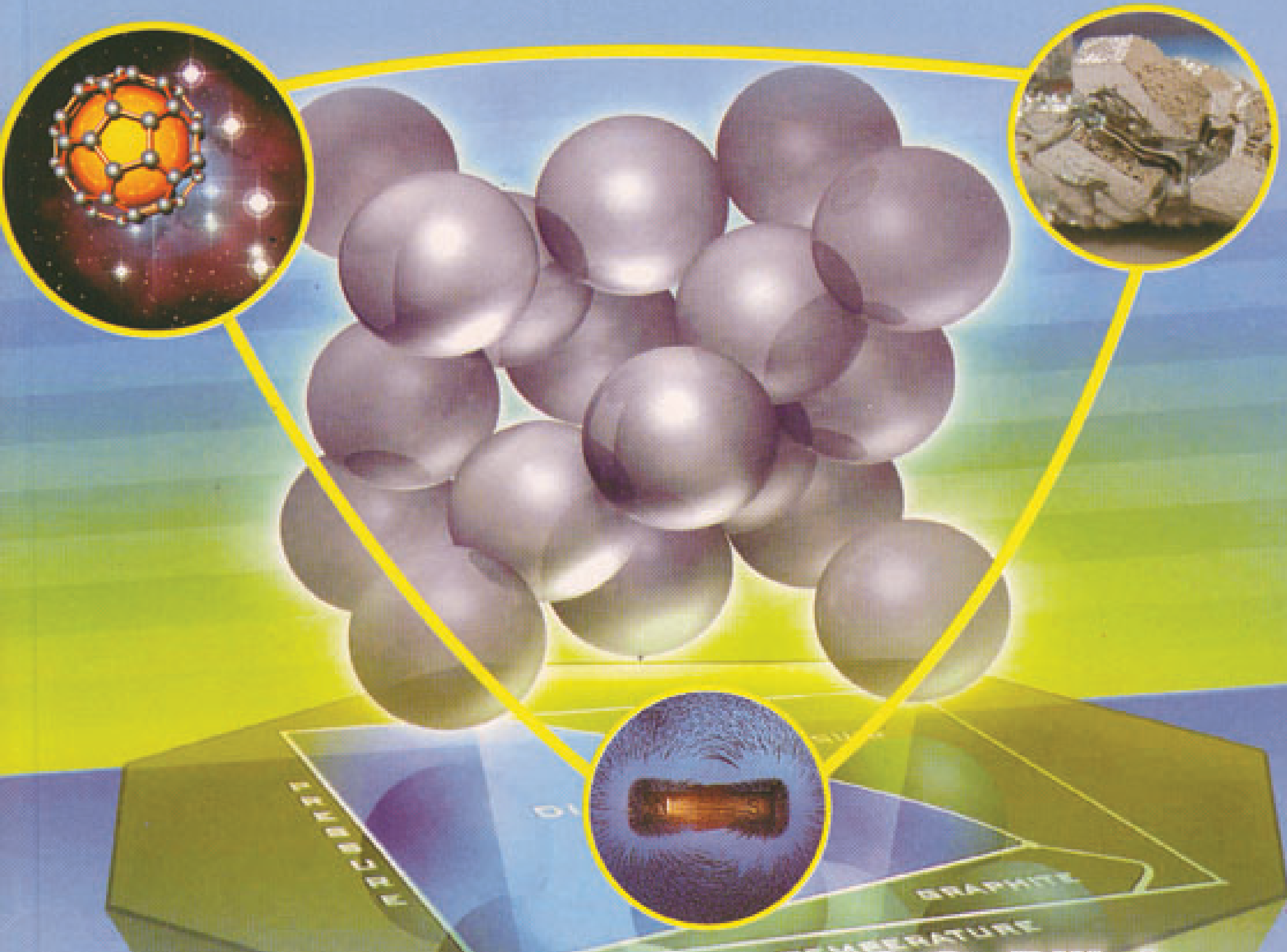
NEW AGE

Second Edition

Rudiments of Materials Science



S.O. Pillai
Sivakami Pillai

NEW AGE INTERNATIONAL PUBLISHERS

Rudiments of
Materials Science

Rudiments of
Materials Science

(For B.Sc., B.E., B.Tech. and AMIE Courses)

(Second Edition)

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Dedicated in memory of the children
who died in the Kumbakonam Fire tragedy.

Oh dear little ones! Oh dear little ones!
For you, we had glorious dreams!
And you were all immersed in your own dreams
Usually, departed old parents are buried by sons
Whereas, Kumbakonam, saw a sad scene!
Crying parents and weeping elders burying the tender ones!!
Oh Almighty! Show your grace on those little ones, and
Bless those parents to have strength to bear this great loss
And bring down their pain and wipe away the burning tears
Oh Almighty! Show your grace on those little ones.

PRESIDENT A.P.J. ABDUL KALAM

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A healthy academic experience, and some views and reviews of the fifth edition of the main book of Dr. S.O. Pillai on Solid State Physics.

Prof. A.P.J. Abdul Kalam, Hon'ble President of India received a copy of the main book on Solid State Physics sent by the author in January 2003. Dr. Pillai's surprise was that Prof. Kalam contacted him over phone and congratulated Dr. S.O. Pillai for the untired efforts, hard work and perseverance in bringing out a fine text book on Condensed Materials using the accumulated lecture notes over a period of forty years providing his own models to expedite the learning process. It was also noted that the copy of the said book has been kept in the Home library of the President. Pillai was also suggested to get the book reviewed by a panel of experts. Dr. Pillai thanks the President through these columns for the kind words and gesture. The review reports from a few outstanding academicians are presented here for the use of the readers and faculty members aspiring for bringing out text-books in many vital areas through reputed publishing houses.

From

Dr. M.G.K. Menon
Distinguished Professor
Indian Space Organization
E-mail: mgkmenon@ren02.nic.in

Dear Dr. Pillai,

Thank you for your recent letter with a copy of the book you have written on Solid State Physics. I am deeply sorry that it will be very difficult for me to go through the book to give comments and suggestions for improving it. This would require a fair amount of work. All I can say is that I am glad that you have written it and it certainly contains the spirit of your approach to teaching of which you have very extensive experience; it is my view that every teacher should impart a sense of excitement and curiosity to the students through their own style of teaching. The book is comprehensive dealing extensively with even newer topic on Superconductivity, Magnetic Properties of Materials, Physics of Semiconductors, Dielectrics and Related Properties, and Optical Properties of Solids. It would have been good for you to have also covered the broad interface of physics and chemistry e.g., Solid State Chemistry, and also the properties of surfaces which have assumed great significance with very new experimental capabilities.

Yours sincerely,
M.G.K. Menon

Formerly

(i) Director of Tata Institute of Fundamental Research
(ii) Science-Advisor to the Prime Minister of India
(iii) Minister for Science and Technology
(iv) Recipient of Padma Shri in 1961 and Padma Bhushan in 1968.

Dr. B.C. Pai
Senior Deputy Director
Regional Research Laboratory (C.S.I.R)
Thiruvananthapuram 675 019

Dear Prof. Pillai

Thank you for the kind letter enclosing with a copy of your book on Solid State Physics. I am extremely sorry that I may not be able to offer specific comments on your book since I am not an expert in the area of Solid State Physics. But all the topics covered in your book have been directly or indirectly relevant in our R and D activities. In this background I have no hesitation in congratulating and complementing you for bringing out an excellent text book presenting the relevant information aptly and precisely. The objective, short and review questions given at the end of each chapter are addressed to the point. Once again let me compliment you for bringing out a nice text book in Solid State Physics, and expect a few more books in the years to come.

Yours sincerely
Dr. B.C. Pai

Dr. B.C. Pai is a Recipient
of many R and D awards
from Government of India,
and from other institutions
and industries.

A Memorable communication from Hon’ble President A.P.J. Abdul Kalam.

President A.P.J. Abdul Kalam added a prologue to the address to the joint sitting of both Houses of Parliament on 7th June 2004 by reciting a few lines from his poem, an idea struck him while on his morning walk.

“I climbed and climbed, where is the peak, my Lord?
I ploughed and ploughed, where is the knowledge treasure, my Lord?
I sailed and sailed, where is the island of peace, my Lord?”

Dr. S.O. Pillai made a soft analysis of this thought provoking poem and found a partial explanation.

“It is: You and in You
It is: in your imparting the knowledge to the illiterates with faith and confidence
It is: in your beneficial contribution to mankind with utmost care and sincerity”.

Dr. S.O. Pillai is extremely grateful to the Hon’ble President for his inspiring encouragement and abundant best wishes which helped Pillai to continue his academic activities with almost all perfectness even at this age.

Rashtrapati Bhavan
New Delhi-110004
June 21, 2004

Dear Dr Pillai,

Thank you for your analysis of my poems. My greetings and best wishes to you and your family.

Yours sincerely,

A.P.J. Abdul Kalam

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Preface

Materials Science is one of the subjects in which considerable advances have been made, both in theoretical understanding and in experimental work, over the last few decades. To teach this subject for undergraduate students whose background is spotty, the major stumbling block proved to be the lack of suitable text books to supplement the lectures. Most of the available books, excellent though they are, rely heavily on the use of concepts completely alien to first or second year science and engineering students, and are largely aimed to cater the needs of post graduate students and research scholars. The main book of the first author on Solid State Physics also belongs to the above said category. The author had the privilege of going through the recent changes introduced in the curriculum and syllabi of undergraduate courses in colleges affiliated to different universities spread all over the county. The inclusion of the fascinating subject Materials Science as a core paper for the undergraduate courses in physics, chemistry, applied sciences, engineering and technology in recent years by a number of universities in India inspired Dr. Pillai to bring out a small book in the present form and format to cater the present day needs, and thereby to improve the workaholic culture and also to enhance the grip of the undergraduate students whose background or pre-requisite in this vital area is not in abundance. It is for this purpose this book is written.

The first author reviewed the accumulated teaching materials prepared for his lecture classes over a period of 35 years. The second author strained in preparing the script in the form of questions and answers providing tables giving physical properties of materials at the end of each chapter. Inclusion of objective questions, problems with solutions under each chapter is the other salient feature of this book. The authors feel that the book now in your hands is handy; and they are prevalently hopeful that it will just serve the purpose.

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KEY WORDS

silicon revolution, electronic structure, electrical conductivity, light emitting diodes (LEDs), solid state lasers, solar cells, bonds, mutual forces of attraction, minimum potential energy, valance electrons, ionic or electrovalent bond, sodium chloride, equilibrium spacing, ionization energy, minimum potential energy, dissociation energy, electrostatic attraction, equilibrium spacing, minimum potential energy, attractive and repulsive forces, cohesion and cohesive energy, interatomic spacing, repulsive exponent, calculation of cohesive energy, bonding energy, energy of dissociation, alkali halides, equilibrium energy, lattice energy, Madelung constant, x-ray diffraction, crystal lattice of NaCl, permittivity, electrolysis, dielectric constant, fundamental absorption frequency, cleave, Born-Haber cycle, sublimation energy, lattice energy, heat of dissociation, covalent or non-polar bond, configuration, non-polar substances, molar orbital, homopolar or electron-pair bonding, the coordination number, brittle, semiconductors, electron cloud or electron gas, lubricant, molecular bonds, van der Waals forces, fracture, condensation, molecular solids, hydrogen bonding.

1.1 INTRODUCTION

We in the beginning turn to a description of the bonding in solids considering the electronic structure in atoms. Some solids consist of molecules bound together by very weak forces. We shall not be concerned with these because their properties are essentially those of the molecules. Nor shall we be much concerned with purely ionic solids alone bound by electrostatic forces between ions. The solids considered here are those in which all the atoms can be regarded as bound together. To illustrate how the bonding is reflected in the properties of the solids, we explore the electronic properties of various types of solids. Solids display a wide variety of interesting and useful electronic properties. Good electronic conductivity is one of the characteristic properties of metals; semiconductors are the foundation of the '*Silicon revolution*'. But why is tin a metal, silicon a semiconductor and diamond an insulator? Many solid state devices (transistors, photocells, light emitting diodes (LEDs), solid state lasers, solar cells) are based on semiconductors containing carefully controlled amounts of impurity. How do these impurity affect the conductivity? These are some of the basic questions to be addressed; but a basic knowledge of bonding theory and the different mechanisms involved is absolutely essential to extend the study.

Q 1.1 What you understand by bonds in solids? What are the main causes and conditions for bond formation?

***Answer*:** The forces which keep or hold together the atoms or molecules of a substance in the form of groups are called *bonds*. The atoms or molecules in the gaseous and liquid states are loosely-packed and a very little binding force exists among them. Therefore, gases and liquids do not possess any definite shape. If a gas (or liquid) is heated, it expands out indefinitely, showing that little binding force exists among its various atoms. However, atoms and molecules in a solid are closely-packed and are held together by strong mutual *forces of attraction*. Therefore, solids have definite shape and occupy well defined space. If a solid is heated, it does not change its shape easily, showing that a very big force exists that binds the various atoms and molecules. In other words the bonds in solids are very strong compared with that in gases and liquids. The law of nature is to make every system to attain a stable state by acquiring *minimum potential energy*. When two atoms come closer and unite to form molecules, their electrons rearrange themselves in such a way so as to form a stable state.

Inference

The formation of bonds between atoms is mainly due to their tendency to attain minimum potential energy. When two atoms tend to form a bond, their *valence electrons* rearrange themselves so as to reach a stable state by acquiring minimum potential energy. In the process, the two atoms lose some energy. The strength of the bond between two atoms would obviously depend upon the energy lost in the process.

Q 1.2 Describe ionic or electrovalent bonds in solids with suitable examples.

***Answer*:** The bond formed between two atoms by the total transfer of valence electrons from one atom to the other is called an *ionic* or *electrovalent bond*. Here one or more electrons from an atom may transfer to the other atom and the resulting positive and negative ions attract each other. A typical example of an ionic bond is sodium chloride (NaCl) where the bond exists between Na^+ and Cl^- ions.

When sodium is burnt in an atmosphere of chlorine, the sodium gives up its valence electron to the chlorine, each of the resulting ions then has a stable filled shell of outer electrons, and a strong *electrostatic attraction* is set up that bonds the Na^+ cation and the Cl^- anion into a very stable molecule NaCl at the *equilibrium spacing*. The relevant equation is:

$$\boxed{2Na + Cl_2 \rightarrow 2Na^+ + 2Cl^- = 2NaCl} \quad \text{(Q 1.2.1)}$$

Magnesium oxide and magnesium chloride are two more examples of ionic crystals and the relevant equations are

$$\boxed{\begin{array}{l} 2Mg + O_2 \rightarrow 2Mg^{++} + 2O^{--} \rightarrow 2MgO \\ Mg + Cl_2 \rightarrow Mg^{++} + 2Cl^- \rightarrow MgCl_2 \end{array}} \quad \text{(Q 1.2.2)}$$

NaCl is one of the best examples of ionic crystal and let the sodium and chlorine atoms be free at infinite distance of separation. The energy required to remove the outer electron from the Na atom (*ionization energy of sodium atom*), leaving it a Na^+ ion is 5.1 eV. i.e.,

$$Na + 5.1\ eV \rightarrow Na^+ + e^-$$

The electron affinity of chlorine is 3.6 eV; thus, when the removed electron from sodium atom is added to chlorine atom, 3.6 eV of energy is released and the chlorine atom becomes negatively charged ion. Hence

$$Cl + e^- \rightarrow Cl^- + 3.6\ eV$$

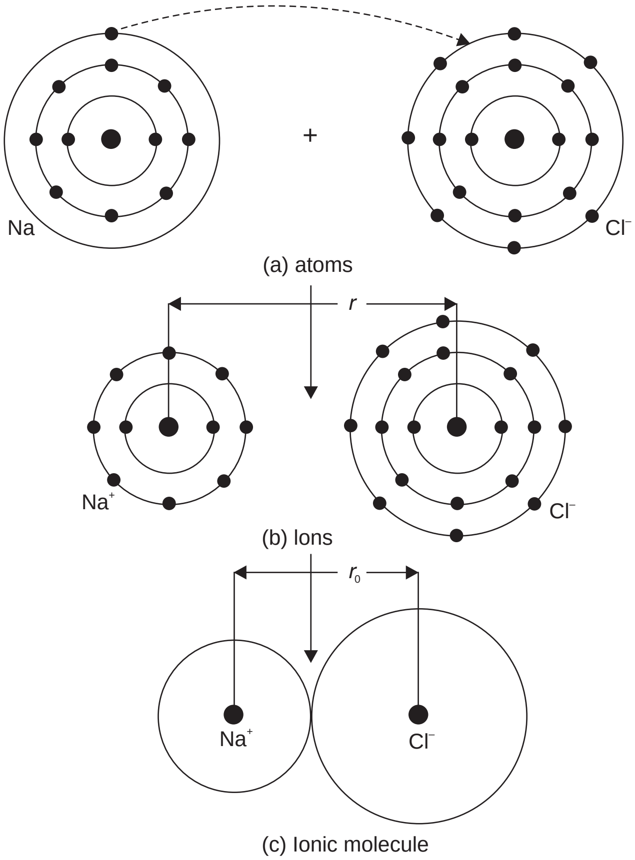


Fig. Q 1.2.1 *Schematic representation of the formation of sodium chloride*

Table Q 1.2.1 *Energy absorbed and energy released in the formation of NaCl*

S. No	*Energy absorbed in the formation of NaCl*	*S. No*	*Energy released in the formation of NaCl*
1	Separation of chlorine atoms of the diatomic Cl_2 molecule	1	Completion of M-shell of chlorine atom
2	Separation of sodium atoms from sodium solid	2	Lattice energy of sodium chloride
3	Separation of electron from sodium atom		

Thus a net energy of (5.1 – 3.6) = 1.5 eV is spent for creating a positive sodium ion and a negative chlorine ion at infinity. Now

$$\mathrm{Na + Cl + 1.5\ eV = Na^+ + Cl^-}$$

What happens when the electrostatic attraction between Na^+ and Cl^- ions brings them together to the *equilibrium spacing* $r_0 = 0.24$ nm? At the equilibrium position, the *potential energy* will be minimum and the energy released in the formation of NaCl molecule is called the *bond energy* of the molecule and it is obtained as follows:

$$\boxed{\begin{aligned} V &= -\frac{e^2}{4\pi \in_0 r_0}\ \text{joule} = -\frac{e}{4\pi \in_0 r_0}\ \text{electron volt} \\ V &= -\frac{1.6\times 10^{-19}}{4\pi \times 8.85 \times 10^{-12} \times 2.4 \times 10^{-10}} = -6\ \text{eV} \end{aligned}} \qquad \text{(Q 1.2.3)}$$

This is the energy released. Thus the entire process evolves an energy of 6 – 1.5 = 4.5 eV. This means that to dissociate a NaCl molecule into Na and Cl ions, an amount of 4.5 eV of energy will be required. Schematically

$$\underset{\xleftrightarrow[\infty]{\hspace{2em}}}{\mathrm{Na^+ + Cl^-}} \rightarrow \underset{\xleftrightarrow[0.24\ \text{nm}]{\hspace{2em}}}{\mathrm{Na + Cl}} \rightarrow \mathrm{NaCl}$$

Q 1.3 Discuss the variation of interatomic force between atoms with spacing between them with a suitable graph. Compute the cohesive energy of this system by drawing a similar curve between potential energy and spacing.

***Answer*:** We assume here that in a solid material the following two types of forces act between the atoms:

(i) *attractive forces* which keep the atoms together forcing them to form a solid.
(ii) *repulsive forces* which come into play when a solid is compressed.

Such forces, however, act in the case of liquids also and even in single molecule. But mere existence of these forces between atoms does not guarantee the formation of a stable chemical bond. This may be established by considering two atoms say A and B exerting attractive and repulsive forces on each other such that the bonding force F, between the atoms may be represented as:

$$\boxed{F(r) = \frac{A}{r^M} - \frac{B}{r^N}} \qquad \text{(Q 1.3.1)}$$

The first term represents the *attractive force* and the second term the *repulsive force*. Near the equilibrium position the second term must increase more rapidly for diminishing value of r than does the first, and N is necessarily greater than M.

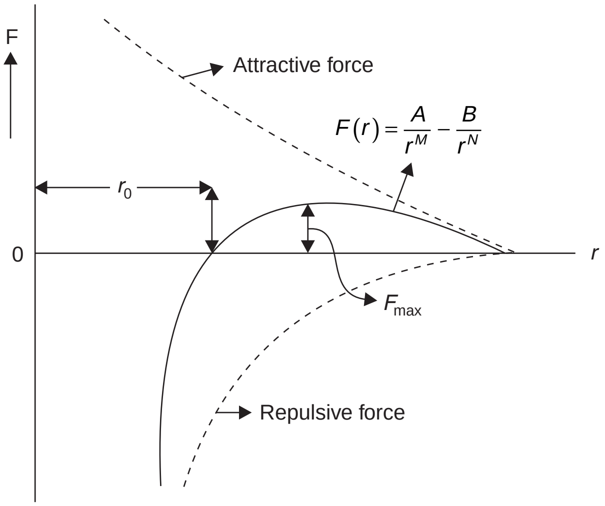


Fig. Q 1.3.1 *Variation of interatomic force with interatomic spacing*

At the equilibrium spacing,
$F(r) = 0$ when $r = r_0$

$$\boxed{\begin{aligned} \frac{A}{r_0^M} &= \frac{B}{r_0^N} \\ r_0 &= \left[\frac{B}{A}\right]^{\frac{1}{N-M}} \end{aligned}} \qquad \text{(Q 1.3.2)}$$

Cohesion and Cohesive Energy

The potential energy representing the interaction between the atoms varies greatly with the *interatomic spacing* and the same is obtained as follows:

$$U(r) = \int F(r)\,dr = \int \left[\frac{A}{r^M} - \frac{B}{r^N}\right] dr$$

$$= -\left[\frac{A}{M-1}\right]\left[\frac{1}{r^{M-1}}\right] + \left[\frac{B}{N-1}\right]\left[\frac{1}{r^{N-1}}\right] + C$$

i.e.,
$$U(r) = -\frac{a}{r^m} + \frac{b}{r^n} + C$$

Setting $U = 0$, when $r = \infty$, we get C = 0 and hence

$$\boxed{U(r) = -\frac{a}{r^m} + \frac{b}{r^n}} \tag{Q 1.3.3}$$

where n is the *repulsive exponent*

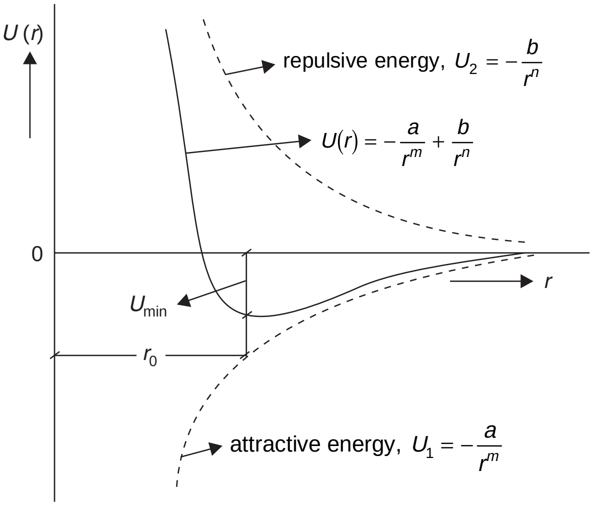


Fig. Q 1.3.2 *Variation of potential energy with spacing*

When $r = r_0$ (the equilibrium spacing), $U(r)$ exhibits a minimum. Thus

$$\left[\frac{dU}{dr}\right]_{r=r_0} = 0 = \frac{am}{r_0^{m+1}} - \frac{bn}{r_0^{n+1}}$$

or
$$r_0 = \left[\left(\frac{b}{a}\right)\left(\frac{n}{m}\right)\right]^{\frac{1}{n-m}}$$

and
$$\left[\frac{d^2U}{dr^2}\right]_{r=r_0} = -\frac{am(m+1)}{r_0^{m+2}} + \frac{bn(n+1)}{r_0^{n+2}} > 0$$

i.e.,
$$r_0^{m+2}\, bn(n+1) - am(m+1)r_0^{n+2} > 0$$

$$bn(n+1) > am(m+1)r_0^{n-m}$$

Substituting for r_o and simplifying, one gets,

$$n > m \qquad \text{(Q 1.3.4)}$$

Computation of Cohesive Energy

The energy corresponding to the equilibrium position ($r = r_0$), symboled by $U(r_0)$ is called the *bonding energy* or the *energy of cohesion* of the molecule. This is the energy required to dissociate the two atoms of the molecules (AB) into an infinite separation. The energy is also therefore called *energy of dissociation*.

Thus

$$\boxed{U_{min} = -\frac{a}{r_0^m} + \frac{b}{r_0^n}} \qquad \text{(Q 1.3.5)}$$

$$\left[\frac{dU}{dr}\right]_{r = r_0} = \frac{ma}{r_0^{m+1}} - \frac{nb}{r_0^{n+1}} = 0$$

Thus

$$\boxed{r_0^n = r_0^m \left[\frac{b}{a}\right]\left[\frac{n}{m}\right]} \qquad \text{(Q 1.3.6)}$$

Substituting this in Eqn. (1.3.5)

$$\boxed{U_{min} = -\frac{a}{r_0^m}\left[1 - \frac{m}{n}\right]} \qquad \text{(Q 1.3.7)}$$

As an example, 4.4 eV of energy is required to break one (H — Cl) bond, or 420 × 10^3 kJ/kmol. The total energy of one ion due to the presence of all others is given by:

$$\boxed{U(r) = -\left[\frac{Z_1 Z_2 Ae^2}{4\pi \in_0 r}\right] + \frac{B}{r^n}} \qquad \text{(Q 1.3.8)}$$

For the univalent *alkali halides*

$$U(r) = -\frac{Ae^2}{4\pi \in_0 r} + \frac{B}{r^n}$$

The total energy per kmol of the crystal is:

$$U(r) = N_A\left[\frac{B}{r^n} - \frac{Ae^2}{4\pi \in_0 r}\right]$$

The potential energy will be zero at $r = r_0$ and

$\frac{dU}{dr} = 0$ and the final equation for the *equilibrium energy* becomes

$$\boxed{U_0 = -\left[\frac{Ae^2 N_A}{4\pi \in_0 r_0}\right]\left[\frac{n-1}{n}\right]} \qquad \text{(Q 1.3.9)}$$

with N_A the Avogadro's number. The *equilibrium energy* U_0 is also called the *lattice energy*. A is called *Madelung constant.*

Q 1.4 Write a note on the properties of ionic crystals.

***Answer*:** (i) *Crystal structure*: Most of the ionic solids have fine crystalline structure. It has been found by *x-ray diffraction* that the constituents of these crystals are ions and not atoms. For instance, in the case of NaCl, each Na^+ ion is surrounded by six Cl^- ions at equal distances. Similarly, each Cl^- is surrounded by six Na^+ ions. The result is, we get *crystal lattice* of NaCl.

(ii) *Melting and boiling points*: Ionic solids have high melting and boiling points. It is because considerable external energy is required to overcome the electrostatic forces existing between the ions in such a solid.

(iii) *Electrical conductivity*: Pure and dry ionic solids are good insulators because all the electrons are tightly bound with the ions involved in the bond formation. However, such solids show electrical conductivity when;

(a) the temperature is raised. At high temperature, the electrostatic forces between the ions are greatly reduced so that some of the ions themselves transport the charge in the material.

(b) dissolve easily in solvents like water. When an ionic solid is dissolved easily in water, the electrostatic forces are considerably weakened (by 80 times) due to high permittivity of water. The result is that the ions become free and wander about in the solution. If now a field is applied, these ions will themselves carry the charge in the solution (*electrolysis*). The permittivity of water is about 80.

(iv) *Solubility*: Ionic compounds easily dissolve in solvents like water (H_2O). It is because molecules of water strongly interact with the crystal ions to destroy the forces of attraction between the ions. Ionic compounds are insoluble in non-polar solvents like benzene (C_6H_6), carbon tetrachloride (CCl_4), because their *dielectric constants* are very low.

(v) *Other properties*: Reaction between ionic compounds in solution state is always fast. This is because in a solution, ionic substances exist as ions and chemical reactions take place between the ions. Ionic crystals are transparent for all frequencies up to the value called the fundamental *absorption frequency*. At frequencies higher than this, they are opaque. High hardness and low conductivity are typical properties of these solids. When subjected to stresses, ionic crystals tend to cleave (break) along certain planes of atoms rather than to deform in a ductile fashion as metals do.

Below are given, some important relations used in the study of other properties of ionic crystals.

(a) The expressions for bulk modulus and compressibility are respectively listed now:

$$K = \frac{Ae^2(n-1)}{72\pi \in_0 r_0^4}$$

and $$\boxed{\beta = \frac{1}{K} = \frac{72\pi \in_0 r_0^4}{Ae^2(n-1)}} \qquad \text{(Q 1.4.1)}$$

where A is Madelung constant and N_A is Avogadro's number.

(b) *The Born-Haber cycle for NaCl crystal*

(i) Initially we start with solid sodium and chlorine molecules. Solid sodium is vaporized by subjecting the *sublimation energy* (S) while chlorine molecule is dissociated into its constituent atoms by supplying *dissociation energy* (D). Hence $\frac{D}{2}$ is the dissociation energy per chlorine atom.

(ii) The outer electron of Na gaseous atom is removed by applying the ionisation energy (I) and this electron is added to Cl atom. As the chlorine atom has the electron affinity E, an energy E is given out.

(iii) The two ions ($Na^+ + Cl^-$) are arranged in the lattice and hence the *lattice energy* (U_0) is released.

(iv) We again reach to the starting point by supplying an energy (ΔH) known as *heat of dissociation*.

Thus

$$S + \frac{D}{2} + I - E + \Delta H - U_0 = 0$$

$$\boxed{U_0 = S + \frac{D}{2} + I - E + \Delta H} \qquad \text{(Q 1.4.2)}$$

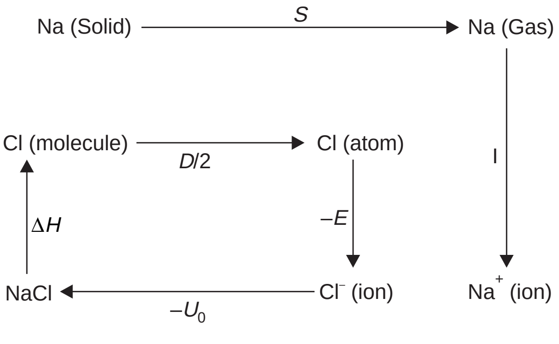


Fig. Q 1.3.3 *Born-Haber cycle for NaCl crystal*

Q 1.5 Discuss briefly the binding mechanism in covalently bonded crystals with suitable sketches.

***Answer*:** The bond formed between two atoms by sharing of valence electrons is called a *covalent* or *non-polar bond*. Such bonds are mainly found in organic molecules and in non-electrolytes. e.g. chlorine, fluorine, methane, hydrogen, etc. In the formation of this bond between two atoms, each atom contributes electrons in equal number and the contributed electrons are shared by both the atoms. In this process, the atoms involved usually acquire the *configuration* of a noble gas. It may be noted in this bond, the shared outer electrons (valence electrons) belong to both the atoms and not to this one or the other. Therefore, both the atoms are neutral even after the formation of bond. It is due to this reason that solids formed by such bond are usually called *non-polar substances.*

Below are discussed a few substances formed by this binding mechanism.

When two isolated H atoms, each with its electron in the ground state 1s orbital approach each other, the 1s clouds begin to overlap. Each electron is attracted to the other nucleus and the overlap increases (provided the electrons have opposite spin). The two atomic orbitals merge into a *molecular orbital*. Within the molecular orbital, the two electrons are attracted to both nuclei. When the repulsive forces have been balanced by the attractive forces a molecule results, having stability greater than that of the two isolated atoms. The covalent bonding is also known as *homopolar* or *electron-pair bonding* and it is common both in organic molecules and in many inorganic molecules. The balance between the attractive and repulsive force in hydrogen molecule occurs at a separation of 0.074 *nm*. Hence some energy must be spent to break the covalent bond in a hydrogen molecule into hydrogen atoms. About 4.5 eV is required to break one bond between the hydrogen atoms. i.e.,

$$H_2 + 4.5 \text{ eV} \rightarrow H + H$$

If *N* represents the number of electrons present in the valence shell of an electrically neutral atom, then (8 – N) is the number of electrons which are required to obtain a stable octet. i.e., it is the maximum number of covalent bonds which an atom can form with the adjacent atoms. Thus (8 – N) is the *co-ordination number* in normal covalent bonding.

The covalent bond between the two hydrogen atoms in a hydrogen molecule is represented as:

$$H : H$$

It is desired to make clear that one electron has come from each atom, it is now indicated as:

$$H \overset{\cdot}{\times} H$$

The total equation is represented as:

$$H^{\bullet} + H^{\bullet} \rightarrow H : H \rightarrow H \overset{\cdot}{\times} H \rightarrow H \bullet H \text{ or } H_2$$

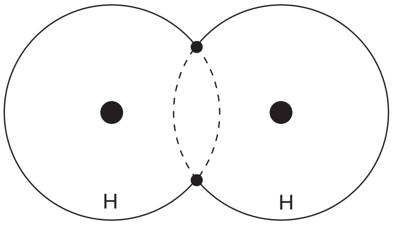
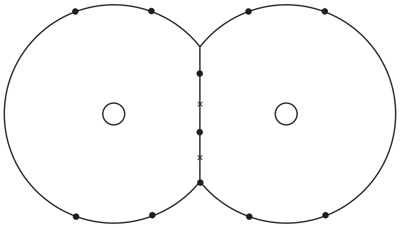
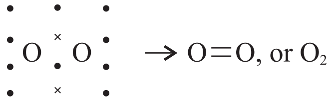


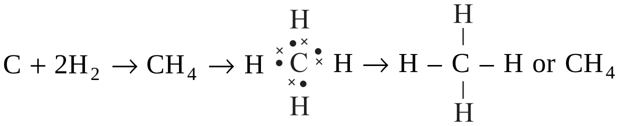
Fig. Q 1.5.1 *Covalent bond in hydrogen molecule*

Other examples are discussed below:





$$\overset{\bullet\ \ \bullet\ \ \bullet}{\underset{\bullet\ \ \times\ \ \bullet}{\vdots O \overset{\times}{\underset{\bullet}{}} O \vdots}} \rightarrow O{=}O, \text{ or } O_2$$



$$C + 2H_2 \rightarrow CH_4 \rightarrow H \overset{H}{\underset{H}{\overset{\bullet\times}{\underset{\times\bullet}{\overset{\times}{\bullet} C \overset{\bullet}{\times}}}}} H \rightarrow H - \overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}} - H \text{ or } CH_4$$

Q 1.6 Briefly explain the properties of covalent compounds.

***Answer*:**

(i) Covalent compounds may be solids, liquids or gases. Generally those substances which have high molecular weights exist as solids. Covalent solids are *hard* as well as *brittle.*

(ii) Covalent solids have crystalline structure i.e., atoms or molecules are arranged in some regular repeatable pattern in the three dimensions.

(iii) Pure covalent solids are good insulators. The reason is that all the valence electrons are tightly held in the covalent bonds. However, when certain impurities are added to such solids, they become reasonably good conductors and are termed as *semiconductors.*

(iv) Since covalent bonds are comparatively weak, therefore, covalent solids have low melting and boiling points

(v) Covalent solids are not readily soluble in water. However, they are easily soluble in organic solvents like benzene.

(vi) A very interesting property of covalent compounds is the apparent lack of sensitivity of their physical properties to their bonding type. For example, carbon in the diamond structure is the hardest substance and has a very high melting point of 3280 K. The hardness and melting point then decrease as we proceed to other elements in column IV of the periodic table from silicon to lead. Tin, for example, is very soft and has a low melting point. The variation in the electrical properties is also pronounced. Diamond is a very good insulator. Silicon and germanium are well known semiconductors while tin is a good conductor. Depending on the number of electrons shared, the bond length and bond energy vary. When the number of electrons shared is more, the bond length between the atoms is decreased and bond energy is increased.

Diamond, silicon, germanium, silicon carbide, tin and rutile are some examples of covalent crystals.

Q 1.7 Explain the nature of the bonds that exist in metals. Discuss the important physical properties of metals.

***Answer*:** Metallic elements have low ionisation energies and hence, in this bonding, atoms of the same element or different elements give their valance electrons to form an *electron cloud* or say '*electron gas*' throughout the space occupied by the atoms. Having given up their valence electrons, the atoms are in reality positive ions. These ions are held together by forces that are similar to those of ionic bond in that they are primarily electrostatic, but are between the ions and the electrons. Most of the atoms in metals have one or two valence electrons. These electrons are loosely held by their atoms and therefore can be easily released to the common pool to form an *electron cloud*. The electrostatic interaction between the positive ions and the electron gas holds the metal together. The high electrical and thermal conductivities of metals follow from the ability of the free electrons to migrate through their crystal lattices while all of the electrons in ionic and covalent crystals are bound to particular atoms.

Unlike other crystals, metals may be deformed without fracture, because the electron gas permits atoms to slide fast one another by acting as a *lubricant*. As we have seen carbon can exist in the covalent form and so it is an extremely poor conductor. However, it may also exist in an alternate form as graphite. In this case, bonds are formed in which covalency is not fully achieved and these bonds can break and reform fairly easily as in metallic bond. For this reason graphite is a conductor. If a potential difference is applied between any two points in a metal piece, the electron gas flows from negatively charged part to the positively charged part, constituting electric current.

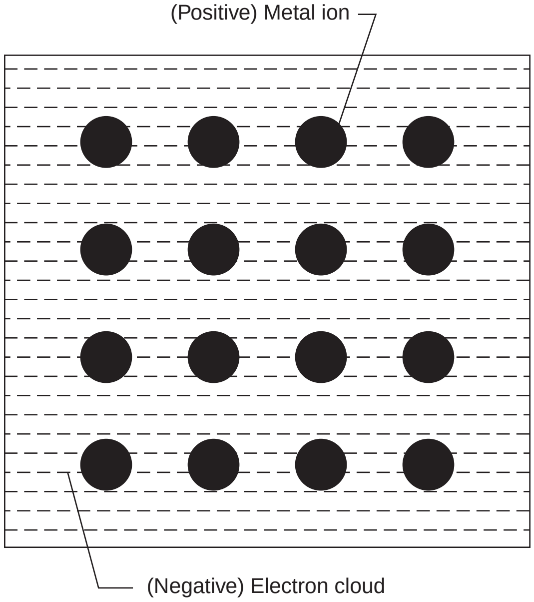


Fig. Q 1.7.1 *Bonding in metals*

Properties of Metallic Crystals

(i) Bonding energies and melting temperatures for some metals are given in Table 1.A. Bonding energies may be weaker or stronger, energies range from 64 × 10^3 kJ/kmol (0.7 eV/atom) for mercury to 850×10^3 kJ/kmol (8.8 eV/atom) for tungsten. Their respective melting points are –39°C and 3410°C.

(ii) Due to the symmetrical arrangements of the positive ions in a space lattice, metals are highly crystalline.

