

## PHY 311: SOLID STATE PHYSICS

### Course Description:

This course is offered to 3rd Year Physics students. The course covers: Intermolecular forces, elementary description of crystal structures; diffraction of X-rays by crystals; lattice vibrations; thermal and dielectric properties of solids. It has a laboratory component that enables easy understanding of the theoretical concept through practical exposure.

### Course Objectives:

At the end of the course students should be able to:

- (i) Describe the intermolecular forces of solids
- (ii) Describe the different crystal structures;
- (iii) Use Bragg's law to index powder diffraction lines;
- (iv) Identify single crystal structures from their diffraction pattern;
- (v) Explain Einstein's and Debye's models of lattice heat capacity.
- (vi) Explain thermal and dielectric properties of solids.
- (vii) Perform experiments linking the theory to practical concepts.
- (viii) Describe the Hall Effect and its applications in semiconductors
- (ix) Illustrate the band theory of solids and explain the difference between metals, Insulators and semiconductors

### Course Content:

#### 1. Intermolecular forces and potential energy

- Attractive and Repulsive forces
- The resultant force
- Potential energy Between atoms and the resultant

#### 2. Elementary description of crystal structures:-

- Crystal periodicity;
- Crystal lattices;
- Symmetry elements;
- Crystal classes,
- Crystal planes and Miller indices,
- Unit cell, crystallographic axes, coordination number, atomic radius and density of packing.

#### 3. Diffraction of X-rays by crystals

- Bragg's law;
- Structure factor;
- Laue, single crystal method and powder diffraction patterns;
- Indexing of powder diffraction lines

#### 4. Lattice vibrations

- Linear monatomic and diatomic lattices;

- Brillouin zone;
  - dispersion curves;
  - acoustic and optic modes;
  - Infrared absorption in ionic crystals.
- 5. Thermal properties of insulating solids**
- Quantization of lattice vibrations – phonons
  - Einstein and Debye models of lattice heat capacity
  - Thermal conductivity of insulators.
- 6. Dielectric properties of solids**
- Electronic, ionic and orientational (dipolar) polarizability;
  - Dielectric constant and electric susceptibility;
  - Resonance absorption in dielectrics;
  - Frequency dependence of dielectric properties of solids.
- 7. Mechanical properties of solids**
- Dislocation
  - Vacancies and interstitials
  - Strength of materials
- 8. The free electron theory of metals**
- Gas of electrons
  - Electronic specific charge
  - Electric and thermo conduction
  - Hall Effect
  - Dielectric Response
- 9. Introduction to the band theory of solids**
- Metals, Insulators and semi-conductors
  - Application of band theory of semi-conductors

#### **MODE OF DELIVERY**

- Two hours of lecture per week and One hour of tutorial / practical per week

#### **COURSE ASSESSMENT**

- Assignments, Tests and Practicals (40%), End of semester examinations (60%)

#### **KEY READINGS:**

- (i) Charles Kittel [1996]. Introduction to solid state physics, John Wiley and Sons Inc, United States of America.
- (ii) J.R Hook and H.E [1991]. Hall. Solid state physics, [2<sup>nd</sup> edition] John Wiley and Sons Ltd, Chichester, England.
- (iii) Ashcroft, N. W and Mermin, D.N; Solid State Physics.(1976), McGraw-Hill
- (iv) J.S Blakemore [1996], solid state physics [2<sup>nd</sup> edition ] the press syndicate of the university of Cambridge, United Kingdom
- (v) E.J.K.B. Banda. Solid State Physics. SEP312. Dist. Ed. Lecture Notes.

## CHAPTER 1: INTERMOLECULAR FORCES AND POTENTIAL ENERGY

Intermolecular forces are forces that hold states together. They exist between all molecules and atoms and responsible for the properties of states including some crystals. For example:

They determine whether the substance is a solid, liquid, or gas at a given temperature. Strong intermolecular forces result in liquids and solids including high melting and boiling points, while weak intermolecular forces result in gases including low melting and boiling points.

Intermolecular forces originate from the interactions between charges, partial charges, and temporary charges on molecules/atoms/ions. They are categorized either as attractive or repulsive forces.

### 1.1 ATTRACTIVE FORCES

Is a force by which one molecule attracts another molecule. They are divided into two groups: strong forces and weak forces. The weak forces responsible for many properties of molecular compounds are the van der Waals forces that includes:

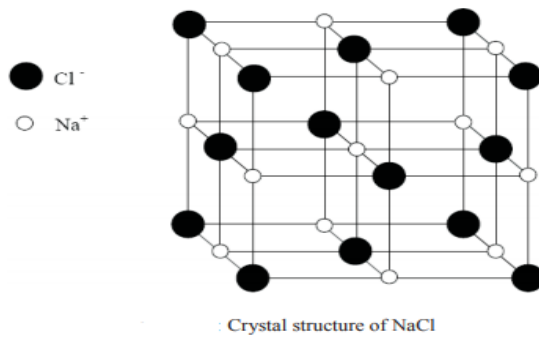
- dispersion forces
- dipole – dipole interactions and
- the hydrogen bond.

The strong forces are the bonding forces of the molecules that include, ionic, covalent and metallic bonds.

#### (a) Ionic bonding

These are strong attractive forces that arise from the electrostatic charges in the molecules or atoms. i.e attraction between the positive and negative ions as a result of complete transfer of electron from one atom (that becomes positive ion) to the other atom participating in the bonding (that becomes negative ion). The most common ionic compounds are the alkali halides such as sodium chloride (NaCl).

The solid sodium chloride crystal normally known as rock salt do not have individual molecules of NaCl. The crystal is just an array of positive ( $\text{Na}^+$ ) ions and negative ( $\text{Cl}^-$ ) ions held together by the coulomb's force that exist between charged particles. The positive sodium ion and the negative chloride ion occupy alternate positions in a cubic crystal lattice. i.e each sodium ion is surrounded by six chloride ion and vice versa as shown below.



### (b) Covalent bonding

This is a strong attractive forces that arise from the concentration of an electron cloud between the positively charged nuclei. i.e the outer most electrons of the unstable atom is shared by other atoms to become stable.

The common crystal where the atoms experience a covalent force is the diamond structure constituted by any group iv elements such as carbon, silicon, germanium or tin. In a diamond, the carbon atoms are arranged tetrahedrally. Each carbon atom is attached to four other carbon atoms.

### (c) Metallic bonding

These are attractive forces that occur in metallic crystals. For example, for sodium with electronic structure (2:8:1), when the sodium atoms come together, the electrons in the outermost shell shares space with the corresponding electron in the neighboring atom to form a molecular orbital. Each sodium atom is touched by eight other sodium atoms – and the sharing occurs between the central atom and all the outermost orbitals of all the eight other atoms. This sharing goes on among all the atoms in that lump of sodium.

The electrons can move freely within these molecular orbitals, and so each electron becomes detached from its parent atom. These electrons appear as a “Sea of free electrons” which fill the space between positive ions. The metal is held together by the strong forces of attraction between the positive ion and the sea of electrons.

## 1.2 Expression for attractive forces

It's quite clear that the attractive force between two opposite ions decreases as the distance (x) between them increases. This can be represented by a simple power law as shown.

$$F_{att} = \frac{A}{X^m}$$

$$F_{att} = AX^{-m}$$

1.0

Where  $x$ , is the distance between the atoms,  $m$  is the positive integer, and  $A$  is the suitable constant

From the equation, if  $m$  is large then the force rapidly reduces to a smaller magnitude and vice versa. However, if  $m$  is large when  $x$ , is greatly small then the force rises rapidly. This shows that attractive forces can still be experienced when the distance between the two atoms are large.

Generally attractive forces between two atoms are regarded as long range forces.

### 1.3 REPULSIVE FORCES

As we already know that when molecules are far apart like in gases, the intermolecular forces are very small and will always be attraction force. At the same time when molecules are relatively close like for liquids and solids, this force increase.

However, when these molecules are made to be closer to each other during compression, a considerable pressure is required. This implies that a repulsive force comes into play when the molecules pushed so close to a distance less than their normal spacing. Hence molecular repulsive force only acts on molecules at very short distance between each other.

#### (a) Origin of repulsive

The repulsive forces may be described as arising from two major sources:

- i. When two atoms (or molecules) are held together by some bond, there will be penetration of one electron shell or orbital by the other. This means that the nuclei are no longer screened from each other, and since they are both positively charged, then they will automatically repel each other.
- ii. The Pauli Exclusion Principle states that “*two electrons of the same energy cannot occupy the same element of space*”. When this happens during bonding, the energy of one must be increased. This is equivalent to force of repulsion.

#### (b) Expression for repulsive force

Generally the repulsive force between two atoms (or molecules) reduces drastically as the separation between them increases, i.e they are significantly great at very short distances. They are therefore short – range forces that can be represented as:

$$F_{rep} = \frac{B}{x^n}$$
$$F_{rep} = Bx^{-n} \quad 1.2$$

Where  $x$  is the distance between atoms (or molecules), and  $n$  is the positive integer, and  $B$  is a suitable constant.

### 1.4 THE RESULTANT FORCE

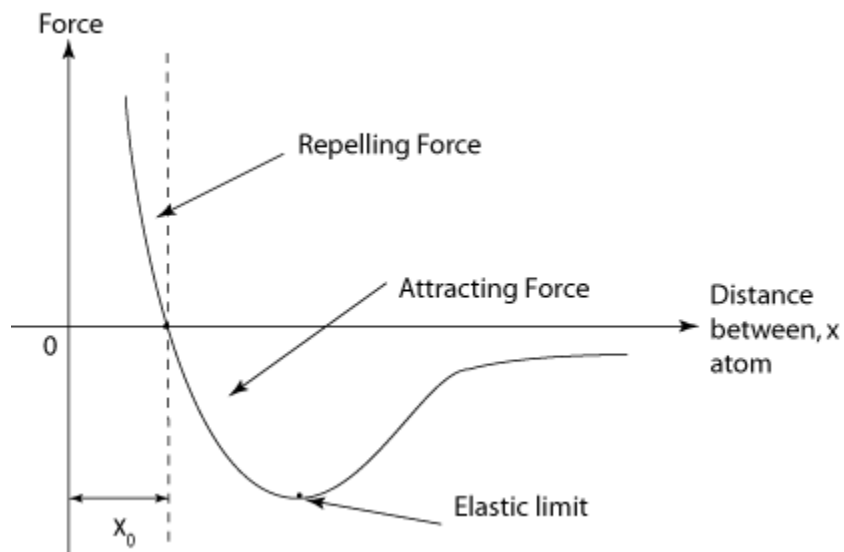
Now that there exist both the repulsive and attractive force between atoms, therefore it's prudent to write the expression of the interatomic force as the resultant of the two forces.

The resultant force  $F$ , between atoms is given by

$$F = F_{att} + F_{rep}$$

$$F = \frac{A}{x^m} - \frac{B}{x^n} \quad 1.3$$

A graph of the intermolecular force against the separation distance between atoms produces a curve as shown in the figure below.



#### Interpretation of the curve

At short distances  $x$  when the molecules are so close to one another like in solids, the force they experience is high and it's repulsive in nature. As the separation begin to increase, the repulsive force decrease greatly to zero at equilibrium when the molecules are at their normal spacing  $x_0$ .

When the separation increases beyond the molecules normal spacing ( $x_0$ ), the force changes to attraction instead acting in the opposite direction that slightly increase to a maximum at a particular distance (due to the influence of repulsive force). The attractive force then decreases gradually as the separation continues according to the equation 1. This force becomes weak and weaker with distance just like for the case of gases.

#### Equilibrium Position

At a separation of  $x_0$ , the two forces balance out each other making the net force between the atoms zero. Substituting for  $F$  in equation 3

$$0 = \frac{A}{x^m} - \frac{B}{x^n} \quad 1.4$$

This gives the constant  $B$  as:  $B = A \frac{x_0^n}{x_0^m} = Ax_0^{n-m}$

Now replacing this  $B$  with the one in equation 3, gives

$$F = A \left[ \frac{1}{x^m} - \frac{x_0^{n-m}}{x^n} \right] \quad 1.5$$

For small displacements,  $dx$  from the equilibrium position, the restoring force is:

$$dF = A \left[ \frac{n-m}{x_0^{m+1}} \right] dx \quad 1.6$$

From the equation above, the restoring force  $dF$  is directly proportional to the displacement implying that the displaced particle is a simple harmonic. Therefore these atoms or molecules oscillate about an equilibrium position as for the case of solids.

## 1.5 POTENTIAL ENERGY

Potential energy between two atoms is the work done in bringing one atom from infinity to a distance  $x$  from another atom.

The relationship between the potential energy  $V_{(x)}$  and the force  $F_{(x)}$

$$V_{(x)} = \int F_{(x)} dx \quad 1.7$$

Expression for potential energy

Consider two atoms that are at infinite distance apart, being pushed together infinitely slowly until they reach a separation  $x$  where they start to experience a repulsive force  $F_{(x)}$

From the previous discussion, the repulsive force,  $F_{(x)} = -\frac{B}{x^n}$ ,  $(n > 1)$  1.8

The potential energy,  $V_{(x)} = -B \int_{\infty}^x \frac{dx}{x^n}$  1.9

This gives  $V_{(x)} = \frac{B}{n-1} \left( \frac{1}{x^{n-1}} \right)$  1.10

Similarly, for attraction force  $F_{(x)} = \frac{A}{x^m}$ , the potential energy will be  $V_{(x)} = \frac{A}{1-m} \left( \frac{1}{x^{1-m}} \right)$

## 1.6 Resultant Potential energy

From the resultant force discussed earlier,  $F = A \left[ \frac{1}{x^m} - \frac{x_o^{n-m}}{x^n} \right]$

The resultant potential energy can then be determined by substituting the resultant force in equation () above.

$$V = A \int \left[ \frac{1}{x^m} - \frac{x_o^{n-m}}{x^n} \right] dx \quad 1.11$$

$$V = A \left[ \left( -\frac{1}{m-1} \cdot \frac{1}{x^{m-1}} \right) + \left( \frac{1}{n-1} \cdot \frac{x_o^{n-m}}{x^{n-1}} \right) \right] \quad 1.12$$

This expression gives the resultant potential energy, where the first term is for attractive and its negative while the second term is for repulsive that is positive.

At equilibrium position when  $x = x_o$ , the potential energy becomes minimum.

$$V_{\min} = -A \frac{1}{x_o^{m-1}} \left[ \frac{1}{m-1} - \frac{1}{n-1} \right] \quad 1.13$$

Therefore the graph of potential energy against separation of atoms is similar to that of the force and the minimum potential energy is achieved when the resultant force is zero ( $x = x_o$ ). Generally any system left on its own will always move so as to reduce its potential energy.

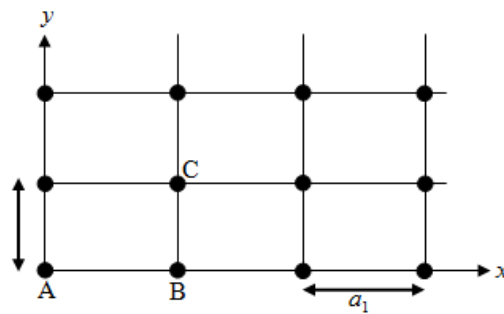


## Chapter 2: Elementary Description of Crystal Structures

### 2.1 Crystal Periodicity

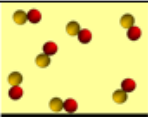
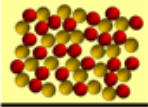
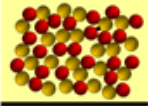
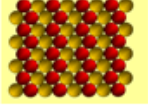
Crystal structure is one of the most important aspects of materials science and engineering as many properties of materials depend on their crystal structures. The basic principles of many materials characterization techniques such as x-ray diffraction and transmission electron microscopy are based on crystallography. Therefore, understanding the basics of crystal structures is of paramount importance.

A solid is said to be a crystal if its atoms are arranged in such a way that their positions are *exactly periodic*. This concept is illustrated in **Fig.1** using a two-dimensional structure. A perfect crystal maintains this periodicity in both the  $x$  and  $y$  directions from  $-\infty$  to  $+\infty$ . As seen from this periodicity, the atoms A, B, C, etc. are *equivalent*.



**Fig.1:** Crystal periodicity

**Definition:** A crystal is a solid composed of atoms, ions or molecules that demonstrate long range periodic order in three dimensions. When a group of atoms is repeated in space, it forms the crystal structure. Non-crystalline or Amorphous materials do not possess such periodicity; rather they have random arrangement of atoms. The periodicity of atoms in crystalline solids can be described by a network of points in space called lattice.

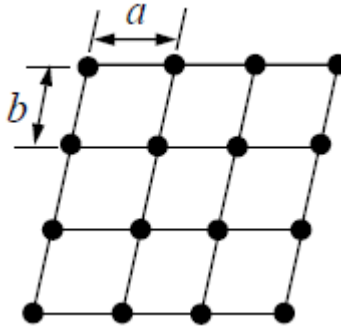
	State of matter	Order	Properties
	Gas	No	Isotropic
	Liquid	Short range	Isotropic
	Solid (amorphous)	Short range	Isotropic
	Solid (crystalline)	Long range	Anisotropic

## 2.2 Crystal Lattice

**Definition:** A lattice is a three-dimensional extended array of points each of which is surrounded in an identical way by its neighbors. The lattice points in a crystal are occupied by atoms and there are a group of atoms attached to each lattice point. This group of atoms is called the *basis* and the distance between adjacent lattice points is called the *lattice space*.

$$\text{Crystal structure} = \text{lattice} + \text{basis}$$

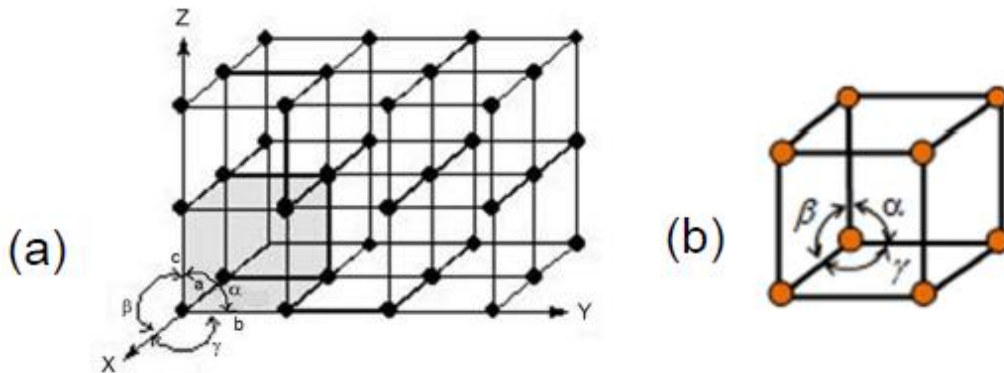
If the periodicity along a line is  $\vec{a}$ , then position of any point along the line can be obtained by a simple translation,  $\vec{r} = u\hat{a}$ ; similarly,  $\vec{r} = u\hat{a} + v\hat{b}$  will repeat the point along a 2D plane, where  $u$  and  $v$  are integers.



**Fig 2:** Illustration of Crystal Lattice

## 2.3 Unit Cell

The position of any atom in a 3D lattice can be described by a vector  $\vec{r} = u\hat{a} + v\hat{b} + w\hat{c}$ , where  $u$ ,  $v$  and  $w$  are integers. The three unit vectors  $\hat{a}, \hat{b}, \hat{c}$  can define a cell as shown by the shaded region in Fig 3(a). This cell is known as unit cell (Fig 3(b)) which when repeated in the three dimensions generates the crystal structure.



**Fig 3:** Unit Cell

**Definition:** A unit cell is the smallest component of a crystal which when repeated in three dimensions generates the crystal structure. A unit cell describes the arrangement of atoms in a crystal. The unit cell is characterized by its lattice parameters which consist of the cell edges and the angles between them.

