COURSE GUIDE

PHL 307
SOLID STATE PHYSICS 1

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INTRODUCTION

Solid state physics is a very wide field, with many branches. It is concerned with the physical properties of solids, particularly the special properties exhibited by atoms and molecules because of their association in the solid phase. The existence of powerful theoretical methods and concepts applicable to a wide range of problems has been an important unifying influence in the field

Learning solid state physics requires a certain degree of maturity, since it involves tying together diverse concepts from many areas of physics. The objective is to understand, in a basic way, how solid materials behave. To do this, requires a good physical and mathematical background. One definition of solid state physics is that it is the study of the physical (e.g. the electrical, dielectric, magnetic, elastic, and thermal) properties of solids in terms of basic physical laws. In one sense, solid-state physics is more like chemistry than some other branches of physics because it focuses on common properties of large classes of materials. It is typical that solid-state physics emphasises how physical properties link to the electronic structure. The rapid rise of interest in solid state physics in recent years has suddenly presented universities with the problem of offering adequate instruction in the subject. For this reason, there should be an introductory or survey course followed by, as a minimum program for graduate students intending to do research in the field, a course in x-ray crystallography and a course in the quantum theory of solids. These two subjects are large, important, and well-developed; it is not possible to deal with them adequately in an introductory course.

COURSE AIMS

The course aims is to provide an understanding of solid state physics.

COURSE OBJECTIVES

To achieve the aim set out, the course has a set of objectives. Each unit has specific objectives which are included at the beginning of the unit. You should read these objectives before you study the unit. Below are the comprehensive objectives of the course as a whole. By meeting these objectives, you should have achieved the aim of the course as a whole. After going through the course, you should be able to:

- Explain crystal structure of solids
- Explain crystal binding
- Explain X-ray diffraction in crystals
- Explain thermal properties of the crystal lattice
- Explain elastic properties of crystals
- Explain lattice vibration
- Explain the concept of free-electron theory of metals
- Understand energy bands in crystals
- Understand semiconductors

- Understand superconductors

WHAT YOU WILL LEARN IN THIS COURSE

The course consists of 21 units and a course guide. This course guide tells you briefly what the course is about, what course materials you will be using and how you can work your' with these, materials. In addition, it advocates some general guidelines for the amount of time you are likely to spend on each unit of the course in order to complete it successfully.

It gives you guidance in respect of your Tutor-Marked Assignment which will be made available in the assignment file. There will be regular tutorial classes that are related to the course. It is advisable for, you to attend these tutorial sessions. The course will prepare you for the challenges you will meet in the field of solid state physics.

COURSE MATERIALS

The main components of the course are:

1. The Course Guide
2. Study Units
3. References/Further Reading
4. Assignments
5. Presentation Schedule

STUDY UNITS

The study units in this course are as follows:

Module 1 Property Of Crystal

Unit 1 Crystal Geometry
Unit 2 Crystal Classification
Unit 3 Simple Lattices
Unit 4 Crystal Diffraction (I)
Unit 5 Crystal Diffraction (II**)**
Unit 6 Experimental Crystal Structure Determination

Module 2 Crystal Elastic Constants And Vibrations

Unit 1 Elastic Constants of Crystals (I)
Unit 2 Elastic Constants of Crystals (II)
Unit 3 Crystals Binding
Unit 4 Lattice Vibration
Unit 5 Thermal Properties

Module 3 Free Electron Fermi Gas

Unit 1 Free Electron Theory of Metals
Unit 2 Electronic Transfer
Unit 3 Energy Band Theory
Unit 4 Electron Dynamics
Unit 5 Fermi Surfaces

Module 4 Semiconductors and Superconductors

Unit 1 Structure and Bonding in Semiconductors
Unit 2 Semiconductor Statistics
Unit 3 Electrical Conductivity and Real Semiconductors
Unit 4 Super Conductivity (I): The Basic Phenomenon
Unit 5 Superconductivity (II): Experiments and Theories

Module 1 which consists of six units, deals with crystal structures and their determination. Module 2 (five units) is devoted to the fundamental determination of elastic constants of crystal. The free electron which discusses the physical basis of the formation of bands, the most important concept in the band – Fermi surfaces were treated in five units which constitute module 3. Module 4, in five units, provides discussions on the properties of semiconductors as well as discussions on basic phenomenon of superconductors.

Each unit consists of either one or two weeks' work and includes an introduction, objectives, definition, conclusion, summary, Tutor-Marked Assignments (TMA) and references. The TMA will help you to achieve the stated learning objectives of the individual units and the course as a whole.

PRESENTATION SCHEDULE

Students are encouraged to complete and submit on time, their TMAs and to guard against falling behind in attending tutorials.

ASSESSMENT

There are three aspects to the assessment of the course. These are the self assessment exercises, Tutor-Marked Assignments and the written examination/end of course examination. The assignments must be dealt with by applying the knowledge and techniques gathered during the course and must be submitted to your facilitator for formal assessment in accordance with the deadlines stated in the presentation schedule. The assessment will account for 40% of the total course work while the examination will count for the remaining 60%.

TUTOR-MARKED ASSIGNMENT (TMA)

The TMA is a continuous assessment component of the course work. It accounts for 40% of the total score. You will be given six (6) TMAs to answer out of which four must be answered before a student is allowed to sit for the end of the course examination. Students are not allowed to present other people's work as their own (including copying another student's work). Make sure that each assignment reaches your facilitator on or before the deadline given. Extension will not be granted after the due date unless in exceptional cases.

FINAL EXAMINATION AND GRADING

The end of course examination for solid state physics will be for three (3) hours and it has a value of 60% of the total course work. All areas of the course will be assessed.

COURSE MARKING SCHEME

Assignment	**Marks**
Assignment 1-6	Six assignments, best four marks at 10% each totaling 40% of the course marks
End of course examination	60% of overall course marks
Total	100% of course materials

FACILITATORS/TUTORS AND TUTORIALS

There will be tutorials provided in support of this course at the end of each unit. Students will be notified of the dates, times and location of these tutorials as well as the name and phone number of your facilitator. Your facilitator will mark and comment on your assignments and return them to you as soon as possible.

MAIN COURSE

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MODULE 1 PROPERTY OF CRYSTAL

Unit 1 Crystal Geometry
Unit 2 Crystal Classification
Unit 3 Simple Lattices
Unit 4 Crystal Diffraction (I
Unit 5 Crystal Diffraction (II**)**
Unit 6 Experimental Crystal Structure Determination

UNIT1 CRYSTAL GEOMETRY

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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.

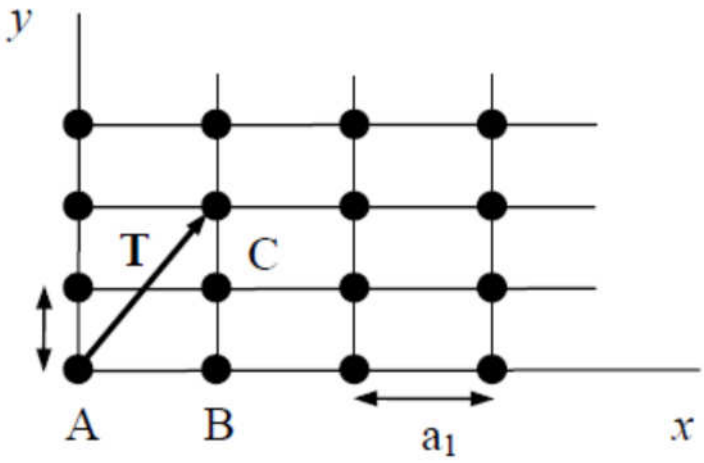


Fig.1.1: Periodicity and concept of symmetry.

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;

$\boldsymbol{r}_{mn} = m\,\boldsymbol{a} + n\,\boldsymbol{b}$ **(1.1)**

Or in three dimensional case

$\boldsymbol{r}_{lmn} = l\,\boldsymbol{a} + m\,\boldsymbol{b} + n\,\boldsymbol{c}$ **(1.2)**

where $\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c}$ 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.

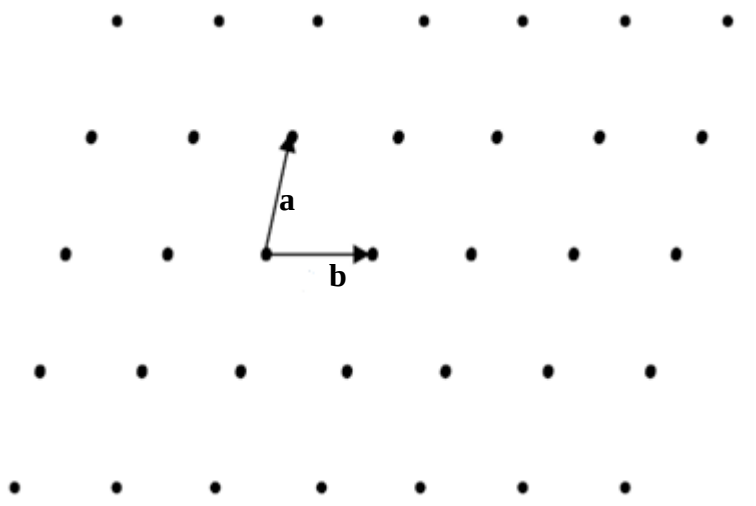


Fig.1.2: Lattice point and Lattice vectors

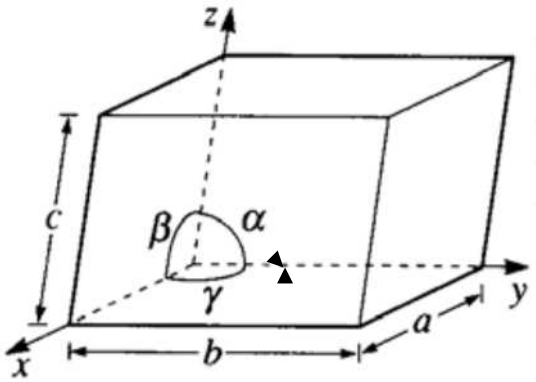


Fig.1.3: Unit cell showing axes lengths and inter axial angles.

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)

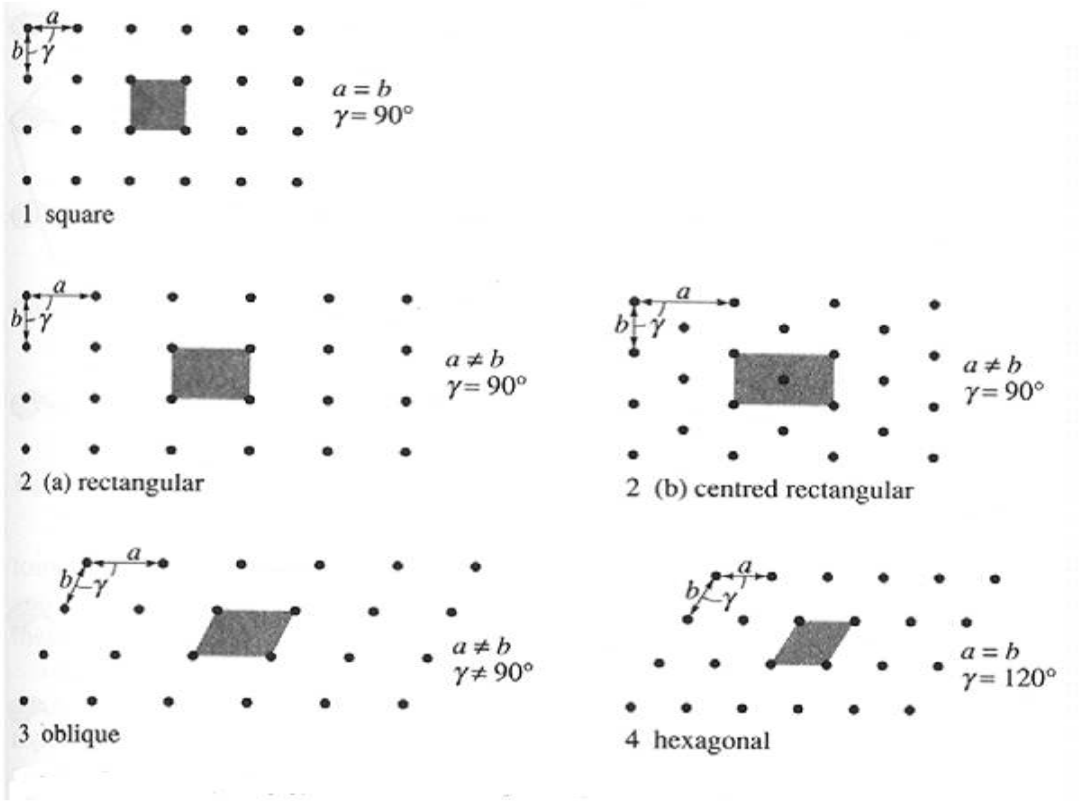


Fig.1.4: Lattice and unit cells in 2-Dimension(After Kittel,1979)

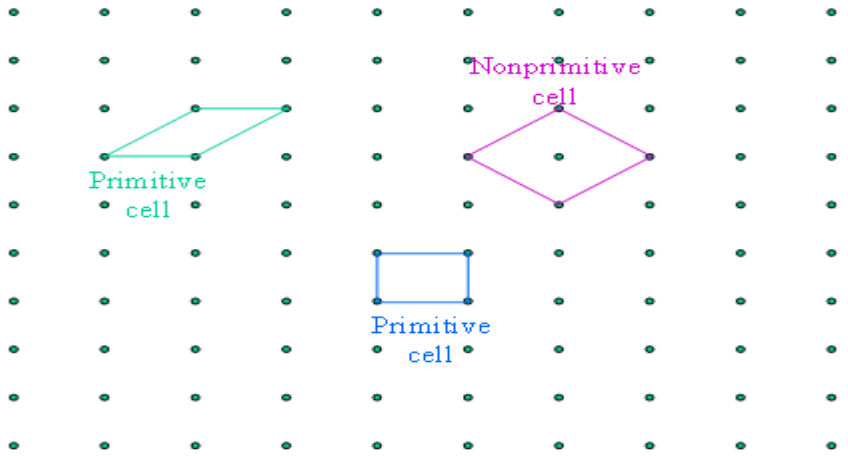


Fig.1.5: Primitive and Non-primitive cells (After Sihv K Gupta, www.4shared.com)

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:

$$\mathbf{r} = k\,\mathbf{a} + l\,\mathbf{b} + m\,\mathbf{c} \quad \textbf{(1.3)}$$

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

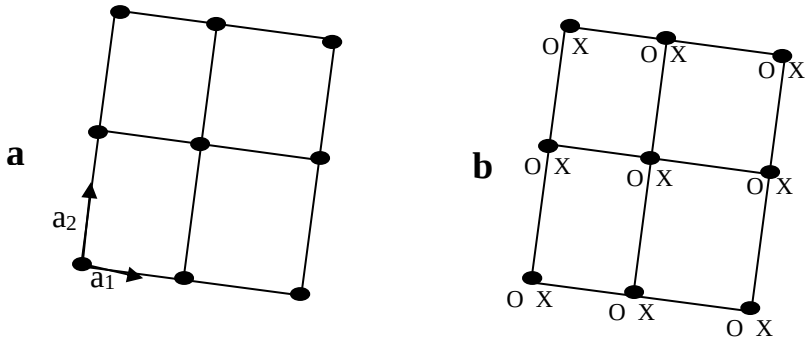


Fig.1.6: Two-dimensional lattices. (a) Bravais lattice; a_1 and a_2 are basis vectors; (b) Lattice with a basis of three atoms; ●, 0, x
(After Kachhava, 1992)

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 $\boldsymbol{R_n} = n_1\mathbf{a} + n_2\mathbf{b} + n_3\mathbf{c}$
- 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

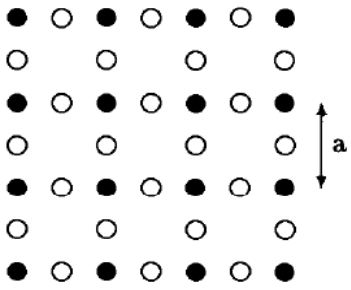
$$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \qquad A = \begin{bmatrix} \alpha & \beta \\ -\beta & \alpha \end{bmatrix} \qquad B = \begin{bmatrix} \alpha & -\beta \\ \beta & \alpha \end{bmatrix}$$

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

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UNIT 2 CRYSTAL CLASSIFICATION

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  3.1 Fundamental types of lattice
  3.2 Direction indices
  3.3 Miller indices
  3.4 Determination of miller indices
  3.5 Some general principles of miller indices
4.0 Conclusion
5.0 Summary
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7.0 Further Reading/References

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$[u_1v_1w_1]$ and $[u_2v_2w_2]$ in a cubic system is given by

$$\cos\theta = \frac{u_1u_2+v_1v_2+w_1w_2}{\left(u_1^2+v_1^2+w_1^2\right)^{1/2}\left(u_2^2+v_2^2+w_2^2\right)^{1/2}} \quad \textbf{(2.1)}$$

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.

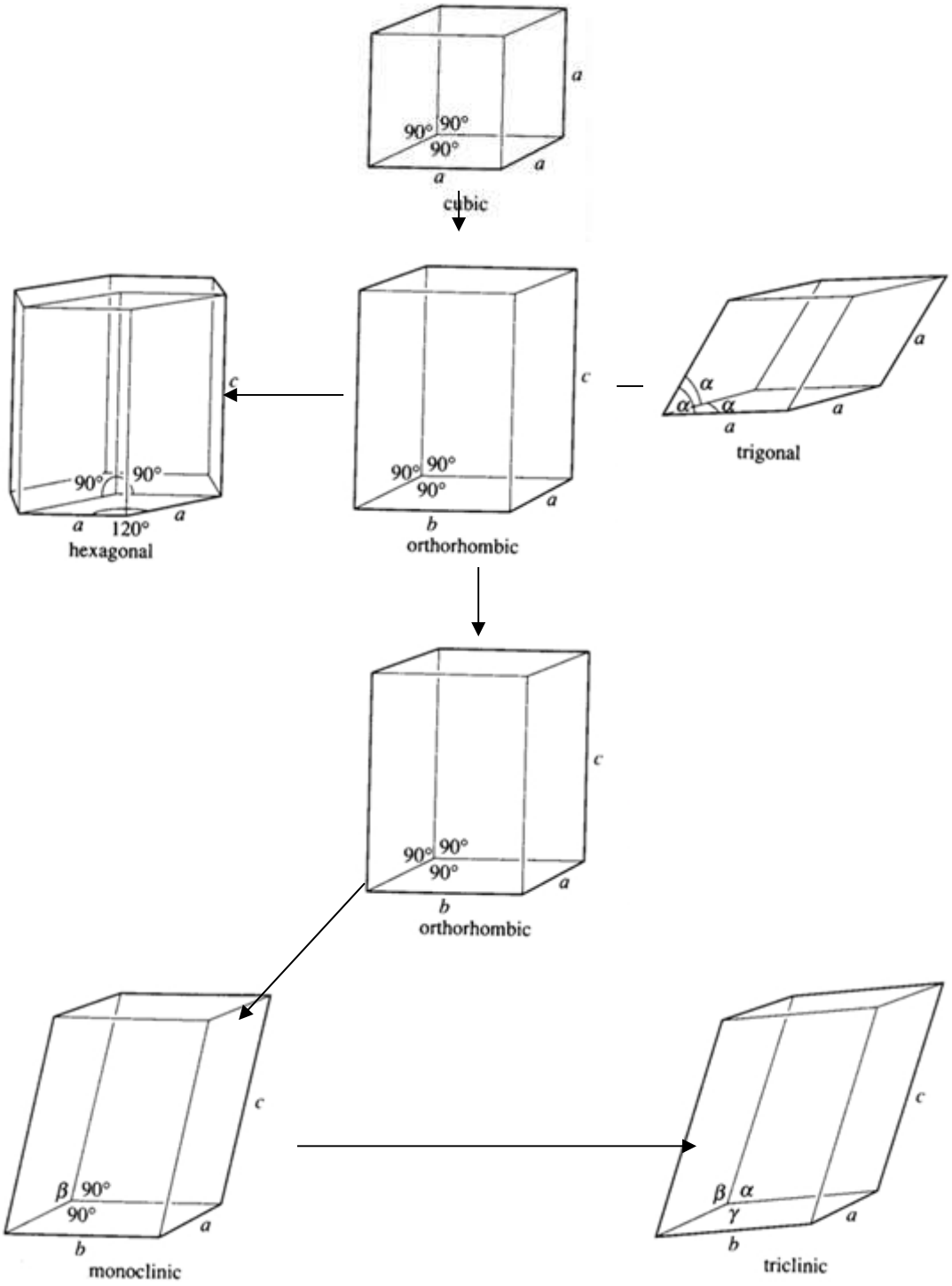

Fig.2.1: seven crystals in three dimensions

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

$$\frac{x}{a}+\frac{y}{b}+\frac{z}{c}=1 \qquad \textbf{(2.2)}$$

Denoting the reciprocal of axial intercepts as $\frac{1}{a}=h, \frac{1}{b}k$ and$\frac{1}{c}=l$,
Eq. (2.2) becomes

$$hx+ky+lz=1 \qquad \textbf{(2.3)}$$

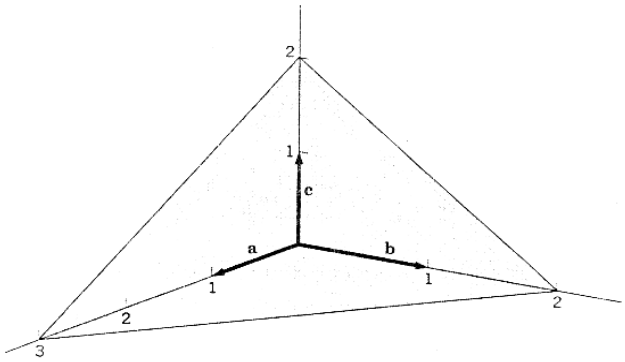

Fig.2.2: Construction for description of a plane. This plane intercepts the **a**, **b**, c axes at 3**a**, 2**b**, 2**c**. (After Kittel, 1979)

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.

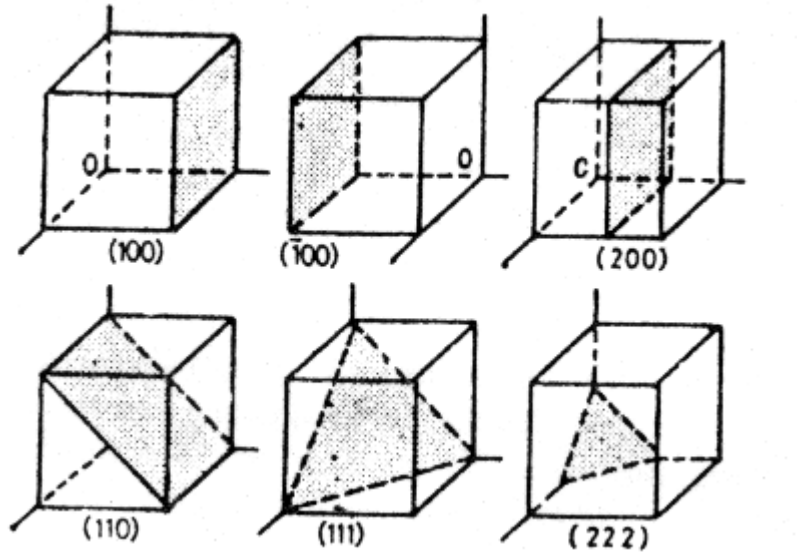

Fig.2.3: Some of the prominent planes for cubic lattices with their Miller indices (After Kachhava, 1992)

Note that:

- ❖ Miller indices are proportional to the direction cosines of the normal to the corresponding plane. Direction cosines are given as
  $\cos\alpha = \frac{hd}{a}, \cos\beta = \frac{kd}{a} = \cos\gamma = \frac{ld}{a}$
- ❖ The normal to the plane with index numbers (hkl) is the direction$[hkl]$
- ❖ The purpose of taking reciprocals is to bring all the planes inside a single unit cell
- ❖ Assume d_{hkl} represent the distance between two adjacent parallel planes having miller indices(hkl), then

$$d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} \qquad \textbf{(2.4)}$$

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.

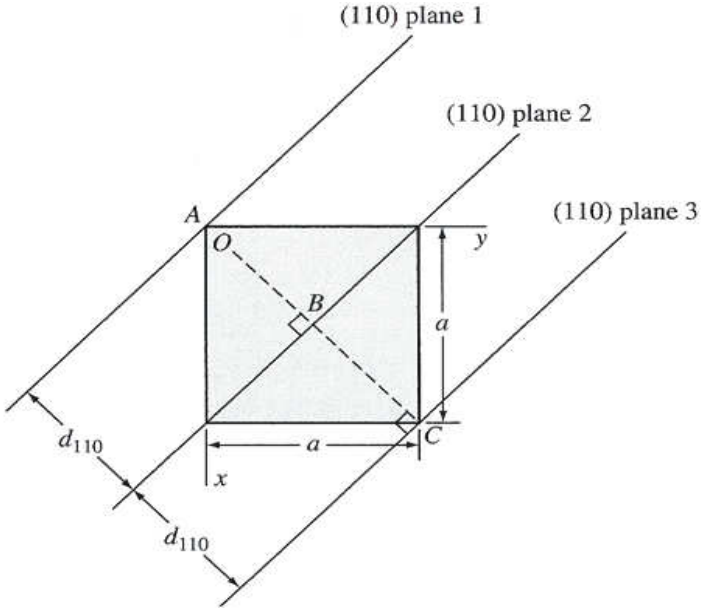

Fig.2.4: inter planer spacing (After Kachhava, 1992)

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

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

- 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

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UNIT 3 SIMPLE LATTICES

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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 **c**rystalline 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

$$\boldsymbol{a_1} = a\boldsymbol{i}, \quad \boldsymbol{a_2} = a\boldsymbol{j}, \quad a_3 = a\boldsymbol{k} \qquad \textbf{(3.1)}$$

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.

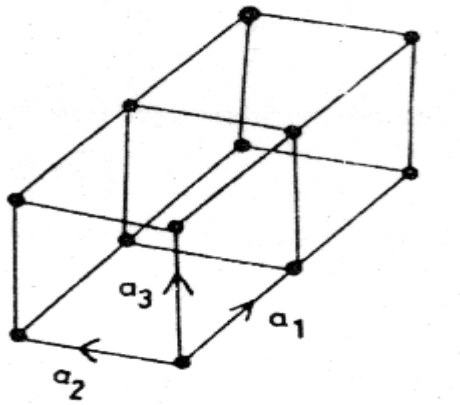

Fig.3.1: Simple cubic lattice (After Kachhava, 1992)

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

$$\boldsymbol{a_1} = \frac{a}{2(-\boldsymbol{i}+\boldsymbol{j}+\boldsymbol{k})}, \quad \boldsymbol{a_2} = \frac{a}{2(\boldsymbol{i}-\boldsymbol{j}+\boldsymbol{k})}, \quad \boldsymbol{a_3} = \frac{a}{2(\boldsymbol{i}+\boldsymbol{j}-\boldsymbol{k})}$$

(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

$$V = \left| \mathbf{a}_1 . \mathbf{a}_2 \times \mathbf{a}_3 \right|$$

(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.

$$\boldsymbol{a_1} = \frac{a}{2(\boldsymbol{j}+\boldsymbol{k})}\,, \boldsymbol{a_2} = \frac{a}{2(\boldsymbol{k}+\boldsymbol{i})}\,,\ \boldsymbol{a_3} = \frac{\boldsymbol{a}}{\boldsymbol{2}(\boldsymbol{i}+\boldsymbol{j})} \qquad \textbf{(3.4)}$$

The primitive cell of the fcc lattice is shown in Fig.3.4 and is a rhombohedron of volume one quarter that of the unit cube. The translation vectors **a**$_1$**, a**$_2$ and **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.

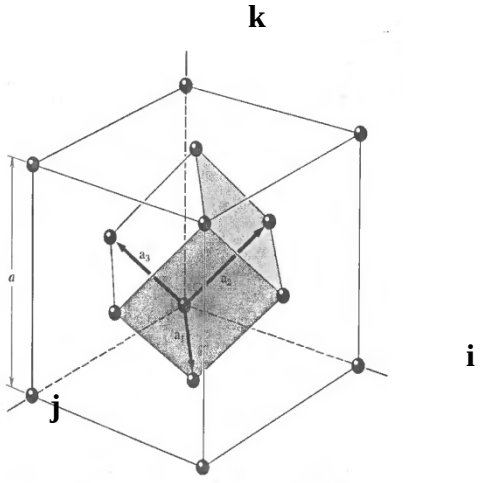

Fig.3.2: Face- centered cubic lattice

3.4 Hexagonal Close-Packed (HCP)

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

$$\boldsymbol{a_1} = a\boldsymbol{i}, \qquad \boldsymbol{a_2} = \frac{\boldsymbol{a}}{\boldsymbol{2}(\boldsymbol{i}+\sqrt{\boldsymbol{3}}\boldsymbol{j})}, \qquad \boldsymbol{a_3} = \boldsymbol{k} \qquad \textbf{(3.5)}$$

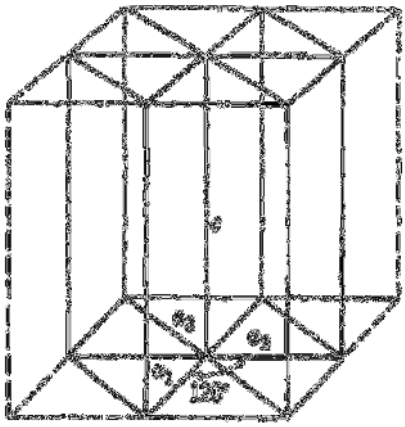

Fig.3.3: Hexagonal Close-packed structure (After Kittel, 1979)

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

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

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.

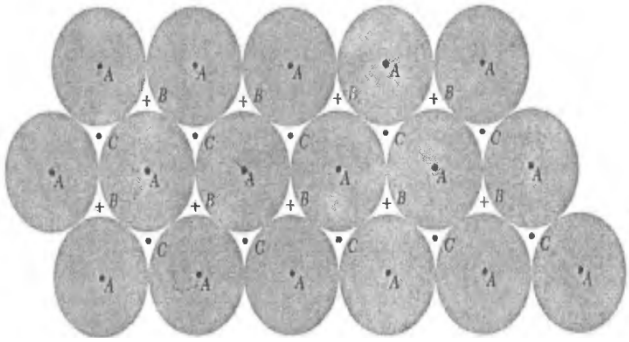

Fig.3.4: A closed- packed layer of spheres (After Kittel, 1979)

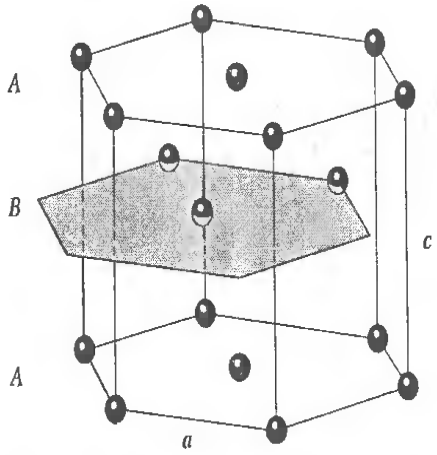

Fig.3.6: The Hexagonal closed packed structures (After Kittel, 1979)

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

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

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	$\frac{a}{2}$	$\frac{a}{2}\sqrt{2}$	$\sqrt{3}\ \frac{a}{4}$	$\frac{a}{2}$
f	**$\pi/6$ = 0.52**	**$\sqrt{2}\frac{\pi}{6}$= 0.74**	**$\sqrt{3}\ \frac{\pi}{8}$ = 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
  $\boldsymbol{a_1}$ = a$\boldsymbol{i}$ $\boldsymbol{a_2}$ = a$\boldsymbol{j}$ $\boldsymbol{a_3}$= a**k**
- 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

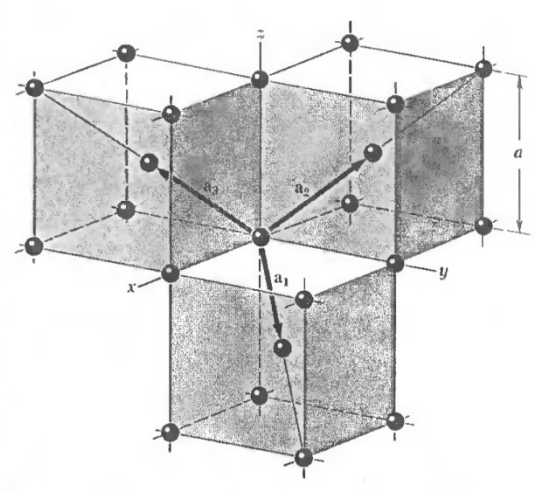

Fig.Q1

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UNIT 4 CRYSTAL DIFFRACTION (I)

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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 $2dsin\theta$. 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

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

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.

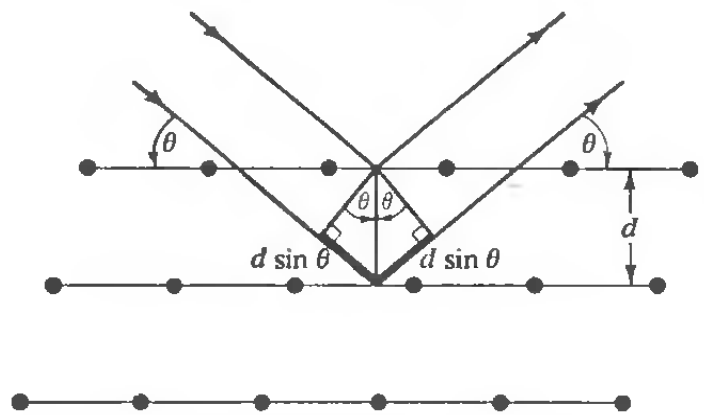

Fig. 4.1: Derivation of the Bragg equation $2d\ sin\theta = n\lambda$ *;* here *d* is the spacing of parallel atomic planes (After Ashcroft and Mermin, 1976).