(iii) Metallic bonds being weak, metals have a melting point moderate to high. i.e., the melting points of metallic crystals are lower than those of the electrovalent crystals.

(iv) Since a large number of free electrons are available, metallic crystals have high electrical conductivity.

(v) Metallic crystals have higher thermal conductivity because of the availability of large number of free electrons which act as carriers of heat.

(vi) They are mechanically strong.

Copper, sodium, aluminum and silver are some examples.

Q 1.8 Discuss briefly molecular bonds. Also write a short note on hydrogen bonding.

***Answer*:** The bonds between atoms of those substances whose electrons have little transferability are known as *molecular bonds*.

Molecular bonds are formed for those elements or compounds whose electronic configuration is such that there is little transfer of electrons between their atoms. (e.g. noble gases like argon, neon, etc.). Unlike the three bonds considered above, in which electrons are either exchanged or shared, molecular bonds involve no transfer or exchange of charge. Rather the bond arises from the *van der Waals forces* of attraction which exist between various atoms as explained below:

All noble gases (neon, argon, etc.) have their last orbits complete. Obviously, they cannot form bonds by exchange or sharing of electrons. Hence, atoms of noble gases have little attraction for each other and consequently they remain in atomic state under ordinary conditions of temperature and pressure. However, at very low temperature, *condensation* of these gases takes place. This condensation would not have been possible if there are no interatomic forces, however weak. These interatomic forces of attraction are called *van der Waals forces*.

van der Waals Forces

An atom is neutral from a distance only. However, close to it, there is always a net charge at any time as seen by a neighbouring atom. This is because all the electrons are not concentrated at one end in an atom. Thus there exists forces of electrostatic attraction between the nucleus of one atom and the electrons of the other. These forces are called *van der Waals* forces. i.e., the forces of attraction between two neighbouring atoms due to the resultant charge are called *van der Waals forces*. These forces are very weak and were first discovered by *van der Waals*.

Characteristics of Molecular Solids

(i) They exist in crystalline form as well as non-crystalline solids

(ii) They have no melting point as the binding arises from *van der Waals* forces which are quite weak

(iii) They are good insulators as free electrons are not available

(iv) They are insoluable in water.

Hydrogen Bonding

Covalently bonded atoms some times produce molecules that behave as permanent dipoles. For example in water molecule, the oxygen atom shares two half filled *p*-orbitals with two hydrogen atoms. A simple way of describing the situation is, the electrons shared between these atoms spend more "time" in between the two atoms so that the oxygen atom tends to act as +ve end of the dipole. So in the formation of ice the bonding tends to become more ionic by the +ve and the –ve ions being arranged alternately forming long chains as shown below:

$$H^+ - O - H^+ - O - H^+$$

TABLES

Table 1.A *Bonding energies and melting temperatures of some selected substances*

Bonding type	*Substance*	*Bonding energy*		*Melting temperature °C*
		kJ/kmol in 10^3	*eV/atom, ion or molecule*	
Ionic	NaCl	640	3.3	801
	MgO	1000	5.2	2800
Covalent	Si	450	4.7	1410
	C (diamond)	713	7.4	3600
Metallic	Hg	68	0.7	–39
	Al	324	3.4	660
	Fe	406	4.2	1538
	W	849	8.8	3410
van der Waals	Ar	7.7	0.08	–189
	Cl_2	30.8	0.32	–101
Hydrogen	NH_3	35	0.36	–72
	H_2O	51	0.52	0

Table 1.B *Bond lengths and bond energy of some diatomic molecules*

Molecule	*Bond length (nm)*	*Bond energy (eV)*
NaCl	0.236	4.4
LiH	0.160	2.5
NaBr	0.250	3.8
KCl	0.267	4.3
NaI	0.271	3.2

Table 1.C *Ionization energy and electron affinity of some elements*

Element	*Ionization energy (eV)*		*Electron affinity eV*
	To remove one electron	*To remove two electron*	
H	13.595		0.7542
Na	5.14	52.43	0.55
C	11.26	35.64	1.27
Si	8.15	24.49	1.39
Cl	13.01	36.81	3.61
Br	11.84	33.40	3.36
I	10.45	29.41	3.06

Table 1.D *Physical properties of some ionic solids*

Ionic solids	*Nearest neighbour separation, r_0 (nm)*	*Bulk modulus, K in 10^{10} N/m^2*	*Repulsive exponent, n*	*Lattice energy in kJ/kmol (in 10^3)*		*Melting temperature ^oC*
				Experimental	*Calculated*	
NaCl	0.2820	2.40	8	788	747	800
NaBr	0.2989	1.99	8.5	736	708	742
KCl	0.3147	1.74	9	717	676	770
KI	0.3533	1.17	10.5	617	605	682
LiCl	0.2570	2.98	7.0	862	807	614
LiI	0.3000	1.71	8.5	732	695	440
RbCl	0.3291	1.56	9.5	687	650	717

Table 1.E *Covalent bond lengths and associated binding energies*

Bond	*Bond length (nm)*	*Binding energy in kJ/kmol (in10^3)*	*Bond*	*Bond length in nm*	*Biding energy in kJ/kmol (in 10^3)*
H—H	0.074	436	O$=$O	0.121	498
O—H	0.097	463	N—N	0.100	390
C—C	0.154	348	H—Cl	0.128	431
C$=$C	0.134	615	Si—O	0.183	368
C—Cl	0.177	327	C—H	0.108	414

Table 1.F *Comparison between ionic bonds and metallic bonds*

Properties	*Ionic Bonds*	*Metallic Bonds*
Bonding force	The bonds exist due to electrostatic force of attraction between positive and negative ions of different elements	The bonds exist due to electro static force of attraction between the electron cloud of valence electrons and positive ions of the same or different metallic elements
Bond formation	Ionic bonds are most easily formed when one of the atoms has smaller number of valence electrons, such as the alkali metals and alkali earths	This type of bond is characteristic of the elements having smaller number of valence electrons, which are loosely held, so that they can be released to the common pool
Conductivity	Low conductivity is the property of the solids formed by ionic bonding	Good thermal and electrical conductivity is the property of most of the solids formed by metallic bonding
Mechanical properties	Solids formed have high hardness. Ionic crystals tend to cleave (break) along certain planes of atoms rather than to deform in a ductile fashion when subjected to stresses	Solids formed mostly have good ductility
Bond strength	These bonds are generally stronger than the metallic bonds	These bonds are generally less stronger than ionic bonds

OBJECTIVE QUESTIONS

1. Ionization energy of sodium atom is
   - (a) 5 joule
   - (b) 8×10^{-19} joule
   - (c) 200×10^{10} joule
   - (d) 1420 joule
2. The net energy required for creating a positive sodium ion and a negative chlorine ion is
   - (a) 5.1 eV
   - (b) 3.6 eV
   - (c) 1.5 eV
   - (d) 2.2 eV
3. Which of the following classes is most likely to produce a semiconductor?
   - (a) ionic
   - (b) covalent
   - (c) metallic
   - (d) van der Waals
4. At high temperature, some of the ions in an ionic crystal transport charge because of interaction
   - (a) true
   - (b) false

5. When an ionic solid is dissolved in water the ions are free and wander in the solution. This is because
   (a) high dielectric constant of water (b) low dielectric constant of water
   (c) low density of water
   (d) none of these

6. Ionic compounds are insoluble in carbon tetrachloride because
   (a) it is a polar solvent (b) it is a non-polar solvent
   (c) it is an organic solvent (d) none of these

7. Which of the following solids are always opaque to visible radiation?
   (a) covalent (b) metallic
   (c) ionic (d) none of these

8. Which of the following has the hydrogen bonding?
   (a) CH_4 (b) CsCl
   (c) NaCl (d) HF

9. If the expression for bond energy of an ionic molecule in electron volt is $-\frac{e}{4\pi \in_0 r_0}$, then it is expressed in joule as
   (a) $-\frac{4\pi \in_0 r_0}{e}$ (b) $-\frac{2e}{4\pi \in_0}$
   (c) $-\frac{e^2}{4\pi r_0}$ (d) $-\frac{e^2}{4\pi \in_0 r_0}$

10. The total number of Cl^- ions in a unit cell of NaCl crystal is
    (a) 4 (b) 2
    (c) 8 (d) 10

11. If the distance between a Na ion and a chlorine ion in NaCl crystal is 0.28 nm, then the lattice parameter of the crystal is
    (a) 0.14 nm (b) 0.8 nm
    (c) 56 A° (d) 0.56 nm

12. At the equilibrium spacing of a diatomic molecule, the resultant force is
    (a) zero (b) minimum
    (c) maximum (d) unity

13. The potential energy in the above said spacing is
    (a) zero (b) minimum
    (c) maximum (d) unity

14. The maximum number of covalent bonds that can be formed by a carbon atom is
    (a) 2 (b) 8
    (c) 4 (d) 1

15. Which of the interatomic bonds are directional?
    (a) covalent (b) metallic
    (c) ionic (d) van der Waals

16. The energy required to break the bond (H — Cl) is 4 eV. This is equal to
    (a) 420×10^6 J/kmol (b) 420×10^4 kJ/kmol
    (c) 120 J/kmol (d) 420 kJ/kmol

17. The number of unshared electrons by each oxygen atom with the carbon atom to form CO_2 is
    (a) 2 (b) 3
    (c) 4 (d) 5

18. Covalent crystals are hard and brittle
    (a) true (b) false

19. The properties of covalent crystals are not sensitive to the nature of the bonding that exist
    (a) true (b) false

20. The absence of electrostatic interaction between the electron gas and positive ions holds the metal together
    (a) true (b) false

21. The endless symmetrical arrangements of positive ions in metals in three dimension is the main cause for the formation of a metal to be single crystal
    (a) true (b) false

22. The electrostatic attraction between the nucleus of one atom and the electrons of the other is called
    (a) coulomb forces (b) gravitational
    (c) van der Waals forces (d) none of these

23. Cohesive energy in the case of van der Waals bonding lies in the range
    (a) 8 – 10 eV (b) 6 – 8 eV
    (c) 0.1 – 0.5 eV (d) 0.002 – 0.1 eV

24. The co-ordination number of Na^+ and Cl^- in the rock salt structure is respectively
    (a) 8 and 6 (b) 6 and 8
    (c) 6 and 6 (d) 4 and 4

PROBLEMS AND SOLUTIONS

1.1 Assuming an overlap interaction between nearest neighbours of the type $\phi(r) = B \exp(-r/\rho)$, where B and ρ are constants, calculate the equilibrium spacing r_0 in terms of B and ρ.

***Solution*:**

$$\phi(r) = B \exp(-r/\rho)$$

At the equilibrium spacing, $r = r_0$

i.e.,

$$B \exp(-r_0/\rho) = 0$$

$$\log_e B - \frac{r_0}{\rho} = 0$$

$$\boxed{r_0 = \rho \log_e B} \ \textbf{\textit{Answer}}$$

1.2 The following figure shows the arrangements of lithium and iodine ions in lithium chloride. If the distance between the lithium and iodine nuclei in lithium iodide is 300 pm, compute the radius of the iodide ion.

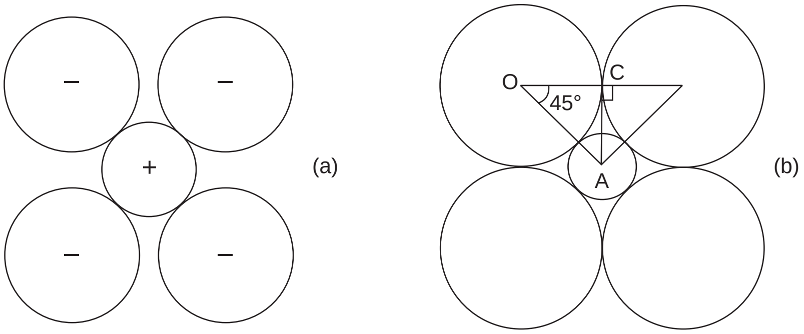


Fig. Q 1.2 *(a) Anions packed around a cation on a horizontal plane (b) Anion-Anion contact on a horizontal plane through an octahedron*

***Solution*:**

$$\cos 45^\circ = \frac{OC}{OA}$$

$$OC = OA \cos 45^\circ = 300 \times 10^{-12} \times 0.707$$

$$OC = I_r = 212 \text{ pm}$$

$$\boxed{I_r = 212 \text{ pm}} \ \textbf{\textit{Answer}}$$

1.3 Given that the compressibility of NaCl is 3.3×10^{-11} m^2/newton. The Madelung constant $\alpha = 1.75$, and the equilibrium nearest neighbour spacing is 0.28 nm, determine the repulsive potential exponent n in the total expression for $2N$ ions using the basic equation $U(r) = -N\left[\frac{\alpha e^2}{r} - \frac{B}{r^n}\right]$.

***Solution*:** A lengthy discussion of the above equation yields,

$$n = 1 + \frac{72\pi \in_0 r_0^4}{Ae^2 \beta} \text{ with } A = 1.75 \text{ the Madelung constant}$$

$$= 1 + \frac{72\pi \in_0 \times \left(0.28 \times 10^{-9}\right)^4}{1.76 \times \left(1.6 \times 10^{-19}\right)^2 \times 3.3 \times 10^{-11}}$$

$$= 1 + 8.3 = 9.3$$

$$\boxed{n = 9.3} \textbf{ Answer}$$

1.4 What is the equilibrium nearest-neighbour separation r_0 at which $U(r_0)$ in the above problem is unchanged by replacing $\frac{B}{r^n}$ by $C \exp\left(-r/\rho\right)$?

***Solution*:**

$$B = r^n\, C \exp\left(-r/\rho\right) \text{ with } r = r_0$$

Differentiating the equation,

$$r^n = \frac{B}{C \exp\left(-r/\rho\right)}, \text{ one gets}$$

$$n r^{n-1} = \frac{B/\rho}{C \exp\left(-r/\rho\right)}$$

Substituting for B

$$n r^{n-1} = \frac{r^n\, C \exp\left(-r/\rho\right)}{C \exp\left(-r/\rho\right)\, \rho}$$

i.e.,

$$\frac{n}{r_0} = \frac{1}{\rho}$$

$$\boxed{r_0 = n\rho} \textbf{ Answer}$$

1.5 The potential energy of a diatomic molecule is given in terms of the interatomic distance r by the expression

$$U\left(r\right) = -\frac{a}{r^2} + \frac{b}{r^{10}}$$

Calculate the equilibrium spacing of the two atoms and the dissociation energy. Given: $a = 1.44 \times 10^{-39}$ J m^2 and $b = 2.19 \times 10^{-115}$ J m^{10}.

***Solution*:**

P.E. of a diatomic molecule is $U(r) = -\dfrac{a}{r^2} + \dfrac{b}{r^{10}}$

$$\left[\frac{dU}{dr}\right]_{r=r_0} = \frac{2a}{r_0^3} - \frac{10b}{r_0^{11}} = 0$$

or
$$r_0^8 = \frac{5b}{a} = \left[\frac{5 \times 2.19 \times 10^{-115}}{1.44 \times 10^{-39}}\right]$$

i.e.,
$$\boxed{r_0 = 0.408 \text{ nm}} \quad \textbf{\textit{Answer (a)}}$$

$$U_{min} = U_{diss} = -\frac{a}{r_0^m}\left[\frac{(n-m)}{n}\right]$$

$$= -\frac{1.44 \times 10^{-39}}{\left(0.408 \times 10^{-19}\right)^2}\left[\frac{(10-2)}{10}\right] = -4.33 \text{ eV}$$

$$\boxed{U_{diss} = 4.33 \text{ eV}} \quad \textbf{\textit{Answer (b)}}$$

1.6 If the repulsive energy is of the form C exp(–*r*/*a*), determine C and *a* for NaCl if the cohesive energy per ion pair is 6.61 eV, and the interatomic separation is 0.282 nm. Given that the ionisation energy of Na is 5.138 eV and the electron affinity of Cl^- is 3.61 eV.

***Solution*:**

(i) cohesive energy/ion pair, E

(ii) ionisation energy of Na, E_1

(iii) electron affinity of Cl, E_a

(iv) coulomb energy, E_c is calculated as follows:

$$E_c = \frac{Ae^2}{4\pi \in_0 r} \text{ joule}$$

$$= \frac{Ae}{4\pi \in_0 r} \text{ eV}$$

with the Madelung constant $A = 1.75$ for NaCl

Thus

$$E_c = \frac{A \times 1.6 \times 10^{-19}}{4\pi \times 8.85 \times 10^{-12} \times r \times 10^{-9}} = \frac{1.44A}{r}$$

Now cohesive energy per ion pair is

$$-E = E_I - E_a - E_c + E_r$$

where E_r is the repulsive energy,

Thus

$$-6.61 = (5.138 - 3.61) - \frac{1.44A}{r} + C\exp(-r/a) \tag{1}$$

But

$$\left[\frac{dU}{dr}\right]_{r=r_0} = 0 = \frac{1.44}{r^2} - \frac{C}{a}\exp(-r/a) \tag{2}$$

Take $r = r_o = 0.282$ nm and A = 1.75, one gets

$$\frac{1.44 \times 1.75}{(0.282)^2} = \frac{C\exp(-r/a)}{a} = 31.69$$

$$C \exp(-r/a) = 31.69a$$

Substituting this in Eqn. (1), we get

$$-6.61 = 1.528 - \frac{1.44A}{0.282} + 31.69a$$

$$\boxed{a = 0.025 \text{ nm}} \quad \textbf{\textit{Answer (a)}}$$

Now equation (1) becomes

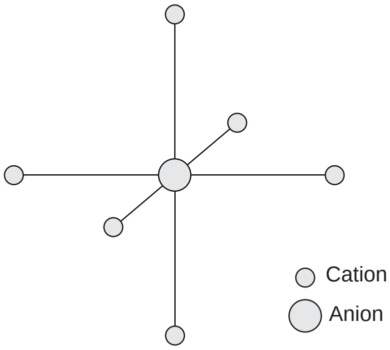
$$C\exp(-r/a) = -6.61 - 1.58 + \frac{1.44 \times 1.75}{0.282} = 0.746$$

$$C = 0.746 \times \exp(r/a) = 0.746 \times \exp(0.282/0.025)$$

$$\boxed{C = 63.22 \text{ eV}} \quad \textbf{\textit{Answer (b)}}$$

EXERCISE

1.1 Calculate the value of the Madelung constant for the structure shown in the following figure. All bond lengths are equal and all bond angles are 90°. Assume that there are no ions other than those shown in figure and that the charges on the cations and anions are +1 and –1. (***Ans:*** 3.99)



1.2 For NaCl, the Na atom has an ionisation energy 8 × 10^{-19} joule and Cl atom has an electron affinity 3.6 eV. The equilibrium separation between the ion-pair is 0.282 nm. What is the energy required to transfer an electron from Na to Cl? Madelung constant is 1.75. (***Ans*:** 7.53 eV)

1.3 The ionic radii of Cs and Cl are 0.165 nm and 1.81 nm and their atomic weights are 133 and 35.5 respectively. Calculate the density of CsCl. (***Ans*:** 4.37 × 10^3 kg/m^3)

1.4 How many kg-atom of potassium will be required to treat with 709.1 kg of chlorine to form KCl. (***Ans*:** 20 kg-atom)

1.5 Assume that the energy of the two particles in the field of each other is given by

$$U(r) = -\frac{\alpha}{r} + \frac{\beta}{r^8}$$

where α and β are constants and r is the distance between the centres of the particles, form a stable compound for $r = r_0 = [8\beta/\alpha]^{1/7}$. Show that in the stable configuration, the energy of attraction is 8 times the energy of repulsion.

2

Crystalline State

2.1 INTRODUCTION

KEY WORDS

array of points, lattice, unit cell, periodic lattice, crystal structure, rock salt crystals, degree of symmetry, periodic arrangements, space lattice, two dimensional space lattice, position vector, fundamental translation vectors, basis or pattern, lattice point, unit cell, crystal lattice, fundamental elementary pattern, translation repetition, identical blocks, Bravais lattices, centre of symmetry/centre of inversion, plane of symmetry, reflection symmetry, axis of symmetry, congruent position, degree of axis/fold of axis, point groups, rotation-inversion axis, self coincidence, translation symmetry elements, glide plane, screw axis, space groups, five-fold rotation axis, packing fraction/density of packing, simple cubic structure, lattice point, primitive cell, coordination number, nearest neighbour distance, loosely packed and closely packed structures, closest packing, fcc and hcp structures, c/a ratio, Avogadro's number, lattice parameter, atomic volume, diamond cubic structure, NaCl structure, lattice planes, interplanar spacings, cleavage planes, Miller indices, reciprocal lattice, x-ray diffraction and electron diffraction, square reciprocal lattice, Ewald, Bragg's condition of reflection, crystal defects, thermal vibrations, point defects, vacancies, Arrhenius plot, powder method, substitutional and interstitial atoms, Debye and Scherrer, Laue, powder method, Bragg diffraction equation, rotating crystal method, stereographic projection, Laue spots.

2.1 INTRODUCTION

By far the most important fact about materials in general and metals in particular is that they are *crystals*. All their mechanical and physical properties are closely related to this fact. We start by neglecting the nature of the ions of the crystal and simply consider a regular *array of points* in space. This array is the *lattice* and we are concerned with its geometric properties. Because it is a periodic structure, it can be described very simply by defining a *unit cell* as a volume containing one or more points, which may be repeated by unit translations so that a *periodic lattice* is generated. The solids of primary interest for us have an arrangement of atoms (or molecules) in which the atoms are arranged in some regular repetitions pattern in three dimensions. The arrangement of atoms is termed the *crystal structure*. The internal regularity of atoms - placement in solids often leads to a symmetry of their external shape. *Rock salt crystals*, for example, are rectangular parrlellopiped with faces which are identical when viewed from many different directions; these crystals have a *high degree of symmetry*.

Prior to the discovery of x-rays, there was no tool to investigate the internal structure of a crystalline solid. However, after the discovery of x-rays in 1895, a systematic study of crystal structure was started—science of crystallography was born.

Q 2.1 Give a brief historical account of the basic terms frequently used in the study of the structure of crystals.

***Answer*:** The study of the *regular* and *periodic arrangements* of atoms or molecules in space is called *crystal structure*. The crystal structure may be described in terms of an idealized geometrical concept called a *space lattice*. It may be defined as an array of points in space such that the environment about each point is the same. The *three dimensional space lattice* may be defined as an infinite array of points in three dimensions in which every point has an identical environment as any other point in the array.

Example

Let us now consider the case of *two dimensional array of points* as shown in Fig. Q 2.1.1. It is obvious from the figure that the environment about any two points is the same; hence it represents a space lattice. In a mathematical form, the space lattice may be defined as follows:

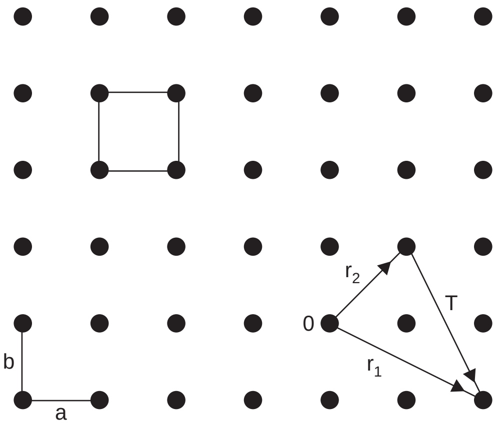


Fig. Q 2.1.1 *Two dimensional array of points*

We choose any arbitrary point 0 as origin and consider the *position vector* $\vec{r}_1$ and $\vec{r}_2$ of any two lattice points by joining them to 0. If the distance $\vec{T}$ of the two vectors $\vec{r}_1$ and $\vec{r}_2$ satisfies the following relation,

$$\vec{T} = n_1 \vec{a} + n_2 \vec{b}$$

where n_1 and n_2 are integers and $\vec{a}$ and $\vec{b}$ are *fundamental translation vectors* characteristic of the array, then the array of points is a *two dimensional lattice*. For *three dimensional lattice*,

$$\vec{T} = n_1 \vec{a} + n_2 \vec{b} + n_3 \vec{c}$$

Hence it should be remembered that a crystal lattice refers to the geometry of a set of points in space whereas the structure of the crystal refers to the actual ordering of its constituent ions, atoms and molecules in the space.

The Basis and Crystal Structure

For lattice to represent a crystal structure, we associate every lattice point with one or more atoms (i.e., a unit assembly of atoms or molecules identical in composition) called the *basis* or *pattern*. When the basis is repeated with correct periodicity in all directions, gives the actual crystal. The *crystal structure* is real, while the lattice is imaginary.

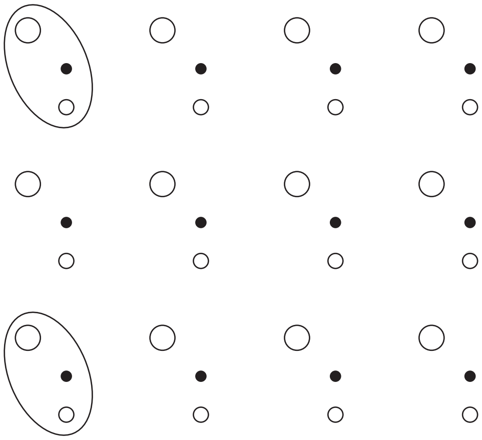


Fig. Q 2.1.2 *Basis or Pattern*

Thus

lattice + basis = crystal structure

Fig. Q 2.1.2 shows the *basis* or *pattern* representing each *lattice point*. It is observed from the figure that the basis consists of three different atoms. It can also be observed that basis is identical in composition, arrangement and orientation. In crystals like aluminium and sodium the basis is a single atom; in NaCl, KCl, etc. the basis is diatomic whereas in crystals like CaF_2 the basis is triatomic.

Unit Cell and Crystal Lattice

For discussing the unit cell, let us consider a two dimensional crystal in which the atoms are arranged as in Fig. Q 2.1.3. If we consider a parallelogram such as ABCD with sides AB = *a* and AD = *b*, then by rotating the parallelogram by any integral multiple of vectors $\vec{a}$ and $\vec{b}$, the whole crystal lattice may be obtained. In this way the fundamental unit ABCD is called a *unit cell*. Thus a unit cell is the smallest geometric figure, the repetition of which gives the actual crystal structure. The unit cell may also be defined as the *fundamental elementary pattern* of minimum number of atoms, molecules or group of molecules—which represent fully all the characteristics of the crystal. It should be noted that the choice of a unit cell is not unique but it can be constructed into a number of ways as EFGH or PQRS shown in Fig. Q 2.1.3. The unit cell should be chosen in such a way that it conveys the symmetry of crystal lattice and makes the mathematical calculations easier.

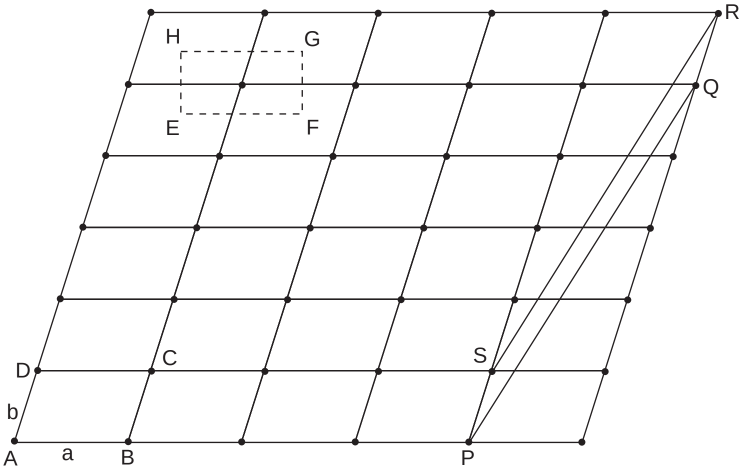
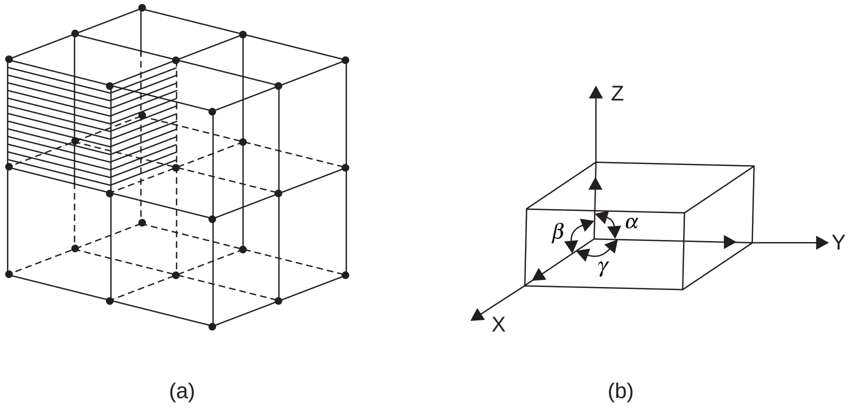


Fig. Q 2.1.3 *Two dimensional arrangement of atoms*



(a) (b)

Fig. Q 2.1.4 *Three dimensional unit cell*

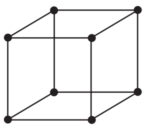
For a three dimensional case, the same procedure may be adopted. A three dimensional unit cell is shown in Fig. Q 2.1.4(*a*). The unit cell is a parallelepiped formed by the basis vectors $\vec{a}, \vec{b}, \vec{c}$ as concurrent edges and including angles α, β, γ between $\vec{b}$ and $\vec{c}$, $\vec{c}$ and $\vec{a}$ and $\vec{a}$ and $\vec{b}$ respectively as shown in Fig. Q 2.1.4(*b*). Thus in general, a unit cell may be defined as that volume of a solid from which the entire crystal may be constructed by *translational repetition* in three dimensions. The entire lattice structure of a crystal is found to consist of *identical blocks* or *unit cells.*

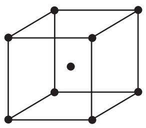
Q 2.2 Discuss the seven systems of crystals and the fourteen types of Bravais lattices with tables and figures.

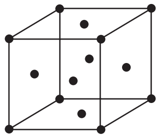
***Answer*:** On the basis of lengths and directions of the axes of symmetry, crystals may be classified into the following systems.

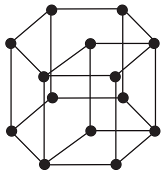
Table Q 2.2.1 *The seven crystal systems*

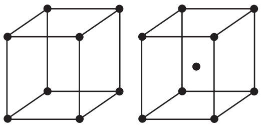
S. No	*Name of the crystal system*	*Relation of length of axes of unit cell*	*Relation of angle between axes*	*Examples*
1	Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Cu, NaCl, CaF_2
2	Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	SnO_2, $NiSO_4$
3	Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	KNO_3, $BaSO_4$
4	Monoclinic	$a = b \neq c$	$\alpha = \beta = 90° \neq \gamma$	Na_2SO_4, $FeSO_4$
5	Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq 90° \neq \gamma$	$CuSO_4$, K_2Cr_2O
6	Trigonal (Rhombohedral)	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	$CaSO_4$, As
7	Hexagonal	$a = b \neq c$	$\alpha = \beta = 90°$ and $\gamma = 120°$	Zn, Cd, SiO_2

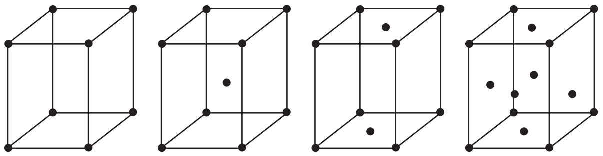

s c

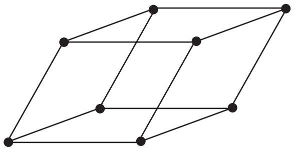

b c c

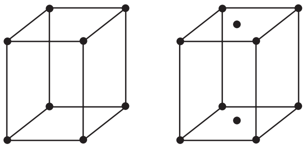

f c c

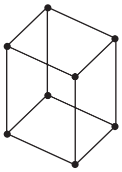

hexagonal


tetragonal


Orthorhombic


Rhombohedral


monoclinic


triclinic

Bravais in 1848 theoretically proved that there are precisely 14 possible ways of arrangement of points in a regular three dimensional pattern. Therefore, 14 types of space lattices possible. These are called *Bravais lattices* after the name of their discoverer. Since the atoms in a crystal are also arranged in a regular and definite pattern as in a space lattice, therefore, there can be only 14 possible types of crystals. Any other type of crystal (or arrangement of atoms) except these 14 is just theoretically impossible.

Table Q 2.2.2 *Fourteen Bravais lattices in three dimensions and conventional unit cells*

S. No.	*System*	*Number of lattices in the system*	*Space lattices or Bravais lattices*	*Lattice symbol*	*Nature of unit cell [Axial length and interaxial angles]*
1	Cube	3	Simple Body centred Face centred	P I F	a = b = c $\alpha = \beta = \gamma = 90°$
2	Tetragonal	2	Simple Body centred	P I	a = b ≠ c $\alpha = \beta = \gamma = 90°$
3	Orthogonal	4	Simple Base centred Body centred Face centred	P C I F	a ≠ b ≠ c $\alpha = \beta = \gamma = 90°$
4	Monoclinic	2	Simple Base centred	P C	a ≠ b ≠ c $\alpha = \beta = 90° \neq \gamma$
5	Triclinic	1	Simple	P	a ≠ b ≠ c $\alpha \neq \beta \neq \gamma \neq 90°$
6	Trigonal	1	Simple	P	a = b = c $\alpha = \beta = \gamma \neq 90°$
7	Hexagonal	1	Simple	P	a = b ≠ c $\alpha = \beta = 90°$ and $\gamma = 120°$

Q 2.3 Explain the following symmetry elements with suitable diagrams for a cubic crystal.

(i) Centre of symmetry (ii) Plane of symmetry (iii) Axis of symmetry

Answer*:** (i) ***Centre of symmetry

This is a point in the cubic crystal such that any line passing through it meets the surfaces of the crystal at equal distances in both directions is known as *centre of symmetry* or *centre of inversion.* Fig. Q 2.3.1(*a*).

(ii) ***Plane of symmetry***

A crystal is said to possess *reflection symmetry* about a plane if it is left unchanged in every respect after being reflected by the plane. Highly regular crystals may be bilaterally symmetrical about several planes cutting them in different directions. They may have several planes of symmetry. However a plane of symmetry is different from a plane of geometrical symmetry in that a plane of symmetry cuts the crystal into two halves such that one is the mirror image of the other (i.e., one is identical to the other in all respects). A cube has three straight planes of symmetry and six diagonal planes of symmetry. Ref. Fig. Q 2.3.1(*a*), Q 2.3.1(*b*) and Q 2.3.1(*c*).

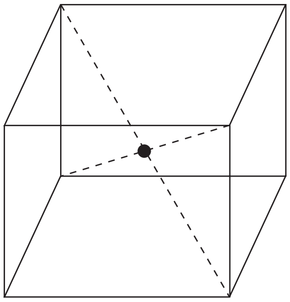


Fig. Q 2.3.1 (a)

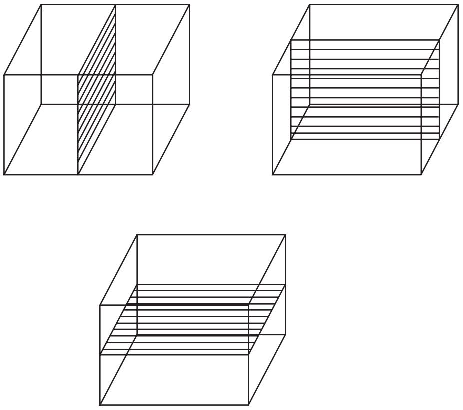


Fig. Q 2.3.1 (b)

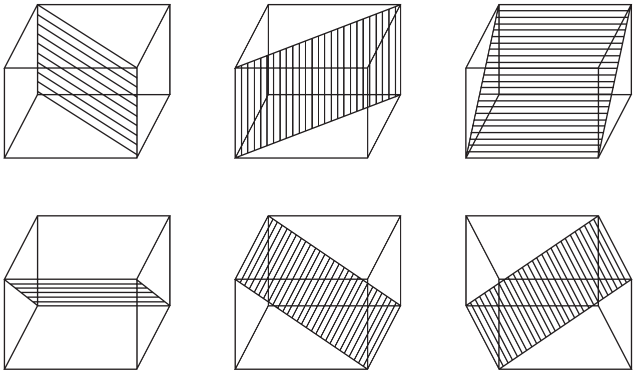


Fig. Q 2.3.1 (c)

(iii) ***Axis of symmetry***

The third kind of symmetry element is the axis of symmetry. Let a cube be rotated anti-clock wise about a line passing through the top face centre, centre of symmetry and bottom face centre. For every rotation of 90^o, the cube comes to a new position indistinguishable from the previous position. This means that rotation of a cube about this perpendicular axis through 90^o brings it into self-coincidence or *congruent position*. The line is then called the *axis of symmetry*. See Fig. Q 2.3.2.

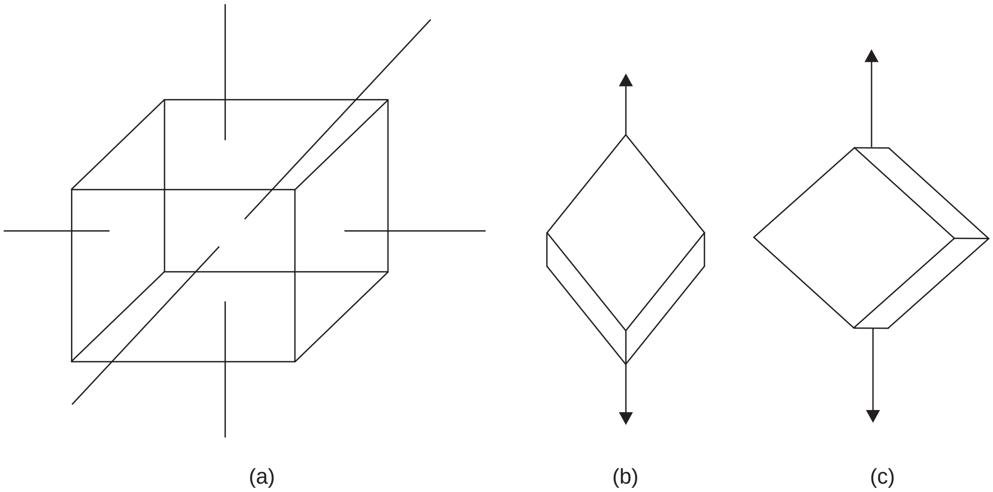


Fig. Q 2.3.2 *Axis of symmetry (a) The three tetrad axes (b) One of the triad axes (c) One of the diad axes*

In general *axis of symmetry* is defined as a line such that the crystal comes to *congruent position* for every rotation of $\left[\frac{360}{n}\right]^\circ$. The value of n decides the degree or *fold of the axis*. A cube possesses 3 tetrad axis, 4 triad axis and 6 diad axis. The total number of crystallographic symmetry elements of the cubic system are:

– centre of symmetry	1	1 point of symmetry
– straight planes	3	9 planes of symmetry
– diagonal planes	6	
– tetrad axes	3	
– triad axes	4	
– diad axes	6	13 axes of symmetry
Total	23	symmetry elements

Q 2.4 Write a small note on the combinations of symmetry elements. Also show that 5 fold or any axis of symmetry for $n > 6$ is not permissible in a single crystal.

