Physics of Materials
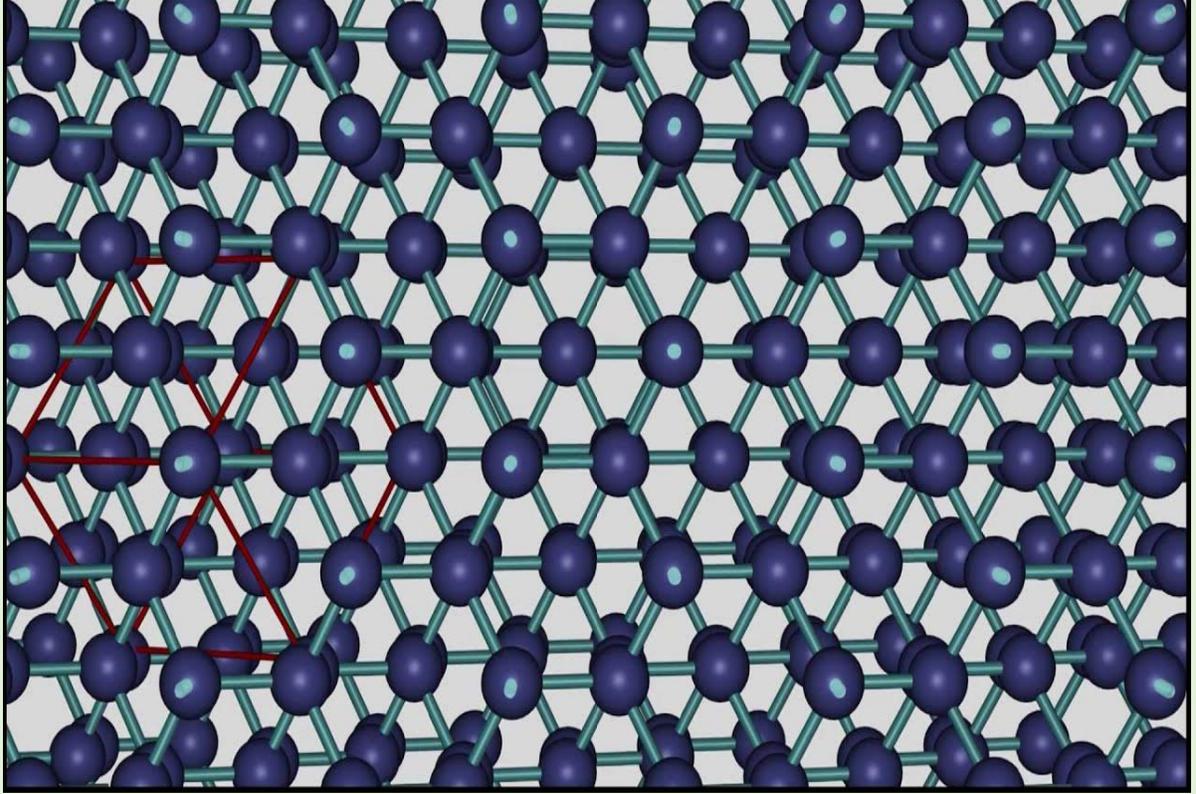
فيزياء المواد

الفرقه الرابعه تعليم أساسى علوم – (انجليزى)

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1.0   Introduction

The physical definition of a solid has several ingredients. We start by defining a solid as a large collection of atoms that attract one another so as to confine the atoms to a definite volume of space. Additionally, in this unit, the term *solid* will mostly be restricted to crystalline solids. A *crystalline solid* is a material whose atoms have a regular arrangement that exhibits translational symmetry. When we say that the atoms have a regular arrangement, what we mean is that the equilibrium positions of the atoms have a regular arrangement. At any given temperature, the atoms may vibrate with small amplitudes about fixed equilibrium positions. Elements form solids because for some range of temperature and pressure, a solid has less free energy than other states of matter. It is generally supposed that at low enough temperature and with suitable external pressure everything becomes a solid. The study of crystal and electrons in crystal is a division of physics known as solid state physics. The solid state physics is an extension of atomic physics following the discovery of X-ray diffractions of crystalline properties.

2.0   Objectives

The candidates should be able to:
- Define crystals
- Explain the crystal structure
- Classify crystals

3.0   Definition of crystal

Crystal may defined on the macroscopic scale as homogeneous solids, in which some of the physical properties are function of direction. Microspically, a crystal may be defined as a solid having an arrangement of atoms (or molecules) in which the atoms are arranged in some repetitive pattern in three dimensions.

3.1   Translational Symmetry

A solid is said to be a crystal if atoms are arranged in such a way that their positions are *exactly periodic*. This concept is illustrated in Fig.1.1 using a two-dimensional (2D) structure. A perfect crystal maintains this periodicity in both the *x* and *y* directions from -∞ to +∞. As follows from this periodicity, the atoms A, B, C, etc. are *equivalent*. In other words, for an observer located at any of these atomic sites, the crystal appears exactly the same. The same idea can be expressed by saying that a crystal possesses a *translational symmetry*. The translational symmetry means that if the crystal is translated by any vector joining two atoms, say **T** in   Fig.1.1, the crystal appears exactly the same as it did before the translation. In other words the crystal remains *invariant* under any such translation.
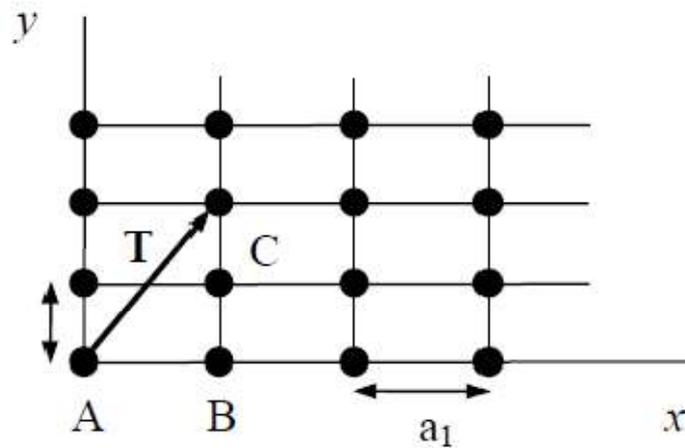
Fig.1.1: Periodicity and concept of symmetry.

3.2 Lattice and Unit cell

The structure of all crystals can be described in terms of a *lattice*. A lattice can be defined as a regular periodic array of points in space (Fig.1.2).Every lattice point can be located as;

$$r_{mn} = m\,a + n\,b \tag{1.1}$$

Or in three dimensional case

$$r_{lmn} = l\,a + m\,b + n\,c \tag{1.2}$$

where a, b, c are called Lattice vectors and *l, m* and *n* are integers.

The network of lattice lines divide the space into identical parts called *unit cells.* Hence, because of inherent periodicity of space lattice; it can thus be represented by a unit cell. A unit cell is a conveniently chosen fundamental block by repeating the entire space lattice which is generated. The unit cell may be in form of a parallelogram (2D) or a parallelepiped (3D) with lattice points at their corners. The size and shape of the unit cell are described by three lattice vectors *a, b, c,* originating from one corner of the unit cell. The axial lengths *a, b, c* and the inter axial angles α, *β* and γ are lattice parameters of the unit cell. Fig.1.3 shows the unit cell with the axes lengths and inter axial angles while Fig.1.4 shows the lattice and unit cells in 2-dimension.
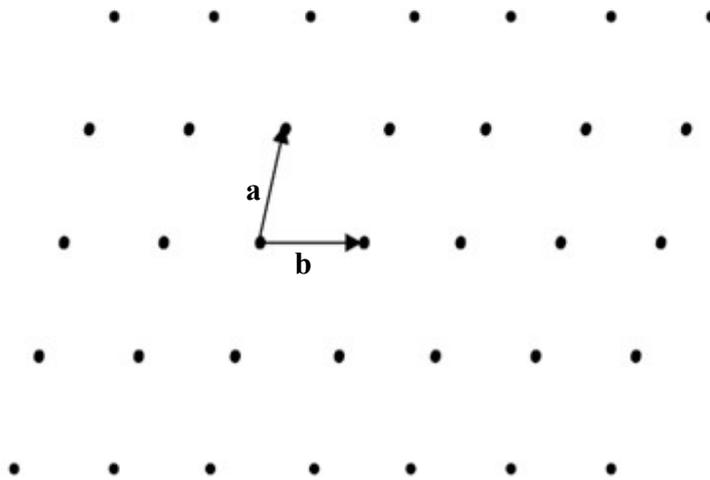
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Fig.1.2: Lattice point and Lattice vectors
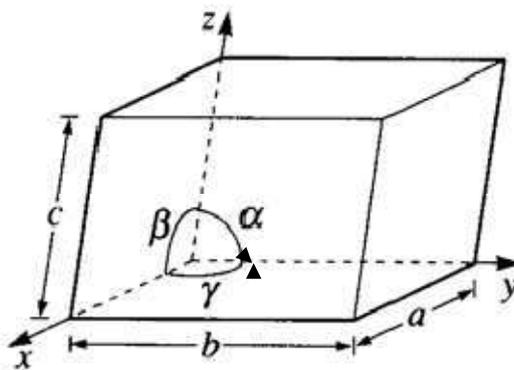
Fig.1.3: Unit cell showing axes lengths and inter axial angles.

The convention for drawing the lattice parameters is as follows:

a   parallel to *x*-axis
b   parallel to *y*-axis
c   parallel to *z*-axis
α   angle between *y* and *z*
β   angle between *z* and *x*
γ   angle between *x* and *y*

3.3   Primitive and Non-Primitive cells

The cell is said to be *primitive* if the lattice points are at the corners of the cell (Fig. 1.5) and if there are lattice points in the cell other than the corners, the cell is said to be *nonprimitive* (Fig.1.5)

Fig.1.4: Lattice and unit cells in 2-Dimension(After Kittel,1979)

Fig.1.5: Primitive and Non-primitive cells (After Sihv K Gupta, www.4shared.com)
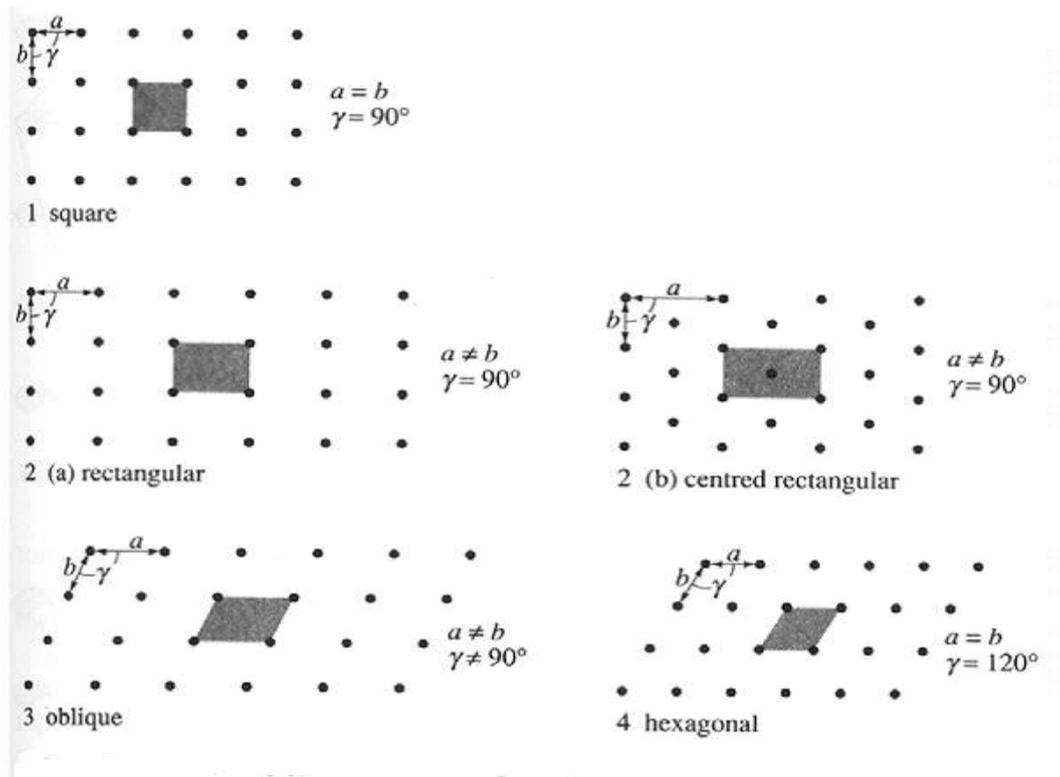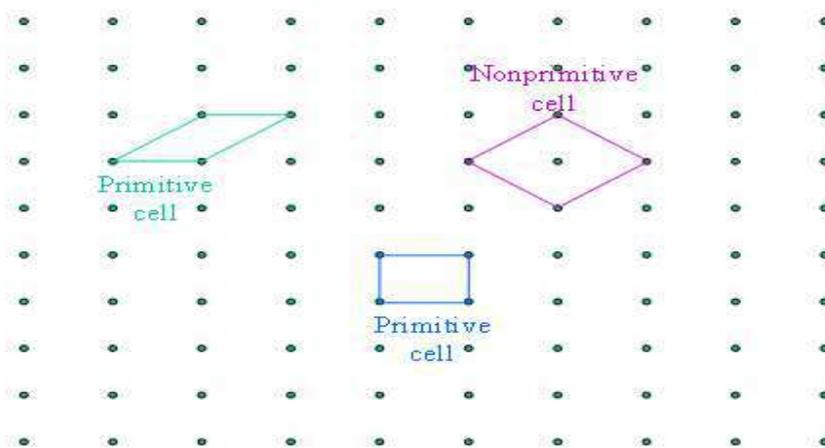
For a single atom, the single atom is placed on the lattice site and is known as *Bravais lattice*. On the other hand, if there are several atoms per unit cell, we have a *lattice with a basis*.

3.4 Bravais Lattice

There are many ways in which an actual crystal may be built, thus possible crystal structures are unlimited. However, the possible schemes of space lattices are highly restricted. Each space lattice has some convenient set of axes which need not be necessarily orthogonal and chosen length along the three axes may not be equal. Bravais in 1848 proved that there are only fourteen space lattices in total which are required to describe all possible arrangement of points in space subject to the condition that each lattice point has exactly identical environment. The fourteen space environments are called Bravais Lattices. The Bravais lattices are the distinct lattice types which when repeated can fill the whole space. The lattice can therefore be generated by three unit vectors, **a**, **b** and **c** and a set of integers k, l and m so that each lattice point, identified by a vector **r**, can be obtained from:

$$\mathbf{r} = k\,\mathbf{a} + l\,\mathbf{b} + m\,\mathbf{c} \tag{1.3}$$

Bravais showed that in two dimensions there are five distinct Bravais lattices, while in three dimensions there exist no more than fourteen space lattices.

3.5 Basis and Crystal structure.

The arrangement of atoms in a solid is termed crystal structure. In order to convert the geometrical array of points in space (lattice) into a crystal structure, we must locate atoms or molecules on the lattice points. The repeating unit assembly of atoms or molecules that are located at each lattice point is called the *basis*. The basis must be identical in composition, arrangement and orientation such that the crystal appears exactly the same at one point as it does not at other equivalent points. No basis contains fewer atoms than a primitive basis contains.

The crystal structure is thus given by two specifications:

   I.   the lattice, and

  II.   The assembly that repeat itself.

Hence, the logical relation is

        Space lattice + basis = crystal structure   **(1.4)**
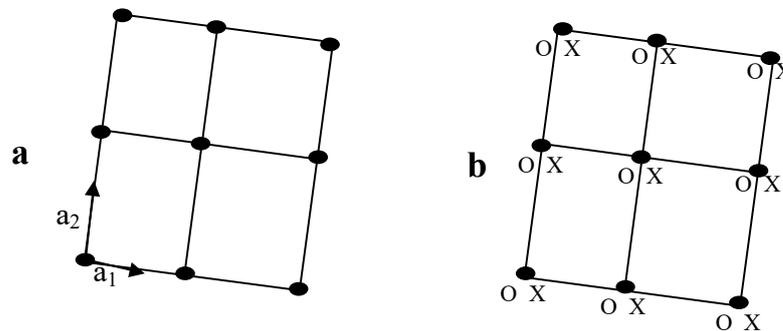
Equation (1.4) is illustrated in Fig.1.6

Fig.1.6: Two-dimensional lattices. (a) Bravais lattice; a_1 and a_2 are basis vectors; (b) Lattice with a basis of three atoms; ●, O, X

(After Kachhava, 1992)

4.0   Conclusion
The fundamental feature of a crystal is the periodicity of the structure.

5.0   Summary
- The size and shape of the unit cell are described by three lattice vectors *a, b, c,* originating from one corner of the unit cell. The axial lengths *a, b, c* and the inter axial angles α, β and γ are lattice parameters of the unit cell.
- A cell is said to be *primitive* if the lattice points are at the corners of the cell and if there are lattice point in the cell other than the corners, the cell is said to be *nonprimitive*
- A lattice is any array of points related by the translational operator
  $R_n = n_1a + n_2b + n_3c$
- The Bravais lattices are the distinct lattice types which when repeated   can fill the whole space   generated by three unit vectors, **a**, **b** and **c** and a set of integers k, l and m

6.0   Tutor marked Assignment
Q1.   A group is represented by three matrices

$$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \qquad A = \begin{bmatrix} \alpha & \beta \\ -\beta & \alpha \end{bmatrix} \qquad B = \begin{bmatrix} \alpha & -\beta \\ \beta & \alpha \end{bmatrix}$$

Where $\alpha = \sin 30^0$ and $\beta = \cos 30^0$.
 (a) Determine the multiplication table for this group.
(b) Give an example of a 2-D crystal with these point group symmetries.

Q2.   (a)   Filled circles in the tetragonal crystal in the figure below represent copper oxide atoms and the copper oxide layers are stacked with   spacing c. assume that there are no other atoms in the crystal, sketch the Bravais lattice and indicate a possible set of primitive vectors for this crystal.
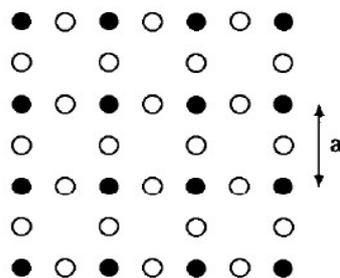
(b)   Define the following terms

(i) Unit cell and

(ii) Basis

7.0   Further reading/References
Ashcroft, N.W., Mermin, D.N, Solid state physics, Saunders College Publishing, 1976

Gupta, S. K, (www.4shared.com)

Kittel, C., Introduction to solid state physics, Wiley Eastern Limited, 1979

Kachhava, C.M., Solid State physics, Tata McGraw-Hill Publishing Company Limited, New Delhi, 1992

UNIT2: CRYSTAL CLASSIFICATION   page

1.0 Introduction

Crystal lattices are classified according to their symmetry properties, such as inversion, reflection and rotation. Also, it is sometimes more convenient to deal with non-primitive or conventional cells, which have additional lattice sites either inside the cell or on its surface. In three dimensions there are 14 different Bravais crystal lattices which belong to 7 crystal systems. These systems are triclinic, monoclinic, orthorhombic, tetragonal, cubic, hexagonal and trigonal.

2.0 Objectives

- To revise the classification of crystal lattices
- To understand direction indices
- To understand miller indices

3.0 Definition of Crystal Lattice

Crystal lattice classification is the regular geometric arrangement of points in the atom of a crystal

3.1 Fundamental types of lattices

The most obvious feature of a crystal is its regularity or symmetry. The basis of classification of crystal is the symmetry exhibited by them. In a well defined crystal, the various symmetry elements (rotation, reflection, inversion etc.) intersect at a point. Each set of symmetry elements intersecting at a point (the centre of unit cell) is called a *point-group*. Since there are 32 point groups, there are equal numbers of crystal classes, which can be grouped together into seven groups known as crystal systems. Table 1.1, consists of the list describing the various systems. Fig 2.1 shows how seven crystal systems can be obtained by successive distortion of a cube.

Table 1.1: Seven Crystal Systems

Crystal System	Axial Lengths and angles	Unit cell	Number of Lattices
Cubic	$a = b = c$, $\alpha = \beta = \gamma = 90^0$	a cube	3
Tetragonal	$a = b \neq c$, $\alpha = \beta = \gamma = 90^0$	a squared-based right prism	2
Orthorhombic	$a \neq b \neq c$, $\alpha = \beta = \gamma = 90^0$	a rectangular-based right prism	4
Rhombohedra	$a = b = c$, $\alpha = \beta = \gamma \neq 90^0$	a rhombohedron	1
Hexagonal	$a = b \neq c$, $\alpha = \beta = 90^0$, $\gamma = 120^0$	a rhombus-based right angles	1
Monoclinic	$a \neq b \neq c$, $\alpha = \gamma = 90^0 \neq \beta$	A parallelepiped-based right prism	2
Triclinic	$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90^0$	a parallelepiped	1

3.2 Direction indices

To find the direction indices, the following rules are used:
  I.   Find any vector in the desired direction.
  II.   Express this vector in terms of the basis (**a, b, c**).
  III. Divide the coefficient of (**a, b, c**) by their greatest common divisor.

The resultant set of three integers u, v, w usually included in parentheses [uvw] defines a direction. $\langle uvw \rangle$ means that all vectors are equivalent to [uvw]. Negative sign in any of the numbers are indicated by placing a bar over the number ($\bar{u}$). Let **a** = 2, **b** = 3, **c** = 4 units and the vector be

$$\mathbf{r} = 6\,\mathbf{i} + 12\,\mathbf{j} + 10\,\mathbf{k}$$

Then $\mathbf{r} = 3(2)\,\mathbf{i} + 4(3)\,\mathbf{j} + 2.5(4)\,\mathbf{k}$

Thus, the coefficients of (**a, b, c**) are 3, 4, 2.5. The relevant greatest common divisor is 0.5. Thus, the three numbers 6, 8, 5 are found. Hence, for the example considered the indices of direction are [685].

In the cubic system, u, v, w are proportional to the direction cosines of the chosen vector. The cube edge **a** would be denoted by [100], that of direction **b** by [010], and **c** by [001].The negative direction of **a** would be [$\bar{1}$00]. When we speak of [200] plane, we mean a plane parallel to [100] but cutting *a* axis at $^1/_2\,a$. Fig 2.1 shows the indices of some important planes and directions in crystals. Note that:
  I.   All parallel rows of atoms have the same [uvw].
  II.   The angle θ between two crystallographic direction[$u_1 v_1 w_1$] and [$u_2 v_2 w_2$] in a cubic system is given by

$$\cos \theta = \frac{u_1 u_2 + v_1 v_2 + w_1 w_2}{\left(u_1^2 + v_1^2 + w_1^2\right)^{1/2}\left(u_2^2 + v_2^2 + w_2^2\right)^{1/2}} \qquad (2.1)$$

3.3 Miller indices

Miller indices are the most commonly used notation for specifying points, directions, and planes in crystal lattice systems. Not only do they simplify the description of locations and directions within the lattice, but they also allow vector operations like dot and cross products. **Miller Indices** are a symbolic vector representation for the orientation of an atomic plane in a crystal lattice and are defined *as the reciprocals of the fractional intercepts which the plane makes with the crystallographic axes*. Before Miller indices can be used, a coordinate system for the crystal structure must first be selected. The right-hand Cartesian coordinate system is the usual choice for this (Fig.2.2). Points within the coordinate system are specified by Miller indices as h, k, l, where h, k, and l are fractions of the lattice parameters a, b, and c. Recall that a, b, and c are the lengths of the edges of the crystal's unit cell in the x, y, and z directions.
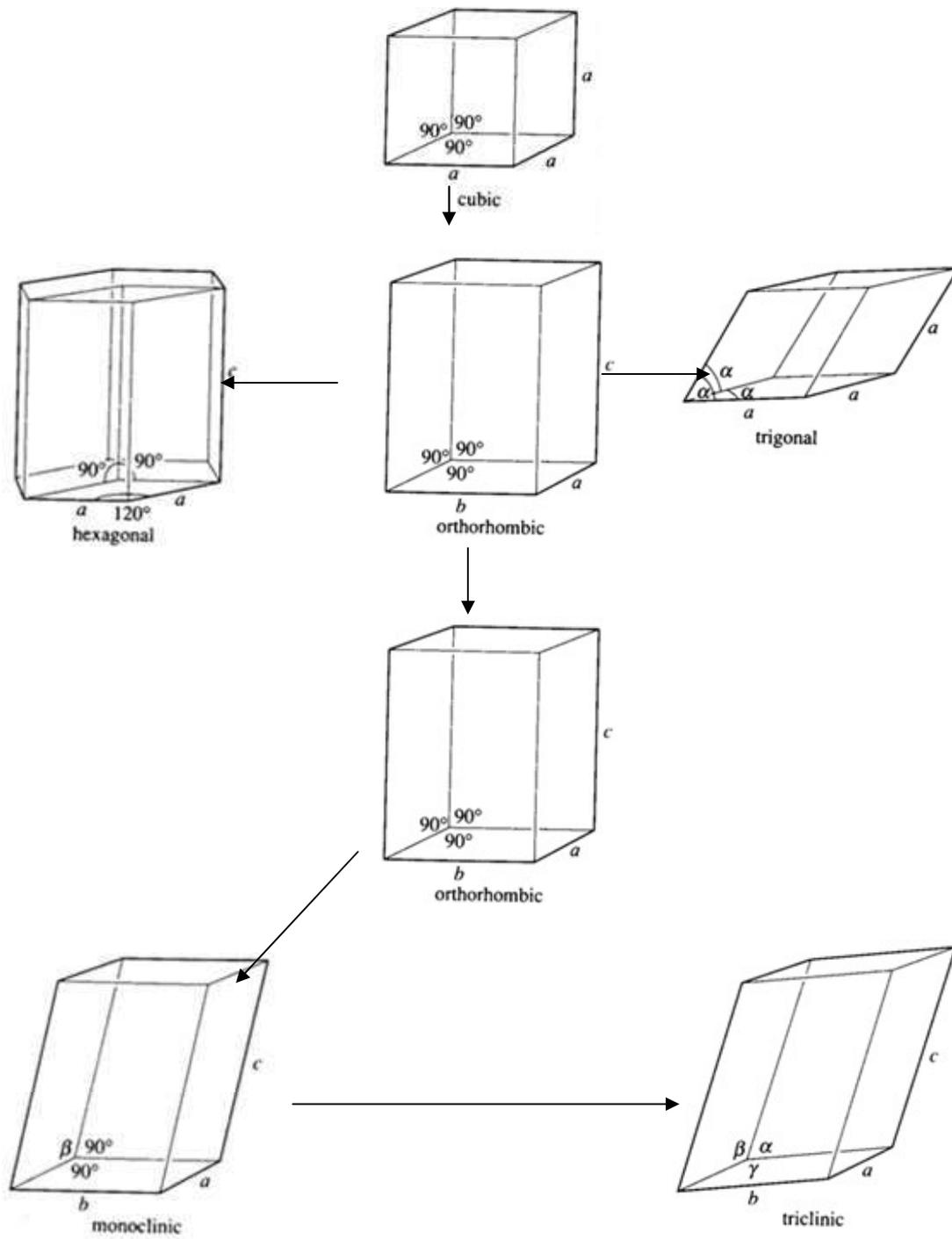
Fig.2.1: seven crystals in three dimensions

A plane oriented with respect to the rectangular coordinate system, which intercepts the x-,y-and z-coordinates at distance a, b and c respectively is represented by the equation

$$\qquad \qquad \overline{} \quad \overline{} \quad \overline{} \qquad \qquad \qquad \text{(2.2)}$$

Denoting the reciprocal of axial intercepts as $\overline{} \qquad \overline{} \quad \text{and} \overline{} \quad$, Eq. (2.2) becomes

$$\qquad \qquad \qquad \qquad \qquad \qquad \qquad \qquad \text{(2.3)}$$
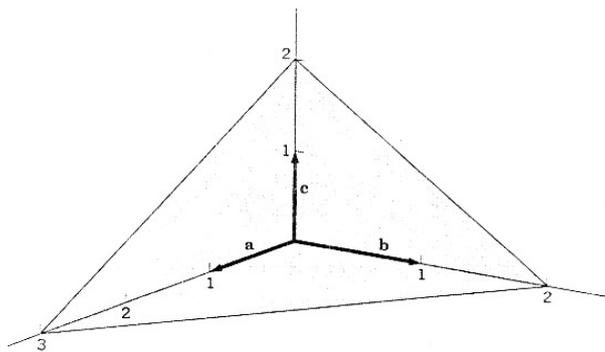

Fig.2.2: Construction for description of a plane. This plane intercepts the **a**, **b**, c axes at 3**a**, 2**b**, 2**c**. (After Kittel, 1979)

3.4 Determination of Miller Indices
The Rules for Miller Indices are:

- Determine the intercepts of the plane along the three crystallographic axes, *in terms of unit cell dimensions.* Coordinates of the points of interception are expressed as integral multiples of the axial lengths in the respective directions. The integers p, q and r are the multiples of axial lengths a, b and c respectively
- Take the reciprocals of the integers p, q and r
- The reciprocals are reduced to the smallest set of integers h, k and l by taking LCM
- The integers are written as (hkl) by enclosing in parenthesis

For example, if the x-, y-, and z- intercepts are 2, 1, and 3, the Miller indices are calculated as:

- The integers are 2, 1, 3
- Take reciprocals: 1/2, 1/1, 1/3
- Clear fractions (multiply by 6): 3, 6, 2
- Reduce to lowest terms (already there)

Thus, the Miller indices are 3, 6, 2. If a plane is parallel to an axis, its intercept is at infinity and its Miller index is zero. A generic Miller index is denoted by *(hkl)*. If a plane has negative intercept, the negative number is denoted by a bar above the number. *Never alter negative numbers*. For example, do not divide -1, -1, -1 by -1 to get 1, 1, 1. This implies symmetry that the crystal may not have!

3.5   General Principles of Miller Indices

- If a Miller index is zero, the plane is parallel to that axis.
- The smaller a Miller index, the more nearly parallel the plane is to the axis.
- The larger a Miller index, the more nearly perpendicular a plane is to that axis.
- Multiplying or dividing a Miller index by a constant has no effect on the orientation of the plane
- Miller indices are almost always small.

Fig.2.3 shows some planes for cubic lattices with their Miller notations.
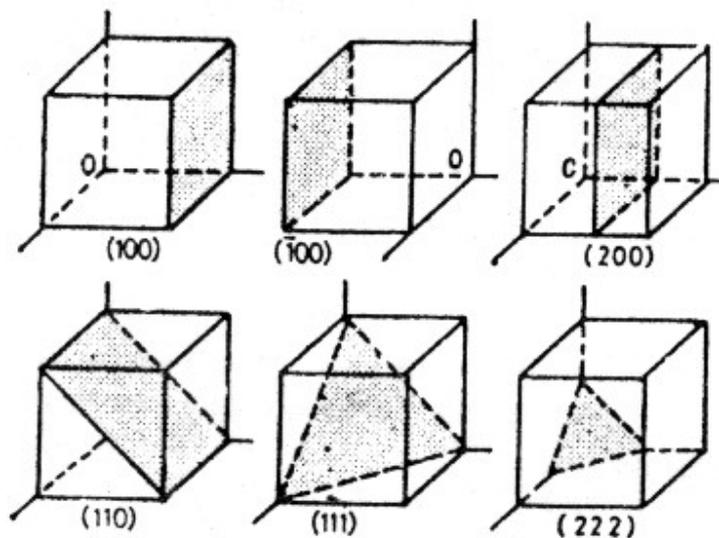
Fig.2.3: Some of the prominent planes for cubic lattices with their Miller indices (After Kachhava, 1992)
Note that:

❖   Miller indices are proportional to the direction cosines of the normal to the corresponding plane. Direction cosines are given as

       —   —   —

❖   The normal to the plane with index numbers   is the direction
❖   The purpose of taking reciprocals is to bring all the planes inside a single unit cell
❖   Assume   represent the distance between two adjacent parallel planes having miller indices   , then

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

(2.4)

Where d_{hkl} = distance between planes

a = lattice constant (edge of unit cell)
h, k,l = Miller indices of planes being considered

Figure 2.4 shows inter planer spacing in terms of the cube edge, a.
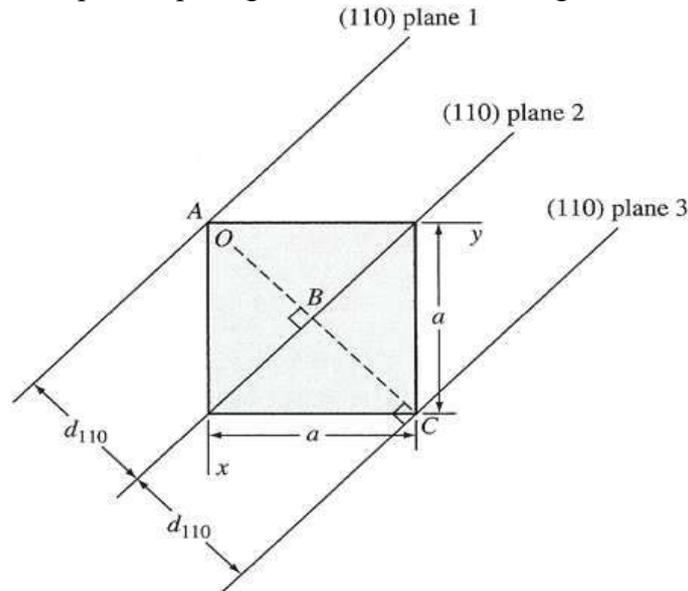
Fig.2.4: inter planer spacing (After Kachhava, 1992)

4.0   Conclusion

Miller indices are the most commonly used notation for specifying points, directions, and planes in crystal lattice systems. Not only do they simplify the description of locations and directions within the lattice, but they also allow vector operations like dot and cross products.