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 was1.540 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 are2θ. 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.,
(c)

$\frac{sin^2\theta_1}{sin^2\theta_2} =$ 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

$\therefore a = 3.18$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

$$P_1B - P_2A = \boldsymbol{r}\cdot\boldsymbol{s} - \boldsymbol{r}\cdot\boldsymbol{s_{0=}}\ \boldsymbol{r}\cdot(\boldsymbol{s}-\boldsymbol{s_0}) \qquad \textbf{(4.2)}$$

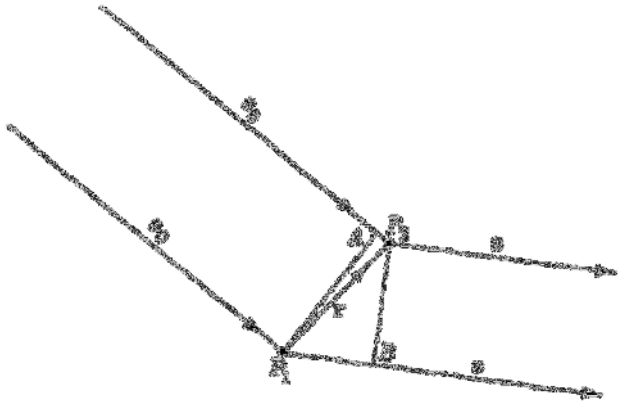

Fig.4.2: Calculation of the Phase difference of the waves scattered from two lattice points (After Kittel, 1979)

The vector $\boldsymbol{s}-\boldsymbol{s_0}$ = **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$\boldsymbol{s_0}$**,** then θ is the angle of incidence, and from the figure (4.3), we see that $|S| = 2sin\theta$, as **s** and $\mathbf{s}_0$ are unit vectors.

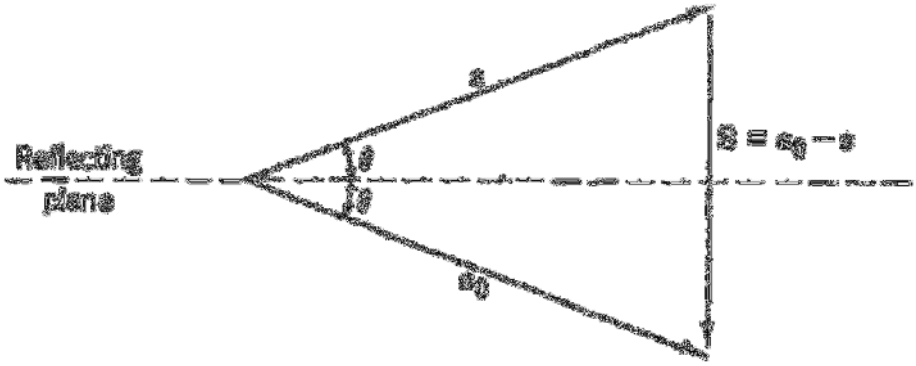

Fig.4.3: Construction of the normal the reflecting plane (After Kittel, 1979)

The phase difference ϕ *is* $^{2\pi}/_{\lambda}$ times the path difference. We have

$$\phi = \left(^{2\pi}/_{\lambda}\right)(\boldsymbol{r}\cdot\boldsymbol{s}) \qquad \textbf{(4.3)}$$

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 of2π. 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

$$\phi_{a=}\left(^{2\pi}/_{\lambda}\right)(\boldsymbol{a}\cdot\boldsymbol{s}) = 2\pi h;$$

$$\phi_{b=}\left(2\pi/\lambda\right)(\boldsymbol{b}\cdot\boldsymbol{s}) = 2\pi k;$$

(4.4)

$$\phi_{c=}\left(2\pi/\lambda\right)(\boldsymbol{c}\cdot\boldsymbol{s}) = 2\pi l;$$

where *h, k; l* are integers.

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

$$\begin{aligned} \boldsymbol{a}\cdot\boldsymbol{s} &= 2a\alpha\ sin\theta = h\lambda \\ \boldsymbol{b}\cdot\boldsymbol{s} &= 2b\beta\ sin\theta = k\lambda \\ \boldsymbol{c}\cdot\boldsymbol{s} &= 2c\gamma\ sin\theta\ = l\lambda \end{aligned} \qquad \textbf{(4.5)}$$

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

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

Then, from (4.5), we have

$$2d(hkl)\ sin\theta = \lambda \qquad \textbf{(4.7)}$$

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

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

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

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

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

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

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.l 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

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

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

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

- 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

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

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. ($h = 6.6 \times 10^{-34} Js$,

$c = 3 \times 10^8\, m/s, 1\, eV = 1.6 \times 10^{-19} J,$

(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. ($\rho_{NaCl} = 2.165\ g/cm^3$)

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UNIT 5 CRYSTAL DIFFRACTION (II)

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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)

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

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:

$$\boldsymbol{A \cdot a = 2\pi}, \quad \boldsymbol{B \cdot a = 0}, \quad \boldsymbol{C \cdot a = 0};$$
$$\boldsymbol{A \cdot b = 0}, \quad \boldsymbol{B \cdot b = 2\pi}, \quad \mathbf{C \cdot b = 0},$$
$$\boldsymbol{A \cdot c = 0}, \quad \boldsymbol{B \cdot c = o}, \quad \boldsymbol{C \cdot c = 2\pi}, \qquad \textbf{(5.2)}$$

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

G = h**A** + k**B**+ l**C,** **(***h, k, l are integers***)** **(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 $[\text{length}]^{-1}$. In dealing with wave properties of crystals, it is convenient to define the reciprocal lattice vector **G** as

$$\mathbf{G} = \boldsymbol{2\pi}(h\boldsymbol{A} + k\boldsymbol{B} + l\boldsymbol{C}) \qquad \textbf{(5.4)}$$

This in conjunction with equation (1.1) yields

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

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

$$exp[\boldsymbol{iG \cdot R_n}] = 1 \qquad \textbf{(5.6)}$$

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 $\mathbf{A_1, B_1, C_1}$ and B for those of $\mathbf{A_2, B_2, C_2}$ **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:

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

Solution:

To solve the problem, we need to use the vector identities:
$\boldsymbol{a.b\times c=b.c\times a=c.a\times b}$
and $\boldsymbol{a\times(b\times c)=(a.c)b-(a.b)c}$
From Eq. (5.1)

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

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

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

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

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 $1/\lambda$ terminating at the origin O. Construct a circle of radius $1/\lambda$(a sphere, called reflex sphere, of radius $1/\lambda$ 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$|\boldsymbol{OA}|<1/2a$ where *a* is the lattice constant), the circle would not pass through any point, showing that X-ray diffraction cannot occur if $\lambda>2a$. 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,OB $=|\mathbf{G}|=1/d$, d is the interplanar for the set.

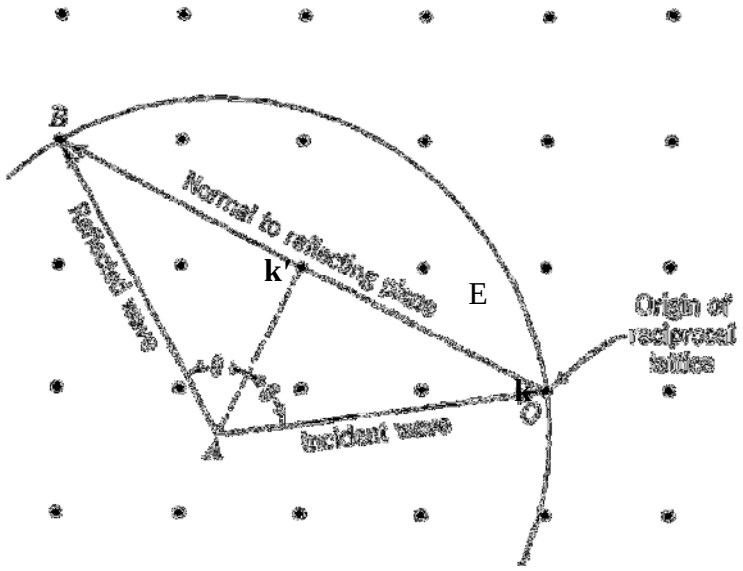

Fig.5.1: Ewald's construction in the reciprocal lattice (After Ashcroft & Mermin, (1976)

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

$$\mathbf{k'} = \mathbf{k} + \mathbf{G} \qquad (5.7)$$

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:**

$$\mathbf{k'^2} = (\mathbf{k} + \boldsymbol{G})^2 = \mathbf{k^2} \qquad (5.8)$$

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

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

Equation (5.10) is Bragg's law in vector form. Its scalar form can be obtained by noting that **AE** = **k + G/2)** is perpendicular to **OB**. Thus OB = 2OE = (2 sin θ)/ λ . 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 **G = OB is** perpendicular to the reflecting plane AE. Thus, corresponding to **G = OB,** the reflecting plane is AE (produced). From the relation **k′ = k + G,** we see that **(AO +OE)·OB** = 0. That is **AE·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.

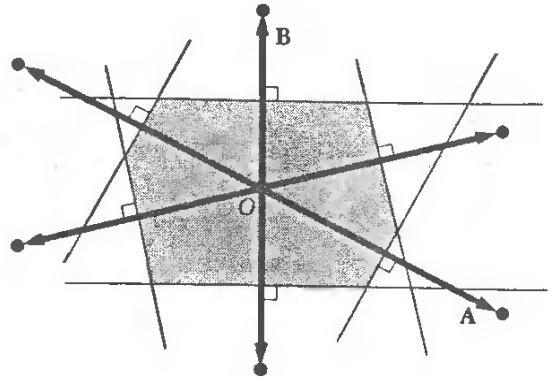

Fig.5.2: Construction of first **BZ** for a two-dimensional oblique lattice (After Kittel.1979).

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

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

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

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

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

$$n_1k_x + n_2k_y = (n_1^2 + n_2^2)\frac{\pi}{a} \qquad \textbf{(5.13)}$$

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

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UNIT 6 EXPERIMENTAL CRYSTAL STRUCTURE DETERMINATION

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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 λ 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.

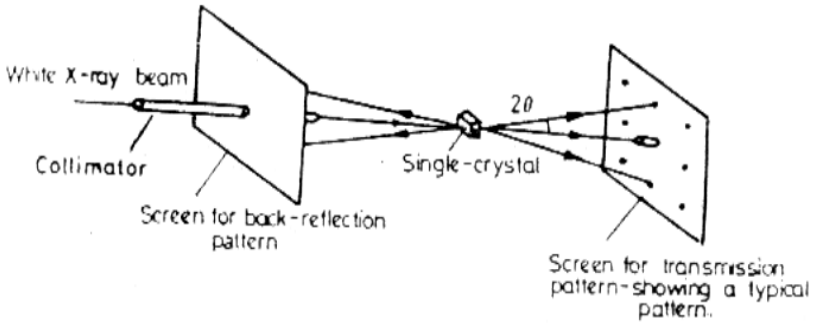

Fig.6.1: Schematic representation of Laue technique (after Kacchava, 1990)

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).

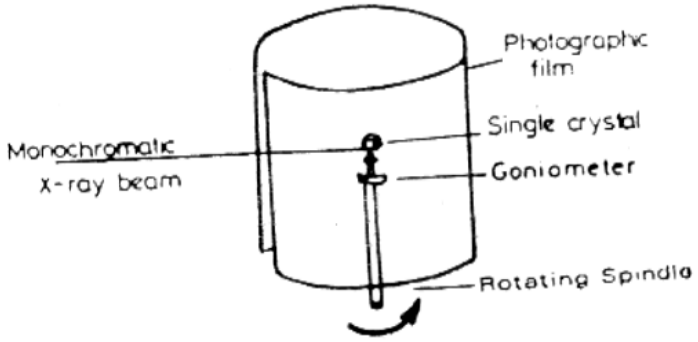

Fig.6.2: Rotating crystal technique (after Kachhava, 1992)

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

$$C \cos \phi_n = n\lambda \qquad \textbf{(6.1)}$$

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)].

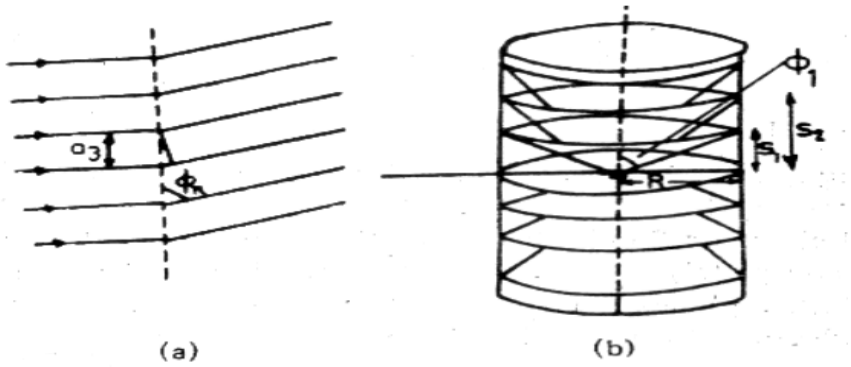

Fig.6.2: Diffraction pattern in rotating crystal technique
(a)Diffraction condition (b) Cones of diffraction (After Kachhava, 1992)

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 $\pm 1, \pm 2, \ldots .$, 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.

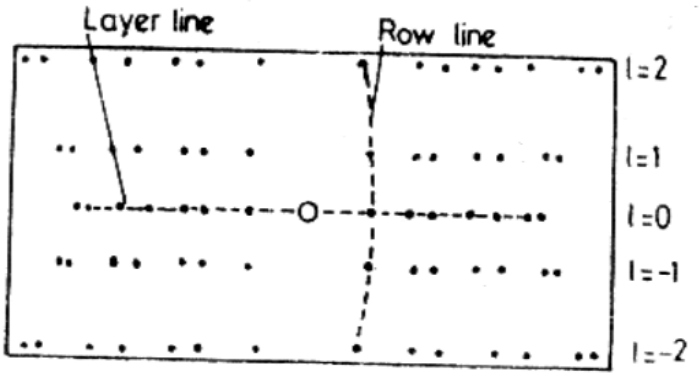

Fig.6.3: Typical Rotation photograph (After Kachhava, 1992)

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

$$S_n = R\ cot\phi_n \qquad \textbf{(6.2)}$$

From equation (6.1) and equation (6.2)

$$S_n = \frac{\left(n\lambda/_C\right)}{\sqrt{1-\left(n\lambda/_b\right)^2}}\text{R}$$

(6.3)

$$\therefore \quad C = \frac{n\lambda}{S_n}(R^2 - S_n^2)^{1/2} \qquad \textbf{(6.4)}$$

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.

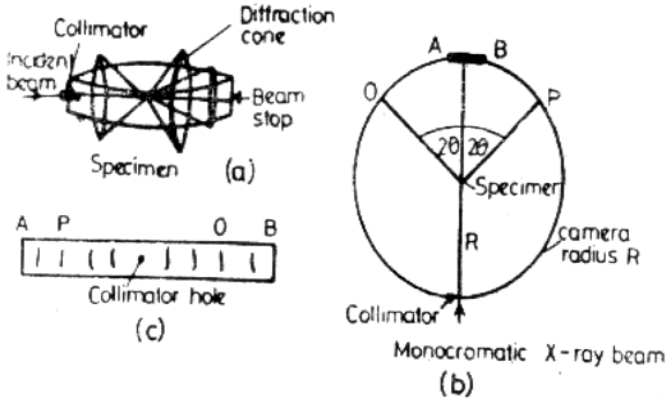

Fig.6.3: Schematic of powder method (a) experimental arrangement (b)Diffraction geometry (c) Developed films (After Kachhava, 1992)

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)

$$\frac{(2\pi - 4\theta)}{2\pi} = \frac{OP}{2\pi R} \quad \textbf{(6.5)}$$

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 $K = 4\pi/\lambda \sin\theta$ can be used to characterize the peak positions (here λ is the wavelength of the X-ray radiation and 2 θ is the scattering angle)

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MODULE 2 CRYSTAL ELASTIC CONSTANTS AND VIBRATIONS

Unit 1 Elastic Constants of Crystals (I)
Unit 2 Elastic Constants of Crystals (II)
Unit 3 Crystals Binding
Unit 4 Lattice Vibration
Unit 5 Thermal Properties

UNIT 1 ELASTIC CONSTANTS OF CRYSTALS

CONTENTS

1.0 Introduction
2.0 Objectives
3.0 Definition
- 3.1 Analysis of elastic strains and stresses
- 3.2 Dilation
- 3.3 Shearing strain
- 3.4 Stress components
- 3.5 Elastic compliance and stiffness constants
- 3.6 Energy density
- 3.7 Cubic crystals

4.0 Conclusion
5.0 Summary
7.0 Tutor Marked Assignment
7.0 Further Reading/References

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, $\boldsymbol{f'}, \boldsymbol{g'}, \boldsymbol{h'}$, are distorted in orientation and in length, so that with the same atom as origin we may write.

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

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

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

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

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

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.

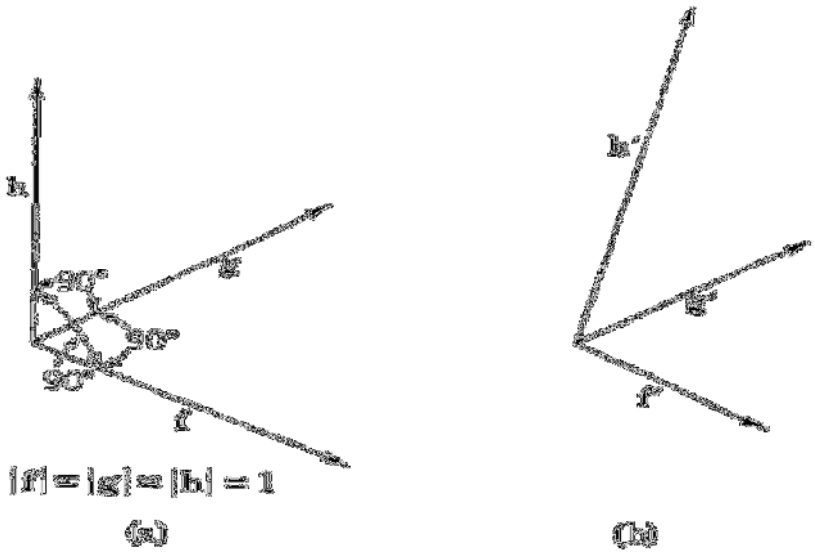

Fig.1.1 Coordinate axes for the description of the state of strain; the orthogonal unit axes in the unstrained state (a) are deformed in the strained state (b).

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

$$\begin{aligned} \boldsymbol{f' - f} &= e_{xx} + \tfrac{1}{2}e_{xy}\boldsymbol{g} + \tfrac{1}{2}e_{zx}\boldsymbol{h}; \\ \boldsymbol{g' - g} &= \tfrac{1}{2}e_{xy}\boldsymbol{f} + e_{yy}\boldsymbol{g} + \tfrac{1}{2}e_{yz}\boldsymbol{h}; \\ \boldsymbol{h' - h} &= \tfrac{1}{2}e_{zx}\boldsymbol{f} + \tfrac{1}{2}e_{yz}\boldsymbol{g} + e_{zz}\boldsymbol{h}; \end{aligned} \qquad \textbf{(1.4)}$$

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

$$\boldsymbol{r} = x\boldsymbol{f} + y\boldsymbol{g} + z\boldsymbol{h} \qquad \textbf{(1.5)}$$

After deformation the particle is at

$$\boldsymbol{r'} = x\boldsymbol{f'} + y\boldsymbol{g'} + z\boldsymbol{h'} \qquad \textbf{(1.6)}$$

so that the displacement is given by

$$\boldsymbol{\varrho = r' - r} = x(\boldsymbol{f' - f}) + y\,(\boldsymbol{g' - g}) + z(\boldsymbol{h' - h}) \qquad \textbf{(1.7)}$$

If we write the displacement as

$$\boldsymbol{\varrho} = u\boldsymbol{f} + v\boldsymbol{g} + w\boldsymbol{h} \qquad \textbf{(1.8)}$$

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

$$\begin{aligned} e_{xx} &= \frac{\partial u}{\partial x}; \quad e_{yy} = \frac{\partial v}{\partial y}; \quad e_{zz} = \frac{\partial w}{\partial z}; \\ e_{xy} &= \frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}; \quad e_{yz} = \frac{\partial w}{\partial y} + \frac{\partial v}{\partial z}; \quad e_{zx} = \frac{\partial u}{\partial z} + \frac{\partial w}{\partial x} \end{aligned} \qquad \textbf{(1.9)}$$

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 $\boldsymbol{\varrho}$ has the components

$$\begin{aligned} \mathrm{u} &= e_{xx}x + \tfrac{1}{2}e_{xy}y + \tfrac{1}{2}e_{zx}z; \\ \mathbf{v} &= \tfrac{1}{2}e_{xy}x + e_{yy}y + \tfrac{1}{2}e_{yz}z; \\ w &= \tfrac{1}{2}e_{zx}x + \tfrac{1}{2}e_{yz}y + e_{zz}z; \end{aligned} \qquad \textbf{(1.10)}$$

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

$$V' = \boldsymbol{f}' \cdot \boldsymbol{g}' \boldsymbol{X}\, \boldsymbol{h}' \cong 1 + e_{xx} + e_{yy} + e_{zz} \qquad \textbf{(1.11)}$$

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

$$\delta = \frac{\Delta V}{V'} = e_{xx} + e_{yy} + e_{zz} \qquad \textbf{(1.12)}$$

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

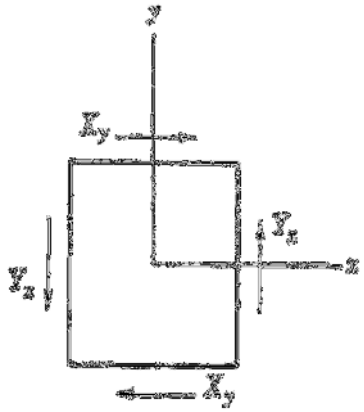

Fig. 1.2: Demonstration that number of independent stress components $Y_x = X_y$ order that the body may be in equilibrium.

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:

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

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

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

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

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

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

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

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

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

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

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

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

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

The quantities s_{11} ..... s_{12} are called the *elastic constants* or *elastic compliance constants;* the quantities c_{11} ..... 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

$$\delta W = \boldsymbol{F} \cdot \boldsymbol{\delta \varrho} \qquad \textbf{(1.15)}$$

where **F** is the applied force and

$$\delta \boldsymbol{\varrho} = \boldsymbol{f}\delta u + \boldsymbol{g}\delta v + \boldsymbol{h}\delta w \qquad \textbf{(1.16)}$$

is the displacement. If *X, Y, Z* denote the components of **F** per unit area, then

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

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

$$\delta u = L\left(\delta e_{xx} + \tfrac{1}{2}\delta e_{xy} + \tfrac{1}{2}\delta e_{zx}\right) \qquad \textbf{(1.18)}$$ etc., so that

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

The increment δU of elastic energy per unit volume is

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

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

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

This leads from Eq. (1.14) to the relation

$$\boldsymbol{c_{12} = c_{21}}$$

and in general we have

$$\boldsymbol{c_{ij} = c_{ji}} \qquad \textbf{(1.21)}$$

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

$$c_{11} = c_{22} = c_{33},$$

and $$c_{12} = c_{13} = c_{21} = c_{23} = c_{31} = c_{32},$$

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:

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

It is readily seen that for a cubic crystal

$$U = {}^1\!/_2\, C_{11}\left(e_{xx}^2 + e_{yy}^2 + e_{zz}^2\right) + C_{12}\left(e_{yy}e_{zz} + e_{zz}e_{xx} + e_{xx}e_{yy}\right) + {}^1\!/_2\, C_{44}\left(e_{yz}^2 + e_{zx}^2 + e_{xy}^2\right) \quad \textbf{(1.23)}$$

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

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

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

(1.24)

$$C_{14} = {}^{1}/_{S_{44}}$$

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 $(C_{11} - C_{12})/2$.

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UNIT 2 ELASTIC CONSTANTS OF CRYSTALS (II)

CONTENT

1.0 Introduction
2.0 Objectives
3.0 Definition
  3.1 Elastic waves in cubic crystals
  3.2 Elastic isotropy
  3.3 Cauchy relations
4.0 Conclusion
5.0 Summary
6.0 Tutor Marked Assignment
7.0 Further Reading/References

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

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

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

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

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

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

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

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

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;

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

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

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

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

$$C_{11} - C_{12} = 2C_{44} \quad \textbf{(2.6)}$$

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:

$$\ddot{\boldsymbol{\varrho}} = C_{44}\nabla^2\boldsymbol{\varrho} + (C_{12} + C_{44})\, grad\ div\, \boldsymbol{\varrho} \quad \textbf{(2.7)}$$

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

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

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

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

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

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

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UNIT 3 CRYSTALS BINDING

CONTENT

1.0 Introduction
2.0 Objectives
3.0 Definition
  3.1 Inter atomic force
  3.2 Vander Waals (Molecular) bonding
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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

$$F(R) = -\frac{\partial U}{\partial R} \qquad \textbf{(3.1)}$$

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.

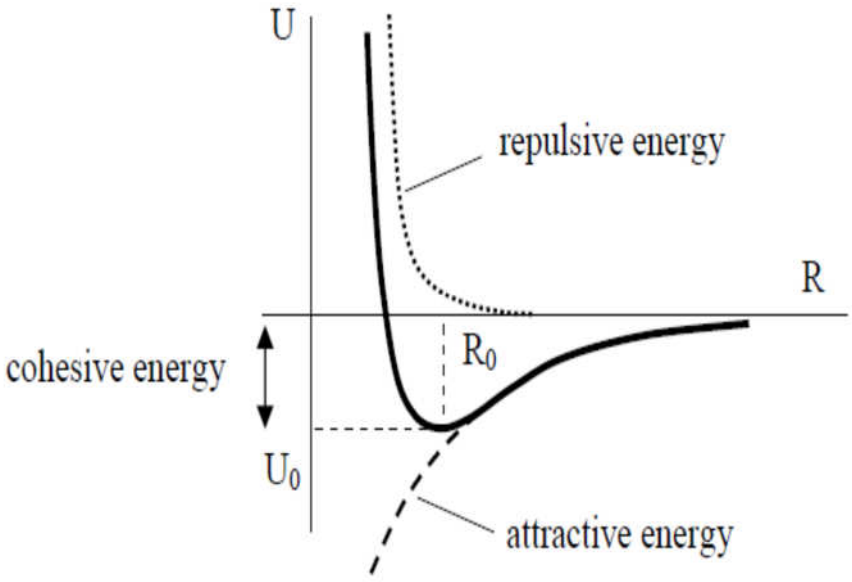

Fig.3.1. A typical curve for the potential energy (binding energy) representing the interaction between two atoms (After Kittel.1979)

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

$$d_2 \propto E \propto \frac{d_1}{R^3} \qquad \textbf{(3.2)}$$

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

$$-\frac{d_1 d_2}{R^3} \propto -\frac{d_1^2}{R^6} \qquad \textbf{(3.3)}$$

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.

$$U \propto -\frac{\langle d_1^2 \rangle}{R^6} \quad \textbf{(3.4)}$$

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

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

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

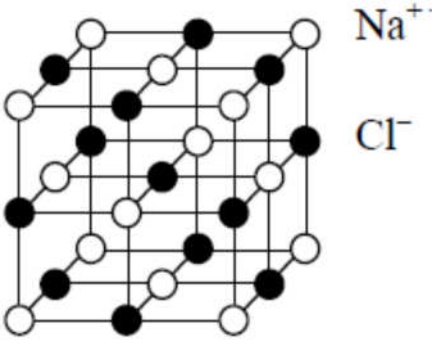

Fig 3.2 structure of $NaCl$(After Kachhava, 1992)

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

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

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

$$U = \frac{1}{2}\sum U_{ij} = N\sum_j \left(\lambda e^{(-r_{ij}/\rho)} \pm q^2/r_{ij}\right) \qquad \textbf{(3.7)}$$

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 $Nacl$ 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

$$U = N\left(Z\lambda e^{-R/\rho} - \alpha\, q^2/R\right) \qquad \textbf{(3.8)}$$

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

$$\alpha = \sum_{j\neq i} \frac{(\pm 1)}{p_{ij}} \qquad \textbf{(3.9)}$$

where p_{ij} is defined by$r_{ij} = p_{ij}R$ .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.

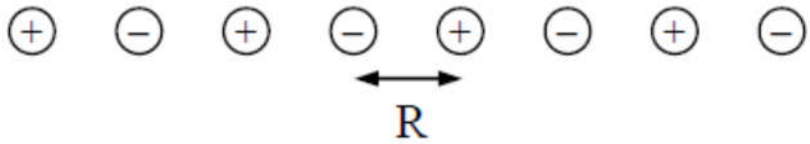

Fig.3.3: 1-D lattice of ions of alternating sign.

In this case

$$\frac{\alpha}{R} = 2\left[\frac{1}{R} - \frac{1}{2R} + \frac{1}{3R} - \frac{1}{4R} + - -\right]$$

Or

$$\alpha = 2\left[1 - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + - -\right] \quad \textbf{(3.10)}$$

The factor 2 occurs because there are two ions, one to the right and one to the left at equal distances r_j.
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 $\alpha = 2\ln 2$.
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.

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UNIT 4 LATTICE VIBRATION

CONTENT

1.0 Introduction
2.0 Objectives
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  3.1 One-dimensional lattice
  3.2 Diatomic one-dimensional lattice
  3.3 Three –dimensional lattice
  3.4 Phonon
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5.0 Summary
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7.0 Further Reading/References

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).

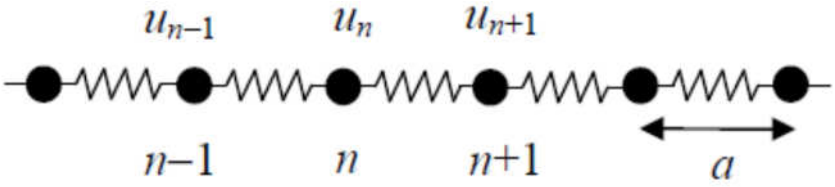


Fig.4.1: Lattice vibration of monatomic lattice
(After www.pa.uk.edu/kwng/phy/525/lec)

Therefore, the force exerted on *n*th atom in the lattice is given by

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

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

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

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

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

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

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

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

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

We find therefore the dispersion relation for the frequency

$$\omega = \sqrt{\frac{4C}{M}}\left|sin\frac{qa}{2}\right| \quad \textbf{(4.6)}$$

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.

$$-\frac{\pi}{a} \leq q \leq \frac{\pi}{a} \quad \textbf{(4.7)}$$

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.

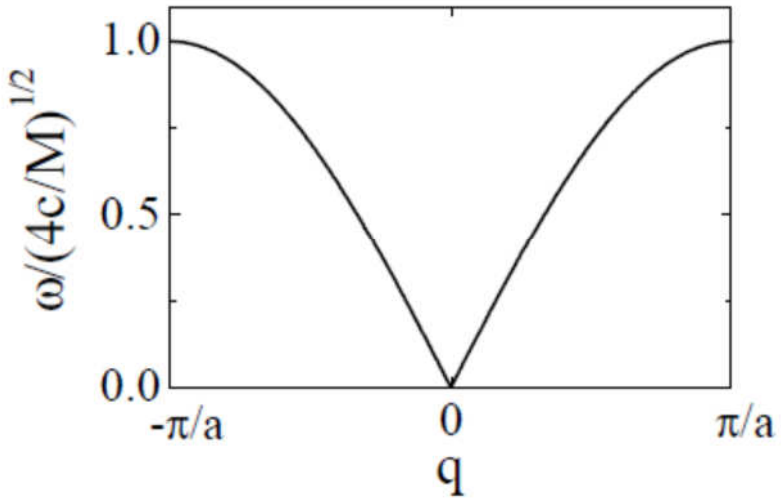


Fig.4.2: Dispersion curve of a one-dimensional monatomic lattice representing the First Brillouin Zone. www.pa.uk.edu/kwng/phy/525/lec)

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

$$v_p = \frac{\omega}{q} \quad \textbf{(4.8)}$$

and the group velocity by

$$v_g = \frac{d\omega}{dq} \qquad \textbf{(4.9)}$$

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

$$v_g = \sqrt{\frac{Ca^2}{M}}\cos\frac{qa}{2} \qquad \textbf{(4.10)}$$

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 $\lambda >> a$. In this limit $qa << 1$. We can then expand the sine in Eq. (4.6) and obtain for the positive frequencies:

$$\omega = \sqrt{\frac{C}{M}}qa \qquad \textbf{(4.11)}$$

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

$$v_p = \frac{\omega}{q} = \sqrt{\frac{C}{M}}a \qquad \textbf{(4.12)}$$

Worked example:

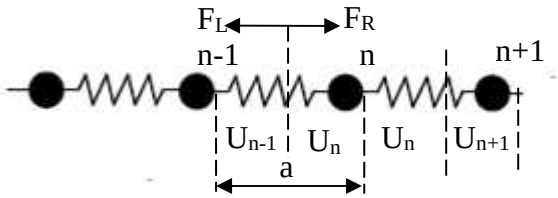
Atoms in crystals are held together by chemical bonds. Consider these bonds to be elastic springs of the same force constants β for one-dimensional crystal lattice. Suppose one of the atoms is displaced from its mean position by an external force and then released;

(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

$$\omega_m = \pm\sqrt{\frac{4\beta}{m}}$$

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 $(n-1)th, nth,$ and $(n+1)th$ atoms from their mean positions at any instant will be U_{n-1}, U_n and U_{n+1} respectively. Also, the extension of the spring between $(n-1)th,$ and nth atoms will be $(a+U_n-U_{n-1})$ and therefore, the restoring force F_L on the nth atom due to the left spring will be

$F_L = \beta(a+U_n-U_{n-1})$ (i)

Similarly, the extension of the spring on the right of nth atom will be $(a+U_{n+1}-U_n)$ and restoring force is given by

$F_R = \beta(a+U_{n+1}-U_n)$ (ii)

The net force on the nth atom will be

$F = F_R - F_L = \beta(a+U_{n+1}-U_n) - \beta(a+U_n-U_{n-1})$

$\therefore F = \beta(U_{n+1}+U_{n-1}-2U_n)$ (iii)

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

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

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

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

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

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

(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,

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

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

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

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

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

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*.