## 2.4 Symmetry Systems

Symmetry refers to certain pattern or arrangement. A body is symmetrical when it is reproduced by certain operation. In the picture below the plane looks identical after a  $90^\circ$  rotation. The plane has 4 fold rotation symmetry as it repeats itself 4 times (shown by the red dot) in a full  $360^\circ$  rotation.

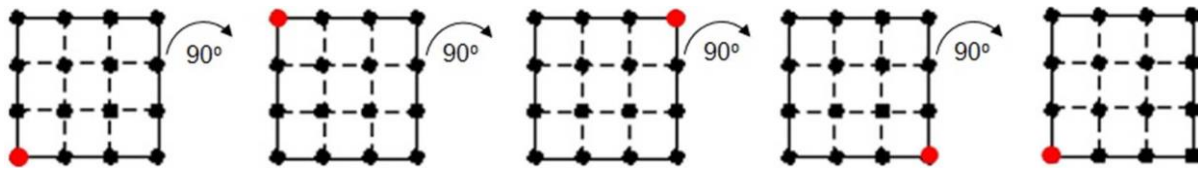


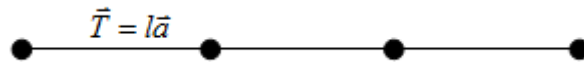
Fig 4: Symmetry rotation

### 1.4.1 Symmetry Operations

Crystals are classified into a number of types or groups according to their symmetry. There are four symmetry operations which include: - translation, rotation, reflection and inversion. These symmetry operations restore a body to its original position.

#### (i) Translation symmetry (T)

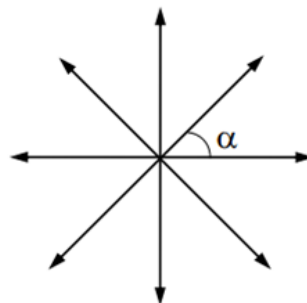
The first point is repeated an infinite number of times along a given axis or line when translated by a vector  $\vec{T} = l\vec{a}$ , where  $\vec{a}$  is the translation vector and  $l$  is an integer. Atoms in the same direction remain exactly identical, so the crystal moves in an identical position.



**NB:** A translation moves every point of a figure or space by the same amount in a given direction. It can also be interpreted as the addition of a constant vector to every point or as shifting the origin of the coordinate system.

#### (ii) Rotation system

This repeats the periodic pattern after a rotation through an angle  $\alpha$ . A rotation can be applied on the translation vector  $\vec{T}$  in all directions, clock or anti-clock wise, through equal angles  $\alpha$  in the 2D space.

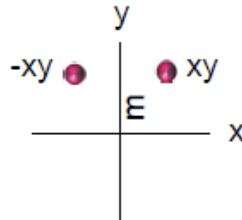


If the motion goes back to the original position, then it is a rotational group (symmetry). **1-fold rotation axis** - An object that requires rotation of a full  $360^\circ$  to repeat itself has no rotational symmetry. **2-fold rotation axis** - If an object appears identical after a rotation of  $180^\circ$ , that is twice in a  $360^\circ$  rotation, then it is said to have 2-fold ( $2\pi/180$ ) rotation symmetry. Similarly we have 3, 4 and 6-fold rotational symmetries. Objects with 5, 7 and 8 or higher order symmetries

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.

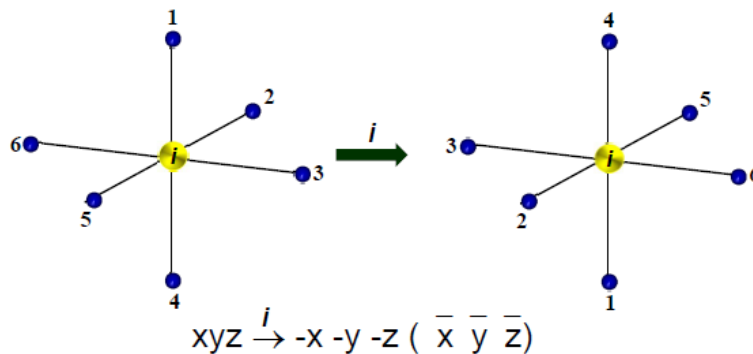
### (iii) Reflection or Mirror symmetry

An object with a reflection symmetry will be a mirror image of itself across a plane called mirror plane ( $m$ ). Reflection operation:  $xy \rightarrow -xy$  across a mirror plane perpendicular to x-axis.



### (iv) Inversion symmetry

In this operation, every part of the object is reflected through an inversion center called center of symmetry which is denoted as  $i$ . The object is reproduced inverted from its original position. A lattice is not a simple lattice if it does not possess inversion symmetry.



Combined symmetry operations also exist. For example, rotation can be combined with inversion which is called **roto-inversion**. The roto-inversion axis is denoted as  $(\bar{n})$ . For example, a 6-fold roto-inversion  $(\bar{6})$  involves rotating the object by  $60^\circ$  ( $360/6$ ), and inverting through a symmetry center.

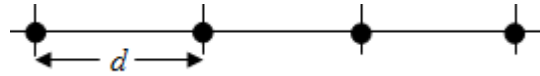
- Symmetry operations generate a variety of arrangements of lattice points in three dimensions. There are **32** unique ways in which lattice points can be arranged in space. These non-translation elements are called **point-groups**.
- A large number of 3D structures are generated when translations [linear translation, translation + reflection (glide plane) and translation + rotation (screw axis)] are applied to the point groups. There are **230** unique shapes which can be generated this way. These are called **space groups**.
- The 32 point groups are denoted by notations called Hermann-Mauguin symbols. These symbols basically describe the unique symmetry elements present in a body.

## 2.5 Lattice Classifications

In terms of lattice orientation, crystal lattices are classified into 1-, 2- and 3-dimensional lattices. These lattices are discussed below.

### 2.5.1 One dimensional lattice (simple lattice)

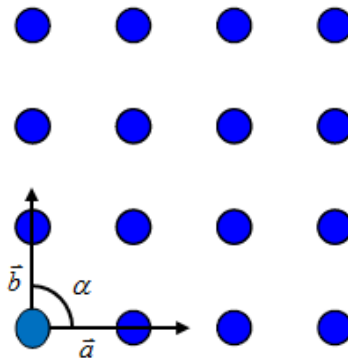
Here there is only one periodic arrangement of points. The lattice points are arranged at equal intervals on a straight line.



The distance,  $d$  between adjacent lattice points is called the lattice space. If  $x$  is the position of any point in the lattice, then  $x = x_o + ld$  (i.e. when the origin coordinate is taken at one point of the lattice points). When  $x_o = 0$ , then  $x = ld$ . Where  $l$  is an integer, and  $x_o$  is a constant.

### 2.5.2 Two dimensional lattices

The position vector  $\vec{r}$  giving points of the simple lattice may be expressed in terms of  $\vec{r} = \vec{r}_o + l\vec{a} + m\vec{b}$  (If origin is at the lattice point), where  $m$  and  $l$  are integers and are vectors. If  $\vec{r}_o = 0$ , then  $\vec{r} = l\vec{a} + m\vec{b}$ . The vectors  $\vec{a}$  and  $\vec{b}$  define the lattice and are called basic vectors.



All of the possible two dimensional lattices fall into one of these 5 categories;

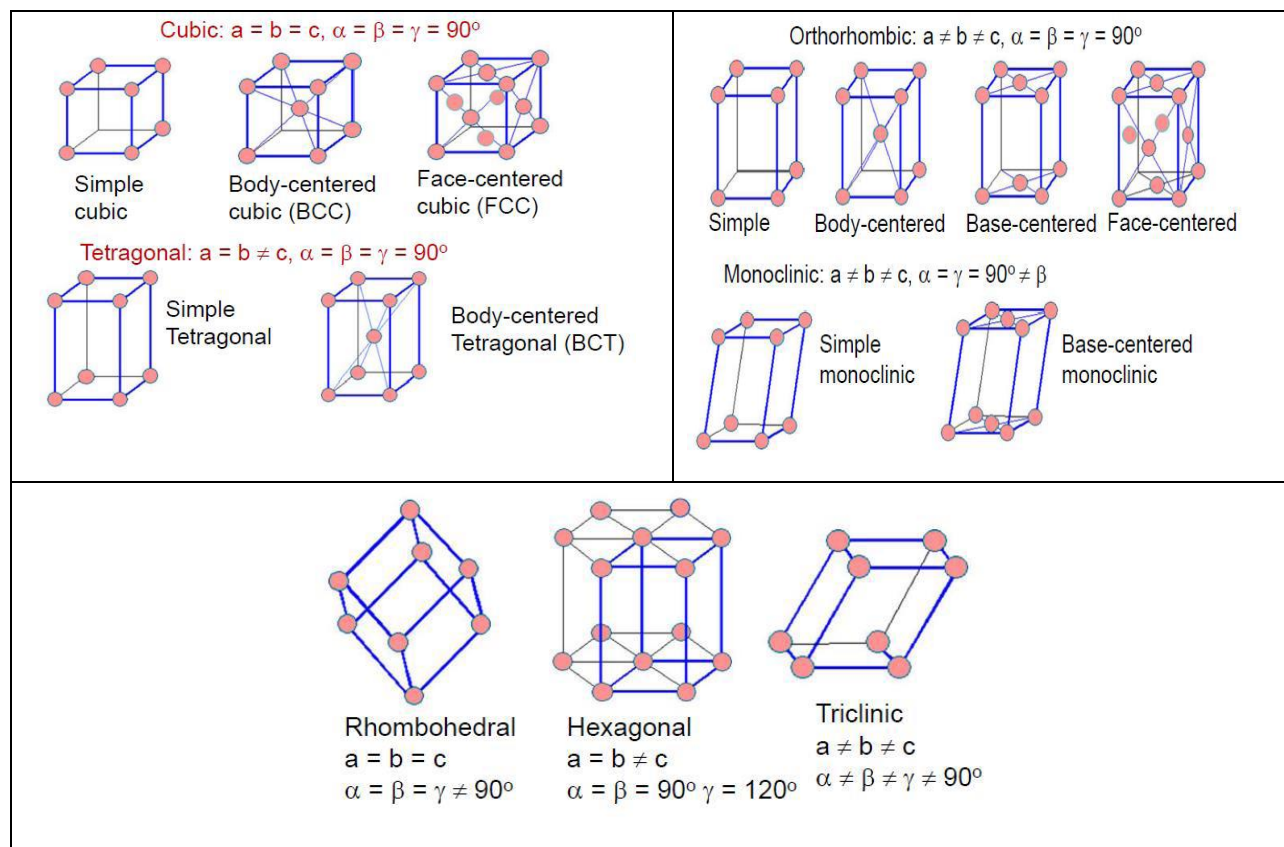
- Square  $|\vec{a}| = |\vec{b}| : \alpha = 90^\circ$  4 fold - 4 mirror planes
- Hexagonal  $|\vec{a}| = |\vec{b}| : \alpha = 120^\circ$  6 fold - 6 mirror planes
- Rectangular  $|\vec{a}| \neq |\vec{b}| : \alpha = 90^\circ$  2 fold - 2 mirror planes
- Centered rectangular  $|\vec{a}| \neq |\vec{b}| : \alpha = 90^\circ$

### 2.5.3 Three dimensional lattices

The simplest lattice in three dimensions is the simple cubic lattice, sometimes known as cubic-primitive lattice). The primitive unit cell in this case can most conveniently be taken to be single cube — which includes 1/8 of each of its eight corners. In fact, real crystals of atoms are rarely

simple cubic. Other three dimensional lattices include; body centered cubic, face centered cubic, orthorhombic and tetragonal lattices. Only slightly more complicated than the simple cubic lattices are the tetragonal and orthorhombic lattices where the axes remain perpendicular, but the primitive lattice vectors may be of different lengths. The orthorhombic unit cell has three different lengths of its perpendicular primitive lattice vectors, whereas the tetragonal unit cell has two lengths the same and one different. In addition to these five (5) lattices, there are nine other types of lattices in three dimensions. All together they form what is commonly known as the *fourteen Bravais lattice types*.

**Definition:** Bravais lattice is an infinite 3D array of points which appears exactly the same when viewed from any one of the points. The 14 Bravais lattices are formed from only 7 different types of unit cells, and incorporate all possible crystalline structures. They result by taking into consideration the space-group symmetry, i.e. the symmetry at translations and the point group symmetry of the lattice (the symmetry with respect to rotation, reflexion or inversion). When the basis consists of only one atom, the Bravais lattice is identical with the crystalline structure. But when the basis is complex and consists of several atoms, say  $s$ , the crystalline structure can be seen as formed by the interpenetration of  $s$  Bravais lattices. The Bravais lattices have always an inversion center in one of the lattice points, whereas such an inversion center can lack in crystals with complex bases.



**Fig.5:** Unit cells for all of the Three Dimensional Bravais Lattice Types.

The figure above shows the full variety of Bravais lattice types in three dimensions. While it is an extremely deep fact that there are only 14 lattice types in three dimensions, the precise statement of this theorem, as well of the proof of it, are beyond the scope of this course. The key result is that any crystal, no matter how complicated, has a lattice which is one of these 14 types.

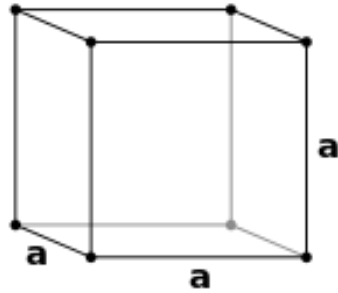
**NB:** By counting the point groups of the possible different crystals (which have bases with different symmetries), one ends with 32 crystalline classes that can be accommodated by the 7 crystal systems. Also, there are 230 space groups that result from the combination of the 32 crystalline structures with the translational symmetry.

Crystal system	Example
Triclinic	$K_2S_2O_8, K_2Cr_2O_7$
Monoclinic	$As_4S_4, KNO_2, CaSO_4 \cdot 2H_2O, \beta\text{-S}$
Rhombohedral	Hg, Sb, As, Bi, $CaCO_3$
Hexagonal	Zn, Co, Cd, Mg, Zr, NiAs
Orthorhombic	Ga, $Fe_3C, \alpha\text{-S}$
Tetragonal	In, $TiO_2, \beta\text{-Sn}$
Cubic	Au, Si, Al, Cu, Ag, Fe, NaCl

## 2.6 Cubic Lattices

### 2.6.1 Simple cubic lattice (SC or P)

A simple cubic lattice has lattice points only at the corners of a cubic unit cell. Unit cells in which there are lattice points only at the eight corners are called primitive. Since the eight sites at the corners are shared by eight adjacent unit cells,  $z = 8 \times (1/8) = 1$ .

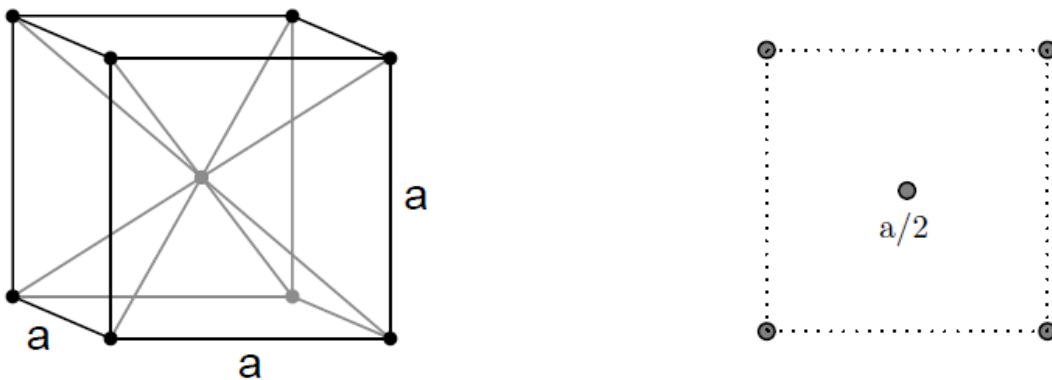


$$a = a = a \quad \text{and} \quad \alpha = \beta = \gamma = 90^\circ$$

### 2.6.2 Body centered cubic lattice (BCC or I)

The body centered cubic lattice is a simple cubic lattice where there is an additional point in the very center of the cube (this is sometimes known as cubic - I). Another way to show this unit cell, which does not rely on showing a three dimensional picture, is to use a so-called plan view of the unit cell, shown in the right of **Fig 5**. A plan view (a term used in engineering and architecture) is a two dimensional projection from the top of an object where heights are labeled to show the third dimension.

In the picture of the bcc unit cell, there are eight lattice points on the corners of the cell (each of which is  $1/8$  inside of the conventional unit cell) and one point in the center of the cell. Thus the conventional unit cell contains exactly two ( $= 8 \times 1/8 + 1$ ) lattice points. Examples of body centered cubic lattice are Li, Na, K, Cs, Rb. Packing together these unit cells to fill space, we see that the lattice points of a full bcc lattice can be described as being points having coordinates  $[x, y, z]$  where either all three coordinates are integers  $[uvw]$  times the lattice constant  $a$ , or all three are odd-half-integers times the lattice constant  $a$ .

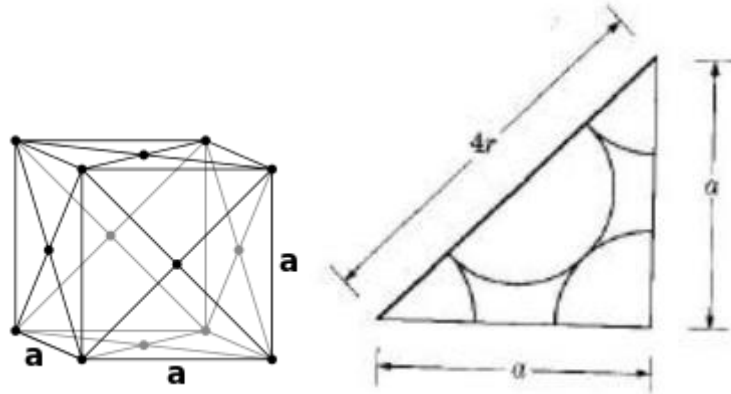


**Fig 5:** Conventional unit cell for the body centered cubic (I) lattice. Left: 3D view. Right: A plan view of the conventional unit cell.



### 2.6.3 Face centered cubic lattice (FCC)

The face centered lattice is a simple cubic lattice where there is an additional point in the center of every face of the cube (this is sometimes known as cubic-F, for “face centered”). Examples include Al, Ca, Ni, Pt, Pb, Cu etc. The unit cell is shown in the left of **Fig 6**. A plan view is of the unit cell is shown on the right of **Fig 6**. In the picture of the fcc unit cell, there are eight lattice points on the corners of the cell (each of which is  $1/8$  inside of the conventional unit cell) and one point in the center of each of the 6 faces, which is  $1/2$  inside the cell. Thus the conventional unit cell contains exactly four ( $= 8 \times 1/8 + 6 \times 1/2$ ) lattice points.



**Fig 6:** Face centered cubic lattice

Packing together these unit cells to fill space, we see that the lattice points of a full fcc lattice can be described as being points having coordinates  $(x, y, z)$  where either all three coordinates are integers times the lattice constant  $a$ , or two of the three coordinates are odd-half-integers times the lattice constant  $a$  and the remaining one coordinate is an integer times the lattice constant  $a$ . Analogous to the bcc case, it is sometimes convenient to think of the fcc lattice as a simple cubic lattice with a basis of four atoms per conventional cell. The simple cubic lattice contains points  $[x, y, z]$  where all three coordinates are integers in units of the lattice constant  $a$ . Within the conventional simple-cubic-unit cell we put one point at position  $[0, 0, 0]$  and another point at the position  $[a/2, a/2, 0]$  another at  $[a/2, 0, a/2]$  and another at  $[0, a/2, a/2]$ .

