \langle \varepsilon \rangle = \frac{\sum \varepsilon_n e^{-\frac{\varepsilon_n}{kT}}}{\sum e^{-\frac{\varepsilon_n}{kT}}} = \frac{\hbar \omega_0}{kT} \frac{\sum (n + \frac{1}{2}) e^{\frac{\varepsilon_n}{kT}}}{\sum e^{\frac{\varepsilon_n}{kT}}} \]

where \[ \chi = \frac{\hbar \omega_0}{kT} \]

After evaluations gives results

average energy: \[ \langle \varepsilon \rangle = \hbar \omega_0 \left[ \frac{1}{2} + \frac{1}{e^{\frac{\hbar \omega_0}{kT}} - 1} \right] \]

The internal energy \( U \rightarrow \) multiply \( \langle \varepsilon \rangle \) by \( 3N \rightarrow \) number of oscillators in 3D.

\[ U_{\text{tot}} = \left[ 3N \langle \varepsilon \rangle \right] = \left[ \frac{3N \hbar \omega_0}{2} + \frac{3N \hbar \omega_0}{e^{\frac{\hbar \omega_0}{kT}} - 1} \right] \]

\[ C_U = \left( \frac{\partial U_{\text{tot}}}{\partial T} \right)_V = 3Nk \left( \frac{\hbar \omega_0}{kT} \right)^2 \frac{C}{e^{\frac{\hbar \omega_0}{kT}} - 1} \]

(5)
\[ \frac{Q_E}{K} = \frac{k w_0}{2} \]

\[ C_v = 3 N k \left( \frac{Q_E}{T} \right) \left[ \frac{e}{Q_{E/T}} \right] \left[ \frac{Q_{E/T}}{\left( e - 1 \right)^2} \right] \]

1. For high \( T \): When \( T >> Q_E \), \( Q_E \approx 0 \)

\[ e = 1 \rightarrow e \approx 1 \]

\[ C_v = 3 N k \text{ at high } T. \]

Compared with the Classical Theory.

2. For low \( T \): \( T << Q_E \rightarrow Q_{E/T} \)

\[ e \approx 1 \]

and \( C_v = 3 N k \left( \frac{Q_E}{T} \right) e^{-Q_{E/T}}. \)

Experimentally, Einstein's theory is found to fit the observations fairly well at all but, at very low \( T \), where the observed \( (T^3) \) behavior is not obtained.

Obviously, this theory provides a much better explanation of the experimental data than the classical theory.
Debye Theory of Cu in 1912.

Since, the atoms of the crystal no longer vibrate independently of one another.

For one Dimensional $\rightarrow$ he said N-atoms Chain $\rightarrow$ there are essentially N-normal modes of vibrations.

For 3D $\rightarrow$ Crystal of N-atoms, each atom can vibrate independently along 3-coordinate $\rightarrow$ So, for this system, there are 3N-possible normal modes.

Internal vibrational energy: $\varepsilon_n = (n+\frac{1}{2}) \hbar \omega_c$

Energy of internal vibrations:

$$dU = \langle \varepsilon (w) \rangle - g(w) \, dw$$

(Average energy at frequency $w$)

(normal vibrational mode of the crystal)

$$U = \frac{9}{8} N k \Theta_D + 9 N k T \left( \frac{T}{\Theta_D} \right) \int_0^\infty \frac{x^2 \, dx}{(e^x - 1)}$$

$$x = \frac{\hbar \omega}{k T} ; \quad x_m = \frac{\hbar \omega_m}{k T} = \frac{\hbar}{k T} \left( \frac{6 N \pi^2}{V} \right)^{1/3}$$

(7)
\[ \Theta_D - \text{Debye temp} = \frac{\hbar \omega_m}{k} = \frac{k \nu_0}{k} \left( \frac{6 \pi n}{V} \right)^{1/2} \]

\[ CV \]

\[ \frac{3Nk}{V} \]

\[ T << \Theta_D \]

\[ T >> \Theta_D \]

\[ \left( \frac{\partial u}{\partial T} \right)_V = C_V = \frac{12 \pi^4}{5} Nk \left( \frac{T}{\Theta_D} \right)^3 \]