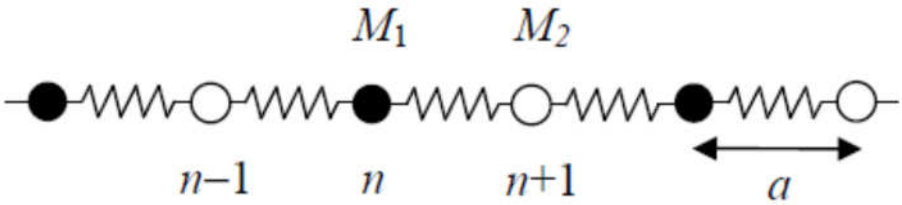


Fig.4.3: Lattice vibration of diatomic lattice (After www.pa.uk.edu/kwng/phy/525/lec)

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:

$$M_1\frac{d^2U_n}{dt^2} = -C(2U_n - U_{n+1} - U_{n-1})$$
$$M_2\frac{d^2U_{n+1}}{dt^2} = -C(2U_{n+1} - U_{n+2} - U_n) \qquad \textbf{(4.13)}$$

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

$$\begin{vmatrix} U_n \\ U_{n+1}\end{vmatrix} = \begin{vmatrix} A_1 e^{iqna} \\ A_2 e^{iq(n+1)a}\end{vmatrix} e^{-i\omega t} \qquad \textbf{(4.14)}$$

$$\begin{vmatrix} 2C - M_1\omega^2 & -2\cos qa \\ -2C\cos qa & 2C - M_2\omega^2\end{vmatrix} = \begin{vmatrix} A_1 \\ A_2\end{vmatrix} = 0 \qquad \textbf{(4.15)}$$

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

$$(2C - M_1\omega^2)(2C - M_2\omega^2) - 4C^2\cos^2 qa = 0 \qquad \textbf{(4.16)}$$

This is a quadratic equation, which can be readily solved

$$\omega^2 = C\left(\frac{1}{M_1} + \frac{1}{M_2}\right) \pm C\sqrt{\left(\frac{1}{M_1} + \frac{1}{M_2}\right)^2 - \frac{4sin^2 qa}{M_1 M_2}} \qquad \textbf{(4.17)}$$

Depending on sign in this formula there are two different solutions corresponding to two different dispersion curves, as is shown in Fig.4.4:

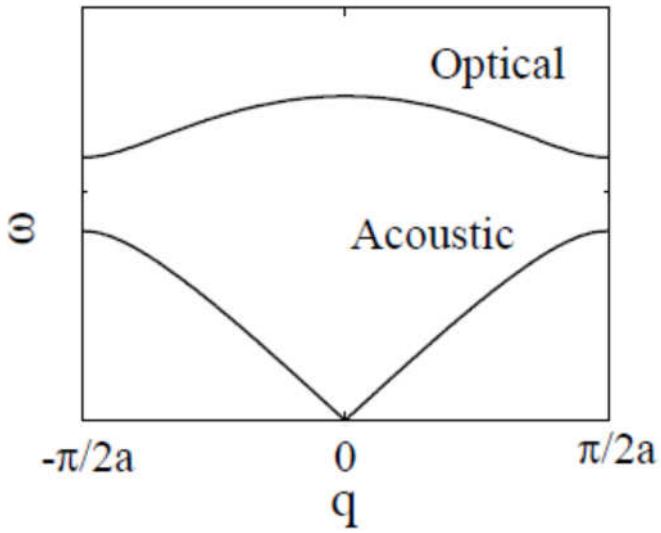


Fig.4.4: Dispersion Curve for one-dimensional diatomic lattice. (After www.pa.uk.edu/kwng/phy/525/lec)

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 ω=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

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

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 ω=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:

$$M_1A_1 + M_2A_2 = 0 \qquad \textbf{(4.19)}$$

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.

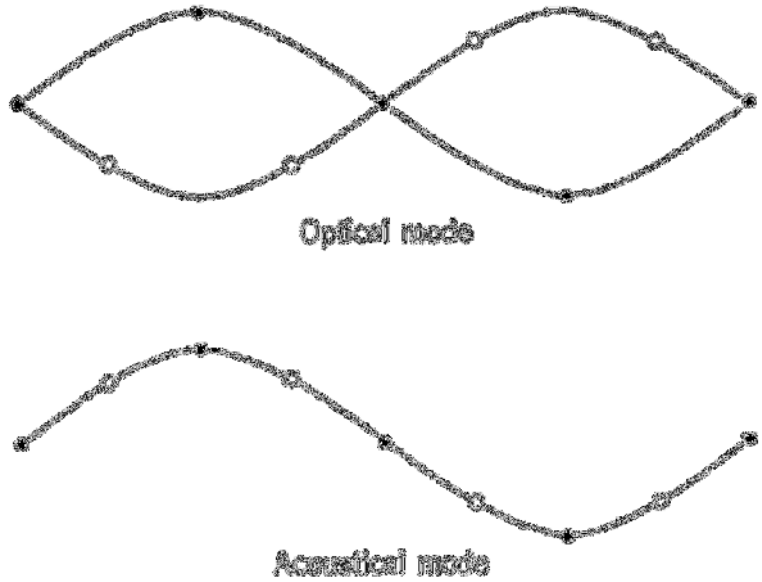


Fig.4.5: Distinction between Acoustic and Optical wave (After Kittel, 1976)

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.*

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

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.

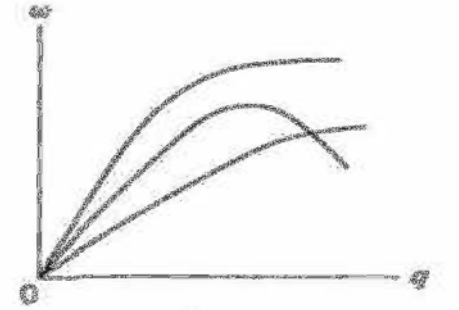


Fig.4.6: Dispersion curve.

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.

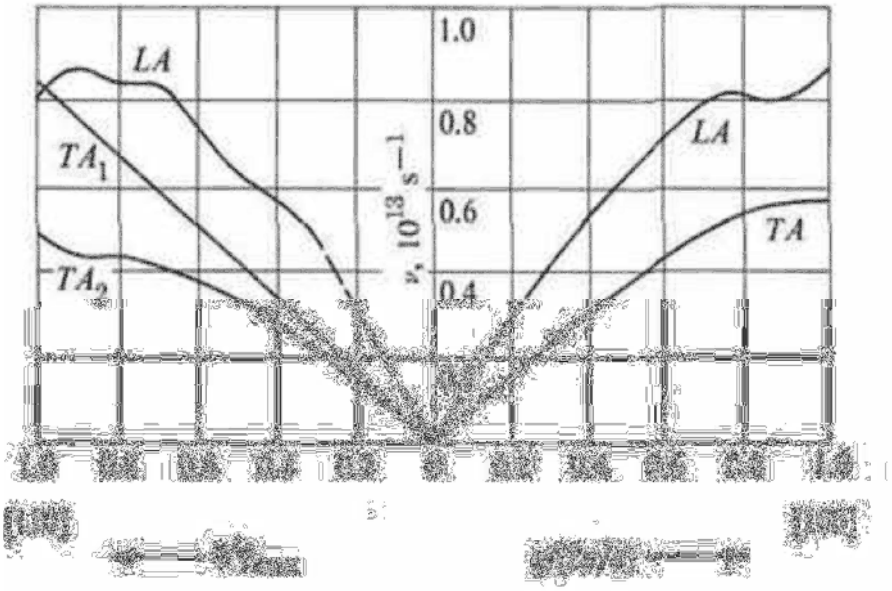


Fig.4.7: Dispersion curve for Al in the [100] and [110] directions (After Kittel, 1979)

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 (3*s* –3) are optical. The mathematical justification for this assertion is as follows: We write the equation of motion for each

atom in the cell, which results in *s* equations. Since these are vector equations, they are equivalent to 3*s* scalar equations, which have 3*s* roots. It can be shown that three of these roots always vanish at $q = 0$, which results in three acoustic branches. The remaining (3*s* –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.

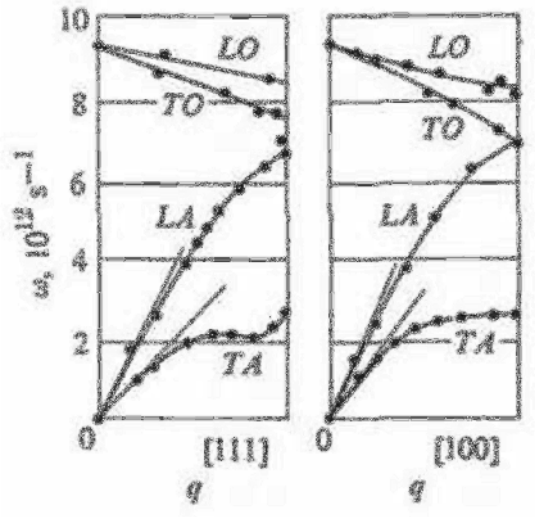


Fig.4.8: Dispersion curve for Ge along [100] and [110] directions (After Kittel, 1979)

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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

$$E = \left(n + {}^{1}/_{2}\right)\hbar\omega \qquad \textbf{(4.21)}$$

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

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

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

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

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.

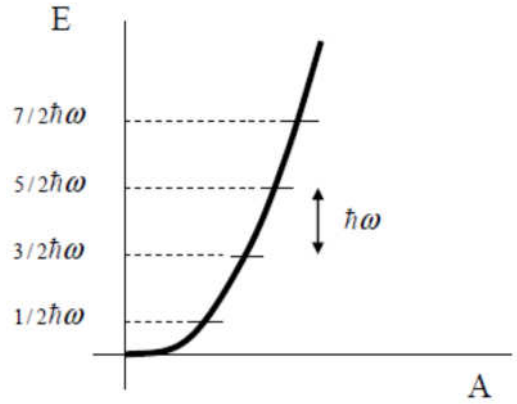

Fig.4.9: Relation between amplitude and frequency (After Kittel, 1979)

The lattice with *s* atoms in a unit cell is described by 3*s* 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,…3*s*. 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 3*s* 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 **G** is a vector in the reciprocal lattice; **k** is the wave

vector of the incident photon and **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

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

where sign (+) corresponds to creation of phonon and sign (–) corresponds to absorption of phonon. Phonon dispersion relations ω_p **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

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

where *M* is the mass of the neutron and $\hbar$**k** and $\hbar$**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 $M_1 >> M_2$.

(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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https://web.pdx.edu/~egertonr/ph311-12/solstate.htm

UNIT 5 THERMAL PROPERTIES

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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.

$$C = \frac{\Delta Q}{\Delta T} \qquad \textbf{(5.1)}$$

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

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

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

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

Where $\langle n_{qp} \rangle$ is the thermal equilibrium occupancy of phonons of wave vector **q** and mode *p* (*p* = 1…3*s*, 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

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

where the constant P_0 is determined from the normalization condition.

$$\sum_{n=0}^{\infty} P_n = 1 \qquad \textbf{(5.5)}$$

so that

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

The average excitation number of the oscillator is given by

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

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

$$\sum_{n=0}^{\infty} x^n = 1 \qquad \textbf{(5.8)}$$

Using this property we find:

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

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

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

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

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

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, ω + $d\omega$. Then the energy is

$$E = \sum_{p} \int d\omega D_p(\omega) \frac{\hbar\omega}{e^{(\hbar\omega/k_B)} - 1} \qquad \textbf{(5.12)}$$

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

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

(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

$$u = Ae^{iqx} \qquad \textbf{(5.14)}$$

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

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

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

$$e^{iqL} = 1 \qquad \textbf{(5.16)}$$

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

$$q = n\frac{2\pi}{L} \qquad \textbf{(5.17)}$$

where *n* = 0, + 1, ±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 2π/*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 2π/*L*, the number of modes is

$$\frac{L}{2\pi}dq \qquad \textbf{(5.18)}$$

We are interested in the number of modes in the frequency range $d\omega$ lying betwe$(\omega, \omega + d\omega)$. The *density of states* $D(\omega)$ is defined such that $D(\omega)d\omega$ 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,

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

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

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

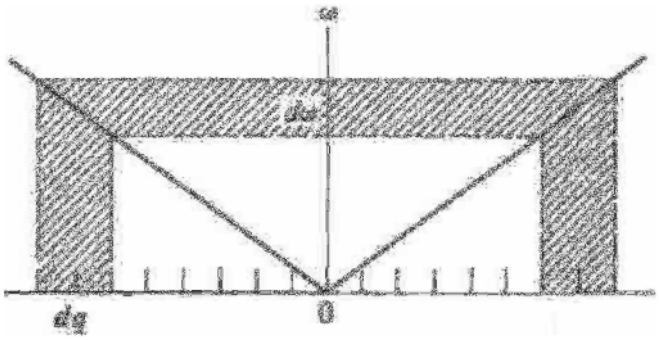

Fig.5.1: Density of state

where the propagation is described by the wave vector **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 ***q*** must satisfy the condition

$$e^{iq_xL} = e^{iq_yL} = e^{iq_zL} \quad \textbf{(5.21)}$$

Therefore, the values are given by

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

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 $(2\pi/L)^3$.

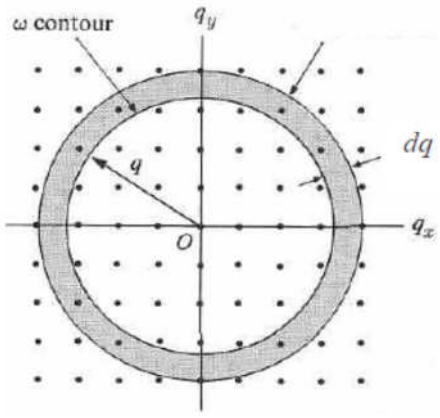

Fig.5.2:Three-dimensional cubic mesh (After Kittel, 1979)

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

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

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

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

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

$$\omega = vq \quad \textbf{(5.25)}$$

where v is the velocity of sound.

In this approximation the density of states is given by

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

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 3*N*. Therefore, we can write

$$\sum_{\boldsymbol{p}} \int_{\mathbf{0}}^{\boldsymbol{\omega_D}} \boldsymbol{D}(\omega)\boldsymbol{d}\omega = 3N \quad (\mathbf{5.27})$$

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

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

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

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

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

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

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

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

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

$$x_D = {\hbar\omega_D}/{k_B T} = {\theta_D}/{T} \quad \textbf{(5.32)}$$

The latter expression defines the Debye temperature

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

The total phonon energy is then

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

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

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

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

In the limit $T>>\theta$, 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. $T<<\theta$. At very low temperatures we can approximate (5.34) by letting the upper limit go to infinity. We obtain

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

(5.36)

and therefore

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

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_BT. The number of these modes may be estimated by drawing a sphere in the q-space whose frequency $\omega = \hbar/k_BT$, 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_BT. 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).

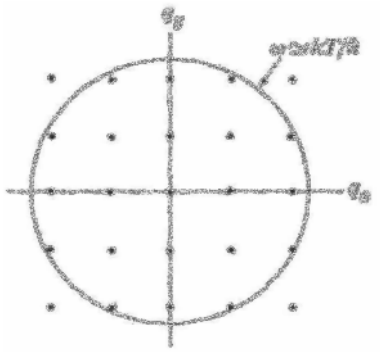

Fig.5.3: The thermal sphere (After Kittel, 1979)

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.

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

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

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

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

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

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,

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

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

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

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 $\frac{1}{2}vE[T(x-l)]$. 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

$$j = \tfrac{1}{2}vE\left[T\left(x-l\right)\right] + \tfrac{1}{2}vE\left[T\left(x+l\right)\right] \qquad \textbf{(5.43)}$$

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:

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

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 $\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle\ {}^1/_3\, v^2$ and since $C_v = \frac{dE}{dT}$ is the heat capacity we obtain,

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

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").

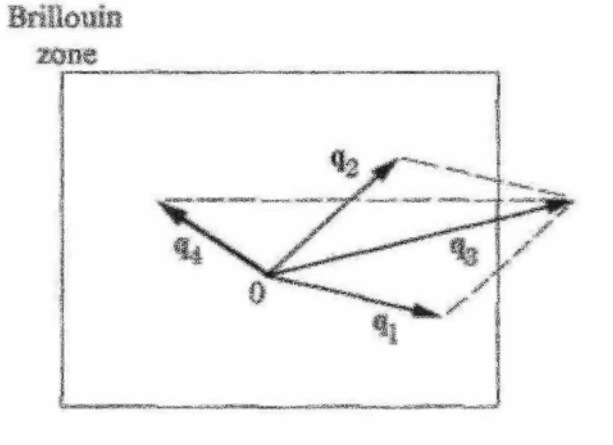

Fig.5.6: Umklapp process(After Kittel, 1979)

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*

6.0 Tutor marked assignment

Q1. Using the dispersion relation for the monatomic linear lattice of *N* atoms with nearest neighbor interactions, show that the density of vibrational modes is given by

$$D(\omega) = \frac{2N}{\pi}\frac{1}{\sqrt{\omega_m^2-\omega^2}}$$ were ω_m is the maximum frequency

Q2. In the Debye approximation, show that the mean square displacement of an atom at absolute zero is

$\langle R^2 \rangle = \frac{3\hbar\omega_D^2}{8\pi^2\rho v^2}$ where v is the velocity of sound. Estimate this value for Cu ($\theta_D = \frac{\hbar\omega_D^2}{k_B} = 343K$, ρ = 8920 kg/m^3, v = 3570 m/s).

7.0 Further reading/References

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MODULE 3 FREE ELECTRON FERMI GAS

Unit 1 Free Electron Theory of Metals
Unit 2 Electronic Transfer
Unit 3 Energy Band Theory
Electron Dynamics
Unit 5 Fermi Surfaces

UNIT 1 FREE ELECTRON THEORY OF METALS

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1.0 Introduction

The free electron theory of metals refers to the case in which the atomic valance electrons are treated as if they are free rather than being bound to the lattice points. Our assumption amounts to supposing that the electrons move in a uniform potential rather than the true periodic potential provided by the positive ions. The basic assumption of the theory is that a metal is equivalent to a gas of free electrons in an otherwise empty box.

2.0 Objective

- To revise the free electron gas (FEG) model and assumptions made.
- To understand how this simple model can be used to derive equations heat capacity of the free electron.
- To employ the time-independent Schrodinger equation to derive the electron wave functions and energies.

3.0 Definition

A free electron model is the simplest way to represent the electronic structure of metals.

3.1 Free electron model

A free electron model is the simplest way to represent the electronic structure of metals. Although the free electron model is a great oversimplification of the reality, surprisingly in many cases it works pretty well, so that it is able to describe many important properties of metals. According to this model, the valence electrons of the constituent atoms of the crystal become conduction electrons and travel freely throughout the crystal. Therefore, within this model we neglect the interaction of conduction electrons with ions of the lattice and the interaction between the conduction electrons. In this sense we are talking about a *free electron gas*. However, there is a principle difference between the free electron gas and ordinary gas of molecules. First, electrons are charged particles. Therefore, in order to maintain the *charge neutrality* of the whole crystal, we need to include positive ions. This is done within the *jelly model*, according to which the positive charge of ions is smeared out uniformly throughout the crystal. This positive background maintains the charge neutrality but does not exert any field on the electrons. Ions form a uniform jelly into which electrons move. Second important property of the free electron gas is that it should meet the Pauli Exclusion Principle, which leads to important consequences.

3.2 One-dimension

We consider first a free electron gas in one dimension. We assume that an electron of mass *m* is confined to a length *L* by infinite potential barriers. The wave function $\psi_n(x)$ of the electron is a solution of the Schrödinger equation, $H\psi(x) = E\psi(x)$ where E_n is the energy of electron in the orbital. Since w can assume that the potential lies at zero, the Hamiltonian *H* includes only the kinetic energy so that

$$H\psi_n(x) = \frac{p^2}{2m}\psi_n(x) = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi_n(x) = E_n\psi_n(x) \qquad \textbf{1.1}$$

Note that this is a one-electron equation, which means that we neglect the electron-electron interactions. We use the term *orbital* to describe the solution of this equation. Since the $\psi_n(x)$ is a continuous function and is equal to zero beyond the length *L*, the boundary conditions for the wave function are $\psi_n(0) = \psi_n(L) = 0$. The solution of Eq. (1.1) is therefore

$$\psi_n(\chi) = A\sin\left(\frac{\pi n}{L}\right)\chi \qquad \textbf{1.2}$$

where *A* is a constant and *n* is an integer. Substituting (1.2) into (1.1) we obtain the eigenvalues

$$E_n = \frac{\hbar^2}{2m}\left(\frac{\pi n}{L}\right)^2 \qquad \textbf{1.3}$$

These solutions correspond to standing waves with a different number of nodes within the potential well as is shown in Fig.1.1

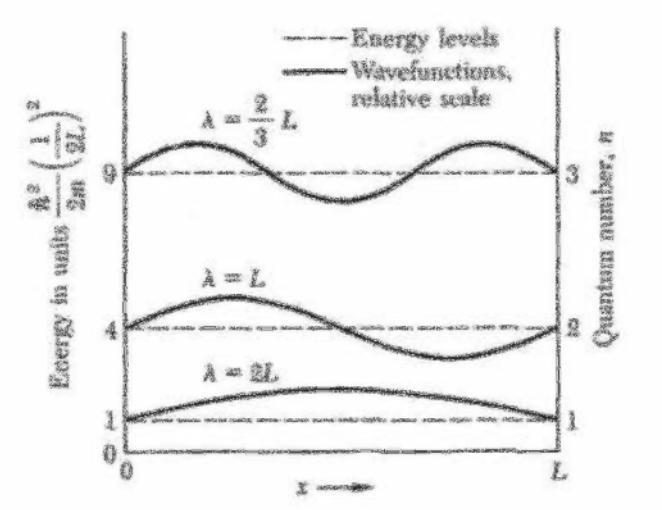

Fig.1.1 First three energy levels and wave-functions of a free electron of mass *m* confined to a line of length *L*.(Kittel, 1979).

Now we need to accommodate *N* valence electrons in these quantum states. According to the Pauli Exclusion Principle no two electrons can have their quantum number identical. That is, each electronic quantum state can be occupied by at most one electron. The electronic state in a 1D solid is characterized by two quantum numbers that are *n* and m_s, where *n* is the positive integer and m_s is the magnetic quantum number such that $m_s = \pm ½$ according to spin orientation.

Therefore, each orbital labeled by the quantum number *n* can accommodate two electrons, one with spin up and one with spin down orientation.

Let n_F denote the highest filled energy level, where we start filling the levels from the bottom *(n* = 1) and continue filling higher levels with electrons until all *N* electrons are accommodated. It is convenient to suppose that *N* is an even number. The condition $2n_F = N$ determines n_F the value of *n* for the uppermost filled level. The energy of the highest occupied level is called the *Fermi energy* E_F. For one - dimensional system of *N* electrons we can define E_F, using Eq. (1.3),

$$E_F = \frac{\hbar^2}{2m}\left(\frac{\pi N}{2L}\right)^2 \qquad \textbf{1.4}$$

In metals the value of the Fermi energy is of the order of 5 eV. The ground state of the *N* electron system is illustrated in Fig.1.2 a: All the electronic levels are filled up to the Fermi energy. All the levels above are empty.

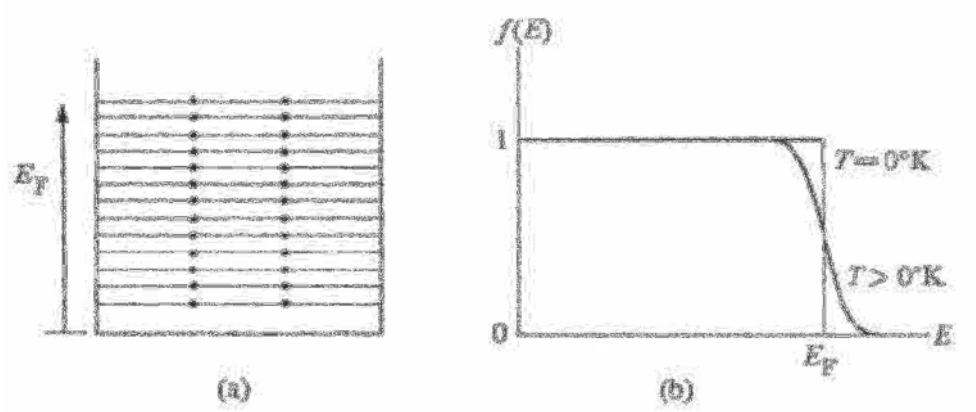

Fig. 1.2 (a) Occupation of energy levels according to the Pauli exclusion principle, (b) The distribution function $f(E)$, at T = 0°K and T> 0°K.

3.3 Fermi distribution

This is the ground state of the N electron system at absolute zero. What happens if the temperature is increased? The kinetic energy of the electron gas increases with temperature. Therefore, some energy levels become occupied which were vacant at zero temperature, and some levels become vacant which were occupied at absolute zero. The distribution of electrons among the levels is usually described by the *distribution function,* $f(E)$, which is defined as the probability that the level E is occupied by an electron. Thus if the level is certainly empty, then, $f(E) = 0$, while if it is certainly full, then $f(E) = 1$. In general, $f(E)$ has a value between zero and unity. It follows from the preceding discussion that the distribution functions for electrons at T = 0°K has the form

$$f(E) = \begin{cases} 1, & E < E_F \\ 0, & E < E_F \end{cases} \qquad \textbf{(1.5)}$$

That is, all levels below E_F are completely filled, and all those above E_F are completely empty. This function is plotted in Fig. 1.2(b), which shows the discontinuity at the Fermi energy.

When the system is heated (T>0°K), thermal energy excites the electrons. However, all the electrons do not share this energy equally, as would be the case in the classical treatment, because the electrons lying well below the Fermi level E_F cannot absorb energy. If they did so, they would move to a higher level, which would be already occupied, and hence the exclusion principle would be violated. Recall in this context that the energy which an electron may absorb thermally is of the order $k_B T$ (= 0.025 eV at room temperature), which is much smaller than E_F, this being of the order of 5 eV. Therefore only those electrons close to the Fermi level can be excited, because the levels above E_F are empty, and hence when those electrons move to a higher level there is no violation of the exclusion principle. Thus only these electrons which are small fraction of the total number - are capable of being thermally excited. The distribution function at non-zero temperature is given by the *Fermi distribution function*. The Fermi distribution function determines the probability that an orbital of energy E is occupied at thermal equilibrium.

$$f(E) = \frac{1}{e^{(\langle E-\mu\rangle/k_B T)}+1} \quad \textbf{(1.6)}$$

This function is also plotted in Fig.1.2(b), which shows that it is substantially the same as the distribution at T = 0°K, except very close to the Fermi level, where some of the electrons are excited from below E_F to above it. The quantity μ is called the chemical potential. The chemical potential can be determined in a way that the total number of electrons in the system is equal to N. At absolute zero $\mu = E_F$.

3.3 Three – dimension

The Schrödinger equation in the three dimensions takes the form

$$H\psi(\boldsymbol{r}) = \frac{p^2}{2m}\psi(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\nabla^2\psi(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r}) \quad \textbf{(1.7)}$$

If the electrons are confined to a cube of edge L, the solution is the standing wave

$$\psi(\boldsymbol{r}) = A\sin\left(\frac{\pi n_x}{L}x\right)\sin\left(\frac{\pi n_y}{L}y\right)\sin\left(\frac{\pi n_z}{L}z\right) \quad \textbf{(1.8)}$$

where $n_{x,}$ $n_{y,}$ and $n_{z,}$ are positive integers.

In many cases, however, it is convenient to introduce periodic boundary conditions, as we did for phonons. The advantage of this description is that we assume that our crystal is infinite and disregard the influence of the outer boundaries of the crystal on the solution. We require then that our wave function is periodic in x, y, and z directions with period L, so that

$\psi(x+L,y,z) = \psi(x,y,z)$, **(1.9)**

and similarly for the y and z coordinates. The solution of the Schrödinger equation Eq. (1.7) which satisfies these boundary conditions has the form of the traveling plane wave:

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = Aexp(i\boldsymbol{k}.\boldsymbol{r}), \quad \textbf{(1.10)}$$

provided that the component of the wave vector **k** are determined from

$$k_x = \frac{2\pi n_x}{L};\ k_y = \frac{2\pi n_y}{L};\ k_z = \frac{2\pi n_z}{L} \quad \textbf{(1.11)}$$

where $n_{x,}$ $n_{y,}$ and $n_{z,}$ are positive or negative integers.
If we now substitute this solution to Eq. (1.7) we obtain for the energies of the orbital with the wave vector **k**

$$E_{\boldsymbol{k}} = \frac{\hbar^2\boldsymbol{k}^2}{2m} = \frac{\hbar^2}{2m}\left(\boldsymbol{k}_x^2+\boldsymbol{k}_y^2+\boldsymbol{k}_z^2\right) \quad \textbf{(1.12)}$$

The wave functions equations (1.10) are the eigenfunctions of the momentum

$\boldsymbol{P} = -i\hbar\nabla$ this can be readily seen by differentiating (1.10):

$$p\psi_k(\boldsymbol{r}) = -i\hbar\nabla\psi_k(\boldsymbol{r}) = \hbar\boldsymbol{k}\boldsymbol{\psi}_{\boldsymbol{k}}(\boldsymbol{r}) \quad \textbf{(1.13)}$$

The eigenvalues of the momentum is $\hbar\boldsymbol{k}$. The velocity of the electron is defined by **v** = **p** /*m* = $\hbar\boldsymbol{k}$ /*m*.

In the ground state a system of *N* electrons occupies states with lowest possible energies. Therefore all the occupied states lie inside a in k space, k_F. The energy at the surface of this sphere is the Fermi energyE_F. The magnitude of the wave vector k_F and the Fermi energy are related by the following equation:

$$E_F = \frac{\hbar^2 k_F^2}{2m} \quad \textbf{(1.14)}$$

The Fermi energy and the Fermi wave vector (momentum) are determined by the number of valence electrons in the system. In order to find the relationship between *N* and k_F we need to count the total number of orbitals in a sphere of radius k_F which should be equal to *N*. There are two available spin states for a given set of k_x, k_y and k_z. The volume in the **k** space which occupies this state is equal to$(2\pi\ /\ L)^3$. Thus in the sphere of $\left({}^{2\pi k_F^3}/_3\right)$ the total number of states is

$$2\,\frac{4\pi\boldsymbol{k_F^3}/3}{(2\pi/L)^3} = \frac{V}{3\pi^2}\boldsymbol{k}_F^3 = N \quad \textbf{(1.15)}$$

where the factor 2 comes from the spin degeneracy. Then

$$k_F = \left(\frac{3\pi^2 N}{V}\right)^{1/3} \quad \textbf{(1.16)}$$

this depends only of the particle concentration. We obtain then for the Fermi energy:

$$E_F = \frac{\hbar}{2m}\left(\frac{3\pi^2 N}{V}\right)^{2/3} \quad \textbf{(1.17)}$$

and the Fermi velocity

$$v_F = \frac{\hbar}{m}\left(\frac{3\pi^2 N}{V}\right)^{1/3} \quad \textbf{(1.18)}$$

An important quantity which characterizes electronic properties of a solid is the *density of states*, which is the *number of electronic states per unit energy range*. To find it we use Eq.(1.17) and write the total number of orbitals of energy $\leq E$:

$$N(E) = \frac{V}{3\pi^2}\left(\frac{2mE}{\hbar^2}\right)^{3/2} \quad \textbf{(1.19)}$$

The density of states is then

$$D(E) = \frac{dN}{dE} = \frac{V}{2\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} . E^{1/2} \quad \textbf{(1.20)}$$

or equivalently

$$D(E) = \frac{3N}{2E} \quad \textbf{(1.21)}$$

So within a factor of the order of unity, the number of states per unit energy interval at the Fermi energy $D(E_F)$, is the total number of conduction electrons divided by the Fermi energy.
The density of states normalized in such a way that the integral

$$N = \int_0^{E_F} D(E)dE \quad \textbf{(1.22)}$$

gives the total number of electrons in the system. At non-zero temperature we should take into account the Fermi distribution function so that

$$N = \int_0^{\infty} D(E)f(E)dE \quad \textbf{(1.23)}$$

This expression also determines the chemical potential.

3.5 Heat capacity

The question that caused the greatest difficulty in the early development of the electron theory of metals concerns the heat capacity of the conduction electrons. Classical statistical mechanics predicts that a free particle should have a heat capacity of $^3/_2\, k_B$, where k_B is the Boltzmann constant. If *N* atoms each give one valence electron to the electron gas and the electrons are freely mobile, then the electronic contribution to the heat capacity should be $^3/_2\, \mathrm{Nk_B}$, just as for the atoms of a monatomic gas. But the observed electronic contribution at room temperature is usually less than 0.01 of this value. This discrepancy was resolved only upon the discovery of the Pauli Exclusion Principle and the Fermi distribution function. When we heat the specimen from absolute zero not every electron gains an energy $\sim k_B T$as expected classically, but only those electrons, which have the energy within an energy range $k_B T$ of the Fermi level, can be excited thermally. These electrons gain an energy, which is itself of the order of$k_B T$, as in Fig. 3. This gives a qualitative solution to the problem of the heat capacity of the conduction electron gas. If *N* is the total number of electrons, only a fraction of the order of $k_B T/E_F$ can be excited thermally at temperature *T*, because only these lie within an energy range of the order of $k_B T$ of the top of the energy distribution. Each of these $Nk_B\, ^T/_{E_F}$ electrons has a thermal energy of the order of $k_B T$. The total electronic thermal kinetic energy *U* is of

the order of $U \cong \left(Nk_B{}^T/_{E_F}\right) k_B T$. The electronic heat capacity is $C_{el} = \frac{du}{dT} = Nk_B\left(k_B{}^T/_{E_F}\right)$and is directly proportional to *T*, in agreement with the experimental results discussed in the following section. At room temperature *C* is smaller than the classical value $\approx Nk_B$ by a factor 0.01 or less, for $T_F \sim 5 \times 10^4 k$

We now derive a quantitative expression for the electronic heat capacity valid at low temperatures $k_B T \ll E_F$. The total energy of a system of *N* electrons at temperature *T* is

$$U = \int_0^\infty ED(E) f(E,T) dE \qquad \textbf{(1.24)}$$

Where f (*E*, *T*) is the Fermi distribution function and *D* (*E*) is the density of states. The heat capacity can be found by differentiating this equation with respect to temperature. Since only the distribution function depends on temperature we obtain

$$C_{el} = \frac{dU}{dT} = \int_0^\infty ED(E) \frac{df(E,T)}{dT} dE \qquad \textbf{(1.25)}$$

It is more convenient to represent this result in a different form:

$$C_{el} = \int_0^\infty (E - E_F) D(E) \frac{df(E,T)}{dT} dE \qquad \textbf{(1.26)}$$

Eq. (1.26) is equivalent to Eq. (1.25) due to the fact which follows from Eq. (1.22):

$$0 = E_F \frac{dN}{dT} = E_F \int_0^\infty D(E) \frac{df(E,T)}{dT} dE \qquad \textbf{(1.27)}$$

Since we are interested only temperatures for which $k_B T \ll E_F$the derivative $df/dT$is large only at the energies which lie very close to the Fermi energy. Therefore, we can ignore the variation of *D* (*E*) under the integral and take it outside the integrand at the Fermi energy, so that

$$C_{el} = D(E_F) \int_0^\infty (E - E_F) \frac{df(E,T)}{dT} dE \qquad \textbf{(1.28)}$$

We also ignore the variation of the chemical potential with temperature and assume that $\mu = E_F$, which is good approximation at room temperature and below. Then

$$\frac{\mathrm{df(E,T)}}{\mathrm{dT}} = \frac{\mathrm{E - E_F}}{\mathrm{k_B T^2}} \frac{\mathrm{e^{\left[(E - E_F)/k_B T\right]}}}{\left[\mathrm{e^{\left[(E - E_F)/k_B T\right]}}\right]^2} \qquad \textbf{(1.29)}$$

Eq. (1.28) can then be rewritten as

$$C_{el} = D(E_F) \int_0^\infty \frac{(E - E_F)^2}{k_B T^2} \frac{e^{(E - E_F/k_B T)}}{\left[e^{(E - E_F)/k_B T} + 1\right]^2} dE = D(E_F) \int_{-E_F/k_B T}^\infty \frac{x^2 (k_B T)^3}{k_B T^2} \frac{e^x}{(e^x + 1)^2} dx \qquad \textbf{(1.30)}$$

Taking into account that $E_F >> k_B T$, we can put the low integration limit to minus infinity and obtain

$$C_{el} = D(E_F)k_B^2 T \int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x+1)^2} dx = \frac{\pi^2}{3} D(E_F)k_B^2 T \quad \textbf{(1.31)}$$

For a free electron gas we should use Eq. (1.21) for the density of states to finally obtain

$$C_{el} = \frac{\pi^2}{2} N k_B \, T/_{T_F}, \quad \textbf{(1.32)}$$

where we defined the Fermi temperature $T_F = \frac{E_F}{k_B}$. This is similar to what we expected to obtain according to the qualitative arguments given in the beginning of this section. Experimentally the heat capacity at temperatures much below both the Debye temperature and the Fermi temperature can be represented in the form:

$$C = C_{el} + C_{ph} = \alpha T + \beta T^3 \quad \textbf{(1.33)}$$

The electronic term is dominant at sufficiently low temperatures. The constants α and β can be obtained by fitting the experimental data.