## 2.7 Geometric properties of a simple 3D crystal structure

Here we consider geometric properties such as; coordination number, atomic radius, volume of primitive cell, and relative density of packing.

### 2.7.1 Coordination number (N)

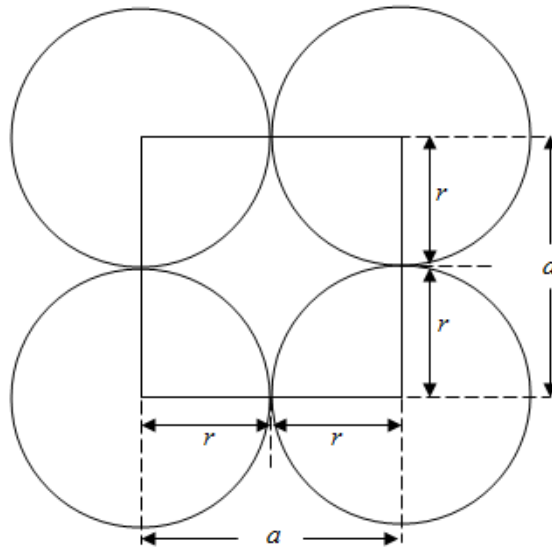
**Definition:** Coordination number is the number of nearest neighbors of points in a space lattice of an atom or ion in the structure. In the FCC lattice each atom is in contact with 12 neighbor atoms. Therefore, the FCC coordination number  $Z = 12$ . For example, the face centered atom in the front face is in contact with four corner atoms and four other face-centered atoms behind it (two sides, top and bottom) and is also touching four face-centered atoms of the unit cell in front of it. The coordination number of BCC crystal is 8. The body centered atom is in contact with all the eight corner atoms. Each corner atom is shared by eight unit cells and hence, each of these atoms is in touch with eight body centered atoms. In Hexagonal lattice  $Z = 12$ . The center atom

of the top face is in touch with six corner atoms, three atoms of the mid layer and other three atoms of the mid layer of the unit cell above it.

### 1.7.2 Atomic radius

It is defined as  $\frac{1}{2}$  the distance between nearest neighbors. To determine the atomic radius, we first identify the length of closest atom.

#### (i) Simple Cubic (SC)

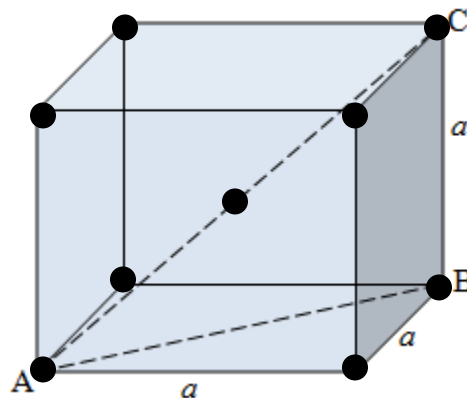


Here,  $a = 2r$

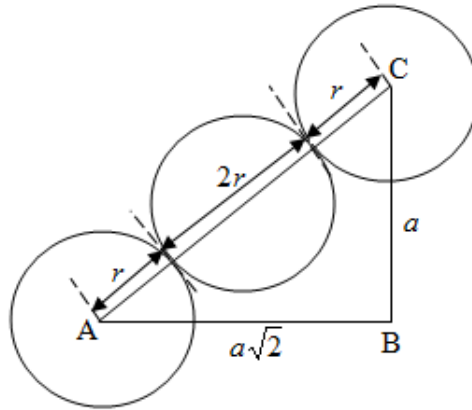
$$\Rightarrow r = \frac{a}{2}$$

#### (ii) Body Centered Cubic (BCC)

Here, the length of closest packing is the body diagonal.



Using Pythagoras theorem, length  $AB = a\sqrt{2}$

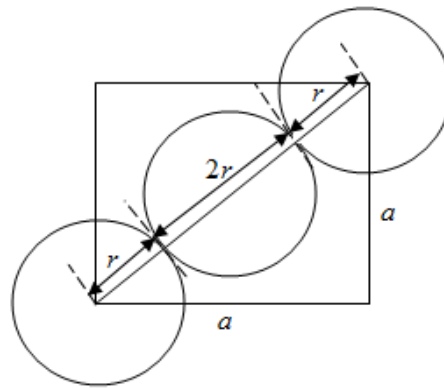


$$(4r)^2 = a^2 + (a\sqrt{2})^2$$

$$\Rightarrow r = \frac{a\sqrt{3}}{4}$$

### (iii) Face Centered Cubic (FCC)

The length of closest packing is the face diagonal.



$$(4r)^2 = a^2 + a^2$$

$$\Rightarrow r = \frac{a\sqrt{2}}{4}$$

### 2.7.3 Relative density of packing

Relative density of packing ( $\rho$ ), also commonly known as *atomic packing factor* (APF) or *packing efficiency* indicates how closely atoms are packed in a unit cell and is given by the ratio of the sum of volume of atoms in the unit cell and volume of the conventional unit cell.

$$\text{i.e. } \rho = \frac{\text{total volume occupied by atoms in a unit cell}}{\text{volume of conventional unit cell}} = \frac{nV_a}{V_c}$$

where,  $n$  - number of atoms (lattice points)

$V_a$  - Atomic volume (sphere)

$V_c$  - Total volume of the conventional unit cell,

$$V_p = \frac{V_c}{n}, \text{ where } V_p - \text{volume of the primitive unit cell}$$

### (i) Simple Cubic

For simple cubic crystals, effective number of atom per unit cell is  $8 \times 1/8 = 1$ . Considering the atoms as hard spheres of radius  $r$ , total volume of atoms is given as  $(4/3)\pi r^3$  and  $V_c = V_p = a^3$ .

$$\Rightarrow \rho_{SC} = \frac{nV_a}{V_c} = \frac{(4/3)\pi r^3}{a^3}$$

$$\text{But } r_{SC} = \frac{a}{2}$$

$$\Rightarrow \rho_{SC} = \frac{(4/3)\pi r^3}{a^3} = \frac{\pi}{6} \approx 0.52 \text{ or } 52\%$$

### (ii) Body Centered Cubic

For BCC crystals, effective number of atoms per unit cell is  $8 \times 1/8 + 1 = 2$ . Here the total volume of atoms is given as  $(4/3)\pi r^3$ ,  $V_c = a^3$  and  $V_p = a^3/2$ .

$$\Rightarrow \rho_{BCC} = \frac{nV_a}{V_c} = \frac{2 \times (4/3)\pi r^3}{a^3} = \frac{8\pi r^3}{3a^3}$$

$$\text{But } r_{BCC} = \frac{a\sqrt{3}}{4}$$

$$\Rightarrow \rho_{BCC} = \frac{8\pi a^3 \times 3\sqrt{3}}{64 \times 3a^3} = \frac{\pi\sqrt{3}}{8} \approx 0.68 \text{ or } 68\%$$

### (iii) Face Centered Cubic

In the case of FCC unit cell, effective number of atoms = 4 and the total volume of atoms is given as  $(4/3)\pi r^3$ ,  $V_c = a^3$  and  $V_p = a^3/4$ .

$$\Rightarrow \rho_{FCC} = \frac{nV_a}{V_c} = 4 \times \frac{(4/3)\pi r^3}{a^3} = \frac{16\pi r^3}{3a^3}$$

$$\text{But } r_{FCC} = \frac{a\sqrt{2}}{4}$$

$$\Rightarrow \rho_{FCC} = \frac{16\pi a^3 \times 2\sqrt{2}}{64 \times 3a^3} = \frac{\pi\sqrt{2}}{6} \approx 0.74 \text{ or } 74\%$$

## 1.7.4 Density of a crystal ( $\rho'$ )

The macroscopic density of a crystal is related to the mass of the atoms and their radii. It does not depend on the crystal structure since this determines how closely the particles are packed. The edge length of a cubic crystal can be obtained from x-ray studies and knowing the crystal structure possessed by it so that the number of particles per unit cell are known, the density of the crystal can be calculated.

$$\text{Density of a crystal} = \frac{\text{mass of unit cell}}{\text{volume of unit cell}}$$

Mass of unit cell = Number of atoms per unit cell x Mass of each atom =  $nm$

$$\text{But mass of each atom} = \frac{\text{mass number}}{\text{Avogadro's number}} = \frac{M}{N_A}$$

$$\therefore \text{Density}(\rho') = \frac{n \times \frac{M}{N_A}}{a^3} = \frac{nM}{N_A a^3}$$

**NB:** For simple cubic crystals,  $n=1$ , for body centered cubic structure,  $n=2$  and for face centered cubic structure,  $n=4$ .

	Simple	Body-centered	Face-centered
Volume of conventional cell	$a^3$	$a^3$	$a^3$
Lattice points per cell	1	2	4
Volume of primitive cell	$a^3$	$a^3/2$	$a^3/4$
Number of nearest neighbors	6	8	12
Nearest-neighbor distance	$a$	$\sqrt{3}a/2$	$a/\sqrt{2}$
Number of second neighbors	12	6	6
Second-neighbor distance	$\sqrt{2}a$	$a$	$a$
Packing fraction	$\pi/6 = 0.524$	$\sqrt{3}\pi/8 = 0.68$	$\sqrt{2}\pi/6 = 0.74$

### Worked Example:

- The unit cell of aluminum is face-centered cubic with  $a = 4.05$  nm. If the mass of the strip of aluminum foil of  $0.005$  cm thickness and  $25$  cm<sup>2</sup> is  $0.0085$  kg, find;
  - The number of atoms present
  - The number of atoms per unit cell

### Solution

- Let the number of atoms in the foil be  $N$

$$N = \frac{N_A m}{M}$$

where  $M = 27$  g,  $m = 0.0085$ kg and  $N_A = 6.02 \times 10^{23}$  atoms

$$\Rightarrow N = \frac{6.02 \times 10^{23} \times 0.0085}{27 \times 10^{-3}} = 1.9 \times 10^{23} \text{ atoms}$$

$$(ii) \text{ Number of atoms per unit cell} = \frac{NV_p}{V_s}$$

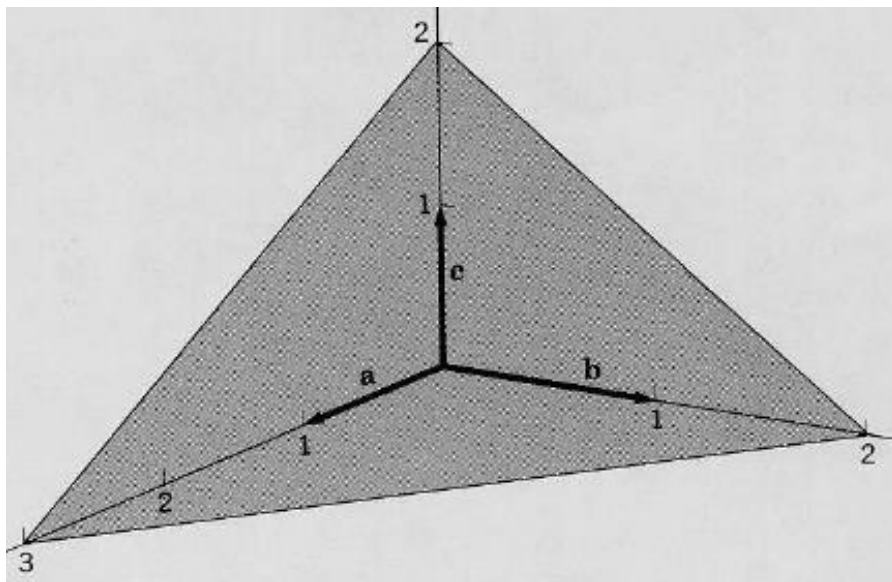
$$\text{where } V_s = 0.005 \times 10^{-2} \times (25 \times 10^{-2})^2 = 3.125 \times 10^{-6} \text{ m}^3$$

$$V_p = a^3 = (4.05 \times 10^{-9})^3 = 6.643 \times 10^{-26} \text{ m}^3$$

$$\Rightarrow \text{Number of atoms per unit cell} = \frac{1.9 \times 10^{23} \times 6.643 \times 10^{-26}}{3.125 \times 10^{-6}} = 4 \times 10^{-9} \text{ atoms}$$

### 1.8 Crystal Planes and Miller Indices

Planes in a crystal are described by notations called Miller indices. Miller indices of a plane are three numbers (h k l) which specify the orientation of planes in a crystal. Miller indices are given by the reciprocal of the intercepts of the plane on the three axes x, y, and z. To determine the Miller indices of a crystal plane, the following procedures are followed.



- Determine the intercepts (x, y, z) of the plane along the crystal axes a, b, c; where a, b, c are unit distances along the axes. For instance, the plane shown here intercepts the a, b, c axes at 3a, 2b, 2c.
- Get the fractions of the intercepts  $\left(\frac{x}{a}, \frac{y}{b}, \frac{z}{c}\right)$ . In this case, fractions of the intercepts are given by  $\left(\frac{3}{1}, \frac{2}{1}, \frac{2}{1}\right)$  since a, b and c are unit distances along the axes.

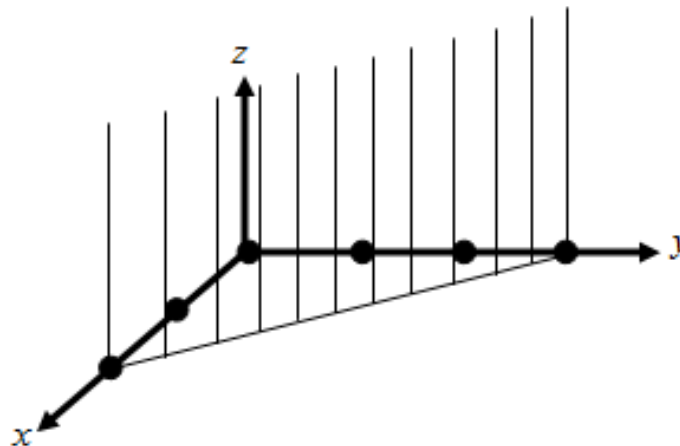
- Take the reciprocals of the fractions, thus giving  $\left(\frac{a}{x}, \frac{b}{y}, \frac{c}{z}\right)$ . In this case, reciprocals of the fractions are given by  $\left(\frac{1}{3}, \frac{1}{2}, \frac{1}{2}\right)$ .
- Multiply the reciprocals of the fractions by their LCM. The results are called Miller indices, normally written as (h k l). In this case, the Miller indices for the above crystal plane are (2 3 3).

**NB:** The reciprocal of  $\infty$  is 0. If any of the intercepts are negative values on the axes, then the negative sign will carry through into the Miller indices; in such cases, the negative sign is actually denoted by overstriking the relevant number.

### Worked Examples:

1. Find the miller indices of the intercepts (2, 3,  $\infty$ ) of a plane.

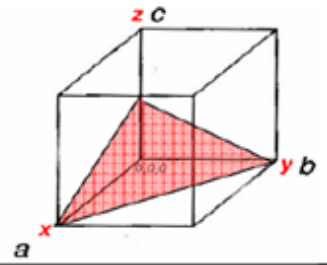
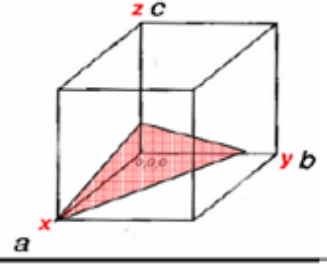
### Solution



- Intercepts as a fraction  $\left(\frac{2}{1}, \frac{3}{1}, \frac{\infty}{1}\right)$
- Reciprocal of the fractions  $\left(\frac{1}{2}, \frac{1}{3}, \frac{1}{\infty}\right)$
- Multiplying the reciprocals by the LCM (6), gives (3, 2, 0)
- Therefore, Miller indices (h k l) = (3 2 0).

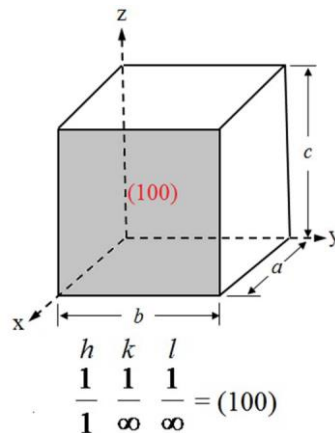
**NB:** Whenever there is a zero in the Miller indices, it implies that the lattice plane does not intersect the corresponding axis.

## Other Examples

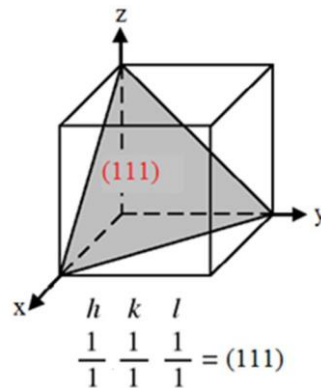
		x (a)	y (b)	z (c)
	Intercept on axes	1	1	$\frac{1}{2}$
	Reciprocal	1	1	2
	Integer Clear	1	1	2
	Miller Indices	(112)		
		x (a)	y (b)	z (c)
	Intercept on axes	1	$\frac{3}{4}$	$\frac{1}{4}$
	Reciprocal	1	$\frac{4}{3}$	4
	Integer Clear	3	4	12
	Miller Indices	(3 4 12)		

## Common Planes

(i) The (100) plane

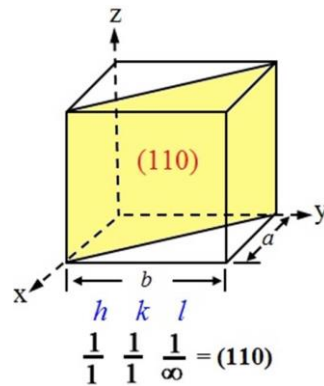


(ii) The (111) plane

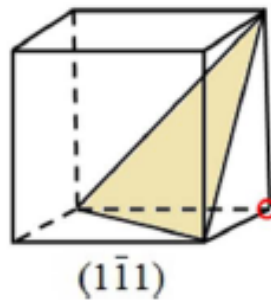




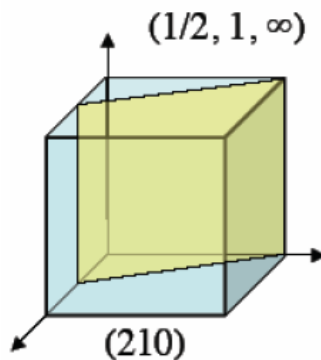
(iii) The (110) plane



(iv) The  $(1\bar{1}1)$  plane



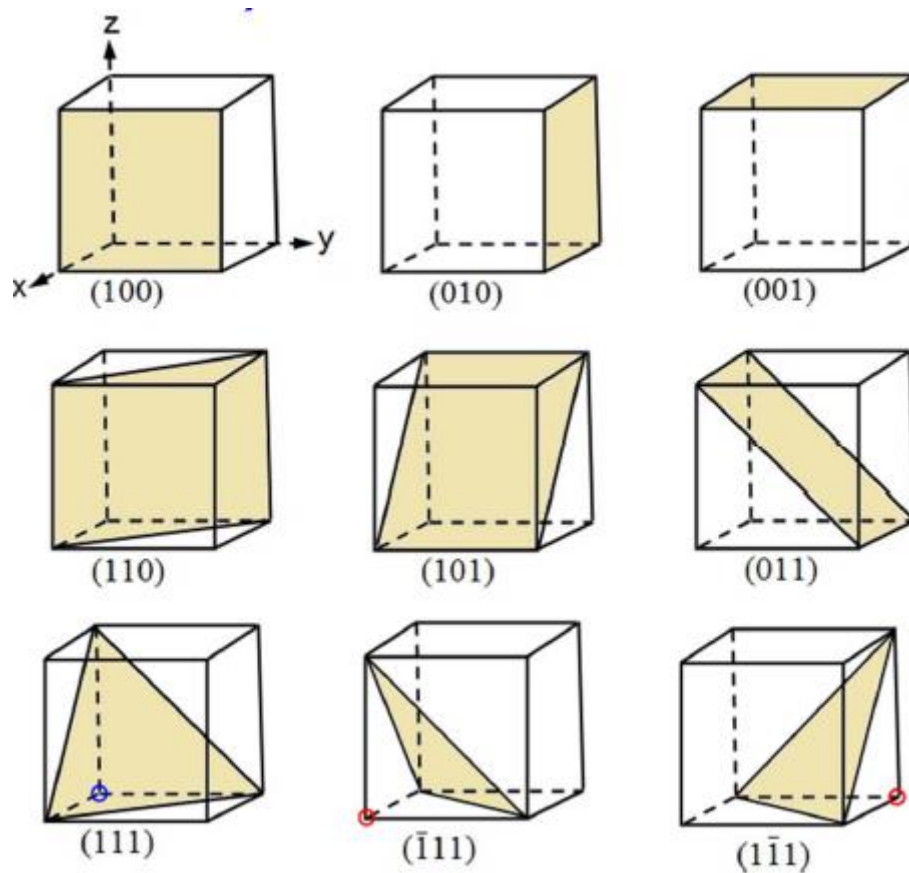
(v) The (210) plane



### 1.9 Symmetry – Equivalent Planes

Certain planes are equivalent to each other. In the following diagrams the first three highlighted surfaces are related by the symmetry elements of the cubic crystal - they are entirely equivalent. In fact there are a total of 6 faces related by the symmetry elements and equivalent to the (100) surface. Any surface belonging to this set of symmetry related surfaces may be denoted by the more general notation  $\{100\}$  where the Miller indices of one of the surfaces is instead enclosed in curly-brackets.