1. at \( T >> \Theta_D \) \( \rightarrow C_V \approx 3Nk \) (high T)
2. at \( T << \Theta_D \) \( \rightarrow C_V \approx \frac{12 \pi^4}{5} Nk \left( \frac{T}{\Theta_D} \right)^3 \) (low T)

\[ F(\frac{\Theta}{T}) \]

1

Debye

Einstein

Debye and Ein. theories.
The essential differences between Debye model and Einstein model is that Debye considers the vibrational modes of a crystal as a whole. Whereas Einstein starting points was to consider the vibration of single atom, assuming the atomic vibration to be independent of each other.

In fact, that the atomic vibrations in crystals are strongly coupled and can not considered as independently simplicity of Einstein model used?
CH-4

Thin Film Deposition.

   1.1 Ideal Solids and Crystal Structure
   1.2 Defects in Solids
   1.3 Bond and Electrons
   1.4 Thermodynamics and Phase Diagrams
   1.5 Kinetics of Diffusion
   1.6 Nucleation and Growth

2. Film Formation
   2.1 Film Formation
   2.2 ...

3. Film Deposition
   3.1 Vac. and K. Theory of gases
   3.2 Evaporation
   3.3 Sputter Deposition
   3.4 Cathodic Arc Deposition
   3.5 Molecular Beam Epitaxy
   3.6 Chemical Vapor Deposition (CVD)

4. Film Characterization (Overview)
   4.1 Imaging Techniques
   4.2 Structural
   4.3 Chemical
4.4 - optical techniques
4.5 - Electrical / Magnetic Techniques
4.6 - Mechanical Techniques

5 - Properties of Thin Films
5.1 - electrical properties
5.2 - Magnetic prop.
5.3 - Mechanical prop.

- Introduction to Scanning E.M.
- FIM.
- AES.
- Introduction to Surface and Thin Films.
- Crystal Growth.
- X-Ray Crystallography.
Solids: amorphous, crystalline
(atoms show short range order only)
(Glass)

Crystal structure

Lattice
(reg. periodic array of points in space)

Simple cubic (bcc) (fcc)

Defined by lattice parameter = \( a_0 \)
= length of a cubic side

- \( \text{Cr} \) - bcc lattice
- one Cr atom basis
  - \( a_0 = 2.88 \text{ Å} \)
- \( \text{Cu} \) - f.c.c. lattice
- 1 Cu atom basis
  - \( a_0 = 3.615 \text{ Å} \)
- \( \text{Si} \) - f.c.c. lattice
  - 2 Si atom basis
  - 1 Si at (0,0,0)
  - other Si at \( (\frac{1}{4}, \frac{1}{4}, \frac{1}{4})a \)
  - \( a_0 = 5.43 \text{ Å} \)

Surfaces
- For thin films, we are interested in surfaces.
- Cut details in different ways.
Describe surfaces by Miller indices (hkl).

Examples: (100), (110), (111) planes of atoms. (See atoms distribution for each for f.c.c. and bcc.)

ex. (100) f.c.c. b.c.c.

Crystal Directions

defined by a vector [hkl]

between two lattice points.

ex.

1-2

Defects in Solids:

- Polycrystalline solid contains several crystalline regions which are randomly oriented.
- Most crystalline materials have many defects.

Ex.: Si can grown with relatively few defects.

Type of defects:

1. Grain boundaries: interfaces between two single crystal regions of different orientation.
At grain boundaries tend to be loosely bound, implying more reactive and accelerated diffusion along grain boundaries.