4.0 Conclusion

The classical free electron theory is an attempt to regard the valence electrons in metal as the non-interacting particles of an ideal gas. The only difference between this gas of electrons and any other ideal gas defined by kinetic theory is that the particles are charged.

5.0 Summary

- The energy of the highest occupied level is called the *Fermi energy*
- Various electronics states of the crystals can be obtained through the application of Schrodinger's wave equation.
- The total energy of a system of *N* electrons at temperature *T* is

$$\mathrm{U} = \int_0^{\infty} \mathrm{ED(E)f(E,T)dE}$$

6.0 Tutor marked assignment

Q1. Consider the free electron energy bands of an fcc crystal lattice in the reduced zone scheme in which all **k**'s are transformed to lie in the first Brillouin zone. Plot roughly in the [111] direction the energies of all bands up to six times the lowest band energy at the zone boundary at **k** = (2π/a)(½,½,½). Explain what happens with these bands in the presence of a weak crystal potential.

Q2. Suppose that the crystal potential in a one-dimensional lattice of lattice constant a is composed of a series of rectangular wells which surround the atom. Suppose that the depth of each well is U_0 and its width *a*/5.

a. Calculate the values of the first three energy gaps. Compare the magnitudes of these gaps.

b. Evaluate these gaps for the case of $U_0 = 5\ eV$ and $a = 4$Å.

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UNIT 2 ELECRONIC TRANSFER

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2.0 Objectives
3.0 Definition
  3.1 Drude model
  3.2 The origin of collision time
  3.3 Thermal conductivity
  3.4. Motion in a magnetic field
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1.0 Introduction

In this unit we are going to study how the classical free electron theory developed by Lorentz, Drude and Debye uses kinetic theory to calculate the transport properties of the free electron of a gas including electrical and thermal conductivity.

2.0 Objective

- To explain the Drude model of the thermal conductivity of solid
- To explain motion in Magnetic field in terms of Cyclotron resonance and Hall Effect

3.0 Definition

Electronic transfer is the determination of the thermal conductivity of electrons treated as classical particles.

3.1 Drude model

The simplest treatment of the electrical conductivity was given by Drude. There are four major assumptions within the Drude model.

i. Electrons are treated as classical particles within a free-electron approximation. Thus, in the absence of external electromagnetic fields each electron is taken to move uniformly in a straight line, neglecting the interactions with other electrons and ions. In the presence of external fields each electron is taken to move according to Newton's laws of motion.

ii. Electrons move free only between collisions with scattering centers. Collisions, as in kinetic theory, are instantaneous events that abruptly alter the velocity of an electron. Drude attributed them to the electrons scattering by ion

cores. However, as we will see later, this is not a correct picture of electron scattering on ordered periodic structures. A particular type of scattering centers does not matter in the Drude model. An understanding of metallic conduction can be achieved by simply assuming that there is *some* scattering mechanism, without inquiring too closely into just what that mechanism might be.

iii. An electron experiences a collision, resulting in an abrupt change in its velocity, with a probability per unit time$1/\tau$. This implies that the probability of an electron undergoing a collision in any infinitesimal time interval of length dt is just dt/τ. The time τ is therefore an average time between the two consecutive scattering events. It is known as, the *collision time* (relaxation time), it plays a fundamental role in the theory of metallic conduction. It follows from this assumption that an electron picked at random at a given moment will, on the average, travel for a time t before its next collision. The relaxation time t is taken to be independent of an electron's position and velocity.

iv. Electrons are assumed to achieve thermal equilibrium with their surroundings only through collisions. These collisions are assumed to maintain local thermo-dynamic equilibrium in a particularly simple way: immediately after each collision an electron is taken to emerge with a velocity that is not related to its velocity just before the collision, but randomly directed and with a speed appropriate to the temperature prevailing at the place where the collision occurred.

Now we consider the application of the Drude model for electrical conductivity in a metal. According to *Ohm's law,* the current *I* flowing in a wire (Fig 2.1) is proportional to the potential drop $V=V_2-V_1$ along the wire: $V = IR$, where *R*, the resistance of the wire, depends on its dimensions. It is much more convenient to express the *Ohm's law* in a form which is independent of the dimensions of the wire because these factors are irrelevant to the basic physics of the conduction We define the conductivity which is the proportionality constant between the current density **j** and the electric field **E** at a point in the metal:

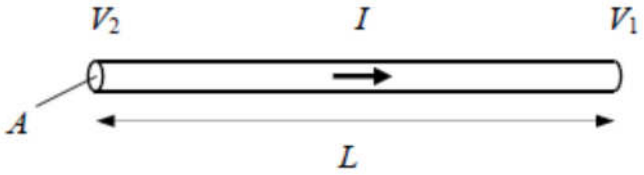

Fig. 2.1: Current flowing in a wire (After www.pa.uk.edu/kwng.phy/525/lec/lecture-8)

$$\boldsymbol{j} = \sigma \boldsymbol{E} \qquad \textbf{(2.1)}$$

The current density **j** is a vector, parallel to the flow of charge, whose magnitude is the amount of charge per unit time crossing a unit area perpendicular to the flow. Thus if a uniform current *I* flows through a wire of length *L* and cross-sectional area

A, the current density will be $j = {}^{I}/_{A}$ Since the potential drop along the wire will be $V = EL$ Eq. (2.1) gives $I/A=\sigma V/L$, and hence $R = L/\sigma A = \rho L/A$, here we have introduced resistivity $\rho=1/\sigma$. Unlike *R*, σ and ρ is a property of the material, since it does not depend on the shape and size. Now we want to express σ is terms of the microscopic properties using the Drude model. If *n* electrons per unit volume all move with velocity **v**, then the current density they give rise to will be parallel to **v**. Furthermore, in a time dt the electrons will advance by a distance vdt in the direction of v, so that $n(vdt)A$ electrons will cross an area *A* perpendicular to the direction of flow. Since each electron carries a charge -*e*, the charge crossing *A* in the time dt will be $-nevAdt$ and hence the current density is

$$\boldsymbol{j} = ne\boldsymbol{v}. \qquad \textbf{(2.2)}$$

At any point in a metal, electrons are always moving in a variety of directions with a variety of thermal energies. The net current density is thus given by Eq. (2.2), where **v** is the average electronic velocity or *drift velocity*. In the absence of an electric field, electrons are as likely to be moving in any one direction as in any other, **v** averages to zero, and, as expected, there is no net electric current density. In the presence of a field **E**, however, there will be a drift velocity directed opposite to the field (the electronic charge being negative), which we can compute as follows. Consider a typical electron at time zero. Let *t* be the time elapsed since its last collision. Its velocity at time zero will be its velocity V_0 immediately after that collision plus the additional velocity $-{}^{e\boldsymbol{E}t}/_{m}$ it has subsequently acquired. Since we assume that an electron emerges from a collision in a random direction, there will be no contribution from $\boldsymbol{v_0}$ to the average electronic velocity, which must therefore be given entirely by the average of $-{}^{e\boldsymbol{E}t}/_{m}$However, the average of *t* is the relaxation time $\boldsymbol{\tau}$. Therefore

$$\boldsymbol{V}_{avg} = -{}^{e\boldsymbol{E}t}/_{m} \qquad \textbf{(2.3)}$$

$$\boldsymbol{j} = -\frac{\boldsymbol{ne^2\tau}}{\boldsymbol{m}}\mathbf{E} \qquad \textbf{(2.4)}$$

The conductivity is, therefore, given by

$$\sigma = \frac{\mathrm{ne}^2\boldsymbol{\tau}}{\mathrm{m}} \qquad \textbf{(2.5)}$$

We see that the conductivity is proportional to the density of electrons, which is not surprising since the higher the number of carriers, the more the current density. The conductivity is inversely proportional to the mass because the mass determine the acceleration of an electron in electric field. The proportionality to τ follows because τ is the time between two consecutive collisions. Therefore, the larger τ is, the more time for electron to be accelerated between the collisions and consequently the larger the drift velocity. The values of relaxation time can be obtained from the measured values of electrical conductivity. For example at room temperature the resistivity of many metals lies in the range of 1-10 $\mu\Omega$cm. The corresponding relaxation time is of the order of $10-14\ s$. In this discussion of electrical conductivity we treated electrons on a classical basis. How are the results modified when the quantum mechanics is taken into account? Let us refer to Fig.2.3. In the absence of an electric

field, the Fermi sphere is centred at the origin (Fig. 2.3a). The various electrons are all moving - some at very high speeds - and they carry individual currents. But the total current of the system is zero, because, for every electron at velocity **v** there exists another electron with velocity -**v** and the sum of their two currents is zero. Thus the total current vanishes due to pair wise cancellation of the electron currents.

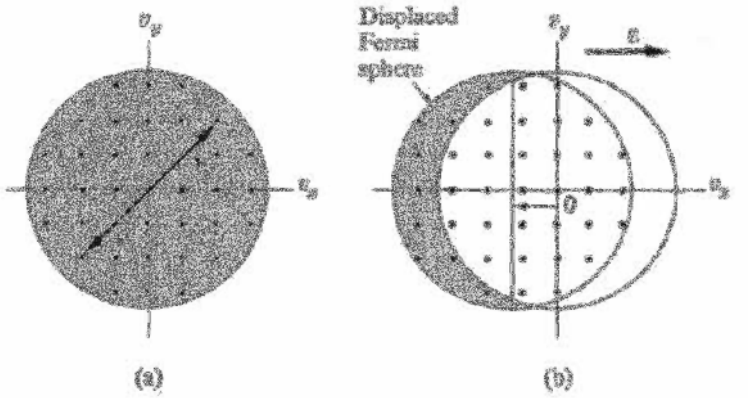

Fig.2.2: (a) The Fermi sphere at equilibrium, (b) Displacement of the Fermi sphere due to an electric field (After www.pa.uk.edu/kwng.phy/525/lec/lecture-8)

The situation changes when a field is applied. If the field is in the positive *x*-direction, each electron acquires a drift velocity, as given by Eq. (2.2). Thus the whole Fermi sphere is displaced to the left, as shown in Fig.2.2 (b). Although the displacement is very small and although the great majority of the electrons still cancel each other pair wise, some electrons - in the shaded crescent in the figure -remain uncompensated. It is these electrons which produce the observed current. The very small displacement is due to a relatively small drift velocity. If we assume that the electric field is 0.1V/cm, we obtain the drift velocity of 1cm/s, which is by 8, orders in magnitude smaller the Fermi velocity of electrons.

Let us estimate the current density. The fraction of electrons which remain uncompensated is approximately v/v_F. The concentration of these electrons is therefore $n(v/v_F)$and since each electron has a velocity of approximatelyv_F, the current density is given by

$$\boldsymbol{j} = -en(v/v_F)V_F = -nev \qquad \textbf{(2.6)}$$

This is the same expression we obtained before. Therefore, formally the conductivity is expressed by the same formula (2.5). However, the actual picture of electrical conduction is thus quite different from the classical one. In the classical picture, we assumed that the current is carried equally by all electrons, each moving with a very small drift velocity **v**. In the quantum-mechanical picture the current is carried only by very small fraction of electrons, all moving with the Fermi velocity. The relaxation time is determined only by electrons at the Fermi surface, because only these electrons can contribute to the transport properties. Both approaches lead to the same result, but the latter is conceptually the more accurate. Since only electrons at the Fermi surface contribute to the conductance, we can define the mean free path of electrons as $l = \boldsymbol{\tau} v_F$. We can make an estimate of the mean free path for metal at room temperature. This estimate gives a value of 100Å. So it is of the order of a few

tens inter atomic distances. At low temperatures for very pure metals the mean free path can be made as high as a few cm.

3.2 The origin of collision time

We see that between two collisions, the electron travels a distance of more than 20 times the inter atomic distance. This is much larger than one would expect if the electron really *did* collide with the ions whenever it passed them. This paradox can be explained only using quantum concepts according to which an electron has a wave character. It is well known from the theory of wave propagation in periodic structures that, when a wave passes through a periodic lattice, it continues propagating indefinitely without scattering. The effect of the atoms in the lattice is to absorb energy from the wave and radiate it back, so that the net result is that the wave continues without modification in either direction or intensity. Therefore we see that, if the ions form a perfect lattice, there is no collision at all - that is, $l = \infty$ - and hence $\tau = \infty$, which in turn leads to infinite conductivity. It has been shown, however, that the observed l is about 10^2 A. The finiteness of σ must thus be due to the deviation of the lattice from perfect periodicity; this happens either because of (1) thermal vibration of the ions, or because of (2) the presence of imperfections or foreign impurities.

In order to consider their contribution we examine the temperature dependence of the electrical conductivity. The electrical conductivity of a metal varies with temperature in a characteristic manner. This variation is usually discussed in terms of the behavior of the resistivity ρ versus T. Figure 2.3 shows the observed curve for Na. At $T \sim 0$°K, ρ has a small *constant* value; above that, ρ increases with T, slowly at first, but afterward ρ increases linearly with T. The linear behavior continues essentially until the melting point is reached. This pattern is followed by most metals, and usually room temperature falls into the linear range.

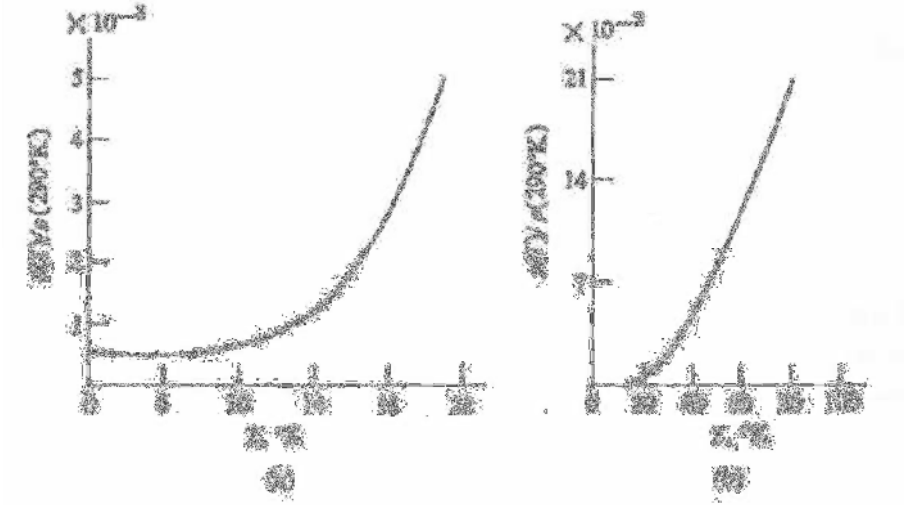

Fig. 2.3 The normalized resistivityρ $(T)/\rho$ (290°K) versus T for Na in the low-temperature region (a), and at higher temperatures (b) (After Kittel, 1979)

We want to explain this behavior in terms of the Drude formula. Recalling that $\rho = \sigma^{-1}$ we have

$$\rho = \frac{m}{ne^2\boldsymbol{\tau}} \quad \textbf{(2.7)}$$

As we have discussed earlier $1/\boldsymbol{\tau}$ which enters equation (2.7), is the probability of the electron scattering per unit time. Thus, if $\boldsymbol{\tau} = 10^{-14}s$, then the electron undergoes 10^{14} collisions in one second. We found that the electron undergoes collisions only because the lattice is not perfectly regular. We group the deviations from a perfect lattice into two classes. a) Lattice vibrations (phonons) of the ions around their equilibrium position due to thermal excitation of the ions. (b) All static imperfections, such as impurities or crystal defects. Of this latter group we shall take impurities as an example. The total probability for an electron to be scattered in a unit time is the sum of the probabilities of scattering by phonons and by impurities. This is because these two mechanisms are assumed to act independently. Therefore we may write

$$\frac{1}{\boldsymbol{\tau}} = \frac{1}{\boldsymbol{\tau}_i} + \frac{1}{\boldsymbol{\tau}_{ph}} \quad \textbf{(2.8)}$$

Where the first term on the right is due to impurities and the second is due to phonons. The scattering by impurities is essentially independent of temperature, whereas the scattering by phonons is temperature dependent because the number of phonons increases with temperature. When equation (2.8) is substituted into equation (2.7), we readily find

$$\rho = \rho_i + \rho_{ph} = \frac{m}{ne^2\tau_i} + \frac{m}{ne^2\tau_{ph}} \quad \textbf{(2.9)}$$

We see that ρ has split into two terms. A term ρ_i due to scattering by impurities, which is independent of *T*, is called the *residual resistivity.* Another term $\rho_{ph}(T)$is due to scattering by phonons; hence it is temperature dependent. Sometimes it is called the *lattice resistivity*.

At very low *T*, scattering by phonons is negligible because the amplitudes of oscillation are very small; in that region $\boldsymbol{\tau}_{ph} > \infty, \rho_{ph} > 0$and hence $\rho = \rho_i$ is a constant. This is in agreement with Fig.2.3. As *T* increases, scattering by phonons becomes more effective, and $\rho_{ph}(T)$,) increases; this is why ρ increases. When *T* becomes sufficiently large, scattering by phonons dominates and ρ ~$\rho_{ph}(T)$. The statement that ρ can be split into two parts, is known as the *Matthiessen rule.* This rule is embodied in (2.9). In general, the *Matthiessen rule* predicts that if there are two distinguishable sources of scattering (like in the case above – phonons and impurities) the resistivity is the sum of the resistivities due to the first and the second mechanism of scattering. The Matthiessen rule is sort of empirical observation which can be used for a qualitative understanding of the contribution from different scattering mechanisms. However, one must always bear in mind the possibility a failure of this rule. In particular, in the case when the relaxation time depends on the wave vector **k**, the Matthiessen rule becomes invalid.

Now let us derive approximate expressions for $\boldsymbol{\tau}_i$ and $\boldsymbol{\tau}_{ph}$ using arguments from the kinetic theory of gases. Consider first the collision of electrons with impurities. We write

$$\boldsymbol{\tau}_i = \frac{l_i}{v_F} \quad \textbf{(2.10)}$$

Where l_i is the mean free path for collision with impurities. In order to find the mean free path we shall assume, for simplicity, that the collision is of the hard-spheres (billiard-ball) type and introduce the *scattering cross section* of an impurity Σ_i which is the area an impurity atom presents to the incident electron. Then, we can argue that the product of the mean free path and the cross section of impurity $l_i\Sigma_i$, is equal to the average volume per impurity, $1/n_i$, where n_i is the impurity concentration, i.e.

$$l_i \sum_i = \frac{1}{n_i} \quad \textbf{(2.11)}$$

and therefore

$$l_i = \frac{1}{n_i \Sigma_i} \quad \textbf{(2.12)}$$

The scattering cross section Σ_i is of the same magnitude as the actual geometrical area of the impurity atom. That is, $\Sigma_i \sim 1\text{Å}^2$. Calculations of the exact value of Σ_i require quantum scattering theory. By substituting Eqs. (2.12) and Eqs. (2.10) into (2.9), we find

$$\rho_i = \frac{mv_F}{ne^2} n_i \Sigma_i \quad \textbf{(2.13)}$$

As expected, ρ_i is proportional to n_i the concentration of impurities. Calculating ρ_{ph} is much more difficult, but equations similar to (2.10) and (2.12) still hold. In particular, one may write

$$I_{ph} = \frac{1}{n_a \Sigma_a} \quad \textbf{(2.14)}$$

where n_a is the concentration of the host atoms in the lattice, and Σ_a is the scattering cross section per atom. We should note here that Σ_a has no relation to the geometrical cross section of the atom. Rather it is the area presented by the thermally fluctuating atom to the passing electron. Suppose that the distance of deviation from equilibrium is *x*, then the average scattering cross section is

$$\sum_a \propto \langle x^2 \rangle \quad \textbf{(2.15)}$$

where $\langle x^2 \rangle$ is the average of x^2. We can easily estimate this value at high temperatures, when the classical approach is valid. Since the ion is a harmonic oscillator, the value $\langle x^2 \rangle$ is proportional to the average of its potential energy is equal to half the total energy. Thus,

$$\sum_a \propto \langle x^2 \rangle \propto \frac{k_B}{2C} T \quad \textbf{(2.16)}$$

where *C* is inter atomic force constant introduced earlier and we used the formula for the energy of a classical oscillator. We see therefore that at high temperatures the resistivity is linear in *T*,

$$\rho_{ph} \propto \frac{m v_F n_a}{n e^2} \frac{k_B}{2C} T \qquad \textbf{(2.17)}$$

which is in agreement with experiment.
In the low-temperature range the lattice resistivity varies with temperature in a different way. Using the Debye model at low temperature range one can find that $\rho_{ph} \sim T^5$.

3.3 Thermal conductivity

When the ends of a metallic wire are at different temperatures, heat flows from the hot to the cold end. The basic experimental fact is that the heat current density, j_Q i.e. the amount of thermal energy crossing a unit area per unit time is proportional to the temperature gradient

$$j_Q = -K \frac{dT}{dx} \qquad \textbf{(2.18)}$$

where *K* is the thermal conductivity. In insulators, heat is carried entirely by phonons, but in metals heat may be transported by both electrons and phonons. The thermal conductivity *K* is therefore equal to the sum of the two contributions

$$K = K_e + K_{ph} \qquad \textbf{(2.19)}$$

where K_e and K_{ph} refer to electrons and phonons, respectively. In most metals, the contribution of the electrons greatly exceeds that of the phonons, because of the great concentration of electrons. Typically $K_e \sim 10^2 K_{ph}$

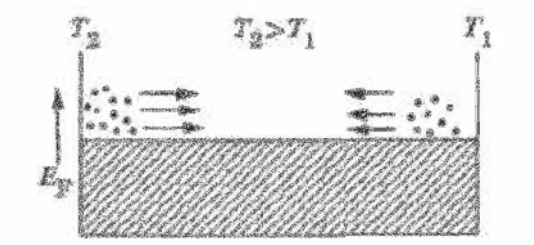

Fig.2.4: Heat conduction process (Afterwww.pa.uk.edu/kwng.phy/525/lec/lecture-8)

The physical process by which heat conduction takes place via electrons is illustrated in Fig.2.4. Electrons at the hot end (to the left) travel in all directions, but a certain fraction travel to the right and carry energy to the cold end. Similarly, a certain fraction of the electrons at the cold end (on the right) travel to the left, and carry energy to the hot end. Since on the average electrons at the hot end are more energetic than those on the right, a net energy is transported to the right, resulting in a current of heat. Note that heat is transported entirely by electrons having the Fermi energy, because those well below this energy cancel each other's contributions.

To evaluate the thermal conductivity *K* quantitatively, we use the formula $K = {}^{1}/_{3}\, C_{el} v_F l$ here C_{el} is the electronic specific heat per unit volume, v is the Fermi velocity of electrons; *l* is the mean free path of electrons at the Fermi energy. Using expression for the heat capacity derived earlier, we find

$$K = \frac{1}{3}\left(\frac{\pi^2}{2} n \frac{k_B^2}{E_F} T\right) v_F l \qquad \textbf{(2.20)}$$

Noting that $E = {}^{1}/_{2}\, m v_F^2$ and that ${}^{l}/_{v_F} = \boldsymbol{\tau}$ we can simplify this expression for *K* to

$$K = \frac{\pi^2 n k_B^2 \boldsymbol{\tau} T}{3m} \qquad \textbf{(2.21)}$$

This expresses thermal conductivity in terms of the electronic properties of the metal. Many of the parameters appearing in the expression for *K* were also included in the expression for electrical conductivityσ. Recalling that $\sigma = {}^{ne^2}/_{m}$ we find

$$\frac{K}{\sigma} = \frac{1}{3}\left(\frac{\pi k_B}{e}\right)^2 T = LT \qquad \textbf{(2.22)}$$

We see from here that the ratio of the thermal conductivity to the electrical conductivity is directly proportional to the temperature. This is called the *Wiedemann-Franz law*. The constant of proportionality *L*, which is called the Lorentz number, is independent of the particular metal. It depends only on the universal constants k_B and *e*, should be the same for *all* metals. The Lorentz number numerical value is$2.45 \times 10^{-8} W\Omega/K^2$. This conclusion suggests that the electrical and thermal conductivities are intimately related, which is to be expected, since both electrical and thermal current are carried by the same agent: electrons.

Worked example:

Solid Ar has an fcc structure with cubic lattice constant $a = 5.26$Å, atomic mass $m_{AR} = 6.67 \times 10^{-26}$ kg and a Debye temperature $\theta_D = 92^0 K$.

a) Estimate the phonon velocity using the Young modulus of Ar, $C_{11} = 1.6 \times 10^9 N/m^2$.

b) Using the expression $K = \frac{1}{3} Cvl$ in which C is the phonon heat capacity per unit volume. Find the thermal conductivity, K (in unit of $Jm^{-1}s^{-1}K^{-1}$) of a $1\, mm^3$ crystal of Ar at $1^0 K$, assuming that phonon scattering occurs only at the boundaries of the sample.

Solution:

a) The phonon velocity is estimated from the velocity of sound which is $v = \sqrt{C_{11}/\rho} = \sqrt{a^3 C_{11}/4m_{AR}}$ since in fcc structure there are 4 atoms in a cubic unit cell and hence, $= \frac{m}{a^3/4} = \frac{4m}{a^3}$, then,

$$v = \sqrt{5.26^3 \times 10^{-30} \times 1.6 \times 10^9 Nm^2 / 4 \times 6.67 \times 10^{-26} kgm^3} \approx 934\, ms^{-1}$$

b) Since $T = 1^0K \ll \theta_D = 92^0K$, we can use the low temperature approximation for heat capacity. Recall Eq.(5.37) in Module 2, unit 5, the heat capacity of a solid which contains N atoms is given,

$$C_v = \frac{12\pi^2}{5} N k_B \left(\frac{T}{\theta_D}\right)^3$$

Dividing the expression by N, we obtain the heat capacity per unit atom and dividing the latter by $a^3/4$, we obtain the heat capacity per unit volume, C. Therefore,

$$C_v = \frac{48\pi^2 k_B}{5a^3}\left(\frac{T}{\theta_D}\right)^3 = \frac{48 \times 3.14^3 \times 1.38 \times 10^{-23}}{5 \times 5.26^3 \times 10^{-30}}\left(\frac{1}{92}\right)^3 J/m^3K \approx 1.14 \times 10^2 J/m^3K$$

Since the scattering of phonons is determined by the boundaries of the sample we can assume that the mean free path is *l*= 1 mm and the thermal conductivity is

$$K = \frac{1}{3} C_v v l = 0.33 \times 1.14 \times 10^2 934 \times 10^{-3} J/m^3K\, m/s\, m \simeq 35 J/msK$$

3.4 Motion in a magnetic field

The application of a magnetic field to a metal gives rise to several interesting phenomena due to conduction electrons. The *cyclotron resonance* and the *Hall Effect* are to be considered

3.4.1 Cyclotron resonance

If a magnetic field is applied to a metal the Lorentz force **F** = –*e*[**E**+(**v** × **B**)] acts on each electron. For a perfect metal in the absence of electric field the equation of motion takes the form

$$m\frac{\boldsymbol{dv}}{\boldsymbol{dt}} = \text{-e}\mathbf{v} \times \boldsymbol{B} \qquad \textbf{(2.23)}$$

If the magnetic field lies along the *z*-direction this results in

$$\frac{dv_x}{dt} = -\omega_c v_{y,} \qquad \textbf{(2.24)}$$

$$\frac{dv_y}{dt} = \omega_c v_x$$

where

(2.25)

$$\omega_c = \frac{e\boldsymbol{B}}{m}$$

is the *cyclotron frequency* in SI system of units ($in\ CGS\ \omega_c = {eB}/{mc}$). For magnetic fields of the order of a few kG the cyclotron frequencies lie in the range of a few GHz. For example for *B*=1kG, the cyclotron frequency is $v_c = {\omega_c}/{2\pi} = 2.8GHz$. Therefore, the magnetic field causes electrons to move in a counterclockwise circular fashion with the cyclotron frequency in a plane normal to the field.

Suppose now that an electromagnetic signal is passed through the slab in a direction parallel to **B**, as shown in figure 2.5. The electric field of the signal acts on the electrons, and some of the energy in the signal is absorbed. The rate of absorption is greatest when the frequency of the signal is exactly equal to the frequency of the cyclotron (see Fig.2.5b), i.e.

$$\omega = \omega_c \qquad \textbf{(2.26)}$$

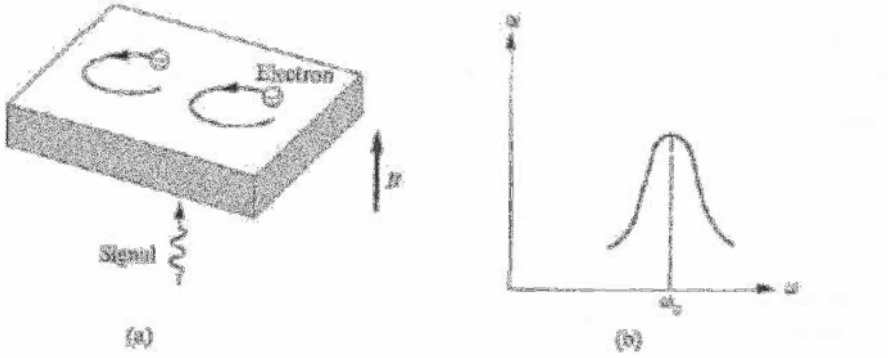

Fig. 2.5 (a) Cyclotron motion, (b) The absorption coefficient versus ω(After www.pa.uk.edu/kwng.phy/525/lec/lecture-8)

This is so because, when this condition holds true, each electron moves with the wave throughout the cycle, and therefore the absorption continues all through the cycle. Thus, Eq. (2.26) is the condition for *cyclotron resonance*. On the other hand, when Eq. (2.26) is not satisfied, the electron is in phase with the wave through only a part of the cycle, during which time it absorbs energy from the wave. In the remainder of the cycle, the electron is out of phase and returns energy to the wave. Cyclotron resonance is commonly used to measure the electron mass in metals and semiconductors. The cyclotron frequency is determined from the absorption curve, and this value is then substituted in Eqs. (2.25) to evaluate the effective mass.

3.4.2 Hall effect

First we derive an equation of motion of an electron in applied magnetic and electric field in the presence of scattering. Assume that that the momentum of an electron is $\boldsymbol{p}(t)$ at time *t*, let us calculate the momentum per electron $\boldsymbol{p}(t + dt)$ an infinitesimal time dt later. An electron taken at random at time *t* will have a collision before time $t + dt$, with probability dt/t, and will therefore survive to time $t + dt$ without suffering a collision with probability $1 - dt/t$. If it experiences no collision,

however, it simply evolves under the influence of the force **F** (due to the spatially uniform electric and/or magnetic fields) and will therefore acquire an additional momentum$\boldsymbol{F}dt$. The contribution of all those electrons that do not collide between *t* and $t + dt$ to the momentum per electron at time $t + dt$ is the fraction $(1 - dt/t)$ they constitute of all electrons, times their average momentum per electron, $\boldsymbol{p}(t) + \boldsymbol{F}dt$. Thus, neglecting the moment the contribution to $\boldsymbol{p}(t + dt)$ from those electrons that *do* undergo a collision in the time between *t* and$t + dt$, we have

$$\mathbf{p}(\mathrm{t} + \mathrm{dt}) = \left(1 - \frac{dt}{\boldsymbol{\tau}}\right)(\mathbf{p}(\mathrm{t}) + \mathbf{F}\mathrm{dt}) \qquad \textbf{(2.27)}$$

Note that if the force is not the same for every electron it should be averaged.