***Answer*:** The different symmetry elements discussed above can be combined if they are *compatible*. The different combinations give rise to different symmetry points in the crystal. It must be noted that all the crystals do not possess all the symmetries enumerated above. The different crystal systems exhibit different symmetries. It is found that there are 32 compatible combinations of the above three point group-symmetry elements, called simply *point groups.* Crystals belonging to different crystal systems can be classified on the basis of point groups.

1. ***Rotation-Inversion Axis***

   A crystal structure is said to possess a rotation-inversion axis if it is brought into *self-coincidence* by rotation followed by an *inversion* about a *lattice point* through which the rotation axis passes.

2. ***Translation Symmetry Elements***

   Glide plane and screw axis are the two symmetry elements discussed here.

   (i) *Glide plane*: When a mirror plane is combined with a simultaneous translation operation in a crystal, one gets a glide plane.

   (ii) *Screw axis*: Just as it is possible to combine a proper rotation with an inversion to produce a hybrid rotation inversion axis, it is possible to combine a proper rotation with a translation parallel to the rotation axis, i.e., the rotation axis coupled with a translation parallel to the rotation axis will give rise to new symmetry element called the *screw axis.*

   (iii) *Space groups*: In a crystal, point group symmetry operations can also be combined with translation symmetry elements, provided they are compatible. Such combinations are called (iv) *space groups*. There are 230 space groups exhibited by crystals. The study of symmetry elements of the different crystals enables one to classify the crystals and their properties based on different symmetries.

Five-fold Rotation Axis is not Compatible with a Lattice

Let us explain this with reference to Fig. Q 2.4.1. Let us rotate the vectors PX and QY through an angle $\phi_n = \left[\frac{360}{n}\right]^\circ$ in the clock-wise and anti clock-wise directions respectively. The tips of vectors P_1 and Q_1 in the two positions must be lattice points if the lattice were to possess *n*-fold rotation axis of symmetry. As per the definition, rotation operation must leave the lattice *invariant*. Clearly P_1Q_1 must be parallel to PQ and must be equal to an integral multiple of the translation *a*; $P_1Q_1 = ma$ where *m* is an integer.

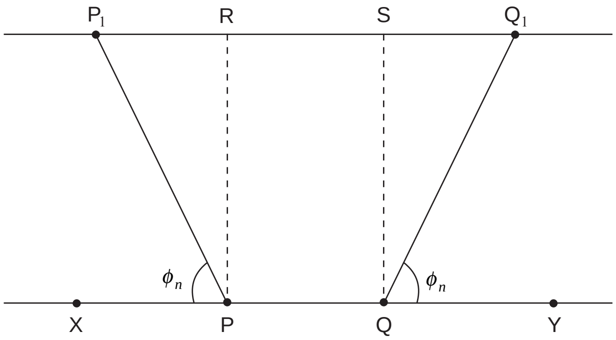


Fig. Q 2.4.1 *The possible rotation axes in a single crystal*

$$\cos\phi_n = \frac{P_1R}{PP_1}$$

$$P_1R = PP_1 \cos\phi_n = a\cos\phi_n$$

Similarly,

$$SQ_1 = a\cos\phi_n$$

Therefore,

$$P_1Q_1 = P_1R + SQ_1 + RS$$

$$P_1Q_1 = 2a\cos\phi_n + a = ma$$

Thus

$$1 + 2\cos\phi_n = m$$

$$2\cos\phi_n = (m-1) = N \text{ where } N \text{ is an integer}$$

$$\cos\phi_n = \left[\frac{m-1}{2}\right] = \frac{N}{2}$$

Table 2.4.1 *Absence of five-fold rotation axis*

N	$\frac{N}{2}$	$\cos\phi_n$	ϕ_n	*Possible fold of axis,* $n = \left[\frac{360}{\phi_n}\right]$
–2	–1	–1	180°	2
–1	–½	–½	120°	3
0	0	0	90°	4
+1	+½	+½	60°	6
+2	+1	+1	360°	1

Q 2.5 What you understand by packing fraction? Compute the packing factor for simple cubic structure and body-centred cubic structure explaining the various terms used with suitable diagrams.

***Answer*:** *Packing fraction* or *density of packing* is defined as the volume occupied by massive atoms in unit volume. Or, it is the ratio of volume occupied by atoms in a unit cell to the total volume of the unit cell. If v and V are the volume occupied by atoms in a unit cell and the volume of the unit cell respectively, then

$$P.F = \frac{v}{V}$$

The packing fraction tells us how closely the atoms are stacked or packed together in the unit cell and hence the name assigned. A high value of *P.F* tells that the atoms are very closely packed in the unit cell or crystal and there is little unoccupied space. A low value of *P.F* is the reverse of the above statement. The very interesting part of it is that the properties of many metals and materials depending on the way in which the atoms are arranged in the unit cell or in the crystal as a whole.

1. ***Simple cubic structure* (sc)**

In this space lattice, the lattice points are situated only at the corners of the unit cells constituting the three dimensional structure. Each cell has eight corners, and eight cells meet at each corner. Thus only one-eight of the lattice point belongs to each cell. That is, there is only one *lattice point* $\left(\frac{1}{8} \times 8\right)$ or one atom per unit cell. A unit cell containing only one lattice is called a *primitive cell*. Since the simple cubic lattice is built of *primitive cells*, it is also known as cubic *P* lattice. The number of nearest neighbours around an atom (or lattice point) is called *coordination number*. In this structure each atom is coordinating 6 atoms one in the front, another at the back and then one at the left and the other at the right. Finally one set of atoms at the top and the other at the bottom. All the atoms touch each other along the edges. Thus the *nearest neighbour distance*, $2r = a$; and the *coordination number* is defined as the number of nearest neighbours around any lattice point (or atom) in the *crystalline lattice*. Let us now compute the packing factor of this structure.

1. the nearest neighbour distance, $2r = a$
2. the lattice parameter, $a = 2r$
3. number of atoms in the unit cell, 1
4. volume of all the atoms in a cell, $v = 1 \times \frac{4}{3}\pi r^3$
5. volume of the unit cell, $V = a^3 = (2r)^3$
6. coordination number, CN = 6

Thus the packing fraction or density of packing of this structure is,

$$P.F = \frac{v}{V} = \left[\frac{4\pi r^3}{3}\right]\left(\frac{1}{a^3}\right) = \frac{4\pi r^3}{3 \times 8 \times r^3} = \frac{\pi}{6} = 0.52$$

$$\boxed{P.F = 0.52 \text{ or } 52\%} \qquad \text{(Q 2.5.1)}$$

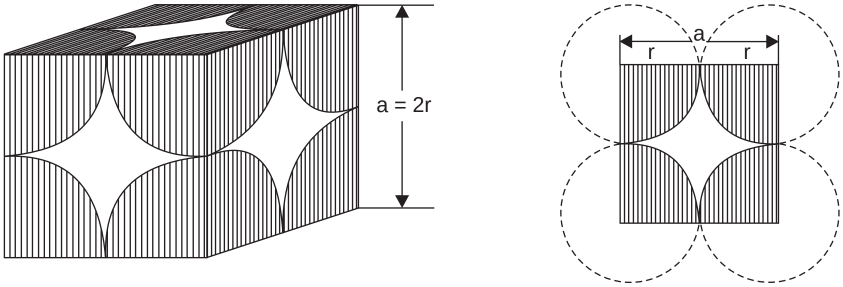


Fig. Q 2.5.1 *Simple cubic structure*

2. ***Body-centred cubic* (bcc) *lattice***

Here the lattice points (or atoms) are situated at each corner of the unit cell. Also one more atom is located at the body centre (centre of symmetry) where the three body diagonals intersect along which the atoms touch each other. Thus the total number of lattice points in a unit cell is $\left(\frac{1}{8} \times 8 + 1\right) = 2$ and $(4r)^2 = 3a^2$. The atom at the body centre is in contact with the 8 corner atoms. Hence the coordination number of bcc structure is 8.

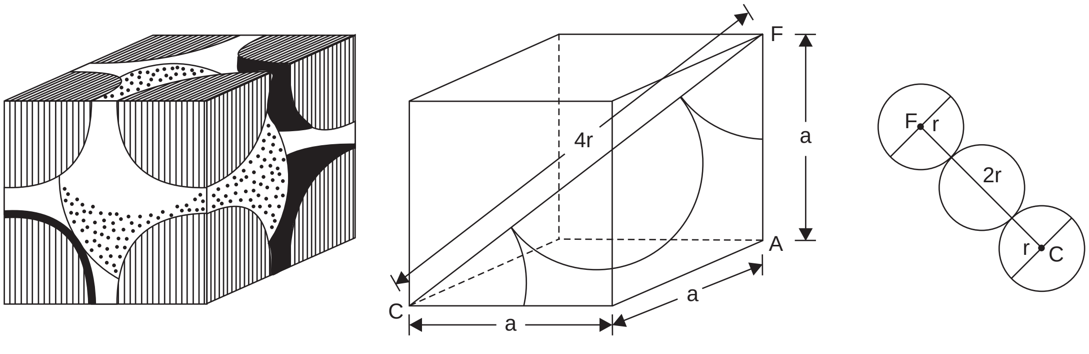


Fig. Q 2.5.2 *Body centred cubic*

The packing fraction of this lattice or structure is computed using the following data:

1. the nearest neighbour distance, $2r = \frac{a\sqrt{3}}{2}$
2. the lattice parameter, $a = \frac{4r}{\sqrt{3}}$
3. number of atoms in the unit cell, 2
4. volume of all the atoms in the unit cell, $v = 2 \times \frac{4}{3}\pi r^3$

5. volume of unit cell, $V = a^3 = \dfrac{64r^3}{3\sqrt{3}}$
6. coordination number, $CN = 8$

Thus packing fraction,

$$P.F = \frac{v}{V} = \frac{8 \times \pi r^3 \times 3\sqrt{3}}{3 \times 64r^3} = 0.68$$

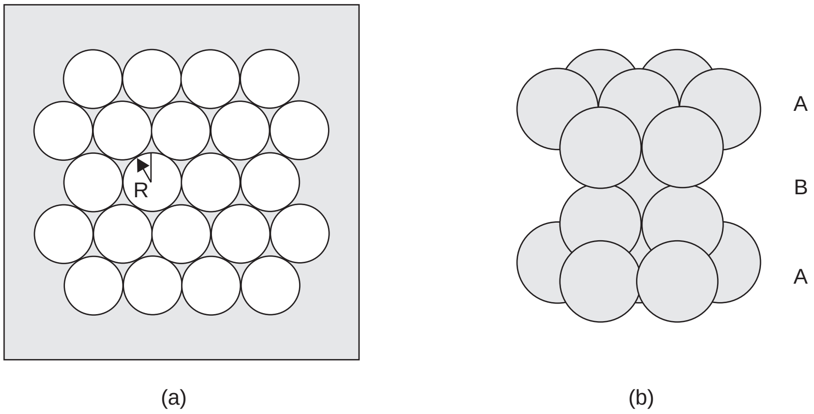
$$\boxed{P.F = 0.68 \text{ or } 68\%} \qquad \text{(Q 2.5.2)}$$

Sodium, iron, chromium and CsCl are some examples of bcc structure; sc and bcc structures are commonly known as loosely packed (respectively) structure and closely packed structure.

Q 2.6 Explain what is meant by closest packing in crystals? Describe face centred cubic lattice and hcp structure which are the two illustrations of closest packing structures.

Answer*:** 1. ***Closest packing

For crystals in which all the atoms are identical, there are two forms of closest packing: face centred cubic (fcc) space lattice and hexagonal close packed structure (hcp). It is a way of arranging equi-dimensional objects in space such that the available space is filled very efficiently. This is achieved only when each object is in contact with the maximum number of like objects as shown in Fig. Q 2.6.1.



(a) (b)

Fig. Q 2.6.1 *Closest packing of spheres in two-dimension and in three-dimension*

Let us now discuss the two well known closest structures, fcc and hcp.

2. ***Face centred cubic structure* (fcc)**

Here the lattice points (or atoms) are situated at all the eight corners as in the previous two cases, but also at the centres of the six faces. The face centre atom shares with two unit cells. Hence the number of atoms in a unit cell is $\left(\frac{1}{8} \times 8 + 3\right) = 4$. This lattice is also known as cubic F lattice. The atoms touch along the face diagonals. The packing fraction is now calculated.

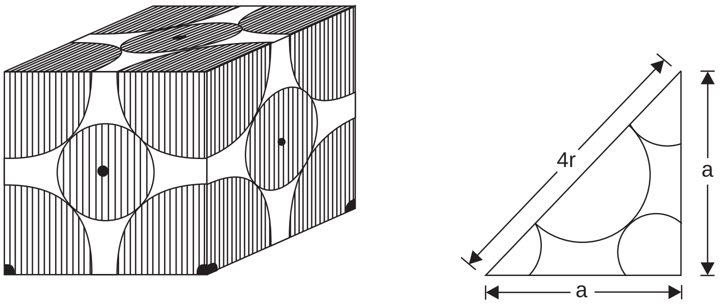


Fig. Q 2.6.2 *Face centred cubic structure*

1. the nearest neighbour distance, $2r$ $= \dfrac{a\sqrt{2}}{2}$
2. the lattice parameter, a $= \dfrac{4r}{\sqrt{2}}$
3. number of atoms in the unit cell, $= 4$
4. volume of all the atoms in the unit cell, v $= 4 \times \dfrac{4}{3}\pi r^3$
5. volume of unit cell, V $= a^3$
6. coordination number, CN $= 8$

Thus density of packing fraction,

$$P.F = \frac{v}{V} = \left[\frac{16\pi r^3}{3}\right]\left[\frac{2\sqrt{2}}{(4r)^3}\right] = \frac{32\pi\sqrt{2}}{3 \times 64} = 0.74$$

$$\boxed{P.F = 0.74 \text{ or } 74\%} \qquad \text{(Q 2.6.1)}$$

3. ***Hexagonal close packed structure*** **(hcp)**

Hexagonal close packed structure is a closest packing one and its packing fraction is almost as that of fcc space lattice. The unit cell contains one atom at each corner, one atom each at the centre of the hexagonal faces and three more atoms within the body of the cell. Each atom touches three atoms in the layer below its plane, six atoms in its own plane, and three atoms in the layer above.

Hence the coordination number of this structure is 12. Further the atoms touch each other along the edge of the hexagon.

Thus $2r = a$.

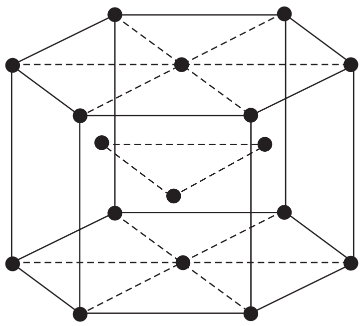


Fig. Q 2.6.3 *Ideal hexagonal close packed structure*

The top layer contains seven atoms. Each corner atom is shared by surrounding hexagon cells and the centre atom is shared by 2 surrounding cells. The three atoms within the body of the cell are fully contributing to the cell.

Thus the total number of atoms in a unit cell is $\frac{3}{2} + \frac{3}{2} + 3 = 6$

$\frac{c}{a}$ *ratio for an ideal hexagonal packed structure*:

Let c and a be respectively the height and edge of the unit cell. The 3 atoms at the bottom and top face in a horizontal plane at $\frac{c}{2}$ from the orthocentres of alternate equilateral triangles at the top or base of the hexagonal cell. These 3 atoms just rest on the three atoms at the corners of the triangles.

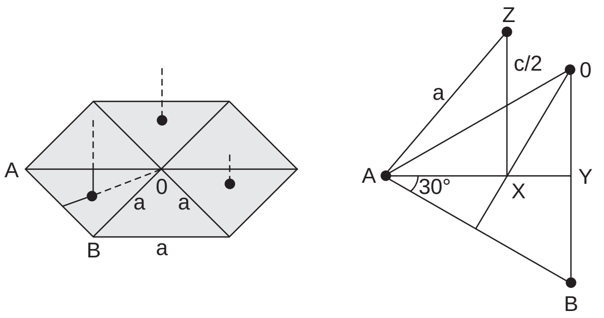


Fig. 2.6.3 (a) *Sketch of the bottom layer*

In the triangle ABY

$$\boxed{\left\{\begin{array}{l}\cos 30° = \dfrac{AY}{AB};\ AY = \dfrac{a\sqrt{3}}{2} \\ \text{and } (AZ)^2 = (AX)^2 + (ZX)^2\end{array}\right\}} \qquad \text{(Q 2.6.2)}$$

In the triangle AXZ,

$$AX = \frac{2}{3}AY = \frac{2a\sqrt{3}}{6} = \frac{a}{\sqrt{3}}$$

Substituting this value in Eqn. (Q 2.6.2), we get

$$a^2 = \frac{a^2}{3} + \frac{c^2}{4};\ \frac{c^2}{4} = a^2 - \frac{a^2}{3} = \frac{2}{3}a^2$$

or
$$\frac{c^2}{a^2} = \frac{8}{3};\ \frac{c}{a} = \sqrt{\frac{8}{3}}$$

i.e.,
$$\boxed{\left\{\frac{c}{a} = \sqrt{\frac{8}{3}}\right\}} \qquad \text{(Q 2.6.3)}$$

Volume of the unit cell

Area of the triangle, AOB = $\frac{1}{2}$ (BO) (AY)

$$= \frac{1}{2}a\left\{a\frac{\sqrt{3}}{2}\right\}$$

Hence area of the base, $\frac{6 \times a^2\sqrt{3}}{4} = \frac{3}{2}\sqrt{3}\left(a^2\right)$

Volume of the unit cell, $V = \frac{3}{2}\sqrt{3}\left(a^2 \times c\right)$

$$\boxed{\left\{V = \frac{3 \times \sqrt{3}a^2 c}{2}\right\}} \qquad \text{(Q 2.6.4)}$$

Packing fraction calculation

1. the nearest neighbour distance, $2r$ $= a$
2. the lattice parameter, a $= 2r$
3. number of atoms in the unit cell, $= 6$
4. volume of all the atoms in the unit cell, v $= 6 \times \frac{4}{3}\pi r^3 = \frac{24\pi r^3}{3} = \pi a^3$
5. volume of unit cell, V $= \frac{3\sqrt{3}a^2 c}{2}$
6. coordination number, CN $= 12$

7. $\dfrac{c}{a} \qquad = \sqrt{\dfrac{8}{3}}$

Thus density of packing fraction,

$$\text{P.F} = \frac{v}{V} = \frac{\pi a^3 \times 2}{3\sqrt{3}\, a^2 c} = \left[\frac{2\pi}{3\sqrt{3}}\right]\left[\frac{a}{c}\right] = \left[\frac{2\pi}{3\sqrt{3}}\right]\left[\frac{3}{8}\right]^{1/2}$$

Thus $$\text{P.F} = \boxed{\left\{\frac{\pi}{3\sqrt{2}} = 0.74 \text{ or } 74\%\right\}} \qquad \text{(Q 2.6.5)}$$

Q 2.7 Copper belongs to fcc space lattice. If M_A and ρ are respectively its atomic weight and density, find an equation connecting the lattice parameter and the said physical quantities. Also briefly discuss diamond cubic structure and the structure of sodium chloride crystal.

***Answer*:** Let N_A be the *Avogadro's number* and $n = 4$ is the number of atoms in a unit cell and a be the *lattice parameter*.

Now M_A/ρ is the *atomic volume* which will contain N_A copper atoms. Hence a^3 (volume of the unit cell) will contain $\dfrac{\rho a^3 N_A}{M_A}$ atoms. This must be equal to n (= 4 in this case).

i.e., $$\frac{a^3 \rho N_A}{M_A} = n$$

or $$a^3 = \frac{n M_A}{\rho N_A}$$

$$\boxed{a = \left[\frac{n M_A}{\rho N_A}\right]^{1/3}} \qquad \text{(Q 2.7.1)}$$

Diamond Cubic Structure

The space lattice of diamond is face-centred cubic (fcc) with a basis of two carbon atoms associated with each lattice point. The figures show the position of atoms in the cubic cell of the diamond structure projected on a cubic face. The fractions denote height above the base in units of a cube edge. The points at 0 and ½ are on the face lattice, those at ¼ and ¾ are on a similar lattice displaced along the body diagonal by one-fourth of its length. Thus the diamond lattice is composed of two interleaved fcc sublattices, one of which is shifted relative to the other by one-fourth of a body diagonal. In a diamond crystal the carbon atoms are linked by directional covalent bonds. Each carbon atom forms covalent bonds with four other carbon atoms that occupy four corners of a cube in a tetrahedral structure. The length of each bond is 0.154 nm and the angle between the bonds is 109.5°. Gray tin, silicon and germanium crystallize in the dc structure. In this structure each atom has four neighbours. The number of atoms per unit cell is 8.

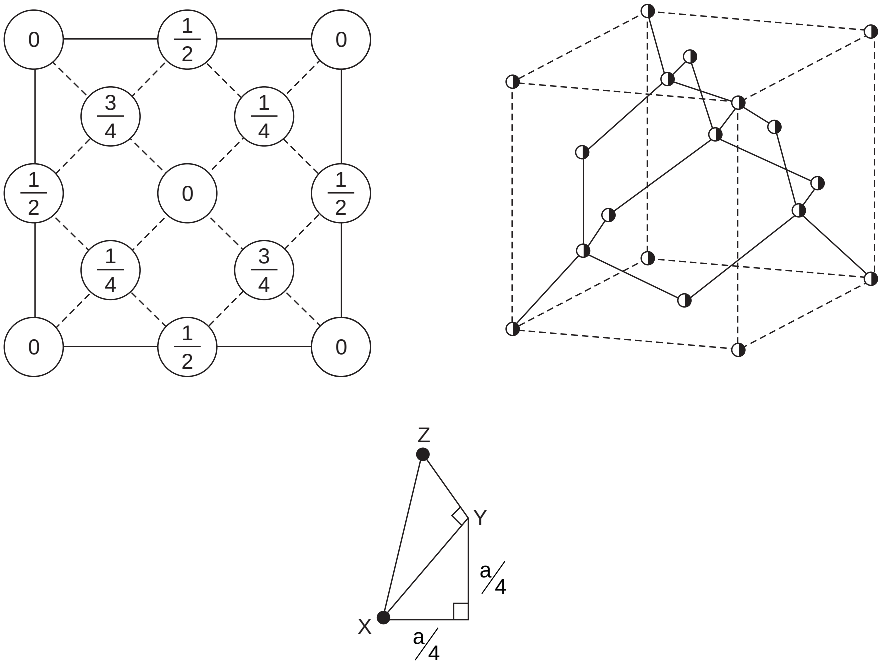


Fig. Q 2.7.1 *Diamond structure*

Computation of Packing Fraction

$$(XY)^2 = \frac{a^2}{16} + \frac{a^2}{16} = \frac{a^2}{8}$$

$$(XZ)^2 = (XY)^2 + (YZ)^2 = \frac{a^2}{16} + \frac{a^2}{8} = \frac{3a^2}{16}$$

i.e.,
$$(2r)^2 = \frac{3a^2}{16}; \text{ or } 2r = a\left[\frac{\sqrt{3}}{4}\right]$$

1. the nearest neighbour distance, $2r$ $= \dfrac{a\sqrt{3}}{4}$
2. the lattice parameter, a $= \dfrac{8r}{\sqrt{3}}$
3. number of atoms in the unit cell, $= 8$
4. volume of all the atoms in the unit cell, v $= 8 \times \dfrac{4}{3}\pi r^3$
5. volume of unit cell, V $= a^3$
6. coordination number, CN $= 4$

Thus the packing fraction is,

$$\text{P.F} = \frac{v}{V} = \frac{32\pi r^3 \times 3\sqrt{3}}{3 \times (8r)^3}$$

$$= \frac{32 \times \pi r^3 \times 3\sqrt{3}}{3 \times 8 \times r^3} = \frac{\pi\sqrt{3}}{2 \times 8} = 0.34$$

$$\boxed{\text{P.F} = 0.34 \text{ or } 34\%} \qquad \text{(Q 2.7.2)}$$

Sodium Chloride Structure

NaCl and KCl crystallize in this structure. Fig. Q 2.7.2 shows NaCl structure.

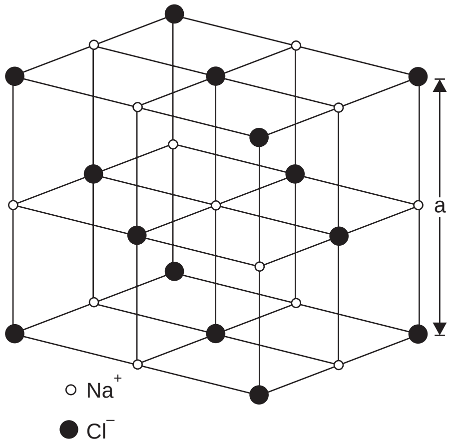


Fig. Q 2.7.2 *Sodium chloride structure*

Here the Na and Cl atoms (strictly ions) occupy alternately the corners of an elementary cube. Let d be the distance between adjacent atoms and hence $a = 2d$ is the lattice parameter or edge of the unit cell. Thus the number of ions in unit volume is $\frac{1}{d^3}$ and number of NaCl molecules in unit volume is $\frac{1}{2a^3}$; where d is interionic distance.

Q 2.8 What are Miller indices? How are they obtained? Sketch the (0 1 0), (1 1 0) and (1 1 1) planes in a cubic crystal.

***Answer*:** A crystal lattice may be considered as an aggregate of a set of parallel, equally spaced planes passing through the lattice points. The planes are called *lattice planes*, and the perpendicular distance between adjacent planes is called *interplanar spacing*. A given space lattice may have an infinite sets of lattice planes, each having its characteristic *interplanar spacing*. Out of these, only those, which have high density of lattice points are significant and show diffraction of x-rays. They are known as *Bragg planes* or *Cleavage planes*. When a crystal is struck, it breaks most easily across its cleavage planes. Hence it is essential to evolve a method to designate these planes in a crystal. Miller evolved a method to designate a set of parallel planes in a crystal by three numbers ($h\ k\ l$) known as *Miller indices*.

The steps in the determination of Miller indices of a set of parallel planes are illustrated with the aid of Fig. Q 2.8.1.

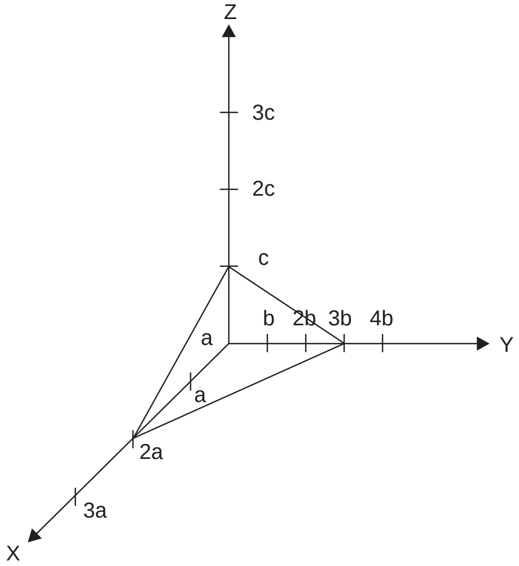


Fig. Q 2.8.1 *Miller indices of an important plane*

i. Determine the coordinates of the intercepts made by the plane along the three crystallographic axes (x, y, z).

x	y	z	
$2a$	$3b$	c	
pa	qb	rc	($p = 2$, $q = 3$, $r = 1$)

ii. Express the intercepts as multiples of the unit cell dimensions, or lattice parameters along the axes, i.e.,

$$\begin{array}{ccc} \dfrac{2a}{a} & \dfrac{3b}{b} & \dfrac{c}{c} \\ 2 & 3 & 1 \end{array}$$

iii. Get the reciprocals of these numbers.

$$\begin{array}{ccc} \dfrac{1}{2} & \dfrac{1}{3} & \dfrac{1}{1} \end{array}$$

iv. Reduce these reciprocals to the smallest set of integral numbers and enclose them in brackets:

$$\begin{array}{ccc} 6 \times \dfrac{1}{2} & 6 \times \dfrac{1}{3} & 6 \times \dfrac{1}{1} \\ 3 & 2 & 6 \end{array}$$

$$(3\ 2\ 6)$$

Thus *Miller indices* may be defined as the reciprocals of the intercepts made by the plane on the crystallographic axes when reduced to smallest numbers.

Conclusions

i. All the parallel equidistant planes have the same *Miller indices*. Thus the *Miller indices* define a set of parallel planes.
ii. A plane parallel to one of the coordinate axes has been intercept of infinity.
iii. If the *Miller indices* of two planes have the same ratio; i.e., (8 4 4) and (4 2 2) or (2 1 1), then the planes are parallel to each other.
iv. If (h k l) are the Miller indices of a plane, then the plane cuts the axes into h, k and l equal segments respectively.

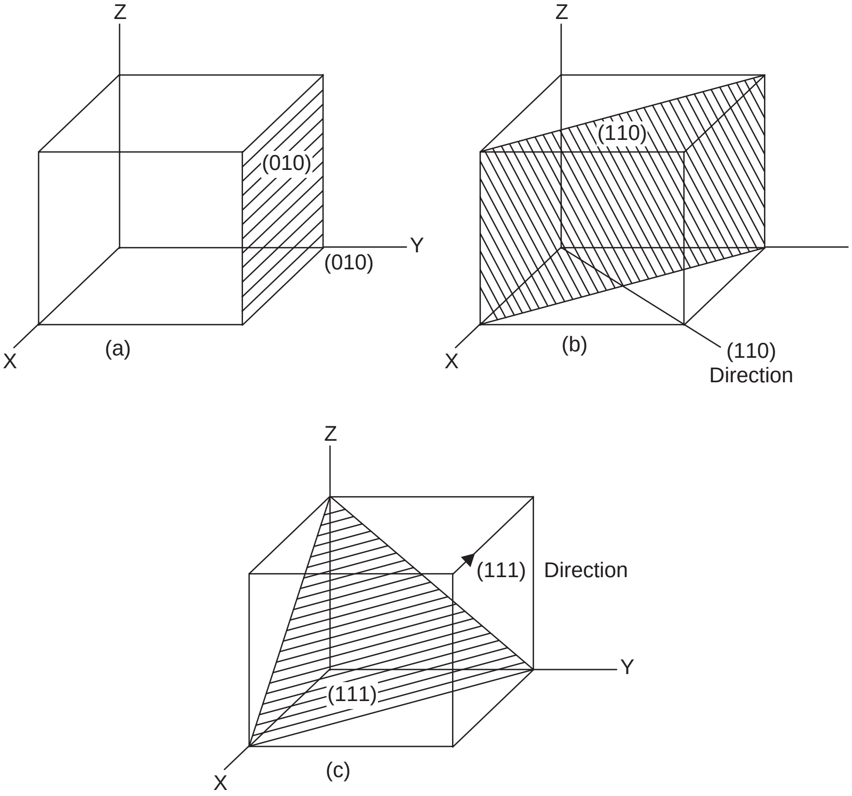


Fig. Q 2.8.2 *Sketch of important planes in a cube*

Q 2.9 Show that in a cubic crystal the spacing between consecutive parallel planes of Miller indices (h k l) is given by:

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

***Answer*:** (*h k l*) represents the *Miller indices* of the plane A B C. This plane belongs to a family of planes whose Miller indices are (*h k l*) because Miller indices represent a set of planes. See Fig. Q 2.9.1.

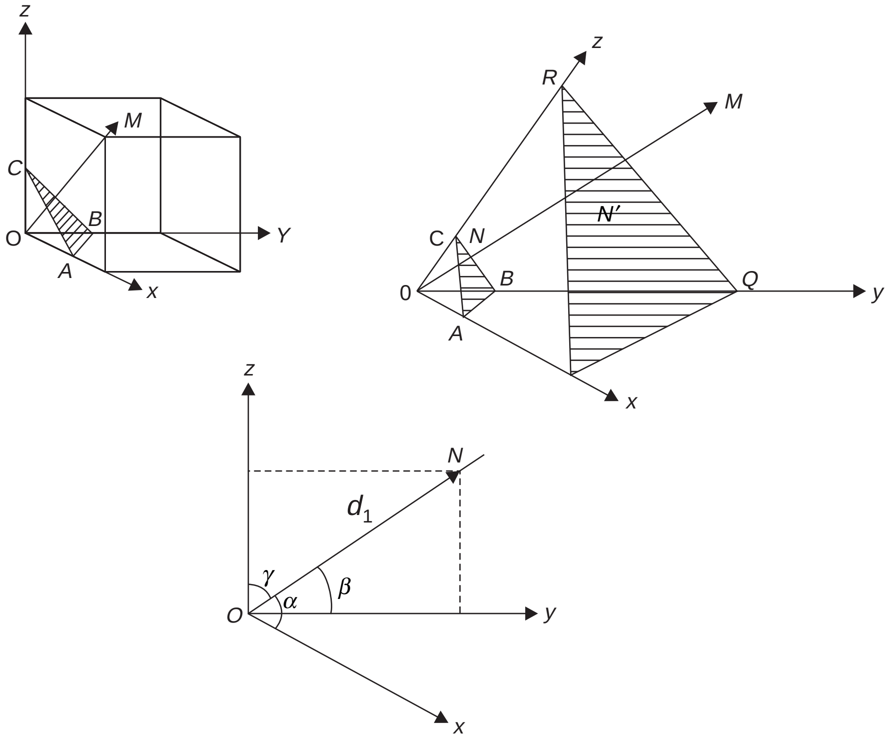


Fig. Q 2.9.1 *Interplanar Spacing*

Let α', β' and γ' (different from the interfacial angles α, β and γ) be the angles between coordinates axes X Y Z respectively and ON.

$$OA = \frac{a}{h}, OB = \frac{a}{k} \text{ and } OC = \frac{a}{l}$$

From Fig. Q 2.9.1 (*a*),

$$\boxed{\cos\alpha' = \frac{d_1}{OA}, \cos\beta' = \frac{d_1}{OB} \text{ and } \cos\gamma' = \frac{d_1}{OC}} \qquad \text{(Q 2.9.1)}$$

From Fig. Q 2.9.1(b),

$$(ON)^2 = x^2 + y^2 + z^2 \text{ with } ON = d_1$$

i.e.,

$$d_1^2 = \left\{d_1^2\left(\cos^2\alpha'\right) + d_1^2\left(\cos^2\beta'\right) + d_1^2\left(\cos^2\gamma'\right)\right\}$$

or

$$d_1 = d_1\left[\cos^2\alpha' + \cos^2\beta' + \cos^2\gamma'\right]^{1/2}$$

In the cartesian system of coordinates the sum of the squares of the direction cosines is equal to 1. So

$$\boxed{\cos^2\alpha' + \cos^2\beta' + \cos^2\gamma' = 1} \qquad \text{(Q 2.9.2)}$$

Substituting this in equation (Q 2.9.1), we get

$$\left[\frac{d_1}{OA}\right]^2 + \left[\frac{d_1}{OB}\right]^2 + \left[\frac{d_1}{OC}\right]^2 = 1$$

i.e.,

$$\left[\frac{d_1 h}{a}\right]^2 + \left[\frac{d_1 k}{b}\right]^2 + \left[\frac{d_1 l}{c}\right]^2 = 1$$

$$\frac{d_1^2}{a^2}\left(h^2 + k^2 + l^2\right) = 1 \text{ for cubic system}$$

$$d_1^2 = \frac{a^2}{h^2 + k^2 + l^2}$$

$$\boxed{d_1 = \frac{a}{\sqrt{h^2 + k^2 + l^2}}} \qquad \text{(Q 2.9.3)}$$

Let $OM = d_2$ be the perpendicular of the next plane P Q R parallel to the plane A B C. The intercepts of this plane on the three crystallographic axes are:

$$OA' = \frac{2a}{h},\ OB' = \frac{2a}{k} \text{ and } OC' = \frac{2a}{l}$$

and

$$\boxed{\cos\alpha' = \frac{d_2}{OA'},\ \cos\beta' = \frac{d_2}{OB'} \text{ and } \cos\gamma' = \frac{d_2}{OC'}} \qquad \text{(Q 2.9.4)}$$

$$(OM)^2 = d_2^2\cos^2\alpha' + d_2^2\cos^2\beta' + d_2^2\cos^2\gamma' \text{ with } OH = d_2$$

i.e.,

$$\cos^2\alpha' + \cos^2\beta' + \cos^2\gamma' = 1$$

Substituting this in equation (Q 2.9.4), and simplifying one gets

$$\left[\frac{d_2 h}{2a}\right]^2 + \left[\frac{d_2 k}{2b}\right]^2 + \left[\frac{d_2 l}{2c}\right]^2 = 1$$

$$\frac{d_2^2}{4a^2}\left(h^2 + k^2 + l^2\right) = 1$$

i.e.,

$$\boxed{d_2 = \frac{2a}{\sqrt{h^2 + k^2 + l^2}}} \qquad \text{(Q 2.9.5)}$$

Thus the interplanar spacing between two adjacent parallel planes of Miller indices (*h k l*) in a cubic lattice is given by:

$$\boxed{d = d_2 - d_1 = \frac{a}{\sqrt{h^2 + k^2 + l^2}}} \qquad \text{(Q 2.9.6)}$$

Q 2.10 Explain how crystal lattice is conveniently represented by *reciprocal lattice*

***Answer*:** The crystal lattice is conveniently represented by what is known as *reciprocal lattice.* The concept of reciprocal lattice is useful in the study of *x-ray diffraction* and *electron diffraction* produced by a crystal. The reciprocal lattice of a real crystal is constructed as follows:

1. choose a point as origin.
2. draw normals to every set of planes from this origin.
3. make the length of the normal equal to the reciprocal of the inter planer spacing of that set of planes.
4. place a point at the end of the normal.

Have a look at Fig. Q 2.10.1. Consider a plane represented by the line (3 2). It is clear that $\frac{OB}{OA} = \frac{OC}{AC}$ (by similarity of triangles).

$$\boxed{\frac{d}{b/h} = \frac{a/k}{\sqrt{\left(a^2/k^2 + b^2/h^2\right)}}} \qquad \text{(Q 2.10.1)}$$

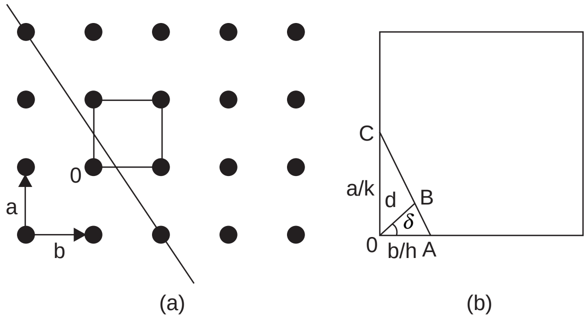


Fig. Q 2.10.1 *(a) A square lattice showing the unit cell and a (h, k) plane; (b) the imagined unit cell*

If $\sigma = \dfrac{1}{d}$, this will give,

$$\boxed{\sigma = \frac{\sqrt{h^2a^2 + k^2b^2}}{ab}} \tag{Q 2.10.2}$$

The direction of σ is

$$\boxed{\tan\delta = \frac{b/h}{a/k}} \tag{Q 2.10.3}$$

The point representing the (3 2) plane in the reciprocal lattice is shown in Fig. Q 2.10.2. The planes of a *square lattice* are represented by a *square reciprocal lattice* and so on. It can be shown that the diffraction of x-rays or of an electron beam by a real crystal lattice will give an array of points identical with its *reciprocal lattice*.