Similarly, simple cubic crystal (111) is equivalent to  $(1\bar{1}1)$ ,  $(\bar{1}11)$ ,  $(\bar{1}\bar{1}\bar{1})$ ,  $(\bar{1}1\bar{1})$ ,  $(111)$  and  $(1\bar{1}\bar{1})$ .



### Exercise

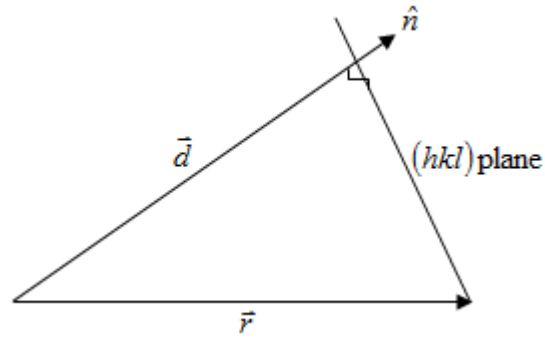
Sketch the planes with the following Miller indices.

- (i) (221)
- (ii) (131)
- (iii) (231)
- (iv) (102)
- (v) (001)
- (vi) (121)

### 1.10 Interplanar Spacing

The spacing between planes in a crystal is known as interplanar spacing and is denoted as  $d_{hkl}$ . Consider a crystal plane with miller indices  $(h\ k\ l)$ . The unit vector  $\hat{n}$  normal to the unit plane makes angles  $\alpha$ ,  $\beta$  and  $\gamma$  with the crystal axes  $\vec{a}$ ,  $\vec{b}$  and  $\vec{c}$ .

Such that  $\hat{n} = (\cos\alpha, \cos\beta, \cos\gamma)$ , where  $\cos^2\alpha + \cos^2\beta + \cos^2\gamma = 1$



The equation of the plane here is given by;

$$(\vec{r} - \vec{d}) \cdot \hat{n} = 0$$

$$\vec{r} \cdot \hat{n} - \vec{d} \cdot \hat{n} = 0$$

$$\vec{r} \cdot \hat{n} = d$$

$$\text{But } \hat{n} = \cos\alpha\vec{a} + \cos\beta\vec{b} + \cos\gamma\vec{c}$$

$$\text{If } \vec{r} = x\vec{a} + y\vec{b} + z\vec{c} \text{ then } d = \vec{r} \cdot \hat{n} = x\cos\alpha + y\cos\beta + z\cos\gamma$$

When  $z = y = 0$

$$\Rightarrow d = \vec{r} \cdot \hat{n} = x\cos\alpha$$

$$\text{But } x = \frac{a}{h}$$

$$\Rightarrow d = \frac{a}{h}\cos\alpha, \Rightarrow \frac{\vec{a} \cdot \hat{n}}{h} = d$$

Also, when  $z = x = 0$  and  $y = \frac{b}{k}$

$$\Rightarrow \frac{b}{k}\cos\beta = d, \Rightarrow \frac{\vec{b} \cdot \hat{n}}{k} = d$$

Similarly for  $x = y = 0$ ,  $z = \frac{c}{l}$ ,

$$\Rightarrow \frac{c}{l}\cos\gamma = d, \Rightarrow \frac{\vec{c} \cdot \hat{n}}{l} = d$$

Substituting for  $\cos\alpha$ ,  $\cos\beta$  and  $\cos\gamma$  into the equation  $d = \vec{r} \cdot \hat{n} = x\cos\alpha + y\cos\beta + z\cos\gamma$  we get;

$$d = x\frac{h}{a}d + y\frac{k}{b}d + z\frac{l}{c}d$$

$$\Rightarrow x\frac{h}{a} + y\frac{k}{b} + z\frac{l}{c} = 1$$

or

$$f(x, y, z) = \left( x \frac{h}{a} + y \frac{k}{b} + z \frac{l}{c} \right) = \text{Constant}$$

This is the equation of the plane with miller indices (h k l).

$$\text{The normal to the plane, } \hat{n} = \frac{\nabla f}{|\nabla f|} = \frac{\left( \frac{h}{a} \hat{a} + \frac{k}{b} \hat{b} + \frac{l}{c} \hat{c} \right)}{\left[ \left( \frac{h}{a} \right)^2 + \left( \frac{k}{b} \right)^2 + \left( \frac{l}{c} \right)^2 \right]^{\frac{1}{2}}}$$

$$\text{But from } d = \frac{\vec{a} \cdot \hat{n}}{h},$$

$$\Rightarrow d = \frac{1}{h} \vec{a} \cdot \left\{ \frac{\left( \frac{h}{a} \hat{a} + \frac{k}{b} \hat{b} + \frac{l}{c} \hat{c} \right)}{\left[ \left( \frac{h}{a} \right)^2 + \left( \frac{k}{b} \right)^2 + \left( \frac{l}{c} \right)^2 \right]^{\frac{1}{2}}} \right\} = \frac{\frac{1}{h} \cdot h}{\sqrt{\left[ \left( \frac{h}{a} \right)^2 + \left( \frac{k}{b} \right)^2 + \left( \frac{l}{c} \right)^2 \right]}}$$

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

In the cubic systems, spacing between the (h k l) planes is given as;

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$\text{In tetragonal system, } \frac{1}{d^2} = \frac{1}{a^2} (h^2 + k^2) + \frac{1}{c^2} l^2$$

$$\text{In orthorhombic system, } \frac{1}{d^2} = \frac{1}{a^2} h^2 + \frac{1}{a^2} k^2 + \frac{1}{c^2} l^2$$

$$\text{In hexagonal systems, } \frac{1}{d^2} = \frac{4}{3a^2} (h^2 + hk + k^2) + \frac{1}{c^2} l^2$$

### Worked Examples

1. Copper has a FCC structure and atomic radius of 0.1273 nm. Find the interplanar spacing for the (111) plane.

#### Solution

For FCC, the densest packing in the structure is the face diagonal. The lattice parameter **a** for the FCC structure is given by;

$$a = \frac{4r}{\sqrt{2}}$$

For this case, since radius of 0.1273 nm,  $\Rightarrow a = \frac{4 \times 0.1273 \times 10^{-9}}{\sqrt{2}} \approx 3.6 \times 10^{-10} \text{ m}$

$$d_{(111)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} = \frac{3.6 \times 10^{-10}}{\sqrt{3}} \approx 2.08 \times 10^{-10} \text{ m}$$

2. The distance between (110) plane in the BCC lattice is 0.203nm.  
(i) What is the size of the unit cell  
(ii) Calculate the radius for the atom in this structure.

#### Solution

For BCC, the densest packing is the body diagonal.

(i) Using  $d_{(hkl)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

$$\Rightarrow a = d_{(110)} \times \sqrt{1^2 + 1^2 + 0^2} = 0.203 \times 10^{-9} \times \sqrt{2} = 2.87 \times 10^{-10} \text{ m}$$

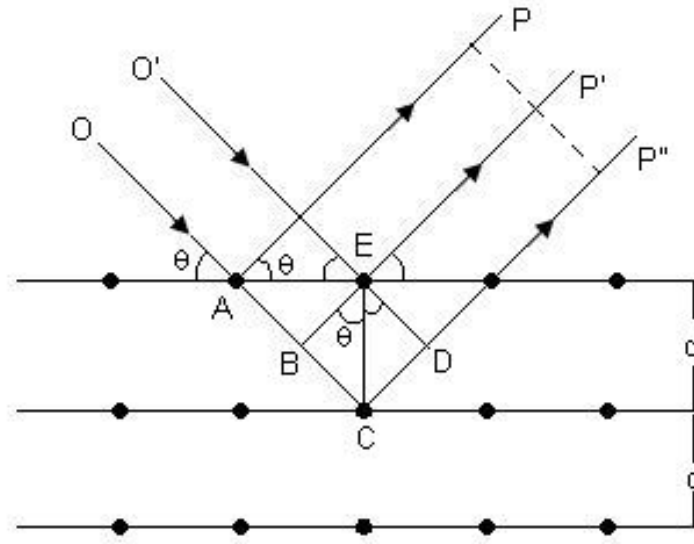
(ii) For BCC,  $r = \frac{a\sqrt{3}}{4} = \frac{2.87 \times 10^{-10} \times \sqrt{3}}{4} = 1.243 \times 10^{-10} \text{ m}$

## Chapter 2: Diffraction of X-rays by Crystals

### 2.1 Bragg's Law

The inter-atomic spacing in crystals is of the order of  $1\text{\AA}$ . Because of the short wavelength (comparable to the inter-planer distance), X-rays are scattered by adjacent atoms in crystals which can interfere and give rise to diffraction effects. When X-rays enter into a crystal, each atom acts as a diffraction center and crystal as a whole acts like a three dimensional diffraction grating. The diffraction pattern so produced can tell us much about the internal arrangement of atoms in crystal.

Let us consider a crystal made up of equidistant parallel planes of atoms with the inter-planer spacing  $d_{hkl}$ . Further, consider a monochromatic x-ray beam of wavelength  $\lambda$  having a common wave front, falls at an angle  $\theta$  on the planes as shown in Figure. Each atom scatters the x-rays more or less uniformly in all directions, but because of the periodic arrangement of atoms, the scattered radiation from all atoms in a set of planes is in phase where they interfere constructively. In all other directions, there is destructive interference.



Consider two of the incoming x-ray  $OA$  and  $O'E$  inclined at an angle  $\theta$  with the topmost plane of the crystal and are scattered in the directions  $AP$  and  $EP'$ , also at an angle  $\theta$  with that plane. Since the path length of the rays  $OEP'$  and  $O'AP$  are the same, they arrive at  $P$  and  $P'$  respectively in phase with each other and again form a common wavefront. This is the condition for scattering in phase by single plane of the crystal.

Now, let us consider X-ray scattering from two adjacent planes  $(hkl)_1$  and  $(hkl)_2$  as shown in Figure. If  $EB$  and  $ED$  are parallel to the incident and scattered wavefront respectively, the total path  $O'CP''$  is longer than the path  $OEP'$  by an amount;

$$\Delta = BCD = BC + BD$$

Now, from the right angle triangle  $EBC$  and  $EDC$ , we have;

$$BC = d \sin \theta = BD$$

$$\text{So, } \Delta = 2d \sin \theta$$

If two consecutive planes scattered in phase with each other then we know that the path difference  $\Delta$  must be equal to an integral multiple of wavelength, i.e.  $\Delta = n\lambda$ , where  $n = 0, 1, 2, \dots$  gives the order of reflection. Thus the condition for constructive interference (in-phase scattering) by a set of equidistant parallel planes in a crystal is given by;

$$2d \sin \theta = n\lambda$$

This is the well-known Bragg's law, which was first derived by the English physicists Sir W.H. Bragg and his son Sir W.L. Bragg in 1913. Thus diffraction (constructive) occurs for certain discrete values of  $\theta$  for which the Bragg's condition is fulfilled.

As  $(\sin \theta)_{\max} = 1$ , we get,  $\frac{n\lambda}{2d} \leq 1$ . That is,  $\lambda$  must not be greater than twice the interplanar spacing, otherwise no diffraction will occur.

This observation is an example of X-ray wave interference, commonly known as X-ray diffraction (XRD), and was direct evidence for the periodic atomic structure of crystals postulated for several centuries. For certain specific wavelengths and incident angles, intense peaks of reflected radiation (known as Bragg peaks) were produced. The concept of Bragg diffraction applies equally to neutron diffraction and electron diffraction processes.

### Worked Examples:

- (i) Determine the angle through which an X-ray of wavelength  $0.440 \text{ \AA}$  be reflected from the cube face of a rocksalt crystal ( $d = 2.814 \text{ \AA}$ ).

#### Solution

Given  $\lambda = 0.440 \text{ \AA}$  and  $d = 2.814 \text{ \AA}$ ,

$$\theta = \sin^{-1} \left( \frac{n\lambda}{2d} \right)$$

$$1^{\text{st}} \text{ order reflection, } n = 1, \theta_1 = \sin^{-1} \left( \frac{1 \times 0.440}{2 \times 2.814} \right) = \sin^{-1}(0.0782) = 4.49^\circ$$

$$2^{\text{nd}} \text{ order reflection, } n = 2, \theta_2 = \sin^{-1} \left( \frac{2 \times 0.440}{2 \times 2.814} \right) = \sin^{-1}(2 \times 0.0782) = 8.98^\circ$$

$$3^{\text{rd}} \text{ order reflection, } n = 3, \theta_3 = \sin^{-1} \left( \frac{3 \times 0.440}{2 \times 2.814} \right) = \sin^{-1}(3 \times 0.0782) = 13.49^\circ$$

- (ii) Determine the wavelength of the diffraction beam when a beam of X-ray having wavelengths in the range  $0.2 \text{ \AA}$  to  $1 \text{ \AA}$  incident at an angle of  $9^\circ$  with the cube face of a rocksalt crystal ( $d = 2.814 \text{ \AA}$ ).

### **Solution**

$$\text{For } n = 1, 1\lambda_1 = 2(2.814)\sin 9^\circ, \quad \Rightarrow \lambda_1 = 0.8804 \text{ \AA}$$

$$\text{For } n = 2, 2\lambda_2 = 0.8804 \text{ \AA}, \quad \Rightarrow \lambda_2 = 0.4402 \text{ \AA}$$

$$\text{For } n = 3, 3\lambda_3 = 0.8804 \text{ \AA}, \quad \Rightarrow \lambda_3 = 0.2935 \text{ \AA}$$

$$\text{For } n = 4, 4\lambda_4 = 0.8804 \text{ \AA}, \quad \Rightarrow \lambda_4 = 0.2201 \text{ \AA}$$

For  $n = 5$ ,  $5\lambda_5 = 0.8804 \text{ \AA}$ ,  $\Rightarrow \lambda_5 = 0.1760 \text{ \AA} < 0.2 \text{ \AA}$ ; which shows the wavelength of the X-rays are 0.8804, 0.4402, 0.2935 and 0.2201 \AA.

**NB:** Bragg's law, as stated above, can be used to obtain the lattice spacing of a particular cubic system through the following relation:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}},$$

where **a** is the lattice spacing or lattice parameter of the cubic crystal, and  $h$ ,  $k$ , and  $l$  are the Miller indices of the Bragg plane.

Combining this relation with Bragg's law we have;

$$\left(\frac{\lambda}{2a}\right)^2 = \frac{\sin^2 \theta}{h^2 + k^2 + l^2}$$

## **2.2 Geometric Structure Factor (*read and make notes*)**

### **2.3 Experimental X-ray Diffraction Methods**

To satisfy Bragg's law, it is necessary to vary either the angle of inclination of the specimen to the beam or the wavelength of the radiation. The three standard methods of X-ray crystallography are:-

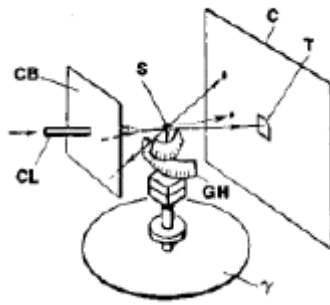
**(a) Laue Method:** A stationary single crystal is irradiated by a range of X-ray wavelengths. This method is used especially for identification of single crystals. The crystal selects out and diffracts given discrete values of  $\lambda$  and each angle of incidence  $\theta$  satisfies the Bragg's condition  $n\lambda = 2d \sin \theta$ .

The diffraction patterns consist of series of spots whose pattern reflects symmetry to the crystal. Each spot on the photographic film will be due to all orders of diffraction i.e.  $n=1, 2, 3, \dots$  superimposed on many single planes.

$$\text{i.e. } 2d_{(hkl)} \sin \theta = n\lambda_1 \quad \text{and} \quad 2d_{(hkl)} \sin \theta = n\lambda_2$$

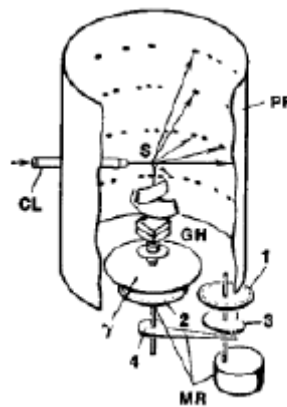
Where  $\lambda_1 \neq \lambda_2$ , otherwise they would overlap.



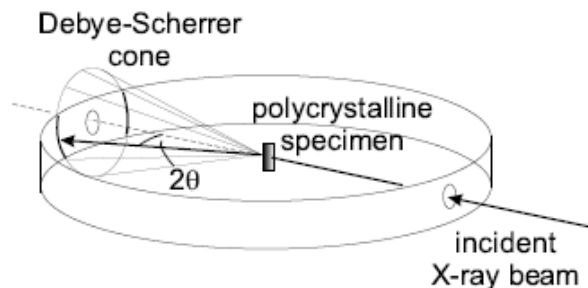


**(b) Rotating Crystal Method:** A single crystal specimen is rotated in a beam of monochromatic X-rays using a spindle. The variation in the angle brings different atomic planes in to position for reflection. The beam is diffracted from a given crystal plane whenever in the course of rotation and the value of  $\theta$  satisfies Bragg's equation,

$$2d_{(hkl)} \sin \theta = n\lambda$$



**(c) Powder (Debye-Scherrer) Method:** A polycrystalline powder specimen is kept stationary in a beam of monochromatic radiation. In this case, the incoming wave can scatter off of any one of many small crystallites which may be oriented in any possible direction.



In spirit, this technique is similar to the rotating crystal method in that there is always some angle at which a crystal can be oriented to diffract the incoming wave. The powder method assumes that all orientations are present in the sample, so that regardless of the angle of incidence, there

will be a grain in the proper orientation for each reflection (diffraction). The patterns are very useful for identification of unknowns. There are compiled indexes of powder diffraction data for minerals, as well as inorganic compounds and organic compounds.

**NB:** If the Miller indices of the diffraction peaks are known, it is possible to determine the unit cell parameters of the material from the peak positions. Cell parameters can then be used to determine composition if the cell variation with composition is known. If more than one mineral is present in the sample it is possible, although not easy, to determine the relative proportions of the minerals. To do this one must have a standard pattern for each pure mineral to obtain the relative intensities of the peaks from each mineral. It is then possible to use the relative intensities of non-overlapping peaks to give an estimate of the mineral proportions, called a *mode*.