The correction to (2.27) due to those electrons that have had a collision in the interval *t* to $t + dt$ is only of the order of$(dt)^2$. To see this, first note that such electrons constitute a fraction dt/τ of the total number of electrons. Furthermore, since the electronic velocity (and momentum) is randomly directed immediately after a collision, each such electron will contribute to the average momentum $\boldsymbol{p}(t + dt)$ only to the extent that it has acquired momentum from the force **F** since its last collision. Such momentum is acquired over a time no longer than dt, and is therefore of order$\boldsymbol{F}dt$. Thus the correction to (2.27) is of order$(dt/t)\boldsymbol{F}dt$, and does not affect the terms of linear order in dt. We may therefore write

$$\frac{\mathbf{p}(\mathrm{t+dt}) - \mathbf{p}(\mathrm{t})}{dt} = \frac{d\mathbf{p}}{dt} = \mathrm{F} = -\frac{\mathbf{p}(\mathrm{t})}{\boldsymbol{\tau}} \qquad \textbf{(2.28)}$$

This simply states that the effect of individual electron collisions is to introduce a damping term into the equation of motion for the momentum per electron. We apply this equation to discuss the Hall Effect in metals using a free electron model. The physical process underlying the Hall Effect is illustrated in Fig.2.6. Suppose that an electric current J_x is flowing in a wire in the *x*-direction, and a magnetic field B_z is applied normal to the wire in the z-direction. We shall show that this leads to an additional electric field, normal to both J_x and B_z, that is, in the *y*-direction. Before the magnetic field is applied, there is an electric current flowing in the positive *x* direction, which means that the conduction electrons are drifting with a velocity **v** in the negative *x*-direction. When the magnetic field is applied, the Lorentz force $\boldsymbol{F} = -e(\boldsymbol{v}\,\boldsymbol{x}\,\boldsymbol{B})$ causes the electrons to bend downward, as shown in the figure. As a result, electrons accumulate on the lower surface, producing a net negative charge there. Simultaneously a net positive charge appears on the upper surface, because of the deficiency of electrons there. This combination of positive and negative surface charges creates a downward electric field$\boldsymbol{E_H}$, which is called the *Hall field*.

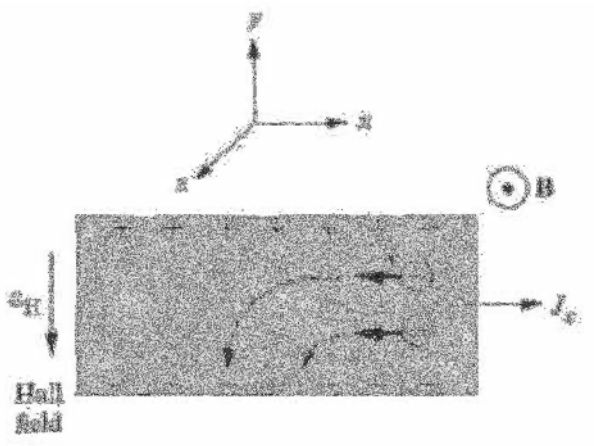

Fig. 2.6: Origin of the Hall field and Hall Effect

(After www.pa.uk.edu/kwng.phy/525/lec/lecture-8)

Let us evaluate this Hall field. We start from the Lorentz force acting on each electron $\mathbf{F} = -e\,[\mathbf{E} + (\mathbf{v} \times \mathbf{B})]$. According to (2.28) we find

$$m\frac{d\mathbf{v}}{dt} = -e\lfloor \mathbf{E} + \mathbf{v} \times \mathbf{B} \rfloor - m\frac{\mathbf{v}}{\boldsymbol{\tau}} \qquad \textbf{(2.29)}$$

where τ is the relaxation time. Note that the Lorentz force is not the same for all electrons because they move with different velocities; therefore it is averaged over ensemble. We are looking for the solution of this equation in the steady state when the current is independent of time and therefore $^{d\boldsymbol{v}}/_{dt} = 0$.

$$0 = -eE_x - eB\mathrm{v}_y - m\frac{\mathrm{v}_x}{\boldsymbol{\tau}}$$

$$0 = -eE_y + eB\mathrm{v}_x - m\frac{\mathrm{v}_y}{\boldsymbol{\tau}} \qquad \textbf{(2.30)}$$

We multiply these equations by $-ne\tau/m$ to introduce current densities components $j_x = -env_x$ and $j_y = -env_y$, so that

$$\sigma \mathrm{E_x} = \omega_c \boldsymbol{\tau} \mathrm{j_y} + \mathrm{j_x}$$

$$\sigma \mathrm{E}_y = -\omega_c \boldsymbol{\tau} j_x + j_y \qquad \textbf{(2.31)}$$

Where σ is the Drude conductivity in the absence of a magnetic field. In the steady state there is no electric current flowing perpendicular to the wire. Therefore the Hall field $E_H = E_Y$ can be determined by the requirement that there be no transverse current j_x. Setting j_x to zero in the second equation of (2.31) we find that

$$E_y = -\left(\frac{\omega_c \boldsymbol{\tau}}{\sigma}\right) j_x = -\frac{1}{ne} j_x B \qquad \textbf{(2.32)}$$

The proportionality constant $^{-1}/_{\mathrm{ne}}$, is known as the *Hall constant,* and is usually denoted by R_H.. Therefore,

$$R_H = -\frac{1}{ne} \quad \textbf{(2.33)}$$

This is a very striking result, which predicts that the Hall coefficient depends on no parameters of the metal except the density of carriers. Since R_H is inversely proportional to the electron concentration *n*, it follows that we can determine *n* by measuring the Hall field. Since we have already calculated *n* assuming that the atomic valence electrons become the metallic conduction electrons, a measurement of the Hall constant provides a direct test of the validity of this assumption.

4.0 Conclusion

The electrical and thermal conductivity of the free electron were obtained through the Drude model.

5.0 Summary

- Drude model provided the simplest treatment of electrical conduction of a metal
- The splitting up of resistivity to two terms (due to impurities and phonon) is known as Matthiessen rule
- Resistivity ((ρ_{ph}) due to scattering of phonons which is independent of temperature is known as lattice resistivity
- Resistivity (ρ_i) due to scattering by impurities which is independent of temperature is known as residual resistivity
- The cyclotron resonance and the Hall Effect are phenomena due to application of a magnetic field to a metal.

6.0 Tutor marked assignment

Q1. A Cu wire of diameter 2mm carries 10A of current. Find the drift velocity

Q2. If the Fermi energy of Na is 3.1 eV and the electrical conductivity is 2.1×10^{17} esu at 0K, calculate the relaxation time.

Q3. Using the Drude formula, calculate the mean free path of K, if its lattice parameter a = 4.2Å. Also calculate the Hall coefficient.

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UNIT 3 ENERGY BAND THEORY

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1.0 Introduction

The free electron model gives us a good insight into many properties of metals, such as the heat capacity, thermal conductivity and electrical conductivity. However, this model fails to help us with other important properties. For example, it does not predict the difference between metals, semiconductors and insulators. It does not explain the occurrence of positive values of the Hall coefficient. Also the relation between conduction electrons in the metal and the number of valence electrons in free atoms is not always correct. We need a more accurate theory, which would be able to answer these questions.

2.0 Objective

The objectives of this unit is

- To explain the general features of band levels
- To explain the periodic potential of an electron
- To explain the properties of the Bloch electron
- To explain the difference between Metals and Insulators.

3.0 Definition

Energy band is the range of energies possessed by electrons in a solid

3.1 Energy band

It is customary to visualize the existence of bands on an energy scale of band structure scheme, according to which, the energy bands for the most tightly bound electrons lie at the bottom, followed by the band of the second most tightly bound electrons, and so on, till we reach the top of the set of completely full energy bands. The top of the band of the set is known as the *valence band.* Next higher energy band is referred to as *conduction band*, which might be completely empty. The characteristic energy that separate the occupied from empty states is called *Fermi energy* E_F and is

characterized by Fermi level existing between the conduction band and the valence band. The two bands are separated by energy gap E_g, defined by

$$E_g = E_c - E_v \quad \textbf{(3.1)}$$

Where E_c and E_v are respectively the energy of the bottom of the conduction band and the top of the valence band. The E_g value for a semiconductor is typically of the order of 1 eV and that for an insulator is 5 eV. based o the relative positions of conduction and valence bands, metals may be classified into two categories. In one, valence band is completely full and conduction band is partially filled, e.g., Na, 2p (valence) band is completely full and conduction (3s) band is half filled. In the other, conduction and valence bands overlap each other. For example, Mg$(1s^2, 2s^2, 2p^6, 3s^2)$, $3s^2$(valence) and $3p$(conduction) bands overlap in energy.

3.2 Periodic Potential

The potential seen by an electron due to the nucleus of an isolated atom of valence z is $-ze^2/r$, where e is the electronic charge and r the nucleus –electron distance. However , the atom in a perfect crystal are arranged in a regular periodic array, therefore, we are led to consider the problem of an electron in a potential U(**r**) with the periodicity of the under-lying Bravais lattice i.e.

U(**r**) = U(**r** + **T**) **(3.2)**

where **T** is a lattice vector. Qualitatively, a typical crystalline potential might be expected to have a form shown in Fig.3.1, resembling the individual atomic potentials as the ion is approached closely and flattening off in the region between ions.

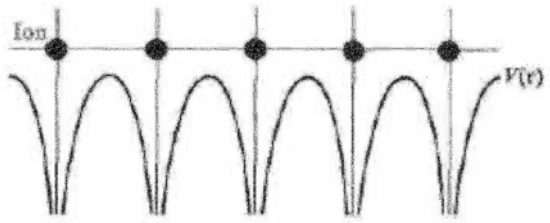

Fig.3.1: The crystal potential seen by the electron (After Kittel, 1979)

Since the scale of periodicity of the potential U (~ 10^{-8} cm) is the size of a typical de Broglie wavelength of an electron, it is essential to use quantum mechanics in accounting for the effect of periodicity on electronic motion. Thus we consider the Hamiltonian.

$$H(\boldsymbol{r}) = -\frac{\hbar^2}{2m}\boldsymbol{\nabla}^2 + U(\boldsymbol{r}) \quad \textbf{(3.3)}$$

Using Eq. (3.2) in Eq. (3.3) leads to

$$H(\boldsymbol{r} + \boldsymbol{T}) = H(\boldsymbol{r}) \quad \textbf{(3.4)}$$

This shows that the Hamiltonian also has the lattice periodicity. Hence, to predict the physical properties of the crystal, one should solve the following Schrodinger equation for a single electron

$$H(\boldsymbol{\psi}) = \left[-\frac{\hbar^2}{2m}\,\boldsymbol{\nabla}^2 + U(\boldsymbol{r})\right]\psi(r) = E\psi(r) \qquad \textbf{(3.5)}$$

in which ψ (**r**) is a wave function for one electron. Independent electrons, which obey a one electron Schrödinger equation (3.5) with a periodic potential, are known as *Bloch electrons*, in contrast to "free electrons," to which Bloch electrons reduce when the periodic potential is identically zero.
Now we discuss general properties of the solution of the Schrödinger equation (3.5) taking into account periodicity of the effective potential (3.2) and discuss main properties of Bloch electrons, which follow from this solution. We represent the solution as an expansion over plain waves.

$$\psi(\boldsymbol{r}) = \sum_{\mathrm{k}} c_k e^{i\boldsymbol{k}\boldsymbol{r}} \qquad \textbf{(3.6)}$$

This expansion in a Fourier series is a natural generalization of the free-electron solution for a zero potential. The summation in (3.6) is performed over all **k** vectors, which are permitted by the periodic boundary conditions. According to these conditions the wave function (3.6) should satisfy

$$\psi(x,y,z) = \psi(x+L,y,z) = \psi(x,y+L,z) = \psi(x,y,z+L) \qquad \textbf{(3.7)}$$

So that

$$\mathrm{k}_x = \frac{2\pi n_x}{L};\ \mathrm{k}_y = \frac{2\pi n_y}{L};\ \mathrm{k}_z = \frac{2\pi n_z}{L} \qquad \textbf{(3.8)}$$

where n_x, n_y, and n_z are positive or negative integers. Note that in general ψ (**r**) is *not* periodic in the lattice translation vectors. On the other hand, according to Eq. (3.2) the potential energy is periodic, i.e. it is invariant under a crystal lattice translation. Therefore, its plane wave expansion will only contain plane waves with the periodicity of the lattice. Therefore, only reciprocal lattice vectors are left in the Fourier expansion for the potential:

$$U(\boldsymbol{r}) = \sum_{\boldsymbol{G}} U_{\boldsymbol{G}} e^{i\boldsymbol{G}r} \qquad \textbf{(3.9)}$$

where the Fourier coefficients U_{G} are related to U(**r**) by

$$U_{\boldsymbol{G}} = \frac{1}{V_c}\int_{cell} e^{-i\boldsymbol{G}r} U(\boldsymbol{r})\,dr \qquad \textbf{(3.10)}$$

where V_c is the volume of the unit cell. It is easy to see that indeed the potential energy represented by (3.9) is periodic in the lattice:

$$\mathrm{U}(\mathbf{r}+\mathbf{T}) = \sum_{\mathbf{G}} \mathrm{U}_{\mathbf{G}} \mathrm{e}^{\mathrm{iG(r+T)}} = \mathrm{e}^{\mathrm{iGT}} \sum_{\mathbf{G}} \mathrm{U}_{\mathbf{G}} \mathrm{e}^{\mathrm{iGr}} = \mathrm{U}(\mathbf{r}) \qquad \textbf{(3.11)}$$

where the last equation comes from the definition of the reciprocal lattice vectors $e^{iGT} = 1$. The values of Fourier components U_G for actual crystal potentials tend to decrease rapidly with increasing magnitude of **G**. For example, for a Coulomb potential U_G decreases as $1/G^2$ .Note that since the potential energy is real the Fourier components should satisfy $U_{-G} = U_G^*$.

We now substitute (3.6) and (3.9) in Eq. (3.5) and obtain:

$$\frac{\hbar^2}{2m}\sum_k k^2 C_k e^{ikr} + \sum_k \sum_G U_G C_k e^{i(k+G)r} = E \sum_K C_k e^{ikr} \qquad \textbf{(3.12)}$$

changing the summation index in the second sum on the left from **k** to **k** +**G** this equation can be rewritten in a form:

$$\sum_{\mathbf{k}} e^{i\boldsymbol{k}r} \left\{ \left(\frac{\hbar^2}{2m} k^2 - E \right) C_k + \sum_G U_{\boldsymbol{G}} C_{\boldsymbol{k}-\boldsymbol{G}} \right\} = 0 \qquad \textbf{(3.13)}$$

Since this equation must be satisfied for any **r** the Fourier coefficients in each separate term of (3.13) must vanish and therefore

$$\left(\frac{\hbar^2}{2m} k^2 - E \right) C_k + \sum_G U_G C_{k-G} = 0 \qquad \textbf{(3.14)}$$

This is a set of linear equations for the coefficients $C_{\mathbf{k}}$. These equations are nothing but restatement of the original Schrödinger equation in the momentum space, simplified by the fact that the potential is periodic. This set of equations does not look very pleasant because, in principle, an infinite number of coefficients should be determined. However, a careful examination of Eq. (3.14) leads to important consequences.

First, we see that for a fixed value of **k** the set of equations (3.14) couples only those coefficients, whose wave vectors differ from **k** by a reciprocal lattice vector. In the one-dimensional case these are k, k±2π/a, k±4π/a, and so on. We can therefore assume that the **k** vector belongs to the first Brillouin zone. The original problem is decoupled to *N* independent problems (*N* is the total number of atoms in a lattice): for each allowed value of **k** in the first Brillouin zone. Each such problem has solutions that are superposition of plane waves containing only the wave vector **k** and wave vectors differing from **k** by the reciprocal lattice vector.

Putting this information back into the expansion (3.6) of the wave function ψ (**r**), we see that the wave function will be of the form

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} C_{k-G} e^{i(\boldsymbol{k}-\boldsymbol{G})\boldsymbol{r}} \quad \textbf{(3.15)}$$

where the summation is performed over the reciprocal lattice vectors and we introduced index **k** for the wave function. We can rearrange this so that

$$\psi_k(\boldsymbol{r}) = e^{i\boldsymbol{k}\boldsymbol{r}} \sum_{\boldsymbol{G}} C_{\boldsymbol{k}-\boldsymbol{G}} e^{-i\boldsymbol{G}\boldsymbol{r}} \quad \textbf{(3.16)}$$

Or

$$\psi_{\boldsymbol{k}}(\boldsymbol{r}) = e^{i\boldsymbol{k}\boldsymbol{r}} u_{\boldsymbol{k}}(\boldsymbol{r}) \quad \textbf{(3.17)}$$

where $u_k(\boldsymbol{r}) = u_k(\boldsymbol{r}+\boldsymbol{T})$ is a periodic function which is defined by

$$u_{\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} C_{\boldsymbol{k}-\boldsymbol{G}} e^{-i\boldsymbol{G}\boldsymbol{r}} \quad \textbf{(3.18)}$$

Equation (3.17) is known as Bloch theorem, which plays an important role in electronic band structure theory. Now we discuss a number of important conclusions which follow from the Bloch theorem.

1. Bloch's theorem introduces a wave vector **k**, which plays the same fundamental role in the general problem of motion in a periodic potential that the free electron wave vector **k** plays in the free-electron theory. Note, however, that although the free electron wave vector is simply $\boldsymbol{p}/\hbar$, where **p** is the momentum of the electron, in the Bloch case **k** is not proportional to the electronic momentum. This is clear on general grounds, since the Hamiltonian does not have complete translational invariance in the presence of a non-constant potential, and therefore its eigenstates will not be simultaneous eigenstates of the momentum operator. This conclusion is confirmed by the fact that the momentum operator, $\boldsymbol{p} = -\boldsymbol{i}\hbar\boldsymbol{\nabla}$, when acting on $\omega_k(\boldsymbol{r})$ gives

$$-i\hbar\nabla\psi_k(\boldsymbol{r}) = -i\hbar\nabla\left[e^{i\boldsymbol{k}\boldsymbol{r}} u_{\boldsymbol{k}}(\boldsymbol{r})\right] = \hbar\boldsymbol{k}\psi_k(\boldsymbol{r}) - i\hbar e^{i\boldsymbol{k}\boldsymbol{r}}\nabla u_{\boldsymbol{k}}(\boldsymbol{r}) \quad \textbf{(3.19)}$$

Which is not, in general, just a constant time $\omega_k(\boldsymbol{r})$; i.e., $\omega_k(\boldsymbol{r})$ is not a momentum eigenstate. Nevertheless, in many ways $\hbar\mathbf{k}$ is a natural extension of **p** to the case of a periodic potential. It is known as the *crystal momentum* or *quasimomentum* of the electron, to emphasize this similarity, but one should not be misled by the name into thinking that $\hbar\mathbf{k}$ is a momentum.

2 The wave vector **k** appearing in Bloch's theorem can always be confined to the first Brillouin zone (or to any other convenient primitive cell of the reciprocal lattice). This is because any **k**' not in the first Brillouin zone can be written as

$$\mathbf{k}' = \mathbf{k} + \mathbf{G} \quad \textbf{(3.20)}$$

where **G** is a reciprocal lattice vector and **k** does lie in the first zone. Since $e^{iGT} = 1$ for any reciprocal lattice vector, if the Bloch form Eq. (3.17) holds for **k**', it will also hold for **k**. An example is given below for a nearly free electron model.

The energy *E* of free electrons which is plotted versus *k* in Fig 3.2a exhibits a curve in the familiar parabolic shape. Figure 3.2b shows the result of translations. Segments of the parabola of Fig.3.2a are cut at the edges of the various zones, and are translated by multiples of $G = 2\pi/a$ in order to ensure that the energy is the same at any two equivalent points. Fig.3.2c displays the shape of the energy spectrum when we confine our consideration to the first Brillouin zone only. The type of representation used in Fig.3.2c is referred to as the *reduced-zone scheme.* Because it specifies all the needed information, it is the one we shall find most convenient. The representation of Fig.3.2 a, known as the *extended-zone scheme* is convenient when we wish to emphasize the close connection between a crystalline and a free electron. Fig.3.2b employs the *periodic-zone* scheme, and is sometimes useful in topological considerations involving the **k** space. All these representations are strictly equivalent; the use of any particular one is dictated by convenience, and not by any intrinsic advantages it has over the others.

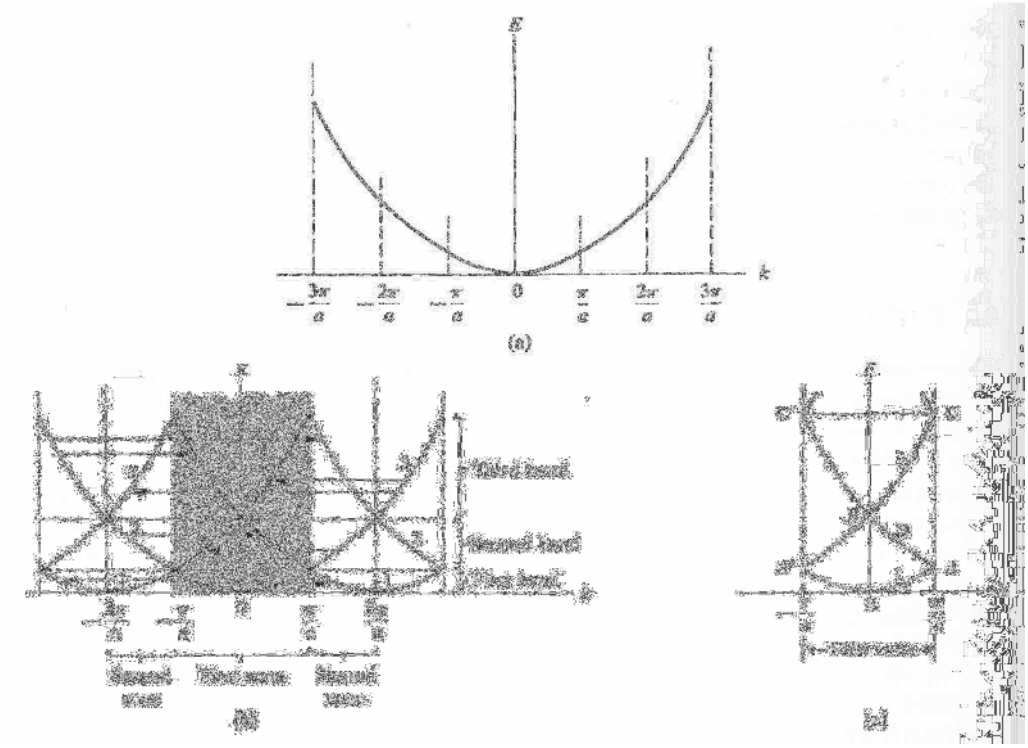

Fig.3.2 Free electron bands within *reduced-* (a), *extended-* (b) and *periodic-zone* (c) scheme (Afterwww.pa.uk.edu/kwng.phy/525/lec/lecture-8)

3 An important consequence of the Bloch theorem is the appearance of the energy bands. All solutions to the Schrodinger equation (3.5) have the Bloch form $\boldsymbol{\omega_k(r) = e^{ikr} u_k(r)}$ where **k** is fixed and $\boldsymbol{u_k(r)}$ has the periodicity of the Bravais lattice. Substituting this into the Schrodinger equation, we find that $\boldsymbol{u_k(r)}$is determined by the eigenvalue problem

$$H(\boldsymbol{k})u_{\boldsymbol{k}}(\boldsymbol{r}) = \left[-\frac{\hbar^2}{2m}(i\boldsymbol{k} + \nabla)^2 + U(\boldsymbol{r})\right]u_{\boldsymbol{k}}(\boldsymbol{r}) = E(\boldsymbol{k})u_{\boldsymbol{k}}(\boldsymbol{r}) \quad \textbf{(3.21)}$$

With boundary condition

$$\boldsymbol{u_k}(\boldsymbol{r}) = u_{\boldsymbol{k}}(\boldsymbol{r} + \boldsymbol{T}) \quad \textbf{(3.22)}$$

Because of the periodic boundary condition we can regard (3.21) as an eigenvalue problem restricted to a single primitive cell of the crystal. Because the eigenvalue problem is set in a fixed finite volume, we expect on general grounds to find an infinite family of solutions with *discretely* spaced eigenvalues, which we label with the band index *n.* The Bloch function can therefore be denoted by $\omega_{nk}(\boldsymbol{r})$ which indicates that each value of the band index *n* and the vector **k** specifies an electron state, or orbital with energy $E_n(\boldsymbol{r})$. Note that in terms of the eigenvalue problem specified by (3.21) and (3.22), the wave vector **k** appears only as a parameter in the Hamiltonian *H* (**k**). We therefore expect each of the energy levels, for given **k**, to vary continuously as **k** varies. In this way we arrive at a description of the levels of an electron in a periodic potential in terms of a family of continuous functions $E_n(\boldsymbol{r})$. For each *n*, the set of electronic levels specified by $E_n(\boldsymbol{r})$ is called an *energy band.* The information contained in these functions for different *n* and **k** is referred to as the *band structure* of the solid.

4 Number of states in a band.

The *number of orbitals in a band within the first Brillouin zone is equal to the number of unit cells N in the crystal.* This is much the same as the statement made in connection with the number of lattice vibrational modes, and is proved in a like manner, by appealing to the boundary conditions. Consider first the one-dimensional case. The allowed values of *k* form a uniform mesh whose unit spacing is 2π/*L.* The number of states inside the first zone, whose length is *2*π/*a*, is therefore equal to (2π/*a*)/ (2π/*L*) = *L*/*a* = *N*, where *N* is the number of unit cells, in agreement with the assertion made earlier. A similar argument may be used to establish the validity of the statement in two- and three-dimensional lattices. It has been shown that each band has *N* states inside the first zone. Since each such state can accommodate at most two electrons, of opposite spins, in accordance with the Pauli Exclusion Principle, it follows that the maximum number of electrons that may occupy a single band is *2N.* This result is significant, as it will be used in a later section to establish the criterion for predicting whether a solid is going to behave as a metal or an insulator.

5. Now we show that an electron in a level specified by band index *n* and wave vector **k** has a nonvanishing mean velocity, given by

$$v_n(\boldsymbol{k}) = \frac{\mathrm{dE_n}(\boldsymbol{k})}{\hbar \mathrm{d}\boldsymbol{k}} \quad \textbf{(3.23)}$$

To show this we calculate the expectation value of the derivative of the Hamiltonian H (**k**) in Eq. (3.21) with respect to **k**:

$$\langle u_n \left| \frac{dH(\boldsymbol{k})}{d\boldsymbol{k}} \right| u_n \rangle = \langle u_n \left| -i\frac{\hbar^2}{m}(i\boldsymbol{k} + \nabla) \right| u_n \rangle = \langle \psi_n \left| \hbar\left(-\frac{i\hbar}{m}\nabla\right) \right| \psi_n \rangle \quad \textbf{(3.24)}$$

Since $v = (-i\hbar/m)\nabla$ is the velocity operator, this establishes (3.23).

This is a remarkable fact. It asserts that there are stationary levels for an electron in a periodic potential in which, in spite of the interaction of the electron with the fixed lattice of ions, it moves forever without any degradation of its mean velocity. This is in striking contrast to the idea of Drude that collisions were simply encounters between the electron and a static ion.

3.3 Weak potential

When the potential is zero the solutions of the Schrödinger equation (3.14) are plane waves

$$E^{\mathbf{0}}(\boldsymbol{k}) = \frac{\hbar^2 \mathrm{k}^2}{2\mathrm{m}}, \quad \textbf{(3.25)}$$

$$\psi_k^0(r) = \frac{1}{\sqrt{V_c}} e^{i\boldsymbol{k}\boldsymbol{r}} \quad \textbf{(3.26)}$$

Where the wave function is normalized to the volume of unit cell V_c. In the reduced-zone representation shown in Fig.3.3, for each **k** there is an infinite number of solutions which correspond to different **G** (and can be labeled by index *n*), as we have already discussed. Each band in Fig.3.3 corresponds to a different value of **G** in the extended scheme.

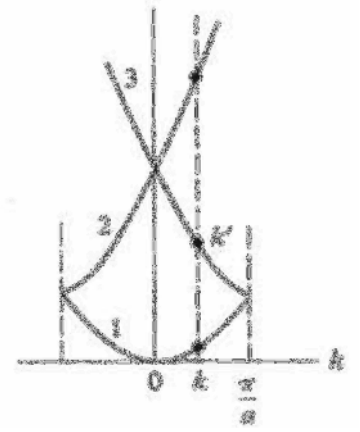

Fig.3.3: Only those states which have the same k in the First Brillouin zone are coupled by perturbation (After Kittel, 1979)

Suppose now that a weak potential is switched on. According to the Schrödinger equation (3.14) only those states, which differ by **G**, are coupled by a perturbation. In the reduced zone scheme those states have same **k** and different *n* (see Fig.3.3). From quantum mechanics, if the perturbation is small compared to the energy difference between the states, which are coupled by the perturbation, we can use the perturbation theory to calculated wave functions and energy levels. Assuming for simplicity that we are looking for the correction to the energy of the lowest band $E^0(\boldsymbol{k})$, the condition for using the perturbation theory is

$$|E^0(\boldsymbol{k}) - E^0(\boldsymbol{k}+\boldsymbol{G})| \gg U \qquad \textbf{(3.27)}$$

For any **G** ≠ 0. According to the perturbation theory the energy is given by

$$E(\boldsymbol{k}) = E^0 + \langle\psi_{\boldsymbol{k}}^0|U|\psi_{\boldsymbol{k}}^0\rangle + \sum_{\boldsymbol{G}\neq 0}\frac{\left|\langle\boldsymbol{\psi_k^0}|U|\psi_{\boldsymbol{k}-\boldsymbol{G}}^0\rangle\right|^2}{E^0(\boldsymbol{k})-E^0(\boldsymbol{k}-\boldsymbol{G})} \qquad \textbf{(3.28)}$$

The first term in Eq. (3.28) is the undisturbed free-electron value for the energy. The second term is the mean value of the potential in the state $\psi_{\boldsymbol{k}}^0(\boldsymbol{r})$:

$$\langle\psi_{\boldsymbol{k}}^0|U|\psi_{\boldsymbol{k}}^0\rangle = \frac{1}{V_c}\int_{cell} U(\boldsymbol{r})dr = U_0 \qquad \textbf{(3.29)}$$

This term gives a constant independent of **k**. Its effect on the spectrum is a rigid shift by a constant value without causing any change in the shape of the energy spectrum. This term can be set equal to zero. The third term can be rewritten as

$$\langle\psi_k^0|U|\psi_{\boldsymbol{k}}^0\rangle = \frac{1}{V_c}\int_{cell}\boldsymbol{e^{-ikr}}U(\boldsymbol{r})e^{i(\boldsymbol{k}-\boldsymbol{G})\boldsymbol{r}}dr = \frac{1}{V_c}\int_{cell}U(\boldsymbol{r})e^{-i\boldsymbol{G}\boldsymbol{r}}dr = U_{\boldsymbol{G}} \qquad \textbf{(3.30)}$$

Finally we obtain for the energy:

$$E(\boldsymbol{k}) = \boldsymbol{E^0} + \sum_{\boldsymbol{G}\neq\boldsymbol{0}}\frac{|U_{\boldsymbol{G}}|^2}{E^{\boldsymbol{0}}(\boldsymbol{k})-E^{\boldsymbol{0}}(\boldsymbol{k}-\boldsymbol{G})} \qquad \textbf{(3.31)}$$

The perturbation theory breaks down, however, in those cases when the potential cannot be considered as a small perturbation. This happens when the magnitude of the potential becomes comparable with the energy separation between the bands, i.e.

$$\left|E^0(\boldsymbol{k}) - E^{\boldsymbol{0}}(\boldsymbol{k}-\boldsymbol{G})\right| \leq U \qquad \textbf{(3.32)}$$

In this case we have to include these levels in the Schrödinger equation and solve it explicitly

There are special **k** points for which the energy levels become degenerate and the relationship (3.32) holds for any non-zero value of the potential. For these **k** points

$$E^0(\boldsymbol{k}) = E^0(\boldsymbol{k}-\boldsymbol{G}) \qquad \textbf{(3.33)}$$

and consequently

$$|\boldsymbol{k}| = |\boldsymbol{k}-\boldsymbol{G}| \qquad \textbf{(3.34)}$$

The latter conduction implies that **k** must lie on a Bragg plane bisecting the line joining the origin of **k** space and the reciprocal lattice point **G**, as is shown in Fig.3.4.

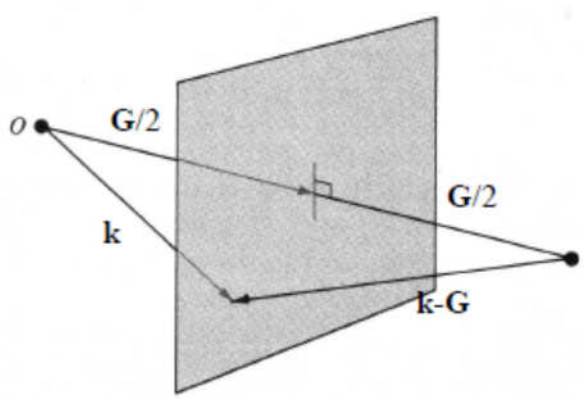

Fig. 3.4 If |**k**| = |**k** – **G**|, then the point **k** must lie in the Bragg plane determined by **G**. (Afterwww.pa.uk.edu/kwng.phy/525/lec/lecture-8)

Therefore, a weak periodic potential has its major effect on those free electron levels whose wave vectors are close to ones at which the Bragg reflection can occur. In order to find the energy levels and the wave functions of near these points we include to the equation (3.14) only the two levels: one which corresponds to **k** and the other which corresponds to $\boldsymbol{k-G}$ assuming that **k** lies near the Bragg plane:

$$(E^0(\boldsymbol{k}) - E)C_{\boldsymbol{K}} + U_{\boldsymbol{G}}C_{\boldsymbol{k-G}} = 0$$
$$(E^0(\boldsymbol{k-G}) - E)C_{\boldsymbol{k-G}} + U_{\boldsymbol{-G}}C_{\boldsymbol{k}} \qquad \textbf{(3.35)}$$

These equations have the solution when the determinant is equal to zero, i.e.

$$\begin{vmatrix} E^0(\boldsymbol{k}) - E & U_{\boldsymbol{G}} \\ U^*_{\boldsymbol{G}} & E^0(\boldsymbol{k-G}) - E \end{vmatrix} = 0 \qquad \textbf{(3.36)}$$

this leads to the quadratic equation

$$(E^0(\boldsymbol{k}) - E)(E^0(\boldsymbol{k-G}) - E) - |U_{\boldsymbol{G}}|^2 \qquad \textbf{(3.37)}$$

The two roots are

$$E = \frac{1}{2}\left(E^0(\boldsymbol{k}) + E^0(\boldsymbol{k-G})\right) \pm \left[\frac{1}{4}\left(E^0(\boldsymbol{k}) - E^0(\boldsymbol{k-G})\right)^2 + |U_{\boldsymbol{G}}|^2\right]^{1/2} \qquad \textbf{(3.38)}$$

These solutions are plotted in Fig.3.4 for **k** parallel to **G**.