Size/Grain sizes \( \Rightarrow \) (0.1 \( \mu \)m - 100 \( \mu \)m)

- How many atoms are at grain bound?
  - Generally:
    - Lower \( T \) \( \Rightarrow \) Smaller grains \( \Rightarrow \) many bound
    - Higher \( T \) \( \Rightarrow \) larger \( \Rightarrow \) fewer bound

- Line Defects: - dislocations

- Point Defects: - vacancy \( \rightarrow \) interstitial atom
  - Impurity atoms - Self-interstitial atom

In principle, you can eliminate all of these except vacancies.

Vacancies arise from thermodynamics (entropy)

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\[ \xrightarrow{\text{Low entropy}} \text{Ef} \xrightarrow{\text{Higher entropy}} \]
\[
\begin{align*}
\text{Fraction of vacancies (} f \text{)} & = \frac{E_f}{k_B T} \\
& \approx 1 \times 10^{-17} \\
\text{at R.T} & = \text{at } 300 \text{ K}
\end{align*}
\]

\[ k_B = 1.38 \times 10^{-23} \, \text{K} \]
\[ E_f = 1 \text{ eV} \]

Note

*Point Defects often arise from:

1. Fast Deposition.
2. Low Substrate T.

\( \Rightarrow \) (No time for atoms to move to crystal lattice sites).

**Surface Roughness**

Films always have some statistical distribution of thickness across the film.

\[
\text{Average thickness} \quad \langle d \rangle \quad \text{and} \quad d \text{ thickness}
\]

**In the worst case:**

\[
\Delta d = \sqrt{d}
\]

*generally observed less Roughness.*
Bonds and Electrons in Solids.

Bonding in Materials:
- Bonds lower the total $E_a$ of a system of atoms $\Rightarrow$ Solids are more stable than free atoms.
- Bonds from electrostatic and quantum attraction and repulsion.
- Electron structures around ion cores lead to different bond types and strengths.

Basic Types of Bonds

- **Metallic**
  - Relatively weak (1-2 eV)
  - Electrostatic and quantum attract. and repuls.
  - Easy to deform
  - Ex: Most Metals Fe, Ni, Cr.

- **Ionic**
  - Strong (2-10 eV)
  - Coulombic of opposite charges.
  - Ex: NaCl, ZnS

- **Covalent**
  - Strong bond
  - Ex: Si, Ge, GaAs

Surface Bonds

$E_{surf}$ - bulk
$E_{surf}$ - Surface.

Surface energy.

Surface Pot.

$P_{bulk}$

$P_{surf}$

$\Delta$ $P_{surf}$

$\Delta$ $P_{bulk}$

$\Delta$ $P$ surf.

$\Delta$ 1/2 atoms

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Thermodynamics and Phase Diagrams

Free energy change

\[ \square = G_{\text{final}} - G_{\text{initial}} = \square - T \square \]

where \( \square \) = enthalpy change
\( T \) = temp.
\( \square \) = entropy change

1. \( \square < 0 \Rightarrow \) process is allowed.
2. \( \square > 0 \Rightarrow \) process is forbidden.
3. \( \square = 0 \Rightarrow \) equilibrium.

Nature will minimize free energy.

Chemical Reactions

\[ aA + bB \rightleftharpoons cC \]

We can relate the FE change for this reaction to the activity, \( a \), (kind of concentration).

\[ \Delta G = RT \ln \left[ \frac{[aC]^{c}}{[aC_{\text{eq}}]^{c}} \right] \frac{[aA]^{a}}{[aA_{\text{eq}}]^{a}} \frac{[aB]^{b}}{[aB_{\text{eq}}]^{b}} \]

\[ R = \text{gas const} = 1.987 \text{ cal/(mole.K)} \]

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Example

\[(\text{oxide formation})\]

\[
\begin{align*}
\Delta G \text{ (Kcal)} & \quad \begin{array}{c}
2 \text{Ni} + \text{O}_2 & \rightarrow 2 \text{NiO} \\
\text{Si} + \text{O}_2 & \rightarrow \text{SiO}_2 \\
\left(\frac{4}{3}\right) \text{Al} + \text{O}_2 & \rightarrow \frac{2}{3} \text{Al}_2\text{O}_3
\end{array}
\end{align*}
\]

\[-300 \quad 400 \quad 800 \quad 1200 \quad 1600 \quad T(\degree C)\]

- IF Al and Al\(_2\)O\(_3\) are in contact with Si and SiO\(_2\)
  - So Al will be oxidized to Al\(_2\)O\(_3\)
  - SiO\(_2\) will be reduced to Si

No information about rate.