## 2.4 Indexing Powder Diffraction Lines

Indexing is the process of determining the unit cell parameters from the peak positions. To index a powder diffraction pattern it is necessary to assign Miller indices ( $h\ k\ l$ ) to each peak. A diffraction pattern cannot be analyzed until it has been indexed. It is always the first step in analysis.

### 2.4.1 Selection rules for indexing powder diffraction lines

Below is a table of possible lattice planes and the selection rules that can occur for the smallest reciprocal lattice vectors.

Lattice Plane Selection Rules					
$\{hkl\}$	$N = h^2 + k^2 + l^2$	Multiplicity	cubic	bcc	fcc
100	1	6	✓		
110	2	12	✓	✓	
111	3	8	✓		✓
200	4	6	✓	✓	✓
210	5	24	✓		
211	6	24	✓	✓	
220	8	12	✓	✓	✓
221	9	24	✓		
300	9	6	✓		
310	10	24	✓	✓	
311	11	24	✓		✓
222	12	8	✓	✓	✓
⋮	⋮				

The selection rules are exactly those listed above: simple cubic allows scattering from any plane, BCC must have  $h + k + l$  be even, and FCC must have  $h, k, l$  either all odd or all even. We have added a column  $N$  which is the square magnitude of the reciprocal lattice vector. We have also added an additional column labeled “multiplicity”. This quantity is important for figuring out the amplitude of scattering. The point here is that the (100) planes have some particular spacing but there are 5 other families of planes with the same spacing (*refer to equivalent planes*). In the powder diffraction method, the crystal orientations are random, and here there would be 6 possible equivalent orientations of a crystal which will present the right angle for scattering from

one of these planes, so there will be scattering intensity which is 6 times as large as we would otherwise calculate — this is known as the multiplicity factor.

It follows therefore that,

- For simple cubic lattice,  $h^2 + k^2 + l^2 = 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12 \dots$  but not 7, 15, 23, 28.
- For body centered cubic,  $h^2 + k^2 + l^2 = 2, 4, 6, 8, 10, 12 \dots$
- For face centered cubic,  $h^2 + k^2 + l^2 = 3, 4, 8, 11, 12, 16, 19, 20, 21 \dots$

### 2.4.2 Procedure for Indexing Powder Diffraction Lines

- (i) Obtain the value of  $\theta$  in radians from the powder diffraction method using the expression

$$\theta = \frac{S}{4R}; \text{ where } S \text{ is the arc through which the rays are spread and } R \text{ is the radius.}$$

- (ii) Calculate  $\theta$  in degrees;  $1 \text{ rad} = \frac{180}{\pi}, \rightarrow \theta = \frac{S}{4R} \left( \frac{180}{\pi} \right)$

- (iii) Find the value of  $\sin^2 \theta$

From Bragg's law,  $2d_{(hkl)} \sin \theta_{(hkl)} = n\lambda$ . For cubic crystal lattice,  $d_{(hkl)} = \frac{a}{\sqrt{h^2 + k^2 + l^2}},$

$$\Rightarrow \frac{4a^2 \sin^2 \theta}{(h^2 + k^2 + l^2)} = n^2 \lambda^2$$

$$\Rightarrow \sin^2 \theta = \frac{\lambda^2}{4a^2} [(h^2 + k^2 + l^2)n^2]$$

Let  $[(h^2 + k^2 + l^2)n^2] = m$ , where  $m$  – is an integer.

$$\Rightarrow \sin^2 \theta = \frac{\lambda^2 m}{4a^2}$$

- (iv) Find the HCF of  $\sin^2 \theta$

- (v) Deduce the lattice type used in the extinction rules

- (vi) The lattice parameter  $a$  is obtained from  $\langle HCF \rangle = \frac{\lambda^2}{4a^2}$ , where  $\lambda$ -wavelength of the radiation.

### Worked Examples

1. In the Debye -Scherrer diffraction with tantalum powder, the following Bragg angles were obtained using  $\text{Cu}_{K\alpha}$  radiation (wavelength 0.154056 nm).

$\theta^0$	19.6	28.1	35.1	41.5	47.7	54.1	60.8	68.9	81.9
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Determine;

- (i) The corresponding reflection plane and deduce the lattice type
- (ii) The lattice parameter.

**Solution**

(i)

$\theta^\circ$	$\sin^2\theta$	$m \times HCF$	hkl
19.6	0.11253	2 x 0.05626	(110)
28.1	0.22185	4 x 0.05546	(200)
35.1	0.33063	6 x 0.05510	(211)
41.5	0.43907	8 x 0.05488	(220)
47.7	0.54705	10 x 0.05471	(310)
54.1	0.65617	12 x 0.05468	(222)
60.8	0.76109	14 x 0.05436	(321)
68.9	0.87640	16 x 0.05478	(400)
81.9	0.97860	18 x 0.05437	(411)

From the table, it is observed by inspection that only even values of (h + k + l) are present. Hence tantalum has a body centered cubic lattice.

$$(ii) \langle HCF \rangle = \frac{\lambda^2}{4a^2},$$

$$\Rightarrow 0.05 = \frac{(0.154056 \times 10^{-9})^2}{4a^2},$$

$$\therefore a =$$

2. In diffraction using aluminum powder, the following  $\theta$  values were obtained using  $\text{Cu}_{K\alpha}$  radiation (wavelength = 0.1540 nm). 19.45<sup>0</sup>, 22.64<sup>0</sup>, 33.00<sup>0</sup>, 39.68<sup>0</sup>, 41.83<sup>0</sup>, 50.35<sup>0</sup>, 57.05<sup>0</sup> and 59.42<sup>0</sup>. Aluminum has molar mass 27 g and density  $2.7 \times 10^{-3} \text{ kgm}^{-3}$ .
  - a. Index the X-ray diffraction lines and deduce the lattice type
  - b. Calculate the Avogadro's constant

**Solution**

a.

$\theta^\circ$	$\sin^2\theta$	$m \times HCF$	hkl
19.45	0.110878	3 x 0.036959	(111)
22.64	0.148179	4 x 0.037045	(200)
33.00	0.296632	8 x 0.037079	(220)
39.68	0.407681	11 x 0.037062	(311)
41.83	0.44479	12 x 0.037066	(222)
50.35	0.592833	16 x 0.037050	(400)
57.05	0.704165	19 x 0.037061	(331)
59.42	0.741183	20 x 0.037059	(420)

From the table, it is observed by inspection that both odd and even values of  $(h + k + l)$  are present. Hence Al powder has a face – centered cubic lattice.

b. From  $\langle HCF \rangle = \frac{\lambda^2}{4a^2}$ ,

$$\Rightarrow 0.04 = \frac{(0.1540 \times 10^{-9})^2}{4a^2},$$

$$\therefore a = 3.85 \times 10^{-9} \text{ m}$$

From density  $\rho = \frac{M}{N_A a^3}$

$$N_A = \frac{M}{\rho a^3} = \frac{27 \times 10^{-3}}{2.7 \times 10^{-3} \times (3.8527 \times 10^{-10})^3}$$

$$\therefore N_A =$$

### **Exercise**

1. An element that has either BCC or FCC structure shows diffraction peaks at following  $2\theta$  angles: 40, 58, 73, 86.8, 100.4 and 114.7. Wavelength of x-ray,  $\lambda = 0.154$ .
  - a. BCC or FCC?
  - b. Determine the lattice constant  $a$ .

## Chapter 3: Lattice Vibrations

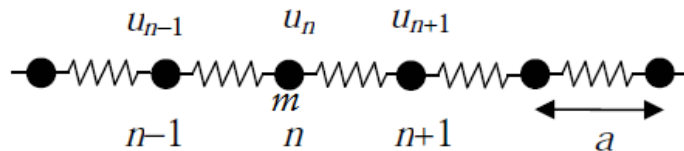
### 3.1 Introduction

So far we have been discussing equilibrium properties of crystal lattices. When the lattice is at equilibrium, each atom is positioned exactly at its lattice site. This is not actually the case; even at the lowest temperatures the atoms perform small vibrations about their equilibrium positions. Now suppose that an atom is displaced from its equilibrium site by a small amount. Due to force acting on this atom, it will tend to return to its equilibrium position. This results in lattice vibrations. Due to interactions between atoms, various atoms move simultaneously, so we have to consider the motion of the entire lattice.

**Definition:** Lattice vibrations are periodic oscillations of atoms in a crystal lattice about their equilibrium positions. Many of the significant features of lattice vibrations can be understood on the basis of simple one-dimensional model; monatomic and diatomic linear chains. For that reason we shall first study the linear chain in some detail.

### 3.2 One-Dimensional Vibration of Monatomic Linear Lattice

For simplicity we consider, first, a one-dimensional crystal lattice of identical atoms of constant lattice spacing  $a$ , and assume that the forces between the atoms in this lattice are proportional to relative displacements from the equilibrium positions. It's also assumed that atoms can move only in one direction parallel to the chain and that forces between them are of such short range that only nearest neighbor forces are considered. This is known as the harmonic approximation, which holds well provided that the displacements are small. One might think about the atoms in the lattice as being identical with masses,  $m$  and interconnected by elastic springs of spring constant  $\beta$ .



Let  $u_n$  be the displacement of the  $n^{th}$  atom from its equilibrium position. Considering nearest neighbor interactions only, the force acting on the  $n^{th}$  atom is due to the  $(n-1)^{th}$  atom and the  $(n+1)^{th}$  atom. Therefore, the force exerted on  $n^{th}$  atom in the lattice is given by;

$$\beta(u_n - u_{n-1}) \text{ ----- (i) to the left}$$

$$\beta(u_{n+1} - u_n) \text{ ----- (ii) to the right}$$

The total force to the right is given by applying Newton's second law to the motion of the  $n^{th}$  atom as;

$$m\ddot{u}_n = \beta(u_{n+1} - u_n) - \beta(u_n - u_{n-1})$$

$$\Rightarrow m\ddot{u}_n = \beta(u_{n+1} - 2u_n + u_{n-1}) \text{ ----- (iii)}$$

A similar equation can be written for each atom in the lattice, resulting in  $N$  coupled differential equations, which should be solved simultaneously ( $N$  is the total number of atoms in the lattice). In addition the boundary conditions applied to the end atom in the lattice should be taken into account.

The trial solution is a wave-like solution in which all the atoms oscillate at the same frequency  $\omega$  and the same amplitude  $A$  and have wave vector  $k$ .

Thus,

$$u_n = Ae^{i(kx_n \pm \omega t)} \quad \text{----- (x)}$$

$$u_{n+1} = Ae^{i(kx_{n+1} \pm \omega t)} \quad \text{----- (xx)}$$

$$u_{n-1} = Ae^{i(kx_{n-1} \pm \omega t)} \quad \text{----- (xxx)}$$

$$\Rightarrow \dot{u}_n = -i\omega Ae^{i(kx_n - \omega t)} \quad \text{and} \quad \ddot{u}_n = -\omega^2 Ae^{i(kx_n - \omega t)} = -\omega^2 u_n$$

Substituting into equation (iii), we have;

$$-\omega^2 mAe^{i(kx_n - \omega t)} = \beta A [e^{i(kx_{n+1} - \omega t)} - 2e^{i(kx_n - \omega t)} + e^{i(kx_{n-1} - \omega t)}]$$

But,

$$x_n = na$$

$$x_{n+1} = (n+1)a$$

$$x_{n-1} = (n-1)a$$

$$\Rightarrow -\omega^2 me^{i(kna - \omega t)} = \beta [e^{i(k(n+1)a - \omega t)} - 2e^{i(kna - \omega t)} + e^{i(k(n-1)a - \omega t)}]$$

$$-\omega^2 mu_n = \beta u_n (e^{ika} + e^{-ika} - 2)$$

$$\text{But } e^{ika} + e^{-ika} = 2 \cos ka$$

$$\Rightarrow -\omega^2 m = 2\beta (\cos ka - 1)$$

$$-\omega^2 m = 2\beta \left[ 1 - 2 \sin^2 \left( \frac{ka}{2} \right) - 1 \right]$$

$$\omega^2 m = 4\beta \sin^2 \left( \frac{ka}{2} \right)$$

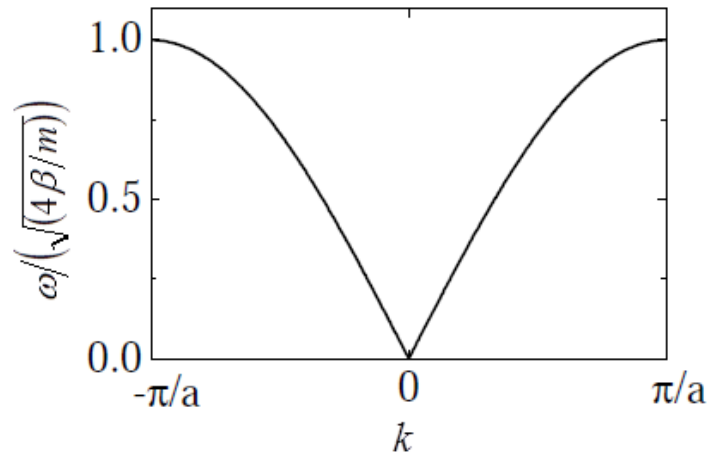
$$\Rightarrow \omega = \pm \sqrt{\left( \frac{4\beta}{m} \right)} \left| \sin \frac{ka}{2} \right|$$

This is the dispersion relation of the wave equation, which is the relationship between the frequency of vibrations and the wave vector  $k$ . This dispersion relation has a number of important properties.

- (i) **The first Brillouin zone:** The Brillouin zone is the primitive unit cell in the reciprocal lattice chosen in such a way that all points in the zone are closer to one reciprocal lattice point than to any other. We usually represent the lattice dynamics in one Brillouin zone. The frequency  $\omega = \sqrt{(4\beta/m)}|\sin(ka/2)|$  and the displacement of the atoms  $u_n = Ae^{i(kx_n \pm \omega t)}$  do not change when we change  $k$  by  $k + 2\pi/a$ . This means that these solutions are physically identical. This allows us to set the range of independent values of  $k$  within the first Brillouin zone, i.e.

$$-\frac{\pi}{a} \leq k \leq \frac{\pi}{a}$$

Within this range of  $k$ ,  $\omega$  versus  $k$  is shown below;



Since the maximum value of  $\sin(ka/2) = 1$ , the maximum possible frequency of the wave is  $\omega = 2\sqrt{(\beta/m)}$ . This is known as the cut off frequency of the lattice. The frequency is symmetric with respect to the sign change in  $k$ , i.e.  $\omega(k) = \omega(-k)$ . This is not surprising because a mode with positive  $k$  corresponds to the wave traveling in the lattice from the left to the right and a mode with a negative  $k$  corresponds to the wave traveling from the right to the left. Since these two directions are equivalent in the lattice the frequency does not change with the sign change in  $k$ .

At the boundaries of the Brillouin zone  $k = \pm\pi/a$ , the solution represents a standing wave  $u_n = A(-1)^n e^{-i\omega t}$ : atoms oscillate in the opposite phases depending on whether  $n$  is even or odd. The wave moves neither right nor left.

In the first Brillouin zone,

$$-\frac{\pi}{a} \leq k \leq \frac{\pi}{a} \quad \text{and} \quad \omega = \omega_{\max}$$



When  $(ka/2) = (\pi/2)$  or  $k = \pi/a$ , this satisfies the Bragg condition  $2d \sin \theta = n\lambda$ . If we take  $\theta = \pi/2$ ,  $d = a$ ,  $k = 2\pi/\lambda$  and  $n = 1$  so that  $\lambda = 2a$ , values off-side the first Brillouin zone merely reproduce the lattice motion described by values within the limits  $\pm a$ .

### (ii) Long wavelength limit

For long wavelength i.e. as  $\lambda \rightarrow +\infty$ ,  $k = (2\pi/\lambda) \rightarrow 0$ . The positive values of

$$\omega = \left(\frac{4\beta}{m}\right)^{\frac{1}{2}} \sin \frac{ka}{2} \text{ becomes } \omega = \left(\frac{4\beta}{m}\right)^{\frac{1}{2}} \frac{ka}{2} \text{ since } \sin \frac{ka}{2} \cong \frac{ka}{2}.$$

$$\Rightarrow \omega = \frac{a}{2} \left(\frac{4\beta}{m}\right)^{\frac{1}{2}} k$$

$$\omega = \left(\frac{a\beta}{m/a}\right)^{\frac{1}{2}} k$$

$$\omega = \left(\frac{\beta'}{\rho}\right)^{\frac{1}{2}} k$$

Where  $\beta'$  = bulk modulus,  $\rho$  = linear mass density and  $k$  = wave vector.

$$\Rightarrow \omega = V_r k$$

Where  $V_r$  is the velocity equivalent to that derived for a homogeneous string.

$\therefore$  for long wave length,  $\omega \propto k$

### (iii) Phase and group velocity

The phase velocity is given by,  $V_p = \frac{\omega}{k}$  and the group velocity by,  $V_g = \frac{d\omega}{dk}$ .

The physical distinction between the two velocities is that  $V_p$  is the velocity of the propagation of the plane wave, whereas the  $V_g$  is the velocity of the propagation of the wave packet. The latter is the velocity for the propagation of energy in the medium.

For the particular dispersion relation, the phase velocity is given by;

$$V_p = \frac{\left(\frac{4\beta}{m}\right)^{\frac{1}{2}} \sin \frac{ka}{2}}{k}$$

$$\Rightarrow V_p = \frac{2a \left(\frac{\beta}{m}\right)^{\frac{1}{2}} \sin \frac{ka}{2}}{ka}$$

For small angles,

$$V_p = a \left( \frac{\beta}{m} \right)^{\frac{1}{2}} = V_r$$

It follows that for the particular dispersion relation, the group velocity is given by;

$$\Rightarrow V_g = a \left( \frac{\beta}{m} \right)^{\frac{1}{2}} \cos \frac{ka}{2}$$

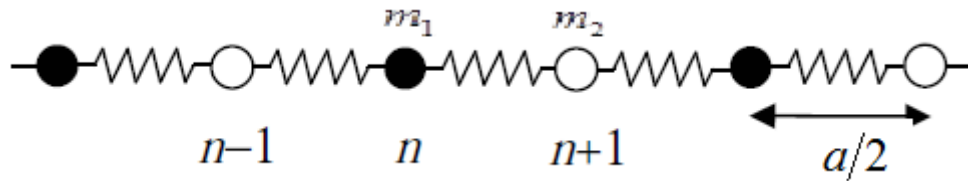
$$\Rightarrow V_g = V_r \cos \frac{ka}{2}$$

$$\text{For } \lambda \rightarrow \infty, k \rightarrow 0, \Rightarrow V_g = V_r = V_p$$

At  $k = \pi/a$ ,  $V_g = 0 \Rightarrow \omega = \omega_{\max}$ . The particles are now vibrating in a standing wave mode and it is at this condition that Bragg's condition is satisfied. Here no energy is propagated.

### 3.3 One –Dimensional Vibration of Diatomic Crystal Lattice

Now we consider a one-dimensional lattice with two non-equivalent atoms in a unit cell. It appears that the diatomic lattice exhibit important features different from the monoatomic case. The figure below shows a diatomic lattice with the unit cell composed of two atoms of masses  $m_1$  and  $m_2$  with the distance between two neighboring atoms  $a/2$ .



Similarly, we assume nearest neighbor interactions only. Also it's necessary to assume that the atoms are equidistant and mass  $m_1 \gg m_2$ .