5.0   Summary

- In a well defined crystal, the various symmetry elements (rotation, reflection, inversion etc.) intersect at a point.
- Each set of symmetry elements intersecting at a point (the centre of unit cell) is called a *point-group.*
- The Miller indices are defined as the reciprocals of the fractional intercepts which the plane makes with the crystallographic axes.
- The angle θ between two crystallographic direction[$u_1v_1w_1$] and [$u_2v_2w_2$] in a cubic system is given by

$$\cos\theta = \frac{u_1u_2 + v_1v_2 + w_1w_2}{\left(u_1^2 + v_1^2 + w_1^2\right)^{1/2}\left(u_2^2 + v_2^2 + w_2^2\right)^{1/2}}$$

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- The distance d_{hkl} between neighboring planes of the family (hkl), is given in terms of the cube edge a as

$$d_{hkl} = \frac{a}{\left(h^2 + k^2 + l^2\right)^{1/2}}$$

6.0. Tutor marked Assignment

Q1 **(a).** Show that the perpendicular distance between two adjacent planes of a set (hkl) in a cubic lattice of lattice constant a is

$$d_{hkl} = \frac{a}{\left(h^2 + k^2 + l^2\right)^{1/2}}$$

(b). The Bragg angle corresponding to the first order reflection from plane

(111) in a crystal is 30^0 when X-rays of wavelength 1.75Å are used.

Calculate the interatomic spacing

Q2. If x, y and z axes intercept 3, 4, and 2, calculate the Miller indices

7.0 Further reading/References
Ashcroft, N.W., Mermin, D.N, Solid state physics, Saunders College Publishing, 1976.
Kachhava, C.M., Solid State physics, Tata McGraw-Hill Publishing Company Limited, New Delhi, 1992 .
Kittel, C., Introduction to solid state physics, Wiley Eastern Limited, 1979.

1.0:   Introduction

The most highly symmetrical lattices which occur naturally are cubic structure. These are, therefore, of some practical interest and also provide useful simple examples which help in visualizing the more general cases. About 90% of metallic crystal structures crystallize into 3 densely packed crystal structures vis-a-vis Body-Centered Cubic cell (BCC), Face-Centered Cubic cell (FCC) and Hexagonal Close-Packed (HCP).

2.0   Objectives

The objectives are to understand metallic crystal structure such as:
- Simple cubic
- Body centered cubic
- Face centered cubic
- Hexagonal Close packed

3.0   Definition of Simple lattices

Simple lattices are crystalline solids that consist of a small group of atoms (unit cells) that contains unique features.

3.1   Simple lattices

The simple lattices have the following elementary properties:

I.   Effective no of atoms/ unit cell, Z, which defines the number of atom per primitive cell

II.   Atomic radius, R usually defines in terms of lattice constant (length of a side of unit cell), **a.**

III.   Nearest neighbor distance which defines the nearest distance between atomic centers.

IV.   Coordinate number which defines the number of nearest neighbor of an atom.

V.   Atomic Packing Fraction (APF) defined as the fraction of volume in a crystal structure that is occupied by atoms.

3.2   The simple cubic lattice.

The simple cubic lattice has basis vectors

$$ \tag{3.1} $$

and the unit cell is a simple cube. The simplest crystal based on this lattice has single atoms at the lattice points, Fig. 3.1. Each atom has six identical nearest neighbors.
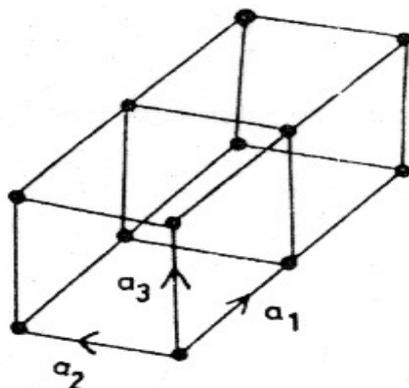

Fig.3.1: Simple cubic lattice (After Kachhava, 1992)

3.2   Body-Centered cubic Lattice

The body-centered cubic (bcc) lattice may be regarded as two interpenetrating simple cubic lattices with atoms at the centre of each cube as well as at the corners. The space lattice may be taken with the basis vectors

$$\underline{\hspace{2cm}} \qquad \underline{\hspace{2cm}} \qquad \underline{\hspace{1.5cm}} \qquad\qquad \textbf{(3.2)}$$

Where **a** is the side of the cube and **i, j, k** are orthogonal unit vectors parallel to the cube edges. The primitive cell of the bcc lattice has a volume one-half that of the unit cube. By elementary vector analysis the volume is given by

$$V = \left| \mathbf{a_1.a_2} \text{ x } \mathbf{a_3} \right| \qquad\qquad \textbf{(3.3)}$$

3.3   Face- Centered Cubic Lattice

The face centered cubic lattice can be considered as four interpenetrating simple cubic lattices giving a cubic unit cell with extra lattice points at the centers of the faces of the fundamental cube. Each point has 12 nearest neighbours. The full translational symmetry has basis vectors.

$$\underline{\hspace{2cm}} \qquad \underline{\hspace{1.8cm}} \qquad \underline{\hspace{1.5cm}} \qquad\qquad \textbf{(3.4)}$$

The primitive cell of the _____ lattice is shown in Fig.3.4 and is a rhombohedron of volume one quarter that of the unit cube. The translation vectors $\mathbf{a_1}$, $\mathbf{a_2}$ and $\mathbf{a_3}$ connect the lattice point at the origin with the lattice points at the face centers. The angles between the axes are 60^0.
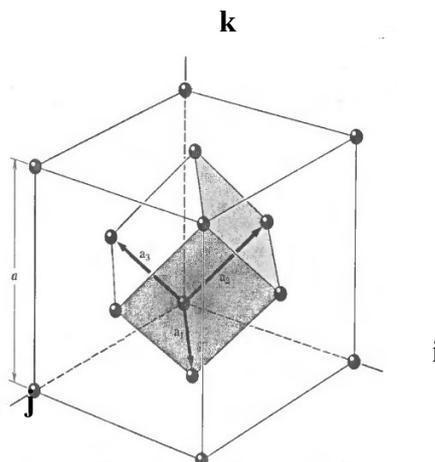

Fig.3.2: Face- centered cubic lattice

3.4   Hexagonal Close-Packed (HCP)

In the hexagonal closed packed   structure, Fig 3.5 the unit cell is a rhombic and the basis vectors are

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$$\boldsymbol{a_1} = a\boldsymbol{i}, \qquad \boldsymbol{a_2} = \frac{a}{2(\boldsymbol{i}+\sqrt{3}\boldsymbol{j})}, \qquad \boldsymbol{a_3} = \boldsymbol{k} \qquad\qquad (3.5)$$
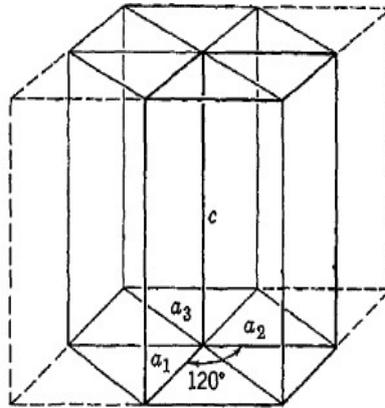
Fig.3.3: Hexagonal Close-packed structure (After Kittel, 1979)

In this structure, there are two atoms per unit cell separated by the vector

$$\boldsymbol{R} = \tfrac{1}{2}\left(a\boldsymbol{i} + \frac{a}{\sqrt{3}}\boldsymbol{j} + c\boldsymbol{k}\right) \qquad\qquad (3.6)$$

Here, as in fcc structure, each atom has twelve neighbours, but the arrangement is slightly different.

3.5   Closed-packed Structures

If the atoms are considered as hard spheres, then the most efficient packing in one plane is the *closed–packed* arrangement shown in Fig 3.6.There are two simple ways in which such planes can be laid on top of one another to form a three-dimensional structures. One leads to the face-centered cubic (cubic close-packed) structure, while the other has hexagonal symmetry and is called the hexagonal closed packed (hcp) structure (Fig3.7). The fraction of the total volume filled by the spheres is 0.74 for both the fcc and hcp structures.

Fig.3.4: A closed- packed layer of spheres (After Kittel, 1979)

Fig.3.6: The Hexagonal closed packed structures (After Kittel, 1979)

Spheres may be arranged in a single closest-packed layer by placing each sphere in contact with six others. Such a layer can either be the basal plane of a *hcp* structure or the (111) plane of *fcc* structure. A second similar layer is added by placing each sphere in contact with three spheres of the bottom layer as in Fig.3.6. A third layer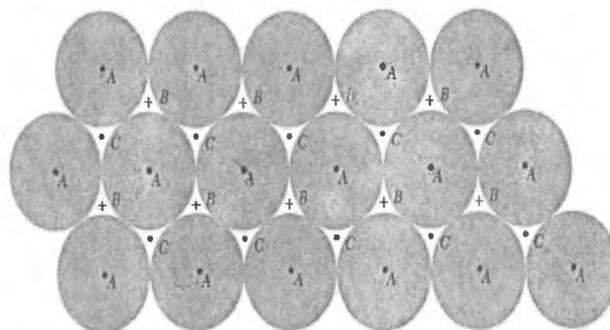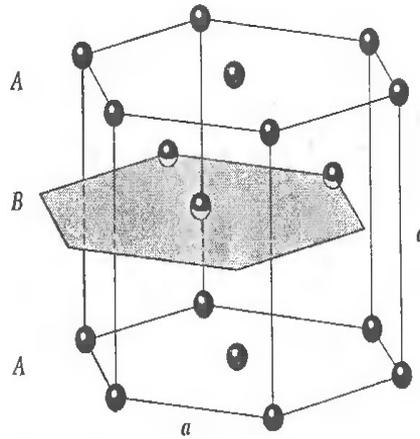 can be added in two ways: in the *fcc* structure the spheres in the third layer are placed over the holes in the first layer not occupied by the second layer; in the hexagonal structure the spheres in the third layer are placed directly over the spheres in the first layer. We say that the packing in the *fcc* structure is ABCABC. ….. , whereas in the *hcp* structure the packing is ABABAB….. The *hcp* structure has a hexagonal primitive cell; the basis contains two atoms. The *fcc* primitive cell contains one atom. The c/a ratio for hexagonal closest-packing of spheres is $(8/3)^{1/2} = 1.633$. We refer to crystals as *hcp* even if the actual c/a ratio departs somewhat from the theoretical value. Thus zinc with c/a = 1.86 is referred to commonly as *hcp*. Magnesium with c/a = 1.623 is close to ideal *hcp*. Many metals transform easily at appropriate temperatures between *fcc* and *hcp*. The coordination number, defined as the number of nearest-neighbor atoms, is 12.

A quantitative measure of the closeness of packing in a crystal structure is provided by the *packing fraction, f,* defined as

$$f = \frac{volume\ occupied\ by\ atoms(hard\ spheres)}{volume\ of\ the\ unit\ cell\ of\ the\ structure} \quad \textbf{(3.5)}$$

The theoretical calculations of *f* requires the knowledge of number of atoms, N, per unit cell and atomic radius, R_a, in terms of a, the length of a side of a cubic lattice. Table 3.1 as reported by (Kachhava, 1992) displayed the values of N, R_a and f along with number (N_n) of nearest neighbors and that (N_{nn}) for next nearest neighbors for simple cubic (sc), body centered cubic (*bcc*), face-centered cubic(*fcc*) and hexagonal close-packed(*hcp*) structures.

Table 3.1 Data for common structures (modified after Kachhava, 1992)

	sc	*bcc*	*fcc*	*hcp*
N	1	2	4	2
N_n	6	8	12	12
N_{nn}	12	6	6	6
R_a	$\dfrac{a}{2}$	$\dfrac{a}{2}\sqrt{2}$	$\sqrt{3}\,\dfrac{a}{4}$	$\dfrac{a}{2}$
f	$\pi/6 = 0.52$	$\sqrt{2}\dfrac{\pi}{6}= 0.74$	$\sqrt{3}\,\dfrac{\pi}{8} = 0.68$	0.74 (ideal)

4.0 Conclusion

The ideal crystal of classical structures is formed by the repetition of identical units in space. The most highly symmetrical lattices which occur naturally are cubic structures which help in visualizing the more general case.

5.0 Summary

- The simple cubic lattice has basis vectors
  $$a_1 = ai \qquad a_2 = aj \qquad a_3 = ak$$
- Important simple structures are the bcc, *fcc* and *hcp*
- The structures differ in the stacking sequence of the planes
- *fcc* have the sequence ABCABC…
- *hcp* have the sequence ABABAB…

6.0   Tutor Marked Assignment

Q1. Use elementary vector analysis to find the value of the angle between the body diagonals of a cube shown in the Figure Q1

Q2 Show that the c/a ratio for an ideal hexagonal closed-packed structure is
$$(8/3)^{1/2} = 1.633.$$

Q3. Sodium transform from *bcc* to *hcp* at about T= 23K. Assuming that the density remain fixed, and the c/a ratio is ideal, calculate the *hcp* lattice spacing a given that the cubic lattice spacing a′ = 4.23Å. What is the difference in the cubic phase

Fig.Q1

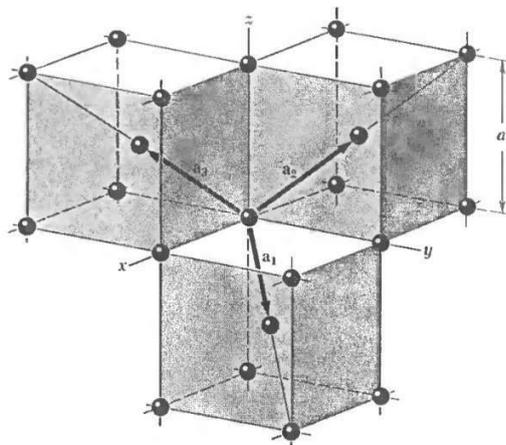**7.0   Further Reading/ References**

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1.0   Introduction

In order to explore the structure of crystals we require waves which interact with atoms and which have a wavelength comparable with the inter atomic spacing in crystals; that is, we require a wavelength of the order of 1 A$(= 10^{-8}\ cm)$. The interaction should be weak enough so that the wave can penetrate in a coherent fashion into the crystal for a distance of the order of perhaps 1000 lattice constants. The most convenient waves suitable for our purpose are those associated with x-rays, while the waves associated with neutrons and electrons have found important special applications. When an atom is exposed to electromagnetic radiation, the atomic electrons are accelerated, and they radiate at the frequency of the incident radiation. The superposition of the waves scattered by individual atoms in a crystal results in the ordinary optical refraction. If the wavelength of the radiation is comparable with or smaller than the lattice constant, we will also under certain conditions have diffraction of the incident beam.

2.0   Objectives

*   To study the use of X-ray as a tool for investigating the structure of crystals.

3.0.   Definition

When a monochromatic beam of x-rays is shone upon a regular crystalline material then the beam will be scattered from the material at definite angles. This produced an interference effect called diffraction between the X-rays from different layers within the crystal.

3.1   Bragg formulation of diffraction by a crystal

W. L. Bragg (1913) found that one could account for the position of the diffracted beams produced by a crystal in an x-ray beam by a very simple model according to which x-rays are reflected from various planes of atoms in the crystal. The diffracted beams are found for situations in which the reflections from parallel planes of atoms interfere constructively. The derivation of the Bragg law is indicated in Fig. 4.1. We consider in the crystal a series of atomic planes which are partly reflecting for radiation of wavelength X and which are spaced equal distances *d* apart. The radiation is incident in the plane of the paper. The path difference for rays reflected from adjacent planes is $2d sin\theta$. Reinforcement of the radiation reflected from successive planes will occur when the path difference is an integral number *n* of wavelengths. The condition for constructive reflection is that

$$2d\ sin\theta = n\lambda \qquad\qquad\qquad (4.1)$$

Equation (4.1) represents the Bragg law. The integer n represents the order of corresponding reflection. It should be emphasized that the Bragg equation results from the periodicity of the structure, without reference to the composition of the unit of repetition.
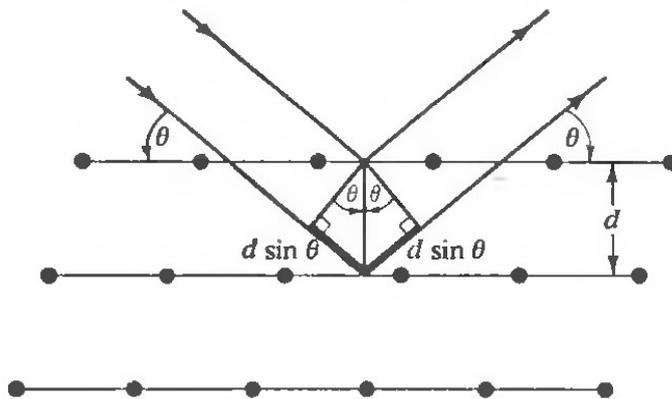
Fig. 4.1: Derivation of the Bragg equation $2d \sin\theta = n\lambda$; here d is the spacing of parallel atomic planes (After Ashcroft and Mermin, 1976).

Worked example:

(a) State Bragg's law of diffraction and give two geometrical facts that are necessary for the derivation of the law.

(b) An X-ray Diffractometer recorder chat for an element, which has a cubic crystal structure, shows diffraction peaks at the following 2θ:40, 58, 73, 86.8, 100.4 and 114.7. The wavelength of the incoming X-rays used was 1.540 Å.

(i) determine the type of the cubic structure possessed by the element

(ii) Determine the lattice constant of the element.

Solution:

(a) Bragg's law of diffraction states that the path difference between two X-rays which are reflected from adjacent planes is an integral multiple of its wavelength i.e.,

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

Where; θ = Bragg's angle

   d= interatomic plane spacing

   λ = Wavelength of the X-rays

   n = order of diffraction

The two geometrical facts are:

(i) The incident beam, the normal to the diffraction plane and the diffracted beam are always coplanar.

(ii) The angle between the diffracted beam is always 2θ. this is known as the diffraction angle.

(b) (i).The values of the angles given are 2θ. Therefore, θ is equal to the half the 2θ values. The ratio of the square of the sine of the 1st two planes gives the true structure of the element, i.e.,

$$\frac{sin^2\theta_1}{sin^2\theta_2} = \text{Structure type}$$

❖ If the ratio is 0.5, the structure is bcc.

❖ If the ratio is 0.75, it is fcc

The 1st two planes have θ values being 20, and 29 and the sines of these angles are 0.3420 and 0.4848 respectively, therefore,

$$\frac{sin^2\theta_1}{sin^2\theta_2} = \frac{0.117}{0.235} \simeq 0.5$$

Hence, the crystal structure is bcc.

(ii). The relationship between Miller indices(hkl) of the Bragg plane and the Bragg angle is given by

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

Where; a is the lattice constant.

For a bcc lattice, the sum $h + k + l$ must be even, hence the 1st set of principal diffraction plane for the bcc structure is {110} and the corresponding value for $sin^2\theta$ is 0.117, then,

$$a = \frac{\lambda}{2}\sqrt{\frac{h^2 + k^2 + l^2}{sin^2\theta}}$$

This implies, $a = \frac{0.154\,nm}{2}\sqrt{\frac{1^2+1^2+0}{0.117}} = 0.318$ nm

$\therefore a = 3.18\text{Å}$

3.2 Von Laue formulation of diffraction by a crystal

Considering the nature of the x-ray diffraction pattern produced by identical atoms located at the corners (lattice points) of primitive cells of a space lattice to investigate scattering from any two lattice points, P_1 and P_2 (Fig. 4.2) separated by the vector **r**. The unit incident wave normal is s_o and the unit scattered wave normal is s. let us examine at a point a long distance away the difference in phase of the radiation scattered by P_1 and P_2. If P_1B and P_2A are the projections of **r** on the incident and scattered wave directions, the path difference between the two scattered waves is

$$P_1B - P_2A = \boldsymbol{r}\cdot\boldsymbol{s} - \boldsymbol{r}\cdot\boldsymbol{s_0} = \boldsymbol{r}\cdot(\boldsymbol{s} - \boldsymbol{s_0}) \quad\quad\quad (4.2)$$
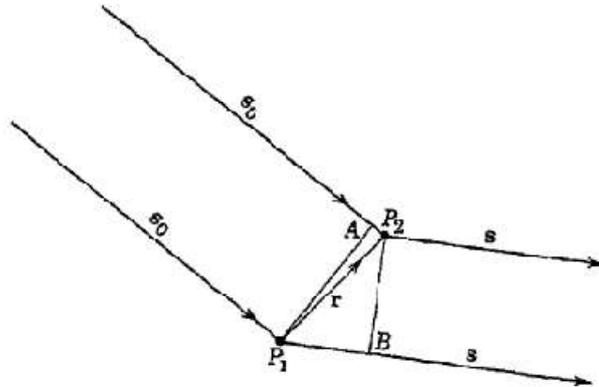

Fig.4.2: Calculation of the Phase difference of the waves scattered from two lattice points (After Kittel, 1979)

The vector $s - s_0 = S$ has a simple interpretation (Fig. 4.3) as the direction of the normal to a plane that would reflect the incident direction into the scattering direction. This plane is a useful mathematical construction and this is called the *reflecting plane.* If 2θ is the angle s makes with s_0, then θ is the angle of incidence, and from the figure (4.3), we see that $|S| = 2sin\theta$, as s and s_0 are unit vectors.
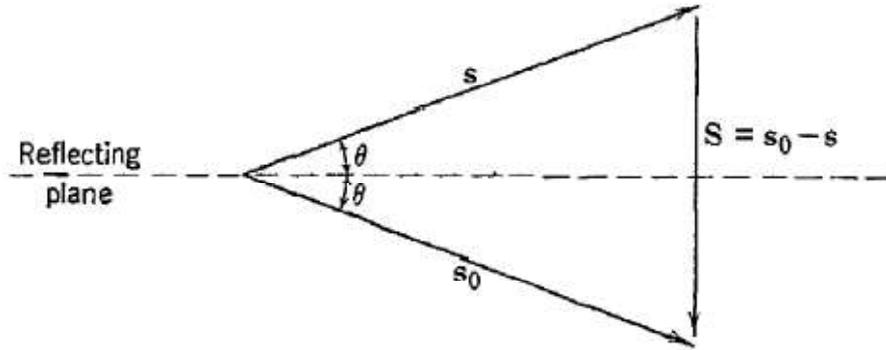
Fig.4.3: Construction of the normal the reflecting plane (After Kittel, 1979)

The phase difference ϕ is $2\pi/\lambda$ times the path difference. We have

$$\phi = \left(2\pi/\lambda\right)(r \cdot s) \qquad (4.3)$$

The amplitude of the scattered wave is a maximum in a direction such that the contributions from each lattice point differ in phase only by integral multiplies of 2π. This is satisfied if the phase difference between adjacent lattice points is an integral multiple of 2π . If **a, b, c** are the basis vectors, we must have for the diffraction maxima

$$\phi_{a=}\left(2\pi/\lambda\right)(a \cdot s) = 2\pi h;$$
$$\phi_{b=}\left(2\pi/\lambda\right)(b \cdot s) = 2\pi k; \qquad (4.4)$$
$$\phi_{c=}\left(2\pi/\lambda\right)(c \cdot s) = 2\pi l;$$

where $h, k; l$ are integers.

If α, β, γ are the direction cosines of **S** with respect to **a, b, c**, we have

$$a \cdot s = 2a\alpha \ sin\theta = h\lambda$$
$$b \cdot s = 2b\beta \ sin\theta = k\lambda \qquad (4.5)$$
$$c \cdot s = 2c\gamma \ sin\theta = l\lambda$$

Equations (4.4 & 4.5) are the Laue equations. They have solutions only for special values of θ and the Wavelength λ. The Laue equations (4.5) have a simple geometrical interpretation. The Laue equations state that in a diffraction direction the direction cosines are proportional to $h/a, k/b, l/c,$ respectively and the adjacent lattice planes (*hkl*)

intersect the axes at intervals *a/h, b/k, c/l* so that by elementary plane geometry the direction cosines of the normal to (*hkl*) are proportional to *h/a, k/b, l/c respectively* Therefore the lattice planes (*hkl*) must be parallel to the   reflecting plane. If $d(hkl)$ is the spacing between two adjacent planes of a set (*hkl*), we have by projection

$$d(hkl) = \frac{a\alpha}{h} = \frac{b\beta}{k} = \frac{c\gamma}{l} \qquad (4.6)$$

Then, from (4.5), we have

$$2d(hkl)\,sin\theta = \lambda \qquad (4.7)$$

We may interpret (4.7) by giving an extended meaning to the spacing d(*hkl*) when *h, k, l* have a common factor n: the diffracted wave actually arises from the nth order reflection from the true lattice planes, but we may as a mathematical device think of the diffracted wave as a first order reflection from a set of planes parallel to the true lattice planes but with a spacing *d(hkl)* equal to l/n of the true spacing.

3.3   Diffraction of crystals by electrons

de Broglie in 1924 predicted that the wavelength associated with a particle of momentum *p= mv* is given by

$$\lambda = \frac{h}{p} \qquad (4.8)$$

where h is plank's constant. One of the most direct pieces of evidence of the wave aspect of particles was provided by the electron diffraction experiments of Davisson and Germer in 1972. They concluded that if one associates a wavelength with the electrons given by (4.9), the diffraction pattern obtained can be interpreted in exactly the same way as the X-ray diffraction patterns. As long as the velocity of the electrons is small compared with the velocity of light, the wavelength of the electrons may be expressed in terms of the accelerating voltage V as follows

$$\tfrac{1}{2}mv^2 = eV \qquad Or \quad \lambda = \frac{h}{(2meV)^{1/2}} \quad \cong \quad \left(\frac{150}{V}\right)^{1/2} \qquad (4.9)$$

λ is obtained in Angstroms if V is expressed in volts. Note that only 150 volts are required to produce electrons of a wavelength of 1Å compared with X-rays, which require approximately 12,000 volts for 1Å. Electrons are scattered by the nucleus as well as by the electrons in the atoms. For spherical charge distribution one can show that the scattering factor is given by

$$E(\theta) = \frac{me^2}{2h^2}(Z - f_s)\frac{\lambda^2}{sin^2\theta} \qquad (4.10)$$

Here f_s is the scattering factor for X-rays, Z is the nuclear charge, and θ is the Bragg angle. As for X-rays the scattering factor decreases with increasing values of θ. However, there is a considerable difference between X-rays and electrons in that, electrons are scattered much more efficiently by atoms than are X-rays. In fact, atoms scattered electrons more strongly by several powers of ten for the energy involved. At normal incidence an electron of about 50 keV has a penetration depth for elastic

scattering of only about 500 Å, while for the small angles of incidence used in reflection techniques this may be about 50 Å measured perpendicularly to the surface. It is evident, therefore, that electron diffraction is particularly useful in investigating the structure of thin surface layers such as oxide on metals. Such layers would not be detected by X-rays diffraction because the patterns obtained are characteristics for the bulk material.

3.4   Diffraction of crystals by neutrons

The mass of a neutron is about 2000 as large as that of an electron, so that according to Eqn.(4.8) the wavelength associated with a neutron is about 1/2000 that for an electron of the same velocity. Thus the energy of a neutron required to give 1 Å is of order of only 0.1eV. Such neutrons can be obtained from a chain-reacting pile, and diffraction from crystals may be observed. Neutrons are scattered essentially by the nuclei of the atoms, except when they are magnetic. The radius of an atomic nuclei is of the order of 10^{-13}cm, and as a consequence, the atomic scattering factor is nearly independent of the scattering angle, because $\lambda \gg 10^{-13} cm$. Also, the scattering power does not vary in a regular manner with the atomic number, so that light elements such as hydrogen and carbon still produce relatively strong scattering. The scattering of X-rays by light element is in contrast, of course, relatively weak. Thus the positions of such atoms in crystalline solids may be determined from neutron diffraction experiments. Another important aspect of neutron diffraction is the fact that scattering from neighboring elements in the periodic system may differ appreciably. For example, neutron diffraction allows one to detect with relative ease ordered phases of an alloy such as FeCo, whereas their detection by X-rays is difficult. A particularly important aspect of neutron diffraction is their use in investigating the magnetic structure of solids. This is a result of the interaction between the magnetic moment of the neutron and that of the atoms concerned. In a paramagnetic substance, in which the magnetic moments are randomly oriented in space, this leads to incoherent scattering, resulting in a diffuse background. This diffuse background of magnetic scattering is then superimposed on the lines produced by the nuclear scattering mentioned above. In a ferromagnetic substance in which the magnetic moments within a domain are lined up in parallel, this diffuse background is absent. In an antiferromagnetic solid, the magnetic moments of particular pairs of atoms are aligned antiparallel and hence, from the point of view of the neutron, such atoms would appear to be different.

4.0   Conclusions

From the discussions of the application of scattering diffraction techniques to the study of the structure of solid crystals that given X-rays of 1 Å it requires energy of the order of 10^4 eV, for electrons of 1 Å it needs 10^2 eV while the energy of a neutron required to give 1 Å is of the order of 0.1 eV. Thus the diffraction technique is a useful tool in the investigation of the structure of solid crystal from surface thin layers to bulky materials.

5.0   Summary

*   Bragg condition for crystal diffraction is given by $2d\ sin\theta = n\lambda$
*   Laue condition for diffraction is given by
*
$$\phi_{a=} \left(2\pi/\lambda\right)(\boldsymbol{a} \cdot \boldsymbol{s}) = 2\pi h;$$

$$\phi_{b=}\left(\frac{2\pi}{\lambda}\right)(\mathbf{b}\cdot\mathbf{s}) = 2\pi k;$$
$$\phi_{c=}\left(\frac{2\pi}{\lambda}\right)(\mathbf{c}\cdot\mathbf{s}) = 2\pi l; \quad \text{and}$$
$$\mathbf{a}\cdot\mathbf{s} = 2a\alpha\ sin\theta = h\lambda$$
$$\mathbf{b}\cdot\mathbf{s} = 2b\beta\ sin\theta = k\lambda$$
$$\mathbf{c}\cdot\mathbf{s} = 2c\gamma\ sin\theta = l\lambda$$

- de Broglie Wavelength equation is given by $\lambda = {}^{h}\!/_{p}$
- wavelength of electron associated with accelerating velocity is given by

$$\lambda = \left(\frac{150}{V}\right)^{1/2}$$

- Scattering factor of electron by neutron is obtained by

$$E(\theta) = {}^{me^2}\!/_{2h^2}\,(Z - f_s)\frac{\lambda^2}{sin^2\theta}$$

6.0. Tutor Marked Assignment

Q1. (a) Discuss the major experimental differences between x-ray, electron, and neutron diffraction from the standpoint of the observed diffraction patterns

(b) Show that the Laue equations for the incident beam parallel to the z cube edge of a simple cubic crystal give diffracted rays in the yz plane when

$$^{\lambda}\!/_{a} = 2l(l^2 + k^2) \quad \text{and} \quad \beta_{z=}\ {}^{(l^2 - k^2)}\!/_{(l^2 + k^2)}$$

Where l and k are integers and β_z is the direction cosine of the diffracted ray relative to the z axis.