The Ewald Construction

Let us take a *two dimensional square reciprocal lattice* (Fig. Q 2.10.3). Let an x-ray beam of wavelength λ strike the surface. The radiation represented by a wave vector k whose length is $1/\lambda$ and its direction is the direction of the beam. Take a point O in the reciprocal lattice as the origin. Let one end of the wave vector be at O and draw circle of radius $1/\lambda$ with the centre at the other end A of the vector.

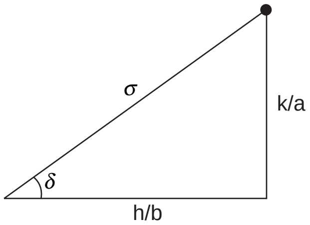


Fig. Q 2.10.2 *The reciprocal lattice point*

Let the circle pass through another point B in the reciprocal lattice. Construct a triangle AOB. Since OB joins origin O to a reciprocal lattice point, it is perpendicular to a set of planes in the real lattice whose interplanar distance $d = \frac{1}{OB}$. Since AC is perpendicular to OB, it is a lattice plane. The angle θ is the angle of incidence of the beam on the lattice plane since it is the angle between AC that is a lattice plane and AO (directions of the beam).

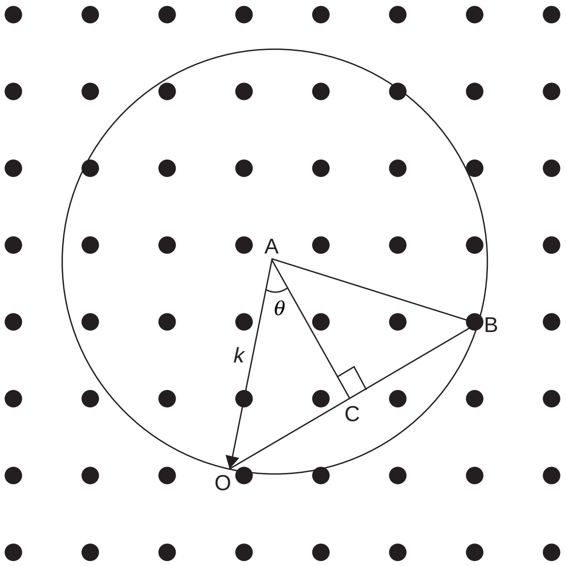


Fig. Q 2.10.3 *The reciprocal lattice point*

For the triangle AOC

$$\sin\theta = \frac{OC}{k} = \frac{OB}{2k}; \text{ but } k = \frac{1}{\lambda} \text{ and } OB = \frac{1}{d}$$

Hence

$$\boxed{\sin\theta = \frac{\lambda}{2d}; \text{ i.e., } 2d\sin\theta = \lambda} \qquad \text{(Q 2.10.4)}$$

This is same as the *Bragg's condition of reflection.* So, the reciprocal lattice is the diffraction pattern of the real lattice. This understanding makes it possible to construct the real lattice based on its diffraction pattern.

Q 2.11 Write a note an crystal defects.

***Answer*:** One hundred percent of ideal crystals do not—cannot exist.

1. ***Thermal vibrations***

The temperature of a solid is a measure of the amplitude of the random vibration of its atoms and these vibrations cause the displacement of the atoms from their ideal positions. This displacement is an important cause of electrical resistance in metals: without it pure metals would have very much less resistance than they do have. At room temperature, for example, copper has about a hundred times the resistivity it has at liquid helium temperature (4.2 K), where thermal vibrations have almost ceased. Other crystal defects may be classified by their dimensionality.

2. ***Zero-dimensional (point) defects***

There are three kinds of point defects in crystalline solids

(i) Vacancies, the sites where atoms are missing

(ii) Substitutional impurities, which are foreign atoms that replace host atoms.

(iii) Interstitial atoms, or interstitialcies, are atoms located in the holes between atoms of the host lattice. They may be foreign atoms or host atoms that have become misplaced.

(a) ***Vacancies***: When a crystal forms, usually at high temperatures, many vacancies are present. As the crystal cools, the equilibrium number of vacancies falls too, by diffusion process. Eventually the rate of diffusion becomes so slow that the vacancies are frozen into the structure. Thus at room temperature, the vacancies in a solid are at equilibrium, but are in concentrations characteristic of some higher temperatures. Vacancies are important because they are responsible for diffusion and void reduction in solids. They play a minor role in the electrical resistivity of pure metals.

Suppose the energy required to form a vacancy is E_v. Then the equilibrium number of vacancies, n, at an absolute temperature, T, is given by the Bolizmann distribution

$$\boxed{n = N \exp\left(-E_v/k_B T\right)} \qquad \text{(Q 2.11.5)}$$

where N is a constant and k_B is Boltzmann's constant. A plot of $ln(n)$ against $1/T$ will give a straight line of slope $(-E_v/k_B)$, sometimes known as *Arrhenius plot*. Now n can be measured by indirect means fairly simply: For example, by measuring the thermal expansion $(\delta l/l)$ of a sample as the temperature rises and comparing it with the change in lattice parameter found by x-rays $(\delta a/a)$. The x-rays do not take any notice of the odd vacant site, so the change in volume that they record is smaller than the actual change in volume. Alternately, the sample can be quenched (cooled rapidly) from high temperature to freeze in the vacancies, and the density at room temperature of the quenched sample can be compared to that of the slowly cooled sample. For aluminium,

$$\frac{E_v}{k_B} = 9700; \; E_v = 9700 \times 1.38 \times 10^{-23} \text{ J}$$

or $E_v = 0.84$ eV for convenience, energies in atoms are given in eV.

(b) ***Substitutional and interstitial atoms***

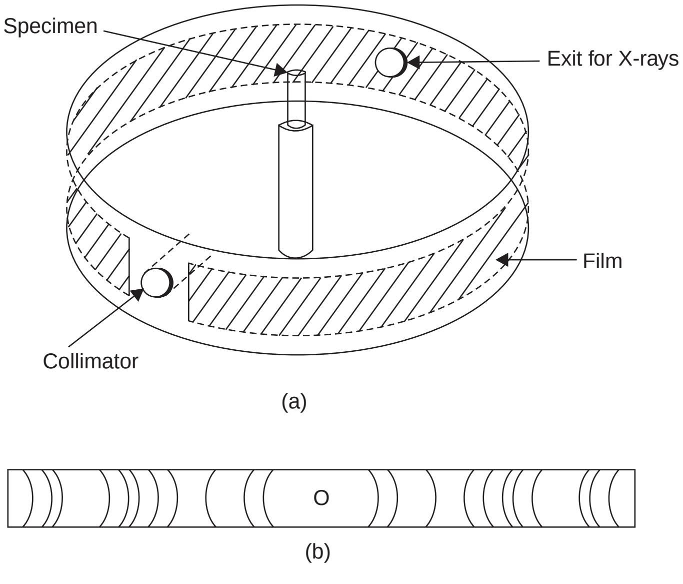
When an impurity atom is dissolved in a solid it can take up a normal lattice by displacing a host atom, or it can squeeze into the spaces between host atoms: which it does depend largely on the relative sizes of host and impurity atoms. In the case of ionic solids the position is complicated by the requirement for charge neutrality. If $CaCl_2$ is dissolved in KCl, for example, the Ca^{2+} ions replace the K^+ ions, but because there must be charge neutrality in the solid, a vacant K^+ site must be formed at the same time. In Cu_2O, there is small fraction of Cu^{2+} ions each requiring a Cu^+ ion vacancy to maintain charge neutrality. The extra positive charge on the cations is mobile and is responsible for *p*-type conductivity in the material: Cu_2O is termed a defect semiconductor.

Q 2.12 Describe powder method of crystal structure study using x-rays.

Answer**:** Bragg's method of crystal analysis can be carried out only if large crystals are available. Hence it is not always possible to adopt this method. Debye and Scherrer adopted a method by means of which analysis can be done using a small amount of powdered crystal. The particles of the powder contain a large number of micro crystals. If a monochromatic x-ray beam falls on a single crystal, then for a Bragg diffraction, it is necessary to provide a range of values of either θ or λ. The various experimental ways to provide such arrangements is the basis of the different x-ray diffraction methods. In the powder method and the rotation crystal method, θ is variable while the powdered crystal and a single crystal is placed in a beam of monochromatic x-rays respectively. In the Laue method, λ is variable as the x-rays of many wavelengths are being used of a single angle of incidence.

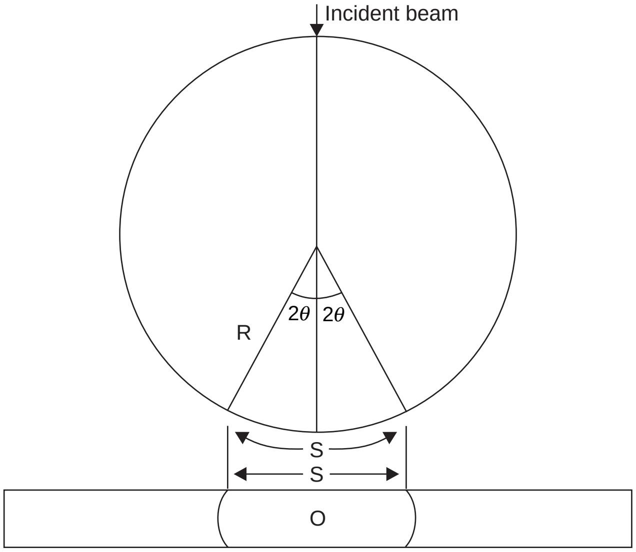
In the powder method, the monochromatic x-rays are falling on a finely powdered or a finally grained polycrystalline specimen as shown in Fig. Q 2.12.1(*a*).

If we consider the diffracted beam from a large number of crystallites which are randomly oriented, then any crystallite giving the reflection will produce a diffracted beam making an angle 2θ with the incident beam and, therefore, the locus of all such diffracted beams is a cone of semiangle 2θ with apex at the specimen. When the film is made flat, the powder diffraction pattern looks like as shown in Fig. Q 2.12.1(b), the cones making a series of concentric rings around the central spot. If *S* is the maximum diameter of a ring and if *R* is the radial distance from specimen to the film, then the Bragg angle θ in radian will be $\frac{S}{4R}$, as can be seen from Fig. Q 2.12.1(b). From the Bragg angle θ, the *interplaner distance d* can be determined with the use of *Bragg diffraction equation*. These distances are related to the *lattice parameters* and the *Miller indices* for any crystal. The observed interplaner spacings are compared with the spacings that would exist in unit cells of various dimensions and angles. In the less symmetrical crystal systems, this trial procedure is quite complicated. However, in highly symmetrical crystal system like cubic, the procedure is quite simple. Therefore, the structure of the simpler crystals can be completely determined by the powder method alone.



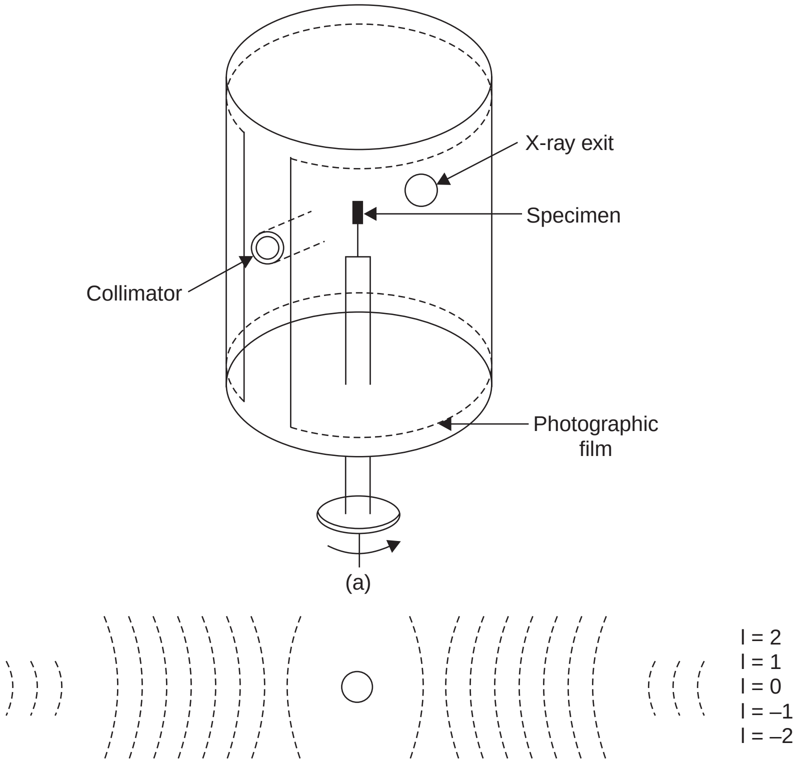
(a)

(b)



(c)

Fig. Q 2.12.1 *(a) X-ray powder diffraction arrangement (b) Typical powder diffraction pattern (c) Conversion of linear distance on the film into Bragg angle*



(b)

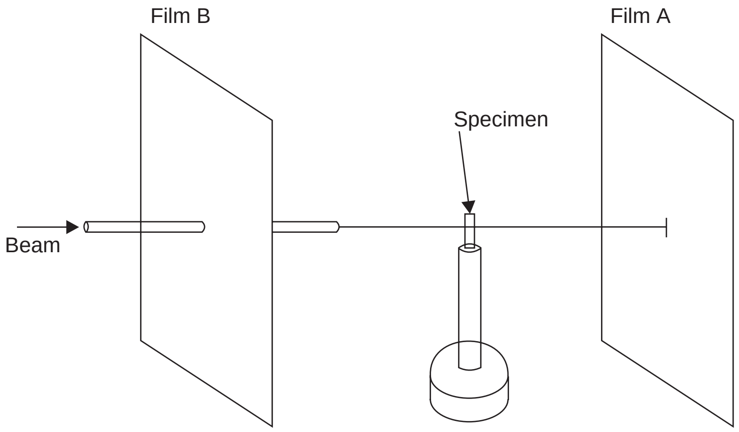
Fig. Q 2.12.2 *(a) X-ray rotating crystal camera (b) Typical rotating crystal diffraction pattern indicating various layer lines*

In order to overcome the difficulties faced in the powder method, the *rotating crystal method* is used whenever single crystals are available. In this method, the single crystal is rotated continuously about an axis that is perpendicular to the x-ray beam as shown in Fig. Q 2.12.2(*a*). The diffracted beams emerge out when the angle of incidence on a certain plane is according to Bragg equation for the monochromatic x-ray radiation. A cylindrical film from such method will give a pattern in Fig. Q 2.12.2(*b*). The characteristic feature of a rotation photograph is the occurrence of diffraction spots along a set of parallel straight lines, known as layer lines. The spots on the central layer line are reflections from planes whose normals are in a horizontal plane whereas the spots on any other layer line are from planes that have the same intercept on the axis of rotation. From the distance between these straight lines, one can find the dimension of the unit cell along the axis of the mounting of the crystal.

The separation of diffraction data into layer line in case of rotating crystal method is somewhat better than the powder diffraction pattern but still there is always some overlap of diffraction spots. Therefore, rotation photographs are rarely used for collection of intensity data. They are more often used for preliminary determination of unit cell dimensions and crystal system. In modern techniques, the photographic film is also replaced with a sensitive counter and a trace is taken of the count rate recorded while the crystal rotates slowly and the computer programmes are used to simplify the problem of crystal structure determination.

In *Laue method*, a narrow beam of non-monochromatic x-rays falls on a single crystal as shown in Fig. Q 2.12.3(*a*). There are two photographic films in this method, film A to record the diffraction pattern and film B to record the back-reflected pattern from the surface of the crystal specimen. On the photographic film A, one obtains a large number of diffraction spots as in Fig. Q 2.13.3(*b*). Laue pattern exhibits the symmetry of a crystal; when the x-ray beam is directed parallel to a six-fold axis of symmetry, the pattern will have the six-fold symmetry about the central point and a 60^o turn will bring coincidence of all the spots. Therefore, the *Laue pattern* has been widely used in determining symmetry axes if the non-monochromatic x-ray beam is incident along or very close to the symmetry axis.

The diffraction pattern on a photographic plate is a two-dimensional representation of the reflection from the three-dimensional crystal planes. Therefore, *stereographic* projection has to be used to determine the relation between *Laue spots* and the actual distribution of lattice points in real space. It will be interesting to mention at this stage that Laue spots correspond to points of a *reciprocal lattice*.



(a)

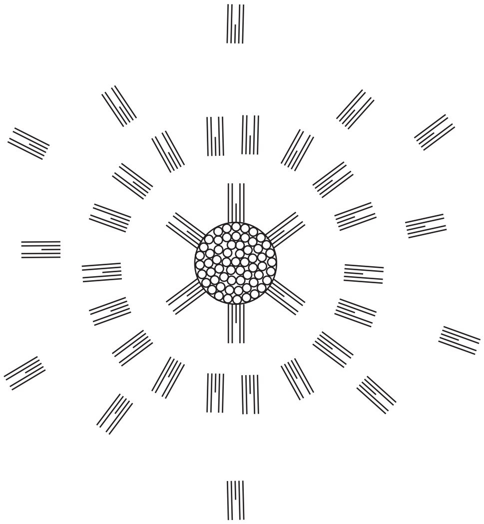

(b)

Fig. Q 2.12.3 *(a) Laue camera (b) Laue pattern*

Table 2. A *Comparison of cell properties of some crystal lattices*

S. No.	*Properties*	*Diamond cube (dc)*	*Simple cube (sc)*	*Body centred cube (bcc)*	*Face centred cube (fcc)*	*Hexagonal close packed structure (hcp)*
1	Volume of unit cell	a^3	a^3	a^3	a^3	$\frac{3}{2}\sqrt{3}\left(a^2 c\right)$
2	Number of atoms per cell	8	1	2	4	6
3	Number of atoms per unit volume	$\frac{8}{a^3}$	$\frac{1}{a^3}$	$\frac{2}{a^3}$	$\frac{4}{a^3}$	$\frac{4}{\sqrt{3}\left(a^2 c\right)}$
4	Number of nearest neighbours	4	6	8	12	12
5	Nearest neighbour distance (2 *r*)	$\frac{a\sqrt{3}}{4}$	a	$\frac{a\sqrt{3}}{2}$	$\frac{a\sqrt{2}}{2}$	a
6	Atomic radius	$\frac{a\sqrt{3}}{8}$	$\frac{a}{2}$	$\frac{a\sqrt{3}}{4}$	$\frac{a\sqrt{2}}{4}$	$\frac{a}{2}$

Contd.

S. No.	*Properties*	*Diamond cube (dc)*	*Simple cube (sc)*	*Body centred cube (bcc)*	*Face centred cube (fcc)*	*Hexagonal close packed structure (hcp)*
7	Atomic packing factor	$\frac{\pi\sqrt{3}}{16} = 0.34$	$\frac{\pi\sqrt{3}}{6} = 0.52$	$\frac{\pi\sqrt{3}}{8} = 0.68$	$\frac{\pi\sqrt{2}}{6} = 0.74$	$\frac{\pi\sqrt{2}}{6} = 0.74$
8	Examples	Germanium, Silicon and Diamond	Polonium	Sodium, Iron, Chromium	Aluminium Copper, Lead	Magnesium Zinc and Cadminum

Table 2. B *Crystal structure and selected properties of representative elements*

Element	*Symbol*	*Atomic weight*	*Density in 10^3 (kg/m^3)*	*Crystal structure*	*Lattice constant (20°C) (nm)*	*Approximate atomic radius*	*Melting point °C*
Aluminium	Al	26.97	2.7	fcc	0.4049	0.1428	660.2
Cadmium	Cd	112.41	8.65	hcp	$a = 0.2979$ $c = 0.5617$	0.1489	320.9
Carbon	C	12.01	2.22	dc	0.3564	0.0770	3700
Chromium	Cr	52.01	7.19	bcc	0.2885	0.1249	1890
Copper	Cu	63.54	8.96	fcc	0.3615	0.1278	1083
Germanium	Ge	72.59	5.36	dc	0.5658	0.1224	937
Iron (α)	Fe	55.85	7.87	bcc	0.2866	0.1238	1539
Lead	Pb	207.21	11.34	fcc	0.4949	0.1750	327
Magnesium	Mg	24.32	1.74	hcp	$a = 0.3209$ $c = 0.5210$	0.1594	650
Potassium	K	39.10	0.86	bcc	0.5339	0.2312	63.7
Silicon	Si	28.09	2.34	dc	0.5428	0.1176	1430
Silver	Ag	107.88	10.49	fcc	0.4086	0.1444	960.5
Sodium	Na	22.99	0.97	bcc	0.4281	0.1857	97.8
Zinc	Zn	65.38	7.13	hcp	$a = 0.2664$ $c = 0.4945$	0.1332	419.5

Table 2.C *Enthalpy of formation of vacancies in some crystals*

Crystal	E_v *(kJ/kmol) in* 10^3	E_v *in eV/vacancy*
Zn	49.0	0.51
Al	68.0	0.70
Mg	56.0	0.58
Kr	7.7	0.08
Cd	38.0	0.39
Pb	48.0	0.50
Ag	106.0	1.10
Cu	120.0	1.24
Ni	168.0	1.74

Table 2. D *Equilibrium vacancies in a metal*

Temperature °C	*Approximate fraction of vacant lattice sites*
500	1×10^{-10}
1000	1×10^{-5}
1500	1×10^{-4}
2000	1×10^{-3}

OBJECTIVE QUESTIONS

1. Which of the following has the least packing fraction
   (a) diamond cubic structure (b) face centred cubic structure
   (c) body centred cubic structure (d) simple cubic structure
2. The number of triad axes of symmetry elements in a cubic system
   (a) 2 (b) 3 (c) 6 (d) 4
3. The volume of the primitive unit cell of a fcc structure with lattice constant a is
   (a) $\frac{a^3}{8}$ (b) $\frac{a^3}{4}$ (c) a^3 (d) $\frac{a^3}{2}$
4. The nearest neighbour distance in the case of bcc structure is
   (a) $\frac{\sqrt{3}}{2}a$ (b) $2a$ (c) $\frac{2}{\sqrt{3}}a$ (d) $\sqrt{3}a$
   where a is the lattice parameter
5. The number of atoms present in the unit cell of hcp structure is
   (a) 2 (b) 4 (c) 6 (d) 7

6. The packing factor of diamond cubic structure is
   (a) 60% (b) 56% (c) 74% (d) none of these
7. Which of the following metals crystallizes in fcc structure?
   (a) zinc (b) sodium (c) aluminium (d) CsCl
8. The ideal *c*/*a* ratio for the hexagonal structure is
   (a) 1 (b) $\frac{\pi}{2}$ (c) $\frac{\sqrt{3}}{2}$ (d) $\sqrt{\frac{8}{3}}$
9. Magnesium crystallizes in hcp structure. If the lattice constant is 0.32 nm, the nearest neighbour distance in magnesium is
   (a) 0.32 nm (b) 0.16 nm (c) 0.64 nm (d) none of these
10. If n is the number of atoms in the unit cell of the cubic system, N_A and M_A are the Avogadro's number and atomic weight respectively and ρ is the density of the element, then the lattice constant a is given by
    (a) $\left[\frac{M_A\,\rho}{nN_A}\right]^{1/2}$ (b) $\left[\frac{nN_A}{M_A\rho}\right]^{1/3}$ (c) $\left[\frac{N_A\,M_A}{n}\right]^{1/4}$ (d) $\left[\frac{nM_A}{\rho\,N_A}\right]^{1/3}$
11. The number of ions in the unit cell of NaCl crystal is
    (a) 8 (b) 6 (c) 2 (d) 4
12. The Miller indices of the plane parallel to the x and y axes are
    (a) (0 1 0) (b) (0 0 1) (c) (1 1 1) (d) (1 0 0)
13. If (3 2 6) are the Miller indices of a plane, the intercepts made by the plane on the three crystallographic axes are
    (a) (2*a* 3b c) (b) (*a* b c) (c) (*a* 2b 3c) (d) none of these
14. In a simple cubic lattice $d_{100} : d_{110} : d_{111}$ is
    (a) 6 : 3 : 2 (b) $6 : 3 : \sqrt{2}$ (c) $\sqrt{6} : \sqrt{3} : \sqrt{2}$ (d) $\sqrt{6} : \sqrt{3} : \sqrt{4}$
15. A plane parallel to one of the co-ordinate axes has an intercept of infinity
    (a) yes (b) no
16. A plane intercepts at *a*, b/2, 3c in a simple cubic unit cell. The Miller indices of the plane are
    (a) (2 6 1) (b) (1 3 2) (c) (1 2 3) (d) (3 6 1)
17. If (*h k l*) are the Miller indices of a plane, then the plane cuts the axes into *h*, *k* and *l* equal segments
    (a) yes (b) no

PROBLEMS AND SOLUTIONS

2.1 Silicon crystallizes in the diamond cubic structure. The radius of silicon atom is 0.1176 nm. The atomic weight and density of silicon are 28.09 and 2.3 ×10^3 kg/m^3. Give me the number of atoms present in a unit cell.

***Solution*:**

$$2r = \frac{a\sqrt{3}}{4}$$

$$a = \frac{8r}{1.732} = \frac{8 \times 0.1176}{1.732}$$

$$a = 0.5432 \text{ nm}$$

$\frac{M_A}{\rho}$ will contain N_A silicon atoms

a^3 m will contain $\frac{\rho N_A a^3}{M_A} = n$

i.e.,

$$n = \frac{2.3 \times 10^3 \times 6.02 \times 10^{26} \times \left(0.5432 \times 10^{-9}\right)^3}{28.9}$$

$$= \frac{2.3 \times 6.02 \times 0.5432^3 \times 10^2}{28.9} = 8$$

$\boxed{n = 8}$ ***Answer***

2.2 Lead is a face centred cubic with an atomic radius of 0.1746 nm. Find the spacing (i) (2 0 0) planes and (ii) (2 2 0) planes

***Solution*:**

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

For fcc structure,

$$a = \frac{4r}{\sqrt{2}} = \frac{4 \times 0.1746}{1.414} = 0.493 \text{ nm}$$

For 2 0 0 plane

$$d_{200} = \frac{0.493}{4} = 0.2465 \text{ nm} \text{ and for the other plane}$$

$$d_{220} = \frac{0.493}{8} = 0.174 \text{ nm}$$

$$\boxed{\begin{aligned} d_{200} &= 0.2465 \text{ nm} \\ d_{220} &= 0.174 \text{ nm} \end{aligned}}$$ ***Answer***

2.3 The Bragg angle corresponding to the first order reflection from (1 1 1) plane in a crystal is 30° when x-rays of wave length 0.175 nm are used. Calculate the iteratomic spacing.

***Solution*:**

We know that

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

$$d_{111} = \frac{a}{\sqrt{3}}$$

and

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

$$2 \times \frac{a}{1.732} \sin 30 = 1 \times 0.175 \times 10^{-9}$$

$$\frac{2a}{2} = 1.732 \times 0.175 \times 10^{-9} = a$$

$$\boxed{a = 0.3031 \text{ nm}}$$ ***Answer***

2.4 A certain orthorhombic crystal has a ratio of a : b : c of 0.429 : 1 : 0.377. Find the Miller indices of the faces whose intercepts are:

0.214 : 1 : 0.183
0.858 : 1 : 0.754
0.429 : ∞ : 0.126

***Solution*:**

The intercepts in terms of the unit axial dimensions are as below:

$$\frac{0.214}{0.429} : \frac{1}{1} : \frac{0.188}{0.377}$$

$$\frac{0.858}{0.429} : \frac{1}{1} : \frac{0.754}{0.377}$$

$$\frac{0.429}{0.429} : \frac{\infty}{1} : \frac{0.126}{0.377}$$

$$\frac{1}{2} : 1 : \frac{1}{2}$$

$$2 : 1 : 2$$

$$1 : \infty : \frac{1}{3}$$

Taking the reciprocals of these numbers and reducing them to the smallest whole numbers, the Miller indices come out as follows:

$$\boxed{\begin{matrix}(2\ 1\ 2)\\(1\ 2\ 1)\\(1\ 0\ 3)\end{matrix}}\quad \textbf{\textit{Answer}}$$

2.5 Find the Miller indices of a set of parallel planes which makes intercepts in the ratio (3a : 4b) on the x-axis and y-axis and parallel to the z-axis; a, b, c being primitive vectors of the lattice.

***Solution*:**

$$pa : qb : rc = 3a : 4b : \infty\ c$$

$$p : q : r = 3 : 4 : \infty$$

$$\frac{1}{p} : \frac{1}{q} : \frac{1}{r} = \frac{1}{3} : \frac{1}{4} : \frac{1}{\infty} = 4 : 3 : 0$$

The Miller indices of the given set of planes are (4 3 0)

$$\boxed{(4\ 3\ 0)}\quad \textbf{\textit{Answer}}$$

2.6 Calculate the ratio of the number of vacancies in equilibrium at 300 K in aluminium to that produced by rapid quenching at 800 K. Enthalpy of formation of vacancies in aluminium is 68 kJ/mol.

***Solution*:**

The general expression for the number of vacancies is given by,

$n_1 = N \exp(-E_v/R_uT_1)$ and $n_2 = N \exp(-E_v/R_uT_2)$

$n_1 = N [\exp(-68 \times 10^3/8.314 \times 300)] = N \exp(-27.3)$

$n_2 = N [\exp(-68 \times 10^3/8.314 \times 800)] = N \exp(-10.2)$

$$\frac{n_1}{n_2} = \frac{\exp(-27.3)}{\exp(-10.2)} = 3.75 \times 10^{-8}$$

$$\boxed{\frac{n_1}{n_2} = 3.75 \times 10^{-8}}\quad \textbf{\textit{Answer}}$$

2.7 A diffraction pattern of a cubic crystal of lattice parameter $a = 0.316$ nm is obtained with a monochromatic x-ray beam of wavelength 0.154 nm. The first four lines on this pattern were observed to have the following values:

Line:	1	2	3	4
$\theta°$:	20.3	29.2	36.7	43.6

Determine the interplanar spacings and Miller indices of reflecting planes.

***Solution*:** $d = \dfrac{\lambda}{\sin\theta}$, or $\sin\theta = \dfrac{\lambda}{d}$

Line	θ	$\sin\theta$	*d (nm)*	$\frac{a^2}{d^2} = h^2 + k^2 + l^2$
1	20.3	0.3460	0.2240	2
2	29.2	0.4886	0.1570	4
3	36.7	0.5980	0.1290	6
4	43.0	0.6990	0.1150	8

For determination of *h*, *k*, *l* one has to resort to trial and error method

$$h^2 + k^2 + l^2 = 2 = 1^2 + 1^2 + 0;\ h\ k\ l = (1\,1\,0)$$

$$h^2 + k^2 + l^2 = 4 = 2^2 + 0 + 0;\ h\ k\ l = (2\ 0\ 0)$$

$$h^2 + k^2 + l^2 = 6 = 2^2 + 1^2\ + 1^2;\ h\ k\ l = (2\,1\,1)$$

$$h^2 + k^2 + l^2 = 8 = 2^2 + 2^2\ + 0;\ h\ k\ l = (2\ 2\ 0)$$

EXERCISE

2.1 Metallic iron changes from bcc to fcc form at 910°C. At this temperature, the atomic radii of the iron atom in the two structures are 0.1258 nm and 0.1292 nm respectively. Calculate the volume change in percentage during this structural change. Also calculate the percentage change in density.

(***Ans*****:** 0.493%, 0.4968%)

2.2 Compare the densities of lattice points in (1 1 1) and (1 1 0) planes in a simple cubic lattice.

(***Ans*****:** $\rho_{111} : \rho_{110} = \sqrt{2} : \sqrt{3}$)

2.3 Cadmium crystallizes in hcp structure. The radius of cadmium atom is 0.1489. What is the height of the unit cell? (***Ans*****:** 0.4862 nm).

2.4 X-ray powder photograph of a cubic material with a wavelength of 0.1542 nm is taken. In the photograph, lines are observed at angles 19.25°, 22.38°, 32.58°, 39.15°, 41.26°, 49.59°, 56.08° and 58.36°. Determine the lattice constant and the nature of the cubic material. (***Ans*****:** fcc, 0.405 nm)

2.5 The unit cell of aluminium is face centred with lattice constant, *a* = 0.405 nm (a) How many unit cells are there in an aluminium foil 0.005 cm thick and side 25 cm square? (b) It weighs 0.0085 kilogram. How many atoms are present? (c) How many atoms are in each unit cell?

(***Ans*****:** 4.7×10^{22}, 1.9×10^{23}, 4)

2.6 The fraction of vacancy sites in a metal is 1×10^{-10} at 500°C. What will be the fraction of vacancy sites at 1000°C? $\left(\textbf{\textit{Ans}}\text{:}\ \frac{n}{N} = 8.8452 \times 10^{-7}\right)$.

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3

Matter Waves and Wave Mechanics of Free Electrons

3.1 INTRODUCTION

Q 3.1 De Broglie's hypothesis
Q 3.2 Electron diffraction experiment
Q 3.3 Heisenberg's uncertainty principle
Q 3.4 Matter waves and Schrödinger wave equation.
Q 3.5 Schrödinger's time independent wave equation
Q 3.6 Particle in a one dimensional potential box
Q 3.7 Graphical representation of ψ_n , E_n and $|\psi_n|^2$
Q 3.8 Particle in a three dimensional potential box
Q 3.9 Degenerate and non-degenerate energy states

- Tables
- Objective questions
- Problems

KEY WORDS

Louis de Broglie, quatum theory, Compton, W. H. Bragg, Maurice, duality, whole numbers, de Broglie wavelength, electron gun, target, Bragg's planes, Heisenberg uncertainty principle, Born, wave packet, uncertainty relation, relativistic formula, radioactive nuclei, beta decay, protons and neutrons, Bohr's radius, duality, orbits, relativistic formula, Bohr radius, uncertainty principle, differential wave equation, complex variable and wave function, physical significance of the wave function, probability density, Schrödinger time-independent wave equation, electron in a one dimensional potential box, complex conjugate, electromagnetic wave, complex variable, plane simple harmonic wave, probability density, complex quantity, one-dimensional potential box, wave function and eign function, degenerate and non-degenerate energy states, three dimensional potential box and the results.

3.1 INTRODUCTION

The discovery of particle/wave duality stemmed from a suggestion made by a French nobleman, *Louis de Broglie*. It sounds so simple, yet it struck to the heart of the matter. "If light waves also behave like particles, "we can imagine de Broglie musing "why shouldn't electrons also behave like waves?" If he had stopped there, of course, he would not have been remembered as one of the founders of *quantum theory*, nor would he have been received a Nobel Prize in 1929. As an idle speculation the idea does not amount to much, and similar speculations had been aired about—x-rays long before *Compton's work*, at least as early as 1912, when the great physicist *W. H. Bragg* said of the state of x-ray physics at the time, "The problem becomes, it seems to me, not to decide between two theories of x-rays, but to find… one theory which possesses the capacity of both". De Broglie's great achievement was to take the idea of particle/wave duality and carry it through mathematically, describing how matter waves ought to behave and suggesting ways in which they might be observed. He had one great advantage as a relatively junior member of the theoretical physics community, an elder brother, *Maurice*, who was a respected experimental physicist who steered him towards the discovery. Louis de Broglie said later that Maurice stressed to him in conversations the "importance and undeniable reality of the dual aspects of particle and wave".

Q. 3.1 Discuss de Broglie's hypothesis of matter waves. If an electron is accelerated by V_p volt, get the equation connecting de Broglie's wave length and the accelerating potential.

***Answer*:** In his thesis, de Broglie started out from the two equations that Einstein had derived for light quanta,

$$\boxed{E = h\upsilon;\ \text{and}\ p = \frac{h\upsilon}{c}} \tag{Q 3.1.1}$$

In both the equations, properties that belong to particles (energy and momentum) appear on the left side and properties that belong to waves (say frequency) appear on the right side of the equations. De Broglie argued that the failure of experiments to settle once and for all whether light is wave or particle must therefore be because the two kinds of behavior are inextricably tangled-even to measure the particle property of momentum you have to know the wave property called frequency. Yet this *duality* did not apply only to photons. Electrons were thought at the time to be good, well-behaved particles, except for the curious way they occupied distinct energy levels inside atoms. But de Broglie realized that the fact that electrons only existed in "*orbits*" defined by *whole numbers* (integers) also looked in some ways like a wave property. The only phenomena involving integers in physics were those of interference and of normal modes of vibration. This fact suggested that electrons too could not be regarded simply as corpuscles, but that periodicity must be assigned to them. De Broglie called the waves associated with a particle as "*matter waves*". The momentum associated with photon is:

$$\boxed{p = \frac{E}{c} = \frac{h\upsilon}{c} = \frac{h}{\lambda}} \tag{Q 3.1.1a}$$

He showed that in an analogous manner the momentum p of a material particle and the wavelength λ of the associated matter waves are related by:

$$\boxed{p = \frac{h}{\lambda};\ \text{or}\ \lambda = \frac{h}{p}} \tag{Q 3.1.2}$$

If we assume that the velocity v of the matter waves is given by:

$$v = \upsilon \lambda$$

Substituting the value of υ and λ from Eqns. Q 3.1.1 and Q 3.1.2,

$$v = \frac{E}{h} = \frac{h}{p}$$

or

$$\boxed{v = \frac{E}{p}} \tag{Q 3.1.3}$$

According to the *special theory of relativity*, we have, for a particle of mass m moving with velocity V,

$$\boxed{E = mc^2,\ p = mV} \tag{Q 3.1.4}$$

Therefore, the velocity v of the associated matter waves is given by:

$$v = \frac{mc^2}{mV} = \frac{c^2}{V}$$

Since we have V not greater than or equal to c, we find that $v \geq c$. Thus the velocity of the matter waves is greater than the velocity of light in vacuum which concludes that the phase velocity of matter waves is not physically meaningful quantity. When an electron is accelerated by a p.d. of V_p volt, the kinetic energy acquired by it (whose rest mass m_0): $(1/2)\, m_0 V^2 = \mathrm{eV}_p$

$$V^2 = \frac{2\,\mathrm{eV}_p}{m_0};\ V = \sqrt{\frac{2\,\mathrm{eV}_p}{m_0}}$$

Thus the momentum is:

$$p = \sqrt{2m_0\,\mathrm{eV}_p}$$

Thus the *de Broglie wavelength* λ associated with the electron is given by:

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{m_0\,\mathrm{eV}_p}} = \frac{6.62 \times 10^{-34}}{\sqrt{9.1 \times 10^{-31} \times 1.6 \times 10^{-19} \times V_p}}$$

i.e.

$$\boxed{\lambda = \frac{1.227}{\sqrt{Vp}}\ \mathrm{nm}} \tag{Q 3.1.5}$$

If the electron is accelerated through very high potential difference, it is necessary to take into account of the relativistic increase in mass of the electron.