If you have a Ni-Al alloy
- Al oxidizes preferentially so end up with Al\(_2\)O\(_3\) film on top

\[
\text{Ni} \quad \text{rich alloy layer} \\
\text{Ni-Al} \\
\text{Al}_2\text{O}_3
\]

Phase Diagrams

arise from minimizing free energy for each phase.
- Gas - Liquid - Solid transitions
- Structural changes (Gr - Diamond)
- Stable alloys

![Diagram showing phases and pressure-temperature relationship]

T.P. has 3 phases coexisting (very well-defined).

**Kinetics of Diffusion**

**Kinetics**: how fast it will happen = atoms diffusing through a solid.

**Diffusion in T-D - Fick's 1st and 2nd Law**

**Fick's 1st law**: (stuff moves from where you have lots to where you have little)

\[ J = -D \frac{dC}{dx} \]

- Mass flux (atoms/cm\(^2\)-sec)
- Diffusion coefficient (cm\(^2\)/sec)
- Concentration gradient (atoms/cm\(^3\))

Depend on moving atoms and solids.
Now let us consider the flux of atoms into and out of a particular volume in the solid.

The fluxes \( J \) may be different at different positions \( (x) \) in the material.

Mathematically \( \frac{\partial J}{\partial x} = \frac{J_2 - J_1}{\Delta x} \)

\[ J_2 = J_1 + \frac{\partial J}{\partial x} \Delta x \]

Rate of increase of matter in the region = Rate of flow in - Rate of flow out = \( (J_1 - J_2) \Delta A = -\frac{\partial J}{\partial x} \Delta x \)

or this = rate of change of concentration in the volume.

So...

\[ \frac{\partial J}{\partial x} = \frac{\partial C}{\partial t} \]

Now using Fick's Law:

\[ \frac{\partial J}{\partial x} = -D \frac{\partial^2 C}{\partial x^2} \]

Fick's 1st law

\[ \frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} \]

Fick's 2nd law
Atomic View: for simplicity consider a cubic lattice.

1. Dark atom moves to Right, where do the neighboring atoms go?
2. Hard to move, like this $\Rightarrow$ slow

- There is always an energy barrier to diffusion (activation energy).

What do we expect mathematically for the flux to the right (from position 1 to 2):

$$J_{1\rightarrow2} = \frac{1}{6} \gamma \left[ e^{-\frac{E_f}{kT}} \right] \left[ C \cdot a_0 \right]$$

- (jump attempt freq.)
- (No. of atoms in any direction in cubic lattice)
- (Activation energy barrier, percent area)

Similarly, we can find the flux to the left:

$$J_{1\rightarrow2} = \frac{1}{6} \gamma \left[ e^{-\frac{E_f}{kT}} \right] \left[ e^{-\frac{E_l}{kT}} \right] \left[ (C + \frac{dC}{dx} \cdot a_0) \right]$$

\((12)\)
the net flux to the right
\[ J_{net} = J_{1-2} - J_{2-1} = \left[ \frac{1}{6} \alpha_0^2 D \right] \left[ E - \frac{(E_f + E_j)}{kT} \right] \frac{dc}{dx} \]

Comparing this to Fick's 1st law:
\[ J = D \frac{dc}{dx} \]

we find
\[ D = D_0 e^{-\frac{E_D}{kT}} \]

where \( D_0 = \frac{1}{6} \alpha_0^2 D \) and \( E_D = E_f + E_j \)