Q2. While sitting in front of a color TV with a 25Kv picture tube potential, you have an excellent chance of being irradiated with X-rays.

(a) Calculate the shortest wavelength (maximum energy) X-ray. ($h = 6.6\times10^{-34}Js$, $c = 3\times10^{8}\ m/s, 1\ eV = 1.6\times10^{-19}J$,

(b) For a rock salt($NaCl$) crystal placed in front of the tube, calculate the Bragg angle for a first order reflection maximum at $\lambda = 0.5$ Å. ($\rho_{NaCl} = 2.165\ g/cm^3$)

7.0 Further readings / References

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1.0 Introduction

To explain the theory of X-ray diffraction by crystal planes, Ewald introduced the concept of reciprocal lattice. According to this concept, the description of interpenetrating planes inside a crystal could be obtained in space by means of a set of points. Thus the properties of planes and points are interchangeable. The space constructed from these points is called *reciprocal lattice*.

2.0 Objective

The objectives of this unit is to explain

- ❖ Reciprocal lattice
- ❖ Ewald's construction
- ❖ Brillouin zones

3.0 Definition

The reciprocal space lattice is a set of imaginary points constructed in such a way that the direction of a vector from one point to another coincides with the direction of a normal to the real space planes and the separation of those points (absolute value of the vector) is equal to the reciprocal of the real inter planar distance

3.1 Reciprocal Lattice

For a perfect single crystal, the reciprocal lattice is an infinite periodic three-dimensional array of points whose spacing is inversely proportional to the distances between the planes in the direct lattice. The axis vectors of the reciprocal lattice is given by Eqn. (5.1)

$$A = 2\pi \frac{b \times c}{a \cdot b \times c}; \qquad B = 2\pi \frac{c \times a}{a \cdot b \times c}; \quad C = 2\pi \frac{a \times b}{a \cdot b \times c}; \qquad (5.1)$$

If **a, b, c** are primitive vectors of the crystal lattice, then A**, B, C** are primitive vectors of the reciprocal lattice. Each vector is orthogonal to two of the axis vectors of the crystal lattice. Thus **A, B, C** has property:

$$
\begin{array}{lll}
A \cdot a = 2\pi, & B \cdot a = 0, & C \cdot a = 0; \\
A \cdot b = 0, & B \cdot b = 2\pi, & C \cdot b = 0, \\
A \cdot c = 0, & B \cdot c = o, & C \cdot c = 2\pi,
\end{array}
\qquad (5.2)
$$

Any arbitrary set of primitive vectors **a, b, c** of a given crystal lattice leads to the same set of reciprocal lattice points.

$$\mathbf{G} = h\mathbf{A} + k\mathbf{B} + l\mathbf{C}, \quad (h,\ k,\ l\ are\ integers) \qquad (5.3)$$

Any vector **G** of the form in Eq. (5.3) is called a reciprocal lattice vector. Every crystal structure has two lattices associated with it, the crystal lattice and the reciprocal lattice. A diffraction pattern of a crystal is a map of the reciprocal lattice of the crystal; a microscopic image, if it could be resolved on a fine scale, represents a map of the crystal structure in real space. When we rotate a lattice crystal, we rotate both the direct lattice and the reciprocal lattice. Vectors in the crystal lattice have the dimensions of [length]; vectors in the reciprocal lattice have the dimensions of [length]$^{-1}$. In dealing with wave properties of crystals, it is convenient to define the reciprocal lattice vector **G** as

$$G = 2\pi(hA + kB + lC) \qquad (5.4)$$

This in conjunction with equation (1.1) yields

$$G \cdot R_n = 2\pi(hn_1 + kn_2 + ln_3) = 2\pi \times integer \qquad (5.5)$$

Thus every vector of the equation (5.3) satisfies the condition

$$exp[iG \cdot R_n] = 1 \qquad (5.6)$$

Some of the elementary properties of the reciprocal lattice are as follows:
I. The unit cell of the reciprocal lattice need not be a parallelepiped.
II. Simple cubic lattice is its own reciprocal, so is the hcp. On the other hand, bcc and fcc are reciprocal of each other.
III. The volume of a unit cell of the reciprocal lattice is inversely proportional to the volume of a unit cell of the direct lattice.
IV. If A is the matrix of the components of A_1, B_1, C_1 and B for those of A_2, B_2, C_2 then B =A^{-1}

The properties of the reciprocal lattice that make it of importance in the diffraction theory are:
i. The vector **G** (hkl) from the origin to the point (h, k, l) of reciprocal lattice is normal to the (hkl) plane of the crystal lattice.
ii. The length of the vector **G**(hkl) is equal to the reciprocal of the spacing of the planes(hkl) of the crystal lattice

Worked example:
Prove that the reciprocal lattice vectors as defined in equation (5.1) satisfy:
$$A.B \times C = \frac{8\pi^3}{a.b \times c}$$
Solution:
To solve the problem, we need to use the vector identities:
$$a.b \times c = b.c \times a = c.a \times b$$
and
$$a \times (b \times c) = (a.c)b - (a.b)c$$
From Eq. (5.1)
$$A.B \times C = A \cdot \frac{(2\pi)^2}{|a.b \times c|^2}\big((b.c \times a)a - (a.c \times a)b\big)$$

$$= A \cdot \frac{(2\pi)^2}{|a.b \times c|^2}\big((b.c \times a)a - 0\big)$$

$$= A \cdot \frac{(2\pi)^3}{|a.b \times c|^3}(a.b \times c)(a.b \times c)$$

Then, $\quad A.B \times C = \frac{8\pi^3}{a.b \times c}$

3.2   Ewald's Construction in the reciprocal lattice

For simplicity, we draw the Ewald construction in two dimensions. Ewald put the information about the wavelength and direction for the incident X-ray beam into reciprocal lattice as follows (Fig.5.1). Draw a vector **AO** in the incident direction of length   terminating at the origin O. Construct a circle of radius   (a sphere, called reflex sphere, of radius   in three dimensions) with centre at A. Two possibilities arise:

1. The circle does not pass through any reciprocal point. This implies that the particular wavelength in question would not be diffracted by that crystal in the orientation. Further, if the magnitude of the vector   where a is the lattice constant), the circle would not pass through any point, showing that X-ray diffraction cannot occur if   . It may also be noticed that the longer the vector **AO** (the shorter the wavelength), the greater is the likelihood of the circle's intersecting a point, and hence of diffraction.

2. The circle passes through any point B of the reciprocal lattice. Join A and O to B. Thus, **OB** is a reciprocal lattice vector, **G** and is normal to some set of lattice planes, e.g., AE. Hence,   , d is the interplanar for the set.
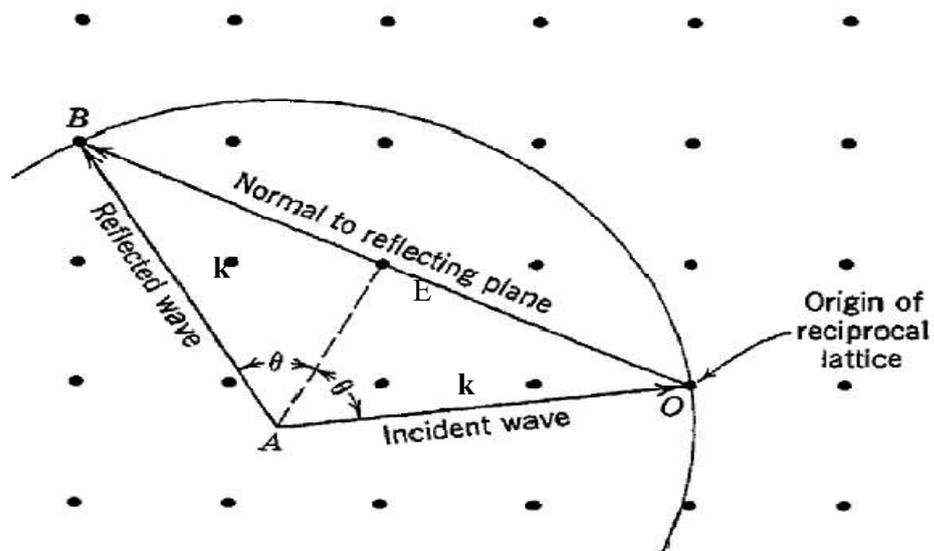
Fig.5.1: Ewald's construction in the reciprocal lattice (After Ashcroft & Mermin, (1976)

Let **k** = **OA** and **k′** = **AB** respectively be the incident wave vector and the reflected wave vector. Thus,

$$\mathbf{k'} = \mathbf{k} + \mathbf{G} \tag{5.7}$$

which shows that (i) scattering changes only the diffraction of **k** and (ii) the scattered wave differs from the incident wave by a reciprocal lattice vector **G.** for diffraction, it is necessary that the vector **k′,** that is the vector **AB,** equal in magnitude to the vector **k:**

$$^2 = \mathbf{k}^2 \tag{5.8}$$

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$$2\mathbf{k}\cdot\mathbf{G} + \mathbf{G}^2 = 0 \qquad\qquad (5.9)$$
$$(\mathbf{k} + \mathbf{G}/2)\cdot\mathbf{G} = 0 \qquad\qquad (5.10)$$

Equation (5.10) is Bragg's law in vector form. Its scalar form can be obtained by noting that $\mathbf{AE} = \mathbf{k} + \mathbf{G}/2)$ is perpendicular to $\mathbf{OB}$. Thus OB = 2OE = $(2 \sin \theta)/ \lambda$. Also OB = $^1/_d$. Hence,

$$(2 \sin \theta)/ \lambda = {}^1/_d$$
$$2d \sin \theta = \lambda$$

This shows that the Bragg equation has a simple geometrical significance in the reciprocal lattice.

3.3   Brillouin Zones

For solid state physics the most important statement of the diffraction condition was given by Brillouin. Fig. 5.1 shows that incident wave and reflected wave make an equal angle with the lattice plane AE, which is, therefore, a reflecting plane. The reciprocal lattice vector $\mathbf{G} = \mathbf{OB}$ is perpendicular to the reflecting plane AE. Thus, corresponding to $\mathbf{G} = \mathbf{OB,}$ the reflecting plane is AE (produced). From the relation $\mathbf{k'} = \mathbf{k} + \mathbf{G,}$ we see that $(\mathbf{AO} + \mathbf{OE})\cdot\mathbf{OB} = 0$. That is $\mathbf{AE}\cdot\mathbf{OB} = 0$. Thus, AE is perpendicular to OB and also bisects it, since E is the midpoint of OB by construction. Hence, for a given reciprocal lattice vector, its right bisector is the reflecting plane. One can extend the procedure for finding the reflecting planes corresponding to reciprocal lattice vectors connecting the reciprocal lattice point O (origin) with its neighbours in reciprocal space. The volume bounded by these planes is referred to as the geometrical definition of the first *Brillouin zone (BZ)*.

Figure 5.2 gives a portion of reciprocal space for a two dimensional oblique lattice showing the lines bisecting some reciprocal lattice from O. The six shortest of these vectors can be right bisected to produce the first **BZ** centered on the reciprocal point O.
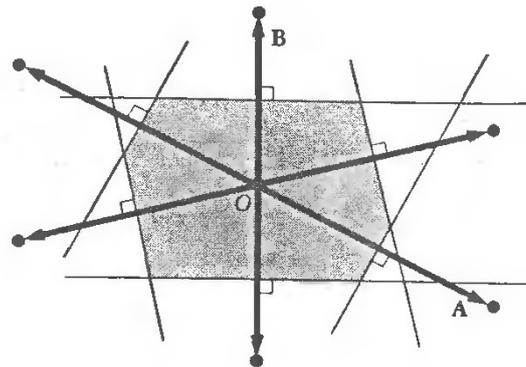

Fig.5.2: Construction of first **BZ** for a two-dimensional oblique lattice (After   Kittel.1979).

Mathematically the reflecting planes and hence the Brillouin zones could be calculated from equation (5.9). For the simple square lattice (of lattice constant *a*), the reciprocal lattice vectors are

$$\mathbf{G} = \frac{2\pi}{a} (n_1\mathbf{i} + n_2\mathbf{j}) \qquad\qquad (5.11)$$

The wave vector for an X-ray measured from the origin of the reciprocal lattice is

$$\boldsymbol{k} = k_x \boldsymbol{i} + k_y \boldsymbol{j} \qquad (5.12)$$

Use of Eq. (5.11) and Eq. (5.12) in Eq.(5.9) gives

$$n_1 k_x + n_2 k_y = (n_1^2 + n_2^2)\frac{\pi}{a} \qquad (5.13)$$

By assigning different value to n_1, n_2, we can obtain various reflection lines. So all $\boldsymbol{k}$-vectors originating at the origin and ending on these lines, will produce Bragg reflection.

4.0   Conclusion
The reciprocal lattice explains the theory of X-ray diffraction by crystal planes while the Brillouin zone gives a vivid interpretation of the diffraction condition.

5.0   Summary
- A wavelength of the order of 1 Å (1 Å $=10^{-8}$ cm) is require to explore the structure of crystals
- The concept of reciprocal lattice explained the theory of X-ray diffraction by crystal planes
- The reciprocal lattice is an infinite periodic three-dimensional array of points whose spacing is inversely proportional to the distance between the planes in the direct lattice.
- Brillouin zone gives a vivid interpretation of the diffraction condition.

6.0   Tutor marked assignment

Q1.   Prove that the volume of the unit cell of the reciprocal lattice is proportional to that   of the corresponding direct lattice.

Q2.   The primitive translational vectors of the hexagonal space lattice may taken as
$$\boldsymbol{A} = \left(3^{\left(\frac{1}{2}\right)} a/2\right) \boldsymbol{i} + \left(a/2\right)\boldsymbol{j} \; ; \quad \boldsymbol{B} = -\left(3^{\left(\frac{1}{2}\right)} a/2\right) \boldsymbol{i} + \left(a/2\right)\boldsymbol{j} \; ; \boldsymbol{C} = c\boldsymbol{k}$$
(a)   Show that the volume of the primitive cell is $\left(3^{\left(\frac{1}{2}\right)} a/2\right) a^2$ c
(b)   Show that the primitive translations of the reciprocal lattice are
$$\boldsymbol{A} = \left(2\pi/3^{1/2}\right) \boldsymbol{i} + \left(2\pi/a\right)\boldsymbol{j}; \; \boldsymbol{B} = -\left(2\pi/3^{1/2}\right) \boldsymbol{i} + \left(2\pi/a\right)\boldsymbol{j} \; ; \boldsymbol{C} = \left(2\pi/c\right)\boldsymbol{k}$$
So that the lattice is its own reciprocal, but with a rotation axes.

Q3. Show that the volume of the first Brillouin zone is given by $(2\pi)^2/V_c$. Where V_c the

volume is is of a crystal primitive cell

7.0   Further reading/References

Brown, J.G., X-rays and their applications, Plenum, 1975

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1.0 Introduction

In practice, to satisfy Bragg's law for X-ray diffraction, it is necessary to vary either the angle of inclination of the specimen to the beam or the wavelength of radiation. The three standard methods of X-ray crystallography to be discussed are the Laue method, the Rotating crystal technique and the Powder method.

2.0 Objective

To explain experimental crystal structure determination according to:
- Laue method
- Rotating crystal technique
- Powder method

3.0 Definition

Experimental crystal structure determination is an experimental method to study scattering of crystal based on Ewald's simple geometric construction.

3.1 Laue method

In the Laue method (Fig 6.1), a single crystal is mounted on a gonimeter, which enables the crystal to be rotated through known angles in two perpendicular planes, and maintained stationary in a beam of X-rays ranging in wavelength from about 0.1 to 2.0 A. The crystal selects out and diffracts those values of for which planes exits, of spacing d and glancing angle θ, satisfying the Bragg equation. A flat photographic film is placed to receive either the transmitted diffracted beam or the reflected diffracted beam.

As shown in the figure (6.1), the resulting Laue pattern consists of a series of spots. Sharp well-defined spots on the film are good evidence of a perfect crystal structure, whereas diffuse, broken or extended spots indicate lattice distortion, defects or other departures from the perfect crystal lattice. The Laue pattern reveals the symmetry of the crystal structure in the orientation used; for example, if a cubic crystal is oriented with a cube edge, i.e., a [100] axis, parallel the incident beam, the Laue pattern will show the four fold symmetry appropriate to this axis.
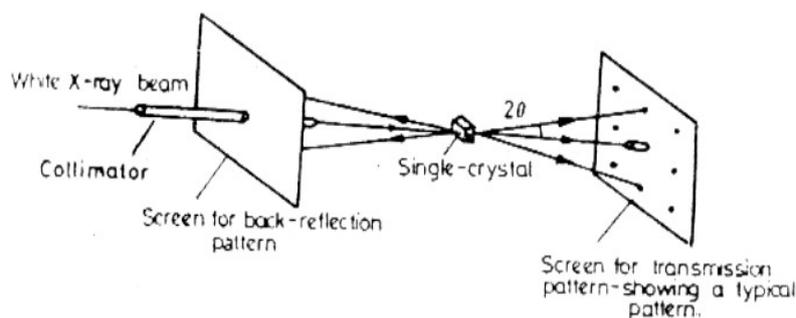
Fig.6.1: Schematic representation of Laue technique (after Kacchava, 1990)

3.2 Rotating Crystal Technique

A small single crystal (1 mm dimension) is mounted on a goniometer which, in turn, is rigidly fixed to a spindle so that the crystal can be rotated about a fixed axis in a beam of monochromatic radiation. The specimen is usually oriented with one of the crystallographic axes parallel to the axis of rotation. The resulting variation in θ brings different lattice planes into position for reflection and diffracted images are recorded on a photographic film placed cylindrically, coaxial with the rotating spindle (Fig.6.2).
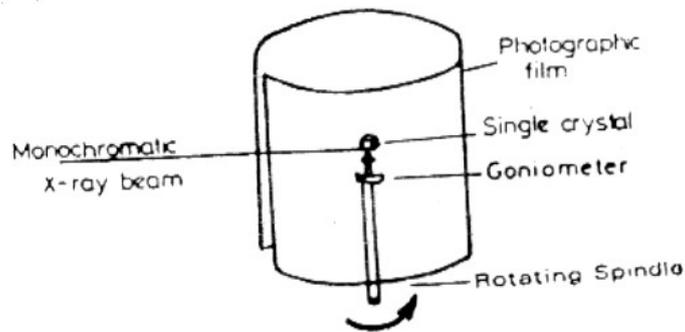
Fig.6.2: Rotating crystal technique (after Kachhava, 1992)

To explain the general nature of the diffraction, consider a crystal mounted so that one of the axes (e.g.   is parallel to the axis of rotation, then diffraction cannot occur from the planes of atoms parallel to this axis unless

(6.1)

where n is an integer [Fig.6.2 (a)]. The diffracted beam will, therefore, be along the surface of a family of cones whose vertices are at the crystal, and whose semi-vertical angles are given by the above equation [Fig.6.2 (b)].

(a)   (b)
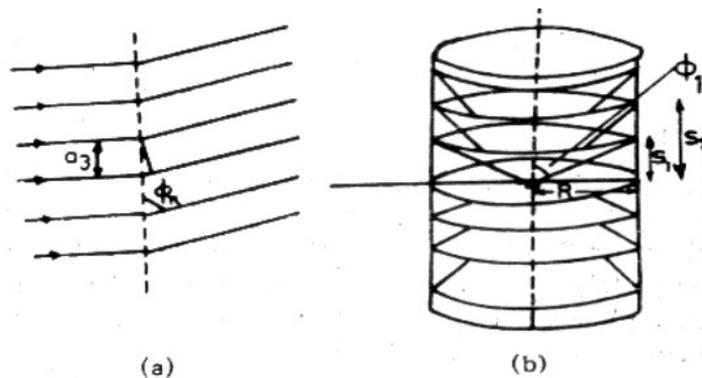
Fig.6.2: Diffraction pattern in rotating crystal technique
(a)Diffraction condition (b) Cones of diffraction (After Kachhava, 1992)

The diffracted beams will only occur along those specific directions lying on the cones for which the correct phase relationship also holds for planes parallel to the other two coordinate axes. When the film is flattened out after development, these diffraction images will lie on a series of lines called layer lines, as illustrated in Fig.6.3. All the

images on the zero layer line come from planes parallel to the axis of rotation, i.e., planes with $l = 0$, and the other layer lines arise from planes with l . . . . ., etc. diffraction images from planes with the same values of h and k but different values of l, all lie on one of a series of curves known as row lines which are transverse to the layer lines and in the particular case when the **A** and **B** axes are perpendicular to **C**, they intersect with the zero layer line at right angles.
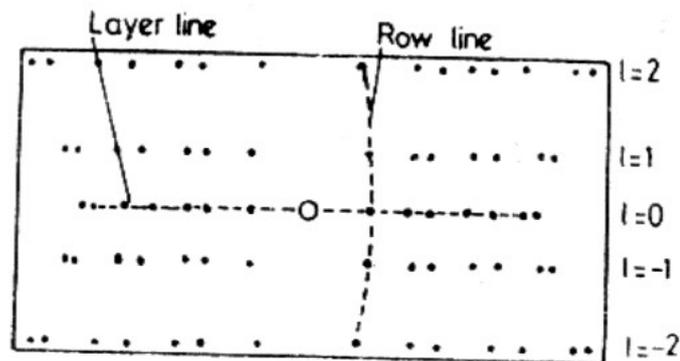
Fig.6.3: Typical Rotation photograph (After Kachhava, 1992)

If is the separation of these layer lines and R is the radius of the camera, then from Fig.6.2 (b),

$$ \tag{6.2} $$

From equation (6.1) and equation (6.2)

$$ \overline{} = R \tag{6.3} $$

$$ \therefore \qquad \overline{} \tag{6.4} $$

By subsequent orientation of the crystal with **A** and **B** axes parallel to the axis of rotation, the other unit cell parameters may be determined.

3.3: Powder method

In this technique, a monochromatic X-ray beam is allowed to irradiate a small specimen of the substance grinded to a fine powder and contained in a thin-walled glass capillary tube. Since the orientation of the minute crystal fragments is completely random, a certain number of them will lie with any set of lattice planes making exactly the correct angle with the incident beam for reflection to occur. Further, these planes in the different crystallites are randomly distributed about the axis of the incident beam so that the corresponding reflections from all the crystallites in the specimen lie on a cone coaxial with the axis and with a semi-apex angle of twice the Bragg angle (i.e.2θ). The specimen

is surrounded by a cylindrical film and two small portions of each cone are recorded as lines on the film (Fig.6.3). If the grain size is fairly large ($> 10^{-6}$ m), there is insufficient room within the irradiated volume for enough crystallites to be in all possible orientations and the resultant powder lines will be rather 'spotty'. This spottiness can be eliminated by rotating the specimen during exposure this considerably increases the number of crystallites which can contribute to each powder line.
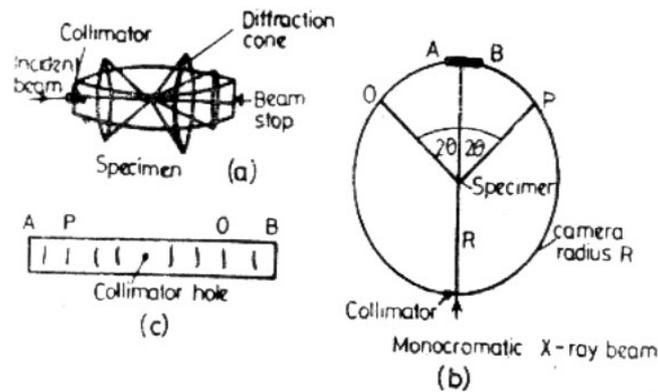
Fig.6.3: Schematic of powder method (a) experimental arrangement (b)Diffraction geometry (c) Developed films (After Kachhava, 1992)

The Bragg angle θ of the various reflections can be calculated by measuring the separation of the pairs of lines since, from the geometry of Fig.6.2 (b)

$$\overline{} \quad \overline{} \qquad\qquad\qquad (6.5)$$

where R is the radius of the camera. The reflections can be indexed and the unit cell parameters evaluated.

4.0   Conclusion
This unit showed that the three methods discussed are tools for better understanding of diffraction phenomena in crystalline samples.

5.0   Summary
- Variation of the angle of inclination of the specimen to the beam or the wavelength of radiation allows better understanding of Bragg's law.
- In the Laue technique , a single stationary crystal is irradiated by a range of X-ray wavelengths
- in the Rotational crystal method, a single crystal specimen is rotated in a beam of monochromatic x-rays wavelength
- in the Powder technique, a polycrystalline powder specimen is kept stationary in a beam of monochromatic radiation.

6.0   Tutor marked Assignment

Q1.   Find the Bragg angles and the indices of diffraction for the three lowest angle lines on the powder photographs of fcc crystal: a = 6.0Å and $\lambda = 1.54$Å

Q2.   Cobalt has two forms: α-Co, with hcp structure (lattice spacing of a= 2.15Å) and β-Co, with fcc structure (lattice spacing of a_{cubic}= 3.55 Å). Assume that the hcp structure has an ideal c/a ration. Calculate and compare the position of the first five X-ray powder diffraction peaks. The quantity $K = \frac{4\pi}{\lambda \sin\theta}$ can be used to characterize the peak positions (here λ is the wavelength of the X-ray radiation and 2θ is the scattering angle)

7.0   Further Reading/References

Kachhava, C.M., Solid State physics, Tata McGraw-Hill Publishing Company Limited, New Delhi, 1992

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Module 2:

CRYSTAL ELASTIC CONSTANTS AND VIBRATIONS

UNIT 1: ELASTIC CONSTANTS OF CRYSTALS

1.0   Introduction

The study of the elastic behavior of solids is very important in the fundamental and technical researches. In technology, it would tell us about the strength of the materials. In fundamental research, it is of interest because of the insight it provides in to the nature of binding forces in solids. They are also of importance for the thermal properties of solids.

2.0   Objective

- To explain elastic constant in solids
- To explain strength of solid materials
- To understand fully the binding forces in solids

3.0   Definition

Elasticity is the study of the ability of crystals to incorporate changes or adapt to new circumstances easily

3.1   Analysis of elastic strains and stresses

The local elastic strain of a body may be specified by six numbers. If α, β, γ are the angles between the unit cell axes **a**, **b**, **c**, the strain may be specified by the changes $\Delta\alpha, \Delta\beta, \Delta\gamma; \Delta a, \Delta b, \Delta c$ resulting from the deformation. This is a good physical specification of strain, but for non-orthogonal axes it leads to mathematical complications. The strain may be specified in terms of the six components $e_{xx}, e_{yy}, e_{zz}, e_{xy}, e_{yz}, e_{zx}$ which are defined below. We imagine that three *orthogonal* axes **f, g, h** of *unit length* are embedded securely in the unstrained solid, as shown in Fig. 1.1(a). We suppose that after a small uniform deformation has taken place the axes, which we now label, $\boldsymbol{f', g', h'}$, are distorted in orientation and in length, so that with the same atom as origin we may write.

$$
\begin{aligned}
\boldsymbol{f'} &= (1 + \varepsilon_{xx})\boldsymbol{f} + \varepsilon_{xy}\boldsymbol{g} + \varepsilon_{xz}\boldsymbol{h}; \\
\boldsymbol{g'} &= \varepsilon_{yx}\boldsymbol{f} + (1 + \varepsilon_{yy})\boldsymbol{g} + \varepsilon_{yz}\boldsymbol{h}; \\
\boldsymbol{h'} &= \varepsilon_{zx}\boldsymbol{f} + \varepsilon_{zy}\boldsymbol{g} + (1 + \varepsilon_{zz})\boldsymbol{h}
\end{aligned}
\qquad (1.1)
$$

The fractional changes of length of the **f, g,** and **h**. axes are $\varepsilon_{xx}, \varepsilon_{yy}, \varepsilon_{zz}$ respectively, to the first order. We define the strain components e_{xx}, e_{yy}, e_{zz} by the relations

$$
e_{xx} = \varepsilon_{xx} \; ; \qquad e_{yy} = \varepsilon_{yy} \; ; \qquad e_{zz} = \varepsilon_{zz} \; ; \qquad (1.2)
$$

The strain components e_{xy}, e_{yz}, e_{zx} may be defined as the changes in angle between the axes, so that to the first order

$$
\begin{aligned}
e_{xy} &= \boldsymbol{f'} \cdot \boldsymbol{g'} = \varepsilon_{yx} + \varepsilon_{xy} \; ; \\
e_{yz} &= \boldsymbol{g'} \cdot \boldsymbol{h'} = \varepsilon_{zy} + \varepsilon_{yz} \; ; \\
e_{zx} &= \boldsymbol{h'} \cdot \boldsymbol{f'} = \varepsilon_{zx} + \varepsilon_{xz} \; ;
\end{aligned}
\qquad (1.3)
$$

This completes the definition of the six strain components. A deformation is *uniform* if the values of the strain components are independent of the choice of origin.
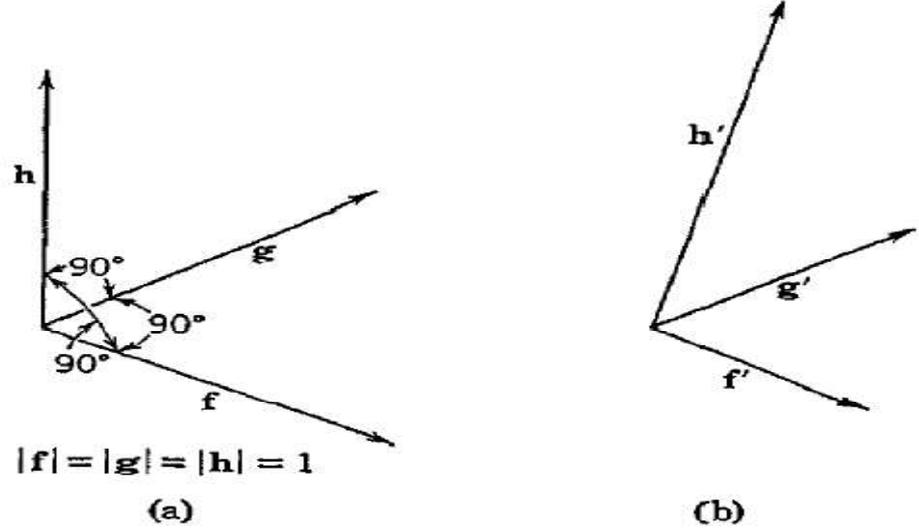
Fig.1.1 Coordinate axes for the description of the state of strain; the orthogonal unit axes in the unstrained state (a) are deformed in the strained state (b).