The equation to be used in such a case is:

$$\boxed{\frac{1.227}{\sqrt{V_p}}\left[1-\frac{eV}{4m_0c^2}\right]} \tag{Q 3.1.6}$$

Q 3.2 Describe the experiment of Davisson and Germer on electron diffraction. i.e., how de Broglie's hypothesis has been verified.

***Answer*:** The first experimental evidence of the wave nature of atomic particles was provided in 1927 by C.J. Davisson and L.H. Germar. They were studying scattering of electrons by a metal target and measuring the intensity of electrons scattered in different directions. The entire arrangement to produce a fine beam of electrons accelerated to a desired velocity is called *electron gun*. The fast moving beam of electrons is made to strike the target (say nickel crystal) capable of rotating about an axis perpendicular to the plane of the diagram. The electrons are now scattered in all directions by the atomic planes of the crystal. The intensity of the electron beam scattered in a direction can be measured by the *electron collector* which can be rotated about the same axis as the target. The collector is connected to a sensitive galvanometer whose deflection is proportional to the intensity of the electron beam entering the collector. The whole unit is kept in an evacuated chamber.

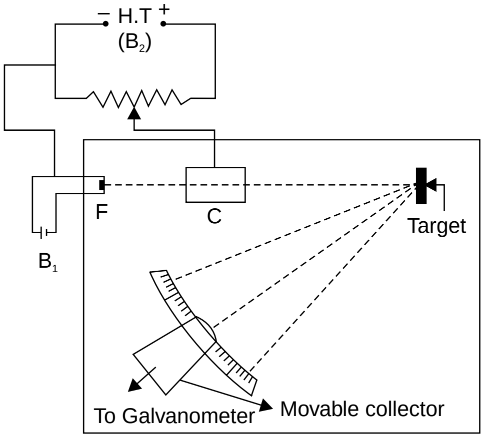

Fig. Q 3.2.1 *Davission-Germer electron diffraction apparatus*

In an investigation, the electron beam accelerated by 54 volt was directed to strike the given nickel crystal and a sharp maximum in the electron distribution occurred at an angle of 50° with the incident beam. The incident beam and the diffracted beam in this experiment make an angle of 65° with the family of *Bragg's planes*. The spacing of planes in this family as determined by x-ray diffraction was 0.091 nm.

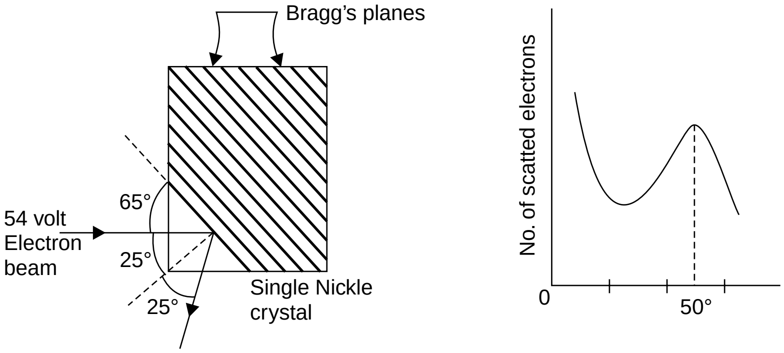

Fig. Q 3.2.2 *Electron diffraction*

Q 3.3 State Heisenberg's uncertainty principle. Discuss its significance and importance.

***Answer*:** In 1927, *Heisenberg* proposed a very useful principle, which is a direct consequence of the dual property of matter, known as *uncertainty principle*. In classical mechanics, a moving particle at any instant has a fixed position in space and a definite momentum which can be determined if the initial values are known. However, in wave mechanics the particle is described in terms of a *wavepacket*. According to *Born's* probability interpretation, the particle may be found any where within the wavepacket. When the *wavepacket* is small, the position of the particle may be fixed but the particle will spread rapidly and hence the velocity becomes indeterminate. On the other hand, when the wave packet is large, the velocity can be fixed but there is large indefiniteness in position. In this way certainty in position involves uncertainly in momentum or velocity and certainty of momentum involves the uncertainty in position. This shows that it is impossible to know where within the wavepacket the particle is and what is its exact momentum.

According to *Heisenberg uncertainty* principle, "it is impossible to specify precisely and simultaneously the values of both members which are particular pairs of physical variables that describe the behavior of an atomic system". Qualitatively this principle states that "the order of magnitude of the product of the uncertainties in the knowledge of two variables must be at least Planck's constant *h*". Considering the pair of physical variables as position and momentum, we have

$$(\Delta p)(\Delta x) \approx h$$

where Δp is uncertainties in determining the momentum and Δx is the uncertainty in determining the position of the particle. Similarly, we have:

$$(\Delta E)\,(\Delta t) \approx h \text{ and } (\Delta J)\,(\Delta \theta) \approx h$$

The exact statement of uncertainty principle is as follows: the product of uncertainties in determining the position and momentum of the particle can never be smaller than the order of $\frac{h}{4\pi}$. So we have:

$$(\Delta p)(\Delta x) \geq \frac{h}{4\pi};\ (\Delta\, E)\,(\Delta\, t) \geq \frac{h}{4\pi} \text{ and } (\Delta\, J)\,(\Delta \theta) \geq \frac{h}{4\pi}$$

Applications of Uncertainty Principle

1. *Presence of protons and neutrons and non-existence of electrons in nucleus*:

The approximate radius of the nucleus of any atom is $10^{-14} m$. If an electron is confined inside the nucleus, then the uncertainty in the position Δx of the electron is equal to the diameter of the nucleus. i.e., $\Delta x \approx 2 \times 10^{-14}$ m. Using the Heisenberg's uncertainty relation, the uncertainty in momentum of electron is given by:

$$\Delta p_x = \frac{h}{2\pi . \Delta x} \geq \frac{6.62 \times 10^{-34}}{2\pi \times 2 \times 10^{-14}}$$

i.e.,

$$\Delta p_x \geq 0.527 \times 10^{-20} \ N\,s$$

Since the mass of the electron is 9.1×10^{-31} kg, the order of magnitude of momentum (0.527×10^{-20} kg m s^{-1}) is relativistic. Using the *relativistic formula* for the energy E of the electron, we have:

$$E^2 = p^2 c^2 + m_0^2 c^4$$

As the rest energy $m_0 c^2$ of the electron is of the order of 0.511 MeV, which is much smaller than the value of first term, it can be neglected. Thus:

$$E^2 = p^2 c^2 ; E = pc$$

Now

$$E = (0.527 \times 10^{-20}) \times (3 \times 10^8) \text{ joule}$$

$$= \frac{0.527 \times 3 \times 10^{-12}}{1.6 \times 10^{-19}}$$

$$\approx 10 \text{ MeV}$$

This means that if the electrons exist inside the nucleus, their energy must be of the order of 10 MeV. However, we know that the electrons emitted by *radioactive nuclei* during *beta decay* have energies only 3 to 4 MeV. Hence, in general electrons cannot exist in the nucleus.

For *protons* and *neutrons*, $m_0 = 1.67 \times 10^{-27}$ kg. This is a non-relativistic problem. Hence the $K. E.$ in this case is,

$$\frac{p^2}{2m_0} = \frac{\left(0.527 \times 10^{-20}\right)^2}{2 \times 1.67 \times 10^{-27}} \text{ joule}$$

i.e.

$$K.E = 52 \text{ keV}$$

Since this energy is smaller than the energy carried by the particles emitted by nuclei, both these particles can exist inside the nuclei.

2. *Calculation of the radius of Bohr's first orbit*:

If (Δx) and (Δp) are the uncertainties in position and momentum of the electron in the first orbit, then according to uncertainty principle,

$$(\Delta x)(\Delta p) \geq \frac{h}{4\pi}$$

$$\Delta p \geq \frac{h}{(\Delta x)\, 2\pi} \text{ using } (\Delta x)(\Delta p) \approx \frac{h}{2\pi}$$

The uncertainty in the kinetic energy (ΔT) of the electron may be written as:

$$\Delta T \geq \frac{1}{2} m(\Delta v)^2 \geq \frac{m^2 (\Delta v)^2}{2m} \geq \frac{(\Delta p)^2}{2m}$$

$$\boxed{\Delta T \geq \left[\frac{1}{2m}\right] \frac{h^2}{4\pi^2 (\Delta x)^2}} \qquad \text{(Q 3. 3.1)}$$

The uncertainty in the potential energy ΔV of the same electron is given by:

$$\Delta V \geq -\frac{Ze^2}{4\pi \in_0 (\Delta x)}$$

Hence the uncertainty in the total energy ΔE is given by:

$$\Delta E \geq \Delta T + \Delta V \geq \frac{h^2}{4\pi^2 \times 2m(\Delta x)^2} - \frac{Ze^2}{(\Delta x) 4\pi \in_0}$$

The uncertainty in the energy will be minimum, if

$$\frac{d(\Delta E)}{d(\Delta x)} = 0 \text{ and } \frac{d^2(\Delta E)}{d^2(\Delta x)} \text{ is positive}$$

Now

$$\frac{d(\Delta E)}{d(\Delta x)} \geq \frac{-2h^2}{8\pi^2 m(\Delta x)^3} + \frac{Ze^2}{4\pi \in_0 (\Delta x)^2} = 0$$

i.e.,

$$\frac{h^2}{4\pi^2 m(\Delta x)^3} = \frac{Ze^2}{4\pi \in_0 (\Delta x)^2}$$

$$\Delta x = \frac{h^2 \in_0}{\pi m Z e^2}$$

Thus the radius of the first orbit of hydrogen is:

$$r \approx \Delta x \approx \frac{h^2 \in_0}{\pi m e^2} \text{ with } Z = 1 \text{ and } n = 1$$

$$\boxed{r = \frac{\in_0 h^2}{\pi m e^2}} \tag{Q 3.3.2}$$

Q 3.4 Set up the time-dependent form of Schrödinger's wave equation for matter waves. What is the physical significance of the wave function?

***Answer*:** In classical mechanics, a wave equation is a second order differential equation in space and time. Solutions of this equation represent wave disturbances in a medium. Therefore, a wave equation is the usual basis of mathematical theory of wave equation.

For example an *Electro-magnetic wave*, travelling in the x-direction, is described by the wave equation,

$$\frac{\partial^2 E_y}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 E_y}{\partial t^2}$$

where E_y is the y-component of the *electric intensity*.

A differential equation for the wave associated with a particle in motion cannot be derived from first principles. The equation may be developed by any one of the following procedures.

1. The equations of motion of classical mechanics are transformed into a wave equation in accordance with wave properties of matter based on de Broglie's hypothesis.
2. A *complex variable* quantity, called the *wave function*, is assumed to represent a *plane simple harmonic wave* associated with a free particle, and the classical expression for the total energy is used.
3. A particle at a given position and at a given time is represented by a wave packet which is obtained by superposition of a group of plane waves of nearly the same wavelength, which interfere destructively every where except at the wave packet, and the classical expression for the total energy is used.
4. In the classical expression for the total energy of a particle, the dynamical quantities are replaced by their corresponding operators. These operators are allowed to operate upon the wave function.

We will follow procedure (2) to develop the Schrödinger equation. If v is the velocity of the given transverse wave and y, the displacement, is a function of both t and x, the total derivatives must be replaced by partial derivatives.

i.e.,

$$\boxed{\frac{\partial^2 y}{\partial t^2} = v^2 \frac{\partial^2 y}{\partial x^2}} \tag{Q. 3.4.1}$$

This wave equation is valid for many other types of waves also. In practice, sound waves in air and light waves in vacuum are two of the important types of waves that obey Eqn. (Q 3. 4. 1). Of the numerous possible solutions for the above equation, the solution corresponding to the case of undamped, monochromatic harmonic waves in the positive x-direction, is of particular interest. The general solution in this case has the form:

$$\boxed{\begin{aligned} y &= A\exp\left[-i\omega\left[t-\frac{x}{v}\right]\right] \\ y &= A\cos\omega\left[t-\frac{x}{v}\right]-i\ A\sin\omega\left[t-\frac{x}{v}\right] \end{aligned}} \tag{Q 3.4.2}$$

Only the real part of equation (Q 3. 4. 2) has some significance in the case of waves in stretched string, where y represents the displacement of the string from its normal position; in this case the imaginary part is discarded as irrelevant. This, however, cannot be directly followed in the case of material particles, because the wave function Ψ of de Broglie, unlike *y*, is not itself a measurable quantity and may, therefore, be complex.

Thus

$$\begin{aligned} \Psi(x,t) &= A\ \exp\left[-i\omega\left[t-\frac{x}{v}\right]\right] \\ &= A\ \exp\left[-2\pi i\left\{\upsilon t-\frac{\upsilon x}{v}\right\}\right] \end{aligned}$$

Using $E = mv^2 = h\upsilon$ and knowing $\upsilon = \frac{E}{h}$ and $\frac{\upsilon}{v} = \frac{p}{h}$, one gets

$$\boxed{\Psi(x,t) = A\ \exp\left[-\frac{i}{\hbar}(Et-px)\right]} \tag{Q 3.4.3}$$

From this one can obtain, the differential equation as:

$$\left\{\text{by knowing } E = \frac{1}{2}mv^2 + V(x);\ E\Psi = \frac{p^2\Psi}{2m} + V\Psi\right\}$$

$$\boxed{\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} = \left[\frac{\hbar^2}{2m}\right]\left[\frac{\partial^2\Psi}{\partial x^2}\right] - V\Psi} \tag{Q 3.4.5}$$

This is the one dimensional Schrödinger’s time- dependent wave equation. In three dimensions the time- dependent form of Schrödinger’s equation is:

$$\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} = \left[\frac{\hbar^2}{2m}\right]\left[\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2}\right] - V\Psi$$

i.e.,

$$\boxed{\frac{\hbar}{i}\frac{\partial\Psi}{\partial t} = \left[\frac{\hbar^2}{2m}\right]\nabla^2\Psi - V\Psi = 0} \tag{Q 3.4.6}$$

Physical significance of the wave function:

The quantity

$$P = \Psi^* \Psi \, dx \, dy \, dz$$

where Ψ^* is the *complex conjugate* of Ψ, gives the probability of finding the particle within the volume element *dx dy dz at* time *t*. If the particle has a definite energy *E*, we can write

$$\Psi(x, t) = \psi(x) \exp(-iEt/\hbar)$$

$$\Psi^*(x, t) = \psi^*(x) \exp(iEt/\hbar)$$

$$\Psi \Psi^* = \psi \psi^*$$

The *probability of finding* the particle within a given volume element is independent of time.

Now

$$P = \psi^*(x) \, \psi(x) \, dx \, dy \, dz$$

gives the probability of findings the particle in the given volume element (at all times).

The meaning of the probability is as follows: suppose we conduct an experiment to find the position of the particle at some instant of time. Let the position (assuming one-dimensional motion along the x-axis) be within an interval Δx_0. Let the particle be brought back to its original state (since the process of measurement might have disturbed its previous state). Let its position be again measured. Let this process be repeated a large number of times. Let us assume that the value Δx_0 of the position occurs *n* times when the total number of trials is *N*. Then the probability of finding the position of the particle within an interval Δx_0 (around a particular value of x_0) is:

$$P = \psi^*(x) \, \psi(x) \, \Delta x_0$$

If $\Delta x_0 = 1$, $\psi^*(x) \, \psi(x)$ is called *probability density*.

Q 3. 5 Arrive at the time-independent form of Schrödinger's equation for free electrons in a metal. Write a note on the physical significance of the wave function.

***Answer*:** The one dimensional time-dependent Schrödinger wave equation is:

$$\boxed{\frac{\hbar}{i}\frac{\partial \Psi}{\partial t} = \left[\frac{\hbar^2}{2m}\right]\left[\frac{\partial^2 \Psi}{\partial x^2}\right] - V\Psi} \tag{Q 3.5.1}$$

This equation can be further simplified for a great variety of problems in which the potential energy of a particle does not dependent on time but only on the position of the particle.

Refer Eqn. (Q. 3. 4. 3):

$$\Psi(x, t) = A \exp\left(-\frac{i}{\hbar}Et\right) \exp\left(\frac{ipx}{\hbar}\right)$$

$= \phi(t)\,\psi(x)$. This $\psi(x)$ is a function of x alone

Now $$\frac{\partial \Psi}{\partial t} = A \exp\left(-\frac{iEt}{\hbar}\right)\left(-\frac{iE}{\hbar}\right)\psi(x)$$

and $$\frac{\partial^2 \Psi}{\partial x^2} = A \exp\left(-\frac{iEt}{\hbar}\right)\frac{d^2 \psi}{dx^2}$$

Substituting these values in Eqn. (Q 3.5.1) and simplifying one gets,

$$\boxed{\frac{d^2 \psi}{dx^2} + \frac{2m}{\hbar^2}(E - V_0)\,\psi = 0} \qquad \text{(Q 3.5.2)}$$

This ψ is independent of time. This is the *steady state* form of Schrödinger equation. In three dimensions, the corresponding equation is:

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2m}{\hbar^2}\left[E - V_0\right]\psi = 0$$

or $$\boxed{\nabla^2 \psi + \frac{2m}{\hbar^2}\left[E - V_0\right]\psi = 0} \qquad \text{(Q 3.5.3)}$$

Here ψ is a function of x, y, z

The physical interpretation of the wave function ψ is now discussed:

Born in 1926 postulated that the square of the magnitude of the function $|\psi|^2$ (or $\psi\psi^*$ assuming ψ is a *complex quantity*), evaluated at a particular point represents the probability of finding the particle at that point. $|\psi|^2$ is called the *probability density* and ψ is called probability amplitude. Thus the probability of finding the particle within an element of volume dv is $|\psi|^2\,dv$. Thus

$$\boxed{\int_{-\infty}^{\infty} |\psi|^2\,dv = 1} \qquad \text{(Q 3.5.4)}$$

A wave function that obeys this equation is said to be *normalized*. Besides being normalizable, an acceptable wave function ψ must fullfill the requirements given below:

(i) The wave function must be finite everywhere. For example, if ψ is infinite at a particular point, it would mean an infinitely large probability of finding the particle at that point. Hence the wave function ψ must have a finite or zero value at any point.

(ii) It must be single-valued. If ψ has more than one value it would mean more than one value of probability of finding the particle at that point which is obviously ridiculous.

(iii) It must be continuous and have a continuous first derivative everywhere. This is necessary from the Schrödinger equation itself which shows that $\frac{d^2\psi}{dx^2}$ must be finite everywhere. This can be so only if $\frac{d\psi}{dx}$ has no discontinuity at any boundary where potential energy changes. Furthermore, the existence of $\frac{d\psi}{dx}$ as a continuous function implies that ψ too is continuous across a boundary.

Q 3.6 You are given a one dimensional potential box of infinite height with *a* as the parameter. Solve the Schrödinger wave equation for a particle in the box and obtain its eign values.

***Answer*:** Let us now consider a particle of mass *m* moving along the *x*-axis between the two rigid walls of the well with $x = 0$ and $x = a$. Since the force acting on the particle between the walls is zero, its potential energy is constant in this region and it is conveniently taken to be zero. Since the walls are assumed to be rigid, the force acting on the particle abruptly increases from zero to finite value at the boundaries and hence the potential energy of the particle becomes infinitely large at $x = 0$ and $x = a$.

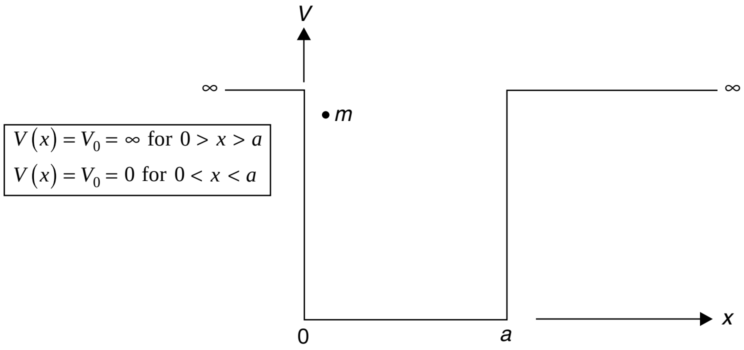

Fig. Q 3.6.1 *Particle in a one dimensional potential box*

As the particle can be found only inside the box, ψ, $\psi\psi^*$ must be zero for $0 \geq x \geq a$ and for zero potential the Schrödinger equation can be written as:

$$\frac{d^2\psi}{dx^2} + k^2\psi = 0$$

with

$$k^2 = \frac{2mE}{\hbar^2}$$

The general solution is of the form:

$$\psi(x) = A\sin kx + B\cos kx$$

Applying the conditions $\psi(x) = 0$ at $x = a$ and $x = 0$, one gets $k = \frac{n\pi}{a}$ where $n = 1, 2, 3, \ldots$ and hence B = 0.

Thus the wave function associated with the electrons is:

$$\boxed{\psi_n = A \sin\left[\frac{n\pi x}{a}\right]} \tag{Q 3.6.1}$$

Also

$$\boxed{E_n = \frac{k^2\hbar^2}{2m} = \frac{n^2 h^2}{8ma^2}} \tag{Q 3.6.2}$$

This equation gives the energy of the particle in the n^{th} energy state. This gives the energy eigen values of the particle; no other values are permitted. We may now evaluate the constant A in Eqn. (Q 3.6.1) by *normalization*. The total probability that the particle is some where in the box must be unity.

i.e.,

$$\int_0^a P_x\,dx = \int_0^a |\psi_n|^2\,dx = 1$$

or

$$A^2 \int \sin^2\left[\frac{n\pi x}{a}\right] dx = 1; \quad A^2 \int_0^a \frac{1}{2}\left[1 - \cos\frac{2\pi n x}{a}\right] dx = 1$$

i.e.,

$$\frac{A^2}{2}\left[x - \frac{a}{2\pi n}\sin\frac{2\pi n x}{a}\right]_0^a = 1; \text{ or } A = \sqrt{\frac{2}{a}}$$

The normalized wave function,

$$\boxed{\psi_n = \left[\sqrt{\frac{2}{a}}\right] \sin\frac{n\pi x}{a}} \tag{Q 3.6.3}$$

Q 3.7 Sketch the graphs for the first two or three wave functions, energy distribution and probability of finding the electrons at various regions in the box. The results of applications of Pauli exclusion principle to the present system may be solicitated.

***Answer*:** The permitted energy values, wave functions and probability of finding the particle in the potential box of length *a* are graphically represented in Fig. Q 3.7.1.

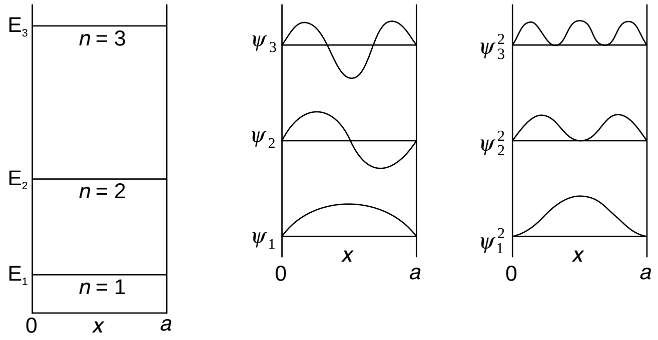

Fig. Q 3.7.1 *Variation of* ψ *and* $|\psi|^2$ *with position*

Conclusions

(i) The electrons can have only discrete energy values and the permitted values are shown in Fig. Q 3.7.1

i.e., $$E_1 = \frac{h^2}{8ma^2},\ E_2 = \frac{4h^2}{8ma^2},\ E_3 = \frac{9h^2}{8ma^2} \ldots$$

(ii) The wave functions associated with the electrons can have positive values as well as negative values including zero.

(iii) The probability function $|\psi|^2$ can have only zero and positive values as shown in the last figure.

Pauli exclusion principle

A metallic crystal can be considered to be a three dimensional infinite potential well whose boundaries are the crystal's surface and to which the free electrons are confined. The electrons may occupy a set of energy states, but only two electrons are allowed in a given state, because of the Pauli exclusion principle. In the allowed states each electron is characterized by a unique set of quantum numbers, including spin, so that the energy level with $n = 2$, say, can only contain two electrons: one spin up and one spin down.

For simplicity, let us consider a one dimensional crystal comprising a line of length 10 mm with atoms of 0.2 nm diameter, so that there are 5×10^7 atom in the line, and suppose that each contributes one free electron. Since two electrons can occupy each level, 2.5×10^7 energy states are filled, and the maximum energy is calculated as follows:

$$E_{\text{max}} = \frac{N^2h^2}{8ma^2} = \frac{\left(2.5 \times 10^7\right)^2 \times \left(6.626 \times 10^{-34}\right)^2}{8 \times 9.1 \times 10^{-31} \times \left(10^{-2}\right)^2 \times 1.6 \times 10^{-19}}\ \text{eV}$$

$$= 2.4\ \text{eV or } 100k_BT \text{ at } 300\ \text{K}$$

This equation shows that E_{max} is proportional to $\left(\frac{N}{a}\right)^2$, that is, it depends only on the linear density of free electrons. We also see that

$$\frac{dE}{dN} = \frac{h^2(2N)}{8ma^2} = \frac{2E_{\text{max}}}{N}$$

i.e.,

$$\boxed{\Delta E = \frac{2(\Delta N)\, E_{\text{max}}}{N}} \qquad \text{(Q 3.7.1)}$$

Now the maximum gap between adjacent energy levels, $(\Delta N = 1)$ when N is 2.5×10^7 is 8×10^{-8} E_{max}, or 0.2 μeV.

Q 3.8 Solve the Schrödinger wave equation for a particle in a rectangular potential box. Hence obtain the expression for the wave functions and permitted energy values.

***Answer*:** The Schrödinger wave equation for particles (say electrons) in a rectangular potential box of dimensions a, b, and c is:

$$\nabla^2 \psi + \frac{2m}{\hbar^2}(E - V_0)\psi = 0$$

when $V_0 = 0$, the said equation becomes

$$\boxed{\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{2mE}{\hbar^2}\psi = 0} \quad \text{(Q 3.8.1)}$$

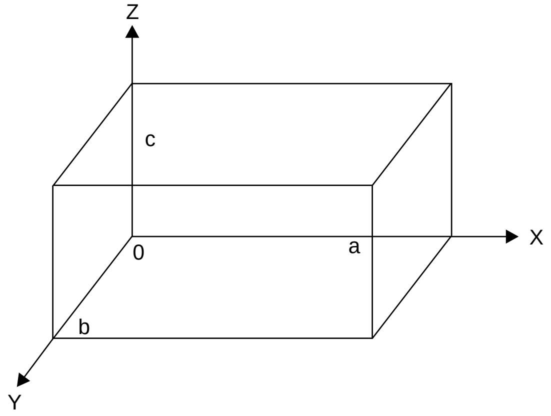

Fig. Q 3.8.1 *Particle in a three dimensional potential box with potential $V_o = 0$ and moving freely within the region $0 < x < a$, $0 < y < b$ and $0 < z < c$*

The above partial differential equation in three independent variables and may be showed by the method of separation of variables. The solution of the Eqn. (Q 3.8.1) is of the form:

$$\psi(x, y, z) = X(x)\,Y(y)\,Z(z)$$

i.e.,

$$\psi = X\,Y\,Z$$

where X-is a function of x alone, Y-is a function of y alone and Z is a function of z alone.

Now $\dfrac{\partial^2\psi}{\partial x^2} = \dfrac{d^2X}{dx^2}YZ$ and $\dfrac{\partial^2\psi}{\partial y^2} = \dfrac{d^2Y}{dy^2}XZ$ and $\dfrac{\partial^2\psi}{\partial z^2} = \dfrac{d^2Z}{dz^2}XY$

Substituting these values in Eqn. (Q 3.8.1) and simplifying and dividing each term by XYZ, we get,

$$\boxed{\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2} + \frac{2mE}{\hbar^2} = 0} \quad \text{(Q 3.8.2)}$$

The first term in this equation is a function of *x* only and the second term is a function of y only, and the third is a function of z only, while the sum of the three terms is a constant. This can only be so, infact, if each term is equal to a constant. Hence we can write,

$$\frac{1}{X}\frac{d^2X}{dx^2} = -k_x^2\,,\ \frac{1}{Y}\frac{d^2Y}{dy^2} = -k_y^2\,,\ \frac{1}{Z}\frac{d^2Z}{dz^2} = -k_z^2$$

with

$$k_x^2 + k_y^2 + k_z^2 = \frac{2mE}{\hbar^2}$$

$$E = \frac{\hbar^2\left(k_x^2 + k_y^2 + k_z^2\right)}{2m}$$

The first equation can be written as:

$$\frac{d^2X}{dx^2} + k_x^2\, X = 0$$

This is similar to the one dimensional case and hence the solution will be of the form:

$$X = \left[\sqrt{\frac{2}{a}}\right]\sin\frac{n_x\pi x}{a} \quad \text{with } k_x = \frac{n_x\pi}{a}$$

Similarly $$Y = \left[\sqrt{\frac{2}{b}}\right]\sin\frac{n_y\pi y}{b} \quad \text{with } k_y = \frac{n_y\pi}{b}$$

and $$Z = \left[\sqrt{\frac{2}{c}}\right]\sin\frac{n_z\pi z}{c} \quad \text{with } k_z = \frac{n_z\pi}{c}$$

where n_x, n_y and n_z are integers

Thus $$\boxed{\psi_{n_x,n_y,n_z} = XYZ = \left[\sqrt{\frac{8}{abc}}\right]\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}\sin\frac{n_z\pi z}{c}} \tag{Q 3.8.3}$$

and $$\boxed{E_{n_x,n_y,n_z} = \left[\frac{h^2}{8m}\right]\left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right]} \tag{Q 3.8.4}$$

For particles in a cubical box

$$\boxed{\psi_{n_x,n_y,n_z} = XYZ = \left[\sqrt{\frac{8}{a^3}}\right]\sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{a}\sin\frac{n_z\pi z}{a}} \tag{Q 3.8.5}$$

and $$\boxed{E_{n_x,n_y,n_z} = \left[\frac{h^2}{8ma^2}\right]\left(n_x^2 + n_y^2 + n_z^2\right) = \frac{n^2h^2}{8ma^2}} \tag{Q 3.8.6}$$

where $n^2 = n_x^2 + n_y^2 + n_z^2$

Q 3.9 List out the possible energy levels of a particle in a cubical box preferably with a chart. What are degenerate and non-degenerate energy states?

***Answer*:** *Some useful results*

(i) The three integers n_x, n_y, and n_z called quantum numbers, are required to specify a given energy state. No quantum number can be zero; because if any one of them is zero, then $\psi(x, y, z) = 0$, which would mean that the particle does not exist in the box.

(ii) It should be noted, however, that the energy E depends only upon the sum of the squares of the quantum numbers n_x, n_y, n_z and not on their individual values.

(iii) Several combinations of the same set of quantum numbers may give different energy states or different wave functions, but of the same energy value. Such states and energy levels are said to be *degenerate*.

Thus for the level for which the energy value is $\frac{6h^2}{8ma^2}$, there are three independent states with quantum numbers (1 1 2), (2 1 1) and (1 2 1). The level is, therefore, called *three fold degenerate* or *triply degenerate*. It will be noted that the ground state (1 1 1), as also several other states like (2 2 2), (3 3 3) are *non-degenerate energy states*. The following table gives the various degenerate and non-degenerate energy states.

Table Q 3.9.1 *Energy levels of a particle in a cubical box*

Energy Levels	*Quantum numbers* (n_x, n_y, n_z)	*Degree of Degeneracy*
21	(421) (142) (214) (412) (241) (124)	Six-fold degenerate
19	(331) (133) (313)	Three-fold degenerate
E ↑ 18	(411) (141) (114)	Three-fold degenerate
17	(322) (232) (223)	Three-fold degenerate
14	(123) (312) (231) (132) (213) (321)	Six-fold degenerate
12	(222)	Non-degenerate
$\frac{n^2h^2}{8ma^2}$ 11	(311) (131) (113)	Three-fold degenerate
9	(221) (122) (212)	Three-fold degenerate
6	(211) (121) (112)	Three-fold degenerate
$\frac{3h^2}{8ma^2}$	(111)	Non degenerate

TABLES

Table 3.A *Wavelengths of electrons under selected voltages*

Voltage applied (volt)	*Wavelength, λ (nm)*
44	0.18
54	0.17
74	0.14
100	0.1227

Table 3.B *Wavelengths of protons accelerated by some selected voltages*

Voltage applied (volt)	*Wavelength, λ (nm)*
25	0.008
36	0.0066
49	0.0057
100	0.0004

Table 3.C *Magnitude of the wave functions and probability of finding the particles at well known positions of electrons in a one dimensional box of side a for*

$n = 2$	ψ	$\lvert\psi\rvert^2$
$x = 0$	0	0
$x = \frac{a}{4}$	$\sqrt{\frac{2}{a}}$	$\frac{2}{a}$
$x = \frac{a}{2}$	0	0
$x = \frac{3a}{4}$	$-\sqrt{\frac{2}{a}}$	$\frac{2}{a}$
$x = a$	0	0

OBJECTIVE QUESTIONS

1. The wavelength associated with a moving particle
   (a) depends upon the charge associated with it
   (b) does not depend upon the charge associated with it
   (c) depends upon the medium in which the particles travel
   (d) none of these
2. Davisson and Germer were the first to demonstrate
   (a) the straight line propagation of light

(b) the diffraction of photons
(c) the diffraction of electrons
(d) none of these

3. Two particles of charges e and $2e$ and masses m_o and $\frac{m_0}{2}$ respectively are accelerated by the same p.d. Their de Broglie's wavelengths are related as

   (a) $\frac{\lambda_1}{\lambda_2} = 5$ (b) $\frac{\lambda_1}{\lambda_2} = 1$
   (c) $\frac{\lambda_1}{\lambda_2} = 2$ (d) $\frac{\lambda_1}{\lambda_2} = 4$

4. The wavelength associated with an electron of mass m and kinetic energy E is given by

   (a) $\lambda = \frac{2mE}{h}$ (b) $\frac{E}{2mh}$
   (c) $\frac{h}{\sqrt{2mE}}$ (d) $\frac{h^2}{\sqrt{2mE}}$

5. An electron, neutron and a proton have the same wavelength; which particle has greater velocity?

   (a) neutron (b) proton (c) electron

6. A proton and an α-particle has the same kinetic energy. If the mass of the α-particle is four times that of a proton, how do their de Broglie wavelength compare?

   (a) $\lambda_p = \frac{\lambda_\alpha}{4}$ (b) $\lambda_p = 2\lambda_\alpha$
   (c) $\lambda_p = 6\lambda_\alpha$ (d) $\lambda_p = 0.25\lambda_\alpha$

7. If an electron is accelerated by 74 volt, the wavelength associated with the electron is

   (a) 0.14 nm (b) 1.4 nm
   (c) 14 nm (d) 114 nm

8. If the kinetic energy of an electron is reduced to half of its original value, then the new de Broglie wavelength is

   (a) unchanged (b) $\frac{h}{\sqrt{mE}}$
   (c) $\frac{h}{\sqrt{2mE}}$ (d) $\frac{2mE}{2}$

9. If Δx is the error in determining the position of an electron and Δp in determining its momentum, then $(\Delta x)(\Delta p)$ is equal to

   (a) $\frac{2\pi}{h}$ (b) $\frac{h}{2\pi}$

(c) $(2\pi - h)$
(d) $(h - 2\pi)$

10. A proton and an α -particle have the same kinetic energy. If the mass of the α -particle is four times that of a proton, how do their frequency compare?

(a) $\upsilon_\alpha = 2\upsilon_p$
(b) $\upsilon_\alpha = 0.5\upsilon_p$
(c) $\upsilon_\alpha = 4.5\upsilon_p$
(d) $\upsilon_\alpha = 1.5\upsilon_p$

11. The wave function associated with an electron in a rectangular box of dimensions a, b and c is

$\psi(n_x, n_y, n_z) = A \sin\frac{n_x\pi x}{a}\sin\frac{n_y\pi y}{b}\sin\frac{n_z\pi z}{c}$ The normalization constant A is:

(a) $\frac{2}{abc}$
(b) $\sqrt{\frac{abc}{2}}$
(c) $\sqrt{\frac{4}{abc}}$
(d) none of these

12. An electron moving in a one dimensional box of length *a* is now considered. If ψ_1 is the wave function at $x = \frac{a}{4}$ with $n = 1$ and ψ_2 is that at $x = a$ for $n = 2$, then $\frac{\psi_2}{\psi_1}$ is

(a) 0
(b) $\sqrt{\frac{2}{a}}$
(c) $\sqrt{\frac{a}{2}}$
(d) ∞

13. If E_1 is the energy of the lowest state in a one dimensional potential box of length *a* and E_2 is the energy of the lowest state when the length of the box is halved, then

(a) $E_2 = E_1$
(b) $E_2 = 2E_1$
(c) $E_2 = 3E_1$
(d) $E_2 = 4E_1$

14. If n_x, n_y, and n_z have either values out of 4 2 1; then the degree of degeneracy of this energy level is

(a) 2 (b) 3 (c) 6 (d) 8

15. The spacing between the n^{th} energy level and the next higher level in a one dimensional potential box increases by

(a) $(n - 1)$
(b) (2n – 1)
(c) (2n + 1)
(d) (n + 1)

16. The energy of free electrons in the state (1 2 1) in a rectangular box of parameters $a = b \neq c$ is

(a) $\frac{h^2}{8m}\left[\frac{5}{a^2} + \frac{1}{c^2}\right]$
(b) $\frac{h^2}{2m}\left[\frac{3}{a^2} + \frac{1}{2c^2}\right]$

(c) $\frac{h^2}{8ma^2}\left[\frac{1}{a^2}+\frac{3}{c^2}\right]$ (d) $\frac{h^2}{8ma^2}\left(3a^2+c^2\right)$

17. E_1 is the lowest energy value of the electron in a one dimensional box of side a and E_2 is the lowest energy value in a cubical side a, then $\frac{E_2}{E_1}$ is

(a) 2 (b) 3 (c) 14 (d) 12

18. The energy level $\frac{27\hbar^2\pi^2}{2ma^2}$ has a degeneracy of

(a) 1 (b) 3 (c) 4 (d) 6

PROBLEMS AND SOLUTIONS

3.1 Using the relation $m = \frac{m_0}{\sqrt{1-\left(v^2/c^2\right)}}$ where m_o is the rest mass of a particle moving with a velocity v, show that the de Broglie wavelength of the particle is equal to its Compton wavelength when its velocity is $0.707c$ where c is the velocity of light.

***Solution*:** The de Broglie wavelength associated with the particle is

$$\lambda_d = \frac{h}{mv} = \frac{h\left[1-\left(v^2/c^2\right)\right]^{1/2}}{m_0 v}$$

The Compton wavelength of the particle with rest mass m_o is given by

$$\lambda_c = \frac{h}{m_0 c}$$

The two wavelengths are equal when

$$\frac{h\left(1-\frac{v^2}{c^2}\right)^{1/2}}{m_0 v} = \frac{h}{m_0 c}$$

$$\left(1-\frac{v^2}{c^2}\right)^{1/2} = \frac{v}{c}$$

$$1-\frac{v^2}{c^2} = \frac{v^2}{c^2}$$

or
$$2\frac{v^2}{c^2} = 1$$

$$\frac{v}{c} = \frac{1}{\sqrt{2}} = 0.707$$

$$\boxed{v = 0.707c} \quad \textbf{\textit{Answer}}$$

This shows that the de Broglie wavelength of the particle is the same as its Compton wavelength if the particle is moving with a velocity $v = 0.707c$.