**Diffusion increases with Temp.**

### Diffusion Coefficients

- Self diffusion (element A in B): \( D_{AB} \)

- Vacancy Diffusion: \( D_V \)

- Chemical Diffusion (element A in B): \( D_{AB} \)

- Grain Boundary Diffusion: \( D_{gb} \)

- Self Diffusion: \( D_s \)

\( D \) is typically **not constant**, but it is a function of...
- \( D \equiv f(\text{position}) \)
  - Jump freq. depends on local atomic arrangement and defect.
  - temp. / gradient S.
- \( D \) function of direction in lattice.
- \( D \) fun of Time.
  ( Defect, Concentrations, T, may vary with time).

**High Diffusivity Paths**

- grain boundaries.
- BD-dislocation networks.
- surfaces.

There are more open structures with higher jump freqs and lower energy barriers.

\[ D_0 \text{ and } D, E_D \text{ are diff for these paths.} \]

Usually the cross sect. areas of these are small compared to the rest of the film.

In general (but not necessarily at high T) \( D_S > D_{gb} > D \)
1.6 Nucleation and Growth

Connection to phase diagrams:

- Can phase diagrams help us with understanding rates?
- Consider cooling a liquid into a solid through a eutectic point.

At point A: Solid is not stable so will not form.

- B: Solid and Liq. are both stable so no driving force to solid.
- C: Liq is unstable - will form solid.
- D: Liq is unstable - will form solid.

Further from equil. = greater driving force to form solid.

Transformation to solid phase

Requires:
1. Nucleation of new phase.
2. Growth of new phase.

That depends on:
1. Liquid phase instabiliy
   - Driving force to equilibrium
   - Increase as we move to lower Temp.
2. Diffusion of atoms into clusters:
   - Increases at higher temperatures.

* Combine these two terms (multiplication) to determine the total nucleation rate

The max. rate of nucleation is at some $T < T_e$

Growth:

- Growth of the phase is diffusion controlled $\Rightarrow$ increases with Temp.

Transformation rate:

Total rate of forming solid is product of nucleation rate and growth rate.
Nucleation Details

When moving into a 2 phase region on phase diagram - how does the new phase form?

Two issues

1. Thermodynamics: Is nucleation possible? (energy minimization)
2. Kinetics: How fast does it happen? (nucleation rate)

Homogenous nucleation

vapor \rightarrow \text{liquid (solid) for pure material with NO substrate}

\vdots \rightarrow \vdots \rightarrow \vdots

Energy minimization involves two terms:

1. Volume Transition.
2. Surface formation.
1. Volume transition:

\[ \Delta G = \frac{4}{3} \pi r^3 \cdot \Delta G_v \]

\( \Delta G_v \) — change in free radiant of lig. phase.

energy per unit Vol. for this system, the activity is essentially the pressure \( P \).

\[ \Delta G_v = \frac{RT}{V} \ln \frac{P_s}{P_v} \]

where \( R \) is the atomic volume, \( P_s \) is the press. above the lig. (solid), and \( P_v \) is the press. in the vapor.

We want \( P_v > P_s \) so that \( \Delta G_v \) is (ve)

2. Surface formation:

\[ \Delta G_{surf} = 4 \pi r^2 \gamma \]

surf. energy per unit area.

change in surf. energy is always (ve) when forming surfaces.

Total Energy Change

\( 18 \)
\[
\Delta G_{\text{tot}} = \frac{4}{3} \pi r^3 \Delta G_V + 4 \pi r^2 \gamma
\]

**Note**

1. Initial formation of nuclei has increase in \( \Delta G \Rightarrow \) metastable
2. If \( r < r^* \), then nuclei shrink to lower \( \Delta G \).
3. If \( r > r^* \), then nuclei grow to lower \( \Delta G \).
4. \( r^* \) is a critical radius for nucleation.