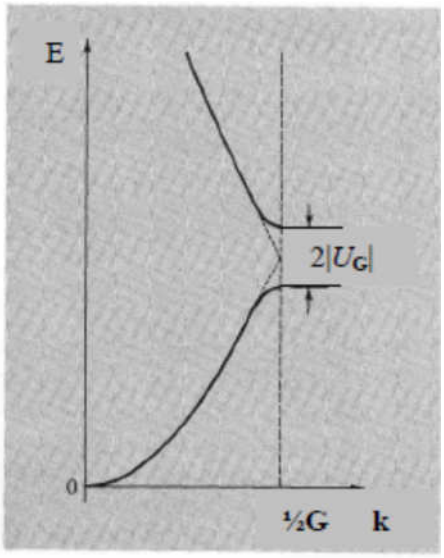

Fig.3.4: Plot of the energy bands given by Eq. (3.38) for **k** parallel to **G**. (Afterwww.pa.uk.edu/kwng.phy/525/lec/lecture-8)

This results is particularly simple for point lying on the Bragg plane, since in this case $E^0(\boldsymbol{k}) = E^0(\boldsymbol{k} - \boldsymbol{G})$ we find from (3.38) then that

$$E = E^0(\boldsymbol{k}) \pm |U_G| \qquad \textbf{(3.39)}$$

Thus, at all points in the Bragg plane, one level is uniformly raised by $|U_G|$and the other is uniformly lowered by the same amount. This means that there are no states in the energy interval between $E_1(\boldsymbol{k}) = E^0(\boldsymbol{k}) + |U_{\boldsymbol{G}}|$ and $E_2(\boldsymbol{k}) = E^0(\boldsymbol{k}) + |U_{\boldsymbol{G}}|$ which implies the creation of the band gap. The magnitude of the band gap is equal to twice the Fourier component of the crystal potential. We illustrate this behavior using a one-dimensional lattice shown in Fig.3.5. We see the splitting of the bands at each Bragg plane in the extended-zone scheme (Fig.3.5b). This results in the splitting of the bands both at the boundaries and at the centre of the first Brillouin zone (Fig.3.5a). There are two important points to note. First, since the energy there increases as k^2, the higher the band, the greater its width. Second, the higher the energy, the narrower the gap; this follows from the fact that the gap is proportional to a Fourier component of the crystal potential and that the order of the component increases as the energy rises. Since the Fourier components of the potential decrease rapidly as the order increases, this leads to a decrease in the energy gap. It follows therefore that, as we move up the energy scale, the bands become wider and the gaps narrower; i.e., the electron behaves more and more like a free particle.

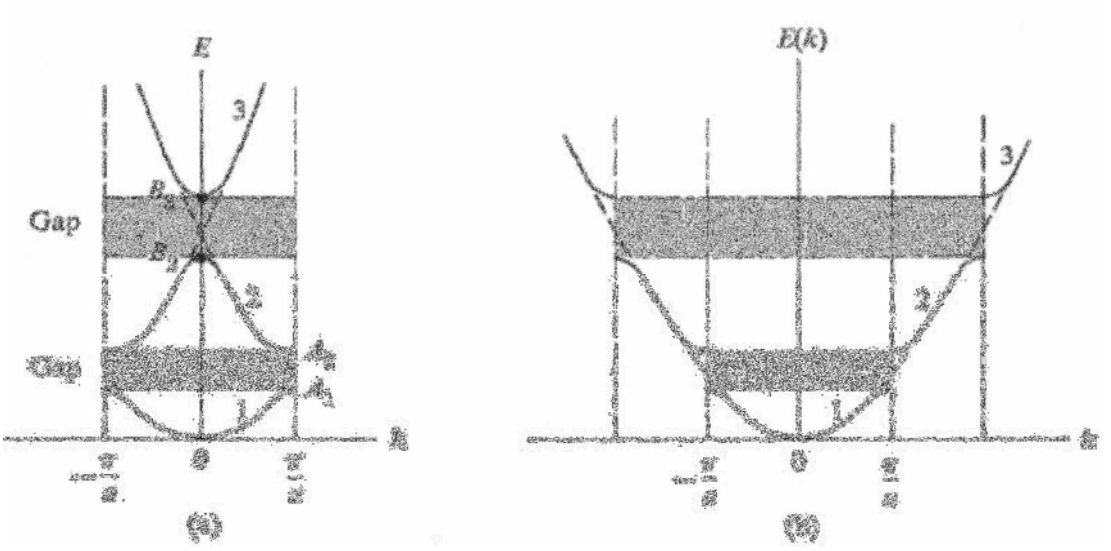

Fig. 3.5 (a) Dispersion curves in the nearly-free-electron model, in the reduced-zone scheme; (b) The same dispersion curves in the extended-zone scheme. (Afterwww.pa.uk.edu/kwng.phy/525/lec/lecture-8)

Now we discuss the origin of the appearance of the band gaps at the Bragg planes. When **k** lies on a Bragg plane we can easily find the form of the wave function corresponding to the two solutions (3.39). Assuming for simplicity that the potential is real we obtain from Eq. (3.35)

$$C_k = \pm C_{k-G} \qquad \textbf{(3.40)}$$

For simplicity we consider a one-dimensional lattice, for which the Bragg reflection occurs at **k**=½**G**. We have then

$$\psi_{\pm} = \frac{1}{\sqrt{2V_c}}\left[e^{iGr/2} \pm e^{iGr/2}\right] \qquad \textbf{(3.41)}$$

We see that at the zone edge, the scattering is so strong that the reflected wave has the same amplitude as the incident wave. The electron is represented there by a *standing* wave, very unlike a free particle.

The distribution of the charge density is proportional to $|\psi|^2$, so that

$$|\psi_+|^2 \propto \cos^2(\mathbf{G}\cdot\mathbf{r}/2),$$
$$|\psi_-|^2 \propto sin^2(\boldsymbol{G}\cdot\boldsymbol{r}/2) \qquad \textbf{(3.42)}$$

Since the origin lies at the ion, the ψ – state distributes the electron so that it is piled predominantly at the nuclei (see Fig.3.6). Since the potential is most negative there, this distribution has a low energy. The function ψ – therefore corresponds to the energy at the top of band 1, that is, point A_1 in Fig. 3.5a.

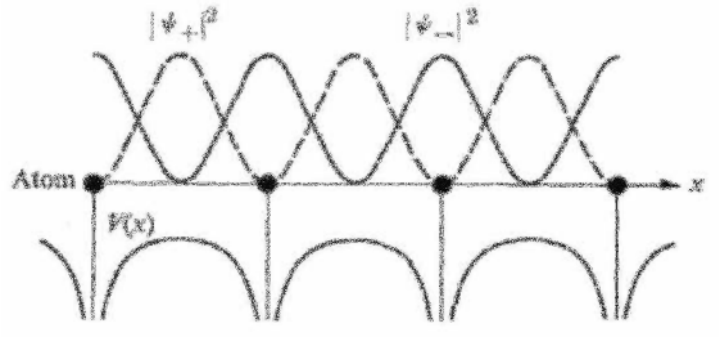

Fig.3.6: Spatial distributions of the charge density described by the functions ψ_+ and ψ_- (Afterwww.pa.uk.edu/kwng.phy/525/lec/lecture-8).

By contrast, the function ψ_+ deposits its electron mostly between the ions (as shown in Fig.3.6), corresponds to the bottom of band 2 in Fig.3.5a, that is, point A_2. The gap arises, therefore, because of the two different distributions for the same value of **k**, the distributions having different energies.

Worked Example:

Consider two-dimensional electrons subjected to a weak periodic potential coming from a square lattice of spacing $a = 5$ Å. For a $\boldsymbol{k}$ vectors far away from the Brillouin zone boundary, the wavefunction can be well described by planes waves. Assume we want to write the wavefunction in the Bloch form, $\psi(\boldsymbol{k}) = e^{\boldsymbol{ik.r}}u(\boldsymbol{r})$ and considering a state of energy $\boldsymbol{E}$ and wavevector $\boldsymbol{k} = \begin{pmatrix} 0.5\ \text{Å}^{-1} \\ 0 \end{pmatrix}$,

a) What will the three lowest energies be at this wavenumber?
b) What are the corresponding $u(\boldsymbol{r})$ functions

Note that $\hbar^2/_{2m} = 3.806\ eV\text{Å}^2$.

Solution:

a) Recall Eq.(3.5), the Schrodinger equation is

$$-\frac{\hbar^2}{2m}\frac{\delta^2\psi}{\delta \boldsymbol{k^2}} + V(\boldsymbol{r})\psi = E\psi(\boldsymbol{r})$$

Where $\frac{\delta^2\psi}{\delta k^2} = \Delta^2$

If the potential is weak, the solutions will be plane waves:
From Eq. (3.25)

$$E_k = \frac{\hbar^2|k^*|^2}{2m}$$

and Eq.(3.25)

$\psi(\boldsymbol{k}^*) = \frac{1}{\sqrt{V}} e^{i\boldsymbol{k}^*\boldsymbol{r}}$

where $\boldsymbol{k}^*$ extends over the entire $\boldsymbol{k}$ space. We can transform the $\boldsymbol{k}^*$wavevector into the first Brillouin zone by using Eq. (3.20) i.e.

$\boldsymbol{k}^* = \boldsymbol{k} + \boldsymbol{G}$

Let $\boldsymbol{k} = nb_1 + mb_2$,

Where b_1 and b_2 are primitive reciprocal lattice vectors and *n* and *m* are integers. The primitive reciprocal lattice vectors are given by

$b_1 = \begin{pmatrix} 1.256\ \text{Å}^{-1} \\ 0 \end{pmatrix}$ and $b_2 = \begin{pmatrix} 0 \\ 1.256\ \text{Å}^{-1} \end{pmatrix}$.

With the value of $k = 0.5\ \text{Å}^{-1}$, the length of the $\boldsymbol{k}^*$vector for several values of *n* and *m* is shown in the table below

n	*m*	$\lvert\boldsymbol{k}^*\rvert$
0	0	0.5
-1	0	0.756
1	0	1.756
0	1	1.351
0	-1	1.351
1	1	2.159

Since the energies increases with $|\boldsymbol{k}^*|$, the three lowest energies obtained using Eq. (3.25) are:

I. $E = 0.95\ eV\ (n = 0, m = 0)$
II. $E = 2.17\ eV\ (n = -1, m = 0)$
III. $E = 6.96\ eV (n = 0,\ \ m \pm 1)$

(b) From

$e^{i\boldsymbol{k}^*\boldsymbol{r}} = e^{i\boldsymbol{k}\boldsymbol{r}} u(\boldsymbol{r})$, $\quad r = \begin{pmatrix} x \\ y \end{pmatrix}$

Solving for $u(\boldsymbol{r})$, we have:

(a) $u(\boldsymbol{r}) = 1$
(b) $u(\boldsymbol{r}) = e^{-ib_1 x} = e^{-i1.256x}$
(c) $u(\boldsymbol{r}) = e^{\pm b_2 y} = e^{\pm 1.256y}$

Note that from Eq. (3.2), the function $u(r)$ has the periodicity of the lattice,$u(\boldsymbol{r}) = u(\boldsymbol{r} + \boldsymbol{T})$. The third energy level is degenerate; there are two corresponding wavefunctions.

3.4 Metals and Insulators

Solids are divided into two major classes: *metals and insulators*. A metal – or a conductor – is a solid in which an electric current flows under the application of electric field. By contrast, application of an electric field produces no electric current in an insulator. There is a simple criterion for distinguishing between the two classes on the basis of the band structure. If the valence electrons exactly fill one or more bands, leaving others empty, the crystal will be an insulator. An external electric field will not cause current flow in an insulator. Provided that a filled band is separated by energy gap from the next higher band, there is no continuous way to change the total momentum of the electrons if every accessible state is filled. Nothing changes when the field is applied.

On the contrary if the valence band is not completely filled the solid is a metal. In a metal there are empty states available above the Fermi level like in a free electron gas. An application of an external electric field results in the current flow. It is possible to determine whether a solid is a metal or an insulator by considering the number of valence electrons. A crystal can be an insulator only if the number of valence electrons in a primitive cell of the crystal is an even integer. This is because each band can accommodate only two electrons per primitive cell. For example, diamond has two atoms of valence four, so that there are eight valence electrons per primitive cell. The band gap in diamond is 7eV and this crystal is a good insulator. However, if a crystal has an even number of valence electrons per primitive cell, it is not necessarily an insulator. It may happen that the bands overlap in energy. If the bands overlap in energy, then instead of one filled band giving an insulator, we can have two partly filled bands giving a metal (Fig.3.7b). For example, the divalent metals, such as Mg or Zn, have two valence electrons per cell. However, they are metals, although a poor ones – their conductivity is small.

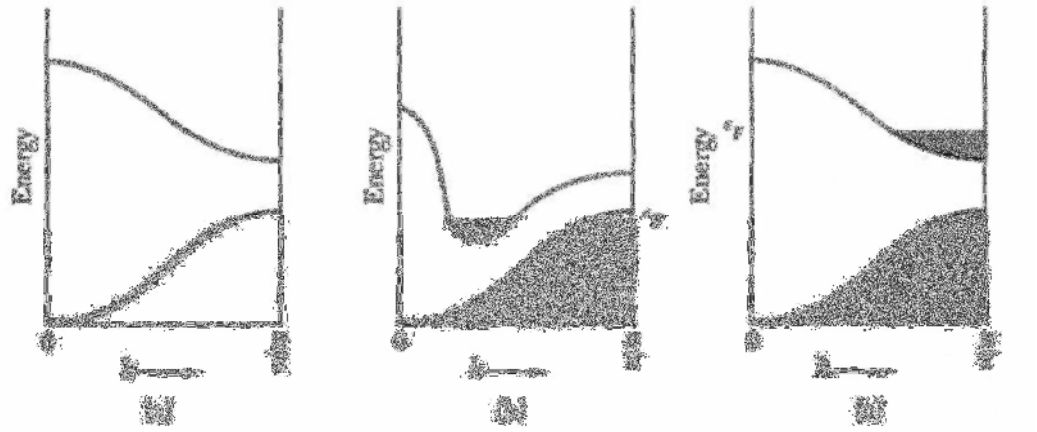

Fig.3.7: Occupied states and band structures giving (a) an insulator, (b) a metal or a semimetal because of band overlap, and (c) a metal because of electron concentration (After Kittel, 1979)

If this overlap is very small, we deal with *semimetals*. The best known example of a semimetal is bismuth (Bi). If the number of valence electrons per cell is odd the solid is a metal. For example, the alkali metals and the noble metals have one valence electron per primitive cell, so that they have to be metals. The alkaline earth metals have two valence electrons per primitive cell; they could be insulators, but the bands

overlap in energy to give metals, but not very good metals. Diamond, silicon, and Germanium each have two atoms of valence four, so that there are eight valence electrons per primitive cell; the bands do not overlap, and the pure crystals are insulators at absolute zero. There are substances, which fall in an intermediate position between metals and insulators. If the gap between the valence band and the band immediately above it is small, then electrons are readily excitable thermally from the former to the latter band. Both bands become only partially filled and both contribute to the electric condition. Such a substance is known as a *semiconductor*. Examples are Si and Ge, in which the gaps are about 1 and 0.7 eV, respectively. Roughly speaking, a substance behaves as a semiconductor at room temperature whenever the gap is less than 2 eV. The conductivity of a typical semiconductor is very small compared to that of a metal, but it is still many orders of magnitude larger than that of an insulator. It is justifiable, therefore, to classify semiconductors as a new class of substance, although they are, strictly speaking, insulators at very low temperatures.

4.0 Conclusion

Solution of Schrodinger equation for a single electron allows the prediction of the physical properties of a crystal while the Bloch theorem plays an important role in electronic band structure theory.

5.0 Summary

- Separation of the valence and conduction band : $E_g = E_c - E_v$
- Periodic potential of an electron is in the form: $U(\boldsymbol{r}) = U(\boldsymbol{r} + \boldsymbol{T})$
- One electron Schrödinger equation with a periodic potential, are known as Bloch electrons
- From the Bloch theorem, The number of orbitals in a band within the first Brillouin zone is equal to the number of unit cells N in the crystal
- Solids are divided into two major classes: metals and insulators which can be distinguished on the basis of band structure.

6.0 Tutor marked assignment

Q1. Using the solution for the energy bands near the zone boundary in the presence of a weak crystal potential. Show that the electron velocity is parallel to the Bragg plane.

Q2. Prove that the current carried by Bloch electrons is given by

$$\boldsymbol{j} = -\left(\frac{\hbar \boldsymbol{e} \boldsymbol{u}_{\boldsymbol{k}}^{\boldsymbol{2}}}{m}\right)\boldsymbol{k}$$

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UNIT 4 ELECTRON DYNAMICS

CONTENT

1.0 Introduction
2.0 Objectives
3.0 Definition
  3.1 Electron dynamics
  3.2 Effective mass
  3.3 Current density
4.0 Conclusion
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6.0 Tutor Marked Assignment
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1.0 Introduction

The Fermi surfaces (FS) concept enables to visualize the relative fullness or occupation of the allowed empty lattice bands geometrically in **k**-space and thus helps in the theoretical determination of the electronic properties of a solid- metal, semiconductor or insulator. In fact, the purpose of the FS construction is to know about the details of the motion of an itinerant electron in three-dimension.

2.0 Objective

- to understand the concept of Fermi surfaces
- to revise the concept of electron dynamic
- to revise the concept of effective mass
- to revise the concept of hole

3.0 Definition

Electron dynamics is using classical equations of motion in a classical way to describe electronic structure quantum-mechanically, i.e. standing waves that distribute electrons to different regions of the bands.

3.1 Electro dynamics

Given the functions $E_n(\mathbf{k})$ the semiclassical model associates with each electron a position, a wave vector and a band index n. In the presence of applied fields the position, the wave vector, and the index are taken to evolve according to the following rules:

(i) The band index is a constant of the motion. The semiclassical model ignores the possibility of interband transitions. This implies that within this model it assumed that the applied electric field is small.

(ii) The time evolution of the position and the wave vector of an electron with band index n are determined by the equations of motion:

$$\frac{d\boldsymbol{r}}{dt} = v_n(\boldsymbol{k}) = \frac{1}{\hbar}\frac{dE_n(\boldsymbol{k})}{d\boldsymbol{k}} \quad \textbf{(4.1)}$$

$$\hbar\frac{d\boldsymbol{k}}{dt} = \boldsymbol{F}(\boldsymbol{r},t) = -e\boldsymbol{E}(\boldsymbol{r},t) \quad \textbf{(4.2)}$$

Strictly speaking Eq. (4.2) has to be proved. It is identical to the Newton's second law if we assume that the electron momentum is equal to$\hbar$**k.** The fact that electrons belong to particular bands makes their movement in the applied electric field different from that of free electrons. For example, if the applied electric field is independent of time, according to Equation (4.2) the wave vector of the electron increases uniformly with time.

$$\boldsymbol{k}(t) = \boldsymbol{k}(0) - \frac{e\boldsymbol{E}t}{\hbar} \quad \textbf{(4.3)}$$

Since velocity and energy are periodic in the reciprocal lattice, the velocity and the energy will be oscillatory. This is in striking contrast to the free electron case, where **v** is proportional to **k** and grows linearly in time. The *k* dependence (and, to within a scale factor, the *t* dependence) of the velocity is illustrated in Fig 4.1, where both *E*(*k*) and v(*k*) are plotted in one dimension. Although the velocity is linear in *k* near the band minimum, it reaches a maximum as the zone boundary is approached, and then drops back down, going to zero at the zone edge. In the region between the maximum of v and the zone edge the velocity actually decreases with increasing *k*, so that the acceleration of the electron is opposite to the externally applied electric force! This extraordinary behavior is a consequence of the additional force exerted by the periodic potential, which is included in the functional form of *E* (*k*). As an electron approaches a Bragg plane, the external electric field moves it in the opposite direction due to the Bragg-reflection.

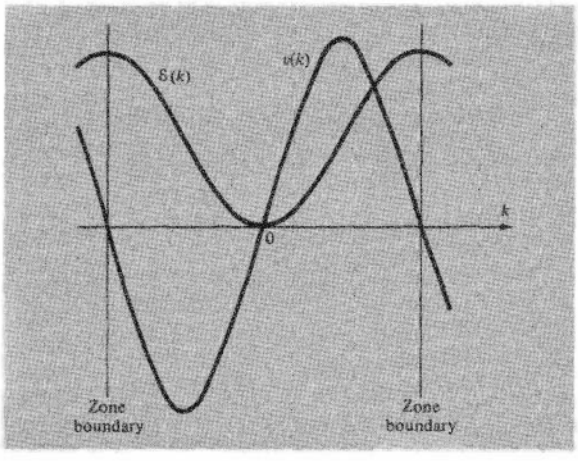

Fig.4.1. *E*(*k*) and v(*k*) vs. *k* in one dimension (After www.pa.uk.edu/kwng.phy/525/lec/lecture-8)

3.2 Effective mass

When discussing electron dynamics in solids it is often convenient to introduce the concept of effective mass. If we differentiate Eq. (4.1) with respect to time we find that

$$\frac{d\boldsymbol{v}}{dt} = \frac{1}{\hbar}\frac{d^2E}{d\boldsymbol{k}dt} = \frac{1}{\hbar}\frac{d^2E}{d\boldsymbol{k^2}}\frac{d\boldsymbol{k}}{dt} \qquad \textbf{(4.4)}$$

Where the second derivative with respect to a vector should be understood as a tensor. Using Eq. (4.2) we find that

$$\frac{d\boldsymbol{v}}{dt} = \frac{1}{\hbar^2}\frac{d^2E}{d\boldsymbol{k}^2}\boldsymbol{F} \qquad \textbf{(4.5)}$$

In one dimensional case this reduces to

$$\frac{dv}{dt} = \frac{1}{\hbar^2}\frac{d^2E}{dk^2}F \qquad \textbf{(4.6)}$$

This has the same form as the Newton's second law, provided that we defined an effective mass by the relation:

$$\frac{1}{m^*}\frac{1}{\hbar^2}\frac{d^2E}{dk^2} \qquad \textbf{(4.7)}$$

The mass m^* is inversely proportional to the curvature of the band; where the curvature is large - that is, $^{d^2E}/_{dk^2}$ is large - the mass is small; a small curvature implies a large mass (Fig.4.2).

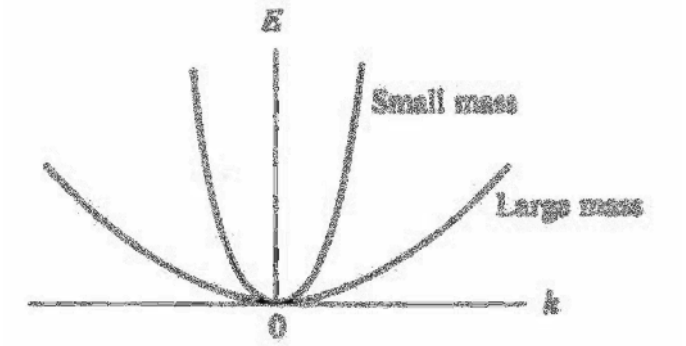

Fig: 4.2. The inverse relationship between the mass and the curvature of the energy band
(After www.pa.uk.edu/kwng.phy/525/lec/lecture-8).

In a general case the effective mass is a tensor which is defined by

$$\left(\frac{1}{m^*}\right)_{\mu\nu} = \frac{1}{\hbar^2}\frac{d^2E}{dk_\mu dk_\nu} \qquad \textbf{(4.8)}$$

Wherek_μ and k_v are Cartesian coordinates. The effective mass can be different depending on the directions on the crystal.

3.3 Current density

The current density within a free electron model was defined as $\boldsymbol{j} = -en\boldsymbol{v}$,
where *n* is the number of valence electrons per unit volume, and **v** is the velocity of electrons. This expression can generalize to the case of Bloch electrons. In this case the velocity depends on the wave vector and we need to sum up over **k** vectors for which there are occupied states available:

$$\boldsymbol{j} = \frac{-e}{V} \sum_{\boldsymbol{k},occupied} \boldsymbol{v}(\boldsymbol{k}) \qquad \textbf{(4.9)}$$

Here the sum is performed within the extended zone scheme and V is the volume of the solid. It is often convenient to replace the summation by the integration. Because the volume of **k**-space per allowed **k** value is $\Delta\boldsymbol{k} = {}^{8\pi^3}/_{V}$ we can write the sum over **k** as

$$\sum_{\boldsymbol{K}} = \frac{V}{8\pi^3} \int d\boldsymbol{k} \qquad \textbf{(4.10)}$$

Taking into account the spin degeneracy we obtain for the current density:

$$\boldsymbol{j} = -e \int_{Occupied} \frac{d\boldsymbol{k}}{4\pi^3} \boldsymbol{v}(\boldsymbol{k}) \qquad \textbf{(4.11)}$$

Using this expression we show now that *completely filled bands do not contribute to the current*. For the filled bands Eq. (4.11) should be replace by

$$\mathbf{j} = -\mathrm{e} \int_{\mathrm{zone}} \frac{\mathrm{d}\mathbf{k}}{4\pi^3} \frac{\mathrm{dE}(\mathbf{k})}{\mathrm{d}\mathbf{k}} \qquad \textbf{(4.12)}$$

This vanishes as a consequence of the theorem that the integral over any primitive cell of the gradient of a periodic function must vanish.

3.4 Hole

One of the most impressive achievements of the semiclassical model is its explanation for phenomena that free electron theory can account for only if the carriers have a positive charge. We now introduce the concept of a hole.

The contribution of all the electrons in a given band to the current density is given by Eq. (4.11), where the integral is over all occupied levels in the band. By exploiting the fact that a completely filled band carries no current, thus we have

$$0 = \int_{zone} \frac{dk}{4\pi^3} \boldsymbol{v}(\boldsymbol{k}) = \int_{occupied} \frac{d\boldsymbol{k}}{4\pi^3} \boldsymbol{v}(\boldsymbol{k}) + \int_{unoccupied} \frac{d\boldsymbol{k}}{4\pi^3} \boldsymbol{v}(\boldsymbol{k}) \quad \textbf{(4.13)}$$

we can equally well write Eq. (4.11), in the form:

$$\boldsymbol{j} = +e \int_{unoccupied} \frac{d\boldsymbol{k}}{4\pi^3} v(\boldsymbol{k}) \quad \textbf{(4.14)}$$

Thus the current produced by electrons occupying a specified set of levels in a band is precisely the same as the current that would be produced if the specified levels were unoccupied and all other levels in the band were occupied with particles of charge +e (opposite to the electronic charge).

Thus, even though the only charge carriers are electrons, we may, whenever it is convenient, consider the current to be carried entirely by fictitious particles of positive charge that fill all those levels in the band that are unoccupied by electrons. The fictitious particles are called *holes.* It must be emphasized that pictures cannot be mixed within a given band. If one wishes to regard electrons as carrying the current, then the unoccupied levels make no contribution; if one wishes to regard the holes as carrying the current, then the electrons make no contribution. One may, however, regard some bands using the electron picture and other bands using the hole picture, as suits one's convenience. Normally it is convenient to consider transport of the holes for the bands which are almost occupied, so that only a few electrons are missing. This happens in semiconductors in which a few electrons are excited from the valence to the conduction bands. Similar to electrons we can introduce the effective mass for the holes. It has a negative sign.

4.0 Conclusion

The electron dynamics in metals is the electronic structure described by quantum mechanics based on semiclassical model

5.0 Summary

- Effective mass of an electron is defined by

$$\frac{1}{m^*} = \frac{1}{\hbar^2} \frac{d^2E}{d\boldsymbol{k}^2}$$

- Current density is defined by

$$\boldsymbol{j} = -e \int_{occupied} \frac{d\boldsymbol{k}}{4\pi^3} \boldsymbol{v}(\boldsymbol{k})$$

6.0 Tutor marked assignment

Q1. Consider a slab of Cu 0.1mm thick, 10.0 mm wide and 10.0mm long.

(a) If a current of 1A is driven down the length of the slab, what is the current density?

(b) If we put the slab in the magnetic field of 1 T with the field perpendicular to the 1 mm x10 mm face, what Hall Effect will be produced, if the Hall coefficient is -0.55×10^{-10} m^3/C.

(c) What Hall voltage will be observed across the slab?

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UNIT 5 FERMI SURFACES

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3.0 Definition
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1.0 Introduction

The Fermi surface is the surface of constant energy ϵ_F in **k** space. The Fermi surface separates the unfilled orbitals from the filled orbitals, at absolute zero. Quantum mechanics showed that the occupation of electron states is governed by the Pauli exclusion and that the chemical potential, μ is equal to ϵ_F. The shape of the Fermi surface may be very intricate but the constructions required the applications of the reduced and the periodic zone schemes. In the reduced zone scheme, it is always possible to select the wavevector index **k** of any Bloch function to lie within the first Brillouin zone. This procedure is known as mapping the band in the reduced zone scheme. In the periodic zone, a given Brillouin zone is repeated periodically through all of the wavevector space. This is achieved by translating the zone by a reciprocal lattice.

2.0 Objective

- to understand Fermi surfaces
- to explain the Brillouin zone
- to explain effect of crystal potential

3.0 Definition

Fermi energy surface is the energy distribution of particles that obey the Pauli Exclusion Principle.

3.1 Fermi surface

The ground state of *N* Bloch electrons is constructed in a similar fashion as that for free electrons, i.e. by occupying all one-electron energy levels with band energies $E_n(\boldsymbol{k})$ less than E_F , where E_F is determined by requiring the total number of levels with energies less than E_F to be equal to the total number of electrons. The wave

vector **k** must be confined to a single primitive cell of the reciprocal lattice. When the lowest of these levels are filled by a specified number of electrons, two quite distinct types of configuration can result:

1. A certain number of bands may be completely filled, all others remaining empty. Because the number of levels in a band is equal to the number of primitive cells in the crystal (and because each level can accommodate two electrons (one of each spin), a configuration with a band gap can arise only if the number of electrons per primitive cell is even.

2 A number of bands may be partially filled. When this occurs, the energy of the highest occupied level, the Fermi energyE_F, lies within the energy range of one or more bands. For each partially filled band there will be a surface in **k**-space separating the occupied from the unoccupied levels. The set of all such surfaces is known as the Fermi surface, and is the generalization to Bloch electrons of the free electron Fermi sphere. The parts of the Fermi surface arising from individual partially filled bands are known as branches of the Fermi surface.

Analytically, the branch of the Fermi surface in the *n*-th band is that surface in **k**-space determined by

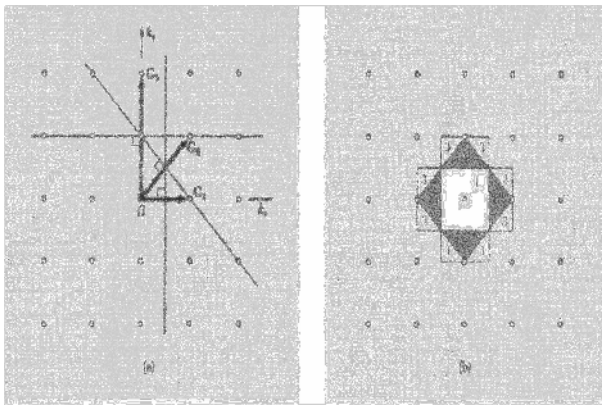
$$E_n(k) = E_F \qquad \textbf{(5.1)}$$

Thus the Fermi surface is a constant energy surface (surfaces) in **k**-space.

Since the $E_n(\boldsymbol{k})$ are periodic in the reciprocal lattice, the complete solution to Eq. (5.1) for each *n* is a **k**-space surface with the periodicity of the reciprocal lattice. When a branch of the Fermi surface is represented by the full periodic structure, it is said to be described in a *repeated zone scheme*. Often, however, it is preferable to take just enough of each branch of the Fermi surface so that every physically distinct level is represented by just one point of the surface. This is achieved by representing each branch by that portion of the full periodic surface contained within a single primitive cell of the reciprocal lattice. Such a representation is described as a *reduced zone scheme*. The primitive cell chosen is often, but not always, the first Brillouin zone.

3.2 Brillouin Zone

We consider now an example of building of a Fermi surface. We start from considering the Fermi surface for free electrons and then investigate the influence of the crystal potential. The Fermi surface for free electrons is a sphere centered at k = 0. To construct the Fermi surface in the reduced-zone scheme, one can translate all the pieces of the sphere into the first zone through reciprocal lattice vectors. This procedure is made systematically through the geometrical notion of the higher Brillouin zones



a **b**

Fig. 5.1: (a) Construction in **k** space of the first three Brillouin zones of a square lattice. (b) On constructing all lines equivalent by symmetry to the three lines in (a) we obtain the regions in **k** space which form the first three Brillouin zones (After Kittel, 1979).

We illustrate this construction for the two dimensional cubic lattice shown in Fig.5.1. Recall that the boundaries of the Brillouin zones are planes normal to **G** at the midpoint of **G**. The first Brillouin zone of the square lattice is the area enclosed by the perpendicular bisectors of $\boldsymbol{G_1}$ and of the three reciprocal lattice vectors equivalent by symmetry to $\boldsymbol{G_1}$ in Fig. 5.1a. These four reciprocal lattice vectors are $\pm\left(2\pi/a\right)\boldsymbol{k}_x^{\cdot}$ and $\pm\left(2\pi/a\right)\boldsymbol{k}_y^{\cdot}$. The second zone is constructed from $\boldsymbol{G_2}$ and the three vectors equivalent to it by symmetry, and similarly for the third zone. The pieces of the second and third zones are drawn in Fig. 5.1b.

In general, the *first Brillouin zone* is the set of points in k-space that can be reached from the origin without crossing *any* Bragg plane. The *second Brillouin zone* is the set of points that can be reached from the first zone by crossing only one Bragg plane. $The\ (n+1)-th$ *Brillouin zone* is the set of points not in the $(n-l)-th$ zone that can be reached from the $n-th$ zone by crossing only one Bragg plane. The free electron Fermi surface for an arbitrary electron concentration is shown in Fig.5.2.