We note that merely rotating the axes does not change the angle between them, so for a pure rotation $\varepsilon_{yx} = -\varepsilon_{xy}$; $\varepsilon_{zy} = \varepsilon_{yz}$; $\varepsilon_{zx} = -\varepsilon_{xz}$. If we exclude pure rotations, we may without further loss of generality take $\varepsilon_{yx} = \varepsilon_{xy}$; $\varepsilon_{zy} = \varepsilon_{yz}$; $\varepsilon_{zx} = \varepsilon_{xz}$. so that in terms of the strain components we have

$$f' - f = e_{xx} + \frac{1}{2}e_{xy}g + \frac{1}{2}e_{zx}h \ ;$$
$$g' - g = \frac{1}{2}e_{xy}f + e_{yy}g + \frac{1}{2}e_{yz}h; \tag{1.4}$$
$$h' - h = \frac{1}{2}e_{zx}f + \frac{1}{2}e_{yz}g + e_{zz}h \ ;$$

We consider under a deformation which is substantially uniform near the origin a particle originally at the position

$$r = xf + yg + zh \tag{1.5}$$

After deformation the particle is at

$$r' = xf' + yg' + zh' \tag{1.6}$$

so that the displacement is given by

$$\varrho = r' - r = x(f' - f) + y(g' - g) + z(h' - h) \tag{1.7}$$

If we write the displacement as

$$\varrho = uf + vg + wh \tag{1.8}$$

we have from Eq.**(1.4)** and Eq.**(1.7)** the following expressions for the strain components:

$$e_{xx} = \frac{\partial u}{\partial x}; \qquad e_{yy} = \frac{\partial v}{\partial y}; \qquad e_{zz} = \frac{\partial w}{\partial z}; \tag{1.9}$$

$$e_{xy} = \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}; \qquad e_{yz} = \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z}; \qquad e_{zx} = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}$$

We have written derivatives for application to non-uniform strain. The expressions (1.9) are frequently used in the literature to define the strain components. Occasionally definitions of e_{xy}, e_{yz}, and e_{zx} are given which differ by a factor ½ from those given here. For a uniform deformation the displacement ϱ has the components

$$u \;=\; e_{xx}x + \frac{1}{2}e_{xy}y + \frac{1}{2}e_{zx}z \; ;$$

$$v \;=\; \frac{1}{2}e_{xy}x + e_{yy}y + \frac{1}{2}e_{yz}z; \tag{1.10}$$

$$w = \frac{1}{2}e_{zx}x + \frac{1}{2}e_{yz}y + e_{zz}z \; ;$$

3.2   Dilation

The fractional increment of volume caused by a deformation is called the *dilation.* The unit cube of edges **f, g,** and **h**. after deformation has a volume

$$V' = \; f' \cdot g'X\,h' \;\cong 1 + \; e_{xx} + e_{yy} + e_{zz} \tag{1.11}$$

where squares and products of strain components are neglected. Thus the dilation is

$$\delta = \frac{\Delta V}{V'} = \; e_{xx} + e_{yy} + e_{zz} \tag{1.12}$$

3.3   Shearing strain

We may interpret the strain components of the type

$$e_{xy} = \; \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}$$

as made up of two simple shears. In one of the shears, planes of the material normal to the x axis slide in the y direction; in the other shear, planes normal to y slide in the x direction.

3.4   Stress Components

The force acting on a unit area in the solid is defined as the stress. There are nine stress components: X_x, X_y, X_z, Y_x, Y_y, Y_z, Z_x, Z_y, Z_z. The capital letter indicates the direction of the force, and the subscript indicates the normal to the plane to which the force is applied. Thus the stress component X_x represents a force applied in the x direction to a unit area of a plane whose normal lies in the x direction; the stress component X_y represents a force

applied in the x direction to a unit area of a plane whose normal lies in the y direction. The number of independent stress components is reduced to six by applying to an elementary cube as in Fig. 1.2 the condition that the angular acceleration vanish, and hence that the total torque must be zero. It follows that

$$Y_z = Z_y, \qquad Z_x = X_z,, \qquad X_y = Y_x$$

and the independent stress components may be taken as X_x, Y_y, Z_z, Y_z, Z_x, X_y The stress components have the dimensions of force per unit area or energy per unit volume, which the strain components are dimensionless
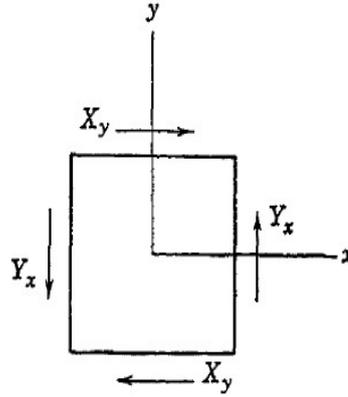
Fig. 1.2: Demonstration that number of independent stress components Y_x = X_y order that the body may be in equilibrium.

3.5   Elastic Compliance and Stiffness Constants

Hooke's law states that for small deformations the strain is proportional to the stress, so that the strain components are linear functions of the stress components:

$$e_{xx} = s_{11}X_x + s_{12}Y_y + s_{13}Z_z + s_{14}Y_z + s_{15}Z_x + s_{16}X_y;$$

$$e_{yy} = s_{21}X_x + s_{22}Y_y + s_{23}Z_z + s_{24}Y_z + s_{25}Z_x + s_{26}X_y;$$

$$e_{zz} = s_{31}X_x + s_{32}Y_y + s_{33}Z_z + s_{34}Y_z + s_{35}Z_x + s_{36}X_y ; \quad (1.13)$$

$$e_{yz} = s_{41}X_x + s_{42}Y_y + s_{43}Z_z + s_{44}Y_z + s_{45}Z_x + s_{46}X_y;$$

$$e_{zx} = s_{51}X_x + s_{52}Y_y + s_{53}Z_z + s_{54}Y_z + s_{55}Z_x + s_{56}X_y;$$

$$e_{xy} = s_{61}X_x + s_{62}Y_y + s_{63}Z_z + s_{64}Y_z + s_{65}Z_x + s_{66}X_y$$

Conversely, the stress components are linear functions of the strain components:

$$X_x = c_{11}e_{xx} + c_{12}e_{yy} + c_{13}e_{zz} + c_{14}e_{yz} + c_{15}e_{zx} + c_{16}e_{xy};$$

$$Y_y = c_{21}e_{xx} + s_{22}e_{yy} + c_{23}e_{zz} + c_{24}e_{yz} + c_{25}e_{zx} + c_{26}e_{xy};$$

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$$Z_z = c_{31}e_{xx} + c_{32}e_{yy} + c_{33}e_{zz} + c_{34}e_{yz} + c_{35}e_{zx} + c_{36}e_{xy} \; ;$$

$$Y_z = c_{41}e_{xx} + c_{42}e_{yy} + c_{43}e_{zz} + c_{44}e_{yz} + c_{45}e_{zx} + c_{46}e_{xy};$$

$$Z_x = c_{51}e_{xx} + c_{52}e_{yy} + c_{53}e_{zz} + c_{54}e_{yz} + c_{55}e_{zx} + c_{56}e_{xy}; \quad \text{(1.14)}$$

$$X_y = c_{61}e_{xx} + c_{62}e_{yy} + c_{63}e_{zz} + c_{64}e_{yz} + c_{65}e_{zx} + c_{66}e_{xy}$$

The quantities $s_{11} \ldots s_{12}$ are called the *elastic constants* or *elastic compliance constants;* the quantities $c_{11} \ldots \ldots c_{11}$ are called the *elastic stiffness constants* or *moduli of elasticity.* Other names are also current. The S's and C's have the dimension of area per unit force or volume per unit energy and force per unit area or energy per unit volume respectively

3.6   Energy Density

We calculate the increment of work δW done by the stress system in straining a small cube of side $L,$ with the origin at one corner of the cube and the coordinate axes parallel to the cube edges. We have

$$\delta W = \mathbf{F} \cdot \delta \boldsymbol{\varrho} \tag{1.15}$$

where $\mathbf{F}$ is the applied force and

$$\delta \boldsymbol{\varrho} = \boldsymbol{f}\delta u + \boldsymbol{g}\delta v + \boldsymbol{h}\delta w \tag{1.16}$$

is the displacement. If X, Y, Z denote the components of $\mathbf{F}$ per unit area, then

$$\delta W = L^2(X\delta u + Y\delta v + Z\delta w) \tag{1.17}$$

We note that the displacement of the three cube faces containing the origin is zero, so that the forces all act at a distance L from the origin. Now by definition of the strain components

$$\delta u = L\left(\delta e_{xx} + \tfrac{1}{2}\delta e_{xy} + \tfrac{1}{2}\delta e_{zx}\right) \tag{1.18}$$

etc., so that

$$\delta W = L^3\left(X_x\delta e_{xx} + Y_y\delta e_{yy} + Z_{zz}\delta e_{zz} + Y_z\delta e_{yz} + Z_{zx}\delta e_{zx} + X_y\delta e_{xy}\right) \text{(1.19)}$$

The increment δU of elastic energy per unit volume is

$$\delta U = X_x\delta e_{xx} + Y_y\delta e_{yy} + Z_z\delta e_{zz} + Y_z\delta e_{yz} + Z_x\delta e_{zx} + X_y\delta e_{xy} \tag{1.20}$$

We have $\delta U/\delta e_{xx} = X_x$ and $\delta U/\delta e_{yy} = Y_y$ and on further differentiation

$$\delta X_x \Big/ \delta e_{yy} = \delta Y_y \Big/ \delta e_{xx}$$

This leads from Eq. (1.14) to the relation

$$c_{12} = c_{21}$$

and in general we have

$$c_{ij} = c_{ji} \tag{1.21}$$

giving fifteen relations among the thirty non-diagonal terms of the matrix of the Cs. The thirty-six elastic stiffness constants are in this way reduced to twenty-one coefficients. Similar relations hold among the elastic compliances. The matrix of the Cs or S's is therefore symmetrical.

3.7   Cubic crystal

The number of independent elastic stiffness constants is usually reduced if the crystal possesses symmetry elements, and in the important case of cubic crystals there are only three independent stiffness constants, as we now show. We suppose that the coordinate axes are chosen parallel to the cube edges. In Eq. (1.14) we must have

$$c_{14} = c_{15} = c_{16} = c_{24} = c_{25} = c_{26} = c_{34} = c_{35} = c_{36} = 0$$

Since the stress must not be altered by reversing the direction of one of the other coordinate axes. As the axes are equivalent, we also have

$$c_{11} = c_{22} = c_{33},$$
$$\text{and} \quad c_{12} = c_{13} = c_{21} = c_{23} = c_{31} = c_{32},$$

so that the first three lines of Eq.(1.14) are described by the two independent constants c_{11} and c_{12}. The last three lines of Eq.(1.14) are described by the independent constant c_{44}, as

$$c_{44} = c_{15} = c_{66}$$

by equivalence of the axes, and the other constants all vanish because of their behavior on reversing the direction of one or other axis. The array of values of the elastic stiffness constant is therefore reduced for a cubic crystal to the matrix below:

$$|c_{ij}| = \begin{vmatrix} X_x & C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ Y_y & C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ Z_z & C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ Y_z & 0 & 0 & 0 & C_{44} & 0 & 0 \\ Z_x & 0 & 0 & 0 & 0 & C_{44} & 0 \\ X_y & 0 & 0 & 0 & 0 & 0 & C_{44} \end{vmatrix} \tag{1.22}$$

It is readily seen that for a cubic crystal

$$U = \frac{1}{2} C_{11}\left(e_{xx}^2 + e_{yy}^2 + e_{zz}^2\right) + C_{12}\left(e_{yy}e_{zz} + e_{zz}e_{xx} + e_{xx}e_{yy}\right)$$
$$+ \frac{1}{2} C_{44}\left(e_{yz}^2 + e_{zx}^2 + e_{xy}^2\right) \tag{1.23}$$

satisfies the Eq.(1.19); for the elastic energy density function.

For example, $\partial U / \partial e_{yy} = C_{11}e_{yy} + C_{12}e_{zz} + C_{12}e_{xx} = Y_y,$

Using Eq. (1.22).

For cubic crystals the compliance and stiffness constants are related by

$$C_{11} = \left[\frac{S_{11}+S_{12}}{(S_{11}-S_{12})(S_{11}+2S_{12})}\right];$$

$$C_{12} = \left[\frac{-S_{12}}{(S_{11}-S_{12})(S_{11}-2S1_{12})}\right]; \tag{1.24}$$

$$C_{14} = \frac{1}{S_{44}}$$

A general review of elastic constant data and of relationships among various coefficients for the crystal classes has been given by **Hearmon (**1946).

4.0   Conclusion
The elastic properties of a crystal considered as homogeneous continuous medium rather than a periodic array of atoms is obtained by Hook's law and Newton second law.

5.0   Summary
- The local elastic strain of a body is specified by six component numbers:
    $e_{xx}, e_{yy}, e_{zz}, e_{xy}, e_{yz}, e_{zx}$
- There are nine stress components: X_x, X_y, X_z, Y_x, Y_y, Y_z, Z_x, Z_y, Z_z
- A deformation is *uniform* if the values of the strain components are independent of the choice of origin
- The fractional increment of volume caused by a deformation is called the *dilation*
- Cubic crystals have only three independent stiffness constants.

6.0 Tutor marked assignment
Q1.   Show that the shear constant $\frac{1}{2}(C_{11} - C_{12})$ in a cubic crystals defined by setting $e_{xx} = - e_{yy} = \frac{1}{2}e$ and all other strains equal to zero.

Q2.   Prove that in a cubical, the effective elastic constant for a shear across the (110) plane in the $[1\bar{1}0]$ direction is equal $(C_{11} - C_{12})/2$.

7.0 Further Reading/ References

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1.0   Introduction

The elastic properties of a homogeneous crystal are generally anisotropic. Even in a cubic crystal, the relationship between stress and strain depends on the orientation of the crystal axes relative to stress. In general, the number of elastic constants characterizing a body is large. However, this number is considerably reduced due to the symmetric nature of both strain and stress tensors.

2.0   Objective

The objectives of this unit are to describe:
- Elastic waves in cubic crystals
- Elastic isotropy
- Cauchy relations
- Lattice theory of elastic coefficients

3.0   Definition

Same as in unit 1

3.1   Experimental determination of elastic constants.

The classic methods for the measurement of the elastic constants of crystals are described in the review by Hearmon (1964). In this method, quartz transducer is transmitted through the test crystal and reflected from the rear surface of the crystal back to the transducer. The elapsed time between initiation and receipt of the pulse is measured by standard electronic methods. The velocity is obtained by dividing the round trip distance by the elapsed time. In a representative arrangement the experimental frequency may be 15 s^{-1}, and the pulse length 1 μsec. The wavelength is of the order of 3 x 10^{-4} cm. The crystal specimen may be of the order of 1 cm in length. The elastic stiffness constants $C_{11}, C_{12,;} C_{44}$ of a cubic crystal may be determined from the velocities of three waves. A longitudinal wave propagates along a cube axis with velocity$\left(C_{11}/\rho\right)^{1/2}$, where ρ is the density. A shear wave propagates along a cube axis with Velocity $\left(C_{44}/\rho\right)^{1/2}$, while a shear wave with particle motion along a $1\bar{1}0$ direction propagates along a 110 direction with velocity$\left[(C_{11}-C_{12})/2\rho\right]^{1/2}$.

3.2   Elastic waves in cubic crystals

By considering the forces acting on an element of volume in the crystal we find for the equation of motion in the x direction

$$\rho \ddot{u} = \frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} \qquad (2.1)$$

With similar equations for the y and z directions; ρ is the density and u is the displacement and $\ddot{u}$ is $\frac{d^2 u}{dt^2}$. From Eq. (1.21) in unit 1, it follows, taking the cube edges as the x, y, z directions, that

$$\rho \ddot{u} = C_{11} \frac{\partial e_{xx}}{\partial x} + C_{12} \left(\frac{\partial e_{yy}}{\partial x} + \frac{\partial e_{zz}}{\partial x}\right) + C_{44} \left(\frac{\partial e_{xy}}{\partial y} + \frac{\partial e_{zx}}{\partial z}\right)$$

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This reduces, using Eq. (1.9) of unit 1, to

$$\rho \ddot{u} = C_{11} \frac{\partial^2 u}{\partial x^2} + C_{44} \left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right) + \left(C_{12} + C_{44} \right) \left(\frac{\partial^2 v}{\partial x \partial y} + \frac{\partial^2 w}{\partial x \partial z} \right) \qquad (2.2)$$

Here u, v and w are components of displacement
One solution is given by a longitudinal wave,

$$u = u_0 e^{i(\omega t - kx)}$$

moving along the x cube edge; from (2.2)

$$-\omega^2 \rho = -k^2 C_{11}$$

Here $k = \frac{2\pi}{\lambda}$ where λ is wave vector and $\omega = 2\pi v$ is the angular frequency
So that the velocity is

$$v = \omega/k = \left(C_{11}/\rho \right)^{1/2} \qquad (2.3)$$

Another solution is given by a transverse or shear wave moving along the y cube edge with the particle motion in the x direction:

$$v = v_0 e^{[i(\omega t - ky)]}$$

which gives, on substitution in Eq. (1.2)

$$-\omega^2 \rho = -k^2 C_{44}$$

so that;

$$v = \left(C_{44}/\rho \right)^{1/2} \qquad (2.4)$$

There is also a solution given by a shear wave moving in the z direction with particle motion in the x direction. In general there are three types of wave motion for a given direction of propagation in the crystal, but only for a few special directions can the waves be classified as pure longitudinal or pure transverse.

3.3   Elastic isotropy
By minor manipulations we may rewrite Eq. (2.2) as

$$\rho_0 \ddot{u} = (C_{11} - \ddot{C}_{12} - 2C_{44}) \frac{\partial^2 u}{\partial x^2} + C_{44} \nabla^2 u + (C_{12} + C_{44}) \frac{\partial}{\partial x} div \, \varrho \qquad (2.5)$$

where the displacement $\varrho = u\boldsymbol{i} + v\boldsymbol{j} + w\boldsymbol{k}$ is not to be confused with density now written as $\boldsymbol{\rho_0}$. if

$$C_{11} - C_{12} = 2C_{44} \tag{2.6}$$

the first term on the right in (2.5) drops out, and we can write on summing with the equations for the y and z motions:

$$\ddot{\varrho} = C_{44} \nabla^2 \varrho + (C_{12} + C_{44}) \; grad \; div \; \varrho \tag{2.7}$$

This equation has the important property that it is invariant under rotations of the reference axes, as each term in the equation is an invariant. Thus the relation (1.6) is the condition that the crystal should be elastically isotropic; that is, that waves should propagate in all directions with equal velocities. However, the longitudinal wave velocity is not necessarily equal to the transverse wave velocity.
The anisotropy factor A in a cubic crystal is defined as

$$A = {2C_{44}}/{(C_{11} - C_{12})} \tag{2.8}$$

and is unity for elastic isotropy.

3.4   Cauchy relation
There are among the elastic stiffness constants certain relations first obtained by Cauchy. The relations reduce to

$$C_{12} = C_{44}$$

in a crystal of cubic symmetry. If this is satisfied, the isotropy condition (2.6) becomes $C_{11} = 3C_{44}$. If then a cubic crystal were elastically isotropic *and* the Cauchy relation is satisfied, the velocity of the transverse waves would be equal to the velocity of the longitudinal waves.
The conditions for the validity of the Cauchy relations are:
 I.   All forces must be central, i.e., act along lines joining the centers of the atoms. This is not generally true of covalent binding forces, nor of metallic binding forces.
 II.   Every atom must be at a center of symmetry; that is, replacing every inter atomic vector should not change the structure.
 III.   The crystal should be initially under no stress. In metallic lattices the nature of the binding is not such that we would expect the Cauchy relation to work out well. In ionic crystals the electrostatic interaction of the ions is the principal interaction and is central in nature. It is not surprising that the Cauchy relation is moderately well satisfied in the alkali halides
Worked example:
   Show that the velocity of a longitudinal wave in the[111] direction of a cubic crystal is given by $v_s = \left[\frac{1}{3}(C_{11} + 2C_{12} + 4C_{44})/\rho\right]^{1/2}$.

Solution:

For a longitudinal phonon in the [111]direction, u = v = w.

Let $u = u_0 e^{ik[x+y+z]/\sqrt{3}} e^{-i\omega t}$

Where $k = \frac{2\pi}{\lambda}$ is the wave number and $\omega = 2\pi\nu$ is angular frequency. From Eq. (2.2),

$$\omega^2 \rho = [C_{11} + 2C_{44} + (C_{12}C_{44})]\, k^2/3$$

Thus, the velocity ω/k of the longitudinal wave in the [111] direction is given by

$$v_s = \omega/k = [(C_{11} + 2C_{12} + 4C_{44}/3\rho)]^{1/2}$$

4.0   Conclusion

The existence of the centre of symmetry of a cubic crystal stable under the central inters atomic forces leads to the well known Cauchy relation, $C_{12} = C_{44}$. This reduces the number of independent elastic constants of a cubic crystal to two only.

5.0   Summary

- The longitudinal wave velocity along the x cube edge is given by

$$v = \omega/k = \left(C_{11}/\rho\right)^{1/2}$$

- The transverse wave velocity along the y cube edge with the particle motion in the x direction is given by

$$v = \omega/k = \left(C_{44}/\rho\right)^{1/2}$$

- The Cauchy relation is $C_{12} = C_{44}$

- Cauchy relation does not work well for metallic lattices while it is moderately well satisfied in the alkali halides.

6.0   Tutor marked assignment

Q1.   Show that the velocity of a longitudinal wave in the [111] direction of a cubic crystal is given by

$$v = \left[\tfrac{1}{3}(C_{11} - 2C_{12} + 4C_{44})/\rho\right]^{1/2}$$

Q2.   Show that the velocity of a transverse wave in the [111] direction of a cubic crystal is given by

$$v = \left[\tfrac{1}{3}(C_{11} - C_{12} + C_{44})/\rho\right]^{1/2}$$

7.0 Further reading/references

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1.0   Introduction

The attractive electrostatic interaction between the negative charges of the electrons and the positive charges of the nuclei is entirely responsible for the cohesion of solid. As the atoms come close together their closed electron shells will start to overlap. The Pauli principle states that each electron state can be occupied by only one electron. In order to have overlap of closed shells, electrons have to be excited to higher states. This costs energy and leads to a repulsive interaction between the atoms. The repulsive interaction dominates for short distances between atoms, while the attractive interaction dominates at large distances. The actual atomic spacing in a crystal is defined by the equilibrium where the potential energy exhibits a minimum.

2.0   Objective

To explain:
- Inter atomic forces
- Vander Waals bonding
- Ionic bonding
- Covalent bonding
- Metallic bonding

3.0   Definition

Crystal binding is the attractive inter atomic force that hold atom together in a crystal.

3.1   Inter atomic forces

Solids are stable structures, and therefore there exist interactions holding atoms in a crystal together. For example a crystal of sodium chloride is more stable than a collection of free Na and Cl atoms. This implies that the Na and Cl atoms attract each other, i.e. there exist an attractive inter atomic force, which holds the atoms together. This also implies that the energy of the crystal is lower than the energy of the free atoms. The amount of energy which is required to pull the crystal apart into a set of free atoms is called the *cohesive energy* of the crystal.

Cohesive energy = energy of free atoms – crystal energy

Magnitude of the cohesive energy varies for different solids from 1 to 10 eV/atom, except inert gases in which the cohesive energy is of the order of 0.1eV/atom. The cohesive energy controls the melting temperature. A typical curve for the potential energy (binding energy) representing the interaction between two atoms is shown in Fig.1.1 It has a minimum at some distance $R=R_0$. For $R>R_0$ the potential increases gradually, approaching 0 as $R\rightarrow\infty$, while for $R<R_0$ the potential increases very rapidly, tending to infinity at $R=0$. Since the system tends to have the lowest possible energy, it is most stable at $R=R_0$, which is *the equilibrium inter atomic distance.* The corresponding energy U_0 is the cohesive energy. A typical value of the equilibrium distance is of the order of a few angstroms (e.g. 2-3Å), so that the forces under consideration are short range. The inter atomic force is determined by the gradient of the potential energy, so that

$$F(R) = -\frac{\partial U}{\partial R}$$

<div align="right">(3.1)</div>

If we apply this to the curve in Fig.3.1, we see that $F(R) < 0$ for $R > R_0$. This means that for large separations the force is *attractive*, tending to pull the atoms together. On the other, hand $F(R) > 0$ for $R < R_0$, i.e. the force becomes *repulsive* at small separations of the atoms, and tends to push the atoms apart. The repulsive and attractive forces cancel each other exactly at the point R_0, which is the point of equilibrium. The attractive inter atomic forces reflect the presence of *bonds* between atoms in solids, which are responsible for the stability of the crystal. There are several types of *bonding*, depending on the physical origin and nature of the bonding force involved.
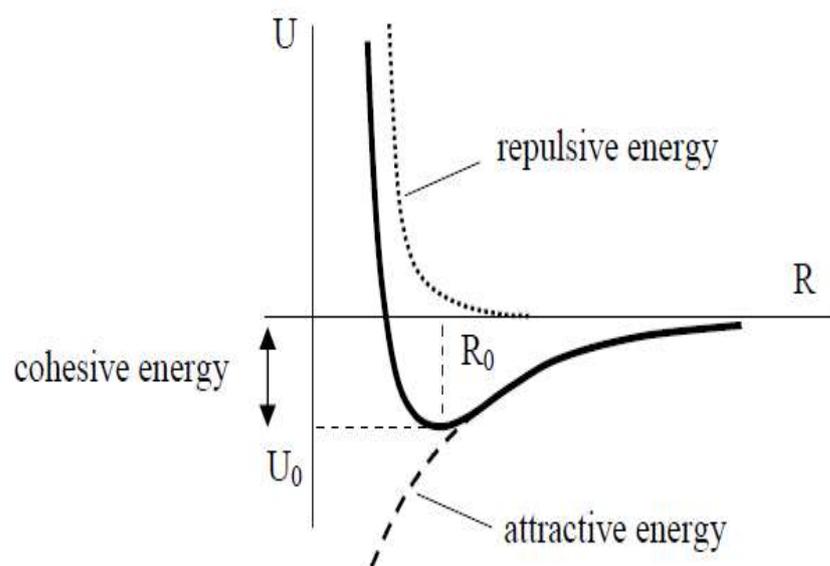
Fig.3.1. A typical curve for the potential energy (binding energy) representing the interaction between two atoms (After Kittel.1979)

Although the nature of the *attractive energy* is different in different solids, the origin of the *repulsive energy* is similar in all solids and it is mainly due to the *Pauli Exclusion Principle*. The elementary statement of this principle is that two electrons cannot occupy the same orbital. As ions approach each other close enough, the orbits of the electrons begin to overlap, i.e. some electrons attempt to occupy orbits already occupied by others. This is, however, forbidden by the Pauli Exclusion Principle. As a result, electrons are excited to unoccupied higher energy states of the atoms. Thus, the electron overlap increases the total energy of the system and gives repulsive contribution to the interaction. The repulsive interaction is not easy to treat analytically from first principles. In order to make some quantitative estimates it is often assumed that this interaction can be described by a central field repulsive potential of the form $\lambda \exp(-r/\rho)$, where λ and ρ are some constants or of the form B/R^n, where n is sufficiently large and B is some constant.

3.2 Vander Waals (Inter atomic) bonding

This type of binding is exhibited by solid noble gas crystals. The outermost electron shell is completely filled and the electron distribution is spherically symmetric. Each atom is neutral and has no permanent dipole moment. The attractive forces between the atoms arise from fluctuations in the electron distribution. These give an instantaneous fluctuating dipole moment in the atom. Its interaction with induced dipole moments in the neighboring atom leads to a weak interaction. The electron distribution in inert gases is very close to that in free atoms. The noble gases such as neon (Ne), argon (Ar), krypton (Kr) and xenon (Xe) are characterized by filled electron shells and a spherical distribution of electronic clouds in the free atoms. In the crystal the inert gas atoms pack together within the cubic fcc structure. Consider two inert gas atoms (1 and 2) separated by distance R. The average charge distribution in a single atom is spherically symmetric, which implies that the average dipole moment of atom 1 is zero: $\langle \boldsymbol{d}_1 \rangle = 0$. Here the brackets denote the time average of the dipole moment. However, at any moment of time there may be a non-zero dipole moment caused by fluctuations of the electronic charge distribution. We denote this dipole moment by $\mathbf{d}_1$. From electrostatics consideration, this dipole moment produces an electric field, which induces a dipole moment on atom 2. This dipole moment is proportional to the electric field which is in its turn proportional to the d_1/R_3 so that

$$d_2 \propto E \propto \frac{d_1}{R^3} \tag{3.2}$$

The dipole moments of the two atoms interact with each other. The energy is therefore reduced due to this interaction. The energy of the interaction is proportional to the product of the dipole moments and inversely proportional to the cube of the distance between the atoms, so that

$$-\frac{d_1 d_2}{R^3} \propto -\frac{d_1^2}{R^6} \tag{3.3}$$

and that the coupling between the two dipoles, one caused by a fluctuation, and the other induced by the electric field produced by the first, results in the attractive force, which is called the *Van der Waals force*. The time averaged potential is determined by the average value of $\langle d_1^2 \rangle$ which is not vanish, even though $\langle \boldsymbol{d}_1 \rangle$ is zero.

$$U \propto -\frac{\langle d_1^2 \rangle}{R^6} \tag{3.4}$$

The respective potential decreases as R^6 reduces with the separation between the atoms. *Van der Waals bonding* is relatively weak; the respective cohesive energy is of the order of 0.1eV/atom. This attractive interaction described by Eq. (3.4) holds only for a relatively large separation between atoms. At small separations a very strong repulsive forces cause by the overlap of the inner electronic shells start to dominate. It appears that for inert gases this repulsive interaction can be fitted quite well by the potential of the
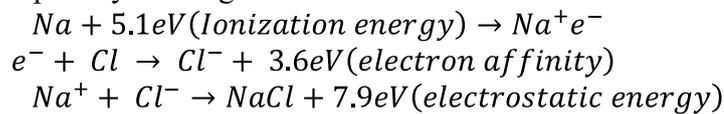
form B/R^{12} where B is a positive constant. Combining this with Eq. (3.4) we obtain the total potential energy of two atoms at separation R which can be represented as

$$U = 4\varepsilon \left[\left(\frac{\sigma}{R} \right)^{12} - \left(\frac{\sigma}{R} \right)^{6} \right] \tag{3.5}$$

where $4\varepsilon\sigma^6 \equiv A$ and $4\varepsilon\sigma^{26} \equiv B$. This potential is known as Lennard-Jones potential.

3.3   Ionic bonding

The ionic bond results from the electrostatic interaction of oppositely charged ions. Let us take sodium chloride as an example. In the crystalline state, each Na atom loses its single valence electron to a neighboring Cl atom, producing Na$^+$ and Cl^- ions which have filled electronic shells. As a result an ionic crystal is formed containing positive and negative ions coupled by a strong electrostatic interaction.

$$Na + 5.1eV \, (Ionization \, energy) \rightarrow Na^+ e^-$$
$$e^- + Cl \rightarrow Cl^- + 3.6eV \, (electron \, affinity)$$
$$Na^+ + Cl^- \rightarrow NaCl + 7.9eV \, (electrostatic \, energy)$$

The cohesive energy with respect to neutral atoms can be calculated as 7.9eV - 5.1eV + 3.6eV, i.e. Na + Cl $\rightarrow$ $NaCl$ + 6.4 eV (cohesive energy). The structure of $NaCl$ is two interpenetrating fcc lattices of Na$^+$ and Cl^- ions as shown in Fig.3.2
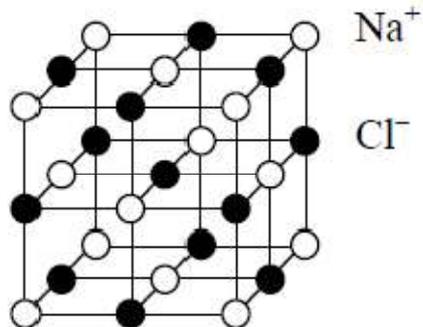
Fig 3.2 structure of $NaCl$(After Kachhava, 1992)

Thus each Na$^+$ ion is surrounded by 6 Cl^- ions and vice versa. This structure suggests that there is a strong attractive Coulombic force between nearest-neighbors ions, which is responsible for the ionic bonding. To calculate binding energy we need to include Coulomb interactions with all atoms in the solid. Also we need to take into account the repulsive energy, which we assume to be exponential. Thus the interaction between two atoms i and j in a lattice is given by

$$U_{ij} = \lambda e^{\left(-r_{ij}/\rho \right)} \pm q^2 / r_{ij} \tag{3.6}$$

Here r_{ij} is the distance between the two atoms, q is the electric charge on the atom, the (+) sign is taken for the like charges and the (−) sign for the unlike charges. The total energy of the crystal is the sum over i and j so that

$$-\hspace{3cm}\text{(3.7)}$$

In this formula ½ is due to the fact that each pair of interactions should be counted only once. The second equality results from the fact in the   structure the sum over j does not depend on whether the reference ion i is positive or negative, which gives the total number of atoms. The latter divided by two gives the number of molecules N, composed of a positive and a negative ion. We assume for simplicity that the repulsive interaction is non-zero only for the nearest neighbors (because it drops down very quickly with the distance between atoms). In this case we obtain

$$\hspace{6cm}\text{(3.8)}$$

Here R is the distance between the nearest neighbors; z is the number of the nearest neighbors, and α is the *Madelung constant*:

$$\overline{\hspace{3cm}}\hspace{4cm}\text{(3.9)}$$

where   is defined by   .The value of the Madelung constant plays an important role in the theory of ionic crystals. In general it is not possible to compute the Madelung constant analytically. A powerful method for calculation of lattice sums was developed by Ewald, which is called *Ewald summation*. This method can be used for the numerical evaluation of the Madelung constants in solids. Example considers a one-dimensional lattice of ions of alternating sign as shown in Fig.3.3 below.
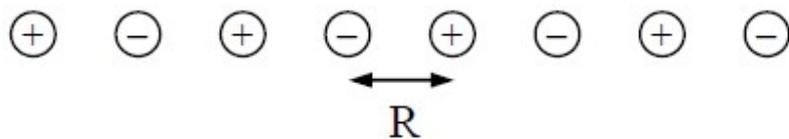
Fig.3.3: 1-D lattice of ions of alternating sign.