3.2 Show that the average kinetic energy of neutrons, atoms and molecules through equipartition law is $K = \frac{3}{2}k_B T$. Write down the de Broglie formula for such particles at T degree kelvin. Hence determine the wavelength of thermal neutrons if the rest mass is 1.67×10^{-27} kg.

***Solution*:** The pressure exerted by a gas of unit volume is

$$P = \frac{1}{3}\rho \bar{c}^2$$

For molar volume,

$$P = \frac{1}{3}\rho \bar{c}^2 = \frac{1}{3}\frac{M_A}{V_m}\bar{c}^2$$

$$P = \frac{mN_A\bar{c}^2}{3V_m}$$

$$PV_m = \frac{m_0 N_A \bar{c}^2}{3} = R_u T$$

or
$$m_0\,\bar{c}^2 = \frac{3R_u T}{N_A} = 3k_B T \text{ and } \bar{c} = \sqrt{\frac{3k_B T}{m_0}}$$

i.e., the kinetic energy associated with each neutron is

$$\frac{1}{2}m_0\,\bar{c}^2 = \frac{3k_B T}{2}$$

or
$$\text{momentum,}\quad p = m_0\,\bar{c} = \sqrt{3m_0 k_B T}$$

According to de Broglie

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{3m_0 k_B T}}$$

$$\lambda = \frac{6.62 \times 10^{-34}}{\sqrt{3 \times 1.67 \times 10^{-27} \times 1.38 \times 10^{-2.3} \times 300}} = 0.146 \times 10^{-9}\, m$$

$$\boxed{\lambda = 0.146 \times 10^{-9}\, m}$$ ***Answer***

3.3 A charged particle such as electron, proton, etc. is accelerated to a particular velocity by subjecting to a potential difference. The uncertainty ΔV in the value of applied voltage leads to an uncertainty principle $(\Delta x)(\Delta p) \approx \frac{h}{4\pi}$ and using the relativistic values, get an expression for the uncertainty in the value of corresponding position coordinate. Hence evaluate the uncertainty in position of an electron accelerated from rest by a potential difference of 500000 ± 500 volt.

***Solution*:** When a charged particle of rest mass m_o with charge *e* is accelerated by a potential difference, its kinetic energy *K* is given by eV. The total energy of the particle would be sum of its kinetic energy *K* plus the rest energy $m_o c^2$, hence

$$E = m_0 c^2 + \text{eV}$$

or

$$E^2 = m_0^2 c^4 + e^2 V^2 + 2 m_0 c^2 \text{eV} \tag{3.3}$$

From special theory of relativity, the energy *E* is given by

$$E^2 = m_0^2 c^4 + p^2 c^2 \tag{3.4}$$

Subtracting one from the other,

$$p^2 c^2 = e^2 V^2 + 2 m_0 c^2 \text{ eV}$$

$$p^2 = \frac{e^2 V^2}{c^2} + 2 m_0 \text{ eV}$$

$$p = \left[\frac{e^2 V^2}{c^2} + 2 m_0 \text{ eV}\right]^{1/2} \tag{3.5}$$

Thus

$$\Delta p = \frac{1}{2}\left[\frac{e^2 V^2}{c^2} + 2 m_0 \text{ eV}\right]^{-1/2} \left[\frac{2e^2}{c^2} V \Delta V + 2 m_0 e \Delta V\right] \tag{3.6}$$

$$= \frac{\frac{1}{2}\left(\frac{2e^2 V}{c^2} + 2 m_0 e\right)\Delta V}{\left[\frac{e^2 V^2}{c^2} + 2 m_0 eV\right]^{1/2}} = \frac{e\left(eV + m_0 c^2\right)\Delta V}{c\left[e^2 V^2 + 2 m_0 c^2 eV\right]^{1/2}}$$

For uncertainty principle, we have

$$\Delta x \geq \frac{h}{4\pi(\Delta p)} \geq \frac{c\left(e^2V^2 + 2m_0c^2eV\right)^{1/2}}{e\left(eV + m_0c^2\right)(\Delta V)}\left[\frac{h}{4\pi}\right] \tag{3.7}$$

In non-relativistic case when $\mathrm{eV} << m_0 c^2$, Eqn. (3.7) yields

$$\Delta x \geq \frac{h}{2\pi}\left(\frac{c}{e(\Delta V)}\right)\left(\frac{eV}{2m_0c^2}\right)^{1/2}$$

$$\boxed{\Delta x \geq \frac{h}{2\pi}\left(\frac{c}{e(\Delta V)}\right)\left(\frac{eV}{2m_0c^2}\right)^{1/2}}$$ ***Answer***

This is the required expression for Δx

For electron,

$e = 1.6 \times 10^{-19}$ coulomb

$m_oc^2 = 9.1 \times 10^{-31} \times 9 \times 10^{16}$ joule $= 0.511$ MeV

and $\Delta V = 500$ volt, $V = 0.5$ MeV

Substituting these values one gets,

$$\boxed{\Delta x \geq 1.7 \times 10^{-10}\, m}$$ ***Answer***

3.4 A particle is moving in a one dimensional box of infinite height of 3 nm. Calculate the probability of finding the particle within an interval of 0.45 nm at the centre of the box when it is in the state of least energy.

***Solution*:**

$$\psi(x) = \left[\sqrt{\frac{2}{a}}\right]\sin\frac{\pi x}{a}$$

The probability of finding the particle at the centre of the box is

$$|\psi(x)|^2 = \frac{2}{a}\left\{\sin\frac{\pi a}{2a}\right\}^2 = \frac{2}{a}$$

The probability of P in the interval Δx is

$$P = |\psi(x)|^2\,\Delta x = \frac{2(\Delta x)}{a} = \frac{2 \times 0.45}{3} = 0.3$$

$$\boxed{P = 0.3}$$ ***Answer***

3.5 The wave function ψ of a particle is given by $\psi = \gamma \exp\left(-x^2/\alpha\right)$ for $-\infty < x < \infty$. Find the value of γ.

***Solution*:**

$$\int_{-\infty}^{\infty} |\psi|^2 \, dx = 1$$

$$2\gamma^2 \int_0^{\infty} \exp\left(-x^2/\alpha\right) dx = 1$$

$$2\gamma^2 \left[\frac{1}{2} \times \frac{\sqrt{\pi}}{\left(\frac{1}{\alpha}\right)^{1/2}} \right] = 1$$

$$\boxed{\gamma = \left[\frac{1}{\pi\alpha}\right]^{1/4}}$$ ***Answer***

3.6 Calculate the value of the difference between the energy of a hydrogen molecule bouncing back and forth on a path of 1 cm long when $n = 2$ and $n = 3$ at 298 K.

***Solution*:**

Mass of the hydrogen molecule, $M = \frac{2}{6.02 \times 10^{26}} = 0.33 \times 10^{-26}\ kg$

$$E_2 = \frac{4h^2}{8ma^2} \text{ and } \frac{9h^2}{8ma^2} = E_3$$

$$E_3 - E_2 = \frac{h^2}{8ma^2}(9 - 4) = \frac{5h^2}{8ma^2}$$

$$= \frac{5 \times \left(6.626 \times 10^{-34}\right)^2}{8 \times 0.33 \times 10^{-26} \times (0.01)^2} = 83.1 \times 10^{-38} \text{ joule}$$

$$= 5.2 \times 10^{-18} \text{ eV}$$

$$\boxed{E_3 - E_2 = 5.2 \times 10^{-18} \text{ eV}}$$ ***Answer***

3.7 Find the expectation value (most probable value) of the position x of a particle in a one-dimensional potential box of infinite height and width a in the lowest state of energy.

***Solution*:** The wave function of the particle is given by

$$\psi = \left[\sqrt{\frac{2}{a}}\right] \sin \frac{n\pi x}{a}$$

In the lowest state of energy, $n = 1$

Hence

$$\psi = \left[\sqrt{\frac{2}{a}}\right] \sin \frac{\pi x}{a}$$

The expectation value of x is

$$< x > = \frac{\int_0^\infty \psi^* x \psi \, dx}{\int_0^\infty \psi\psi^* dx} = \frac{\int_0^\infty \psi\psi^* x \, dx}{1}$$

$$= \frac{2}{a}\int_0^a x \sin^2 \frac{\pi x}{a} = \frac{2}{a}\int_0^a \left[\frac{x\left(1 - \cos \frac{2\pi x}{a}\right)}{2}\right] dx$$

$$= \frac{1}{a}\left[\int_0^a x \, dx - \int_0^a x \cos \frac{2\pi x}{a} \, dx\right]$$

$$= \frac{1}{a}\left[\frac{a^2}{2} - \frac{a}{2\pi}\left\{x \sin \frac{2\pi x}{a}\right\}_0^a - \int_0^a \sin \frac{2\pi x}{a} \, dx\right]$$

$$= \frac{1}{a}\left[\frac{a^2}{2} + \frac{a}{2\pi}\left\{\cos \frac{2\pi x}{a}\left(\frac{a}{2\pi}\right)\right\}_0^a\right] = \frac{a}{2}$$

$$\boxed{<x> = \frac{a}{2}}$$ ***Answer***

3.8 Get the probability of finding an electron in a cubical box of parameter *a* from 0.45*a* to 0.55*a*

***Solution*:**

$$\psi_n(x) = \left[\sqrt{\frac{2}{a}}\right] \sin \frac{\pi x}{a}$$

Hence,

$$P = \int_{x_1}^{x_2} |\psi_n|^2 \, dx$$

$$= \frac{2}{a} \int_{x_1}^{x_2} \sin^2 \frac{\pi x}{a} dx$$

$$= \frac{2}{a} \int_{x_1}^{x_2} \left[\frac{1}{2}\left(1 - \cos \frac{2\pi x}{a}\right)\right] dx$$

$$= \frac{1}{a} \left[x - \frac{a}{2\pi} \sin \frac{2\pi x}{a}\right]_{x_1 = 0.45a}^{x_2 = 0.55a}$$

$$= \frac{1}{a} \left[\left(0.55a - \frac{a}{2\pi} \sin 1.10\pi\right) - \left(0.45a - \frac{a}{2\pi} \sin 0.90\pi\right)\right]$$

$$= \left(0.55 - \frac{1}{2\pi} \sin 198^0\right) - \left(0.45 - \frac{1}{2\pi} \sin 162^0\right)$$

$$= (0.55 - 0.45) - \frac{1}{2\pi}\left(\sin 198^0 - \sin 162^0\right)$$

$$= 0.10 - \frac{1}{\pi}\left(\cos 180^0 \; \sin 18^0\right) = 0.10 + (0.30/\pi) = 0.198$$

$\boxed{19.8\%}$ ***Answer***

EXERCISE

3.1 Find the uncertainty in the momentum of a particle when its position is determined within 0.01 cm. Find also the uncertainty in the velocity of an electron and an α-particle when they are located within 50 *nm*. (***Ans*:** 1.05 × 10^{-30} kg–m/s, 2.33 × 10^5 m/s, 31.4 m/s)

3.2 If the electron having de Broglie wavelength as 1.21×10^{-10}m is confined in a one dimensional box, how far apart must be the walls of the box when five loops of the de Broglie wave span are formed from one wall to the other. (***Ans*:** 0.303 nm)

3.3 A particle is confined to one dimensional infinite potential well of width 0.2 nm. It is found that when the energy of the particle is 230 eV, its eign function has 5 antinodes. Find the mass of the particle and show that it can never have energy equal to 1 keV.

(***Ans*:** $m = 9.3 \times 10^{-31}$ kg, $n = 10.4$. Since n is not an integer, $E_n = 1$ keV is not allowed)

3.4 For a particle show that the Schrödinger wave equation leads to the de Broglie wavelength, $\lambda = \dfrac{h}{p}$.

3.5 Find the lowest energy of a neutron confined to a nucleus of size 10^{-14} metre. Given mass of neutron as 1.6×10^{-27} kg. (***Ans*:** 2.1 MeV)

3.6 Consider a grain dust ($m = 1\ \mu$gm) confined to move between two right walls separated by 0.1 mm. It requires 100 sec to cross the gap. What quantum number describes this motion?

(***Ans*:** 3×10^{14})

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4

Theories of Metals and their Limitations

4.1 INTRODUCTION

KEY WORDS

polytetrafluoro ethylene (PTFE), valance electrons, free electrons, electron gas, zig-zag motion, drift velocity, Drude-Lorentz, non-interacting particles, root mean square velocity, Boltzmann constant, unidirectional motion, memory of momentum, thermal velocity, drift velocity, mobility of charge, current density, lattice scattering, random velocity, mean free path, molar electronic specific heat, lattice positions, computation of mean free path, Fermi-Dirac statistics, thermal conductivity, Wiedemann-Franz law, Fermions, Fermi function, electrical resistivity, Lorentz number, octant, discrete energy levels, Pauli's exclusion principle, mean energy of electron, trivalent metal, occupied and unoccupied levels, probability occupation, Fermi temperature, Fermi velocity, heat capacity of electrons, lattice contribution, electronic contribution, thermal equilibrium, Fermi surface, zero momentum, Fermi sphere, effective mass of electron, Debye temperature, Bloch-Gruneisen law, superconductors, Matthiessen's rule, Wiedemann-Franz law, Lorentz number, Sommerfeld, Richardson-Dushman, thermionic emission, Fermi surface, anomalous expansion of water, the coefficient of expansion, periodic lattice, Kronig-Penney model, Sommerfeld quantum theory, periodicity character, Schrödinger equation, Bloch, forbidden energy, potential barrier strength, points of discontinuity, (E–k) curve, Brillouin zones, effective mass, gauge factor, Bridgeman constant, Electrical strainometer, nichrome, Wheatstone's bridge, electrical engineering materials, low resistivity materials, temperature coefficient of resistance, ductility, high resistivity materials, heating elements, resistance thermometers, precision resistors, high frequency conduction.

4.1 INTRODUCTION

Metals are to be considered as an important class of solids on account of their favourable electrical, thermal and mechanical properties at normal temperature and pressure. The other interesting point is the electrical resistivities of materials at room temperature vary over a wide range of values than any physical property—from $1.5 \times 10^{-8}\ \Omega$ m for silver to about $10^{16}\ \Omega$ m for *polytetrafluoro ethylene* (PTFE). This range over 24 orders of magnitude may be compared with the ratio of the earth's orbit (1.5×10^{11} m) to the Bohr radius of hydrogen atom (5×10^{-11} m). Because of the special features of metals, it has to be assumed that the outer electrons (valance electrons) of atoms of metals are free to move randomly, just as the molecules of a gas. These electrons are called '*free electrons*', and their aggregate in a given metal is called an '*electron gas*'. These electrons are free to move throughout the lattice and do not belong to any particular atom. For a monovalent metal, the number of free electrons in a given volume is equal to the number of atoms in the same volume. In the absence of an electric field, the random velocity due to the *zig-zag motion* is determined by the absolute temperature with zero *drift velocity* in a particular direction.

Q 4.1 Discuss classical free electron theory of metals and obtain the expression for electrical conductivity.

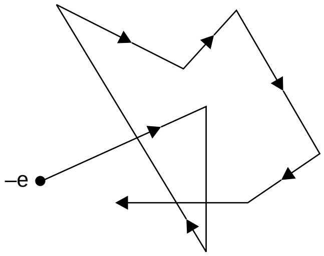
***Answer*:** The free electron theory of metals using classical laws was developed by *Drude* and *Lorentz* in the beginning of the last century where the valance electrons in metals were regarded as the non-interacting particles of an ideal gas. The only difference is that electrons are charged. If we assume that the kinetic theory of gases can be applied to the free-electron gas, then the *root mean square velocity* of the electron is

$$\boxed{\bar{c} = \sqrt{\frac{3k_BT}{m}}} \tag{Q 4.1.1}$$

where k_B is *Boltzmann's constant* and T is absolute temperature. Refer Fig. Q. 4.1.1(a).

Thus $\bar{c} \propto \sqrt{T}$

Let us now sound the system with an external electric field. i.e., the given copper rod of uniform cross-section (say 1 sq. m) is subjected to a field of strength E applied in the direction as shown in Fig. Q 4.1.1(b). The possessive nature of the electrons is now suppressed. The random motion is discouraged and the charged electrons prefer to have a *unidirectional motion* in a direction opposite to the direction of the applied electric field as sketched in Fig. Q 4.1.1(c).



(a)

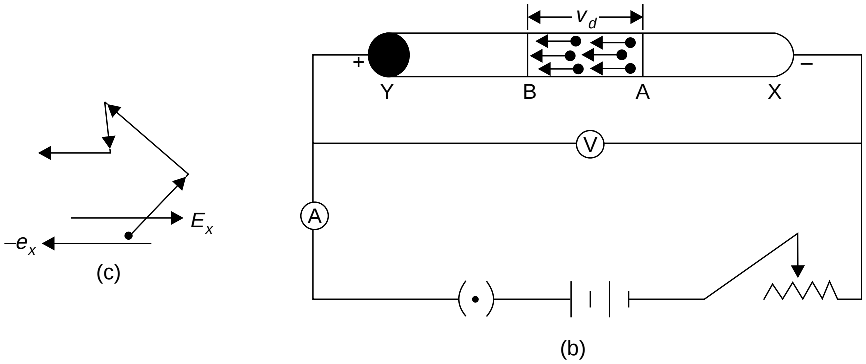


Fig. Q 4.1.1 *(a) zig-zag motion (b) Drift in a field*

Now it appears reasonable to expect that the free electrons will bump into a cation of the lattice from time to time. Let the average time between such collisions be τ sec. Immediately after a collision we further suppose that the velocity of the electron averages to zero; that is to say, the electron has no *memory* of the momentum acquired from the field and that its *thermal velocity* averages to zero. In a time τ sec the electron will attain a velocity given by:

$$v_d = a\tau$$

Here v_d is called *drift velocity* and the magnitude of $a = \frac{eE}{m}$

Thus

$$\boxed{v_d = -\frac{eE\tau}{m}} \qquad \text{(Q 4.1.2)}$$

Usually the term $\frac{e\tau}{m}$ is replaced by μ called the *mobility* of charge carriers, or defined as the *drift velocity in unit field*

Thus

$$\boxed{v_d = -\mu E} \qquad \text{(Q 4.1.3)}$$

If n is the density of electron and $-e$ is the charge of the electron, then charge flowing through unit area for one sec (or the *current density*) J_x (in A/m^2) is

$$J_x = -n\,e\,v_d$$

Substituting for v_d from Eqn. (Q 4.1.2), we get,

$$\boxed{J_x = \frac{ne^2E\tau}{m}} \qquad \text{(Q 4.1.4)}$$

Thus the *electric conductivity*, $\sigma = \frac{1}{\rho}$ is:

$$\frac{J_x}{E} = \frac{ne^2\tau}{m}$$

i.e.,
$$\sigma = \frac{ne^2\tau}{m}; \text{ or } \rho = \frac{m}{ne^2\tau}$$

Also
$$\boxed{\sigma = \text{ne}\,\mu \text{ and } \rho = \frac{1}{ne\,\mu}} \quad \text{(Q 4.1.5)}$$

In a metal, when temperature increases, n remains constant, but μ decreases as *lattice scattering* increases and therefore conductivity decreases.

Q 4.2 Discuss with a simple theory, the temperature dependence of the electrical resistivity of a metal (say copper).

***Answer*:** Let us consider a copper rod of uniform cross-section a sq. m and length l (say 1 m) and totally free from the influence of the external electric field. The free electrons have now the liberty of receiving thermal energy (of the order $k_B T$) from the atmosphere in all possible directions. The result is the *zig-zag motion* for the electrons and will be in thermal equilibrium. The *kinetic energy* associated with the electron is:

$$\boxed{\frac{1}{2}m\bar{c}^2 = \frac{3}{2}k_B T} \quad \text{(Q 4.2.1)}$$

When an electric field is applied, the electron will acquire a *drift velocity* and the resulting acceleration is, $a = \frac{eE}{m}$. The *drift velocity* is small compared to the *random velocity*, $\bar{c}$. Further the drift velocity is not retained after a collision with an atom because of the relatively large mass of the atom. Hence just after a collision the drift velocity is reduced to zero. If the *mean free path* is λ, then the time that elapses before the next collision takes place is $\frac{\lambda}{\bar{c}}$. Hence the drift velocity acquired just before the next collision takes place is,

$$u = \text{acceleration} \times \text{time interval} = \frac{eE}{m}\left(\frac{\lambda}{\bar{c}}\right)$$

The *average drift velocity* is:

$$\boxed{\frac{u}{2} = \frac{eE\lambda}{2m\bar{c}} = v_{ad}} \quad \text{(Q 4.2.2)}$$

If n is the number of electrons per unit volume and hence the current flowing through unit area for unit time is

$$J_x = \frac{neu}{2} = \frac{ne^2E\lambda}{2m\bar{c}} \text{ where } \bar{c} = \sqrt{\frac{3k_BT}{m}}$$

or
$$\sigma = \frac{J_x}{E} = \frac{ne^2\lambda}{2m\bar{c}} = \frac{ne^2\lambda}{\sqrt{12mk_BT}}$$

$$\boxed{\rho = \frac{\sqrt{12mk_BT}}{ne^2\lambda}} \qquad \text{(Q 4.2.3)}$$

It was assumed by Drude and Lorentz that λ is independent of temperature and that it is of the order of interatomic distance. Also $\rho \propto \sqrt{T}$. This means that the specific resistance of an electric conductor is directly proportional to the square root of the absolute temperature. This is not in agreement with the experimental observation that $\rho \propto T$.

Q 4.3 Outline the important drawbacks of the classical free electron theory of metals bringing out the bad assumptions made while explaining them.

Answer*:** (i) ***Molar electronic specific heat

In many solids the most important types of internal energy are (a) the vibrational energy of the atoms about their mean *lattice positions* and (b) the kinetic energy of the free electrons. The kinetic energy with one kmol of a monovalent metal is:

$$U = \frac{1}{2}m\bar{c}^2 N_A = \frac{mN_A}{2}\left(3k_BT/m\right) = \frac{3}{2}R_uT$$

The molar electronic specific heat is:

$$\boxed{C_{ve} = \frac{dU}{dT} = 1.5R_u = 12.5 \times 10^3 \text{ J/kmol/K}} \qquad \text{(Q 4.3.1)}$$

This value of 1.5 R_u is about hundred times greater than the experimentally predicated value. Our assumption that all the free electrons make contribution to the specific heat may be wrong and hence to be corrected.

(ii) ***Computation of mean free path***

The microscopic relation for the resistivity of a metal is:

$$\rho = \frac{m}{ne^2\tau}; \text{ or } \tau = \frac{m}{ne^2\rho}$$

For copper, $n = 8.5 \times 10^{28}/\text{m}^3$ and $\rho = 1.69 \times 10^{-8}\,\Omega\,\text{m}$

Thus

$$\tau = \frac{9.1 \times 10^{-31}}{8.5 \times 10^{28} \times \left(1.6 \times 10^{-19}\right)^2 \times 1.69 \times 10^{-8}} = 2.47 \times 10^{-14} \text{ sec}$$

$$\lambda = \tau\bar{c} = 2.47 \times 10^{-14} \times 1.154 \times 10^5 = 2.85 \times 10^{-9} \text{ metre}$$

$$\boxed{\lambda = 2.85 \text{ nm}} \tag{Q 4.3.2}$$

The experimentally found value for λ is about ten times greater than this value of 2.85 nm. Probably the application of Fermi-Dirac statistics (instead of classical statistics) to the free electrons in metals may help us to explain the difference in the values of λ.

Q 4.4 Obtain the expression for the thermal conductivity of a metal in terms of well known microscopic parameters. Get Wiedemann-Franz law and Lorentz number.

***Answer*:** The following figure shows the view of a copper rod of an appreciable length in the steady state with a cross-section 1 sq. m.

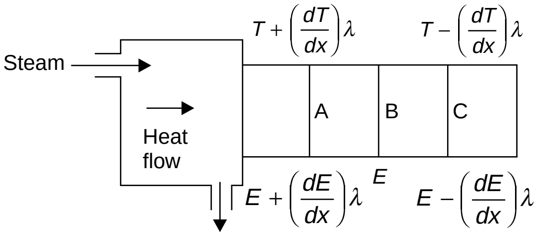


Fig. Q 4.4.1 *Flow of heat through a copper rod at the steady state*

The excess of energy carried by an electron from A to B is $\left[\frac{dE}{dx}\right]\lambda$. Hence the excess of energy transported by the process of conduction through unit area in unit time at the middle layer B is $\frac{n\bar{c}\,\lambda}{6}\left[\frac{dE}{dx}\right]$. Similarly the deficit of energy transported through B in the opposite direction is $\frac{1}{6}n\bar{c}\,\lambda\left[\frac{dE}{dx}\right]$ assuming $\frac{1}{6}n\bar{c}$ is the number of free electrons flowing in a given direction through unit area in unit time.

Thus the net energy transported through unit area in unit time from A to B is:

$$\frac{1}{6}n\bar{c}\,\lambda\left[\frac{dE}{dx}\right] - \left\{-\frac{1}{6}n\bar{c}\,\lambda\left[\frac{dE}{dx}\right]\right\} = \frac{n\bar{c}\lambda}{3}\left(\frac{dE}{dT}\right)\left(\frac{dT}{dx}\right)$$

i.e.,

$$\boxed{\sigma_T\left(\frac{dT}{dx}\right) = \frac{n\bar{c}\,\lambda}{3}\left[C_v\right]_{el}\left(\frac{dT}{dx}\right)} \tag{Q 4.4.1}$$

Knowing $\left[\frac{dE}{dT}\right] = \left[C_v\right]_{el} = \frac{3}{2}k_B$ (with respect to one electron) and $\bar{c} = \sqrt{\frac{3k_BT}{m}}$ and equating the above value with the general expression for *thermal conductivity*, one gets

$$\sigma_T\left[\frac{dT}{dx}\right] = \frac{n\lambda}{3}\left[\frac{3k_B}{2}\right]\left[\sqrt{\frac{3k_BT}{m}}\right]\left(\frac{dT}{dx}\right)$$

or
$$\boxed{\sigma_T = \left(\frac{n\lambda k_B}{2}\right)\sqrt{\frac{3k_BT}{m}}} \qquad \text{(Q 4.4.2)}$$

The general expression for electrical conductivity is:

$$\sigma = \frac{ne^2\lambda}{\sqrt{12mk_BT}}$$

i.e.,
$$\boxed{\frac{\sigma_T}{\sigma} = 3\left(\frac{k_B}{e}\right)^2 T} \qquad \text{(Q 4.4.3)}$$

This is known as *Wiedemann–Franz* law and the multiplying constant $3\left(\frac{k_B}{e}\right)^2$ is called *Lorentz number* (L).

***Example*:** For copper at 20°C, the thermal conductivity and electrical resistivity are respectively 386 W $m^{-1}K^{-1}$ and 1.7×10^{-8} Ω m. Computation of Lorentz number is done as follows:

$$L = \frac{\sigma_T}{\sigma \times T} = \frac{\sigma_T\rho}{T} = \frac{386 \times 1.7 \times 10^{-8}}{293} = 2.26 \times 10^{-8}$$

$$\boxed{L = 2.26 \times 10^{-8}\, W\Omega\ \mathrm{K}^{-2}} \qquad \text{(Q 4.4.4)}$$

This value of L does not match with the one calculated using the RHS of Eqn. (Q 4.4.3). This is another failure of classical theory.

Q 4.5 Get the standard expression for the density of energy states using Fermi-Dirac statistics.

***Answer*:** Some of the results of wave mechanics discussed earlier combined with *Fermi-Dirac statistics* may help us to over come the difficulties arised in the classical treatment of free electron theory of metals. In order to account for the unexpectedly low specific heat compared with the one predicted by classical theory and also the unacceptable values of mean free path of electrons and *Lorentz–number*, it was assumed that the free electrons obey Fermi–Dirac statistics and not the classical one. Such particles are then called *Fermions*.

If $N(E)$ is the number of electrons in a system that have energy E, and $Z(E)$ is the number of energy states have energy E, then the number of electrons having energy values lying between E and $E + dE$ or in the energy interval dE is:

$$\boxed{N\ (E)\ dE\ =\ Z(E)\ dE\quad F\ (E)} \tag{Q 4.5.1}$$

with $F\left(E\right)=\dfrac{1}{1+\exp\left[\left(E-E_F\right)/k_BT\right]}$

This *Fermi function* is unity at 0 K.

The number of energy states with a particular energy E, depends on the number of combinations of the three quantum numbers n_x, n_y, n_z to give the same n-value.

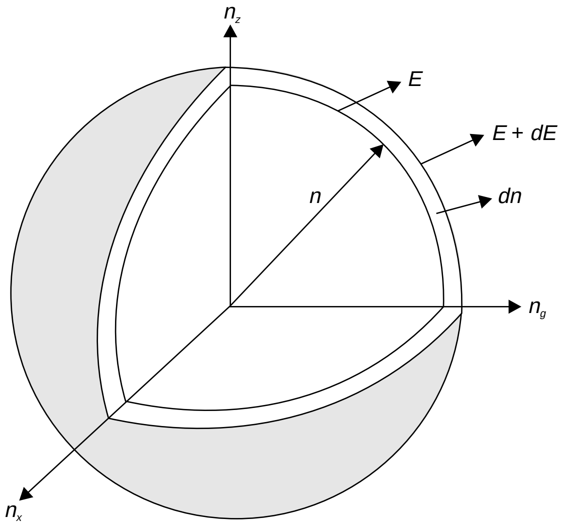


Fig. Q 4.5.1 *Density of energy states calculation*

Let us now draw a radius vector n (from the origin) to a point n_x, n_y and n_z such that all the points on the surface of the sphere with $n=\sqrt{n_x^2+n_y^2+n_z^2}$ will have the same energy value. This reveals that a unit cube will have only one energy state. Hence the number of energy states in any volume is just equal to the volume. Hence the number of energy states having energy values lying between E and $E + dE$, or in the energy interval dE with respect to the sphere is:

$$\boxed{Z\left(E\right)dE=\frac{1}{8}\left(\frac{4\pi}{3}\right)\left[\left(n+dn\right)^3-n^3\right]=\frac{\pi}{2}n^2dn} \tag{Q 4.5.2}$$

The term $\dfrac{1}{8}$ indicates that only in one *octant* of a sphere, all the *quantum numbers* will be positive. The general expression for the *discrete energy* values from Eqn. (Q 3.8.6) is:

$$\boxed{\begin{array}{l} E = \dfrac{n^2h^2}{8ma^2};\ n^2 = \dfrac{8ma^2E}{h^2};\ \text{and } n = \sqrt{\dfrac{8ma^2E}{h^2}} \\ \text{and} \\ 2ndn = \left[\dfrac{8ma^2}{h^2}\right]dE;\ (\text{or})\ dn = \dfrac{1}{2n}\left[\dfrac{8ma^2}{h^2}\right]dE \end{array}} \tag{Q 4.5.3}$$

Substituting these values in the expression (Q 4.5.2) for $Z(E)dE$ and then simplifying, one gets

$$Z(E)dE = \frac{\pi}{4}\left[\frac{8ma^2}{h^2}\right]^{3/2} E^{1/2}\,dE$$

Effecting Pauli's exclusion principle, the effective number of states available is:

$$Z(E)dE = 2 \times \frac{\pi}{4}\left[\frac{8ma^2}{h^2}\right]^{3/2} E^{1/2}\,dE$$

or

$$\boxed{Z(E)dE = \frac{\pi}{2}\left[\frac{8ma^2}{h^2}\right]^{3/2} E^{1/2}\,dE} \tag{Q 4.5.4}$$

Now the number of energy states in one cubic metre having energy values lying between E and $(E + dE)$ (or in the energy interval dE) is called *density of energy states* and it is given by:

$$\boxed{Z(E)dE = \frac{\pi}{2}\left[\frac{8m}{h^2}\right]^{3/2} E^{1/2}\,dE} \tag{Q 4.5.5}$$

Q 4.6 Bring out the general equation for computing the Fermi energy of electrons in solids at zero degree kelvin. Show that the mean energy at 0 K is (3/5)th of the Fermi energy.

***Answer*:** The actual number of electrons $N(E)dE$ in the given energy interval dE is:

$N(E)dE = Z(E)dE\ F(E)$

At 0 K, $F(E) = 1$

Thus

$$\int N(E)dE = \frac{\pi}{2}\left[\frac{8ma^2}{h^2}\right]^{3/2} \int_0^{E_F} E^{1/2}\,dE$$

i.e.,

$$\boxed{N = \frac{\pi}{2}\left[\frac{8ma^2}{h^2}\right]^{3/2} E_F^{3/2}\,(2/3)} \tag{Q 4.6.1}$$

Now the number of electrons in unit volume is:

$$\boxed{n = \frac{N}{a^3} = \frac{\pi}{3}\left[\frac{8m}{h^2}\right]^{3/2} E_F{}^{3/2}} \tag{Q 4.6.2}$$

or

$$E_F = \left[\frac{h^2}{2m}\right]\left[\frac{3n}{8\pi}\right]^{2/3} = 0.584 \times 10^{-37} \times n^{2/3} \text{ joule}$$

$$= \frac{n^{2/3} \times 0.584 \times 10^{-37}}{1.6 \times 10^{-19}} \text{ eV}$$

i.e.,

$$\boxed{E_F = 3.65 \times 10^{-19} \times n^{2/3} \text{ eV}} \tag{Q 4.6.3}$$

Mean energy of the electron gas at 0 K

To do *this* proposition, one must get the total energy using the equation,

$$U_0 = \int Z(E)\, F(E)\, E \quad \text{with } F(E) = 1$$

$$= \left[\frac{\pi}{2}\right]\left[\frac{8ma^2}{h^2}\right]^{3/2} \int_0^{E_F} E^{3/2}\, dE$$

Thus the *mean energy* at 0 K is:

$$\bar{E}_0 = \frac{U_0}{N}$$

Substituting for N from Eqn. (Q 4.6.1) and then simplifying, one gets

$$\boxed{\bar{E}_0 = \frac{3}{5} E_F} \tag{Q 4.6.4}$$

***Example*:** Aluminium is a *trivalaent metal* with 6 × 10^{28} atoms in a cubic metre. Find the mean energy of the electron.

Formula used: $E_F = 3.65 \times 10^{-19} \times n^{2/3}$

$n^{2/3} = (18 \times 10^{28})^{2/3} = 3.19 \times 10^{19}$

$E_F = 3.65 \times 10^{-19} \times 3.19 \times 10^{19}$ eV

$E_F = 11$ eV

The mean energy of the electron in this metal is:

$$\bar{E}_0 = \frac{3}{5} E_F = \frac{3}{5} \times 11$$

i.e.,

$$\bar{E}_0 = 6.6 \text{ eV}$$

Q 4.7 Discuss Fermi distribution with the help of suitable graphs and arrive at the expression for the heat capacity of the electron gas and compare it with the classical results.

***Answer*:** The probability $F(E)$ of an electron occupying particular energy level is given by:

$$\boxed{F(E) = \frac{1}{\left[1 + \exp\left(E - E_F\right)/k_B T\right]}} \tag{Q 4.7.1}$$

***Conclusions*:**

1. At 0 K and for $E < E_F$, the function $F(E)$ attains the value 1.
2. At 0 K and for $E > E_F$, $F(E)$ becomes zero. This means at absolute zero, all the quantum states above E_F are unoccupied while the quantum states below E_F are occupied. This means the Fermi level is the highest energy level for the free electron to stay at 0 K.

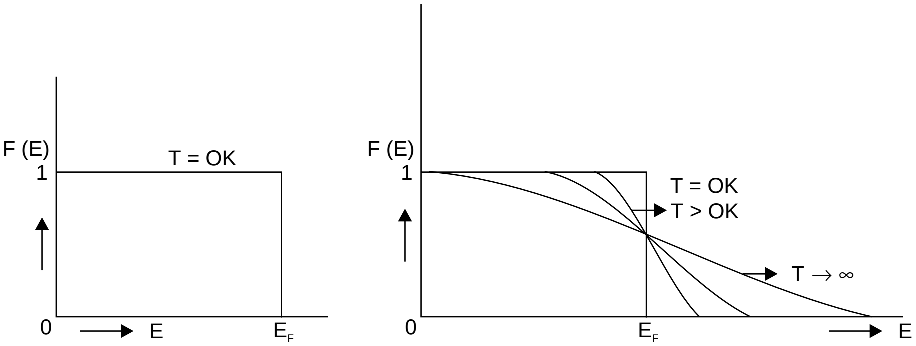


Fig. Q 4.7.1 *Variation of Fermi distribution at different temperatures*

3. The *Fermi function* plot at a temperature greater than zero (say 300 K) shows very little change from the Fermi plot at 0 K. It is now very clear that near E_F, $F(E)$ begins to fall and $F(E) = \frac{1}{2}$ at $E = E_F$. So Fermi level is also known as the level at which the *probability of occupation* is $\frac{1}{2}$.
4. *Fermi temperature* and *Fermi velocity* (T_F and v_F) are two familiar terms referred in the literature. They can be easily computed for any monovalent metal. Here it is done for copper with one valence electron. The given data is the Fermi energy of copper ($E_F = 7$ eV).

(i) $\frac{1}{2} m v_F^2 = E_F \,;\, v_F = \sqrt{\frac{2E_F}{m}} = \sqrt{\frac{2 \times 7 \times 1.6 \times 10^{-19}}{9.1 \times 10^{-31}}}$

i.e., $$\boxed{v_F = 1.57 \times 10^6 \text{ m/s}}$$

(ii) $k_B\, T_F = E_F$

or
$$T_F = \frac{E_F}{k_B} = \frac{7 \times 1.6 \times 10^{-19}}{1.38 \times 10^{-23}} = 81000 \text{ K}$$

$$\boxed{T_F = 81000\,\text{K}}$$

Heat Capacity of Electrons

The difference here is that the electrons very near to the Fermi level alone are agitated at 300 K (unlike in classical theory) and then move to the excited empty states and make their contribution to the specific heat. Thus the fraction of electrons that will be excited at 300 K is given by,

$$\frac{k_B T}{E_F} = \frac{0.025}{5} = 0.005 = 0.5\%$$

This result tells us that at ordinary temperatures, less than 1% of the valence electrons alone contribute to the heat capacity. This result is sharply in contrast to the classical inferences where it was assumed that all the electrons would absorb energy, and contribute to the heat capacity. Each of the electron may absorb a kinetic energy of the order $(3/2)k_BT$. Hence the energy associated with 1 kmol of the metal will be,

$$U = N_A \left[\frac{k_B T}{E_F}\right]\left[\left(\frac{3}{2}\right)k_B T\right]$$

Thus

$$\left[C_v\right]_{el} = \frac{dU}{dT} = 3R_u \left[\frac{k_B T}{E_F}\right] = 3R_u\,(0.005) \text{ with } E_F = 5 \text{ eV and } k_BT = 0.025 \text{ eV}$$

$$\boxed{\left[C_v\right]_{el} = 0.015 R_u} \qquad \text{(Q 4.7.2)}$$

This value of $0.015R_u$ well agrees with the experimental value. However, at low temperatures, the *lattice contribution* is small and falls as T^5 and the *electronic contribution* becomes significant.