We can treat the motion of this lattice in a similar fashion as for monoatomic lattice. However, in this case because we have two different kinds of atoms, we should write two equations of motion:

$$(i) \text{ For } m_1, m_1 \ddot{u}_n = \beta(u_{n+1} - 2u_n + u_{n-1}) \quad [1]$$

$$(ii) \text{ For } m_2, m_2 \ddot{u}_{n-1} = \beta(u_n - 2u_{n-1} + u_{n-2}) \quad [2]$$

In analogy with the monoatomic lattice we are looking for the solution in the form of traveling mode for the two atoms. The trial solution for mass  $m_1$  is,

$$\left. \begin{aligned} u_n &= Ae^{i(kx_n - \omega t)} = Ae^{i\left(\frac{kna}{2} - \omega t\right)} \\ \Rightarrow \ddot{u}_n &= -\omega^2 Ae^{i\left(\frac{kna}{2} - \omega t\right)} = -\omega^2 u_n \\ u_{n+1} &= Be^{i(kx_{n+1} - \omega t)} = Be^{i\left(\frac{k(n+1)a}{2} - \omega t\right)} \\ u_{n-1} &= Be^{i(kx_{n-1} - \omega t)} = Be^{i\left(\frac{k(n-1)a}{2} - \omega t\right)} \end{aligned} \right\} \quad [3]$$

Substituting equation [3] into equation [1] we've;

$$\begin{aligned} -m_1 \omega^2 Ae^{i\left(\frac{kna}{2} - \omega t\right)} &= \beta \left[ Be^{i\left(\frac{k(n+1)a}{2} - \omega t\right)} - 2Ae^{i\left(\frac{kna}{2} - \omega t\right)} + Be^{i\left(\frac{k(n-1)a}{2} - \omega t\right)} \right] \\ -m_1 \omega^2 Ae^{i\left(\frac{kna}{2} - \omega t\right)} &= \beta \left[ Be^{ik\frac{a}{2}} - 2A + Be^{-ik\frac{a}{2}} \right] e^{i\left(\frac{kna}{2} - \omega t\right)} \\ -m_1 \omega^2 A &= \beta \left[ 2B \cos\left(\frac{ka}{2}\right) - 2A \right] \\ \Rightarrow (2\beta - m_1 \omega^2)A - \left(2\beta \cos\frac{ka}{2}\right)B &= 0 \end{aligned} \quad [4]$$

Considering mass  $m_2$ , the trial solution will be;

$$\left. \begin{aligned} u_n &= Ae^{i(kx_n - \omega t)} = Ae^{i\left(\frac{kna}{2} - \omega t\right)} \\ u_{n-1} &= Be^{i(kx_{n-1} - \omega t)} = Be^{i\left(\frac{k(n-1)a}{2} - \omega t\right)} \\ \Rightarrow \ddot{u}_{n-1} &= -\omega^2 Be^{i\left(\frac{k(n-1)a}{2} - \omega t\right)} \\ u_{n-2} &= Ae^{i(kx_{n-2} - \omega t)} = Ae^{i\left(\frac{k(n-2)a}{2} - \omega t\right)} \end{aligned} \right\} \quad [5]$$

Substituting [5] into [2] we've;

$$\begin{aligned} -m_2 \omega^2 Be^{i\left(\frac{k(n-1)a}{2} - \omega t\right)} &= \beta \left[ Ae^{i\left(\frac{kna}{2} - \omega t\right)} - 2Be^{i\left(\frac{k(n-1)a}{2} - \omega t\right)} + Ae^{i\left(\frac{k(n-2)a}{2} - \omega t\right)} \right] \\ -m_2 \omega^2 Be^{i\left(\frac{k(n-1)a}{2} - \omega t\right)} &= \beta \left[ Ae^{i\left(\frac{k(n-1)a}{2} - \omega t\right)} e^{i\frac{ka}{2}} - 2Be^{i\left(\frac{k(n-1)a}{2} - \omega t\right)} + Ae^{i\left(\frac{k(n-1)a}{2} - \omega t\right)} e^{-i\frac{ka}{2}} \right] \\ -m_2 \omega^2 B &= \beta \left[ Ae^{i\frac{ka}{2}} - 2B + Ae^{-i\frac{ka}{2}} \right] \end{aligned}$$

$$\begin{aligned}
-m_2\omega^2 B &= \beta \left[ 2A \cos\left(\frac{ka}{2}\right) - 2B \right] \\
\Rightarrow \left( 2\beta \cos\frac{ka}{2} \right) A + (m_2\omega^2 - 2\beta) B &= 0
\end{aligned} \tag{6}$$

Equations [4] and [6] are homogeneous linear equations in the two amplitudes  $A$  and  $B$  which can be written in the obvious matrix form.

$$\begin{bmatrix} 2\beta - m_1\omega^2 & -2\beta \cos(ka/2) \\ 2\beta \cos(ka/2) & m_2\omega^2 - 2\beta \end{bmatrix} \begin{bmatrix} A \\ B \end{bmatrix} = 0 \tag{*}$$

The equations will have non-trivial solutions only if the determinant of the coefficients of  $A$  and  $B$  vanishes.

$$\begin{aligned}
\Rightarrow (2\beta - m_1\omega^2)(m_2\omega^2 - 2\beta) - \left( 2\beta \cos\frac{ka}{2} \right) \left( -2\beta \cos\frac{ka}{2} \right) &= 0 \\
m_1m_2\omega^4 - (2\beta m_1 + 2\beta m_2)\omega^2 + 4\beta^2 \left( 1 - \cos^2\left(\frac{ka}{2}\right) \right) &= 0 \\
\Rightarrow \omega^4 - 2\beta \left( \frac{1}{m_2} + \frac{1}{m_1} \right) \omega^2 + \frac{4\beta^2}{m_1m_2} \sin^2\left(\frac{ka}{2}\right) &= 0
\end{aligned} \tag{7}$$

The quadratic solution in  $\omega^2$  can be got to give solutions for  $\omega^2$ . This solution will be denoted by  $\pm \omega^2$  according to whether the positive or negative sign in the solution is taken.

$$\begin{aligned}
\text{i.e. } \omega^2 \pm &= \frac{2\beta}{2} \left( \frac{1}{m_2} + \frac{1}{m_1} \right) \pm \frac{1}{2} \sqrt{4\beta^2 \left( \frac{1}{m_2} + \frac{1}{m_1} \right) - \frac{16\beta^2}{m_1m_2} \sin^2\left(\frac{ka}{2}\right)} \\
\Rightarrow \omega^2 \pm &= \beta \left( \frac{m_1 + m_2}{m_1m_2} \right) \pm \beta \sqrt{\left( \frac{m_1 + m_2}{m_1m_2} \right)^2 - \frac{4\beta^2}{m_1m_2} \sin^2\left(\frac{ka}{2}\right)} \\
\Rightarrow \omega^2 \pm &= \beta \left( \frac{m_1 + m_2}{m_1m_2} \right) \left[ 1 \pm \sqrt{1 - \frac{4m_1m_2}{(m_1 + m_2)^2} \sin^2\left(\frac{ka}{2}\right)} \right]
\end{aligned} \tag{8}$$

The significance of equation [8] is appreciated if we consider the following limiting cases:

**(i) Limiting case 1**

For very long wavelength,  $\lambda \rightarrow \infty$ ,  $k = (2\pi/\lambda) \rightarrow 0$ .

$$\Rightarrow \omega^2 = 2\beta \left( \frac{m_1 + m_2}{m_1m_2} \right)$$

$$\therefore \omega = \left[ 2\beta \left( \frac{m_1 + m_2}{m_1 m_2} \right) \right]^{\frac{1}{2}}$$

Otherwise for  $\frac{ka}{2}$  being small,  $\sin \frac{ka}{2} \cong \frac{ka}{2}$

$$\Rightarrow \omega^2 = \beta \left( \frac{m_1 + m_2}{m_1 m_2} \right) \left[ 1 \pm \sqrt{1 - \frac{m_1 m_2 k^2 a^2}{(m_1 + m_2)^2}} \right]$$

Using the binomial expansion,  $(1-x)^n \approx 1-nx$  we've;

$$\Rightarrow \left( 1 - \frac{m_1 m_2 k^2 a^2}{(m_1 + m_2)^2} \right)^{\frac{1}{2}} \approx 1 - \frac{1}{2} \frac{m_1 m_2 k^2 a^2}{(m_1 + m_2)^2}$$

$$\Rightarrow \omega^2 = \beta \left( \frac{m_1 + m_2}{m_1 m_2} \right) \cdot \frac{1}{2} \left( \frac{m_1 m_2 k^2 a^2}{(m_1 + m_2)^2} \right)$$

$$\therefore \omega = \pm \left( \frac{\beta k^2 a^2}{2(m_1 + m_2)} \right)^{\frac{1}{2}} \quad \text{where } \frac{ka}{2} \ll \frac{\pi}{2}$$

## (ii) Limiting case 2

The second limiting case is given when  $\sin^2 \frac{ka}{2}$  is a maxima i.e. when  $\frac{ka}{2} = \frac{\pi}{2}$ . Working out the determinant of the coefficients of  $A$  and  $B$  we shall have;

$$\begin{vmatrix} 2\beta - m_1 \omega^2 & 0 \\ 0 & m_2 \omega^2 - 2\beta \end{vmatrix}$$

$$\Rightarrow (2\beta - m_1 \omega^2)(m_2 \omega^2 - 2\beta) = 0$$

$$\text{Either } 2\beta - m_1 \omega^2 = 0$$

$$\Rightarrow \omega_- = \pm \left( \frac{2\beta}{m_1} \right)^{\frac{1}{2}}$$

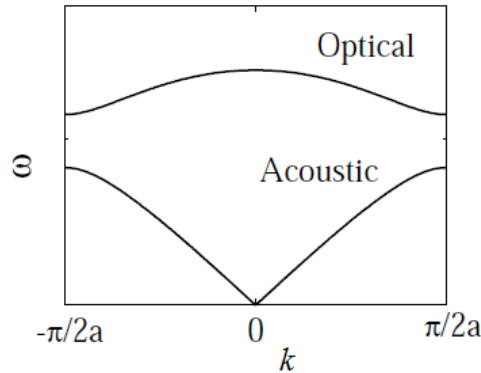
$$\text{Or } m_2 \omega^2 - 2\beta = 0$$

$$\Rightarrow \omega_+ = \pm \left( \frac{2\beta}{m_2} \right)^{\frac{1}{2}}$$

$$\text{Hence } \omega_+ \left( \frac{\pi}{2} \right) > \omega_- \left( \frac{\pi}{2} \right) \text{ since } m_1 \gg m_2$$

In this case, the dispersion relationship has two branches as shown in the figure below;

- $\omega_+(k)$  is called the optical branch
- $\omega_-(k)$  is called the acoustic branch

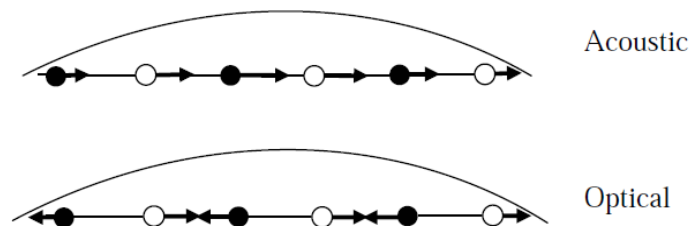


The lower curve is called the *acoustic branch*, while the upper curve is called the *optical branch*. The acoustic branch begins at  $k = 0$  and  $\omega = 0$ . Then with increasing  $k$  the frequency increases in a linear fashion. This is why this branch is called acoustic: it corresponds to elastic waves or sound. Eventually this curve saturates at the edge of the Brillouin zone.

On the other hand, the optical branch has a nonzero frequency at zero  $k$  and it does not change much with  $k$ ;

$$\omega_0 = \left( 2\beta \left( \frac{1}{m_1} + \frac{1}{m_2} \right) \right)^{\frac{1}{2}} \quad [**]$$

The distinction between the acoustic and optical branches of lattice vibrations can be seen most clearly by comparing them at  $k = 0$  (infinite wavelength). As follows from equation [\*], for the acoustic branch  $\omega = 0$  and  $A = B$ . So in this limit the two atoms in the cell have the same amplitude and the phase. Therefore, the molecule oscillates as a rigid body for the acoustic mode as shown in the figure below.



On the other hand, for the optical vibrations, substituting equation [\*\*] into equation [\*], we obtain for  $k = 0$ :

$$m_1 A + m_2 B = 0$$

The vibrations of atoms are in opposite directions and the ratio of the amplitudes is equal to the inverse ratio of the masses so that the center of the mass of a unit cell remains fixed during

motion. The two atoms move in out of phase as shown in the figure above. The frequency of these vibrations lies in infrared region which is the reason for referring to this branch as optical.

**NB:**

- If masses  $m_1$  and  $m_2$  are equal, then the frequency is the same in the diatomic as in the lattice monatomic there is no forbidden gap.
- At the first Brillouin zone edge (i.e. when  $ka/2 = \pi/2$ ), only one of the lattices is vibrating. In the optical branch, it is the light atom. In the acoustic branch, it is the heavier atom. Both branches represent standing waves which have a phase difference of  $\pi/2$ .
- If then heavier mass  $m_1 \rightarrow \infty$ , the acoustic branch disappears backwards  $\omega_-(k) \rightarrow 0$ . The optical branch flattens in such a way that all the values have the same frequency.
- If the lighter mass,  $m_2 \rightarrow 0$ , the optical branch disappears upwards, the acoustic branch is unchanged and we return to monatomic lattice.

## Chapter 4: Thermal Properties of Insulating Solids

### 4.1 Introduction

Thermal property of a material is the response of the material to heat. This is manifested by changes in temperature and dimensions of the material. In order to determine the thermal properties of solids (particularly the heat capacity), it's important to note that there are two contributions: one comes from *phonons* (or lattice vibrations) and another from *electrons*. In conductors, heat transmission is carried out by the free valence electrons whereas in insulators, heat is transmitted by the lattice vibration. This section is devoted to the thermal properties of solids due to lattice vibrations (the contribution from electrons in metals will be considered in Solid State Physics II).

### 4.2 Quantization of lattice vibrations: Phonons

Quantum Mechanics tells us that the energy levels of harmonic oscillators are quantized. Similarly the energy levels of lattice vibrations are quantized. The coupling of atomic vibrations of adjacent atoms in solids results in waves of atomic displacements; each of which is characterized by its wavelength and frequency. For a wave of a given angular frequency  $\omega$ , there is the smallest “quantum” of vibrational energy,  $E = \hbar\omega$  and momentum  $P = \hbar k$ , called *phonon* in analogy with photon, which are the quanta of electromagnetic field. Therefore, ***phonons are quanta of thermal lattice oscillations***. Phonons are bosons and they obey the Bose-Einstein statistics.

#### 4.2.1 Number of phonons

The number of phonon is not a fixed value. If an atom starts to oscillate, then we created some phonons. If the oscillation stops, the phonons disappear. Although we cannot determine the number of phonons, at a fixed temperature we know the probability of having  $n$  phonons.

Let's consider a lattice wave with a fixed wave vector  $k$  and a fixed frequency  $\omega$  and ask how many phonons we will have in this wave. The probability of having  $n$  phonons here is;

$$P(n) \propto e^{\left(\frac{-E_n}{k_B T}\right)}$$

where  $K_B$  is the Boltzmann constant,  $T$  is the absolute temperature in kelvin and  $E_n$  is the energy carried by these  $n$  phonons. Because each phonon carries energy  $\hbar\omega$ ,  $E_n = n\hbar\omega$ . The expression  $\exp(E_n/k_B T)$  is known as the Boltzmann factor, which is one fundamental assumption in statistical Physics.

$$\Rightarrow P(n) = \frac{1}{Z} e^{\left(\frac{-n\hbar\omega}{k_B T}\right)}$$

where  $Z$  is the normalization factor (which is called the partition function) and  $\hbar = \frac{h}{2\pi}$ .



Total probability is 1. We can use this condition to fix  $Z$ .

$$1 = \sum_{n=0}^{\infty} P(n) = \sum_{n=0}^{\infty} \frac{1}{Z} e^{\left(\frac{-n\hbar\omega}{k_B T}\right)} = \frac{1}{Z} \sum_{n=0}^{\infty} e^{\left(\frac{-n\hbar\omega}{k_B T}\right)} = \frac{1}{Z} \left[ \frac{1}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} \right]$$

Here we used the fact that  $1 + x + x^2 + x^3 + \dots = \frac{1}{1-x}$ .

$$Z = \left[ \frac{1}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} \right]$$

Average number of phonons

$$\begin{aligned} \langle n \rangle &= \sum_{n=0}^{\infty} n P(n) = \sum_{n=0}^{\infty} \frac{n}{Z} \exp\left(-\frac{n\hbar\omega}{k_B T}\right) = \frac{1}{Z} \sum_{n=0}^{\infty} n \exp\left(-\frac{n\hbar\omega}{k_B T}\right) \\ \Rightarrow \langle n \rangle &= \frac{1}{Z} \frac{k_B T}{\hbar} \sum_{n=0}^{\infty} \frac{d}{d\omega} \exp\left(-\frac{n\hbar\omega}{k_B T}\right) = -\frac{1}{Z} \frac{k_B T}{\hbar} \frac{d}{d\omega} \sum_{n=0}^{\infty} \exp\left(-\frac{n\hbar\omega}{k_B T}\right) \\ &= -\frac{1}{Z} \frac{k_B T}{\hbar} \frac{d}{d\omega} \frac{1}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} \\ &= \frac{1}{Z} \frac{k_B T}{\hbar} \left( \frac{1}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} \right)^2 \exp\left(-\frac{\hbar\omega}{k_B T}\right) \frac{\hbar}{k_B T} = \frac{\exp\left(-\frac{\hbar\omega}{k_B T}\right)}{1 - \exp\left(-\frac{\hbar\omega}{k_B T}\right)} \\ \therefore \langle n \rangle &= \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} \end{aligned}$$

The average phonon number depends on temperature  $T$ , the frequency of the phonons  $\omega$  and some fundamental physics constants  $\hbar$  and  $k_B$ . This relation is known as the Planck distribution or the Bose-Einstein distribution. After the above Planck discovery, Bose and Einstein later discovered that for any bosonic particles, the average number of particles is;

$$\langle n \rangle = \frac{1}{\exp\left(\frac{\epsilon - \mu}{k_B T}\right) - 1}$$

where  $\epsilon$  is the energy of this particle and  $\mu$  is the chemical potential. The Planck distribution is therefore a special case of the Bose-Einstein distribution, where  $\mu$  is 0. (Photons and phonons are both bosonic particles (bosons), so they obey the Bose-Einstein distribution).

#### 4.2.2 Energy carried by phonons

From the Planck's theory, one phonon has energy  $\hbar\omega$ , so the average energy carried by these waves is;

$$\langle E_n \rangle = \langle n \rangle \hbar\omega = \frac{\hbar\omega}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

**NB:** This is the energy carried by phonons per oscillator in a 1-dimensional lattice with frequency  $\omega$  when temperature  $T$  is applied. However, in the real sense, even at 0° K atoms vibrate in the crystal and have zero-point energy given as  $(\hbar\omega)/2$ . This is the minimum energy of the system.