In this case

$$-\quad-\quad\overline{\ }\quad\overline{\ }\quad\overline{\ }$$

Or

$$-\quad-\quad-\hspace{4cm}\text{(3.10)}$$

The factor 2 occurs because there are two ions, one to the right and one to the left at equal distances   .
we sum this series by the expansion

$$\ln(1 + x) = \sum_{n=1}^{\infty} (-1)^{n-1} \frac{X^n}{n}$$

Thus the Madelung constant for 1-dimensional chain is $\alpha = 2\ln2$.

In three dimensions calculation of the series is much more difficult and cannot be performed so easy. The values of the Madelung constants for various solids are calculated, tabulated and can be found in literature (e.g.Kittel, 1996).

3.4   Covalent bonding

The covalent bond is another important type of bond which exits in many solids. The covalent bond between two atoms is usually formed by two electrons, one from each atom participating in the bond. The electrons forming the bond tend to be partly localized in the region between the two atoms joined by the bond. Normally the covalent bond is strong: for example, it is the bond, which couples carbon atoms in diamond. The covalent bond is also responsible for the binding of silicon and germanium crystals. In a two-atomic molecule (one electron per atom) the energy levels are split into a binding and an antibinding one. The two electrons are shared between the two atoms and fill the lowest, binding, molecular orbital. In a solid the energy levels are no longer discrete but the binding and antibinding levels become broad **energy bands**. The structure of covalent crystals is determined by the direction of the bonds, they have often fewer nearest neighbor atoms (lower coordination number).

Compounds where the atoms have different number of valence electrons exhibit a mixture of ionic and covalent binding. Ex: $GaAs$. Ga has 3 valence electrons and As has 5. On the average we have 4 electrons per atom which can be shared in tetrahedral bonds with neighboring atoms. However if the bonds are to be symmetrical the Ga will be negatively charged and As positively charged. Hence partial ionic binding cannot be avoided in this and similar cases.

3.5   Metallic bonding

Metals are characterized by a high electrical conductivity, which implies that a large number of electrons in a metal are free to move. The electrons capable to move throughout the crystal are called the *conductions electrons*. Normally the valence electrons in atoms become the conduction electrons in solids. The main feature of the metallic bond is the lowering of the energy of the valence electrons in metal as compared to the free atoms. Below, some qualitative arguments are given to explain this fact. According to the Heisenberg uncertainty principle the indefiniteness in coordinate and in the momentum are related to each other so that $\Delta x \Delta p = \hbar$. In a free atom the valence electrons are restricted by a relatively small volume. Therefore, Δp is relatively large which makes the kinetic energy of the valence electrons in a free atom large. On the other hand in the crystalline state the electrons are free to move throughout the whole crystal, the volume of which is large. Therefore the kinetic energy of the electrons is greatly reduced, which leads to diminishing the total energy of the system in the solid. This mechanism is the source of the metallic bonding. Figuratively speaking, the negatively charged free electrons in a metal serve as glue that holds positively charged ions together. The metallic bond is somewhat weaker than the ionic and covalent bond. For instance the melting temperature of metallic sodium is about 400^0 which is smaller than 1100^0 in

$NaCl$ and about 400^0 in diamond. Nevertheless, this type of bond should be regarded as strong. In transition metals like Fe, Ni, Ti, Co the mechanism of metallic bonding is more complex. This is due to the fact that in addition to s electrons which behave like free electrons we have 3d electrons which are more localized. Hence the d electrons tend to create covalent bonds with nearest neighbors. The d electrons are normally strongly hybridized with s electrons making the picture of bonding much more complicated.

4.0 Conclusion

Solids are stable structures, and therefore there exist interactions holding atoms in a crystal together. Depending on the distribution of the outer electrons with respect to the ions, different binding types can occur.

5.0 Summary

- The cohesive energy is the energy that must be added to the crystal to separate it to neutral free atoms at rest, at infinite separation.
- Crystals of inert gas atoms are bound by Vander Waals interaction.
- Ionic crystals are bound by electrostatic attraction of charged ions of separate signs.
- A covalent bound is characterized by the overlap of charge distributions of antiparallel spin.
- Metals are bound by reduction in kinetic energy of the valence electrons in the metal as compared with the free atom.

6.0 Tutor marked assignment

Q1. Repulsive potential between two atoms is represented by A/R^n, where constants A and n are phenomenological parameters.

(a) Show that the equilibrium inter atomic distance is given by

$$R_0 = \left(\frac{6nA}{\alpha q^2}\right)^{\frac{n}{n-1}}$$

(b) Demonstrate that the cohesive energy per molecule at equilibrium is

$$U_0 = -\frac{\alpha q^2}{R_0}\left(1 - \frac{1}{n}\right)$$

(c) Calculate the constant n for $NaCl$, taking into account that the lattice constant is a=5.63Å, α=1.75, $q=e$ and the measured binding energy per molecule for this crystal is -7.94 eV.

Q2. Using the Lennard-Jones potential with e=1.04ÿ10^{-2} eV and s=3.40Å and taking into account only nearest-neighbor atoms, calculate the lattice parameter and the cohesive energy of the fcc crystal of Ar.

7.0 Further reading/References.

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1.0   Introduction

An important aspect of the study of solid state physics is the lattice dynamics, which concerns itself with the vibrations of atoms about their equilibrium sites in a solid. These vibrations occur at any temperature, even at absolute zero. They are responsible for the thermal properties - heat capacity, thermal conductivity, thermal expansion, etc. of insulators and contribute the greater part of the heat capacity of metals.

2.0   Objective

To describe:
- One-dimensional monatomic lattice.
- One-dimensional diatomic lattice
- Three- dimensional lattice.

3.0   Definition

Lattice vibration is a continuing periodic oscillation relative to a fixed reference point, or a single complete oscillation.

3.1   One-dimensional monatomic lattice

Consider one-dimensional crystal lattice and assume that the forces between the atoms in this lattice are proportional to relative displacements from the equilibrium positions. 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 interconnected by elastic springs (Fig.4.1).
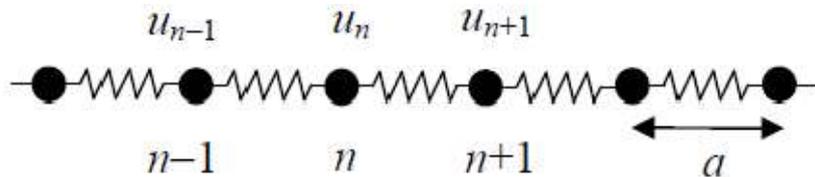
Fig.4.1: Lattice vibration of monatomic lattice
(After www.pa.uk.edu/kwng/phy/525/lec)

Therefore, the force exerted on nth atom in the lattice is given by

$$F_n = C(u_{n+1} - u_n) + C(u_{n-1} - u_n) \tag{4.1}$$

where C is the interatomic force (elastic) constant. Applying Newton's second law to the motion of the $n - th$ atom we obtain

$$M\frac{d^2u_n}{dt^2} = F_n = C(u_{n+1} - u_n) + C(u_{n-1} - u_n) = -C(2u_n - u_{n+1} - u_{n-1}) \tag{4.2}$$

where M is the mass of an atom. Note that we neglected here the interaction of the $n - th$ atom with all but its nearest neighbors. A similar equation should 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.

Now let us attempt a solution of the form

$$U_n = Ae^{i(qx_n - \omega t)} \tag{4.3}$$

where x_n is the equilibrium position of the $n - th$ atom so that $x_n = na$. This equation represents a traveling wave, in which all the atoms oscillate with the same frequency ω and the same amplitude A and have wave vector q. Note that a solution of the form Eq. (4.3) is only possible because of the transnational symmetry of the lattice. Now substituting Eq. (4.3) into Eq.(4.2) and canceling the common quantities (the amplitude and the time-dependent factor) we obtain

$$M(-\omega^2)e^{iqna} = -C\left[2e^{iqna} - e^{iq(n+1)a} - e^{iq(n-1)a}\right] \tag{4.4}$$

This equation can be further simplified by canceling the common factor e^{iqna} which leads to

$$M\omega^2 = C\left(2 - e^{iqa} - e^{-iqa}\right) = 2C(1 - \cos qa) = 4C\sin^2\frac{qa}{2} \tag{4.5}$$

We find therefore the dispersion relation for the frequency

$$\omega = \sqrt{\frac{4C}{M}}\left|sin\frac{qa}{2}\right| \tag{4.6}$$

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

(**i**) *Reducing to the first Brillouin zone*. The frequency (4.6) and the displacement of the atoms (5.3) do not change when we change q by $q+2\pi/a$. This means that these solutions are physically identical. This allows us to set the range of independent values of q within the first Brillouin zone, i.e.

$$-\frac{\pi}{a} \leq q \leq \frac{\pi}{a} \tag{4.7}$$

Within this range of q the ω versus q is shown in Fig.4.2. The maximum frequency is $\sqrt{4C/M}$. The frequency is symmetric with respect to the sign change in q, i.e. $\omega(q)=\omega(-q)$). This is not surprising because a mode with positive q corresponds to the wave traveling in the lattice from the left to the right and a mode with a negative q 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 q. At the boundaries of the Brillouin zone $q=\pm\pi/a$ 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.
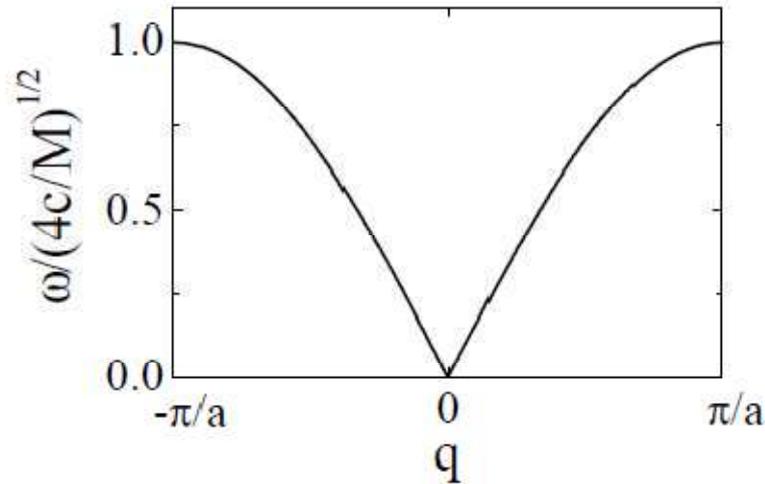
Fig.4.2: Dispersion curve of a one-dimensional monatomic lattice representing the First Brillouin Zone. www.pa.uk.edu/kwng/phy/525/lec)

(ii) *Phase and group velocity.* The phase velocity is defined by

$$v_p = \frac{\omega}{q} \tag{4.8}$$

and the group velocity by

$$v_g = \frac{d\omega}{dq} \tag{4.9}$$

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 Eq. (4.6) the group velocity is given by

$$v_g = \sqrt{\frac{Ca^2}{M}} \cos\frac{qa}{2} \tag{4.10}$$

As is seen from Eq. (4.10) the group velocity is zero at the edge of the zone where $q=\pm\pi/a$. Here the wave is standing and therefore the transmission velocity for the energy is zero.

(iii) *Long wavelength limit.* The long wavelength limit implies that $\lambda \gg a$. In this limit $qa \ll 1$. We can then expand the sine in Eq. (4.6) and obtain for the positive frequencies:

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$$—$$
$$—$$ (4.11)

We see that the frequency of vibration is proportional to the wave vector. This is equivalent to the statement that velocity is independent of frequency. In this case

$$—$$
$$— \quad —$$ (4.12)

Worked example:
Atoms in crystals are held together by chemical bonds. Consider these bonds to be elastic springs of the same force constants for one-dimensional crystal lattice. Suppose one of the atoms is displaced from its mean position by an external force and then released;

    (a) derive an expression for its periodic motion with respect to its nearest neighbours

    (b) prove that these atoms can vibrate with a number of discrete frequencies up to a maximum value given by

$$—$$
$$—$$

Solution:
(a) Consider a linear chain of atoms connected by elastic springs, each of spring constants β (Fig below). If the atoms are each of mass m and the distance between any two consecutive atoms is 'a', then a small displacement by some external force on one of them will result into an oscillatory motion?
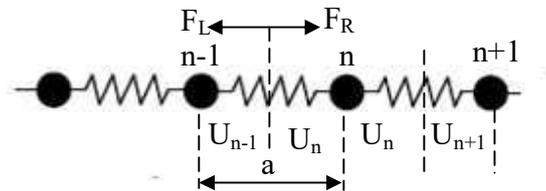
The displacements of   and   atoms from their mean positions at any instant will be   and   respectively. Also, the extension of the spring between   and   atoms will be   and therefore, the restoring force F_L on the   atom due to the left spring will be

                                                   (i)

Similarly, the extension of the spring on the right of   atom will be and restoring force is given by

                                                   (ii)

The net force on the   atom will be

                                                   (iii)

Applying Newton's second law of motion to the displacement of the   atom, we obtain

$$\overline{\quad\quad}$$

$$\therefore m\frac{d^2 U_n}{dt^2} - \beta(U_{n+1} + U_{n-1} - 2U_n) = 0 \qquad\qquad (iv)$$

Hence, Eq.(iv) is the equation of periodic motion of the nth atom with respect to $(n-1)th$ and $(n+1)th$ atoms.

(b)The general solution of Eq. (iv), if the amplitude of this motion is U, is given by

$$U_n = Ue^{i(\omega t + kX_n)} \qquad\qquad (v)$$

Where X_n is the distance of the nth atom from the origin i.e. $X_n = na$. Similarly, if X_{n-1} and X_{n+1} are the distances of $(n-1)th$ and $(n+1)th$ atom from the origin, then $X_{n-1} = (n-1)a$ and $X_{n+1} = (n+1)a$. Thus, we have

$$U_{n-1} = Ue^{i(\omega t + kX_{n-1})}$$
$$\qquad\qquad (vi)$$
$$U_{n+1} = Ue^{i(\omega t + kX_{n+1})}$$

Where ω is the angular frequency and $k = \frac{2\pi}{\lambda}$

Substituting Eq.(v) and Eq.(vi) into Eq.(iv) with $X_n = na$, $X_{n-1} = (n-1)a$ and $X_{n+1} = (n+1)a$, gives,

$$-m\omega^2 U e^{i\omega t} e^{ikna} = \beta U e^{i\omega t} e^{ikna}\left[e^{ika} + e^{-ka} - 2\right]$$

$$-m\omega^2 U e^{i\omega t} e^{ikna} = \beta\left[\left(e^{\frac{ika}{2}}\right)^2 + \left(e^{-\frac{ika}{2}}\right)^2 - 2\right] = \beta\left[e^{\frac{ika}{2}} - e^{-\frac{ika}{2}}\right]^2$$

$$-m\omega^2 = 4\beta i^2 \left[\frac{e^{\frac{ika}{2}} - e^{-\frac{ka}{2}}}{2i}\right]^2 = -4\beta\left[\sin\frac{ka}{2}\right]^2$$

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

$$\therefore \omega = \sqrt{\frac{4\beta}{m}}\,\sin\frac{ka}{2} \qquad\qquad (vii)$$

E.(vii) gives a number of frequencies with which the atoms of the 1-dimensional lattice can vibrate. When $\sin\frac{ka}{2} = \pm 1$ i.e. when $\frac{ka}{2} = \frac{\pi}{2}$, the maximum frequency is obtained from Eq.(vii) as $\omega_m = \pm\sqrt{\frac{4\beta}{m}}$

3.2   Diatomic one-dimensional lattice

Now we consider a one-dimensional lattice with two non-equivalent atoms in a unit cell. Fig.4.3 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.
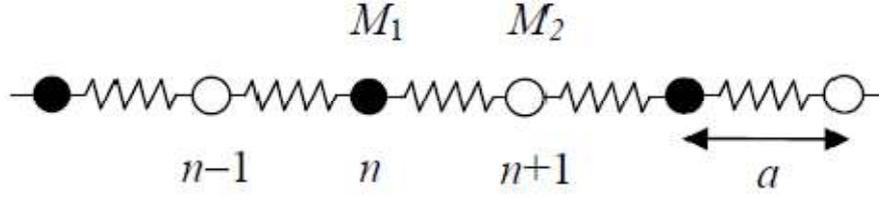
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Fig.4.3: Lattice vibration of diatomic lattice (After
www.pa.uk.edu/kwng/phy/525/lec)

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

$$M_1 \frac{d^2 U_n}{dt^2} = -C(2U_n - U_{n+1} - U_{n-1})$$

$$M_2 \frac{d^2 U_{n+1}}{dt^2} = -C(2U_{n+1} - U_{n+2} - U_n)$$

(4.13)

In analogy with the monatomic lattice we are looking for the solution in the form of traveling mode for the two atoms:

$$\begin{vmatrix} U_n \\ U_{n+1} \end{vmatrix} = \begin{vmatrix} A_1 e^{iqna} \\ A_2 e^{iq(n+1)a} \end{vmatrix} e^{-i\omega t}$$

(4.14)

$$\begin{vmatrix} 2C - M_1\omega^2 & -2\cos qa \\ -2C\cos qa & 2C - M_2\omega^2 \end{vmatrix} = \begin{vmatrix} A_1 \\ A_2 \end{vmatrix} = 0$$

(4.15)

This is a system of linear homogeneous equations for the unknowns A_1 and A_2. A nontrivial solution exists only if the determinant of the matrix is zero. This leads to the secular equation

$$(2C - M_1\omega^2)(2C - M_2\omega^2) - 4C^2 \cos^2 qa = 0$$

(4.16)

This is a quadratic equation, which can be readily solved

$$\omega^2 = C\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \pm C\sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^2 - \frac{4\sin^2 qa}{M_1 M_2}}$$

(4.17)

Depending on sign in this formula there are two different solutions corresponding to two different dispersion curves, as is shown in Fig.4.4:
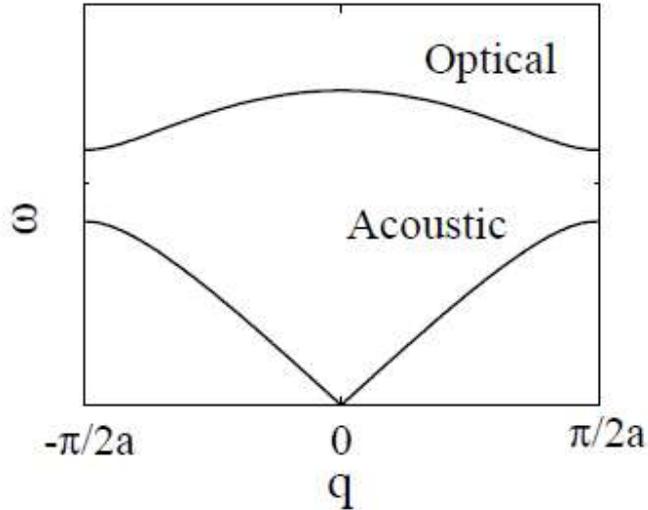
Fig.4.4: Dispersion Curve for one-dimensional diatomic lattice.
(After www.pa.uk.edu/kwng/phy/525/lec)

The lower curve is called the *acoustic branch*, while the upper curve is called the *optical branch*. The optical branch begins at $q=0$ and $\omega=0$. Then with increasing q 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 q

$$\omega_0 = \sqrt{2C\left(\frac{1}{M_1} + \frac{1}{M_2}\right)} \tag{4.18}$$

and it does not change much with q.
The distinction between the acoustic and optical branches of lattice vibrations can be seen most clearly by comparing them at $q=0$ (infinite wavelength). From Eq. (4.15), for the acoustic branch $\omega=0$ and $A_1=A_2$. 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, as shown in Fig.4.5 for the acoustic mode. On the other hand, for the optical vibrations, substituting Eq. (4.18) to Eq. (4.15), we obtain for $q=0$:

$$M_1 A_1 + M_2 A_2 = 0 \tag{4.19}$$

It implies that the optical oscillation takes place in such a way that the center of mass of a molecule remains fixed. The two atoms move in out of phase as shown in Fig.4.5. The frequency of these vibrations lies in infrared region which is the reason for referring to this branch as optical.
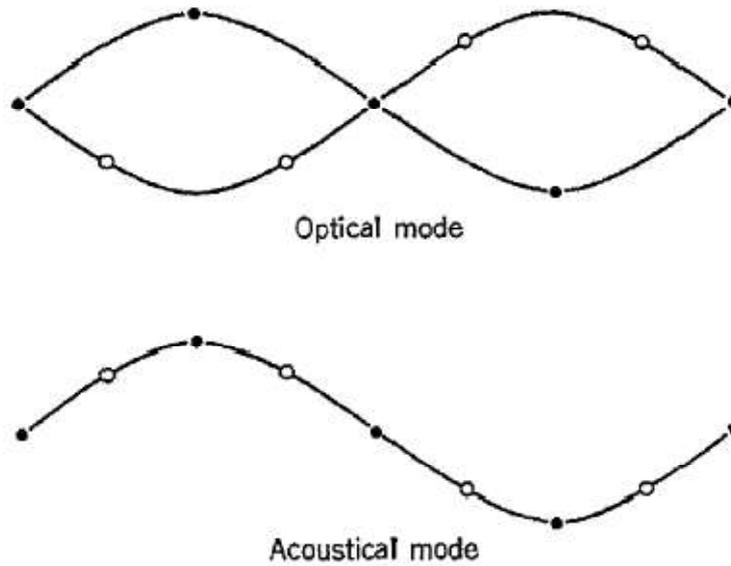
Optical mode

Acoustical mode

Fig.4.5: Distinction between Acoustic and Optical wave (After Kittel, 1976)

3.3   Three- dimension

The concept of the division of the vibrational modes into acoustic and optical branches can be generalized to be applicable to three-dimensional structure. To avoid mathematical details we shall present only a qualitative discussion. Consider, first, the monatomic Bravais lattice, in which each unit cell has a single atom. The equation of motion of each atom can be written in a manner similar to that of Eq. (4.2). The solution of this equation in three dimensions can be represented in terms of *normal modes.*

$$\boldsymbol{U_n} = \boldsymbol{A}e^{i(qr-\omega t)} \qquad\qquad (4.20)$$

where the wave vector **q** specifies both the wavelength and direction of propagation. The vector **A** determines the amplitude as well as the direction of vibration of the atoms. Thus this vector specifies the *polarization* of the wave, i.e., whether the wave is *longitudinal* (**A** parallel to **q**) or *transverse* (**A** perpendicular to **q**). When we substitute Eq.(5.20) into the equation of motion, we obtain three simultaneous equations involving A_x, A_y. and A_z, the components of **A**. These equations are coupled together and are equivalent to a 3 x 3 matrix equation. The roots of this equation lead to three different dispersion relations, or three dispersion curves, as shown in Fig.4.6. All the three branches pass through the origin, which means all the branches are acoustic. This is of course to be expected, since we are dealing with a *monatomic* Bravais lattice.
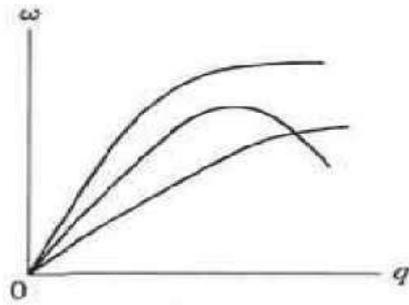
Fig.4.6: Dispersion curve.

The three branches in Fig.4.6 differ in their polarization. When **q** lies along a direction of high symmetry - for example, the [100] or [110] directions − these waves may be classified as either pure longitudinal or pure transverse waves. In that case, two of the branches are transverse and one is longitudinal. One usually refers to these as the TA - *transverse acoustic* and LA − *longitudinal acoustic* branches, respectively. However, along non-symmetry directions the waves may not be pure longitudinal or pure transverse, but have a mixed character.
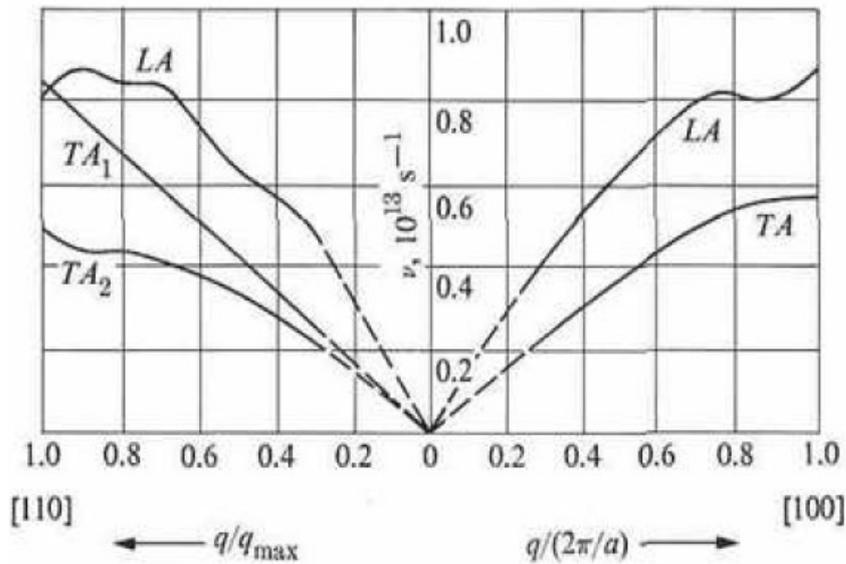
Fig.4.7: Dispersion curve for Al in the [100] and [110] directions (After Kittel, 1979)

Figure 4.7 shows the dispersion curves for Al in the [100] and [110] directions. Note that in certain high-symmetry directions, such as the [100] in Al, the two transverse branches coincide. The branches are then said to be *degenerate*.
 We turn our attention now to the non-Bravais three-dimensional lattice. Here the unit cell contains two or more atoms. If there are s atoms per cell, then on the basis of our previous experience we conclude that there are *3s* dispersion curves. Of these, *three* branches are acoustic, and the remaining ($3s$ −3) are optical. The mathematical justification for this assertion is as follows: We write the equation of motion for each

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atom in the cell, which results in s equations. Since these are vector equations, they are equivalent to $3s$ scalar equations, which have $3s$ roots. It can be shown that three of these roots always vanish at $q = 0$, which results in three acoustic branches. The remaining ($3s$ -3) roots, therefore, belong to the optical branches, as stated above. The acoustic branches may be classified, as before, by their polarizations as TA_1, TA_2, and LA. The *optical* branches can also be classified as longitudinal or transverse when q lies along a high symmetry direction, and one speaks of LO and TO branches. As in the one-dimensional case, one can also show that, for an optical branch, the atoms in the unit cell vibrate out of phase relative to each other. As an example of a non-Bravais lattice, the dispersion curves for Ge are shown in Fig.4.8. Since there are two atoms per unit cell in germanium, there are six branches: three acoustic and three optical. Note that the two transverse branches are degenerate along the [100] direction, as indicated earlier.
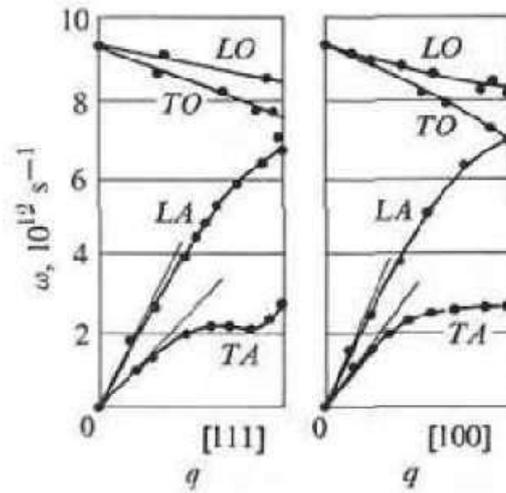
Fig.4.8: Dispersion curve for Ge along [100] and [110] directions (After Kittel, 1979)

3.4   Phonons

So far we discussed a classical approach to the lattice vibrations. As we know from quantum mechanics the energy levels of the harmonic oscillator are quantized. Similarly the energy levels of lattice vibrations are quantized. The quantum of vibration is called a *phonon* in analogy with the photon, which is the quantum of the electromagnetic wave. We know that the allowed energy levels of the harmonic oscillator are given by

$$E = \left(n + \frac{1}{2}\right)\hbar\omega \qquad\qquad (4.21)$$

where n is the quantum number. A normal vibration mode in a crystal of frequency ω is given by Eq. (4.20). If the energy of this mode is given by Eq. (4.21) we can say that this mode is occupied by n *phonons* of energy $\hbar\omega$. The term $\frac{1}{2}\hbar\omega$ is the zero point energy of the mode.