Find \( r^* \) from

\[
0 = \frac{4}{3} \pi r^3 \Delta G_V + 4 \pi r^2 \gamma \Rightarrow \frac{4}{3} \pi r^3 \Delta G_V = -4 \pi r^2 \gamma
\]

give \( r^* = \frac{-4 \gamma}{\Delta G_V} \)

and \( \Delta G^* = \frac{16 \pi \gamma^3}{3 (\Delta G_V)^2} \)

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Nucleation Rate

How fast will the critical nucleus continue to grow?

Consider the rate at which atoms will join the critical nuclei?

\[ \text{term 1:} \quad \frac{N}{N^*} = n_s \exp \left\{ \frac{-\Delta G^*/kT}{q} \right\} \]

\[ \text{term 2:} \quad A^* = 4\pi (r^*)^2 \]

\[ \text{Term 3:} \quad \omega = \frac{\alpha (P_v - P_s) N_A}{\sqrt{2\pi M R T}} \]

from kinetic theory of gases.

\[ N = \left[ n_s \exp \left\{ \frac{-\Delta G^*/kT}{q} \right\} \right] \left[ \frac{4\pi (r^*)^2}{A} \right] \left[ \frac{\alpha (P_v - P_s) N_A}{2\pi M R T} \right] \]

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Film Formation II

Island Growth

observe 3 growth modes especially:

1 Island growth (Volmer-Weber):
   - form 3D islands.
   - Source:
     1 film atoms more strongly bound to each other than to substrate.
     2 and/or slow diffusion.

2 Layer by layer growth (Frank-vander Merwe)
   - generally highest crystalline quality.
   - Source:
     1 film atoms more strongly bound to substrate than to each other.
     2 and/or fast diffusion.

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3. Mixed growth (Stranski-Krastanov)
- Initially layer by layer
- Then forms 3D islands.

\[ \gamma_{sf} \sim \gamma_{vf} \]

\[ \gamma_{sy} = \gamma_{fs} + \gamma_{vf} \quad (0 \leq \theta \leq 90) \]

For islands growth when $0 < \theta < 90$

\[ \cos \theta < 1 \]

\[ \frac{\gamma_{sv}}{\gamma_{vf}} \]

\[ \gamma_{sv} < \gamma_{fs} + \gamma_{vf} \]

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For layer growth $\theta = 0$ or undefined.

$$\hat{y}_{sv} = \hat{y}_{fs} + \hat{y}_{uf}$$

For mixed growth

$$\hat{y}_{sv} \approx \hat{y}_{fs} + \hat{y}_{uf}$$

The layer growth condition with cosine $\theta$ greater than 1 looks odd. This is the case where the angle theta is undefined because for layer growth there is no point where the substrate, vapor and film come together and therefore no way to define the angle.

**Thick Films - Zone Models**

- Furthermore growth depends on:
  - Bulk diffusion
  - Surface diffusion
  - Desorption
  - Geometry

- Shadowing (line of sight impingement)
  - Atoms can not impinge here

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Relative importance of these processes depends on:
1. Substrate Temp. (T)
2. Deposition Rate (R)

Grain size dependence on deposition rate and Subst. Temp.
- Grain size typically increase with increasing film thickness, decreasing T_{subst.}, and increasing annealing temp. and decreasing deposition rate.

Grain size ↑ with ↑ film thickness and ↑anneal. Rate

\[ T_{subst} \]

![Graphs showing grain size vs. substrate temperature, film thickness, and annealing temperature](image-url)
Other factors affecting film growth

1. Substrate:
   ① not really a featureless plane
   ② atomic structure = epitaxy
   ③ Defects - relationship of film cryst. to subst. cryst. str.

2. Contamination

   from:
   ① poor back ground pressure
   ② impure deposition source
   ③ dirty substrate

Changes the energies ($\gamma_s \neq \gamma_v \neq \gamma_f$)

(dirty surf.)

Changes $\gamma_s$ and $\gamma_f$.

$\gamma_{sv}$

Dirt:

Change $\gamma_{sv}$ and $\gamma_{sv}$.