Therefore, the total energy per oscillator in a vibrating 1-dimensional lattice is the sum of zero-point energy and the phonon contribution to the thermal energy;

$$\Rightarrow \langle E_n \rangle = \left( \frac{1}{2} + \langle n \rangle \right) \hbar\omega = \hbar\omega \left( \frac{1}{2} + \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} \right)$$

#### 4.3 Heat capacity

Heat capacity is the ability of a material to absorb heat (thermal energy). Heat capacity,  $C$ , is defined as the amount of energy  $\Delta Q$  required to produce a unit temperature rise by  $\Delta T$ .

$$C = \frac{\Delta Q}{\Delta T} \text{ (J/mol-K)}$$

On the other hand, specific heat,  $c$ , is the heat capacity per unit mass (J/kg-K). Heat capacity can be measured under conditions of constant pressure or constant volume. In this case,  $\partial Q$  must be replaced by  $\partial U$ , which represents the increase in the internal energy  $U$  of the system. Thus, two distinct heat capacities can be defined as;

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \text{ and } C_P = \left( \frac{\partial U}{\partial T} \right)_P$$

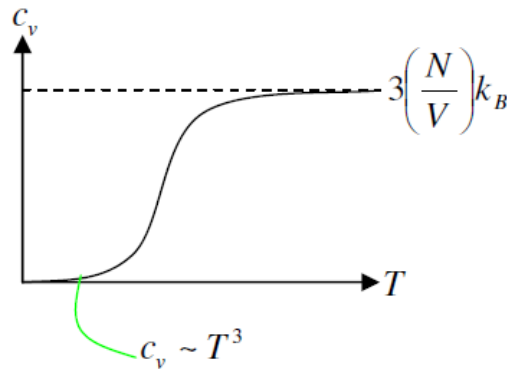
#### 4.4 Classical Statistical Theory

In a classical statistical theory, based on the classical partition function, the mean internal energy of a one-dimensional oscillator is  $k_B T$ , value that becomes  $3k_B T$  for a three-dimensional oscillator. Then for  $N$  three-dimensional oscillators  $\langle E \rangle = 3Nk_B T$ , and the phononic heat capacity at constant volume is;

$$C_V = \left( \frac{\partial E}{\partial T} \right)_V = 3Nk_B$$

i.e.  $C_V = 3k_B$  per atom, or  $C_V = 3N_A k_B = 3R$

This result is known as the Dulong-Petit law, found experimentally by Dulong and Petit in 1819. This law predicts a temperature-independent heat capacity. This prediction agrees with experimental data at high temperatures but not at low temperatures, where experiments indicate that  $C_V \propto T^3 \rightarrow 0$  as  $T \rightarrow 0$ . The general temperature dependence of  $C_V$  for solid insulators has the form shown below.



**NB:** Any theory used to calculate lattice heat capacities of crystalline solids must explain two things:

1. Near room temperature, the heat capacity of most solids is around  $3k_B$  per atom. This is the well-known Dulong and Petit law.
2. At low temperatures,  $C_V$  decreases, becoming zero at  $T=0$ . Heat capacities have a temperature dependence of the form  $\alpha T^3 + \gamma T$ , where the  $T^3$  term arises from lattice vibrations, and the linear term from conduction electrons.

Classical mechanics would predict  $C_V = 3k_B$  at all temperatures, in violation of both experiment and the third law of thermodynamics. Therefore, in order to explain the low-temperature behavior of lattice heat capacity, one should disregard the classical statistical theory and instead use the *quantum theory*.

The first explanation was proposed by Einstein in 1906. He considered a solid as an ensemble of independent quantum harmonic oscillators vibrating at a frequency  $\omega_E$ . Debye advanced the theory by treating the quantum oscillators as collective modes in the solid (phonons).

#### 4.5 Einstein's model of lattice heat capacity

In this model, Einstein treated each atom or molecule in a crystal as  $N$  simple harmonic oscillators that oscillate independently in the average field of its neighbors with the same frequency  $\omega_E$ . In this theory the correlation between the motions of neighboring atoms were ignored. The frequency  $\omega_E$  depends on the strength of the restoring force acting on the atom, i.e.

the strength of the chemical bonds within the solid. Considering the fact that the equation of motion for each atom decomposes into three independent equations for the  $x$ ,  $y$  and  $z$  components of displacement, Einstein considered  $3N$  harmonic oscillators and obtained the energy levels of the harmonic oscillators as;

$$U = 3N\langle E_n \rangle = 3N\left(\frac{1}{2} + \langle n \rangle\right)\hbar\omega_E = 3N\hbar\omega_E\left(\frac{1}{2} + \frac{1}{\exp\left(\frac{\hbar\omega_E}{k_B T}\right) - 1}\right)$$

$$\Rightarrow U = 3N\hbar\omega_E\left(\frac{1}{2} + \frac{1}{\exp\left(\frac{\hbar\omega_E}{k_B T}\right) - 1}\right)$$

### **Limiting Cases:**

#### **(i) At high temperatures**

$$\frac{\hbar\omega_E}{k_B T} \ll 1, \quad \Rightarrow \hbar\omega_E \ll k_B T$$

$$\text{From } e^x = 1 + x + \frac{x^2}{2!} + \dots$$

$$\Rightarrow U = 3N\hbar\omega_E\left(\frac{1}{2} + \frac{1}{1 + \frac{\hbar\omega_E}{k_B T} + \frac{1}{2}\left(\frac{\hbar\omega_E}{k_B T}\right)^2 + \dots - 1}\right)$$

$$\Rightarrow U = 3N\hbar\omega_E\left(\frac{1}{2} + \frac{k_B T}{\hbar\omega_E}\right)$$

The lattice heat capacity is then defined as;

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 3N\hbar\omega_E \frac{d}{dT}\left(\frac{1}{2} + \frac{k_B T}{\hbar\omega_E}\right) = 3Nk_B$$

$$\therefore \underline{C_V = 3R}$$

Thus at higher temperatures, Einstein's model gives results close to the classical model.

#### **(ii) At low temperatures**

$$\hbar\omega_E \gg k_B T$$

$$\Rightarrow U = 3N\hbar\omega_E\left(\frac{1}{2} + \exp\left(-\frac{\hbar\omega_E}{k_B T}\right)\right), \text{ since } \frac{\hbar\omega_E}{k_B T} \text{ becomes too large and hence 1 is neglected.}$$

The lattice heat capacity is then defined as;

$$C_V = \left( \frac{\partial U}{\partial T} \right)_V = 3N\hbar\omega_E \frac{d}{dT} \left( \frac{1}{2} + \exp\left(-\frac{\hbar\omega_E}{k_B T}\right) \right)$$

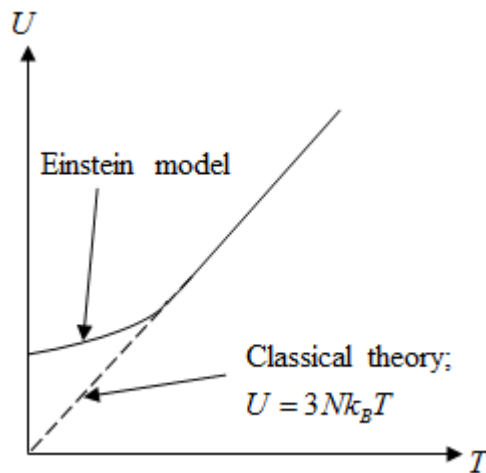
$$\Rightarrow C_V = 3N\hbar\omega_E \frac{d}{dT} \left( \exp\left(-\frac{\hbar\omega_E}{k_B T}\right) \right) = 3N \left( \frac{\hbar^2 \omega_E^2}{k_B T^2} \right) e^{-\frac{\hbar\omega_E}{k_B T}}$$

$$\therefore C_V = 3Nk_B \left( \frac{\hbar^2 \omega_E^2}{k_B^2 T^2} \right) e^{-\frac{\hbar\omega_E}{k_B T}}$$


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Thus when  $T$  is reduced to zero,  $C_V$  decreases very fast to zero as  $e^{-\frac{\hbar\omega_E}{k_B T}}$ . This result agrees with the third law of thermal dynamics:  $C_V = 0$  at  $T = 0$ .

#### Variation of $U$ against $T$



At high temperatures, classical model agrees with Einstein model and the reverse is true at low temperatures.

#### 4.6 Debye model of lattice heat capacity

The disagreement between Einstein's result and the experimental data is due to the fact that Einstein's assumptions about the atoms in a crystal do not strictly apply to real crystals. The main problem lies in the assumption that a single frequency of vibration characterizes all  $3N$  oscillators. Debye improved on Einstein's theory by considering the vibrations of a body as a whole, regarding it as a **continuous elastic solid**. He associated the internal energy of the solid with stationary elastic sound waves. Each independent mode of vibration (or normal mode) is treated as a degree of freedom.

The Debye model assumes that the acoustic modes give the dominant contribution to the heat capacity. Within the Debye approximation the velocity of sound is taken a constant independent of polarization as it would be in a classical elastic continuum. The dispersion relation is written as  $\omega = vk$ , where  $v$  is the acoustic (sound) velocity.

In this approximation the number of modes with wave vectors less than  $k$  is given by;

$$N = \frac{\text{volume of sphere with radius } k}{\text{volume assigned to each lattice point in the } k\text{-space}} = \frac{(4/3)\pi k^3}{(2\pi/a)^3} = \frac{4a^3\pi k^3}{24\pi^3}$$

where  $a$  is the lattice parameter,  $k = \omega/v$  and  $a^3 = \text{volume}, V$ .

$$\Rightarrow N = \frac{V\omega^3}{6\pi^2 v^3} \quad [*]$$

The Debye angular frequency which is the cut-off frequency for  $N$  is given by;

$$\omega_D = \left( \frac{6\pi^2 v^3 N}{V} \right)^{\frac{1}{3}}$$

Therefore, the cut-off wave vector (Debye wave vector),  $k_D = \frac{\omega_D}{v}$  is given as;

$$k_D = \left( \frac{6\pi^2 N}{V} \right)^{\frac{1}{3}}$$

This implies that modes of wave vector larger than  $k_D$  are not allowed. This is due to the fact that the number of modes with  $k \leq k_D$  exhausts the number of degrees of freedom of the lattice.

The density of state is defined from equation [\*] as;

$$D(\omega) = \frac{dN}{d\omega} = \frac{V\omega^2}{2\pi^2 v^3}$$

i.e. the density of states increases quadratically with the frequency.

Usually it's convenient to assume that in the frequency range  $\omega$  and  $(\omega + d\omega)$ , there are  $D(\omega)d\omega$  number of modes. Then the energy for  $3N$  harmonic oscillator is given by;

$$U = 3 \int D(\omega) d\omega N \hbar \omega$$

$$\text{where } N = \sum n = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1}$$

$$\Rightarrow U = \frac{3V\hbar}{2\pi^2 v^3} \int_0^{\omega_D} \frac{\omega^3}{e^{\hbar\omega/k_B T} - 1} d\omega = \frac{3Vk_B^4 T^4}{2\pi^2 v^3 \hbar^3} \int_0^{x_D} \frac{x^3}{e^x - 1} dx, \quad [**]$$

$$\text{where } x = \frac{\hbar\omega}{k_B T} \text{ and } x_D = \frac{\hbar\omega_D}{k_B T} = \frac{\theta_D}{T}$$

The latter expression defines the Debye temperature;  $\theta_D = \frac{\hbar\omega_D}{k_B} = \frac{\hbar v}{k_B} \left( \frac{6\pi^2 N}{V} \right)^{\frac{1}{3}}$ .

The total phonon energy is then;

$$\Rightarrow U = 9Nk_B T \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1} dx,$$

where  $N$  is the number of atoms in the crystal

The lattice heat capacity can simply be found by differentiating the middle expression of equation [\*\*] with respect to temperature

$$\Rightarrow C_V = \left( \frac{\partial U}{\partial T} \right)_V = \frac{3V\hbar^2}{2\pi^2 v^3 k_B T^2} \int_0^{\omega_D} \frac{\omega^4 e^{\hbar\omega/k_B T}}{(e^{\hbar\omega/k_B T} - 1)^2} d\omega,$$

$$C_V = 9Nk_B T \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx.$$

### **Limiting Cases:**

#### **(i) High temperatures**

In the limit  $T \gg \theta_D$ ,  $x \ll 1$ . We can expand the expression under the integral and obtain:  $C_V = 3Nk_B$ . This is exactly the classical value for the heat capacity, which is known from the elementary physics. Recall that according to the elementary thermodynamics the average thermal energy per a degree of freedom is equal to  $E = k_B T$ . Therefore for a system of  $N$  atoms in 3-dimensions,  $E = 3Nk_B T$  which results in  $C_V = 3Nk_B$ . This is known as the *Dulong-Petit* law.

#### **(ii) Low temperatures**

Now consider an opposite limit, i.e.  $T \ll \theta_D$ . At very low temperatures we can approximate the total phonon energy by letting the upper limit go to infinity. We obtain;

$$U = 9Nk_B T \left( \frac{T}{\theta_D} \right)^3 \int_0^\infty \frac{x^3}{e^x - 1} dx = 9Nk_B T \left( \frac{T}{\theta_D} \right)^3 \frac{\pi^4}{15} = \frac{3\pi^4}{5} Nk_B T \left( \frac{T}{\theta_D} \right)^3$$

$$\Rightarrow C_V = \frac{12\pi^4}{5} Nk_B \left( \frac{T}{\theta_D} \right)^3.$$

We see that within the Debye model at low temperatures the heat capacity is proportional to  $T^3$ . This result agrees with the third law of thermal dynamics:  $C_V = 0$  at  $T = 0$ .

### Worked Examples

1. Calculate the specific heat for aluminum at 300 K, given its Debye temperature is 375 K.

#### **Solution**

Given  $\theta_D = 375\text{K}$

Specific heat of material by Debye method is given by;

$$C_V = \frac{12\pi^4}{5} Nk_B \left( \frac{T}{\theta_D} \right)^3; \text{ if } T \ll \theta_D.$$

#### **Known values:**

$$\pi \text{ (pi constant)} = 3.14$$

$$N_A \text{ (Avogadro number)} = 6.023 \times 10^{23} \text{ mol}^{-1}$$

$$k_B \text{ ( Boltzmann constant)} = 1.38 \times 10^{-23} \text{ JK}^{-1}$$

Therefore, specific heat for aluminum at 300 K,  $C_V = 995 \text{ kJ/kmol-K}$

#### **Exercise**

1. What is the Debye frequency for copper, if it has the Debye temperature of 315 K?. Find its Debye specific heat at 10 K and 300 K.
2. Find the Debye temperature for sodium chloride at 10, 15 and 20 K with corresponding specific heat values of 0.066, 0.249 and 0.649 kJ/kmol-K.

### **4.7 Thermal Conductivity**

When the two ends of the sample of a given material are at two different temperatures,  $T_1$  and  $T_2$  ( $T_2 > T_1$ ), heat flows down the thermal gradient, i.e. from the hotter to the cooler end. Observations show that the *heat current density*  $j$  (amount of heat flowing across unit area per unit time) is proportional to the temperature gradient ( $dT/dx$ ). That is,

$$j = -K \frac{dT}{dx}.$$

The proportionality constant  $K$ , known as the *thermal conductivity*, is a measure of the ease of transmission of heat across the bar (the minus sign is included so that  $K$  is a positive quantity).

Heat may be transmitted in the material by several independent agents. In metals, for example, the heat is carried both by electrons and phonons, although the contribution of the electrons is much larger. In insulators, on the other hand, heat is transmitted entirely by phonons, since there are no mobile electrons in these substances. Here we consider only transmission by phonons.

When we discuss transmission of heat by phonons, it is convenient to think of these as forming a phonon gas. In every region of space there are phonons traveling randomly in all directions, much like the molecules in an ordinary gas. The concentration of phonons at the hotter end of the sample is larger and they move to the cooler end. The advantage of using this gas model is that



many of the familiar concepts of the kinetic theory of gases can also be applied here. In particular, thermal conductivity in a generalized three dimensional case is given by;

$$K = \frac{1}{3} C_v v l$$

where  $C_v$  is the specific heat per unit volume,  $v$  the velocity of the particle, and  $l$  its *mean free path*. In the present case,  $v$  and  $l$  refer, of course, to the velocity and the mean free path of the phonon, respectively. The mean free path is defined as the average distance between two consecutive scattering events, so that  $l = v\tau$ , where  $\tau$  is the average time between collisions which is called *collision time* or *relaxation time*.

Since  $C_v = \frac{dE}{dT}$  is the heat capacity, we obtain

Since  $j = \frac{1}{3} C_v v l \left( -\frac{dT}{dx} \right)$ , where  $v$  is phonon velocity.

#### 4.7.1 Dependence of the thermal conductivity $j$ on temperature

The dependence of  $C_v$  on temperature has already been studied in detail, while the velocity  $v$  is found to be essentially insensitive to temperature. The mean free path  $l$  depends strongly on temperature. Indeed,  $l$  is the average distance the phonon travels between two successive collisions. Three important mechanisms may be distinguished:

- a) The collision of a phonon with other phonons,
- b) the collision of a phonon with imperfections in the crystal, such as impurities and dislocations, and
- c) The collision of a phonon with the external boundaries of the sample.

Phonon-phonon collisions become particularly important at high temperature, at which the atomic displacements are large. In this region, the corresponding mean free path is inversely proportional to the temperature, that is,  $l \sim 1/T$ . This is reasonable, since the larger  $T$  is, the greater the number of phonons participating in the collision.

The second mechanism (b) which results in phonon scattering results from defects and impurities. Real crystals are never perfect and there are always crystal imperfections in the crystal lattice, such as impurities and defects, which scatter phonons because they partially destroy the perfect periodicity of the crystal.

At very low temperature (say below  $10^0\text{K}$ ), both phonon-phonon and phonon-imperfection collisions become ineffective, because, in the former case, there are only a few phonons present, and in the latter the few phonons which are excited at this low temperature are long-wavelength ones. These are not effectively scattered by objects such as impurities, which are much smaller in size than the wavelength. In the low-temperature region, the primary scattering mechanism is the external boundary of the specimen, which leads to the so-called *size* or *geometrical effects*. This mechanism becomes effective because the wavelengths of the excited phonons are very long - comparable, in fact, to the size of the specimen. The mean free path here is  $l \sim L$ , where  $L$  is roughly equal to the diameter of the specimen, and is therefore independent of temperature.

## Chapter 5: Dielectric Properties of Solids

### 5.1 Introduction

In electromagnetics we classify materials generally into four broad categories;

1. Conductor – free charge moves easily through the material
2. Semi-conductor – free charge moves somewhat
3. Dielectrics (insulators) – no free charge, but material produces change to electric field
4. Magnetic – material produces change to magnetic field

**Dielectrics** are insulating materials having electric dipoles permanently or temporarily by inducement during the application of electric field. Electric dipole is formed from two charges of opposite sign and equal magnitude located close together. The process of producing electric dipoles out of neutral atoms or molecules is known as *polarization*.

### 5.2 Types of dielectric polarizations

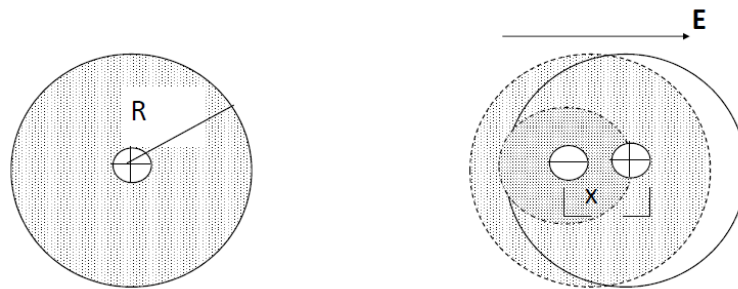
At the atomic level, all matter consists ultimately of positively and negatively charged particles whose charges balance each other macroscopically in the absence of an electric field giving rise to overall charge neutrality. Once the electric field is applied, the balances of charges are perturbed by the following three basic polarization mechanisms:

- Electronic polarization
- Atomic/ionic polarization
- Dipolar/orientational polarization

#### 1. Electronic Polarization

Electronic polarization is due to the displacement of charge centers of electron cloud (negative charge centre) and nucleus (positive charge centre) of an atom in the presence of an applied electric field. Thus electronic polarization is an induced polarization effect.

Consider an atom of a dielectric material of atomic number ' $Z$ ' and atomic radius ' $R$ '. In the absence of an electric field (**Fig.5.a**), the centers of gravity of charges of electron cloud and positive nucleus are at the same point and hence there is no displacement.



If the atom is placed in a *dc* electric field of strength  $\vec{E}$ , the nucleus and the electron cloud experience *Lorentz forces* in opposite directions. The magnitude of these *Lorentz forces* is  $\vec{F}_L = Ze\vec{E}$ .