  Let us now make a comparison between the classical and quantum solutions in one-dimensional case. Consider a normal vibration

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$$u = Ae^{i(qx - \omega t)} \qquad \textbf{(4.22)}$$

where u is the displacement of an atom from its equilibrium position x and A is the amplitude. The energy of this vibrational mode averaged over time is

$$E = \tfrac{1}{2}\, M\omega^2 A^2 = \left(n + \tfrac{1}{2}\right)\hbar\omega \qquad \textbf{(4.23)}$$

It is evident from Eq.(4.23) above that there is a relationship between the amplitude of vibration and the frequency and the phonon occupation of the mode. In classical mechanics any amplitude of vibration is possible, whereas in quantum mechanics only discrete values are allowed. This is shown in Fig.4.9.
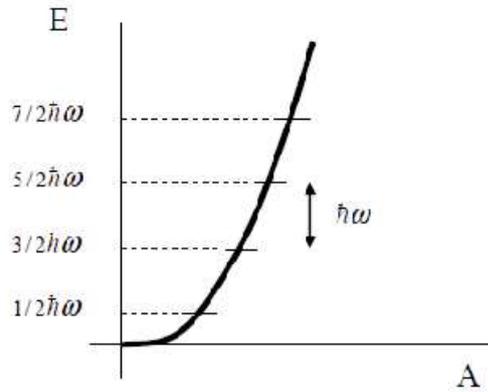

Fig.4.9: Relation between amplitude and frequency (After Kittel, 1979)

The lattice with s atoms in a unit cell is described by $3s$ independent oscillators. The frequencies of normal modes of these oscillators will be given by the solution of 3s linear equations as we discussed before. They are $\omega_p(\boldsymbol{q})$, where p denotes a particular mode, i.e. $p = 1,\dots 3s$. The energy of this mode is given by

$$E_{qp} = \left(n_{qp} + \frac{1}{2}\right)\hbar\omega_p(\boldsymbol{q}) \qquad \textbf{(4.24)}$$

where n_{qp} the occupation is number of the normal mode and is an integer. A vibrational state of the entire crystal is specified by giving the occupation numbers for each of the $3s$ modes. The total vibrational energy of the crystal is the sum of the energies of the individual modes, so that

$$E = \sum_{qp} E_{qp} = \sum_{qp} \left(n_{qp} + \frac{1}{2}\right)\hbar\omega_p(\boldsymbol{q}) \qquad \textbf{(4.25)}$$

Phonons can interact with other particles such as photons, neutrons and electrons. This interaction occurs such as if photon had a momentum $\hbar\mathbf{q}$. However, a phonon does not carry real physical momentum. The reason is that the center of mass of the crystal does not change it position under vibrations (except $q=0$). In crystals there exist selection rules for allowed transitions between quantum states. We saw that the elastic scattering of

an x-ray photon by a crystal is governed by the wave vector selection rule $\mathbf{k'} = \mathbf{k} + \mathbf{G}$, where $\mathbf{G}$ is a vector in the reciprocal lattice; $\mathbf{k}$ is the wave vector of the incident photon and $\mathbf{k'}$ is the wave vector of the scattered photon. This equation can be considered as condition for the conservation of the momentum of the whole system, in which the lattice acquires a momentum $-\hbar\mathbf{G}$. If the scattering of photon is inelastic and is accompanied by the excitation or absorption of a phonon the selection rule becomes

$$\mathbf{k'} = \mathbf{k} \pm \mathbf{q} + \mathbf{G} \qquad (4.26)$$

where sign (+) corresponds to creation of phonon and sign (–) corresponds to absorption of phonon. Phonon dispersion relations ω_p $\mathbf{q}$ can be determined by the inelastic scattering of neutrons with emission or absorption of phonons. In this case in addition to the condition of the momentum conservation we have the requirement of conservation of energy. The latter condition can be written as

$$\frac{\hbar^2 k^2}{2M} = \frac{\hbar^2 k^2}{2M} \pm \hbar\omega \qquad (4.27)$$

where M is the mass of the neutron and $\hbar\mathbf{k}$ and $\hbar\mathbf{k'}$ are the momenta of the incident and scattered neutron. Once we know in experiment the kinetic energy of the incident and scattered neutrons from Eq. (4.27) we can determine the frequency of the emitted or absorbed phonon. Then experimentally we need to determine those directions, which characterized by highest intensity of the scattered beam. For these directions the conditions (5.26) are satisfied and therefore from Eq. (4.26) we can find the wave vector of the phonon. Therefore, this is the way to obtain the dispersion conditions for the frequency of phonons which we discussed before.

4.0   Conclusion
Lattice vibrations are elastic waves propagating within crystals and the quantum unit of vibration is a phonon. The general equation of motion provides the phonon dispersion or phonon spectrum, ω.

5.0   Summary
- All lattice waves can be described by wave vectors that lie within the first Brillouin zone
- The quantum unit of vibration is a phonon.
- The energy of the phonon is $\hbar\omega$

6.0   Tutor marked assignment
Q1.   Consider a linear chain in which alternative ions have masses M_1 and M_2 and only nearest neighbors interact.
 (a) Discuss the form of the dispersion relation and the nature of the vibrational modes when $M_1 \gg M_2$.
(b) Show that for $M_1 = M_2$ the dispersion relation becomes identical to that for the   monatomic lattice

Q2. Consider the normal modes of a linear chain in which the force constants between nearest-neighbor atoms are alternatively C and 10C. Assuming that the masses are equal and the nearest neighbor separation is $a/2$ find $\omega(q)$ at $q=0$ and $q=\pi/a$. Sketch the dispersion curve. This problem simulates a crystal of diatomic molecules such as H_2.

7.0   Further reading/References

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1.0   Introduction

This unit is devoted to the description of certain thermal properties of solid materials. The properties considered on the basis of atomic point of view are specific heat, thermal expansion, equation of state and thermal conductivity. The most fundamental approach for the theoretical evaluation of these characteristics for a solid is to relate them to the internal energy, the total kinetic energy and potential energy of its constituents.

2.0   Objective

To explain
- Lattice specific heats
- Debye model
- Einstein model
- Lattice thermal conductivity

3.0   Definition

Specific heat is a measure of the number of degrees of freedom of oscillating lattice.

3.1   Heat capacity

The heat capacity C is defined as the heat ΔQ which is required to raise the temperature by ΔT, i.e.

$$C = \frac{\Delta Q}{\Delta T} \tag{5.1}$$

If the process is carried out at constant volume V, then $\Delta Q = \Delta E$, where ΔE is the increase in internal energy of the system. The heat capacity at constant volume C_V is therefore given by

$$C_v = \left(\frac{\partial E}{\partial T}\right)_v \tag{5.2}$$

The contribution of the phonons to the heat capacity of the crystal is called the *lattice heat capacity*.

The total energy of the phonons at temperature T in a crystal can be written as the sum of the energies over all phonon modes, so that

$$E = \sum_{qp} \langle n_{qp} \rangle \hbar \omega(\boldsymbol{q}) \tag{5.3}$$

Where $\langle n_{qp} \rangle$ is the thermal equilibrium occupancy of phonons of wave vector $\mathbf{q}$ and mode p ($p = 1\ldots3s$, where s is the number of atoms in a unit cell). The angular brackets denote the average in thermal equilibrium. Note that we assumed here that the zero-point energy is chosen as the origin of the energy, so that the ground energy lies at zero. The average thermal equilibrium can be calculated.

Consider a harmonic oscillator in a thermal bath. The probability to find this oscillator in an excited state, which is characterized by a particular energy E_n is given by the Boltzmann distribution

$$P_n = P_0 e^{\left(-n\hbar\omega / k_B T\right)} \tag{5.4}$$

where the constant P_0 is determined from the normalization condition.

$$\sum_{n=0}^{\infty} P_n = 1 \tag{5.5}$$

so that

$$P_0 = \left(\sum_{n=0}^{\infty} e^{\left(-n\hbar\omega / k_B T\right)}\right)^{-1} \tag{5.6}$$

The average excitation number of the oscillator is given by

$$\langle n \rangle = \sum_{n=0}^{\infty} n P_n = \frac{\sum_{n=0}^{\infty} n e^{-n\hbar\omega / k_B T}}{\sum_{n=0}^{\infty} e^{-n\hbar\omega / k_B T}} \tag{5.7}$$

The summation in the numerator can be performed using the known property of geometrical progression:

$$\sum_{n=0}^{\infty} x^n = 1 \tag{5.8}$$

Using this property we find:

$$\sum_{n=0}^{\infty} n x^n = x \frac{d}{dx} \sum_{n=0}^{\infty} x^n = x \frac{d}{dx} \frac{1}{1-x} \frac{x}{(1-x)^2} \tag{5.9}$$

Where $x = e^{-\frac{\hbar\omega}{kT}}$, then we obtain

$$\langle n \rangle = \frac{x}{1-x} = \frac{1}{x^{-1}-1} = \frac{1}{e^{\left(\hbar\omega / k_B\right)}-1} \tag{5.10}$$

The distribution given by Eq. (5.10) is known as the Planck distribution. Coming back to the expression for the total energy of the phonons, we find that

$$E = \sum_{n=0}^{\infty} \frac{e^{\hbar\omega(q)}}{e^{\hbar\omega(q)} - 1} \tag{5.11}$$

Usually it is convenient to replace the summation over **q** by an integral over frequency. In order to do this we need to introduce the *density of modes* or the *density of states* $D_P(\omega)$. $D_p(\omega)d\omega$ represents the number of modes of a given number s in the frequency range (ω, $\omega + d\omega$. Then the energy is

$$E = \sum_p \int d\omega D_p(\omega) \frac{\hbar\omega}{e^{(\hbar\omega/k_B)} - 1} \tag{5.12}$$

The lattice heat capacity can be found by differentiation of this equation with respect to temperature, so that

$$C_v = \frac{\partial E}{\partial T} = k_B \sum \int d\omega D_p(\omega) \frac{\left(\frac{\hbar\omega}{k_B T}\right)^2 e^{\left(\hbar\omega/k_B T\right)}}{\left(e^{(\hbar\omega/k_B)} - 1\right)^2} \tag{5.13}$$

We see that the central problem is to find the density of states $D_P(\omega)$, the number of modes per unit frequency range.

3.2   Density of state

Consider the longitudinal waves in a long bar. The solution for the displacement of atoms is given by

$$u = Ae^{iqx} \tag{5.14}$$

where we omitted a time-dependent factor it is irrelevant for the present discussion. We shall now consider the effects of the boundary conditions on this solution. These boundary conditions are determined by the external constraints applied to the ends of the bar. The most convenient type of boundary condition is known as the *periodic boundary condition.* By this we mean that the right end of the bar is constrained in such a way that it is always in the same state of oscillation as the left end. It is as if the bar were deformed into a circular shape so that the right end joined the left. Given that the length of the bar is *L*, if we take the origin as being at the left end, the periodic condition means that

$$u(x = 0) = u \ (x = L) \tag{5.15}$$

where *u* is the solution given by Eq.(5.14). If we substitute (5.14) into (5.15), we find that

$$e^{iqL} = 1 \tag{5.16}$$

This equation imposes a condition on the admissible values of *q*:

$$q = n\frac{2\pi}{L} \tag{5.17}$$

where $n = 0, +1, \pm 2$, etc. When these values are plotted along *q-axis,* they form a one-dimensional mesh of regularly spaced points. The spacing between the points is $2\pi/L$. When the bar length is large, the spacing becomes small and the points form a quasi-continuous mesh. Each *q*-value of Eq. (5.17) represents a *mode* of vibration. Suppose we choose an arbitrary interval dq in *q*-space, and look for the number of modes whose *q*'s lie in this interval. We assume here that *L* is large, so that the points are quasi-continuous, which is true for the macroscopic objects. Since the spacing between the points is $2\pi/L$, the number of modes is

$$\frac{L}{2\pi}dq \tag{5.18}$$

We are interested in the number of modes in the frequency range $d\omega$ lying betwe$(\omega, \omega + d\omega$. The *density of states D(ω)* is defined such that *D(ω)dω* gives this number. Comparing this definition with Eq.(5.18), one may write $D(\omega)d\omega = (L/2\pi)\,dq, or\, D(\omega) = (L/2\pi)/(d\omega/dq)$. We note from Fig.5.1, however, that in calculating $D(\omega)$ we must include the modes lying in the negative *q*-region as well as in the positive region. The effect is to multiply the above expression for $D(\omega)$ by a factor of two. That is,

$$D(\omega) = \frac{L}{\pi}\frac{1}{d\omega/dq} \tag{5.19}$$

We see that the density of states $D(\omega)$ is determined by the dispersion relation

$$\omega = \omega(q).$$

Now we extend these results to the 3D case. The wave solution analogous to (5.14) is

$$u = Ae^{i(q_x x + q_y y + q_z z)} \tag{5.20}$$

Fig.5.1: Density of state

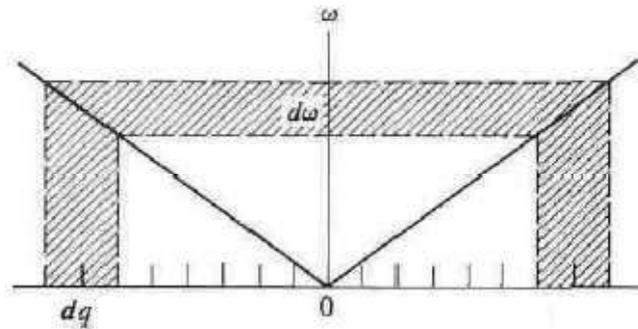where the propagation is described by the wave vector $\mathbf{q} = (q_x, q_y, q_z)$, whose direction specifies the direction of wave propagation. Here again we need to take into account the boundary conditions. For simplicity, we assume a cubic sample whose edge is *L*. By imposing the periodic boundary conditions, one finds that the allowed values of $\boldsymbol{q}$ must satisfy the condition

$$e^{iq_xL} = e^{iq_yL} = e^{iq_zL} \tag{5.21}$$

Therefore, the values are given by

$$(q_x, q_y, q_z) = (l\frac{2\pi}{L}, m\frac{2\pi}{L}, n\frac{2\pi}{L}) \tag{5.22}$$

where *l, m, n* are some integers

if we plot these values in a *q*-space, as in Fig.5.2, we obtain a three-dimensional cubic mesh. The volume assigned to each point in this *q*-space is $(2\pi/L)^3$.
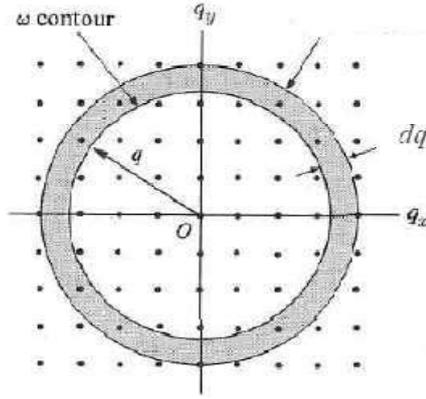

Fig.5.2:Three-dimensional cubic mesh (After Kittel, 1979)

Each point in Fig.5.2 determines one mode. We now wish to find the number of modes lying in the spherical shell between the radii q and $q + dq$, as shown in Fig.2. The volume of this shell is, $4\pi q^2 dq$ and since the volume per point is $(2\pi/L)^3$, it follows that the number we seek

$$\left(\frac{L}{2\pi}\right)^3 4\pi q^2 dq = \frac{V}{(2\pi)^3} 4\pi q^2 dq \tag{5.23}$$

where $V = L^3$ is the volume of the sample. By definition of the density of modes, this quantity is equal to $D(\omega)d\omega$. Thus, we arrive at

$$D(\omega) = \frac{Vq^2}{2\pi^2} \frac{1}{d\omega/dq} \tag{5.24}$$

We note that Eq. (5.24) is valid only for an *isotropic solid*, in which the vibrational frequency, ω, does not depend on the direction of **q**. Also we note that in the above discussion we have associated a single mode with each value of *q*. This is not quite true for the 3D case, because for each *q* there are actually three different modes, one longitudinal and two transverse, associated with the same value of *q*. In addition, in the case of non-Bravais lattice we have a few sites, so that the number of modes is 3*s*, where *s* is the number of non-equivalent atoms. This should be taken into account by index *p*=1…3*s* in the density of states because the dispersion relations for the longitudinal and transverse waves are different, and acoustic and optical modes are different.

3.2.1 Debye model

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

$$\omega = vq \tag{5.25}$$

where v is the velocity of sound.

In this approximation the density of states is given by

$$D(\omega) = \frac{V\omega^2}{2\pi^2 v^3} \tag{5.26}$$

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

The normalization condition for the density of states determines the limits of integration over ω. The lower limit is obviously ω=0. The upper limit can be found from the condition that the number of vibrational modes in a crystal is finite and is equal to the number of degrees of freedom of the lattice. Assuming that there are N unit cells is the crystal, and there is only one atom per cell (so that there are N atoms in the crystal), the total number of phonon modes is $3N$. Therefore, we can write

$$\sum_p \int_0^{\omega_D} D(\omega) d\omega = 3N \tag{5.27}$$

where the cutoff frequency ω_D is known as Debye frequency. Assuming that the velocity of the three acoustic modes is independent of polarization and substituting Eq.(5.26) in Eq.(5.27) we obtain

$$\omega_D = \left(\frac{6\pi^2 v^3 N}{V}\right)^{1/3} \tag{5.28}$$

The cutoff wave vector which corresponds to this frequency is given by

$$q_D = \frac{\omega_D}{v} = \left(\frac{6\pi^2 N}{V}\right)^{1/3} \tag{5.29}$$

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

The thermal energy is given by Eq. (5.12), so that

$$E = 3 \int_0^{\omega_D} d\omega \frac{V\omega^2}{2\pi^2 v^3} \frac{\hbar\omega}{e^{(\hbar\omega/k_B)} - 1} \tag{5.30}$$

where a factor of 3 is due to the assumption that the phonon velocity is independent of polarization. This leads to

$$E = \frac{3V\hbar}{2\pi^2 v^3} \int_0^{\omega_D} d\omega \frac{\omega^3}{e^{(\hbar\omega/k_B T)} - 1} = \frac{3V k_B^4 T^4}{2\pi^2 v^3 \hbar^3} \int_0^{x_D} dx \frac{x^3}{e^x - 1} \qquad (5.31)$$

Where $x = \dfrac{\hbar\omega}{k_B T}$ and

$$x_D = \frac{\hbar\omega_D}{k_B T} = \frac{\theta_D}{T} \qquad (5.32)$$

The latter expression defines the Debye temperature

$$\theta_D = \frac{\hbar v}{k_B}\left(\frac{6\pi^2 N}{V}\right)^{1/3} \qquad (5.33)$$

The total phonon energy is then

$$E = 9Nk_B T \left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} dx \frac{x^3}{e^x - 1} \qquad (5.34)$$

where N is the number of atoms in the crystal and $x_D = \dfrac{\theta_D}{T}$.

The heat capacity is most easily found by differentiating the middle expression of Eq.(5.31) with respect to the temperature so that

$$C_v = \frac{3V\hbar^2}{2\pi^2 v^3 k_B T^2} \int_0^{\omega_D} d\omega \frac{\omega^4 e^{\hbar\omega/k_B T}}{\left(e^{\hbar\omega/k_B T} - 1\right)^2} = 9Nk_B \left(\frac{T}{\theta_D}\right)^3 \int_0^{x_D} dx \frac{x^4 e^x}{(e^x - 1)^2} \qquad (5.35)$$

In the limit $T \gg \theta$, 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 $E = 3Nk_B T$ which results in $C_v = 3Nk_B$. This is known as the *Dulong-Petit* law.

Now consider an opposite limit, i.e. $T \ll \theta$. At very low temperatures we can approximate (5.34) by letting the upper limit go to infinity. We obtain

$$E = 9Nk_B T \left(\frac{T}{\theta_D}\right)^3 \int_0^\infty dx \frac{x^3}{e^x - 1} = 9Nk_B T \left(\frac{T}{\theta_D}\right)^3 \frac{\pi^4}{15} = \frac{3\pi^4}{5} Nk_B T \left(\frac{T}{\theta_D}\right)^3 \qquad (5.36)$$

and therefore

$$C_v = \frac{12\pi^4}{5} Nk_B T \left(\frac{T}{\theta_D}\right)^3 \qquad (5.37)$$

We see that within the Debye model at low temperatures the heat capacity is proportional to T^3. The cubic dependence may be understood from the following qualitative argument. At low temperature, only a few modes are excited. These are the modes whose quantum energy $\hbar\omega$ is less than $k_B T$. The number of these modes may be estimated by drawing a sphere in the q-space whose frequency $\omega = \hbar/k_B T$, and counting the number of points inside, as shown in Fig. 5.3. This sphere may be called the *thermal sphere,* in analogy with the Debye sphere discussed above. The number of modes inside the thermal sphere is proportional to $q^3 \sim \omega^3 \sim T^3$. Each mode is fully excited and has an average energy equal to $k_B T$. Therefore the total energy of excitation is proportional to T^3, which leads to a specific heat proportional to T^3, in agreement with Eq. (5.37).
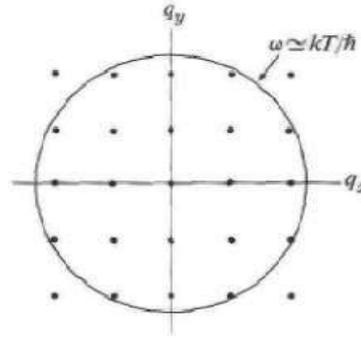

Fig.5.3: The thermal sphere (After Kittel, 1979)

3.2.2 Einstein model

Within the Einstein model the density of states is approximated by a delta function at some frequency ω_E i.e.

$$D(\omega) = N\delta(\omega - \omega_E) \qquad (5.38)$$

where N is the total number of atoms (oscillators). ω_E is known as the Einstein frequency. The thermal energy of the system is then

$$E = \frac{3N\hbar\omega_E}{e^{(\hbar\omega_E/k_B T)}-1} \qquad (5.39)$$

where a factor of 3 reflects the fact that there are three degree of freedom for each oscillator. The heat capacity is then

$$C_v = \left(\frac{\partial E}{\partial T}\right)_V = 3Nk_B \frac{\hbar\omega_E}{k_B T}\frac{e^{\hbar\omega_E/k_B T}}{\left(e^{(\hbar\omega_E/k_B T)}-1\right)} \qquad (5.40)$$

The high temperature limit for the Einstein model is the same as that for the Debye model, i.e. $C_v = 3Nk_B$, which is the Dulong-Petit law. At low temperatures however Eq.(5.40) decreases as $C_v \sim e^{-\frac{\hbar\omega_E}{k_B T}}$, while the experimental form of the phonon is known to be T^3 as given by the Debye model. The reason for this disagreement is that at low temperatures only acoustic phonons are populated and the Debye model is much better approximation that the Einstein model. The Einstein model is often used to approximate the optical phonon part of the phonon spectrum. Concluding our discussion about the heat capacity we note that a real

density of vibrational modes could be much more complicated than those described by the Debye and Einstein models.

3.3 Thermal conductivity

When the two ends of a given sample 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,

$$j = -K \frac{dT}{dx} \qquad (5.41)$$

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 to make a positive quantity).

Heat may be transmitted in the material by several independent agents. In metals, for example, the heat is carried by both 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, corresponding to all the q's in the Brillouin zone (BZ), 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 is given by

$$K = \frac{1}{3} C_v v l \qquad (5.42)$$

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 distances between two consecutive scattering events, so that $l = v\tau$, where τ is the average time between collisions which is called *collision time* or *relaxation time*.

Let us give a qualitative explanation for Eq. (5.42). For simplicity we consider a one-dimensional picture, in which phonons can move only along the x axis. We assume that a temperature gradient is imposed along the x axis. We also assume that collisions between phonons maintain local thermodynamic equilibrium; so that we can assign local thermal energy density to a particular point of the sample $E[T(x)]$. The phonons which originate from this point have this energy on average. At a given point x half the phonons come from the high temperature side and half phonons come from the low temperature side. The phonons which arrive to this point from the high-temperature side will, on the average, have had their last collision at point $x-l$, and will therefore carry a thermal energy density of $E[T(x-l)]$. Their contribution to the thermal current density at point x will therefore be the ½$vE[T(x-l)]$. The phonons arriving at x from the low temperature side, on the other hand,

will contribute $-\frac{1}{2}vE[T(x+l)]$, since they come from the positive x-direction and are moving toward negative x. Adding these together gives

$$j = \frac{1}{2}vE\big[T(x-l)\big] + \frac{1}{2}vE\big[T(x+l)\big] \tag{5.43}$$

Provided that the variation in the temperature over the mean free path is very small we may expand this about the point x to find:

$$j = vl\frac{dE}{dT}\left(-\frac{dT}{dx}\right) = v^2\tau\frac{dE}{dT}\left(-\frac{dT}{dx}\right) \tag{5.44}$$

This result can be easily generalized to the three dimensional case. We need to replace v by the x-component v_x, and then average over all the angles. Since $\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle$ $\frac{1}{3}v^2$ and since $\quad C_v = \dfrac{dE}{dT}$ is the heat capacity we obtain,

$$j = \frac{1}{3}C_v vl\left(-\frac{dT}{dx}\right) \tag{5.45}$$

where v is the phonon velocity.

Let us now discuss the 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.

Consider a collision of type (a). The phonon-phonon scattering is due to the *anharmonic* interaction between them. When the atomic displacements become appreciable, this gives rise to anharmonic coupling between the phonons, causing their mutual scattering. Suppose that two phonons of vectors $\mathbf{q}_1$ and $\mathbf{q}_2$ collide, and produce a third phonon of vector $\mathbf{q}_3$. Since momentum must be conserved, it follows that $\mathbf{q}_3 = \mathbf{q}_1 + \mathbf{q}_2$. Although both $\mathbf{q}_1$ and $\mathbf{q}_2$ lie inside the Brillouin zone (Brillouin zones are primitive cells that arise in the theories of electronic levels - Band Theory), $\mathbf{q}_3$ may not do so. If it does, then the momentum of the system before and after collision is the same. Such a process has no effect at all on thermal resistivity, as it has no effect on the flow of the phonon system as a whole. It is called a *normal* process. By contrast, if $\mathbf{q}_3$ lies outside the BZ, such a vector is not physically meaningful according to our convention. We reduce it to its equivalent $\mathbf{q}_4$ inside the first BZ, where $\mathbf{q}_3 = \mathbf{q}_4 + \mathbf{G}$ and $\mathbf{G}$ is the appropriate reciprocal lattice vector. As is seen from Fig.5.6, the phonon $\mathbf{q}_4$ produced by the collision travels in a direction almost opposite to either of the original phonons $\mathbf{q}_1$ and $\mathbf{q}_2$. The difference in momentum is transferred to the center of mass of the lattice. This type of process is highly efficient in changing the momentum of the phonon, and is responsible for phonon scattering at high temperatures. It is known as the *umklapp process* (German for "flipping over").
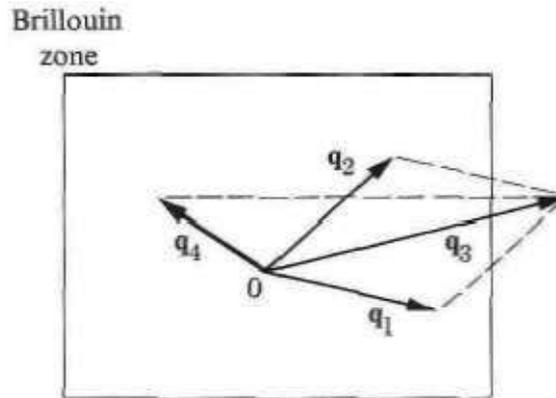
Fig.5.6: Umklapp process(After Kittel, 1979)

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, $l \propto 1/T$. 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 $10^0 K$), 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.

4.0   Conclusion

There are two contributions to thermal properties of solids: one comes from *phonons* (or lattice vibrations) and another from *electrons*. In most solids, the energy given to lattice vibrations is the dominant contribution to specific heat.

5.0   Summary

- Lattice heat capacity is the contribution of phonon to heat capacity
- Debye model at low temperature is proportional to T^3
- Dulong Petit law results in $Cv = 3Nk_B$ for N atoms
- Einstein model is used to approximate the optical part of the phonon spectrum
- Changing the momentum of the phonon which is responsible for phonon scattering at high temperatures is known as the *umklapp process*

Module 4:

SEMICONDUCTORS AND SUPERCONDUCTORS

1.0 Introduction

In a semiconductor the valence band is almost completely filled while the conduction band is empty. Thermal excitation or (energy) absorption processes may cause some electrons to cross the band gap, making it similar to semimetals. Semiconductors tend to be bonded tetrahedrally and covalently, although binary semiconductors may have polar, as well as covalent character.

2.0 Objective

- The objective of this unit is to
- Understand the structure and bonding in semiconductors.
- Explain intrinsic semiconductors.
- Understand the importance of impurity states of semiconductors.

Definition

Semiconductors are electronic conductors with electrical resistivity values generally in the range of 10^{-2} to 10^9 ohm-cm at room temperature, intermediate between good conductors(10^{-6} ohm-cm) and insulators (10^{14} to 10^{22} ohm-cm).

3.1 Crystal structure and bonding

Semiconductors include a large number of substances of widely different chemical and physical properties. These materials are grouped into several classes of similar behavior, the classification being based on the position in the periodic table of the elements.

The best-known class is the Group IV semiconductors - C (diamond), Si, *Ge,* - all of which lie in the fourth column of the periodic table. They have been studied intensively, particularly Si and Ge, which have found many applications in electronic devices. The elemental semiconductors all crystallize in the diamond structure. The diamond structure has an fcc lattice with a basis composed of two identical atoms, and is such that each atom is surrounded by four neighboring atoms, forming a regular tetrahedron. Group IV semiconductors are covalent crystals, i.e., the atoms are held together by covalent bonds. These bonds consist of two electrons of opposite spins distributed along the line joining the two atoms. The covalent electrons forming the bonds are hybrid sp^3 atomic orbitals.

Another important group of semiconductors is the Group III-V compounds, so named because each contains two elements, one from the third and the other from the fifth column of the periodic table. The best-known members of this group are *GaAs* and InSb (indium antimonite), but the list also contains compounds such as *GaP*, InAs, *GaSb,* and many others. These substances crystallize in the zinc blend structure which is the same as the diamond structure, except that the two atoms forming the basis of the lattice are now different. Thus, in *GaAs*, the basis of the fcc lattice consists of two atoms, Ga and As. Because of this structure, each atom is surrounded by four others of the opposite kind, and these latter atoms form a regular tetrahedron, just as in the diamond structure.

The bonding in the III-V compounds is also primarily covalent. The eight electrons required for the four tetrahedral covalent bonds are supplied by the two types of atoms, the trivalent atom contributing its three valence electrons, and the pentavalent atom five electrons. The bonding in this group is not entirely covalent. Because the two elements in the compound are different, the distribution of the electrons along the bond is not symmetric, but is displaced toward one of the atoms. As a result, one of the atoms

acquires a net electric charge. Such a bond is called *heteropolar,* in contrast to the purely covalent bond in the elemental semiconductors, which is called *homopolar.*

The distribution of electrons in the bond is displaced toward the atom of higher *electronegativity.* In *GaAs* for instance, the *As* atom has a higher electronegativity than the Ga, and consequently the *As* atom acquires a net negative charge, whose value is $-0.46e$ per atom (a typical value in Group III-V compounds). The Ga atom correspondingly acquires a net positive charge of $0.46e$. Charge transfer leads to an ionic contribution to the bonding in Group III-V compounds. Their bonding is therefore actually a mixture of covalent and ionic components, although covalent ones predominate in most of these substances.

3.2 Bonding structure

A semiconductor is a solid in which the highest occupied energy band, the *valence band,* is completely full at $T = 0°K$, but in which the gap above this band is also small, so that electrons may be excited thermally at room temperature from the valence band to the next-higher band, which is known as the *conduction band*. Generally speaking, the number of excited electrons is appreciable (at room temperature) whenever the energy gap E_F is less than 2 eV. The substance may then be classified as a semiconductor. When the gap is larger, the number of electrons is negligible, and the substance is an insulator. When electrons are excited across the gap, the bottom of the conduction band (CB) is populated by electrons, and the top of the valence band (VB) by holes. As a result, both bands are now only partially full, and would carry a current if an electric field were applied. The conductivity of the semiconductor is small compared with the conductivities of metals of the small number of electrons and holes involved, but this conductivity is nonetheless sufficiently large for practical purposes. The simplest band structure of a semiconductor is indicated in Fig.1.1. Since we are interested only in the region which lies close to the band gap, where electrons and holes lie, we can ignore a more complex variation of the energy bands far away from the gap. The energy of the CB has the form.

$$E_c(k) = E_c + \frac{\hbar^2 k^2}{2m_e} \qquad (1.1)$$

where k is the wave vector and m_e the effective mass of the electron. The energy E_g represents the energy gap. The zero-energy level is chosen to lie at the top of the VB. The energy of the VB (Fig.1.1) may be written as

$$E_v(k) = E_v - \frac{\hbar^2 k^2}{2m_h} \qquad (1.2)$$

Where m_h is the effective mass of the hole which is positive. (Because of the inverted shape of the VB, the mass of an electron at the top of the VB is negative, but the mass of a hole is positive).
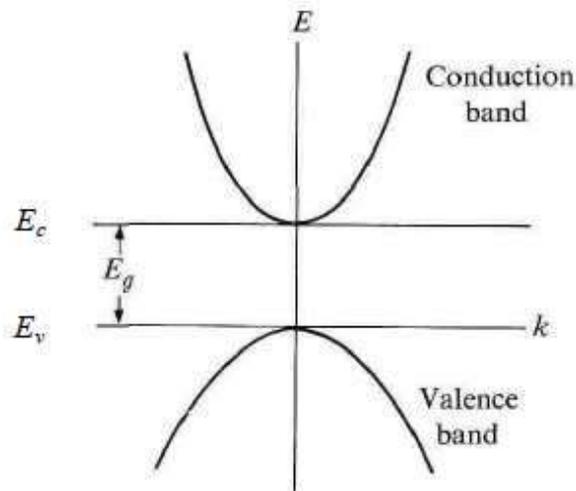
Fig. 1.1: Band structure in a semiconductor.