N: **B** *Can you discuss the above problem at higher temperatures*?

Yes. The mean energy of the electron at higher temperatures is given by the equation,

$$\boxed{\bar{E} = \bar{E}_0 \left[1 + \frac{5\pi^2}{12}\left(\frac{k_B T}{E_F}\right)^2\right]} \qquad \text{(Q 4.7.3)}$$

Thus
$$\left[C_v\right]_{el} = \frac{\partial \bar{E}}{\partial T} = \frac{\bar{E}_0 5\pi^2 2T}{12}\left(k_B^2/E_F\right) \text{ with } \bar{E}_0 = \frac{3}{5}E_F$$

Thus for a monovalent metal, the *heat capacity* per kmol of the metal due to free electron is:

$$[C_v]_{el} = \left[\frac{\pi^2}{2}\right](k_B N_A)\left[\frac{k_B T}{E_F}\right] \text{ with } E_F = k_B T_F$$

$$\boxed{[C_v]_{el} = \frac{R_u \pi^2}{2}\left[\frac{k_B T}{k_B T_F}\right] = \frac{\pi^2}{2}\left[\frac{T}{T_F}\right] R_u = AT} \qquad \text{(Q 4.7.4)}$$

For $E_F = 5$ eV and $T = 300$ K

$$[C_v]_{el} = \frac{\pi^2}{2}\left[\frac{0.025}{5}\right] R_u$$

i.e., $$\boxed{[C_v]_{el} = 0.025 R_u} \qquad \text{(Q 4.7.5)}$$

This value is much higher than that at 0 K, but fairly agrees with the experimental values.

Q 4.8 On the basis of quantum mechanical considerations, obtain the expression for electrical conductivity and then compute the value of mean free path.

***Answer*:** In *thermal equilibrium*, the valence electrons obeying classical free electron theory do random motion with no preferential velocity in any direction. It is now conveniently plotted the velocities of these free electrons in velocity space with v_F as the maximum velocity that an electron can assume. i.e., v_F is the actual value of the velocity of the electron at the Fermi level. The shape having v_F as a radius represents, the *Fermi surface.* Under normal conditions the origin and the centre of the sphere coincide so that the net momentum is zero. When the electrons are accelerated by an electric field, motion in the direction of the force is favoured. The whole *Fermi sphere* is then moved from the origin and move steadily further as time proceeds. See Fig. Q 4.8.1.

For a free electron, $$\boxed{\vec{v} = \left[\frac{\hbar \vec{k}}{m}\right]; \; m\vec{v} = \hbar \vec{k}} \qquad \text{(Q 4.8.1)}$$

Now $$m\frac{d\vec{v}}{dt} = \hbar\frac{d\vec{k}}{dt} = e\vec{E}$$

This is the equation of motion of each electron in the *Fermi surface* under the influence of the field $\vec{E}$.

i.e., $$d\vec{k} = \frac{e\vec{E}\,dt}{\hbar}$$

Integrating

$$\vec{k}(t) - \vec{k}(0) = \frac{e\vec{E}\,t}{\hbar}$$

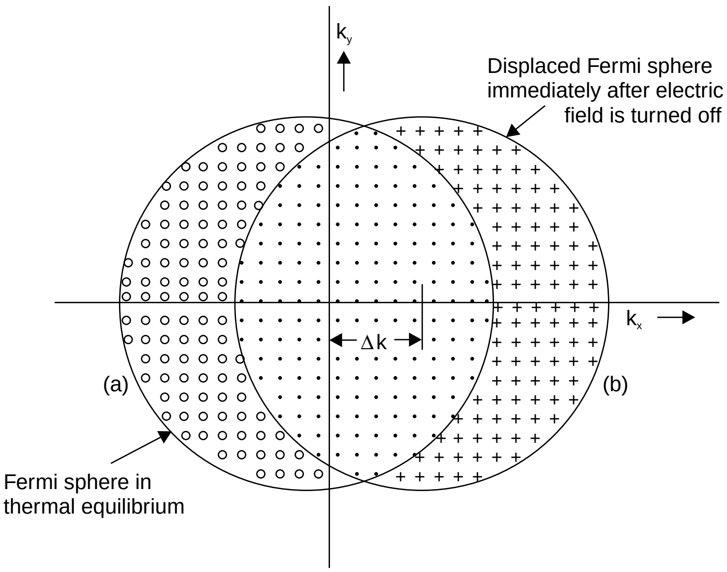


Fig. Q 4.8.1 *Fermi sphere in (a) absence (b) presence of electric field*

Thus if the electric field is applied at a time $t = 0$ to a filled *Fermi sphere* centred at the origin of $\vec{k}$ – space in the characteristic time,

$\tau = \tau_F = \dfrac{\lambda_F}{v_F}$ the sphere might have moved to a new centre at

$$\boxed{\Delta \vec{k} = \frac{e\vec{E}\lambda_F}{\hbar v_F} \text{ with } \tau_F = \frac{\lambda_F}{v_F}} \quad \text{(Q 4.8.2)}$$

A steady current is ultimately reached with,

$$\vec{J} = ne\Delta\vec{v} = \left[\frac{ne\hbar\Delta\vec{k}}{m^*}\right] = \sigma\vec{E} \quad \text{[Refer Eqn. Q 4.8.1]}$$

with m^* is the effective mass of the electron

or

$$ne\hbar\left[\frac{e\vec{E}\lambda_F}{\hbar v_F m^*}\right] = \sigma\vec{E}$$

i.e.,

$$\boxed{\sigma = \frac{ne^2\lambda_F}{m^* v_F} = \frac{ne^2\tau_F}{m^*}} \quad \text{(Q 4.8.3)}$$

***Example*:** If the *effective mass* of electron in copper is $m^* = 1.01\ m$ and the electric conductivity of copper is 5.76×10^7 ohm^{-1} m^{-1} with $E_F = 7$ eV, the Fermi mean free path is now calculated as given below.

Formula used: $\tau_F = \dfrac{m^* \times \sigma}{ne^2} = \dfrac{1.01 \times 9.1 \times 10^{-31} \times 5.76 \times 10^7}{8.5 \times 10^{28} \times \left(1.6 \times 10^{-19}\right)^2} = 2.4 \times 10^{-14}$ sec

$$\frac{1}{2} m v_F^2 = E_F = 7 \times 1.6 \times 10^{-19}$$

$$v_F = 1.55 \times 10^6 \ m/s$$

$$\tau_F = \frac{\lambda_F}{v_F}$$

or $$\lambda_F = v_F \, \tau_F = 2.4 \times 10^{-14} \times 1.55 \times 10^6 = 37.8 \text{ nm}$$

$$\boxed{\lambda_F = 37.8 \text{ nm}} \qquad \text{(Q 4.8.4)}$$

This value agrees with the experimental value fairly well.

Q 4.9 What are the sources of resistances in metals? Explain Matthiessen's rule.

***Answer*:** The special features of metals with regard to their conductivities are summarized below:

1. The current density in the steady state is proportional to the electric field strength (*Ohm's law*)
2. For pure specimens, the electric conductivity (σ) and the thermal conductivity (σ_T) vary with temperature as follows:

   $\sigma \propto T^{-1}$ and σ_T = constant for $T > \theta_D$

   so that $\dfrac{\sigma_T}{\sigma \times T}$ is independent of temperature (Wiedemann-Franz law); and

   $\sigma \propto T^{-5}$ and $\sigma_T \propto T^{-2}$ for $T < \theta_D$ where θ_D is the characteristic *Debye temperature*.

   The relation $\rho \propto T^5$ is known as *Bloch-Gruneisen law*.
3. The resistivity of some metals becomes zero at very low temperatures near absolute zero (e-g) mercury, aluminium, lead, etc. These metals are called *superconductors*.
4. The resistivity of metals having trace of impurities, the total electrical resistivity is given by the equation,

   $$\boxed{\rho = \rho_0 + \rho_p(T)} \qquad \text{(Q 4.9.1)}$$

   where ρ_0 is a constant that increases with increasing impurity content and $\rho_p(T)$ is the temperature dependent part of the resistivity. This is known as *Matthiessen's rule*.
5. For most metals electrical resistivity decreases with increase of pressure.

6. The resistivity of alloys that exhibit order-disorder transitions shows pronounced minima corresponding to order phases.

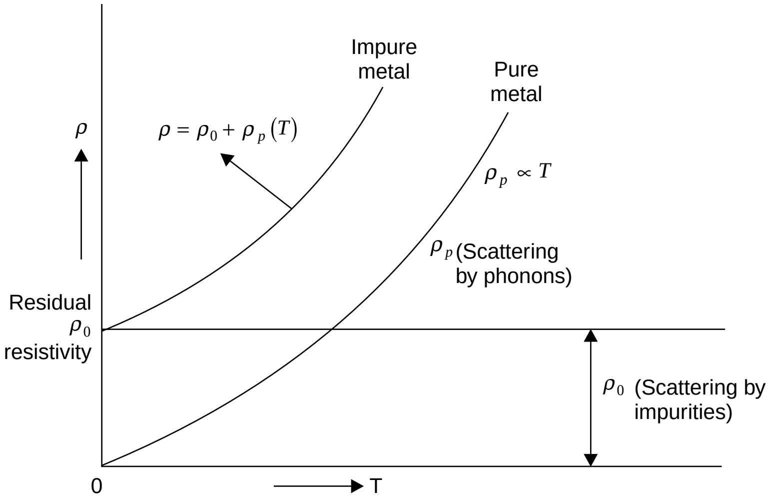


Fig. Q 4.9.1 *Sketch showing the variation of electrical resistivity with temperature*

Q 4.10 Study Wiedemann-Franz law using quantum mechanical principles. What is the corresponding equation for computing *Lorentz number*?

***Answer*:** Refer Eqn (Q 4.4.1)

$$\sigma_T = \frac{n\bar{c}\lambda}{3} C_{ve}$$

Remembering quantum mechanical approach and substituting for $[C_v]_{el}$ from Eqn. (Q 4.7.4), we get,

$$\sigma_T = \frac{nv_F\lambda_F}{3}\left[\frac{\pi^2}{2}\left\{\frac{k_BT}{E_F}\right\}k_B\right] \text{ with } E_F = \frac{1}{2}mv_F^2$$

The expression for electrical conductivity from Eqn. (Q 4.8.3)

$$\sigma = \frac{ne^2\lambda_F}{m^* v_F} = \frac{ne^2\tau_F}{m^*}$$

i.e.,

Thus the quantum mechanical form of *Wiedemann-Franz law* is:

$$\boxed{\frac{\sigma_T}{\sigma} = \left(\frac{\pi^2}{3}\right)\left(\frac{k_B}{e}\right)^2 T} \tag{Q 4.10.1}$$

and *Lorentz number*

$$\boxed{L = \frac{\sigma_T}{\sigma \times T} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 = 2.45 \times 10^{-8}\ \mathrm{W}\,\Omega\,\mathrm{K}^{-2}} \qquad \text{(Q 4.10.2)}$$

This is an acceptable result compared with the one predicted by classical theory; also well agrees with experimental values.

Q 4.11 What are the drawbacks of quantum free electron theory of metals proposed by Sommerfeld. Author a small note on anomalous expansion of water.

***Answer*:** Sommerfeld theory assuming the free electrons as a Fermi gas provides amazingly good predictions of the properties of alkali metals and some monovalent metals such as copper, silver and gold. *Richardson-Dushman* equation of *thermionic emission* is obeyed well. The reasons for the unexpected value of specific heats of the said metals predicted by classical theory are explained very well here. But the interactions between electrons and the ion cores are of transcendent importance for a qualitative understanding of other metals and of alloys. This theory also failed to explain why some solids are metals and others are semiconductors and insulators. Another interesting feature is that the electronic contribution to magnetic susceptibility is about 1% of the predicted value. The other major shortcomings of the free electron theory are its contradiction of results from experiments which determine the sign of the conductors or shape of the *Fermi surface*. Many metals give results which suggest positive charge carriers-a result in flat contradiction with free electron theory. In addition the Fermi surface turns out to be non-spherical even in the case of arachetypal metals like copper and aluminium.

The other plus point of this theory is that it provides a basis for the understanding of the effects of the uncertainty and exclusion principles in metals. Indeed the system which describes electron behaviour in terms of wave number space (the Fermi space) is essential to study the more advanced theories on free electrons.

Anomalous Expansion of Water

In majority of liquids, the increase in temperature produces an increase in volume of the liquids but water is a ***notable*** exception. The expansion of water is so markedly irregular that even ordinary laboratory methods can detect the anomaly. In the case of water, from 0°C to 4°C, instead of expanding, actually, contracts, from 4°C upwards it expands, far from uniformity. In the range 5°C to 10°C, the *coefficient of expansion* is only 0.53×10^{-4}, where as in the range of 20°C to 40°C it is 3.02×10^{-4} and between 60°C and 80°C, it is 5.87×10^{-4}. Hence for a given mass of water, the volume is minimum or density is maximum at 4°C. In other words, in the expression for the volume coefficient, $\frac{dV}{dT}$ is negative for temperature less than 4°C and positive for temperature greater than 4°C.

At 4°C, $\frac{dV}{dT} = 0$. This means that the specific volume decreases first, reaching a minimum value at 4°C and then increases; it is evident that the density curve will follow an inverse path, increasing from 0°C to 4°C where it reaches a maximum and then decreases. It may be noted that the curve is not linear and hence the expansion is not uniform even beyond 4°C. This *anomalous behaviour* of water has been explained on the assumption that the three types of water molecules, H_2O, $(H_2O)_2$ and $(H_2O)_3$ which have different specific volumes and mixed in different proporations at different temperatures, so that the maximum density at 4°C is probably due to greater proportions of the higher types of molecules. The result is, water at 4°C sinks to the bottom. A close *lookism* of this wonderful behaviour of water on either side of 4°C reveals that *Nature* has bestowed this special property to water to enable aquatic life to survive even during severe winter.

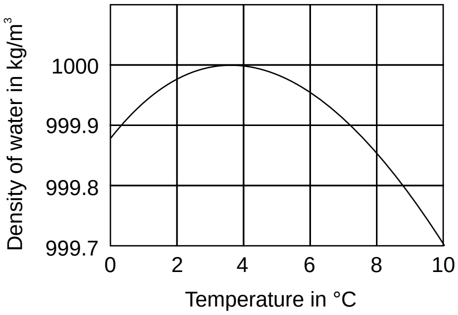


Fig. Q 4.11.1 *Anomalous expansion of water*

Q 4.12 Discuss the potential experienced by electron in a perfectly periodic lattice. Explain Kronig-Penney model to assess the behaviour of an electron in a periodic potential.

***Answer*:** While discussing free electron theory of metals, it was assumed that the conduction electron in a metallic crystal experiences a constant (zero) potential, i.e., it is completely free to move about in the crystal. This assumption does not seem to be reasonable.

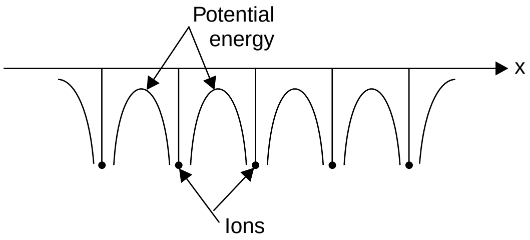


Fig. Q 4.12.1 *Potential experienced by electron in a perfectly periodic potential*

Even though both *Drude* and *Sommerfeld* theories explain many important properties of metals, it fails to explain a number of other properties such as the presence of energy band, effective mass of electrons, etc. Further the working of semiconductors do not find any explanation from this theory. The shortcomings of the Sommerfeld quantum theory are on account of the over simplified potential. A more reasonable approximation of the potential experienced by an electron in passing through the crystal is one which is perfectly *periodic* with the period of the lattice. This is shown in Fig. Q 4.12.1. At smaller distances from the nuclei, the potential energy of the valence electron will be low while the kinetic energy will be high. As the distance of the electron from the ion increases, its potential energy increases while kinetic energy decreases. Between neighbouring ions, the potential energy variation of valence electron is also shown in Fig. Q 4.12.1. The *periodicity character* of the potential extends to infinity in all directions inside the crystal. At the surface of the crystal, the potential is interrupted and look some what as shown at the edges of the above figure. This is because there are no ions to reduce the potential again.

Kronig-Penney Model

With the sinusoidal type of potential inside the crystal as shown in Fig. Q 4.12.1, the Schrödinger equation is not easily tractable. So Kronig and Penney introduced a simpler model for the shape of the potential variation. The potential inside the crystal is approximated to the shape of rectangular step as shown in Fig. Q 4.12.2. The potentials in the different regions are defined by

$V = 0$ when $0 < x < a$

and $V = V_0$ when $-b < x < 0$

Electrons moving in a crystal are not really free, but must be influenced to some degree by the periodic potential of the atoms in the lattice. In this model, the potential energy of electron moving in a one dimensional crystal lattice, is represented in the form of rectangular wells with $V(x) = 0$ for $0 < x < a$ and $V(x) = V_0$ for $-b < x < 0$. Although this model is highly artificial yet it illustrates many of the characteristics features of the behaviour of electrons in a *periodic lattice*. The wave functions related to this model may be obtained by solving Schrödinger equation for the following two regions:

$$\frac{d^2\psi}{dx^2} + \left[\frac{2m}{\hbar^2}\right]E\psi = 0 \text{ for } 0 < x < a \text{ with } V(x) = 0$$

and

$$\frac{d^2\psi}{dx^2} + \left[\frac{2m}{\hbar^2}\right](E - V_0)\,\psi = 0 \text{ for } -b < x < 0 \text{ with } V(x) = V_0$$

Let us now define the real quantities;

$$\alpha^2 = \frac{2mE}{\hbar^2} \text{ and } \beta^2 = \frac{2m}{\hbar^2}\left[V_0 - E\right]$$

Thus the two equations with the conditions said above are:

$$\boxed{\frac{d^2\psi}{dx^2} + \alpha^2\,\psi = 0} \qquad \text{(Q 4.12.1)}$$

and

$$\boxed{\frac{d^2\psi}{dx^2} - \beta^2\,\psi = 0} \qquad \text{(Q 4.12.2)}$$

Bloch has shown that the solutions are of the form:

$$\psi = u_k(x)\exp(ikx) \qquad \text{(Q 4.12.3)}$$

where $u_k(x)$ has the periodicity of the lattice, so that

$u_k(x) = u_k(x + a) = u_k(x + na)$ where n is an integer and k the wave number is:

$$\frac{2\pi}{\lambda} = \frac{p}{\hbar}$$

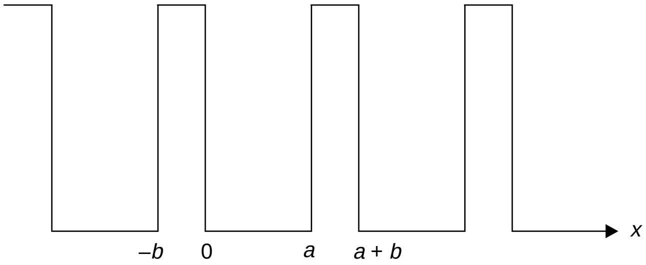


Fig. Q 4.12.2 *Kronig-Penney model of potential*

The common solution applicable to both the equations (Q 4.12.1) and (Q 4.12.2) suggested by *Bloch* is:

$$\psi(x) = u_k(x) \exp(ikx)$$

where $u_k(x)$ is a periodic function in x such that

$u_k(x) = u_k(x + a) = u_k(x + na)$ where n is an integer.

It turns out after some tedious manipulation with the wave equation, that only those values of k are allowed which satisfy the following equation:

$$\frac{\beta^2 - \alpha^2}{2\alpha\beta} \sinh \beta b \sin \alpha a + \cosh \beta b \cos \beta b = \cos k(a + b) \tag{Q 4.12.4}$$

A fruitful discussion of this equation and arriving at useful results is not very easy. Hence Kronig-Penney suggested that when V_o tends to infinity, b approaches zero in such a way that the product $V_o b$ remains finite. Under such a situation, $\sinh \beta \to \beta b$ and $\cosh \beta b \to 1$ as $b \to 0$. Now Eqn. (Q 4.12.4) becomes

$$\beta b \left[\frac{\beta^2 - \alpha^2}{2\alpha\beta}\right] \sin \alpha a + \cos \alpha a = \cos ka \tag{Q 4.12.5}$$

But
$$\beta^2 - \alpha^2 = \frac{2m}{\hbar^2}[V_0 - E + E]$$

$$\left[\frac{2mV_0}{2\hbar^2}\right](ab)\frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos ka \tag{Q 4.12.6}$$

$$\left[\frac{mV_0 ab}{\hbar^2}\right]\left(\frac{\sin \alpha a}{\alpha a}\right) + \cos \alpha a = \cos k a$$

or
$$\boxed{P\frac{\sin \alpha a}{\alpha a} + \cos \alpha a = \cos k a} \tag{Q 4.12.7}$$

where $P = \frac{mV_0ab}{\hbar^2}$

Since V_o tends to infinity, the quantity P is a measure of V_ob which is the area of the potential barrier. The physical significance of P is that as it increases, the area of the potential barrier increases. i.e., the electron is bound more strongly to a particular potential well. When P tends to zero, the potential barrier becomes very weak. i.e., the electron becomes free. Equation (Q 4.12.7) will be satisfied only for those values of αa for which the left hand side lies between + 1 and –1. Such values of αa alone will give a solution for the equation obtained by Bloch (Eqn 4.12.7). In Fig. (Q 4.12.3) $\frac{P\sin\alpha a}{\alpha a} + \cos\alpha a$ is plotted against αa for $P = \frac{3}{2}$. The part of the vertical axis lying between horizontal lines represents the range acceptable to the left hand side $\left(P\frac{\sin\alpha a}{\alpha a} + \cos\alpha a\right)$. The abscissa αa is a measure of energy, because $\alpha^2 = \frac{2mE}{\hbar^2}$. By finding the value of αa at any point, the energy represented by the function at that point is calculated. The following interesting conclusions are being drawn:

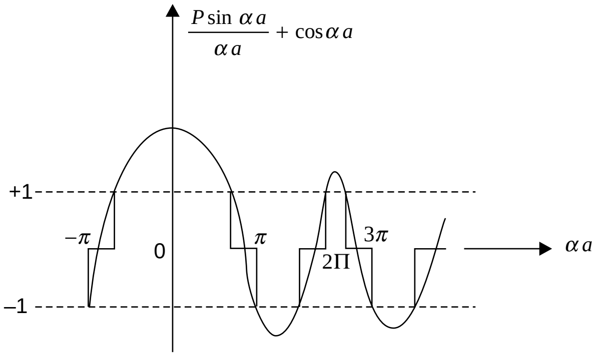


Fig. Q 4.12.3 *Plot of* $\frac{P\sin\alpha a}{\alpha a} + \cos\alpha a$ *versus* αa

1. It is very clear from Fig. (Q 4.12.3) that the energy spectrum of the electron consists of alternate regions of allowed energy which are drawn heavily and unallowed energy which are shown by white portion in between. These regions are called *allowed* and *forbidden energy bands.* The boundaries of allowed ranges of αa corresponds to the values of $\cos ka = \pm 1$ or $ka = n\pi$, $k = \frac{n\pi}{a}$.
2. As the value of αa increases, the width of allowed energy band also increases while the width of forbidden band decreases.

3. It is known that P is a measure of the *potential barrier strength*. If P is large, the function described by the left hand side of the Eqn. (Q 4.12.7) crosses + 1 and –1 region at a steeper angle; hence the allowed bands are narrower and the forbidden bands are wider. Also in equation (Q 4.12.7), when $\alpha a = \pm n\pi, \cos\alpha a = \cos ka$ with again $ka = \pm n\pi$, or $k = \pm\frac{n\pi}{a}$. These values of k are *points of discontinuity* in the $(E - k)$ curve for electron in the crystal.
4. The energy spectrum in the two extreme cases using Eqn. (Q 4.12.7) can now be discussed.

   (i) When $P \to \infty$, Eqn. (4.12.7) will have a solution only when $\sin\alpha a = 0$.

   or

   $\alpha a = \pm n\pi$ where n is an integer.

   Now

   $$\alpha = \pm\frac{n\pi}{a} \text{ or } \alpha^2 = \frac{n^2\pi^2}{a^2} = \frac{2mE}{\hbar^2}$$

   or

   $$E = \frac{n^2\pi^2\hbar^2}{2ma^2}; \text{ or } \frac{n^2h^2}{8ma^2} \tag{Q 4.12.8}$$

   The conclusion is that the energy is independent of k. The energy levels in this case are discrete and the electron is completely bound. It will be well within the potential well and moves only in the cell of width a.

   (ii) When $P \to 0$, we have

   $$\cos ka = \cos\alpha a$$

   or

   $$\alpha^2 = k^2 = \frac{2mE}{\hbar^2}$$

   i.e.,

   $$\boxed{E = \frac{\hbar^2k^2}{2m} = \frac{h^2}{8\pi^2m}\left(\frac{2\pi}{\lambda}\right)^2} \tag{Q 4.12.9}$$

   $$\boxed{E = \left(\frac{h^2}{2m}\right)\frac{1}{\lambda^2} = \frac{h^2}{2m}\left(\frac{p^2}{h^2}\right) = \frac{p^2}{2m} = \frac{1}{2}mv^2} \tag{Q 4.12.10}$$

   This energy corresponds to a completely free particle. No energy level in this case exist. i.e., all energies are allowed to the electrons.

Q 4.13 Discuss the features of $(E - k)$ curve. What are Brillouin zones? Illustrate your answer by constructing two Brillouin zones for a square lattice.

***Answer*:** Equation (Q 4.12.9) gives an $(E - k)$ curve which is parabolic one, as shown by the dotted line in Fig. Q 4.13.1 while an electron acted on by the lattice potential of a crystal has an $(E - k)$ curve shown by the solid lines. Near the energy gaps at $ka = \pm n\pi$, the solid lines deviate markedly from the *parabola*.

When $k = \pm \frac{n\pi}{a}$, Eqn. (Q 4.12.10) gives the free electron energy.

i.e.,
$$\boxed{E = \frac{\hbar^2 n^2 \pi^2}{2ma^2} = \frac{n^2 h^2}{8ma^2}} \qquad \text{(Q 4.12.1)}$$

which is exactly the same as the equation for a free particle in the potential well problem. If the size of the well is replaced by the distance between the atoms, say 0.3 nm, then the Eqn. (4.13.1) becomes

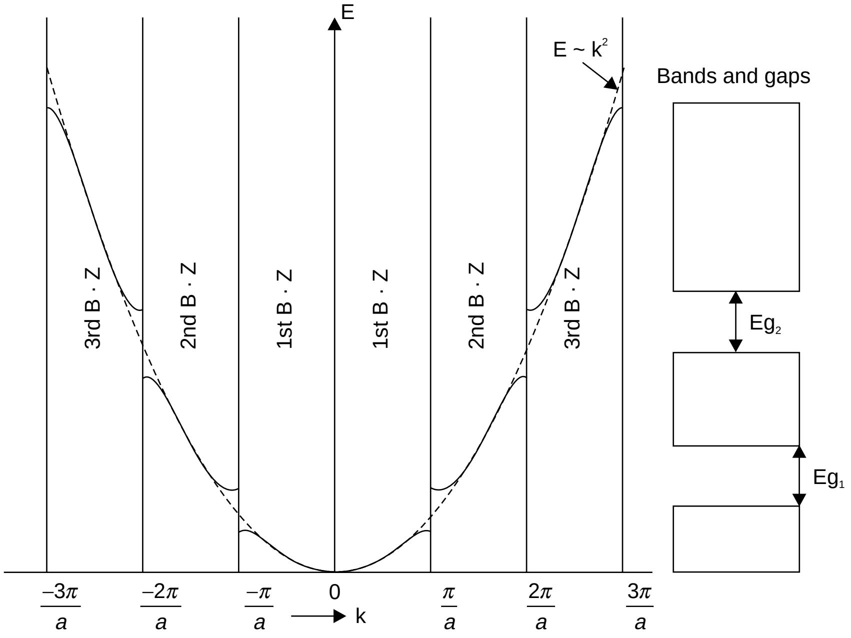


Fig. Q 4.13.1 *The (E – k) curve for nearly fee electron*

$$E \approx 4n^2 \text{ eV} \qquad \text{(Q 4.13.2)}$$

The inference is that beyond few discontinuities in the ($E - k$) curve, the electrons energy becomes very large and we are not usually concerned with them. The regions between the energy discontinuities are called *Brillouin zones* labelled 1st Brillouin zone, 2nd Brillouin zone, etc. as shown in Fig. Q 4.13.2.

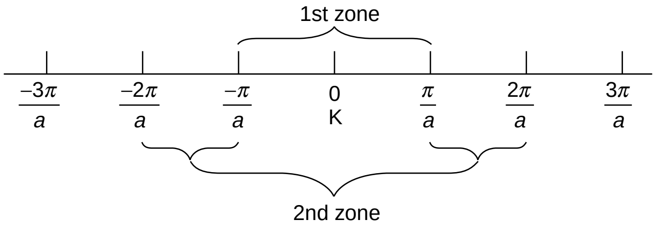


Fig. Q 4.13.2 *The first two Brillouin zones in a one dimensional case*

Brillouin zones in two dimensions

In general, the condition for any energy discontinuity is

$$\boxed{k = \pm \frac{n\pi}{a}} \tag{Q 4.13.3}$$

The corresponding condition for the two dimensional case is:

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

where n_1 and n_2 are integers referring to each of the axes. To sketch the first zone, n_1 and n_2 are made equal in turn to ± 1, or 0. The equations giving the borders of the first zone are:

$$n_1 = +1,\, n_2 = 0 \text{ giving } k_x = \pm\frac{\pi}{a}$$

$$n_1 = 0,\, n_2 = \pm 1 \text{ giving } k_y = \pm\frac{\pi}{a}$$

i.e., a square passing through the points A, B, C and D gives the *first Brillouin zone*. The *second Brillouin zone* should naturally pass through the points P, Q, R and S. To get the sketch of the second zone, we must use the next set of integers above those used for the first zone.

i.e.,
$$n_1 = +1,\, n_2 = +1 \text{ giving } k_x + k_y = \frac{2\pi}{a}$$

$$n_1 = -1,\, n_2 = +1 \text{ giving } -k_x + k_y = \frac{2\pi}{a}$$

$$n_1 = +1,\, n_2 = -1 \text{ giving } k_x - k_y = \frac{2\pi}{a}$$

$$n_1 = -1,\, n_2 = -1 \text{ giving } -k_x - k_y = \frac{2\pi}{a}$$

The above four equations describe a set of four lines at 45° to the k_x and k_y axes passing through the points P, Q, R and S. This means the second Brillouin zone is the area or region between P, Q, R, S and A, B, C, D. Similarly the third Brillouin zone may be obtained by giving n_1 and n_2 values of 0, ± 1, and ± 2.

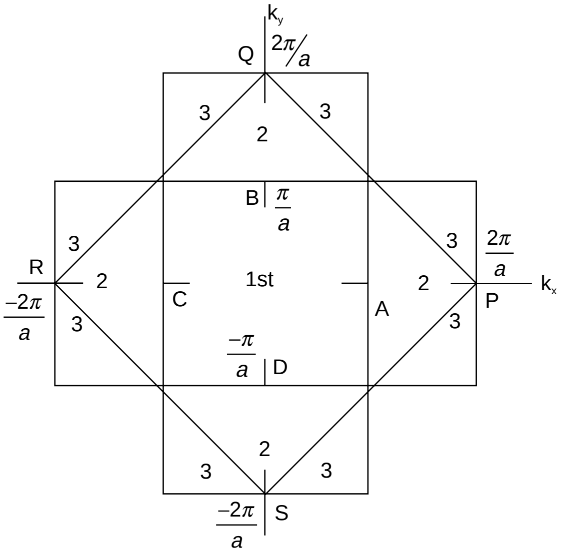


Fig. Q 4.13.3 *Brillouin zone for a square lattice*

Q 4.14 Write a note on effective mass approximation of electrons.

***Answer*:** For a completely free electron, the kinetic energy $\text{K.E.} = \frac{p^2}{2m}$ with $p = \frac{h}{\lambda}$ or $\hbar k$. The $(E - k)$ curve is the parabola with $E = \frac{\hbar^2 k^2}{2m}$. Obviously the latter equation does not apply to the heavy curve of Fig. Q 4.13.1. This problem may be discussed introducing the concept of *effective mass*, m^*. The concept of effective mass is freely and widely used in physics of condensed materials. When a free electron is subjected to an electric field $\vec{E}$, it experiences an acceleration $\vec{a} = -\frac{e\vec{E}}{m}$. However, when the external electric field is applied to solids say a metallic crystal, only completely free electrons, if any, have an acceleration $-\frac{e\vec{E}}{m}$. For example a copper *K* electron is so tightly bound to its atom that it is not accelerated at all; its "*effective mass*" is infinite. For an electron which is not bound to any single atom, *Newton's second law* gives $m\vec{a} = -e\vec{E}$ + forces due to neighbouring ion cores and electrons. These latter forces we do not know quantitatively, but we can transfer our ignorance to the left side of the equation by writing,

$$\boxed{m^*\vec{a} = -e\vec{E}} \qquad \text{(Q 4.14.1)}$$

where m^* is the effective mass.

Q 4.15 Explain the variation of electrical resistivity with necessary equations under mechanical stress.

***Answer*:** The application of mechanical loading produces changes which play a vital role in electromechanical *transducers*. We know that

$$R = \rho \frac{l}{A}$$

i.e.,

$$\boxed{\frac{dR}{R} = \frac{d\rho}{\rho} + \frac{dl}{l} - \frac{dA}{A}} \qquad \text{(Q 4.15.1)}$$

However, the resistivity itself is also affected by changes in dimensions. We know that

$$\rho = \left[\frac{m}{ne^2}\right]\left[\frac{\bar{c}}{\lambda}\right] = \left[\frac{m}{e^2}\right]\bar{c}\,\lambda^{-1}\,n^{-1}$$

$$\boxed{\frac{d\rho}{\rho} = \frac{d\bar{c}}{c} - \frac{d\lambda}{\lambda} - \frac{dn}{n}} \qquad \text{(Q 4.15.2)}$$

If N is the total number of electrons in the specimen of length l and area of cross-section A, then

$$n = \frac{N}{Al}$$

or

$$\boxed{\frac{dn}{n} = \frac{dN}{N} - \frac{dA}{A} - \frac{dl}{l}} \qquad \text{(Q 4.15.3)}$$

Thus Eqn. (Q.4.15.2) becomes

$$\boxed{\frac{d\rho}{\rho} = \frac{d\bar{c}}{c} - \frac{d\lambda}{\lambda} - \frac{dN}{N} + \frac{dA}{A} + \frac{dl}{l}} \qquad \text{(Q 4.15.4)}$$

This total relative change in resistivity is partly due to a change in intrinsic resistivity, ρ_i, associated with changes in the average electron velocity, $\bar{c}$, the mean free path λ and the total number of electrons *N*; and partly due to changes in dimensions of *A* and *l*. Thus Eqn. (Q 4.15.1) becomes

$$\boxed{\frac{dR}{R} = \frac{d\rho_i}{\rho_i} + 2\frac{dl}{l}} \qquad \text{(Q 4.15.5)}$$

Thus an increase in the length of the conductor, not only increases the distance to be travelled by the electrons but also decreases the number of electrons per unit length. This is the double effect of a change in length. $\frac{dl}{l}$ is the tensile strain in the direction of the flow of current and it is usually represented by ε_x.

Thus $\frac{dR}{R} = \frac{d\rho_i}{\rho_i} + 2\varepsilon_x$

It has been found experimentally that $\frac{dR}{R}$ varies linearly with ε_x over a considerable range of strains, an indication that if it varies at all, ρ_i varies linearly with ε_x

Thus $\frac{dR}{R} = c\varepsilon_x + \varepsilon_x = \varepsilon_x(c+2)$

or $\frac{dR}{R} = G_s\varepsilon_x$ where G_s = (c + 2), a constant called *gauge factor* and *c* is called *Bridgeman constant.*

i.e., $$\boxed{G_s = \frac{\frac{dR}{R}}{\varepsilon_x}} \qquad \text{(Q 4.15.6)}$$

Electrical Strainometer

The bonded electrical resistance wire gauge is commonly used for measuring strains. The strain gauge is either a grill of fine wire attached to thin sheet of paper or a maze of fine material deposited on a thin plastic sheet. These gauges have the materials of high electrical resistance. These strain gauges show variation of resistivity when subjected to a varying force or mechanical stress. The sensitivity of the strain gauge is determined by the gauge factor ε_x which is a measurement of the amount of change of resistance for a given strain.

i.e., $$\varepsilon_x = \frac{dR/R}{dl/l}$$

The features of a good strain gauge are:

(i) high gauge factor to get more resolution
(ii) high resistance material
(iii) low temperature coefficient
(iv) linear relationship between strain and resistance
(v) no hysteresis

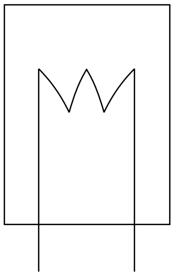


Fig. Q 4.15.1 *A strain gauge*

Nickel and Chromium in the ratio 8 : 2 known as nichrome is the popular strain gauge material. The resistivity of nichrome is of the order of $10^{-6}\,\Omega$ m; the temperature coefficient of resistance is 1. The *Bridgeman constant* (c) and Poisson's ratio (σ) are 1.13 and 0.3 respectively. The gauge factor is 2.05.

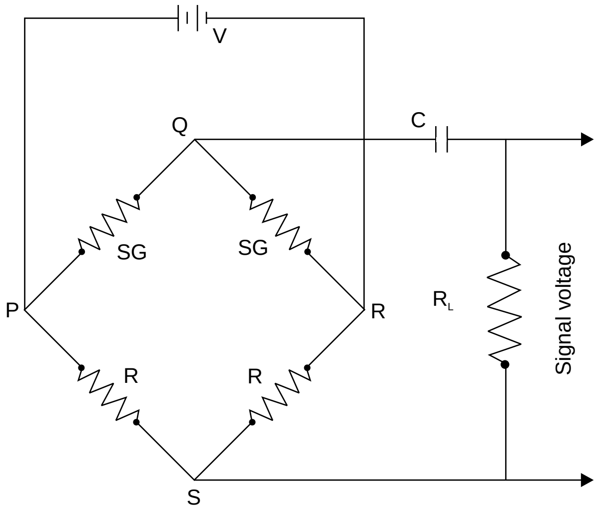


Fig. Q 4.15.2 *Circuit of a strain gauge*

Fig. Q 4.15.2 shows the circuit of a strain gauge bridge to measure stress directly. The strain gauge is firmly attached to the body on which the stress is to be determined. The strain gauge forms one arm of the Wheatstone's bridge PQ. To compensate temperature variations, an identical strain gauge should be attached to the same body where opposite strain occurs. This forms the arm QR. Two identical resistors are used in the other two arms. When no force is applied to the body, the *Wheatstone bridge* is balanced and hence there will be no signal voltage: when the body is subjected to stress, resistance SG changes resulting in unbalanced condition. This produces signal voltage. This voltage is a measure of the stress in the body. These voltages can be calibrated in terms of stress. Then one can measure stress directly using this bridge circuit.