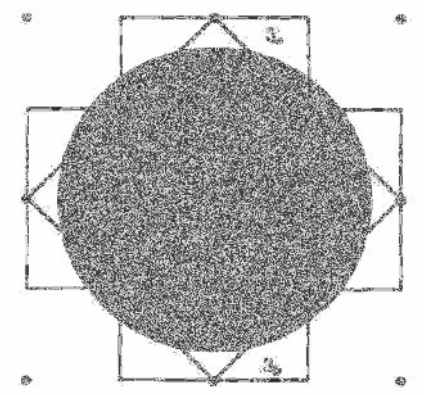
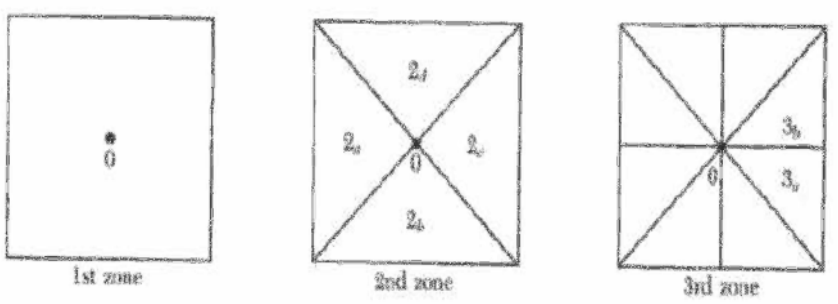


Fig.5.2: Brillouin zones of a square lattice in two dimensions (After Kittel, 1979).

Now we perform a transformation to the reduced zone scheme as is shown in Figs.5.3 and 5.4. We take the triangle labeled 2a (Fig 5.2) and move it by a reciprocal lattice vector $\boldsymbol{G} = -\left(2\pi/a\right)\boldsymbol{k}_x^{\cdot}$ such that the triangle reappears in the area of the first Brillouin

zone (Fig.5.3). Other reciprocal lattice vectors will shift the triangles 2_b, 2_c, 2_d to other parts of the first zone, completing the mapping of the second zone into the reduced zone scheme. The parts of the Fermi surface falling in the second zone are now connected, as shown in Fig. 5.4.



a **b** **c**

Fig.5.3 Mapping of the first, second, and third Brillouin zones in the reduced zone scheme. The sections of the second zone in Fig. 5.1 are put together into a square by translation through an appropriate reciprocal lattice vector (After Kittel, 1979).

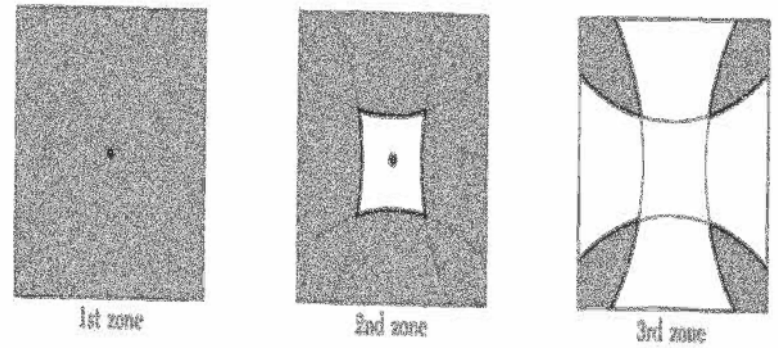
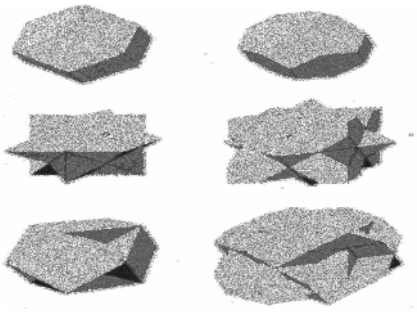


Fig.5.4: The free electron Fermi surfaces of Fig.5.3, as viewed in the reduced zone scheme. The shaded areas represent occupied electron states. Parts of the Fermi surface fall in the second and third zones. The first zone is entirely occupied (After Kittel, 1979).

Construction of Brillouin zones and Fermi surfaces in three-dimensions is more complicated. Fig5.5 shows the first three Brillouin zones for bcc and fcc structures.



a **b**

Fig.5.5: Surfaces of the first, second, and third Brillouin zones for (a) body-centered cubic and (b) face-centered cubic crystals. (Only the *exterior* surfaces are shown (After Kittel, 1979)..

The free electron Fermi surfaces for fcc cubic metals of valence 2 and 3 are shown in Fig.5.6.

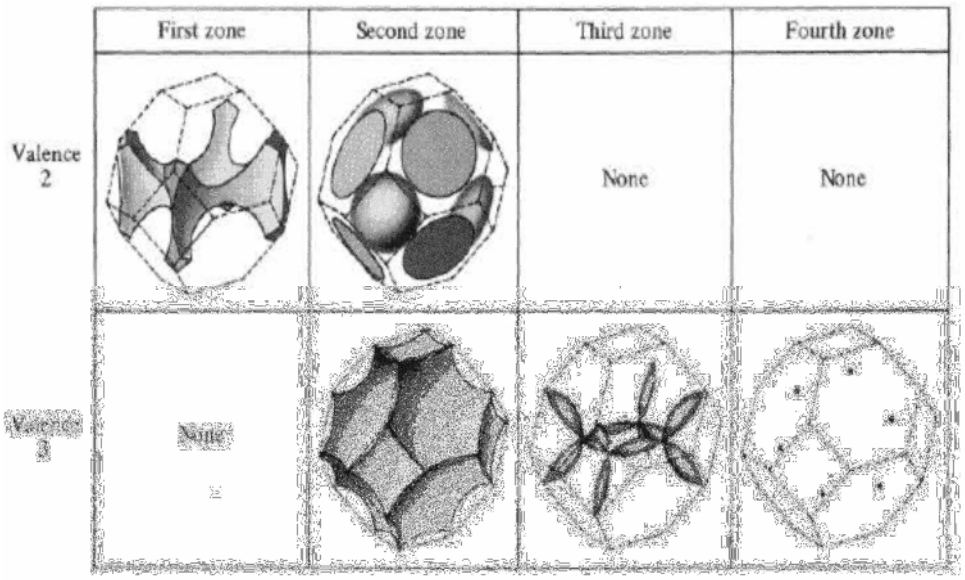


Fig.5.6: The free electron Fermi surfaces for face-centered cubic metals of valence 2 and 3(After Kittel, 1979).

3.3 Effect of a crystal potential

How do we go from Fermi surfaces for free electrons to Fermi surfaces in the presence of a weak crystal potential? We can make approximate constructions freehand by the use of the following facts:

(i) The interaction of the electron with the periodic potential of the crystal causes energy gaps at the zone boundaries.

(ii) Almost always the Fermi surface will intersect zone boundaries perpendicularly. Using the equation for the energy near the zone boundary it is easy to show that $\frac{dE}{d\boldsymbol{k}} = \frac{\hbar^2}{m}\left(\boldsymbol{k} - \frac{1}{2}\boldsymbol{G}\right)$ which implies that on the Bragg plane the gradient of energy is parallel to the Bragg plane. Since the gradient is perpendicular to the surfaces on which function is constant, the constant energy surfaces at the Bragg plane are perpendicular to the plane.

(iii) The crystal potential will round out sharp corners in the Fermi surfaces.

(iv) The total volume enclosed by the Fermi surface depends only on the electron concentration and is independent of the details of the lattice interaction.

(v) If a branch of the Fermi surface consists of very small pieces of surface (surrounding either occupied or unoccupied levels, known as "pockets of electrons" or "pockets of holes"), then a weak periodic potential may cause these to disappear. In addition, if the free electron Fermi surface has parts

with a very narrow cross section, a weak periodic potential may cause it to become disconnected at such points.

Below we give a few examples for real metals.

3.3.1. Alkali metals

The radius of the Fermi sphere in bcc alkali metals is less than the shortest distance from the center of the zone to a zone face and therefore the Fermi sphere lies entirely within the first Brillouin zone. The crystal potential does not distort much the free electron Fermi surface and it remains very similar to a sphere. Fig 5.7 shows Fermi surface for sodium.

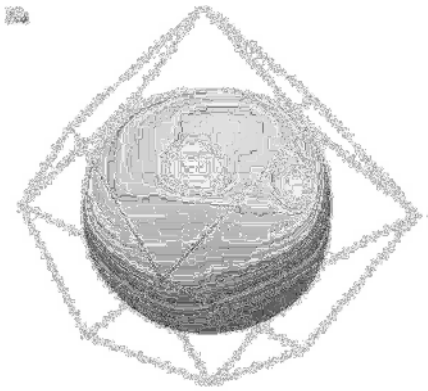


Fig.5.7: Fermi surface of sodium (After www.pa.uk.edu/kwang.phy/525/lec-8)

3.3.2. Noble metals

The Fermi surface for a single half-filled free electron band in fcc Bravais lattice is a sphere entirely contained within the first Brillouin zone, approaching the surface of the zone most closely in the [111] directions, where it reaches 0.903 of the distance from the origin to the center of the hexagonal face. For all three noble metals therefore their Fermi surfaces are closely related to the free electron sphere. However, in the [111] directions contact is actually made with the zone faces, and the measured Fermi surfaces have the shape shown in Fig.5.8. Eight "necks reach out to touch the eight hexagonal faces of the zone, but otherwise the surface is not grossly distorted from spherical.

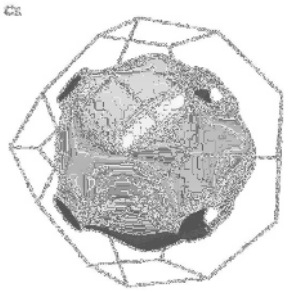


Fig. 5.8: In the three noble metals the free electron sphere bulges out in the [111] directions to make contact with the hexagonal zone faces.

3.3.3. Cubic divalent metals

With two electrons per primitive cell, calcium, strontium, and barium could, in principle, be insulators. In the free electron model, the Fermi sphere has the same volume as the first zone and therefore intersects the zone faces. The free electron Fermi surface is thus a fairly complex structure in the first zone, and pockets of electrons in the second. The question is whether the effective lattice potential is strong enough to shrink the second-zone pockets down to zero volume, thereby filling up all the unoccupied levels in the first zone. Evidently this is not the case, since the group II elements are all metals. Calculations show that the first Brillouin zone is completely filled and a small number of electrons in the second zone determine the non-zero conductance.

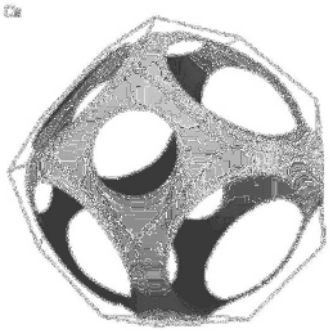


Fig.5.9: Fermi surface of calcium (Afterwww.pa.uk.edu/kwng.phy/525/lec/lecture-8)
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3.3.4. Trivalent metals

The Fermi surface of aluminum is close to that of the free electron surface for fcc cubic monatomic lattice with three conduction electrons per atom. The first Brillouin zone is filled and the Fermi surface of free electrons is entirely contained in the second, third and fourth Brillouin zones. When displayed in a reduced-zone scheme the second-zone surface is a closed structure containing unoccupied levels, while the third-zone surface is a complex structure of narrow tubes (Fig.5.6). The amount of surface in the fourth zone is very small, enclosing tiny pockets of occupied levels. The effect of a weak periodic potential is to eliminate the fourth-zone pockets of electrons, and reduce the third-zone surface to a set of disconnected "rings" (Fig.5.10). Aluminum provides a striking illustration of the theory of Hall coefficients. The high-field Hall coefficient should be,$R_H = -1(n_e - n_h)e$ where n_e and n_h are the number of levels per unit volume enclosed by the particle-like and hole-like branches of the Fermi surface. Since the first zone of aluminum is completely filled and accommodates two electrons per atom, one of the three valence electrons per atom remains to occupy second- and third-zone levels. Thus

$$n_e^{II} + n_e^{III} = \frac{n}{3} \qquad (5.2)$$

where *n* is the free electron carrier density appropriate to valence 3. On the other hand, since the total number of levels in any zone is enough to hold two electrons per atom, we also have

$$n_e^{II} + n_h^{II} = 2\frac{n}{3} \qquad (5.3)$$

Subtracting (5.3) from (5.2) gives

$$n_e^{III} + n_h^{II} = -\frac{n}{3} \qquad (5.4)$$

Thus the high-field Hall coefficient should have a positive sign and yield an effective density of carriers a third of the free electron value. This is precisely what is observed.

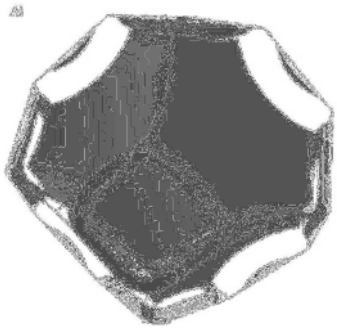

Fig.5.10: Fermi surface of aluminum (After www.pu. uk.edu/kwang.phys/525/lecture8)

4.0 Conclusion

The Fermi surfaces (FS) concept enables to visualize the relative fullness or occupation of the allowed empty lattice bands geometrically in **k**-space and thus helps in the theoretical determination of the electronic properties of a solid.

6.0 Summary

- The N Bloch electron is constructed when the wave vector k is confined to single primitive cell.
- In Alkali metals, the Fermi surface is very much like a sphere
- In Noble metals, the Fermi surface is a sphere entirely contained within the first Brillouin zone.
- In Cubic divalent metals, the Fermi surface has the same volume as the first Brillouin zone.
- In Trivalent metals, the Fermi surface is entirely contained in the 2^{nd} , 3^{rd} and the 4^{th} Brillouin zone.

6.0 Tutor marked assignment

Q1. A two-dimensional metal has one atom of valence one in a simple rectangular primitive cell of a_1 = 2Å and a_2 = 4Å.

(a) Draw the first and the second Brillouin zones.

(b) Calculate the radius of the free electron Fermi sphere and draw this sphere to scale on the drawing of the Brillouin zones.

(c) Draw the Fermi surface in reduced zone scheme and show schematically the effect of a weak crystal potential.

Q2 Suppose that some atoms in a Cu crystal, which has an fcc lattice, are gradually replaced by Zn atoms. Considering that Zn is divalent while Cu is monovalent, calculate the atomic ratio of Zn to Cu in a $CuZn$ alloy (brass) at which the Fermi sphere touches the zone faces. Use the free-electron model. This particular alloy is interesting because the solid undergoes a structural phase change at this concentration ratio.

7.0 Further reading/References

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MODULE 4 SEMICONDUCTORS AND SUPERCONDUCTORS

Unit 1 Structure and Bonding in Semiconductors
Unit 2 Semiconductor Statistics
Unit 3 Electrical Conductivity and Real Semiconductors
Unit 4 Super Conductivity (I): The Basic Phenomenon
Unit 5 Superconductivity (II): Experiments and Theories

UNIT 1 STRUCTURE AND BONDING (SEMICONDUCTORS)

CONTENT

1.0 Introduction
2.0 Objectives
3.0 Definition
- 3.1 Crystal structure and bonding
- 3.2 Bonding structure
- 3.3 intrinsic semiconductor
- 3.4 Impurities states
- 3.5 Acceptors

4.0 Conclusion
5.0 Summary
6.0 Tutor Marked Assignment
7.0 Further Reading/References

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.

3.0 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.

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

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

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

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).

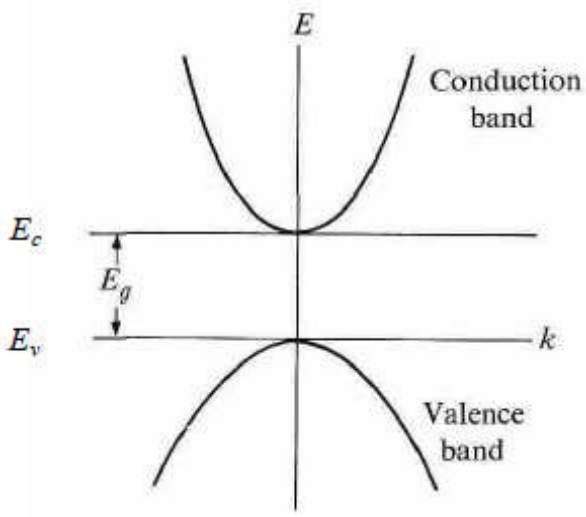

Fig. 1.1: Band structure in a semiconductor.

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.

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

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.

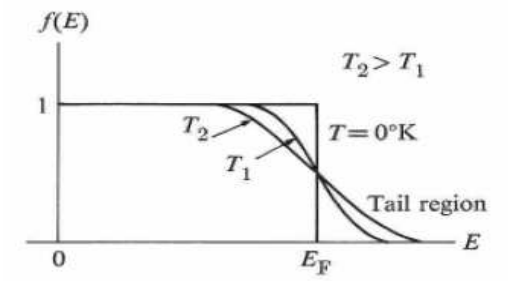

Fig. 1.2: The Fermi-Dirac distributions function (After Kittel, 1979)

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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.

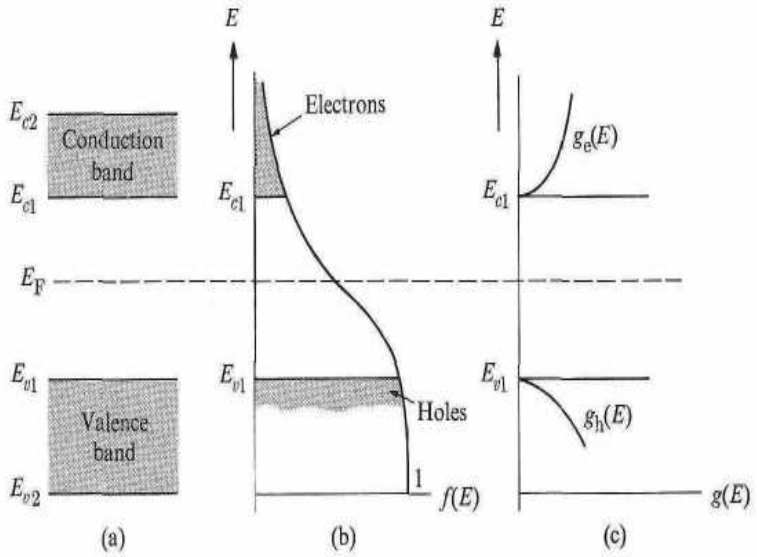

Fig.1.3: (a) conduction and valence bands (b) the distribution function
(c) Density of states for electrons and holes (After Kittel, 1979)

.

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.

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

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 $(E-\mu) >> k_B T$ and we can neglect the unity term in the denominator of the distribution function Eq. (1.3), so that

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

The density of the conduction band is given by

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

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

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

By changing the variable, and using the result

$$\int_0^\infty x^{1/2} e^{-x} dE = \frac{\sqrt{\pi}}{2} \quad \textbf{(1.8)}$$

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

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

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

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

The density of states for the holes is

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

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

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

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 **(1.13)**

and

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

We obtain then, for the Fermi energy

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

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.

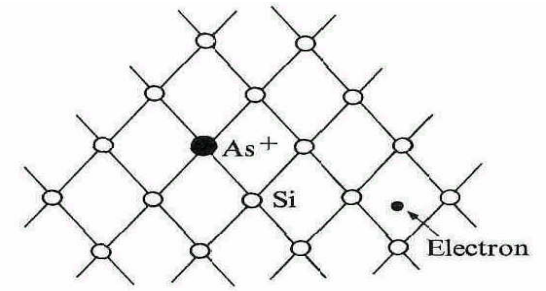

Fig.1.4: An As impurity in a Si crystal. The extra electron migrates through the crystal.

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

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

where ε is the reduced dielectric constant of the medium . The dielectric constant ε = 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

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

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 ε ~ 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.

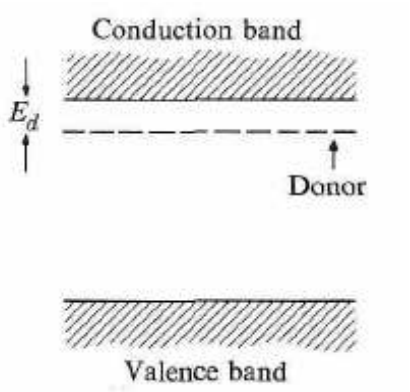

Fig. 1.5: The donor level in a semiconductor

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

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

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.

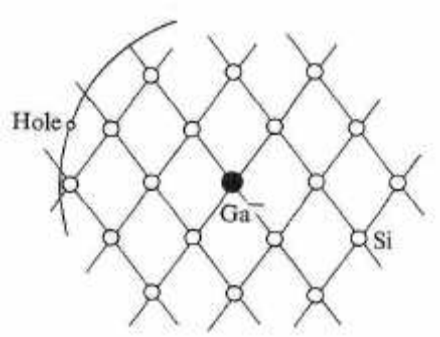

Fig. 1.6: A Ga impurity in a Si crystal. The extra hole migrates through the crystal

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.

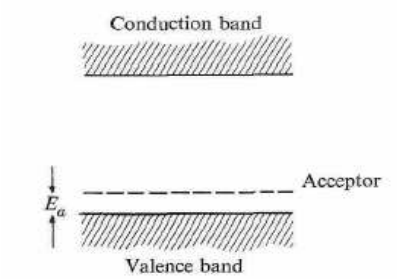

Fig.1.7: The acceptor level in a semiconductor.

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 $E - \mu >> kT$, 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.

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UNIT 2 SEMICONDUCTOR STATISTICS

1.0 Introduction
2.0 Objectives
3.0 Definition
 3.1 Semiconductor statistics
  3.1.1 Intrinsic region
  31.2 extrinsic region
4.0 Conclusion
5.0 Summary
6.0 Tutor Marked Assignment
7.0 Further Reading/References

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.

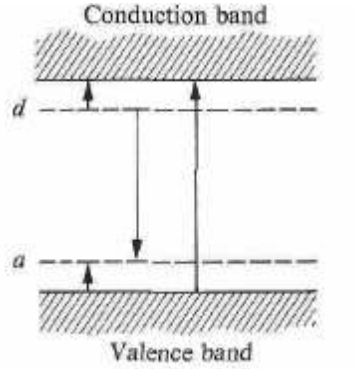

Fig. 2.1: The various electronic processes in a semiconductor

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 primarily by 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

$$n \gg N_d, N_a \qquad \textbf{(2.1)}$$

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,

$$n = N_d \qquad \textbf{(2.2)}$$

A semiconductor in which $n >> p$ 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,

$$p = N_a \qquad \textbf{(2.3)}$$

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.

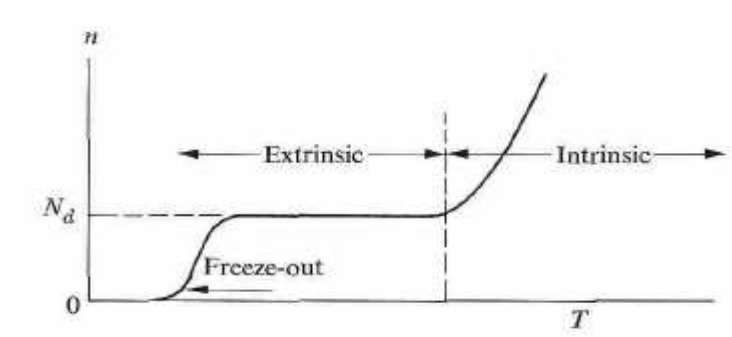

Fig.2.2: Variation of electron concentration n with temperature in an n-type semiconductor.

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 $E_g \gg k_B T$.

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UNIT 3 ELECTRICAL CONDUCTIVITY AND REAL SEMICONDUCTORS

CONTENT

1.0 Introduction
2.0 Objectives
3.0 Definition
 3.1 Electrical conductivity
  3.1.1 Dependence on temperature
  3.1.2 Mobility Vs Temperature
 3.2 Band structure of real semiconductors
 3.3 Excitons
4.0 Conclusion
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7.0 Further Reading/References

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:

$$\sigma_e = \frac{ne^2\tau_e}{m_e} \qquad \textbf{(3.1)}$$

where m_e is an effective mass and $\tau_e$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.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.

$$|V_e| = \mu_e E \qquad \textbf{(3.2)}$$

Where $|V_e|$ is the absolute value of the velocity. Taking into account that $\boldsymbol{j}_e = -en_e\boldsymbol{V}_e$ and $\boldsymbol{j}_e = \sigma_e\boldsymbol{E}$ we find that

$$\mu_e = \frac{e\tau_e}{m_e} \qquad \textbf{(3.3)}$$

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

$$\sigma_e = ne\mu_e \qquad \textbf{(3.4)}$$

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

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

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

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

where $\mu_h$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

$$\sigma = \sigma_e + \sigma_h \qquad \textbf{(3.7)}$$

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

$$\sigma = ne\mu_e + pe\mu_h \quad \textbf{(3.8)}$$

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

$$\sigma = ne(\mu_e + \mu_h) \quad \textbf{(3.9)}$$

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

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

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.

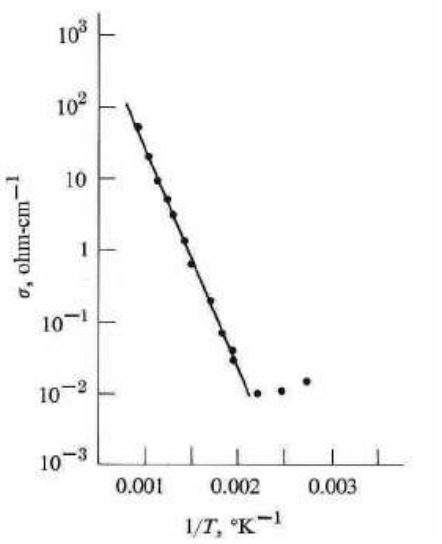

Fig. 3.1: Conductivity of Si versus $1/T$ in the intrinsic range.

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

$$\sigma = ne\mu_e \quad \textbf{(3.11)}$$

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.

3.1.2 Mobility versus temperature

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

$$\mu_e = \frac{e\tau_e}{m_e} = \frac{el_e}{m_e V_e} \quad \textbf{(3.12)}$$

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:

$$^1/_2\, m_e V_e^2 = {}^3/_2\, kT \quad \textbf{(3.13)}$$

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

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

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.

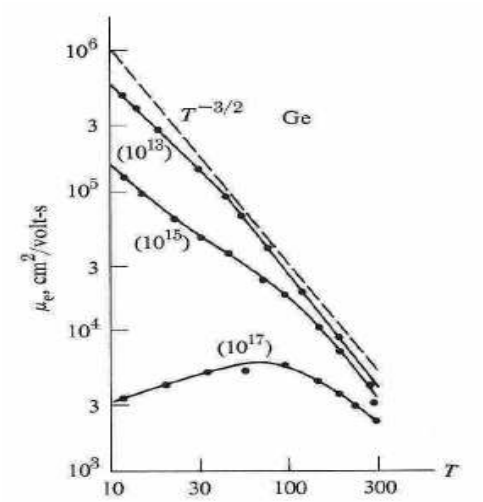

Fig.3.2: Electron mobility versus T in Ge. The dashed curve represents pure phonon scattering; numbers in parentheses refer to donor concentrations.

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,$E(k) = \frac{\hbar^2 k^2}{m_e}$, 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.

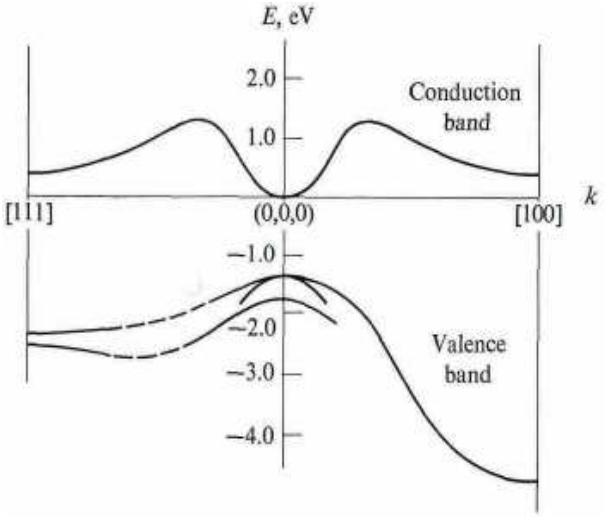

Fig. 3.3 Band structure of GaAs plotted along the [100] and [111] directions.

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 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.

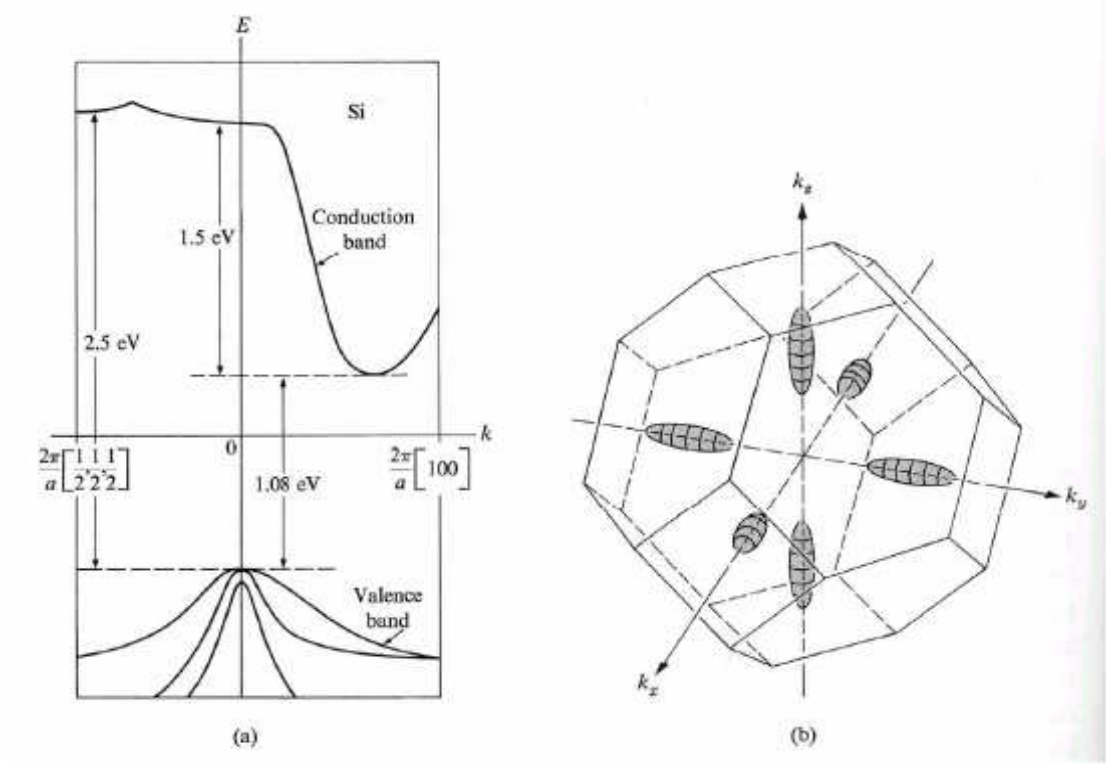

Fig.3.4 (a) Band structure of Si plotted along the [100] and [111] directions, (b) Ellipsoidal energy surfaces corresponding to primary valleys along the [100] directions (After Kittel, 1979)

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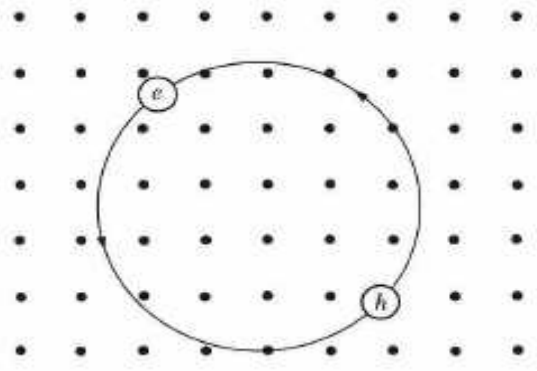

Fig.3.5: An Excitons, a bound electron-hole pair.

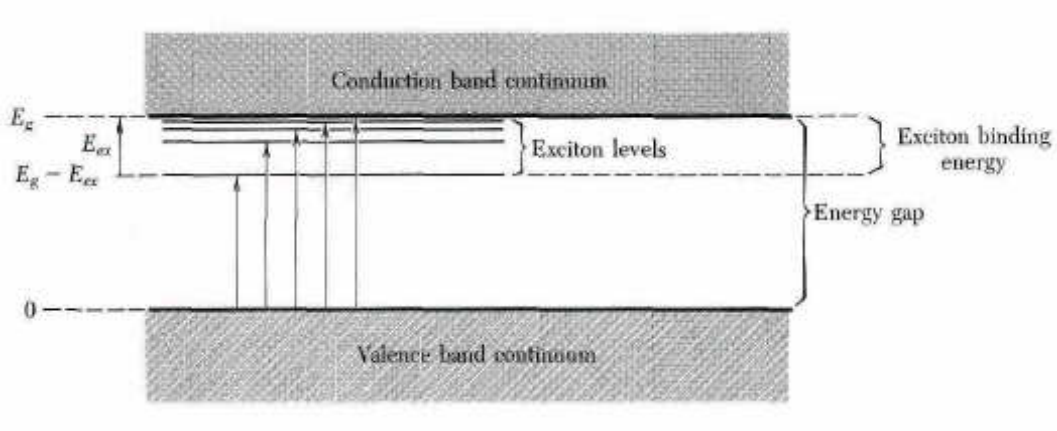

Fig.3.6: Energy levels of Excitons.

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

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

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

$$E_n = E_c - \frac{e^4\mu}{2\varepsilon^2\hbar^2 n^2} \qquad \textbf{(3.16)}$$

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

$$\frac{1}{\mu} = \frac{1}{m_e} + \frac{1}{m_h} \qquad \textbf{(3.17)}$$

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, $k_BT/e = 26\ mV$. 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 $n = 10^{22}m^{-3}$, $= 1.6 \times 10^{-19}$, $\mu_e = 10^{-2}m^2V^{-1}s^{-1}$,

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

(b) From Eq.(3.6), the free electron model of metals gives
$\sigma = \frac{ne^2\tau}{m^*}$, 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

- $\sigma_e = \frac{ne^2\tau_e}{m_e}$ defines electrical conductivity according to free electron model.
- $\mu_e = \frac{e\tau_e}{m_e}$ 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 $m^2V^{-1}s^{-1}$. Calculate the extrinsic resistivity of the sample (for Si, atomic weight = 28, density = 2300 kg/m3).

Q2. Given the data for Si: μ_e = 1350 cm^2/V·s, μ_h = 475 cm^2/V·s, m_e = 0.19*m*, m_h = 0.16*m* 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 reading/References

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UNIT 4 SUPER CONDUCTIVITY (I): THE BASIC PHENOMENON

1.0 Introduction
2.0 Objectives
3.0 Definition
- 3.1 Empirical criteria
- 3.2 Transition Temperature
- 3.3 Energy Gap
- 3.4 Properties dependent on Energy gap
  - 3.4.1 Microwave and Infrared absorption
  - 3.4.2 Density of states
  - 3.4.3 Specific Heat
  - 3.4.4 Acoustic attenuation
  - 3.4.5 Thermal Conductivity

4.0 Conclusion
5.0 Summary
6.0 Tutor Marked Assignment
7.0 Further Reading/References

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 $3x10^{-6}\Omega$ 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.