Within this simple picture of the semiconductor, the primary band-structure parameters are thus the electron and hole masses m_e and m_h, and the band gap E_g. Table 1.1 gives these parameters for various semiconductors. Note that the masses differ considerably from the free-electron mass. In many cases they are much smaller than the free-electron mass. The energy gaps range from 0.18 eV in *InSb* to 3.7 eV in ZnS. The table also shows that the wider the gap, the greater the mass of the electron. The energy gap for a semiconductor varies with temperature, but the variation is usually slight. That a variation with temperature should exist at all can be appreciated from the fact that the crystal, when it is heated, experiences a volume expansion, and hence a change in its lattice constant. This, in turn, affects the band structure, which is a sensitive function of the lattice constant. The band structure in Fig 1.1 is the simplest possible structure. Band structures of real semiconductors are somewhat more complicated, as we shall see later.

3.3   Intrinsic Semiconductors

In the field of semiconductor, electrons and holes are usually referred to as *free carriers,* or simply *carriers,* because it is these particles which are responsible for carrying the electric current. The number of carriers is an important property of a semiconductor, as this determines its electrical conductivity. *Intrinsic semiconductors* are semiconductors in which the number of carries and the conductivity is not influenced by impurities. Intrinsic conductivity is typical at relatively high temperatures in highly purified specimens. In order to determine the number of carriers, we need some of the basic results of statistical mechanics.

Table 1.1. Band Structure parameters of Semiconductors

Group	Crystal	E_g(eV)	m_e/m	m_h/m
IV	C	5.3		
IV	Si	1.1	0.19	0.16
IV	Ge	0.7	0.08	0.04
III-V	GaAs	1.4	0.07	0.09
III-V	GaP	2.3	0.12	0.50
III-V	InSb	0.2	0.01	0.18
II-VI	ZnS	3.6	0.40	5.41
II-VI	ZnSe	2.7	0.1	0.6
II-VI	CdSe	1.7	0.13	0.45

The most important result in this regard is the Fermi-Dirac (FD) distribution function.

$$f(E) = \frac{1}{e^{\left[(E-\mu)/k_B T\right]}+1} \tag{1.3}$$

This function, gives the probability that an energy level E is occupied by an electron when the system is at temperature T. The function is plotted versus E in Fig.1.2. Here we see that, as the temperature rises, the unoccupied region below the Fermi level E_F becomes longer, which implies that the occupation of high energy states increases as the temperature is raised, a conclusion which is most plausible, since increasing the temperature raises the overall energy of the system.
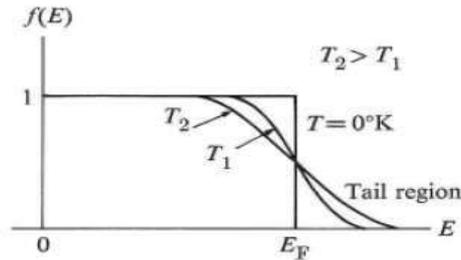
Fig. 1.2: The Fermi-Dirac distributions function (After Kittel, 1979)

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We will see later that the Fermi level in intrinsic semiconductors lies close to the middle of the band gap. Therefore we can represent the distribution function and the conduction and valence bands of the semiconductor as shown in Fig.1.3.
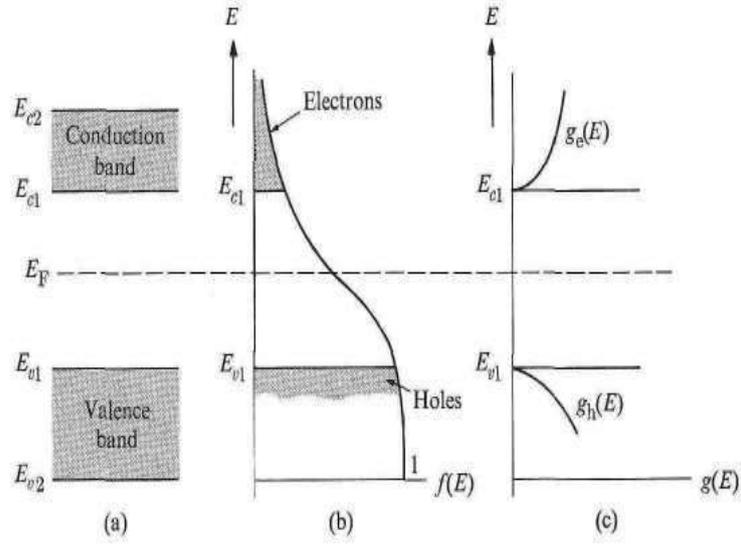
Fig.1.3: (a) conduction and valence bands (b) the distribution function
(c) Density of states for electrons and holes (After Kittel, 1979)

.

First we calculate the concentration of electrons in the CB. The number of states in the energy range (E, E + dE) is equal to $D_e(E)dE$, where $D_e(E)$ is the density of electron states. Since each of these states has an occupation probability f (E), the number of electrons actually found in this energy range is equal to $f(E)D_e(E)dE$. The concentration of electrons throughout the CB is thus given by the integral over the conduction band.

$$n = \int_{E_c}^{\infty} f_e(E)D_e(E)dE \tag{1.4}$$

where E_c is the bottom the conduction band, as shown in Fig.1.3.

The band gap in semiconductors is of the order of 1eV, which is much larger than kT. Therefore $(E-\mu) \gg k_B T$ and we can neglect the unity term in the denominator of the distribution function Eq. (1.3), so that

$$f_e(E) \approx e^{-(E-\mu)/k_B T} \tag{1.5}$$

The density of the conduction band is given by

$$D_e(E) = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2}(E - E_c)^{1/2} \tag{1.6}$$

Note that $D_e(E)$ vanishes for $E < E_c$ and is finite only for $E > E_c$ as shown in Fig.1.3. When we substitute equations for $f(E)$ and $D_e(E)$ into Eq. (1.4), we obtain

$$n = \frac{1}{2\pi^2}\left(\frac{2m_e}{\hbar^2}\right)^{3/2} e^{\mu/kT} \int_{E_n}^{\infty} (E - E_c)^{1/2} e^{-E/k_B T} dE \tag{1.7}$$

By changing the variable, and using the result

$$\int_0^{\infty} x^{1/2} e^{-x} dE = \frac{\sqrt{\pi}}{2} \tag{1.8}$$

one can readily evaluate the integral in (1.7). The electron concentration then reduces to the expression

$$n = 2\left(\frac{m_e kT}{2\pi\hbar^2}\right)^{3/2} e^{(\mu - E_c)/k_B T} \tag{1.9}$$

The electron concentration is still not known explicitly because the Fermi energy μ is so far unknown. Essentially the same ideas employed above may also be used to evaluate the number of holes in the VB. The probability that a hole occupies a level E in this band is equal to $1-f(E)$, since $f(E)$ is the probability of electron occupation. Assuming that the Fermi level lies close to the middle of the band gap, i.e. $(\mu-E)>>k_B T$ for the valence band, we find for the distribution function of holes

$$f_h(E) = 1 - \frac{1}{e^{[(E-\mu)/k_B T]} + 1} = \frac{1}{e^{[(\mu-E)/k_B T]}} \approx e^{-(\mu-E)/k_B T} \tag{1.10}$$

The density of states for the holes is

$$D_h(E) = \frac{1}{2\pi^2}\left(\frac{2m_h}{\hbar^2}\right)^{3/2} (E_v - E)^{1/2} \tag{1.11}$$

where E_v is the energy of the valence band edge. Proceeding in a similar fashion as we did for electrons we find for the concentration of holes in the valence band

$$p = \int_{-\infty}^{E_v} f_h(E) D_h(E) dE = 2\left(\frac{m_h kT}{2\pi\hbar^2}\right)^{3/2} e^{(E_v - \mu)/k_B T} \tag{1.12}$$

The electron and hole concentrations have thus far been treated as independent quantities. For intrinsic semiconductors the two concentrations are, in fact, equal, because the electrons in the CB are due to excitations from the VB across the energy gap, and for each electron thus excited a hole is created in the VB. Therefore,

n = p

$$\tag{1.13}$$

and

$$(m_e)^{3/2}e^{(\mu - E_c)/k_B T} = (m_h)^{3/2}e^{(E_v - \mu)/k_B T} \qquad \textbf{(1.14)}$$

We obtain then, for the Fermi energy

$$\mu = \frac{E_v - E_c}{2} + \frac{3}{4}k_B T \ln \frac{m_h}{m_e} \qquad \textbf{(1.15)}$$

The second term on the right of (1.15) is very small compared with the first, and the energy level is close to the middle of the energy gap. This is consistent with earlier assertions that both the bottom of the CB and the top of the VB are far from the Fermi level. The concentration of electrons may now be evaluated explicitly by using the above value of μ. Substitution of Eq. (1.15) into Eq. (1.9) yields

$$n = 2\left(\frac{k_B T}{2\pi\hbar^2}\right)^{3/2}(m_e m_h)^{3/4}e^{-E_g/2k_B T} \qquad \textbf{(1.16)}$$

where $E_g = E_c - E_v$ is the band gap. The important feature of this expression is that n increases very rapidly - exponentially - with temperature, particularly by virtue of the exponential factor. Thus as temperature is raised, a vastly greater number of electrons is excited across the gap. Our discussion of carrier concentration in this section is based on the premise of a pure semiconductor. When the substance is *impure,* additional electrons or holes are provided by the impurities. In that case, the concentrations of electrons and holes may no longer be equal, and the amount of each depends on the concentration and type of impurity present. When the substance is sufficiently pure so that the concentrations of electrons and holes are equal, we speak of an *intrinsic semiconductor.* That is, the concentrations are determined by the intrinsic properties of the semiconductor itself. On the other hand, when a substance contains a large number of impurities which supply most of the carriers, it is referred to as an *extrinsic semiconductor.*

3.4   Impurity states

A pure semiconductor has equal numbers of both types of carriers, electrons and holes. In most applications, however one needs specimens which have one type of carrier only, and none of the other. By doping the semiconductor with appropriate impurities, one can obtain samples which contain either electrons only or holes only. Consider, for instance, a specimen of Si which has been *doped* by As. The *As* atoms (the impurities) occupy some of the lattice sites formerly occupied by the Si host atoms. The distribution of the impurities is random throughout the lattice. But their presence affects the solid in one very important respect. The *As* atom has valence 5 while Si has valence 4. Of the five electrons of *As,* four participate in the tetrahedral bond of Si, as shown in Fig. 1.4. The fifth electron cannot enter the bond, which is now saturated, and hence this electron detaches from the impurity and is free to migrate through the crystal as a conduction electron, i.e., the electron enters the CB. The impurity is now actually a positive ion, As^+ (since it has lost one of its electrons), and thus it tends to capture the free electron, but we shall show shortly that the attraction force is very weak, and not enough to capture the electron in most circumstances. The net result is that the *As* impurities contribute

electrons to the CB of the semiconductors, and for this reason these impurities are called *donors*. Note that the electrons have been created *without* the generation of holes.
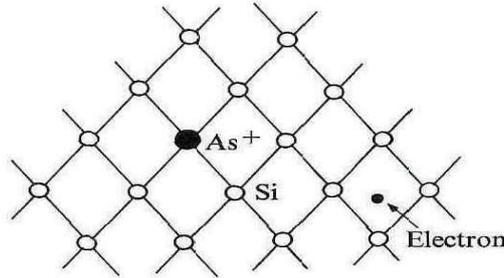

Fig.1.4: An As impurity in a Si crystal. The extra electron migrates through the crystal.

When an electron is captured by an ionized donor, it orbits around the donor much like the situation in hydrogen. We can calculate the binding energy by using the familiar Bohr model. However, we must take into account the fact that the coulomb interaction here is weakened by the screening due to the presence of the semiconductor crystal, which serves as a medium in which both the donor and ion reside. Thus the coulomb potential is now given by

$$V(r) = -\frac{e^2}{\varepsilon r} \qquad (1.17)$$

where ε is the reduced dielectric constant of the medium . The dielectric constant $\varepsilon = 11.7$ in Si, for example, shows a substantial decrease in the interaction force. It is this screening which is responsible for the small binding energy of the electron at the donor site. Using this potential in the Bohr model, we find the binding energy, corresponding to the ground state of the donor, to be

$$E_d = -\frac{e^4 m_e}{2\varepsilon^2 \hbar^2} \qquad (1.18)$$

Note that binding energy of the hydrogen atom, which is equal to 13.6 eV. The binding energy of the donor is reduced by the factor $1/\varepsilon^2$, and also by the mass factor m_e/m which is usually smaller than unity. Using the typical values $\varepsilon \sim 10$ and $m_e/m \sim 0.1$, we find that the binding energy of the donor is about 10^{-3} of the hydrogen energy, i.e., about 0.01 eV. This is indeed the order of the observed values. The donor level lies in the energy gap, very slightly below the conduction band, as shown in Fig.1.5. Because the level is so close to the CB, almost all the donors are ionized at room temperature, their electrons have been excited into CB.
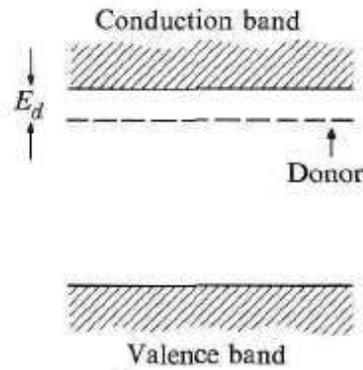
Fig. 1.5: The donor level in a semiconductor

It is instructive to evaluate the Bohr radius of the donor electron. Straightforward adaptation of the Bohr result leads to

$$r_d = \varepsilon \frac{m}{m_e} a_0 \qquad (1.19)$$

where a_0 is the Bohr radius, equal to 0.53 Å. The radius of the orbit is thus much larger than a_0, by a factor of 100, if we use the previous values for ε and m_e. A typical radius is thus of the order of 50 Å. Since this is much greater than the inter atomic spacing, the orbit of the electron encloses a great many host atoms, and our picture of the lattice acting as a continuous, polarizable dielectric is thus a plausible one. Since the donors are almost all ionized, the concentration of electrons is nearly equal to that of the donors. Typical concentrations are about $10^{15} cm^3$. But sometimes much higher concentrations are obtained by doping of the sample, for example, $10^{18} cm^{3}$ or even more.

3.5   Acceptors

An appropriate choice of impurity may produce holes instead of electrons. Suppose that the Si crystal is doped with Ga impurity atoms. The Ga impurity resides at a site previously occupied by a Si atom, but since Ga is trivalent; one of the electron bonds remains vacant (Fig.1.6). This vacancy may be filled by an electron moving in from another bond, resulting in a vacancy (or hole) at this latter bond. The hole is then free to migrate throughout the crystal. In this manner, by introducing a large number of trivalent impurities, one creates an appreciable concentration of holes, which lack electrons. The trivalent impurity is called an *acceptor,* because it accepts an electron to complete its tetrahedral bond. The acceptor is negatively charged, by virtue of the additional electron it has entrapped. Since the resulting hole has a positive charge, it is attracted by the acceptor. We can evaluate the binding energy of the hole at the acceptor in the same manner followed above in the case of the donor. Again this energy is very small, of the order of 0.01 eV. Thus essentially all the acceptors are ionized at room temperature.
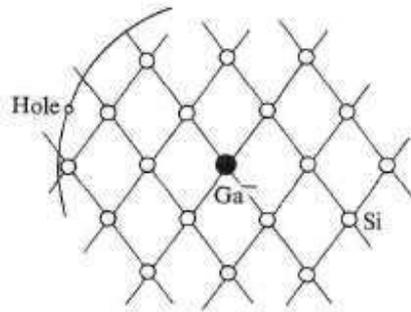
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Fig. 1.6: A Ga impurity in a Si crystal. The extra hole migrates through the crystal

The acceptor level lies in the energy gap, slightly above the edge of the VB, as shown in Fig.1.7. This level corresponds to the hole being captured by the acceptor. When an acceptor is ionized (an electron excited from the top of the VB to fill this hole), the hole falls to the top of the VB, and is now a free carrier. Thus the ionization process, indicated by upward transition of the electron on the energy scale, may be represented by a downward transition of the hole on this scale.
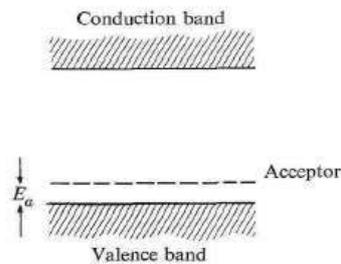

Fig.1.7: The acceptor level in a semiconductor.

4.0   Conclusion
Semiconductors include a large number of substances of widely different chemical and physical properties. The number of carriers (electrons and holes) is an important property of a semiconductor, as this determines its electrical conductivity.

5.0   Summary

- The best-known class of semiconductors is the Group IV (diamond, Silicon, Germanium).
- The valence band is completely full at $T = 0°K$.
- Electrons at room temperature may be excited thermally from the valence band to the next-higher band, known as the *conduction band.*
- The energy of the CB has the form.

$$E_c(k) = E_c + \frac{\hbar^2 k^2}{2m_e}.$$

- The energy of the VB

$$E_v(k) = E_v - \frac{\hbar^2 k^2}{2m_e}$$

- In an intrinsic semiconductor the number of electrons is equal to the number of holes.

6.0   Tutor marked assignment

Q1.   For the nondegenerate case where $E - \mu \gg kT$, calculate the number of electrons per unit volume in the conduction band from the integral

$$n = \int_{E_c}^{\infty} D(E) f(E) dE$$

$D(E)$ is the density of states, $f(E)$ is the Fermi function

Q2.   **(a)**   Compute the concentration of electrons and holes in an intrinsic semiconductor $InSb$ at room temperature (E_g=0.2eV, $m_e = 0.01m$ and $m_h =$ 0.018 m).

(b)   Determine the position of the Fermi.

7.0   Further readings/Reference

Kittel, C., Introduction to solid state physics, Wiley Eastern Limited, 1979
Kachhava, C.M., Solid State physics, Tata McGraw-Hill Publishing Company   Limited, New Delhi, 1992.
Long, D., Energy bands in semiconductors, Wiley, 1968
Smith, R.A., Semiconductors, Cambridge, 1959
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www.pa.uk.edu/kwng.phy/525/lec/lecture-8

1.0   Introduction

In this unit, we are going to study the concentration of the carriers both in the conduction and valence bands and the difference between intrinsic region and the extrinsic region.

2.0   Objective
The objective of this unit is to differentiate
- the intrinsic region from
- the extrinsic region
-

3.0   Definition
3.1   Semiconductor statistics
Semiconductors usually contain both donors and acceptors. Electrons in the CB can be created either by thermal excitation or by thermal ionization of the donors. Holes in the VB may be generated by interband excitation or by thermal excitation of electrons from the VB into the acceptor level. And in addition, electrons may fall from the donor levels to the acceptor level. Figure 2.1 indicates these various processes.
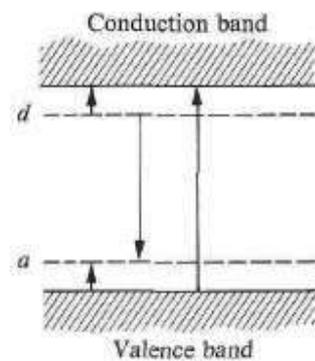

Fig. 2.1: The various electronic processes in a semiconductor

Finding the concentrations of carriers, both electrons and holes, taking all these processes into account, is quite complicated. We shall treat a few special cases, which are often encountered in practice. Two regions may be distinguished, depending on the physical parameters involved: The *intrinsic* and the *extrinsic* regions.

3.1.1. Intrinsic region
The concentration of carriers in the intrinsic region is determined   primarilyby thermally induced interband transitions. In this region *n=p*. The intrinsic region obtains when the impurity doping is small. When we denote the concentrations of donors and acceptors by N_d and $N_a,$ the requirement for the validity of the intrinsic condition is

$$n \gg N_d, N_a \qquad (2.1)$$

Since *n* increases rapidly with temperature, the intrinsic condition becomes more favorable at higher temperatures. All semiconductors, in fact, become intrinsic at sufficiently high temperatures (unless the doping is unusually high).

3.1.2 Extrinsic region

Quite often the intrinsic condition is not satisfied. For the common dopings encountered, about $10^{15} \, cm^{-3}$, the number of carriers supplied by the impurities is large enough to change the intrinsic concentration appreciably at room temperature. The contribution of impurities, in fact, frequently exceeds those carriers that are supplied by interband excitation. When this is so, the sample is in the *extrinsic region.*

Two different types of extrinsic regions may be distinguished. The first occurs when the donor concentration greatly exceeds the acceptor concentration, that is, when $N_d \gg N_a$. In this case; the concentration of electrons may be evaluated quite readily. Since the donor's ionization energy (i.e. the binding energy) is quite small all the donors are essentially ionized, their electrons going into the CB. Therefore, to a good approximation,

$$n = N_d \tag{2.2}$$

A semiconductor in which $n \gg p$ is called an *n-type semiconductor* (*n* for negative). Such a sample is characterized, as we have seen, by a great concentration of electrons. The other type of extrinsic region occurs when $N_a \gg N_d$ that is, the doping is primarily by acceptors. Using an argument similar to the above, one then has,

$$p = N_a \tag{2.3}$$

i.e., all the acceptors are ionized. Such a material is called a *p-type semiconductor.* It is characterized by a preponderance of holes. In discussing ionization of donors (and acceptors), we assumed that the temperature is sufficiently high so that all of these are ionized. This is certainly true at room temperature. But if the temperature is progressively lowered, a point is reached at which the thermal energy becomes too small to cause electron excitation. In that case, the electrons fall from the CB into the donor level, and the conductivity of the sample diminishes dramatically. This is referred to as *freeze-out,* in that the electrons are now "frozen" at their impurity sites. The temperature at which freeze-out takes place is $E_d \sim kT,$ which gives a temperature of about 100°K. The variation of the electron concentration with temperature in an *n-type* sample is indicated schematically in Fig. 2.2.
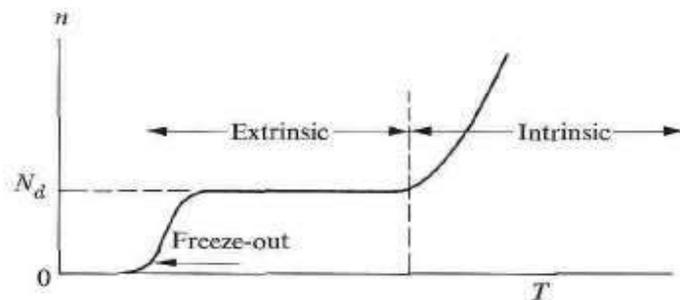

Fig.2.2: Variation of electron concentration n with temperature in an n-type semiconductor.

4.0 Conclusion

Both holes and electrons contribute to conductivity.

5.0 Summary

- Thermal vibration or energy can be used to create a hole by exciting an electron from the valence band to the conduction band.
- In an intrinsic semiconductor (undoped), the number of holes in the valence band is equals the number of electrons in the conduction band.
- an n-type semiconductor is one characterized by a great concentration of electrons.
- a p-type semiconductor is one characterized by a preponderance of holes.

6.0 Tutor marked assignment

Q1. Indium antimonide has E_g = 0.23 eV; dielectric constant ε = 18; electron effective mass m_e = 0.015 m. Calculate

(a) the donor ionization energy and

(b) the radius of the ground state orbit.

Q2. In a particular semiconductor there are 10^{13} donor/cm^3 with an ionization energy E_d of 1 meV and an effective mass 0.01 m.
Estimate the concentration of conduction electrons at 4 K
What is the value of the Hall coefficient? Assume no acceptor atoms are present and that $E_g \gg k_B T$.

7.0 Further readings/References

Kittel, C., Introduction to solid state physics, Wiley Eastern Limited, 1979
Kachhava, C.M., Solid State physics, Tata McGraw-Hill Publishing Company Limited, New Delhi, 1992.
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www.pa.uk.edu/kwng.phy/525/lec/lecture-8

1.0 Introduction

In this unit, we are going to study the electrical conductivity and mobility which are the primary interest in semiconductors, the band structure so that the observed phenomenon in the model structure can be used to obtain quantitative agreement between experiments and theoretical analysis.

2.0 Objective

The objectives of this unit is to

- Understand electrical conductivity which measures both scattering and electron concentration
- Understand electrical mobility which measures scattering
- Understand band structure of real semiconductor

3.0 Definition

Electrical conductivity is the ability of a material to conduct electrical current.

3.1 Electrical conductivity

Electrical conductivity is, of course, the quantity of primary interest in semiconductors. Both electrons and holes contribute to electric current. Assume first that a sample is strongly n-type and contains only one type of carrier: electrons. The conductivity can be treated according to the free- electron model:

$$\sigma_e = \frac{ne^2\tau_e}{m_e} \tag{3.1}$$

where m_e is an effective mass and τ_e is the lifetime of the electron. To estimate the value for σ_e, we substitute $n = 10^{14}\ cm^{-3}$, which is eight orders in magnitude less than that in metals, and $m_e = 0.\text{lm}$. This leads to $\sigma_e \sim 10^{-7}(\mu\ ohm \cdot cm)^{-1}$ which is a typical figure in semiconductors. Although this is many orders of magnitude smaller than the value in a typical metal, where $\sigma_e \sim 1(\mu\ ohm \cdot cm)^{-1}$ the conductivity in a semiconductor is still sufficiently large for practical applications. Semiconductor physicists often use another transport coefficient: *mobility*. The mobility μ_e is defined as the proportionality coefficient between the electron drift velocity and the applied electric field, i.e.

$$|V_e| = \mu_e E \tag{3.2}$$

Where $|V_e|$ is the absolute value of the velocity. Taking into account that $j_e = -en_e V_e$ and $j_e = \sigma_e E$ we find that

$$\mu_e = \frac{e\tau_e}{m_e} \tag{3.3}$$

As defined, the mobility is a measure of the rapidity of the motion of the electron in the field. The longer the lifetime of the electron and the smaller its mass, the higher the mobility. We can now express electrical conductivity in terms of mobility. We can write

$$\sigma_e = ne\mu_e \qquad\qquad (3.4)$$

Indicating that σ_e is proportional to μ_e. A typical value for μ_e may be obtained by substituting $\sigma_e = (\mu\, ohm \cdot cm)^{-1}$ and $n = 10^{14}\, cm^{-3}$ in Eq. (3.4). This yield

$$\mu_e \sim 10^3 cm^3 V^{-1} s^{-1} \qquad\qquad (3.5)$$

What we have said about electrons in a strongly n-type substance can be   carried over to a discussion of holes in a strongly p-type substance. The conductivity of the holes is given by

$$\sigma_h = \frac{pe^2\tau_e}{m_h} = pe\mu_h \qquad\qquad (3.6)$$

where μ_h is the hole mobility.

Let us now treat the general case, in which both electrons and holes are present. When a field is applied, electrons drift opposite to the field and holes drift in the same direction as the field. The currents and conductivities of the two carriers are both additive. Therefore

$$\sigma = \sigma_e + \sigma_h \qquad\qquad (3.7)$$

i.e., both electrons and holes contribute to the currents. In terms of the mobilities, one may write

$$\sigma = ne\mu_e + pe\mu_h \qquad\qquad (3.8)$$

The carriers' concentrations n and p may be different if the sample is doped, as discussed before. And one or the other of the carriers may dominate, depending on whether the semiconductor is $n-$ or $p-type$. When the substance is in the intrinsic region, however, $n = p,$ and Eq. (3.8) becomes

$$\sigma = ne(\mu_e + \mu_h) \qquad\qquad (3.9)$$

where n is the intrinsic concentration. Even now the two carriers do not contribute equally to the current. The carrier with the greater mobility usually the electron contributes the larger share.

3.1.1 Dependence on temperature

Conductivity depends on temperature, and this dependence is often pronounced. Consider a semiconductor in the intrinsic region. Its conductivity is expressed by (3.9). But in this situation the concentration n increases exponentially with temperature, as may be recalled from Eq. (1.16). We may write the conductivity in the form

$$\sigma = F(T)e^{(-E_g/2kT)} \tag{3.10}$$

where $F(T)$ is a function which depends only weakly on the temperature. (This function depends on the mobilities and effective masses of the carriers.) Thus conductivity increases exponentially with temperature as shown in Fig.3.1.
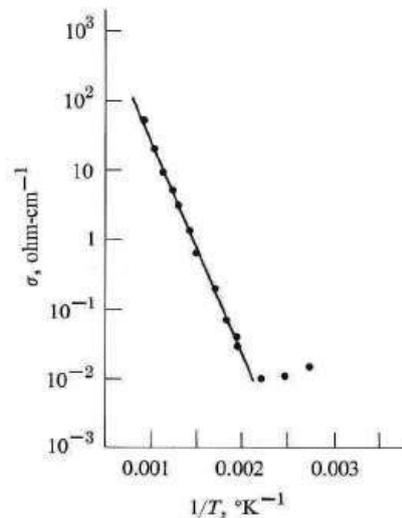

Fig. 3.1: Conductivity of Si versus $1/T$ in the intrinsic range.

This result can be used to determine the energy gaps in semiconductors. In the early days of semiconductor this was the standard procedure for finding the energy gap. Nowadays, however, the gap is often measured by optical methods. When the substance is not in the intrinsic region, its conductivity is given by the general expression (3.8). In that case the temperature dependence of the conductivity on T is not usually as strong as indicated above. To see the reason for this, suppose that the substance is extrinsic and strongly *n-type*. The conductivity is

$$\sigma = ne\mu_e \tag{3.11}$$

But the electron concentration n is now a constant equal to N_d, the donor (hole) concentration. And any temperature dependence present must be due to the mobility of electrons or holes.

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3.1.2 Mobility versus temperature

Mobility of electrons (or holes) varies with temperature. In n-type semiconductor

$$\mu_e \;=\; \frac{e\tau_e}{m_e} = \frac{el_e}{m_e V_e} \tag{3.12}$$

Since the lifetime of the electron, or its collision time, varies with temperature,   its mobility also varies with temperature. Normally, both lifetime and mobility diminish as the temperature rises. The relaxation time is given by $\tau_e = l_e/V_e$ where l_e is the mean free path of the electron and V_e is the drift velocity. The velocity of electrons is different depending on their location in the   conduction band. Electrons at the   bottom of the conduction band in a semiconductor obey the classical statistics and not the highly degenerate Fermi statistics prevailing in metals. The higher electrons are in the band, the greater their velocity. We can evaluate the conductivity by assuming that V_e is the average velocity. The average velocity can be estimated using the   procedure   of   the   kinetic theory of gases:

$$\tfrac{1}{2}\, m_e\, V_e^2 \;=\; \tfrac{3}{2}\, kT \tag{3.13}$$

This introduces a factor of T$^{-1/2}$ dependence in the mobility:

$$\mu_e = \frac{el_e}{m_e^{1/2}(3kT)^{1/2}} \tag{3.14}$$

The mean free path l_e also depends on the temperature, and in much the same way as it does in metals. l_e is determined by the various collision mechanisms acting on the electrons. These mechanisms are the collisions of electrons with thermally excited phonons and collisions with impurities. At high temperatures, at which collisions with phonons is the dominant factor, l_e is inversely proportional to temperature, that is, $l_e \propto T^{-1}$. In that case, mobility varies as $\mu_e \propto T^{3/2}$. Figure 3.2 shows this for *Ge*. Another important scattering mechanism in semiconductors is that of *ionized* impurities. When a substance is doped the donors (or acceptors) lose their   electrons (or holes) to the conduction band. The impurities are thus ionized, and are quite effective in scattering the electrons (holes). At high temperatures this scattering is masked by the much stronger phonon mechanism, but at low temperatures this latter mechanism becomes weak and the ionized-impurity scattering gradually takes over.
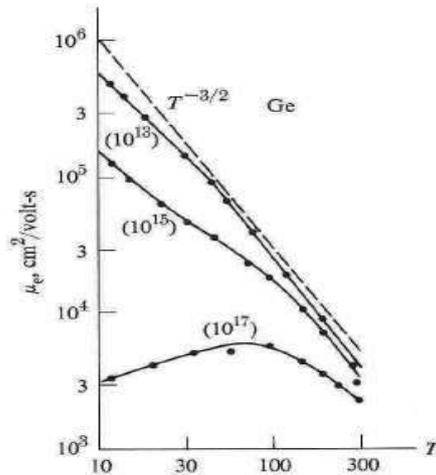
Fig.3.2: Electron mobility versus T in Ge. The dashed curve represents pure phonon scattering; numbers in parentheses refer to donor concentrations.