Since the nucleus and electron cloud are pulled apart, an attractive force (Coulomb force) develop between them.

Recall Coulomb's law;  $\vec{F}_C = \frac{q_+ q_-}{4\pi\epsilon_0 R^2}$ .

When the Lorentz force and coulomb attractive forces are equal and opposite, there will be a new equilibrium between the nucleus and the electron cloud and the electric dipole forms. Let the distance of separation between the centers of the displaced nucleus and electron cloud be  $x$ . The negative charge enclosed in the sphere of radius ' $x$ ' is equal to;

$$q_- = \frac{4}{3}\pi x^3 \rho$$

where  $\rho$  is the charge density of electron cloud, and is equal to;

$$\rho = \left[ \frac{-Ze}{\frac{4}{3}\pi R^3} \right]$$

Therefore charge enclosed in the sphere of radius,  $x$  is,

$$q_- = \frac{4}{3}\pi x^3 \left[ \frac{-Ze}{\frac{4}{3}\pi R^3} \right] = \left[ \frac{-Zex^3}{R^3} \right]$$

The charge due to positive charges in the nucleus is given as  $q_+ = Ze$

Therefore Coulomb force of attraction;  $\vec{F}_C = \frac{Ze \cdot [\text{charge enclosed in the sphere of radius } x]}{4\pi\epsilon_0 x^2}$ .

$$\Rightarrow \vec{F}_C = \frac{-Ze \cdot Zex^3}{4\pi\epsilon_0 x^2 R^3} = \frac{-Z^2 e^2 x}{4\pi\epsilon_0 R^3}$$

Lorentz force of repulsion experienced by the electron cloud due to applied field  $\vec{E}$  is;

$$\vec{F}_L = -Ze\vec{E}.$$

In equilibrium condition,  $\vec{F}_C = \vec{F}_L$

$$\begin{aligned} \Rightarrow \frac{-Z^2 e^2 x}{4\pi\epsilon_0 R^3} &= -Ze\vec{E} \\ \Rightarrow x &= \frac{4\pi\epsilon_0 R^3}{Ze} \vec{E} \end{aligned}$$

Thus the separation between the two charge centers is proportional to the applied field  $\vec{E}$ .

The induced electric **dipole moment** or **added polarization** which is the product of *magnitude* of either of the charges of a dipole and the *separation* between them is given by;  $p_e = Zex$ .

$$\Rightarrow p_e = 4\pi\epsilon_0 R^3 \cdot \vec{E}$$

$$\therefore p_e = \alpha_e \vec{E}, \Rightarrow \alpha_e = 4\pi\epsilon_0 R^3$$

where  $\alpha_e$  is called electric polarizability.

**NB:**  $\alpha_e$  is independent of  $Z$ ,  $e$  and  $T$ . It only depends on atomic radius,  $R$ .

The polarization, i.e., total dipole moment per unit volume is given as;

$$\vec{P} = Np_e = N\alpha_e \vec{E};$$

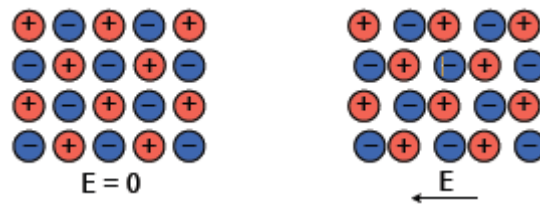
where ' $N$ ' is the number of dipoles, atoms or molecule per unit volume

$$\text{But } \frac{\vec{P}}{\vec{E}} = N\alpha_e = \chi_e;$$

where  $\chi_e$  is the electronic susceptibility

## 2. Ionic Polarization

Ionic polarization is due to the displacement of positive and negative ions of a molecule in the presence of an applied electric field. In case of *sodium chloride* molecule, it is composed of  $Na^+$  and  $Cl^-$  separated by inter atomic distance,  $r_0$ . The permanent dipole moment is then  $er_0$  in the absence of applied field. When field is applied to the molecule, the sodium and chlorine atoms get displaced in opposite directions until ionic bonding forces stop the process. Thus the dipole moment increases.



In this case, two forces are created; a stretching force  $\vec{F}_s = \gamma x$  and the Lorentz force  $\vec{F}_L = q\vec{E}$ .

At equilibrium,  $\vec{F}_s = \vec{F}_L$ .

$$\Rightarrow \gamma x = q\vec{E},$$

where  $\gamma$  and  $x$  are string constant and charge separation distance respectively

$$\Rightarrow x = \frac{q\vec{E}}{\gamma}$$

The induced ionic **dipole moment** or **added polarization** is given by;  $p_i = qx$ .

$$\Rightarrow p_i = \frac{q^2 \vec{E}}{\gamma}$$

$$\therefore p_i = \alpha_i \vec{E}, \Rightarrow \alpha_i = \frac{q^2}{\gamma}$$

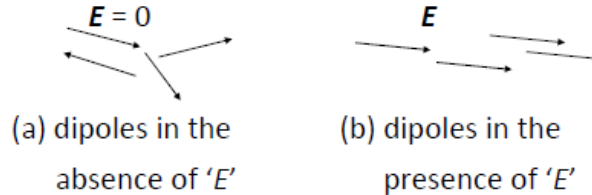
where  $\alpha_i$  is the ionic polarizability.

## 3. Orientation Polarization

Orientation polarization is due to the alignment of dipoles of polar molecules (molecules possessing permanent dipole moments) in the presence of applied electric field. This type of polarization occurs in polar substances (dielectrics). Polar substances show random distribution of their dipoles in space in the absence of electric field. This leads to the zero net dipole moment of the substance.

When dielectric is kept under an electric field, the field produces a torque in individual dipoles and dipoles align with the field. If the field is so strong enough, the dipoles may completely be aligned along the field direction. With increasing temperature, orientational polarizability,  $\alpha_d$  decreases.

$$\text{i.e. } \alpha_d = \frac{p_d^2}{3k_B T}$$



### 5.3 Polarization, dielectric constant and electric susceptibility

Consider a dielectric slab placed between two charged plates. The external electric field between the conducting plates induces charge on the opposite sides of the dielectric. The dielectric is then said to be polarized.

The electric field intensity in the dielectric is given by;

$$\begin{aligned}\vec{E} &= \frac{1}{\epsilon_0} (\vec{D} - \vec{P}) \\ \Rightarrow \vec{E}\epsilon_0 &= \vec{D} - \vec{P} \\ \Rightarrow \vec{D} &= \vec{P} + \vec{E}\epsilon_0\end{aligned}$$

For linear homogeneous isotropic dielectrics,

$$\begin{aligned}\vec{P} &= \epsilon_0 \chi_e \vec{E} \\ \Rightarrow \vec{D} &= \epsilon_0 \chi_e \vec{E} + \vec{E}\epsilon_0 = \epsilon_0 (\chi_e + 1) \vec{E}\end{aligned}$$

We define the dielectric constant  $\epsilon_r$  through the relation;

$$\begin{aligned}\vec{D} &= \epsilon_0 \epsilon_r \vec{E} \\ \Rightarrow \epsilon_0 (\chi_e + 1) \vec{E} &= \epsilon_0 \epsilon_r \vec{E} \\ \therefore \epsilon_r &= \chi_e + 1\end{aligned}$$

This is the relation between  $\epsilon_r$  and  $\chi_e$ .

In the presence of electronic, ionic and dipolar polarization mechanisms, the average induced dipole moment per molecule will be the sum of all the contributions in terms of the local field (effective field) acting on each individual molecule.

$$P_{av} = \alpha_e \vec{E}_{loc} + \alpha_i \vec{E}_{loc} + \alpha_d \vec{E}_{loc}$$

where  $\alpha_e$ ,  $\alpha_i$  and  $\alpha_d$  are the electronic, ionic and dipolar polarizabilities.  $\vec{E}_{loc}$  is the local field or the effective field at the site of an individual molecule that causes the individual polarization. Each effect adds linearly to the net dipole moment of the molecule.

#### 5.4 Clausius and Mossotti relation for dielectric permittivity

Consider a molecule of a dielectric medium situated in a uniform electric field  $\vec{E}$ . The total electric field acting on this molecule  $\vec{E}_{loc}$  will have three main components-  $\vec{E}_1$ ,  $\vec{E}_2$ , and  $\vec{E}_3$ . Here  $\vec{E}_1$  is the applied electric field  $\vec{E}$ ,  $\vec{E}_2$  is the field from the free ends of the dipole chain and  $\vec{E}_3$  is the near field arising from the individual molecular interactions. In solids we have to consider the actual effective field acting on a molecule in order to estimate the dielectric permittivity. For electronic and ionic polarization, the local field for cubic crystals and isotropic liquids can be given by the Lorentz field, given by;

$$\vec{E}_{loc} = \vec{E} + \frac{1}{3\epsilon_0} \vec{P}$$

By assuming the near field  $\vec{E}_3 = 0$ , Clausius and Mossotti derived a relation for the dielectric constant of a material under electronic and ionic polarization.

The total polarization vector can be written as;

$$\vec{P} = \sum N_j \alpha_j \vec{E}_{loc} \quad [*]$$

where  $N_j$  - number of atoms/m<sup>3</sup> of type  $j$ , and  $\alpha_j$  - electric polarization of type  $j$ .

$$\text{But } \vec{P} = \epsilon_0 \chi_e \vec{E} \text{ and } \chi_e = \epsilon_r - 1$$

$$\Rightarrow \vec{P} = \epsilon_0 (\epsilon_r - 1) \vec{E} \quad [**]$$

From equations [\*] and [\*\*];

$$\begin{aligned} \epsilon_0 (\epsilon_r - 1) \vec{E} &= \sum N_j \alpha_j \vec{E}_{loc} \\ \text{But } \vec{E}_{loc} &= \vec{E} + \frac{1}{3\epsilon_0} \vec{P} \\ \epsilon_0 (\epsilon_r - 1) \vec{E} &= \sum N_j \alpha_j \left( \vec{E} + \frac{1}{3\epsilon_0} \vec{P} \right) \\ \Rightarrow \epsilon_0 (\epsilon_r - 1) \vec{E} &= \sum N_j \alpha_j \left[ \vec{E} + \frac{1}{3\epsilon_0} (\epsilon_0 [\epsilon_r - 1] \vec{E}) \right] \\ \Rightarrow \epsilon_0 (\epsilon_r - 1) \vec{E} &= \sum N_j \alpha_j \vec{E} \left( \frac{2 + \epsilon_r}{3} \right) \\ \therefore \left( \frac{\epsilon_r - 1}{\epsilon_r + 2} \right) &= \frac{1}{3\epsilon_0} (N_e \alpha_e + N_i \alpha_i) \end{aligned}$$

This equation is known as the Clausius – Mossotti relation for electronic and ionic polarization. It relates the macroscopic dielectric constant with the microscopic polarizability. Here,  $\epsilon_r$  is the relative permittivity at low frequencies,  $\alpha_i$  is the effective ionic polarizability per ion pair,  $N_i$  is the number of ions pair per unit volume,  $\alpha_e$  is the electronic polarizability and  $N_e$  is the number of ions (or atoms) per unit volume exhibiting electronic polarization.

The atomic/ionic polarizability  $\alpha_i$  and the electronic polarizability  $\alpha_e$  cannot be separated at low frequencies and hence they are together represented as the induced polarizability  $\alpha_{ind}$  and

$$N_i = \frac{N_A \rho}{M} = N_m.$$

$$\Rightarrow \left( \frac{\epsilon_r - 1}{\epsilon_r + 2} \right) = \frac{1}{3\epsilon_0} (\alpha_{ind} N_m)$$

This is known as the Clausius –Mossotti equation for non-polar dielectrics.

### 5.5 Debye theory for polar dielectrics

In addition to the induced polarization present in all dielectrics, the polar dielectrics possess an orientational polarization that exists even in the absence of an applied electric field. It should be noted that the polarizability  $\alpha_d$  corresponding to the orientational polarization is related to the orientation of the molecules which are heavier than that of atoms or electrons that are involved in induced polarization. Hence  $\alpha_d$  contributes to the total molecular polarizability  $\alpha$  at much lower frequencies than  $\alpha_{ind}$  does. So the dielectric constant that remains after the relaxation of orientational polarization (the dielectric constant due to the induced polarization) can be designated separately.

To account for the orientational contribution to the dielectric constant, Debye used classical Boltzmann statistics and the Langevin function  $L(\alpha) = \coth \alpha - 1/\alpha$  from the theory of paramagnetism, to estimate the temperature dependence of permanent dipole orientation.

Assuming that these dipoles do not interact with each other, Debye derived the following equation for the orientational polarizability.

$$\alpha_d = \frac{p_d^2}{3k_B T}$$

where  $p_d$  is the permanent dipole moment created by polar molecules

Using Clausius-Mossotti internal field argument discussed above, this additional polarization contributes to the static dielectric constant according to the following formulae:

$$\left( \frac{\epsilon_r - 1}{\epsilon_r + 2} \right) = \frac{1}{3\epsilon_0} (\alpha_{ind} N_m + N_d \alpha_d)$$

This is the Debye equation

## 5.6 Frequency dependence of dielectric properties of insulators

### (i) For gases

Suppose an alternating electric field  $E = E_0 e^{-i\omega t}$  is applied to a non-polar gaseous dielectric, the electron cloud of an atom in the dielectric will be displaced relative to the nucleus. In the absence of dissipative forces, the equation of motion is;

$$m \frac{d^2 x}{dt^2} + kx = eE_0 e^{-i\omega t}, \quad \text{where } e = q = \text{charge}$$

After sufficiently long time, the displacement  $x$  will follow the periodicity of the applied field so that:

$$\begin{aligned} x &= x_0 e^{-i\omega t} \\ \dot{x} &= -i\omega x_0 e^{-i\omega t} \\ \ddot{x} &= -\omega^2 x_0 e^{-i\omega t} \\ \Rightarrow m(-\omega^2 x_0 e^{-i\omega t}) + k(x_0 e^{-i\omega t}) &= eE_0 e^{-i\omega t} \\ \Rightarrow (-m\omega^2 + k)x &= eE \\ \left(\omega^2 - \frac{k}{m}\right)x &= -\frac{eE}{m} \\ \text{Let } \omega_0^2 &= \frac{k}{m} \\ \Rightarrow (\omega^2 - \omega_0^2)x &= -\frac{eE}{m} \\ \Rightarrow x &= \frac{eE}{m(\omega_0^2 - \omega^2)} \end{aligned}$$

The added polarization or induced dipole moment,  $\vec{p} = qx = ex$

$$\vec{p} = \frac{e^2 E}{m(\omega_0^2 - \omega^2)}$$

Also, recall:  $\vec{p} = \alpha_e \vec{E}$

$$\alpha_e = \frac{e^2}{m(\omega_0^2 - \omega^2)}$$

Recall: total polarization, i.e., total dipole moment per unit volume is given as;

$$\begin{aligned} \vec{P} &= Np_e = N\alpha_e \vec{E} \\ \Rightarrow \vec{P} &= \frac{Ne^2 \vec{E}}{m(\omega_0^2 - \omega^2)} \end{aligned}$$

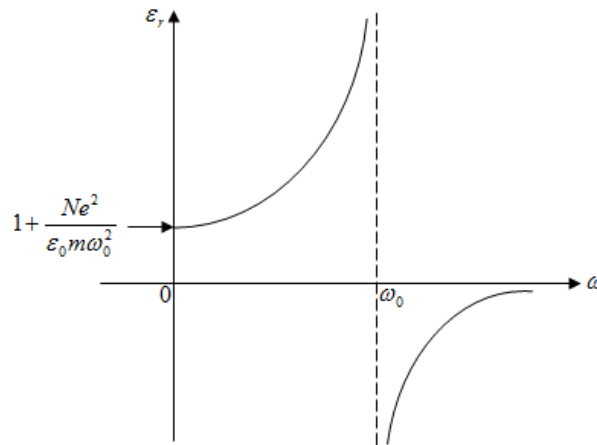
Also recall:  $\vec{P} = \epsilon_0(\epsilon_r - 1)\vec{E}$



$$\Rightarrow \epsilon_0(\epsilon_r - 1)\vec{E} = \frac{Ne^2\vec{E}}{m(\omega_0^2 - \omega^2)}$$

$$\therefore \epsilon_r = 1 + \frac{Ne^2}{\epsilon_0 m(\omega_0^2 - \omega^2)}$$

**Sketch of frequency dependence of dielectric constant**



**NB:**  $\epsilon_r - \epsilon_0 = \frac{Ne^2}{m(\omega_0^2 - \omega^2)}$  diverges at  $\omega = \omega_0$ . At this frequency, oscillations build up without limit, but this is not physical. The divergence is removed by considering a more realistic picture in which dissipative forces are considered. The damping effect results from:

- Charges which have been accelerated and decelerated when the electric field is applied. The charges radiate energy.
- In elastic atomic collisions which occur at random times during an oscillation cycle, the energy of the dielectric oscillation is dissipated as heat by the collisions.

Both effects can be described by a damping term in the equation of motion.

$$\text{Thus } m \frac{d^2 x}{dt^2} + m\gamma \frac{dx}{dt} + kx = eE_0 e^{-i\omega t}$$

$$\text{Recall: } \omega_0^2 = \frac{k}{m} \quad \Rightarrow k = m\omega_0^2$$

$$\Rightarrow m \frac{d^2 x}{dt^2} + m\gamma \frac{dx}{dt} + m\omega_0^2 x = eE_0 e^{-i\omega t}$$

where  $\gamma$  - damping coefficient

After sufficiently long time, the displacement of an electric cloud will assume the time dependence of the applied field.

$$\text{Let } x = x_0 e^{-i\omega t}$$

$$\dot{x} = -i\omega x_0 e^{-i\omega t}$$

$$\ddot{x} = -\omega^2 x_0 e^{-i\omega t}$$

$$\Rightarrow (-m\omega^2 - im\omega\gamma + m\omega_0^2)x = e\vec{E}$$

$$\Rightarrow x = \frac{e\vec{E}}{m[(\omega_0^2 - \omega^2) - i\omega\gamma]}$$

The added polarization or induced dipole moment,  $\vec{p} = qx = ex$

$$\vec{p} = \frac{e^2 \vec{E}}{m[(\omega_0^2 - \omega^2) - i\omega\gamma]}$$

Recall: total polarization, i.e., total dipole moment per unit volume is given as;

$$\vec{P} = N\vec{p}_e$$

$$\vec{P} = \frac{Ne^2 \vec{E}}{m[(\omega_0^2 - \omega^2) - i\omega\gamma]}$$

$$\text{But } \vec{P} = \epsilon_0(\epsilon_r - 1)\vec{E}$$

$$\Rightarrow \epsilon_0(\epsilon_r - 1) = \frac{Ne^2}{m[(\omega_0^2 - \omega^2) - i\omega\gamma]}$$

Putting  $\epsilon_r = \epsilon'_r + \epsilon''_r$ , where  $\epsilon'_r$  - real part and  $\epsilon''_r$  - imaginary part.

$$\Rightarrow \epsilon'_r + \epsilon''_r = 1 + \frac{Ne^2}{\epsilon_0 m[(\omega_0^2 - \omega^2) - i\omega\gamma]}$$

Rationalizing, we get;

$$\epsilon'_r = 1 + \frac{Ne^2(\omega_0^2 - \omega^2)}{\epsilon_0 m[(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2]} \quad \text{and} \quad \epsilon''_r = 1 + \frac{iNe^2 \gamma \omega}{\epsilon_0 m[(\omega_0^2 - \omega^2)^2 + \gamma^2 \omega^2]}$$

**Limiting case:**

For static limit,  $\omega = 0$

$$\epsilon'_r = 1 + \frac{Ne^2}{\epsilon_0 m \omega_0^2} \quad \text{and} \quad \epsilon''_r = 0$$

Real part of the dielectric constant is strongly frequency dependent in the region about  $\omega_0$ .