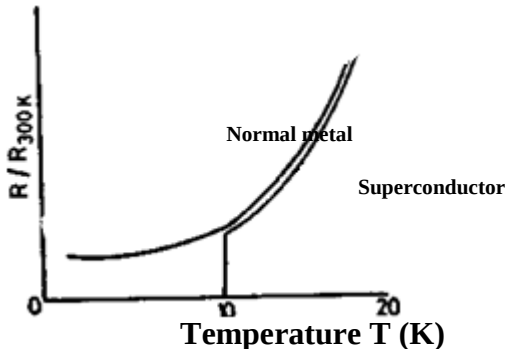

Fig.4.1: Temperature dependence of the resistance: of a normal and superconducting material (After Kachhava, 1992)

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.

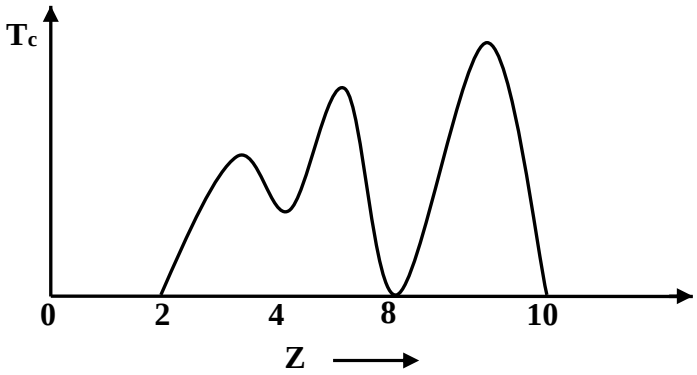

Fig 4.2: Variation of transition temperature with number of valence electron

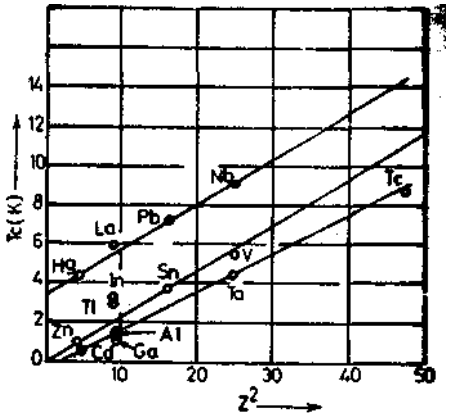

Fig 4.3: Empirical correlation between transition temperature and Z^2(After Kachhava, 1992)

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 = Δ 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. 2Δis typically of the order of 10^{-4} eV.

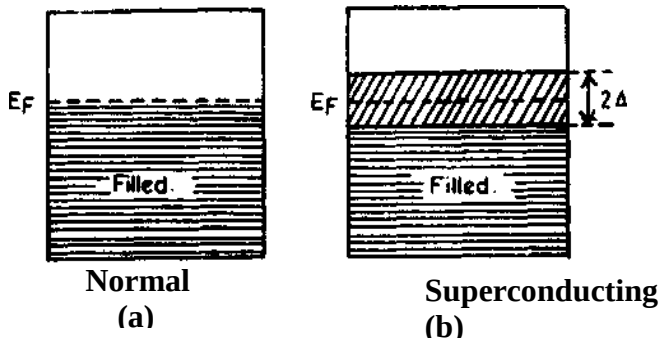

Fig.4.4: (a) Conduction band in the normal metal (b) Energy gap at the Fermi level in the superconducting state (After Kachhava, 1992)

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)/ Δ (0) as a function of the reduced temperature T/T_c. Elementary theory predicts that

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

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.

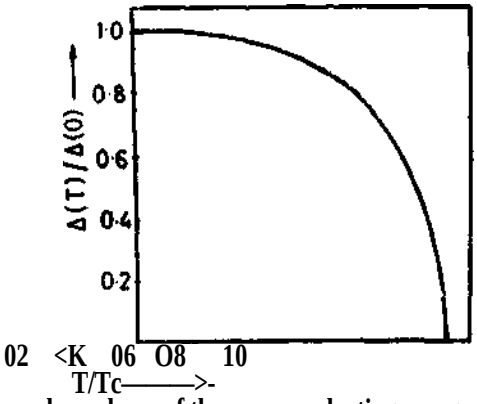

Fig. 4.5: Temperature dependence of the superconducting energy gap (After Kachhava, 1992)

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 ± $\Delta(0)$ 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 $\Lambda(0)$ is now smaller than $\Lambda(0)$. 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).

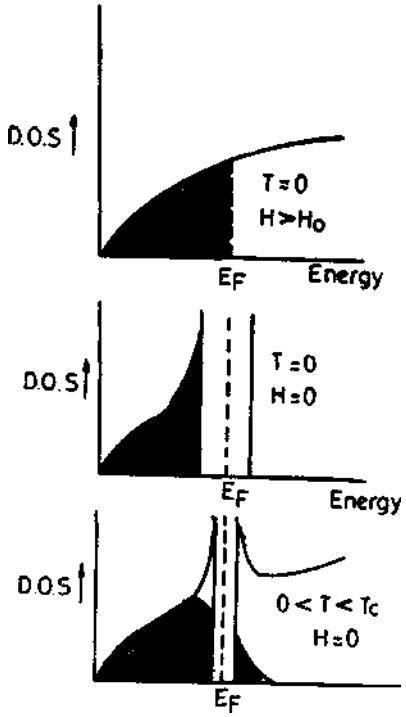

Fig. 4.6: Density and occupancy of states (D.O.S) for a normal and a superconductor (After Kachhava, 1992)

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

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

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.

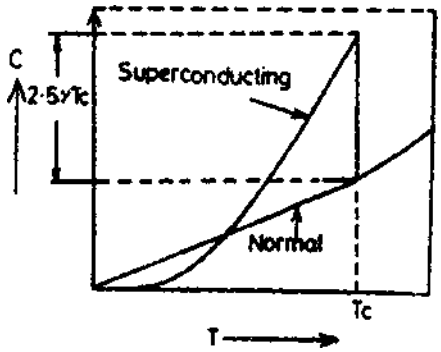

Fig.4.7: Specific heat of normal and superconductor (After Kachhava, 1992)

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

$$C_s = AT^3 C_{es} \qquad (4.3)$$

Where

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

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

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

At low temperatures

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

The exponential decay ratio is represented in Fig. 4.8

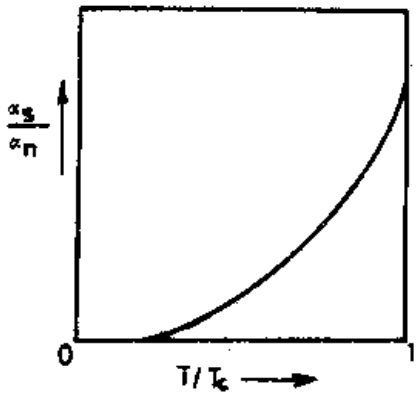

Fig.4.8: Ratio of attenuation coefficients for acoustic waves in superconducting and normal metal as a function of temperature (After Kachhava, 1992).

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

$$\frac{k_{es}}{k_{en}} \sim exp\left(-\Delta/k_B T\right) \qquad (4.7)$$

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

($\sim 10^3$) 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.

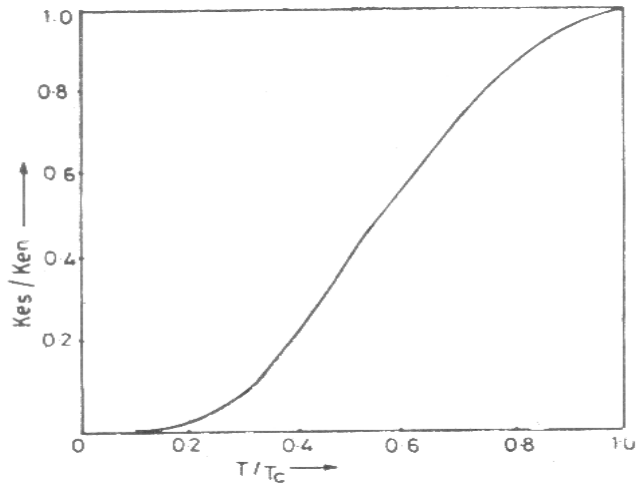

Fig.4.9: Ratio of the electronic contribution to the thermal conduction of Al (After Kachhava, 1992)

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 reading/References

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UNIT 5 SUPERCONDUCTIVITY (II): EXPERIMENTS AND THOERIES

1.0 Introduction
2.0 Objectives
3.0 Definition
- 3.1 Meissner effect
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- 3.6 Thermodynamics of Superconducting transition
- 3.7 Isotope effect

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1.0 Introduction

In this unit, we are going to study both the experimental and theoretical situations concerning superconductivity. The experimental survey includes the effects of magnetic field on superconductivity(the Meissner effect), the minimum magnetic field (critical field) necessary to destroy superconductivity as well as the minimum current (critical current) that can be passed without destroying superconductivity. Thermodynamics, London equation and type I and II of semiconductors constitute the theoretical surveys.

2.0 Objective

The objectives of this unit are:

- To survey the central experimental facts concerning superconductivity
- To discuss the theoretical situations of superconductivity

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 Meissner effect

Meissner and Ochsenfeld (1933) showed that, if a long superconductor is cooled in a longitudinal magnetic field from above the transition temperature, the lines of induction are pushed out (Fig. 5.1) at the transition. The Meissner effect shows that a super- conductor behaves as if inside the specimen $B = 0$ or $\chi = -1/4\pi$; that is, a superconductor exhibits perfect diamagnetism. This very important result cannot be derived merely from the characterization of a superconductor as a medium of zero resistivityρ: from E = ρj we see that, if ρ is zero while j is finite, then E must be zero and with it curl E must be zero. Therefore from Maxwell's equations

$$dB/dt = -curl\ E = 0 \qquad \textbf{(5.1)}$$

so that the flux through the metal cannot change on cooling through the transition. The Meissner effect contradicts this result and suggests that perfect diamagnetism and zero resistivity are two independent essential properties of the superconducting state.

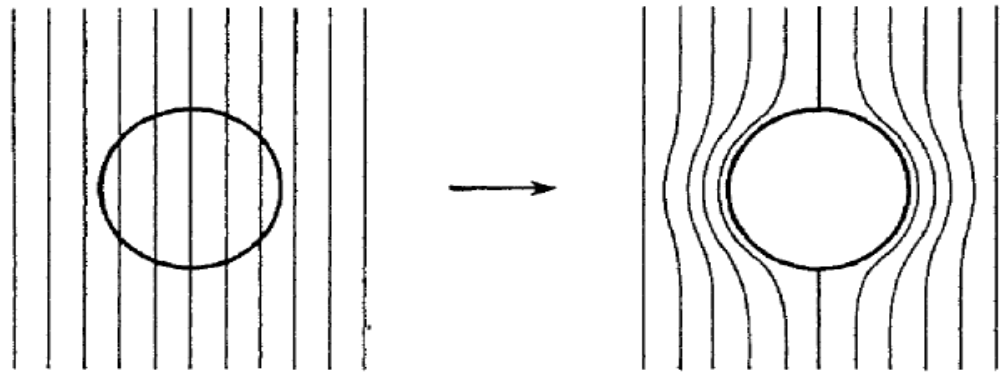


Fig.5.1: Meissner effect in a sphere cooled in a constant applied magnetic field; on passing below the transition temperature the lines of induction are ejected from the sphere. (After Kittel,

3.2 Critical Field

The minimum applied magnetic field necessary to destroy superconductivity and restore the normal resistivity is called the *critical field*, H_c. H_c depends on the temperature. Fig.5.2 shows the critical field as a function of temperature. The curve is nearly parabolic and can be reasonably well represented by the relation

$$H_c = H_0\left[1 - \left(\frac{T}{T_c}\right)^2\right] \qquad \textbf{(5.2)}$$

Where H_0 is the critical field at absolute zero. This equation is really the equation of phase boundary between the normal and superconducting state. The typical value of H_0 is 5000A/m.

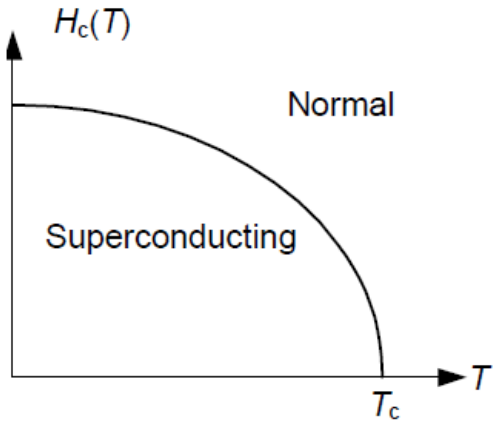
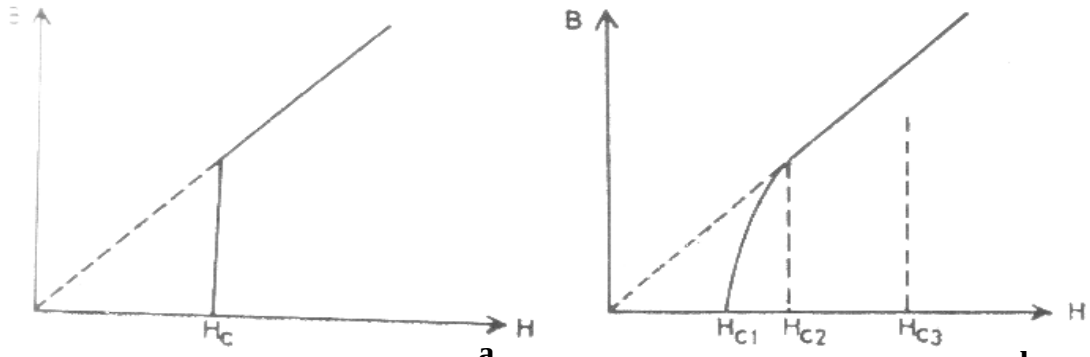


Fig.5.2: Critical magnetic field as a function of temperature (After James and Bernard, 2005).

3.3 Type I and Type II Superconductors

Superconductors may be divided into two classes which depend on the way in which the transition from the superconducting to the normal state proceeds when the applied field exceeds H_c. In type-**I** materials, as H_c is reached entire specimen enters the normal state practically simultaneously, the resistance returns, the diamagnetic moment becomes zero and $B_{internal} = B_{external}$ (Fig5.2a).



a b

Fig.5.2: Flux penetration as a function of magnetic filed in (a) type-I superconductor and (b) type-II superconductor

In type-II superconductors, the transition to a completely normal specimen is much more gradual. As shown in Fig. 5.2b, there is a partial penetration of the magnetic field between the critical field H_{c1} and H_{c2}. Small surface super currents may still flow up to an applied field H_{c3}.

3.4 Critical Currents

The minimum current that can be passed in a sample without destroying its superconductivity is called *critical current* I_c. If a wire (radius *r)* of a type-**I** superconductor carries a current I, there is a surface magnetic field $H_I = I/2\pi r$ associated with the current. If H_I exceeds H_c, the material will go normal. If in addition, a transverse magnetic field *H* is applied to the wire, the condition for the transition to the normal state at the surface is that the sum of the applied field and the field due to the current should equal the critical field. Thus, as seen from Fig. (5.3b), we have

$$H_c = H_I + 2H$$

$$H_I = \frac{I_c}{2\pi r} = H_c - 2H$$

Hence $I_c = 2\pi r(H_c - 2H)$ **(5. 3)**

The critical current I_c will decrease linearly with increase of the applied field until it reaches zero at $H = H_c/2$. If the applied field is zero, $I_c = 2\pi r H_c$, similar considerations apply to type-**II** superconductor for $H \ll H_{c1}$, that is when the superconductor is not in the mixed state.

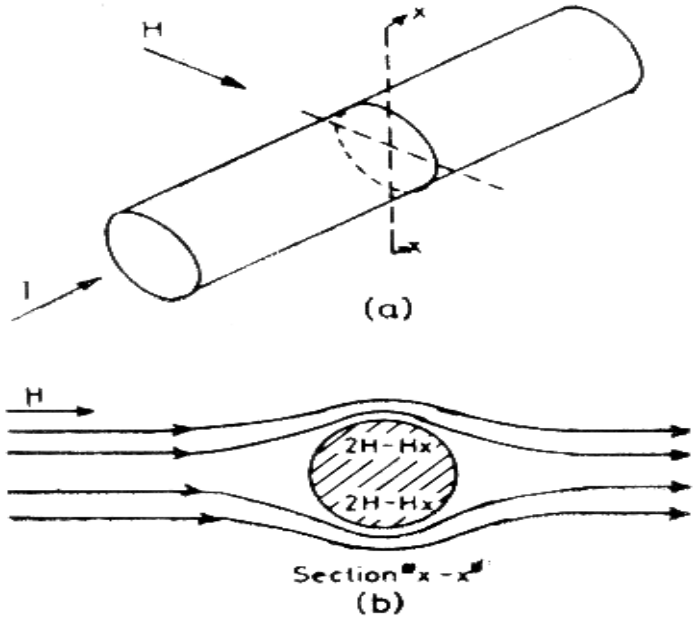


Fig.5.3 :(a) wire carrying current I subjected to transverse field H.(b) Cross-section of wire showing fields at equatorial position on the surface(After Kachhava,1990)

3.5 London Equations

In 1935, two brothers F. and H. London, proposed two equations to govern the microscopic electric and magnetic fields (two basic electrodynamics properties) which give superconductivity its unique interest. The London theory is based on rather old ideas of the two –fluid model according to which a superconductor can be thought to be composed of both normal and superfluid electrons. Let n_n, v_n and n_s, v_s be respectively the density, and velocity of the normal and superfluid electrons. If n_0 is the number of electrons per unit volume, then on the average

$$n_0 = n_n + n_s$$

The equation of motion for the superfluid electrons is

$$m\frac{dv_s}{dt} = -eE \qquad \textbf{(5.4)}$$

The density of the superfluid electrons is

$$j_s = -en_s v_s \qquad \textbf{(5.5)}$$

Then Eq. (5.4) and (5.5) yield

$$\frac{dj_s}{dt} = \frac{n_s e^2}{m}E \qquad \textbf{(5.6)}$$

This is the first London equation.
Taking curl of Eq. (5.6)

$$\nabla \times \frac{dj_s}{dt} = \frac{n_s e^2}{m} \text{ curl } E$$

and using Maxwell's equation

$$\text{curl } E = -\frac{\partial B}{\partial t}$$

we get

$$\nabla \times \frac{dj_s}{dt} = -\frac{n_s e^2}{m} \frac{\partial B}{\partial t} \quad \textbf{(5.7)}$$

Integrating this equation with respect to time, and choosing the constant of integration to be zero consistent with the Meissner effect, we have

$$\nabla \times \mathbf{j}_s = -\frac{n_s e^2}{m} B \quad \textbf{(5.8)}$$

This is the second London equation.
We may derive the Meissner effect from the second London equation by using the Maxwell equation

$$\nabla \times \mathbf{B} = \mu_0 j_s \quad \textbf{(5.9)}$$

Taking curl of this equation

$$Curl\ curl\ \mathbf{B} = \mu_0 \nabla \times j_s \quad \textbf{(5.10)}$$

Then using the condition div **B** = 0 of a superconductor in the identity

$$Curl\ curl\ \mathbf{B} = \text{grad div } \mathbf{B} - \nabla^2 \mathbf{B}$$

We get

$$Curl\ curl\ \mathbf{B} = -\nabla^2 \mathbf{B} \quad \textbf{(5.11)}$$

On combining Eq. (5.10) and (5.11),

$$-\nabla^2 \mathbf{B} = \mu_0 \nabla \times j_s \quad \textbf{(5.12)}$$

This along with Eq. (5.8) gives

$$\nabla^2 \mathbf{B} = \frac{1}{\lambda^2} \mathbf{B} \quad \textbf{(5.13)}$$

Where is called the London penetration depth and is defined by

$$\lambda = \left(\frac{m}{\mu_0 n_s e^2}\right)^{1/2} \quad \textbf{(5.14)}$$

For a superconductor to the right of the plane x = 0, Eq. (5.13) has the solution

$$B(x) = B(0)\exp\left(-\frac{x}{\lambda}\right) \qquad \textbf{(5.15)}$$

This equation indicates that B does not penetrate very deeply into superconductor, and therefore it implies the Meissner effect. The field penetrates only a distance λ within the surface. λ is typically of the order of 1000Å. The graphical form of Eq. (5.15) is shown in Fig.5.4. The penetration depth is also found to depend strongly on temperature and to become much larger as T approaches T_c. The observation can be fitted extremely well by a simple expression of the form

$$\left[\frac{\lambda(T)}{\lambda(0)}\right]^2 = \left[1 - \left(\frac{T}{T_c}\right)^4\right]^{-1} \qquad \textbf{(5.16)}$$

This equation implies that

$$n_s = n_s\left[1 - \left(\frac{T}{T_c}\right)^4\right]^{-1} \qquad \textbf{(5.17)}$$

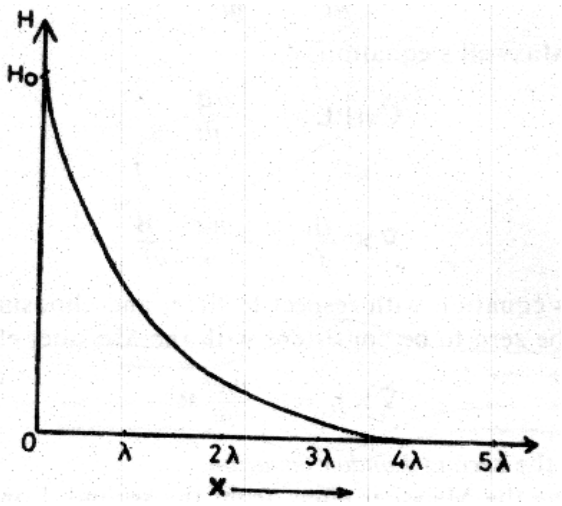


Fig.5.4: Magnetic field penetration at surface of a superconductor (After Kachhava, 1992).

The density superconducting electrons increase from zero at T_c to n_0 at absolute zero as shown in Fig.5.5, which also depicts the temperature variation of λ. n_s is called the *order parameter* because it characterizes the *order* in the superconducting state.

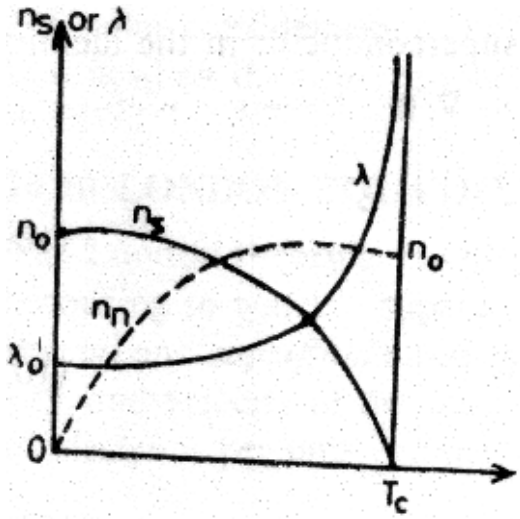


Fig.5.5: Density of superconducting electrons as a function of temperature (After Kachhava, 1992)

Worked example:

The London equation for simple superconductor is a phenomenological equation relating the supercurrent $\boldsymbol{j_s}$ to the magnetic vector potential **A**:

$$\boldsymbol{j_s} = \frac{-n_e e^2}{m_e c}\boldsymbol{A}$$

Where m_e is the electron mass. Using the appropriate Maxwell equation, show how the above equation leads to Meissner effect.

Solution:

The Meissner effect refers to the fact that in the superconducting state magnetic induction vanishes and materials become strongly diamagnetic. From London equation (Eq.58),

$$\boldsymbol{\nabla} \times \mathbf{j_s} = -\frac{n_s e^2}{m}\boldsymbol{B} \qquad \textbf{(i)}$$

Since $\lambda^2 = \frac{m_e}{n_s e^2}$, we get

$$\boldsymbol{\nabla} \times \mathbf{j_s} = -\frac{\mathbf{1}}{\boldsymbol{c\lambda^2}}\boldsymbol{B} \qquad \textbf{(ii)}$$

Inside a superconductor, the electrical field vanishes and we have the Maxwell equation

Error! Bookmark not defined. $\boldsymbol{\nabla \times B} = \frac{\boldsymbol{4\pi}}{\boldsymbol{c}}\boldsymbol{j_s}$

Hence $\boldsymbol{B} = -c\lambda^2 \nabla \times \boldsymbol{j_s} = -\frac{\boldsymbol{c^2\lambda^2}}{4\pi}[\nabla(\nabla \cdot \boldsymbol{B}) - \boldsymbol{\nabla^2 B}]$,

Or, using Maxwell's equation $\nabla^2 \boldsymbol{B} = \frac{1}{\lambda^2}\boldsymbol{B}$

Where $\lambda = \left(\frac{m}{\mu_0 n_s e^2}\right)^{1/2}$

For a superconductor to the right of x= 0, Eq. (ii) has the solution

$$\boldsymbol{B} = \boldsymbol{B_0} e^{\left(-\frac{x}{\lambda}\right)}$$

This shows that $\boldsymbol{B}$ decays exponentially such that $\boldsymbol{B} = \frac{1}{e}\boldsymbol{B}_0$ at x = λ.

For $x \gg \lambda$, B→ 0, indicating that the magnetic field exists only in a thin layer of thickness≈ λ beneath the surface of the superconductor. Thus the magnetic field inside a superconductor is zero. This is the Meissner effect.

3.6 Thermodynamics of Superconducting transition

It has been demonstrated experimentally that the transition between the normal and superconducting states is thermodynamically reversible, in the same sense that with slow evaporation the transition between liquid and vapor phases of a substance is reversible. The Meissner effect also suggests that the transition is reversible and would not subsist if the superconducting currents die away with the production of Joule heat when superconductivity is destroyed. As the transition is reversible we may apply thermodynamics to the transition, obtaining an expression for the entropy difference between normal and superconducting states in terms of the critical field curve H_c versusT_c.
The Gibbs free energy per unit volume in a magnetic field

$$G = U - TS + PV - \frac{MH}{\mu_0} \qquad \textbf{(5.18)}$$

Then the differential Gibbs free energy dG is

$$dG = -SdT + PdV - \frac{MdH}{\mu_0} \qquad \textbf{(5.19)}$$

At constant T and P, the free energy difference, because of the presence of a magnetic field, is found by integration. Thus

$$\int_{T,0}^{T,H} dG = -\int_0^H \frac{M}{\mu_0} dH \qquad \textbf{(5.20)}$$

$$G(T,H) - G(T,0) = -\int_0^H \frac{M}{\mu_0} dH \qquad \textbf{(5.21)}$$

For superconductor, $I = -H$ or $M = -VH$ and

$$G_s(T,H) - G_s(T,0) = -\int_0^H \frac{VH}{\mu_0} dH$$

$$G_s(T,H) - G_s(T,0) = \frac{1}{2\mu_0} VH^2 \qquad \textbf{(5.22)}$$

Here G_s is the free energy of a superconducting phase

Along the phase boundary between normal and superconducting state, the normal phase must have a free energy indistinguishable from that of the superconducting phase. Therefore

$$G_n(T, H_c) - G_s(T, 0) = \frac{1}{2\mu_0} V H_c^2 \qquad \textbf{(5.23)}$$

Where G_n is the free energy of the normal phase. Fig.5.6 shows the variation of G_n and G_s below T_c, where the normal phase is obtained by applying the field in excess of H_c.

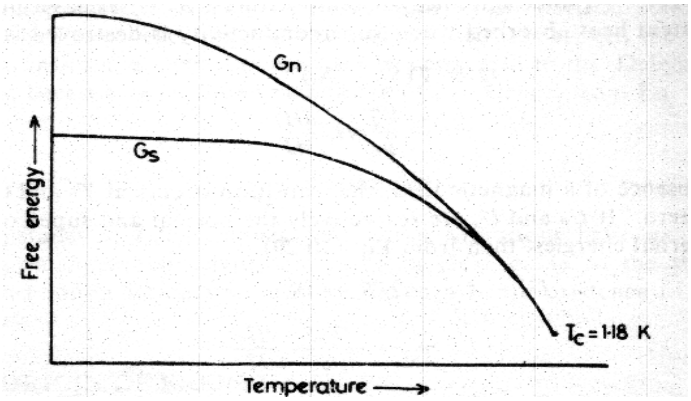


Fig.5.6: Experimental values of free energy of Al in the normal and superconducting state as a function of temperature (After Kachhava, 1992)

Let us now calculate the difference in entropy of the two phases. For solids, the entropy S is given by $-dG/dT$. Hence, differentiating Eq. (5.23) with respect to T, we have

$$S_n - S_s = -\frac{d}{dT}\left(\frac{1}{2\mu_0} V H_c^2\right)$$

$$= -\frac{V H_c}{\mu_0}\frac{dH_c}{dT} \qquad \textbf{(5.24)}$$

Where the entropies S_n and S_n refer to normal and superconducting phases respectively. Thus $S_n \geq S_s$ as illustrated in Fig.5.7.

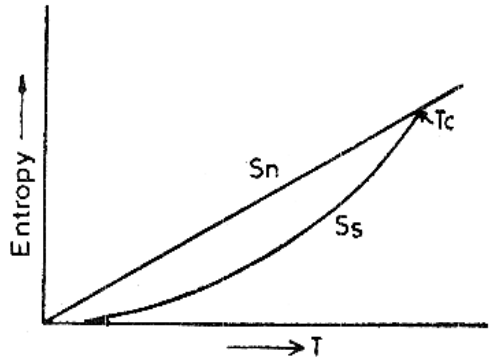


Fig.5.7: Entropy S of Al in the normal and superconducting state as a function of temperature (After Kachhava, 1992).

As $\frac{dH_c}{dT}$ is always negative, $S_n - S_s$ is always positive and the superconducting state is observed to be more ordered than the normal state. At the transition temperature $S_n - S_s = 0$ because $H_c = 0$, and at 0K, $S_n - S_s = 0$ from the third law of thermodynamics, which is satisfied, because $\frac{dH_c}{dT}$ tends to zero. At some intermediate temperatures, $S_n - S_s$ has a maximum. The latent heat absorbed when superconductivity is destroyed is

$$Q = T(S_n - S_s)$$

$$= -\frac{VT}{\mu_0} H_c \frac{dH_c}{dT} \qquad \textbf{(5.25)}$$

In the absence of a magnetic field, the transition occurs at T_c and the latent heat is zero. If U_n and U_s are respectively the normal and superconducting state internal energies, then from Eq. (5.25)

$$U_n - U_s = T(S_n - S_s)$$

$$= -\frac{VTH_c}{\mu_0} \frac{dH_c}{dT} \qquad \textbf{(5.26)}$$

From experiment, $S_n - S_s \approx 10^{-7} eV$, which is extremely small compared to the band energies. For a unit volume, the difference of the of the heat capacities, from Eq. (5.26), will be

$$(C_s - C_n) = T\frac{d}{dT}(S_s - S_n)$$

$$= \frac{TH_c}{\mu_0}\frac{d^2H_c}{dT^2} + \frac{T}{\mu_0}\left(\frac{dH_c}{dT}\right)^2 \qquad \textbf{(5.27)}$$

On substituting $T = T_c$, $H_c = 0$ in this equation, we get the *Rugers formula*

$$(C_s - C_n) = \frac{T_c}{\mu_0}\left(\frac{dH_c}{dT}\right)^2_{T=T_c} \qquad \textbf{(5.28)}$$

This equation reproduces the experimental data very well.

3.7 Isotope effect

It has been found by early experimentalists that the transition temperature is strongly dependent on the average isotopic mass, M, of the constituents of a superconductor. In particular

$$T_c \propto M^{-1/2} \qquad \textbf{(5.29)}$$

More recent experiments have suggested the following general form

$$T_c \propto M^{-\alpha} \quad \textbf{(5.30)}$$

In which α is called the isotope effect coefficient and is defined by

$$\alpha = -\frac{\partial \ln T_c}{\partial \ln M} \quad \textbf{(5.31)}$$

Recent theories lead to the result

$$\alpha = 0.5[1 - 0.01\{N(0)V\}^{-2}] \quad \textbf{(5.32)}$$

where the parameter $N(0)$ is the density of single states for one spin at the Fermi level and *V* is the model potential between the electrons. The transition temperature can be connected to the Debye temperature, θ_D, because $\theta_D \propto$ sound velocity $\propto M^{-1/2}$. Hence, from Eq. (5.30),

$$T_c \propto \theta_D$$

i.e. $\frac{T_c}{\theta_D}$ = constant **(5.33)**

The constant of $\frac{T_c}{\theta_D}$ implies that the lattice vibrations have an important bearing on superconductivity, and gives a clear guide to the theory that electron-phonon interaction must be the basis of the existence of superconductivity.

4.0 Conclusion

The magnetic properties exhibited by superconductors are as dramatic as their electrical properties. The magnetic properties cannot be accounted for by the assumption that the superconducting state is characterized properly by zero electrical resistivity.

5.0 Summary

- A bulk specimen of metal in the superconducting state exhibits perfect diamagnetism, with the magnetic induction **B = 0.** This is Meissner effect.
- There are two types of superconductors, **I** and **II**
- In type **I**, the superconducting state is destroyed and the normal state is restored by application of critical value H_c.
- A type II superconductor has two critical fields $H_{c1} < H_c < H_{c2}$
- The London 1st and 2nd equations

$$\frac{d\mathbf{j}_s}{dt} = \frac{n_s e^2}{m}\boldsymbol{E} \quad \text{Or} \quad \nabla \times \mathbf{j}_s = -\frac{n_s e^2}{m}\boldsymbol{B}$$

Leads to the Meissner effect through the penetration equation $\nabla^2 \mathbf{B} = \frac{1}{\lambda^2}\mathbf{B}$

6.0 Tutor marked assignment

Q1. A superconducting tin has a critical temperature of 3.7 K in zero magnetic fields and a critical field of 0.0306 T at 0 K. Find the critical field at 2 K.

Q2. Estimate the London penetration depth from the following data:

Critical temperature = 3.7 K
Density = 7.3 g cm^{-3}
Atomic weight = 118.7
Effective mass* = 1.9m, where m is the mass of a free electron

7.0 Further reading/References

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