3.2 Band structure of real semiconductor

So far, we have assumed the simplest possible band structure, namely, a   conduction band of a standard form, centered at the origin, k = 0, and a valence band of a standard inverted form, also centered at the origin. Such a simple structure is applicable for elucidating many observed phenomena, but it does not represent the actual band structures of many common semiconductors. Only when one uses the actual band structure is it possible to obtain a quantitative agreement between experiments and theoretical analysis.

A material whose band structure comes close to the ideal structure is $GaAs$ (Fig. 3.3). The conduction band has a minimum at the origin k = 0 and the region close to the origin

is well represented by quadratic energy dependence, $E(k) = \dfrac{\hbar^2 k^2}{m_e}$, where me = 0.072 m.

Since the electrons are most likely to populate this region, one can represent this band by a single effective mass. Note, however, that as k increases, the energy $E(k)$ is no   longer quadratic in k, and those states may no longer by represented by a   single,   unique effective mass. In particular that the next-higher energy minimum occurs along the [100] direction. The dependence of energy on k in the neighborhood of this *secondary* minimum is quadratic, and hence an   effective mass may be defined locally, but its value is much greater than   that of the primary minimum (at the center). The actual value is 0.36 m. Due to cubic symmetry there are six equivalent secondary minima, or   *valleys*, in all along the [100] directions.
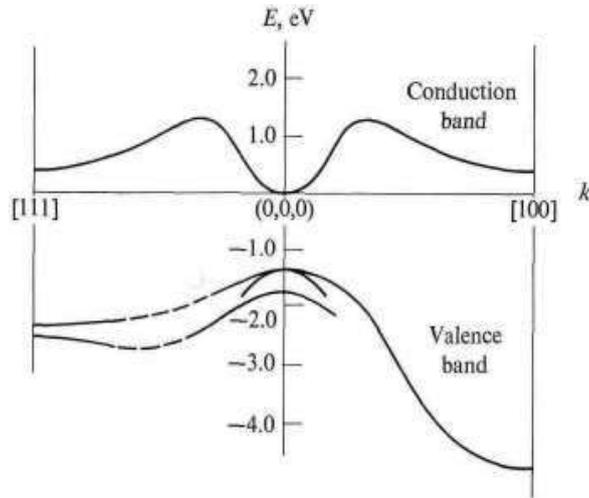
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Fig. 3.3 Band structure of GaAs plotted along the [100] and [111] directions.

These secondary valleys do not play any role under most circumstances, since the electrons usually occupy only the central or primary valley. In such situations, these secondary valleys may be disregarded altogether. There are also other secondary valleys in the [111] directions, as shown in Fig. 3.3. These are higher than the [100] valleys, and hence are even less likely to be populated by electrons. The valence band is also illustrated inFig.3.3. Here it is composed of three closely spaced subbands. Because the curvatures of the bands are different, so are the effective masses of the corresponding holes .One speaks of *light holes* and *heavy holes*. Other III- V semiconductors have band structures quite similar to that of *GaAs*.

Figure 3.4a shows the band structure of Si. An interesting feature is that the conduction band has its lowest (primary) minimum not at k=0. The minimum lies along the [100] direction, at about 0.85 the distance from the center to the edge of the zone. Note that the bottom of the conduction does not lie directly above the top of the valence band. This type of semiconductors is known as *indirect gap semiconductors*. These should be distinguished from *direct gap semiconductors* such as *GaAs*. Because of the cubic symmetry, there are actually six equivalent primary valleys located along the [100] directions. These are illustrated in Fig. 3.4b. The energy surfaces at these valleys are composed of elongated ellipsoidal surfaces of revolution, whose axes of symmetry are along the [100] directions. There are two different effective masses which correspond to these surfaces: the *longitudinal* and the *transverse* effective masses. The longitudinal mass is $m_l = 0.97m$, while the two identical transverse masses are $m_t = 0.19m$. The mass anisotropy ratio is about 5. The valence band in silicon is represented by three different holes (Fig.3.4a). One of the holes is heavy ($m_h = 0.5m$), and the other two are light. The energy gap in Si, from the top of the valence band to the bottom of the conduction band, is equal to 1.08 eV. The fact that the bottom of the conduction does not lie directly above the top of the valence band, is irrelevant to the definition of the band gap.

3.3 Excitons

An electron and a hole may be bound together by their attractive coulomb interaction, just as an electron is bound to a proton to form a neutral

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hydrogen atom. The bound electron-hole pair is called an *Excitons*, Fig.3.5. Excitons can move through the crystal and transport energy; it does not transport charge because it is electrically neutral. It is similar to positronium, which is formed from an electron and a positron. Excitons can be formed in every insulating crystal. All Excitons are unstable with respect to the ultimate recombination process in which the electron drops into the hole. The binding energy of the Excitons can be measured by optical transitions from the valence band, by the difference between the energy required to create an Excitons and the energy to create a free electron and free hole, Fig.3.6.
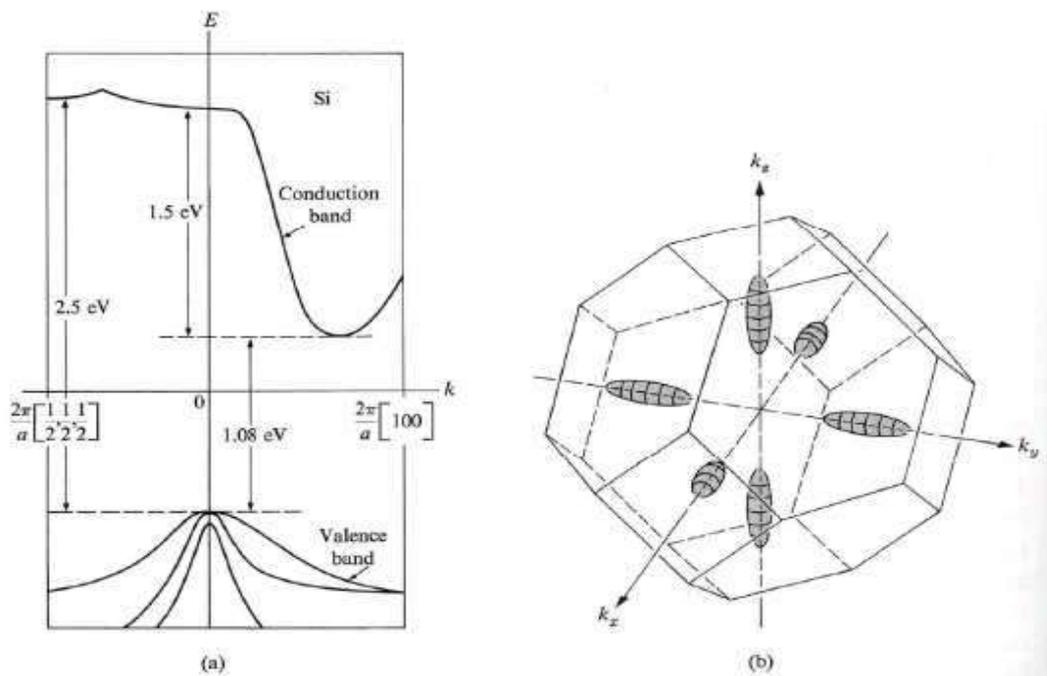

Fig.3.4 (a) Band structure of Si plotted along the [100] and [111] directions, (b) Ellipsoidal energy surfaces corresponding to primary valleys along the [100] directions (After Kittel, 1979)
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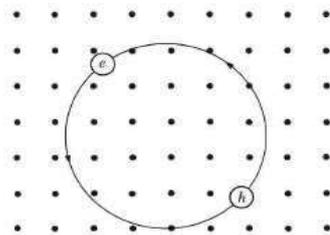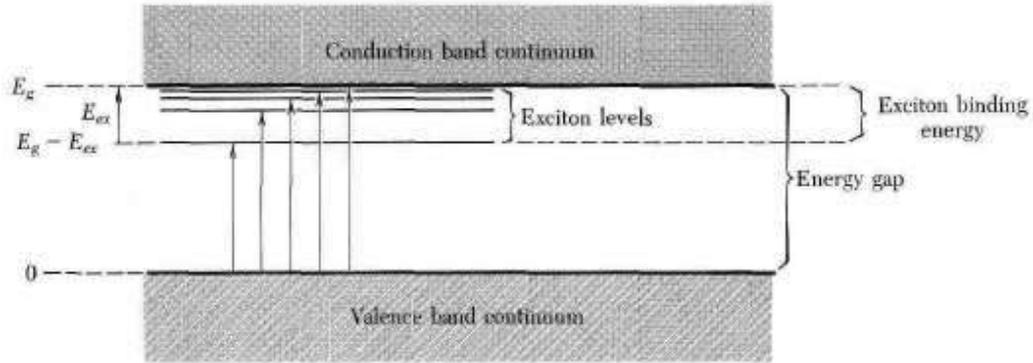**Fig.3.5:** An Excitons, a bound electron-hole pair.

Fig.3.6: Energy levels of Excitons.

Energy levels of Excitons can be calculated as follows. Consider an electron in the conduction band and a hole in the valence band. The electron and hole attract each other by the Coulomb potential

$$V(r) = -\frac{e^2}{\varepsilon r} \tag{3.15}$$

where r is the distance between the particles and ε is the appropriate dielectric constant. There will be bound states of the Excitons system having total energies lower than the bottom of the conduction band. The problem is the hydrogen atom problem if the energy surfaces for the electron and hole are spherical and nondegenerate. The energy levels are given by

$$E_n = E_c - \frac{e^4 \mu}{2\varepsilon^2 \hbar^2 n^2} \tag{3.16}$$

Here *n is* the principal quantum number and μ is the reduced mass:

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h} \tag{3.17}$$

formed from the effective masses of the electron and hole. The Excitons ground   state energy is obtained on setting $n = 1$ in Eq. (316); this is the ionization energy of the Excitons.

Worked example:
At room temperature, $k_B T / e = 26\ mV$. A sample of cadmium sulfide displays a mobile carrier density of 10^{16} cm^{-3} and a mobility coefficient $\mu = 10^2\ cm^2 / volt\ sec$
   (a)   Calculate the electrical conductivity of this sample
   (b)   If the charge carriers have an effective mass equal to 0.1 times the mass of a free electron, what is the average time between successive scatterings
Solutions:
   (a)   From Eq. (3.4), the electrical conductivity in terms of mobility is given by

$$\sigma_e = ne\mu_e$$

With $n = 10^{22} m^{-3}$, $e = 1.6 \times 10^{-19}$, $\mu_e = 10^{-2} m^2 V^{-1} s^{-1}$,

we have $\sigma_e = 16 \Omega^{-1} m^{-1}$

   (b)   From Eq.(3.6), the free electron model of metals gives

$\sigma = \dfrac{ne^2\tau}{m^*}$,   where m^* *is* the effective mass of an electron is, then the average time between successive scattering is

$$\tau = \frac{0.1\sigma}{ne}\left(\frac{m}{e}\right) = 5.7 \times 10^{-15} s$$

4.0   Conclusion

The number of carriers (electrons and holes) is an important property of a semiconductor, as this determines its electrical conductivity. Both   conductivity and mobility (a measure of the rapidity of the motion of the   electron in the field) depend on temperature.

5.0   Summary

- $\sigma_e = \dfrac{ne^2\tau_e}{m_e}$ defines electrical conductivity according to free electron   model.

- $\mu_e = \dfrac{e\tau_e}{m_e}$ defines mobility

- electrical conductivity in terms of mobility is defined as $\sigma_e = ne\mu_e$

- $\sigma = ne\mu_e + pe\mu_h$ defines contribution to the currents by both electrons and holes in terms of the mobilities

- A material whose band structure comes close to the ideal structure is GaAs

- The bound electron-hole pair is called an *Excitons*

6.0   Tutor marked Assignment

    Q1.   A sample of Si contains 10^{-4} atomic per cent of phosphorous donors that are all singly ionized at room temperature. The electron mobility is 0.15 $m^2 V^{-1} s^{-1}$. Calculate the extrinsic resistivity of the sample (for Si, atomic weight = 28,   density = 2300 kg/m3).

    Q2.   Given the data for Si: $\mu_e = 1350$ cm^2/V·s, $\mu_h = 475$ cm^2/V·s, $m_e = 0.19m$, $m_h = 0.16m$ and $E_g = 1.1$ eV, calculate

    (a) The lifetimes of electrons and holes.

    (b) The intrinsic conductivity σ at room temperature

7.0   Further readings/References

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UNIT 4: SUPER CONDUCTIVITY (I): THE BASIC PHENOMENON   page

1.0 Introduction

Superconductivity was first discovered and so named by Kamerlingh Onnes in 1911. In the course of an investigation of the electrical resistance of various metals at liquid helium temperatures, he observed that the resistance of a sample of mercury dropped from 0.08 Ω at about 4 K to less than $3 \times 10^{-6} \Omega$ over a temperature interval of 0.01K. Subsequent attempts showed that the width of the transition region in a particular specimen depends on a number of factors, such as the purity and metallurgical history and can be as sharp as one millidegree or spread over several degrees. While the breadth of the transition may increase if the sample is metallurgically imperfect, the extraordinary smallness of the resistance in the superconducting state appears to hold for all superconductors. Thus, the first characteristic property of a superconductor is that its electrical resistance, for all practical purposes, is zero, below a well-defined temperature T_c, called the critical, or transition temperature. Thus, the conductivity in this range of temperature is infinite; hence the nomenclature of superconductivity.

Figure 4.1 shows how the electrical resistivity in a superconductor becomes immeasurably small at the transition temperature. The figure also contrasts the behaviour of a normal metal for which at very low temperatures, the remanent resistivity is characteristic of residual impurities. The resistance of a superconductor is believed to be zero rather than just very small.
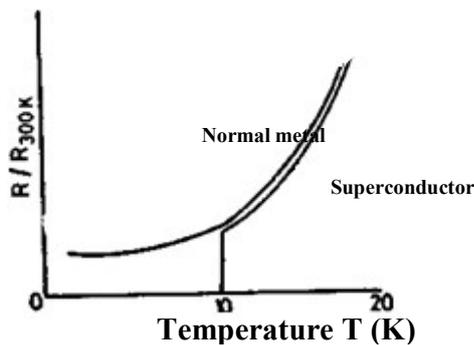

Fig.4.1: Temperature dependence of the resistance: of a normal and superconducting material (After Kachhava, 1992)

2.0 Objective

The objective of this unit is to revise the basics of Superconductors in terms of:
- Empirical criteria
- Transition temperature
- Energy gap

3.0 Definition

Superconductivity is the phenomenon on which the electrical resistivity of metals or alloys drop to zero (infinite conductivity) when cooled into its critical temperature.

3.1   Empirical criteria

There are found to be a number of regularities in the appearance of superconductivity, the principal of which are the following:

I.   Superconductivity has been observed only for those metallic substances for which the number of valence electrons Z lies between 2 and 8.

II.   In all cases involving transition metals, the variation of T_c with number of valence electrons shows sharp maxima for Z = 3, 5 and 7, as shown in Fig. 4.2.

III.   A rather striking correlation (a straight line graph) exists between 3 and Z^2 for elements along given rows of periodic table (Fig. 4.3).

IV.   For a given value of Z, certain crystal structures seem more favourable than others. For example, β-tungsten and α-manganese structure are conductive to the phenomenon of superconductivity.

V.   Ferromagnetic and ferroelectric ordering are found to inhibit superconductivity.

VI. T_c increases with a high power of the atomic volume and inversely as the atomic mass.

VII.   Superconductivity occurs in materials having high normal resistivities. The condition n p > 10^6 is a good criterion for the existence of superconductivity, where n is the number of valence electrons per c.c. and p is the resistivity in electrostatic units at 20°C.

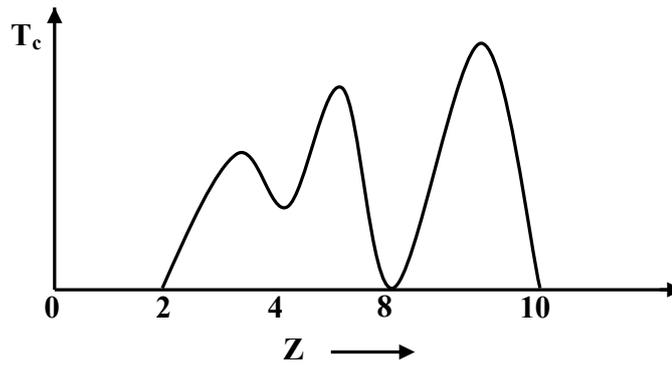These empirical rules have played an important role in the discovery of new superconductors.

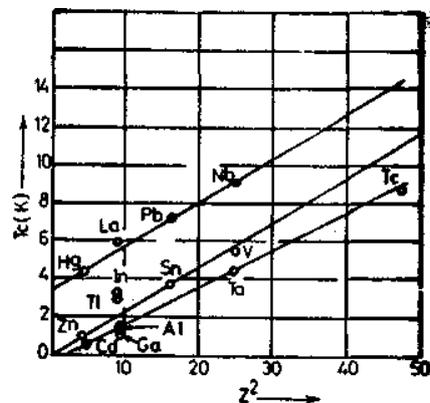Fig 4.2: Variation of transition temperature with number of valence electron

Fig 4.3: Empirical correlation between transition temperature and Z^2(After Kachhava, 1992)

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3.2 Transition Temperature

The temperature at which the normal metal passes into superconducting state is called the transition temperature, T_c. The transition temperature is generally affected by the application of pressure though no specific regularity in the behaviour has been found. The value of T_c for most of the metals lies below 4K; e.g., for Al, it is 1.20 K. For C-15 structure (e.g., V2 Hf), it is 10K; for B-1 structure (e.g., NbN), it is near 13 K, whereas NbZr and NbT1 [BCC (A-2) structure] have the values of T_c as 11.0 and 10.0 K respectively. For A-15 structure, the highest $T_c = 23.2$ K has been observed in NB_3Ge.

3,3 Energy Gap

Experiments have shown that in superconductors, for temperatures in the vicinity of absolute zero, a forbidden energy gap just above the Fermi level is observed. Figure 4.4(a) shows the conduction band in the normal state, while (b) depicts an energy gap equal to 2Δ at the Fermi level in the superconducting state. Thus, the Fermi level in a superconductor is midway between the ground state and the first excited state so that each lies an energy distance $= \Delta$ away from the Fermi level. Electrons in excited states above the gap behave as normal electrons. At absolute zero, there are no electrons above the gap. 2Δ is typically of the order of 10^{-4} eV.
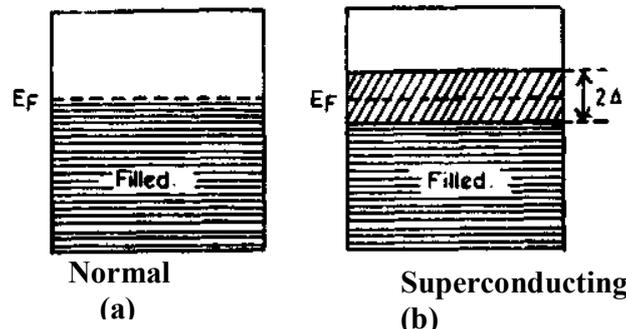

Fig.4.4: (a) Conduction band in the normal metal (b) Energy gap at the Fermi level in the superconducting state (After Kachhava, 1992)

Δ is found to be a function of temperature T. Thus, (T) represents energy gap at temperature T. Figure 4.5 shows reduced values of observed energy gap $(T)/\Delta(0)$ as a function of the reduced temperature T/T_c. Elementary theory predicts that

$$\frac{\Delta(T)}{\Delta(0)} = 1.74 \left(1 - \frac{T}{T_c}\right)^{1/2} \tag{4.1}$$

We observe that the energy gap decreases continuously to zero as the temperature is increased *to* T_c . Numerically, experiments show that for most of the metals. The transition from the superconducting state to the normal state is observed to be a second-order phase transition. In such a transition, there is no latent heat, but there is a discontinuity in the heat capacity.
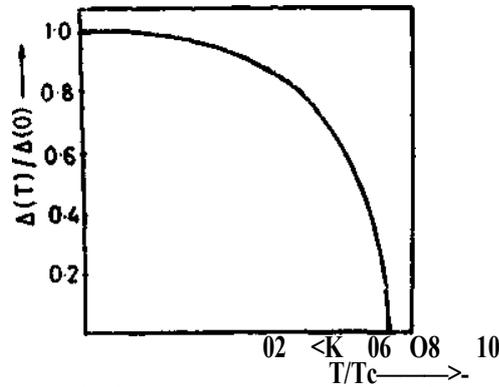
Fig. 4.5: Temperature dependence of the
superconducting energy gap (After Kachhava, 1992)

3.4. Properties Dependent on Energy Gap

3.4.1 Microwave and Infrared Absorptions

The response of a metal to electromagnetic radiation is determined by the frequency dependent conductivity. This in turn depends on the available mechanisms for energy absorption by the conduction electrons at the given frequency. Because the electronic excitation spectrum in the superconducting state is characterized by an energy gap 2Δ, one would expect the AC conductivity to differ substantially from its normal state form at frequencies small compared with $2\Delta/\hbar$, and to be essentially the same in the superconducting and normal states at frequencies large compared with $2\Delta/\hbar$. The value of $2\Delta/\hbar$, is typically in the range between microwave and infrared frequencies. In the superconducting state, an AC behaviour is observed which is indistinguishable from that in the normal state at optical frequencies. Deviations from normal state behaviour first appear in the infrared, and only at microwave frequencies does AC behaviour fully displaying the lack of electronic absorption characteristic of an energy gap becomes completely developed.

3.4.2 Density of States

The three parts of Fig. 4.6 give a highly exaggerated picture of the difference between the spectrum and occupancy of states in a normal metal and those in a superconductor. Part (a) considers the density of states at T = 0 in the absence of superconductivity (which can be arranged by applying a suitable magnetic field). The superconducting ground state for zero temperature is pictured in part (b). This shows a zero density of states for energies within $\pm \Delta(0)$ on either side of the Fermi energy, and a piling up of the displaced states on either side of the gap. At T — 0, no electrons are excited to higher states. Part (c) of the figure imagines the consequences of a finite temperature less than T_c. The superconducting energy gap $\Delta(0)$ is now smaller than $\Delta(0)$. Fractions of number of electrons are in states above $E_F + \Delta T$ leaving behind some unoccupied states below $E_F - \Delta T$. Finally, the gap decreases to zero when T reaches T_c and the corresponding density of states is the one depicted in part (a).
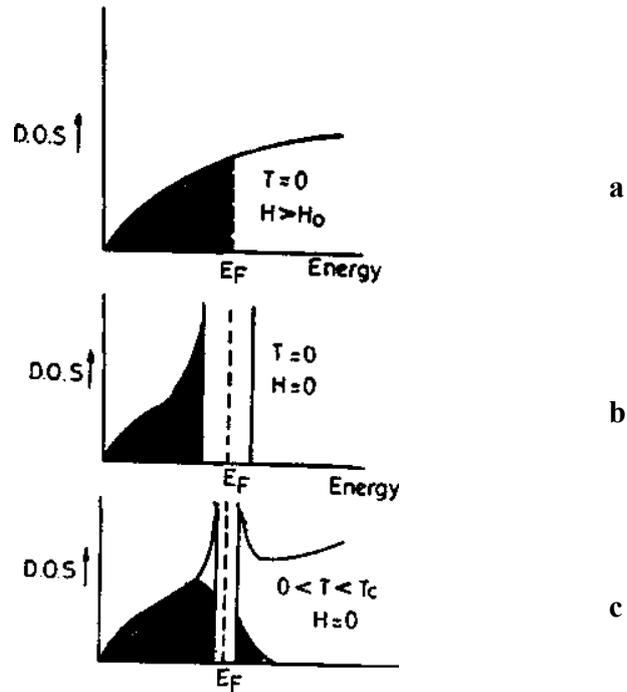
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Fig. 4.6: Density and occupancy of states (D.O.S) for a normal and a superconductor (After Kachhava, 1992)

3.4.3 Specific Heat

There is no heat of transformation associated with the superconducting-normal transition in a metal, but there is an anomaly in the electronic component of the specific heat. An example of this is illustrated in Fig. 4.7. The discontinuity in the specific heat reflects the second-order transition from a relatively disordered (normal) state to a more highly ordered (superconducting) state of lower entropy. At low temperatures, the specific heat of a normal metal has the form

$$C_n = AT + BT^3 \qquad \qquad (4.2)$$

where the linear term is due to electronic excitations- and the cubic term is due to lattice vibrations. Below the superconducting critical temperature, this' behaviour is substantially altered. As the temperature drops below T_c, the specific heat jumps to a higher value and then slowly decreases, eventually falling well below the value one would expect for a normal metal. By applying a magnetic field to drive the metal into the normal state, one can compare the specific heats of the superconducting and normal states below the critical temperature.
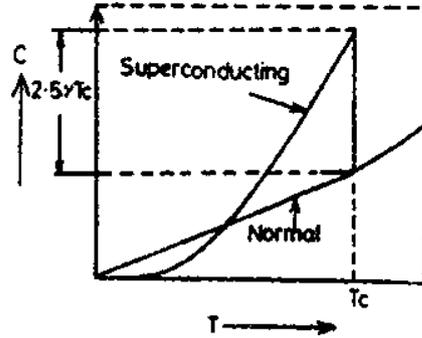
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Fig.4.7: Specific heat of normal and superconductor (After Kachhava, 1992)

Such an analysis reveals that in the superconducting state, the linear electronic contribution to the specific heat is replaced by term that vanishes much more rapidly at very low temperatures, having dominant low-temperature behaviour of the form $\exp(-\Delta/k_B T)$. This is the characteristic thermal behaviour of a system whose excited levels are separated from the ground state by energy 2Δ, thus, the total specific heat of the superconducting state is

$$C_s = AT^3 C_{es} \tag{4.3}$$

Where

$$\frac{C_{es}}{\gamma T} = a \, exp\left(-b\left(\frac{T_c}{t}\right)\right) \tag{4.4}$$

where γT is the low-temperature electronic specific heat of the normal state (obtained by applying suitable magnetic field), and $a \approx 9$ and $b \approx 1.5$. These parameters are themselves weakly temperature dependent. In Fig.4.7 the size of the discontinuity in specific heat at $T = T_c$ is 2.5 in units of γT_c. The exponential decrease in specific heat below T_c can be interpreted as follows. Because, of the energy gap, the number of electrons excited across the gap is given roughly by a Boltzmann factor, $\exp(-\Delta/k_B T)$. Hence, the heat capacity varies exponentially with temperature.

3.4.4   Acoustic Attenuation

When a sound wave propagates through a metal, the microscopic electric fields due to the displacement of the ions can impart energy to electron near the Fermi level, thereby removing energy from the wave. This is expressed by the *attenuation coefficient, α,* of acoustic waves. The ratio of α for superconducting and normal state is given by

$$\frac{\alpha_s}{\alpha_n} = \frac{2}{1+exp(\Delta/k_B T)} \tag{4.5}$$

At low temperatures

$$\frac{\alpha_s}{\alpha_n} = 2 \exp\left(-\Delta/k_B T\right) \tag{4.6}$$

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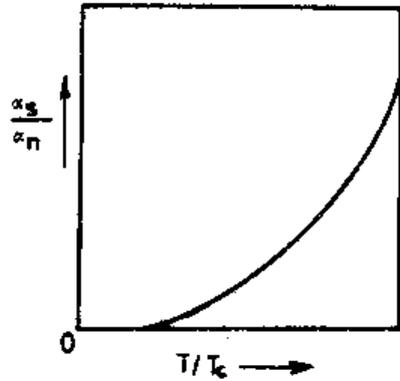The exponential decay ratio is represented in Fig. 4.8

Fig.4.8: Ratio of attenuation coefficients for acoustic waves in superconducting and normal metal as a function of temperature (After Kachhava, 1992).

3.4.5 Thermal Conductivity

In normal metals, the heat current is predominantly carried by the conduction electrons and at low temperatures, the electronic contribution to the thermal conductivity K_{en} is given by the Wiedemann-Franz law. In a superconductor, however, the electron pairs have zero energy so they cannot contribute to energy transport and hence to the heat current (but being charged, they can still contribute to the electric current). Hence, the electronic contribution to the heat current depends on the number of normal electrons and like the electronic specific heat represented by Eq. (4.4), we have the ratio of superconducting to normal phase conductivities as

$$\frac{k_{es}}{k_{en}} \sim exp\left(-\frac{\Delta}{k_B T}\right) \tag{4.7}$$

This is illustrated in Fig.4.9. When $T \ll T_c$, $K_{es} \rightarrow 0$ and the only thermal current will be carried by the phonons (as in insulator). Under suitable conditions, $\frac{k_{es}}{k_{en}}$ may be very large

($\sim 10^5$) and this property can be used to make a heat switch, the heat flow being controlled by a magnet. The phonon contribution to thermal conduction will actually increase in the superconducting state since the scattering of phonons by electrons is reduced by the formation of pairs. In extreme cases when K_{en} is made small by the introduction of impurities, the increase in the phonon contribution to the thermal conductivity below T_c may outweigh the reduction in the electronic contribution so that the total conductivity increases in the superconducting state. To achieve this condition, an impurity of similar mass but different valence, which will reduce K_{en} without greatly affecting phonon transport, should be used. An example is Bi in Pb.
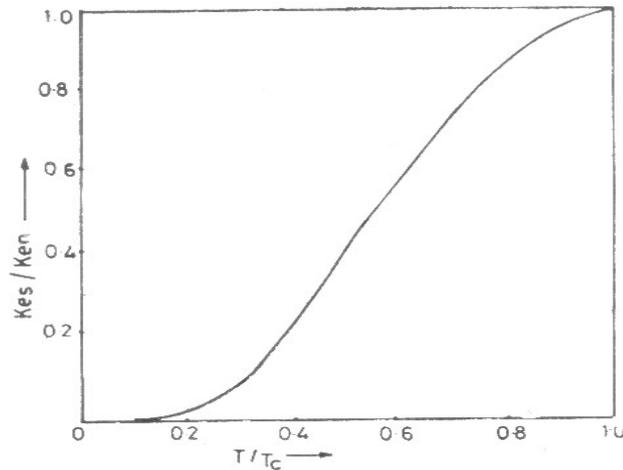
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Fig.4.9: Ratio of the electronic contribution to the thermal conduction of Al (After Kachhava, 1992)

4.0   Conclusion

At a critical temperature T_c, many metals and alloy undergo a phase transition from a state of normal electrical resistivity to a superconducting state.

5.0   Summary

- Superconductivity has been observed only for those metallic substances for which the number of valence electrons Z lies between 2 and 8.
- The temperature at which the normal metal passes into superconducting state is called the transition temperature, T_c
- In superconductors, for temperatures in the vicinity of absolute zero, a forbidden energy gap just above the Fermi level is observed.
- The ratio of attenuating coefficient for superconducting and normal state is given by

$$\frac{\alpha_s}{\alpha_n} = \frac{2}{1 + esp\left(\Delta/k_B T\right)}$$

- The ratio of superconducting to normal phase conductivities is given as

$$\frac{k_{es}}{k_{en}} \sim exp\left(-\Delta/k_B T\right)$$

6.0   Tutor marked assignment

Q1.   Prove that the Meissner effect is consistent with the disappearance of resistivity in a super conductor.

Q2.   Show that when superconductivity is destroyed by the of a magnetic field, the magnet will cool.

7.0   Further readings/References

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