Q 4.16 Write a note on selection of electrical engineering materials.

***Answer*:** The choice of conducting materials depends on the following factors:

1. resistivity of the material
2. temperature coefficient of resistance
3. resistiance against corrosion
4. oxidation characteristics
5. easy in soldering and welding
6. drawability/rollability
7. mechanical strength
8. flexibility and abundance

9. durability and low cost
10. resistivity to chemicals and weathers

Conducting materials are broadly classified into:

1. Low resistivity materials-copper, aluminium, steel, etc.
2. High resistivity materials-tungsten, platinum, etc.
3. Metals with zero resistivity are called superconductors

Low Resistivity Materials

A low resistivity material such as copper $\left(\rho = 1.2 \times 10^{-7}\ \Omega m\right)$ must possess low temperature coefficient resistance to avoid variation in voltage drop and power loss with changes in temperature. These types of conducting material should possess sufficient mechanical strength to withstand the stresses in transmission lines. Mechanical stresses are common in generators and transformers when loaded. Over head transmission is another area where stress is common. Ductility is another preferred property as they have to be drawn into different sizes and shapes. Conducting materials should be such that they are not easily corroded or rusted without insulation. Conductors are required to be jointed very often. The joint should offer minimum contact resistance. The two metals aluminium and copper possess the above said properties though the degree of the properties of aluminium are different from that of copper. Cost wise aluminium is much cheaper than copper.

High Resistivity Materials

The materials should have high resistivity. They should have high melting point and low temperature coefficient of resistance. They must not undergo oxidation even at high temperatures. High resistivity materials are used as heating elements, resistance thermometers and for manufacturing precision resistors. Tungsten, Platinum and Nichrome are some examples.

Q 4.17 Discuss high frequency conduction in metals and show that the frequency dependence of the conductivity is given by:

$$\sigma_\omega = \frac{\sigma_{\text{static}}}{1 + \omega^2 \tau^2}$$

***Answer*:** Alternating electric fields differ from static fields in that they do not penetrate uniformly through a conductor, but decay in magnitude exponentially from the surface inward. Let an alternating field of strength $E_0 \cos \omega\tau$ be applied in the x– direction, ω being the angular frequency. The force on the electron cloud resulting from the field is $-e\ E_0 \cos \omega\tau$ and the equation of motion in the a.c field is:

$$\boxed{m\frac{dv_x}{dt} + \frac{mv_x}{\tau} = -eE\cos \omega t} \qquad \text{(Q 4.17.1)}$$

To solve this equation for v_x, it is convenient to use the complex notation.

$$E \cos \omega t = E_0 \text{ Real } \exp\left(i\omega t\right)$$

and we shall assume the solution to be of the form

$$v_x(t) = \text{Re}\left[A^* \exp(i\omega t)\right]$$

where A^* is in general a complex amplitude.

Thus $$\frac{dv_x}{dt} = \text{Re}\left[A^* \exp(i\omega t) i\omega\right]$$

Now Eqn. (Q 4.17.1) becomes

$$\text{Re}\left[mA^* i\omega \exp(i\omega t)\right] + \text{Re}\left[A^* \frac{m}{\tau} \exp(i\omega t)\right] + eE_0 \,\text{Re}\left[\exp(i\omega t)\right] = 0$$

$$\text{Real}\left[\left\{A^* i\tau\omega + A^* + \frac{eE_0\tau}{m}\right\} \exp(i\omega t)\right] = 0$$

But $\exp(i\omega t)$ cannot be zero

Hence $$A^* i\tau\omega + A^* + \frac{eE_0\tau}{m} = 0$$

$$A^*(1 + i\omega\tau) = -\frac{eE_0\tau}{m}$$

$$A^* = -\frac{eE_0\tau/m}{(1+i\tau\omega)}$$

Thus $$v_x(t) = \text{Real}\left[-\frac{(eE_0\tau/m)\exp(i\omega t)}{(1+i\tau\omega)}\right]$$

$$= -\left[\frac{eE_0\tau}{m}\right] \text{Real}\left[\frac{1 - i\tau\omega}{1 + \tau^2\omega^2} \exp(i\omega t)\right]$$

$$v_x(t) = -\frac{(eE_0\tau)}{m} \text{Real}\left[\frac{1}{1+\omega^2\tau^2} - \frac{i\tau\omega}{1+\tau^2\omega^2}\right](\cos\omega t + i\sin\omega t)$$

$$= -\frac{(eE_0\tau)}{m}\left[\frac{\cos\omega t}{1+\omega^2\tau^2} + \frac{\omega\tau\sin\omega t}{1+\omega^2\tau^2}\right]$$

$$j_x = -nev_x(t)$$

$$= \frac{ne^2\tau E_0}{m}\left[\frac{\cos\omega t}{1+\omega^2\tau^2} + \frac{\omega\tau\sin\omega t}{1+\omega^2\tau^2}\right]$$

In this equation, $\frac{ne^2\tau}{m}$ represents the static conductivity, σ_s

$$\boxed{j_x = \sigma_s (E_0) \left[\frac{\cos \omega t}{1 + \omega^2\tau^2} + \frac{\omega\tau \sin \omega\tau}{\left(1 + \omega^2\tau^2\right)} \right]} \qquad \text{(Q 4.17.2)}$$

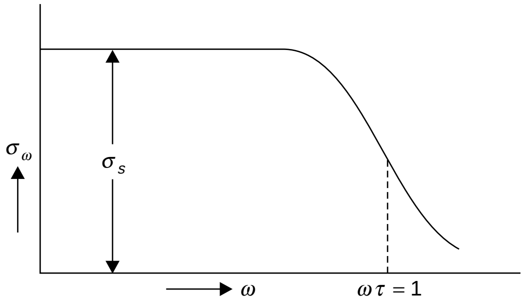


Fig. Q 4.17.1 *Variation of conductivity with angular frequency*

Thus the current density, according to Eqn. (Q 4.17.2), depends upon σ_s, the relaxation time of the electron distribution, and the angular frequency of the field (ω). Eqn. (Q 4.17.2) further indicates that the current density consists of two parts, one in phase with the applied field and the other shifted by $\frac{\pi}{2}$ from the applied field. Also we notice that as long as $\omega\tau << 1$

$$j_x = \sigma_s E_0 \cos \omega t$$

$$\boxed{\frac{j_x}{E_0 \cos \omega t} = \sigma_\omega = \sigma_s} \qquad \text{(Q 4.17.3)}$$

i.e; metal behaves as a pure resistance with conductivity given by the static value, $\sigma_s = \frac{ne^2\tau}{m}$. The variation of σ_s with the angular frequency of the applied field is shown in Fig. Q 4.17.1. In the region of $\omega\tau = 1$, the conductivity drops sharply and reaches zero.

For $\omega\tau = 1$, equation (4.17.2) becomes

$$j_x = \frac{\sigma_s E_0 \cos \omega t}{2}$$

i.e.,
$$\boxed{\sigma_\omega = \frac{j_x}{E_0 \cos \omega t} = \frac{\sigma_s}{2}} \tag{Q 4.17.4}$$

This occurs at approximately a frequency 10^{14} Hz remembering τ for electrons in metal is approximately 10^{-14} sec. For the conductivity to decrease sharply, the frequency of the applied field must be in the region of ultraviolet light. The loss of conductivity under such conductions is reasoned by the fact that the electrons cannot move fast enough with the field and hence lag behind.

TABLES

Table 4.A *Root mean square velocities of molecules of some well known gases at 0°C*

Gas	*Velocity* $(\bar{c})$ *in* 10^2 *m/s*
Oxygen	4.22
Hydrogen	16.92
Helium	12.01
Carbon dioxide	3.61
Chlorine	2.86
Nitrogen	4.52
Argon	3.81

Table 4.B *Physical properties of some selected metals*

Name of metal	*Atomic number* Z	*Atomic weight* M_A	*Density* ρ *kg/m*^{3}	*Young's modulus in* 10^{10} *(N/m*^{2}*)*	*Linear expansivity* α *in* 10^{-5}	*Poisson's ratio*
Aluminium	13	27	2700	7.0	2.4	0.34
Chromium	24	52	7100	2.5	0.85	-
Copper	29	63.5	8930	12.0	1.6	0.29
Iron	26	55.8	7860	22.0	1.2	0.30
Lead	82	207.2	11301	1.49	2.9	0.44
Nickel	28	58.7	8900	20	1.3	0.30
Platinum	78	39.1	21400	16.6	0.92	-
Silver	47	107.9	10500	7.9	1.9	0.38
Tin	50	118.7	7300	5.5	2.7	0.33
Tungsten	74	183.9	19300	36	0.43	-

Table 4.C *Thermal properties of some metals*

Metal	*Specific heat capacity, C_v J kg^{-1} K^{-1}*	*Thermal conductivity σ_T W m^{-1} K^{-1}*	*Melting point (T_m) K*	*Specific latent heat in 10^5 J kg^{-1}*	*Temperature coefficient of resistance (α) in 10^{-3} K^{-1}*
Aluminium	900	200	933	3.9	4.2
Cobalt	420	70	1769	2.6	6.2
Copper	410	390	1335	2.1	4.3
Iron	450	75	1810	2.75	6.5
Mercury	140	10.4	234	0.12	0.92
Nickel	450	70	1730	3	6.52
Molybdenum	260	140	2890	2.9	4.31
Silver	230	422	1234	1.05	3.9
Tin	220	65	505	0.59	4.3
Zinc	390	110	692	1.12	4.1

Table 4.D *Classical velocity of free electrons at different temperatures*

Temperature °C	*Root mean square velocity, ($\bar{c}$) (m/s)*
0	1.11×10^5
27	1.17×10^5
40	1.19×10^5
55	1.22×10^5
75	1.26×10^5
100	1.30×10^5

Table 4.E *Familiar alloys and their properties*

Name of alloy	*Composition %*	*Density, ρ kg/m^3*	*Young's modulus in 10^{10} N/m*	*Linear expansivity α in 10^{-5} K^{-1}*	*Thermal conductivity σ_T (W/mK)*	*Melting point T_m K*	*Specific heat capacity C_v (J/kg K)*	*Electrical resistivity ρ in 10^{-8} Ωm*	*Temperature coefficient of resistance α in 10^{-3} K^{-1}*
Constantan (Eureka)	58 Cu, 41 Ni, 1 Mn	8900	11	1.5×10^{-5}	22	1540	410	45×10^{-8}	0.05
Bronze	90 Cu, 10 Sn	8850	10	1.9×10^{-5}	45	1280	381	-	-
Brass	50 – 70 Cu 30 – 45 Zn	8500	10	2.1×10^{-5}	120	1170	380	6×10^{-8}	2
Soft iron	0.04 – 0.4C	7600	22	1.2×10^{-5}	60	1800	460	14×10^{-8}	-
Steel	0.85 C	7800	20	1.2×10^{-5}	50	1630	480	18×10^{-8}	-
Stainless steel	0.1 C, 12 Cr	7200	20	1.0×10^{-5}	50	1780	460	-	-
Cast iron	3 – 4 C, 2.5 Si	7300	10	1.1×10^{-5}	60	1450	500	-	-
Invar	64 Fe, 36 Ni	8100	14.5	0.21×10^{-5}	16	1720	505	10×10^{-8}	2
Manganin	34 Cu, 12 Mn, 4 Ni	8500	13.1	1.7×10^{-5}	22	1270	412	43×10^{-8}	0.02

Table 4.F *Selected electrical properties of some familiar metals*

Metal	*Resistivity at 0 °C* Ω *m in* 10^{-8}	*Number of atoms/*m^3 *in* 10^{28}	*Debye temperature* $\theta_D(K)$	*Hall coefficient at 293 K* R_H *in* 10^{-10} m^3/C^3	*Crystal structure*	*Lattice parameters (a, c) (nm)*
Cu	1.55	8.5	330	–0.55	fcc	0.3615
Ag	1.49	5.8	224	+0.85	fcc	0.4086
Au	2.04	5.9	175	–0.722	fcc	0.4078
Zn	5.52	6.6	213	–0.33	hex	0.2659,0.5936
Pb	1.92	3.3	85	+0.085	fcc	0.4949
Fe	8.9	8.5	419	+0.244	bcc, fcc	0.2867
Co	6.25	9.0	400	–1.340	fcc, hex	0.2507,0.4070
Ni	6.7	9.0	476	–0.612	fcc	0.3524
W	5.0	6.3	334	+1.18	bcc	0.3150
Al	2.5	6.0	395	–0.30	fcc	0.4041

Table 4.G *Fermi energy and other related parameters of some selected elements*

Valency	*Metal*	*Electron concentration n in* $10^{28}/m^3$	*Fermi energy at 0 K* E_F *(eV)*	*Fermi velocity at 0 K* v_F *in* 10^6 *m/s*	*Fermi temperature* T_F *in* 10^4 *K*
1	Li	4.72	4.71	1.29	5.48
	Na	2.66	3.24	1.07	3.75
	Ag	5.86	5.48	1.39	6.37
	Au	5.90	5.51	1.39	6.39
	Cu	8.50	7.05	1.57	8.12
2	Mg	8.61	7.13	1.58	8.28
	Ca	4.60	4.68	1.28	5.43
	Ba	3.16	3.65	1.13	4.23
3	Al	18.06	11.63	2.02	13.49
	In	11.49	8.60	1.74	9.98

Table 4.H *Electrical conductivity and other transport properties of some selected metals*

Metal	*Electrical Conductivity σ in 10^5 $ohm^{-1}\ m^{-1}$*	*Concentration of free electrons n in $10^{28}/m^3$*	*τ_F in 10^{-14} s*	*v_F in 10^6 m/s*	*λ_F (in nm)*	$\frac{m^*}{m}$
Li	1.07×10^7	4.62	0.90	1.21	10.8	1.2
Na	2.09×10^7	2.65	3.20	1.11	34	1.2
Cu	5.76×10^7	8.50	2.70	1.60	53	1.01
Al	3.64×10^7	18.06	0.71	2.02	14.1	0.97
Ag	6.14×10^7	5.9	4.11	1.41	57.1	0.99
Zn	1.69×10^7	13.1	0.411	1.98	7.8	0.85

Table 4.I *Lorentz number of some useful metals*

Metal	*Electrical resistivity ρ in $10^{-8}\ \Omega$ m*	*Thermal conductivity σ_T $W m^{-1} K^{-1}$*	*Lorentz number (L)*	
			at 273 K in 10^{-8} $W\ \Omega\ K^{-2}$	*at 373 K in 10^{-8} $W\ \Omega\ K^{-2}$*
Al	2.74	422	2.01	2.06
Cu	1.72	388	2.23	2.33
Ag	1.60	231	2.31	2.37
Zn	5.92	129	2.31	2.33
Pb	2.08	36	2.47	2.56
Cd	7.69	101	2.42	2.44
Au	2.23	295	2.35	2.40

OBJECTIVE QUESTIONS

1. The electrical resistivity of metal is of the order of

   (a) $10^{-8}\ \Omega$ m (b) $10^6\ \Omega$ m (c) 100 Ω (d) $10^{-26}\ \Omega$ m

2. If *c* and *T* are the root mean square velocity and absolute temperature respectively, the dependence of them during the zig-zag motion is

   (a) $c \propto \frac{1}{T}$　　(b) $c \propto \sqrt{T}$

   (c) $c \propto T$　　(d) $c \propto T^2$

3. Metallic bond in the formation of metals is

   (a) due to the transference of electrons

   (b) due to sharing of electron

(c) due to interaction between the electron gas and ions
(d) none of these

4. If n, v_d and e are density of electrons, the electron's drift velocity and its charge respectively, then the current density is
   (a) $J_x = n\ v_d$
   (b) $J_x = n\ e\ v_d$
   (c) $J_x = \frac{ne}{v_d}$
   (d) $J_x = \frac{1}{nev_d}$
5. Drift velocity for unit electric field is
   (a) thermal conductivity
   (b) electric conductivity
   (c) electric polarization
   (d) mobility of charge carriers
6. The kinetic energy associated with the electron is
   (a) $\frac{2}{3}k_BT$
   (b) $\frac{3}{2}k_BT$
   (c) $2k_BT$
   (d) k_BT
7. The relation between resistivity and absolute temperature is
   (a) $\rho \propto T$
   (b) $\rho \propto \sqrt{T}$
   (c) $\rho \propto T^2$
   (d) $\rho \propto \frac{1}{T}$
8. When temperature increases lattice scattering increases and hence mobility
   (a) decreases
   (b) increases
   (c) remains unaltered
   (d) none of these
9. The classical value of molar electronic specific heat of metal is
   (a) 12.5 kJ/kmol/K
   (b) 12.5×10^3 kJ/kmol/K
   (c) 1000 J/kg/K
   (d) 14200 J/kg/K
10. The experimental value of mean free path of electrons in metals is
    (a) ten times greater than the classical value
    (b) hundred times greater than the classical value
    (c) ten times lower than the classical value
    (d) hundred times lower than the classical value
11. The Widemann-Franz law as per Drude-Lorentz theory is given by the following expression, where k_B Boltzmann constant, e is the charge of the electron and T is absolute tempertaure
    (a) $1.5\left(\frac{k_B}{e}\right)T$
    (b) $1.5\left(\frac{k_B}{e}\right)^2$
    (c) $3\left(\frac{k_B}{T}\right)$
    (d) $3\left(\frac{k_B}{T}\right)^2 T$

12. Fermi energy level is the highest energy state for an electron to occupy at 0 K in a metal

    (a) true (b) false

13. If E_F is Fermi energy of the metal at 0 K, the mean energy of the electron in the metal at the said temperature is

    (a) $\frac{3}{5}E_F$ (b) $\frac{5}{3}E_F$

    (c) $2\ E_F$ (d) $\frac{E_F}{2}$

14. If the mean energy of the electron in sodium is 3 eV, the Fermi energy of the metal is

    (a) 10 eV (b) 7 eV (c) 1 eV (d) 5 eV

15. The Fermi energy of the electron at 0 K is proportional to

    (a) $n^{2/3}$ (b) n^2 (c) n (d) $\frac{1}{n^{2/3}}$

    where n is the density of free electrons

16. The relation between Fermi energy and Fermi temperature is

    (a) $T_F = \frac{E_F}{k_B}$ (b) $T_F = k_B E_F$

    (c) $T_F = \frac{k_B}{E_F}$ (d) $T_F = E_F$

    where k_B is Boltzmann constant

17. The quantum mechanical value of molar electronic specific heat at high temperatures is about

    (a) $0.1\ R_u$ (b) $0.025\ R_u$ (c) $0.5\ R_u$ (d) $10\ R_u$

    where R_u is universal gas constant

18. The quantum mechanical expression for electrical conductivity

    (a) $\frac{m^*}{ne^2\tau_F}$ (b) $ne^2\tau_F$

    (c) $\frac{1}{ne^2\tau_F}$ (d) $\frac{ne^2\tau_F}{m^*}$

    where m^* and e are the effective mass and charge of the electron. τ_F is the relaxation time of the electron in the Fermi surface.

19. The experimental value of mean free path of the electron in copper is about

    (a) 38 nm (b) 380 nm (c) 2.8 nm (d) 0.1 nm

20. For temperatures greater than θ_D the Debye temperature $\sigma \propto T^5$ is known as Bloch-Gruneisen law:
    (a) true (b) false
21. If ρ_0 and $\rho_p(T)$ where ρ_0 is the residual resistivity and $\rho_p(T)$ is resistivity due to scattering phonons, then the total resistivity $\rho = \rho_0 + \rho_p(T)$ is
    (a) Bloch-Gruneisen law (b) Wiedemann-Franz law
    (c) Matthiessen's law (d) none of these
22. The quantum mechanical form of Wiedemann-Franz law is
    (a) $\frac{\sigma_T}{\sigma} = \pi^2 \left(\frac{k_B}{e}\right)^2$ (b) $\frac{\sigma_T}{\sigma} = \frac{\pi^2}{3} \left(\frac{k_B}{e}\right)^2 T$
    (c) $\frac{\sigma_T}{\sigma} = \frac{\pi^2}{2} \left(\frac{k_B}{e}\right)^2$ (d) $\frac{\sigma_T}{\sigma} = k_B T$
23. Anomalous expansion of water is due to the smaller proportions of the higher types water molecules H_2O, $(H_2O)_2$ and $(H_2O)_3$.
    (a) true (b) false
24. In the $(E - k)$ curve, the condition for energy discontinuity is
    (a) $k = \pm \frac{n\pi}{a}$ (b) $k = \pm \frac{a}{n\pi}$
    (c) $\frac{2a}{n\pi}$ (d) $\frac{n\pi}{2a}$
25. Since the *K* electron of copper is so tightly bound to the nucleus, its effective mass is infinite.
    (a) true (b) false
26. The energy level $\frac{27\hbar^2 \pi^2}{2ma^2}$ has a degeneracy of
    (a) 1 (b) 3 (c) 4 (d) 6
27. The density of energy states having energy values between E and E + dE is proportional to
    (a) $E^{1/2}$ (b) E (c) $E^{3/2}$ (d) $\frac{1}{E}$
28. Which of the following increases when copper is hard drawn into wires?
    (a) diameter (b) cross sectional area
    (c) specific gravity (d) resistivity

29. At very high temperatures, the mean free path and collision time in a conductor are proportional to

    (a) $\frac{1}{T}$ (b) $\frac{1}{T^2}$

    (c) T^3 (d) independent of temperature

30. On increasing the impurity concentration in the metal, the residual part of the resistivity

    (a) decreases (b) increases

    (c) remains constant (d) none of these

31. Which of the following group of elements are added to iron to improve its oxidation effect

    (a) magnesium and copper (b) silver and copper

    (c) chromium and aluminium (d) none of these

32. Which of the following metals has the lowest temperature coefficient of resistance?

    (a) copper (b) aluminium

    (c) silver (d) gold

33. Temperature coefficient of resistance is given by

    (a) $\frac{1}{R}\frac{dR}{dT}$ (b) $\frac{dR}{dT}$

    (c) $\frac{1}{R}\frac{dT}{dR}$ (d) $R\frac{dT}{dR}$

34. We have copper wires of 18 gauge, 20 gauge and 24 gauge. Which of the following will be lower for 18 gauge wire?

    (a) strength (b) cost

    (c) weight (d) resistance

35. Lead and copper is used in soldering

    (a) true (b) false

36. When temperature increases, scattering of free electrons increases and hence mobility decreases; thus resistivity

    (a) increases (b) decreases (c) remains constant

37. 60% of copper and 40% nickel gives constantan

    (a) true (b) false

38. Which of the following is used for making heating elements?

    (a) phosphor bronze (b) lithium

    (c) nichrome (d) none of these

39. Which of the following combination gives brass

    (a) 50% copper 50% aluminium (b) 70% copper 30% zinc

    (c) 30% zinc 70% copper (d) equal proportion of iron and copper

40. Nickel and chromium in the ratio 2:8 known as invar is used for fabricating a strain gauge

    (a) true (b) false

PROBLEMS AND SOLUTIONS

4.1 If Widemann-Franz law is valid under quantum mechanical treatment, compute the electrical resistivity of copper at 20ºC if the thermal conductivity at this temperature is 380 W m^{-1} K^{-1}.

***Solution*:**

Formula used:

$$\frac{\sigma_T}{\sigma} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T$$

$$\sigma_T \times \rho = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 T$$

$$\rho = \frac{\pi^2 \times k_B^2 \times T}{3 \times e^2 \times \sigma_T} = \frac{\pi^2 \times \left(1.38 \times 10^{-23}\right)^2 \times 293}{3 \times \left(1.6 \times 10^{-19}\right)^2 \times 380}$$

$$= \frac{\pi^2 \times 1.38^2 \times 10^{-46} \times 293}{4.8 \times 380 \times 1.6 \times 10^{-38}} = 1.89 \times 10^{-8}\ \Omega$$

i.e., $\boxed{\rho = 1.89 \times 10^{-8}\ \Omega m}$ ***Answer***

4.2 The Fermi energy of silver is 5 eV. Calculate the number of energy states for the free electrons in a cubical box of side 0.02 *m* lying below an energy of 3 eV.

***Solution*:**

Formula used:

$$\frac{\pi V}{2}\left[\frac{8m}{h^2}\right]^{3/2} E^{1/2}\, dE = Z(E)\, dE$$

$$\int Z(E)\, dE = \frac{\pi V}{2}\left[\frac{8m}{h^2}\right]^{3/2} \int_0^3 E^{1/2}\, dE$$

$$= \frac{\pi V}{3}\left[\frac{8m}{h^2}\right]^{3/2} \left[E^{3/2}\right]_0^3$$

$$= \frac{\pi \times 0.02^3}{3}\left[\frac{8 \times 9.1 \times 10^{-31}}{6.62^2 \times 10^{-68}}\right]^{3/2} \left[\left(3 \times 1.6 \times 10^{-19}\right)^{3/2}\right.$$

$$= \frac{\pi \times 0.02^3}{3}\left[\frac{72.8 \times 10^{37}}{6.62^2}\right]^{3/2} \left[\left(4.8 \times 10^{-19}\right)^{3/2}\right.$$

$$= 8.4 \times 10^{-6} \times 6.77 \times 10^{55} \times 3.3 \times 10^{-28} = 1.89 \times 10^{21}$$

$$\boxed{\int Z(E)\,dE = 1.89 \times 10^{21}} \quad \textbf{\textit{Answer}}$$

4.3 An alloy of a metal is found to have a resistivity of the order of 10^{-6} Ω m at 27°C. When it is heated to a temperature of 1000 K, the resistivity increases by 6.5%. Using Matthiessen's rule, determine the resistivity of the alloy.

***Solution*:**

$$\rho = \rho_0 + \alpha T_1$$

$$\rho + 0.065\,\rho = \rho_0 + \alpha T_2$$

$$0.065\,\rho = \alpha(T_2 - T_1)$$

$$\alpha = \frac{0.065\rho}{(T_2 - T_1)} = \frac{0.065 \times 10^{-6}}{700} = 0.9 \times 10^{-10}\,\Omega m K^{-1}$$

$$\rho_0 = \rho - \alpha T_1 = 10^{-6} - 0.9 \times 10^{-10} \times 300$$

$$\rho_0 = 10^{-6} - 2.7 \times 10^{-8} = 10^{-6}(1 - 0.0027)$$

i.e., $$\boxed{\rho_0 = 0.973 \times 10^{-6}\,\Omega\, m} \quad \textbf{\textit{Answer}}$$

4.4 Compute the average kinetic energy of a gas molecule at 27° C. Express the result in electron volt. If the gas is hydrogen, what is the order of magnitude of the velocity of the molecule at 27° C.

***Solution*:**

The equation used is

$$E = \frac{1}{2} m\bar{c}^2 = \frac{3}{2} k_B T$$

i.e., $$E = 1.5 \times 1.38 \times 10^{-23} \times 300 \text{ joule}$$

$$= \frac{1.5 \times 300 \times 1.38 \times 10^{-23}}{1.6 \times 10^{-19}} \text{ electron volt}$$

$$\boxed{E = 0.039 \text{ eV}} \quad \textbf{\textit{Answer}}$$

Also

$$\bar{c} = \sqrt{\frac{3k_B T}{M_H}} = \sqrt{\frac{3 \times 1.38 \times 10^{-23} \times 300}{2 \times 1.008 \times 1.67 \times 10^{-27}}}$$

$$= \sqrt{\frac{900 \times 1.38 \times 10^{4}}{2 \times 1.008 \times 1.67}} = 1920 \text{ metre/sec}$$

$$\boxed{\bar{c} = 1920 \text{ m/s}}$$ ***Answer***

4.5 The relaxation time of conduction electron in copper is 2.5 × 10^{-14} sec. Find the thermal conductivity of copper at 0°C. Assume density of electrons to be 8.5 × $10^{28}/\text{m}^3$.

***Solution*:**

The general expression for thermal conductivity is

$$\sigma_T = \frac{k_B n \bar{c}\, \lambda}{2}$$

and $$\lambda = \tau \bar{c}$$

Thus $$\sigma_T = \frac{k_B n \tau (\bar{c})^2}{2}$$

with $$\bar{c} = \sqrt{\frac{3k_B T}{m}}$$

i.e., $$\sigma_T = \left[\frac{k_B n \tau}{2}\right]\left[\frac{3k_B T}{m}\right]$$

$$= \frac{1.5 \times \left(1.38 \times 10^{-23}\right)^2 \times 2.5 \times 10^{-14} \times 273 \times 8.5 \times 10^{28}}{9.1 \times 10^{-31}}$$

$$\boxed{\sigma_T = 182\ W m^{-1} K^{-1}}$$ ***Answer***

4.6 In the Kronig-Penney model, determine the energy of the lowest band for P << 1.

***Solution*:**

We infer from Eqn. (Q 4.12.7) the energy of the lowest band corresponds to $k = \pm\frac{\pi}{a}$ as

$$\frac{P}{a\alpha}\sin\alpha a + \cos\alpha a = \pm 1$$

Considering only the magnitude of ± 1, we can write, $\frac{P}{\alpha a}\sin\alpha a = (1 - \cos\alpha a)$

$$\frac{P}{a\alpha}\left(2\sin\frac{\alpha a}{2} \times \cos\frac{\alpha a}{2}\right) = \left(1 - \cos\alpha a\right) = 2\sin^2\frac{\alpha a}{2}$$

i.e., $$\frac{P}{a\alpha} = \frac{2\sin^2\frac{\alpha a}{2}}{\left(2\sin\frac{\alpha a}{2} \times \cos\frac{\alpha a}{2}\right)}$$

or
$$\tan\frac{\alpha a}{2} = \frac{P}{a\alpha}$$

when 1 >> P, then

$$\frac{P}{a\alpha} = \frac{\alpha a}{2};\ \alpha^2 = \frac{2P}{a^2} = \frac{2mE}{\hbar^2} \quad \text{[Refer Eqn. Q 4.12.2]}$$

or
$$E = \frac{\hbar^2}{ma^2}P = \frac{h^2}{4\pi^2 ma^2}P$$

i.e.,
$$\boxed{E = \frac{\hbar^2}{ma^2}P} \quad \textbf{\textit{Answer}}$$

4.7 (a) Show that the wave length associated with an electron having an energy equal to the Fermi energy is given by

$$\lambda_F = 2\left[\frac{\pi}{3n}\right]^{1/3}$$

(b) If this wave length is 0.68 nm, identify the metal with the following table giving Fermi temperatures:

Metal	Li	Al	Na	Cu
T_F(K)	5.48×10^4	13.52×10^4	3.75×10^4	8.18×10^4

***Solution*:**

(a)
$$\frac{1}{2}mv_F^2 = E_F$$

$$m^2v_F^2 = 2mE_F$$

$$mv_F = p_F = \sqrt{2mE_F}$$

$$\lambda_F = \frac{h}{mv_F} = \frac{h}{\sqrt{2mE_F}}$$

∴ Substituting the value of E_F from Eqn. (Q 4.6.2), one gets,

$$\lambda_F = \left[\frac{h}{\sqrt{2m}}\right]\left[\frac{2m}{h^2}\right]^{1/2}\left[\frac{8\pi}{3n}\right]^{1/3}$$

or
$$\boxed{\lambda_F = 2\left[\frac{\pi}{3n}\right]^{1/3}} \quad \textbf{\textit{Answer (a)}}$$

(b) $\lambda_F^3 = \dfrac{8\pi}{3n};\ n = \dfrac{8\pi}{3 \times \left(0.68 \times 10^{-9}\right)^3} = 26.6 \times 10^{27}$

Refer Eqn. (Q 4.6.2):

$$E_F = 0.584 \times 10^{-34} (26.6 \times 10^{27})^{2/3} \text{ J}$$

or $$k_B T_F = E_F = 0.584 \times 8.91 \times 10^{-19} \text{ J}$$

$$T_F = \frac{0.584 \times 8.91 \times 10^{-19}}{1.38 \times 10^{-23}} = 3.77 \times 10^4$$

$$\boxed{T_F = 3.77 \times 10^4\ K}$$ ***Answer***

The metal is therefore sodium.

4.8 A copper wire of length 0.5 metre and diameter 0.3 mm has a resistance 0.12 Ω at 20°C. If the thermal conductivity of copper at 20°C is 390 W m⁻¹ K⁻¹, calculate Lorentz number. Compare this value with the value predicted by classical free electron theory.

***Solution*:**

The resistance,

$$R = \rho \frac{l}{a};\ \rho = \frac{aR}{l}$$

$$\sigma = \frac{l}{\left(\pi r^2\right) R} = \frac{0.5}{\pi \times \left(0.15 \times 10^{-3}\right)^2 \times 0.12} = 5.89 \times 10^7 \text{ ohm}^{-1} \text{ m}^{-1}$$

$$\frac{\sigma_T}{\sigma} = L = 1.5 \left(\frac{k_B}{e}\right)^2 = \frac{1.5 \times \left(1.38 \times 10^{-23}\right)^2}{\left(1.6 \times 10^{-19}\right)^2} = 1.116 \times 10^{-8}$$

i.e., $$\boxed{L = 1.116 \times 10^{-8}\ \text{W}\,\Omega\,\text{K}^{-2}}$$ ***Answer (a)***

The experimental value of L is obtained as follows:

$$L = \frac{\sigma_T}{\sigma \times T} = \frac{390}{5.89 \times 10^7 \times 293} = 2.26 \times 10^{-8}\ W\,\Omega\,K^{-2}$$

$$\boxed{L = 2.26 \times 10^{-8}\ \text{W}\,\Omega\,\text{K}^{-2}}$$ ***Answer (b)***

4.9 A copper wire has a resistivity of 1.7×10^{-8} at room temperature of 300 K. If copper is highly pure, find the resistivity at 700 K.

***Solution*:**

The equation used is

$$\rho = \rho_0 + \rho_p\left(T\right) = \rho_0 + \alpha T$$

Since copper is highly pure,

$$\rho_0 = 0$$

Thus $\rho = \alpha T$

$$1.7 \times 10^{-8} = 300\alpha$$

$$\alpha = \frac{1.7 \times 10^{-8}}{300}$$

Resistivity at 700° C is given by,

$$\rho = \alpha T = \frac{1.7 \times 10^{-8} \times 973}{3} = 5.52 \times 10^{-8}$$

$$\boxed{\rho = 5.52 \times 10^{-8}\,\Omega\,\text{m}}$$ ***Answer***

EXERCISE

4.1 The resistivity of aluminium at room temperature is $2.62 \times 10^{-8}\ \Omega$ m. Calculate (i) the drift velocity of the conduction electrons in a field of 50 V/m, (ii) their mobility, (iii) their relaxation time and mean free path on the basis of classical free electron theory. Density of aluminium is 2700 kg/m^3.

(***Ans*:** 0.666 m/s, 1.32×10^{-3} m^2 V^{-1} s^{-1}, 0.75×10^{-14} s and 0.88 nm)

4.2 The resistivity of aluminium at room temperature is $2.62 \times 10^{-8}\ \Omega$ m. Calculate the incremental velocity acquired by the free electrons in a field gradient of 100 volt/metre. (***Ans*:** 0.13 m/s)

4.3 Find the difference in energy between the neighbouring levels at the highest energy state in a cubical box of sodium of side 1 cm. The Fermi energy of sodium is 3 eV. Given: $n_x = n_y = n_z$.

(***Ans*:** 1.2×10^{-7} eV)

4.4 Evaluate the Fermi function for an energy k_BT above Fermi energy. (***Ans***: 0.269)

4.5 Given that the Fermi energy of copper is 7 eV at room temperature, what is the number of electrons per unit volume with energy greater than 8 electron volt. (***Ans*:** 9.8×19^9 /m^3)

4.6 Calculate the heat capacity of the electron gas at room temperature in copper assuming one free electron per atom. Compare this with the lattice specific heat value of 2.4×10^4 J/kmol/kelvin. Fermi energy of copper is 7 eV. (***Ans*:** 1.45×10^2 J $kmol^{-1}$ K^{-1}, 0.608%)

4.7 A sample of pure copper has resistivity of $1.5 \times 10^{-8}\ \Omega$ m at 0°C. If nickel is added to copper, the resistivity increases by $1.2 \times 10^{-8}\ \Omega$ m per added atomic percent silver. If the alloy consists of 0.25 atomic percent copper and 0.2 atomic percent silver, calculate the theoretical resistivity of the alloy at 300 K and 4 K. (***Ans*:** $1.945 \times 10^{-8}\ \Omega$ m, $0.42 \times 10^{-8}\ \Omega$ m)

4.8 Show that for a simple square lattice (two dimensions), the kinetic energy of a free electron at a corner of the first zone is higher than that of an electron at mid point of a side face of the zone by a factor of 2.

4.9 Assuming that a current density of 10^4 amp/m^2 flows through a sample of standard metal and $\tau = 10^{-13}$ sec, calculate the electric field to derive this current. What is the average drift velocity of the electrons? Compare it with the Fermi velocity.

(***Ans*:** 5.9×10^{-5} V/m, $v_d = 1.04 \times 10^{-6}$ m/s, $v_F = 10^{12}\ v_d$)

4.10 If the size of the one dimensional potential well is replaced by interatomic distance 0.3 nm, show that the energy of the particle becomes approximately $4n^2$ eV.

4.11 If the fermi energy of a metal is 0.365 eV at 0 K with a concentration of 10^{27} atom/m^3, compute the constant of proportionality. (***Ans*:** 3.65×10^{-19})

5

Superconductivity

5.1 INTRODUCTION

KEY WORDS

resistivity, thermal vibrations, impurity scattering, residual resistivity, critical temperature, phase diagram, Kamerlingh Onnes, electrical resistance and superconductivity, refrigeration, cryostatic apparatus, critical temperature, phenomenon of superconductivity, ceramic materials, critical magnetic field, magnetic induction, Meissner effect, thermal conductivity, bound system, infinite conductivity, neutron scattering, critical temperature, Faraday's law of induction, flux, transition temperature, critical field, phase diagram, free energy, condensation energy, Type I and Type II superconductors, perfect diamagnetism, hysteresis, flux pinning, hard superconductors, flux jumping, quench, critical field and transition temperature, London penetration depth, current density, characteristic length, Ginsberg-Landu theory, characteristic length, intrinsic coherence length, mean free path, normal conduction electrons, penetration depth, fluxoid, lower critical field, upper critical field, specific heat, Sommerfeld constant, Fermi surface, lattice contribution, lattice specific heat, Boltzmann factor, isotopic effect, ionic mass, electron-electron interaction, cooper-pairs, thermodynamic aspects, reversible transition, free energy density, internal energy, entropy, pressure, volume, external field, magnetic moment, first law of thermodynamics, BCS microscopic theory, correlated system, third law of thermodynamics, second order phase transition, Ruter's formula, mechanical properties, thermal conductivity, superelectrons, exchange energy, thermal switches, thermoelectric effects, Thomson relations, Peltier and Thomson coefficients, London's theory, superelectrons and normal electrons, conduction electron density, Meissner effect, scattering and lattice vibrations, density of charge carriers, Ohm's law, current density, magnetic induction vector, London equation, London's penetration depth, coherence length, condensed state, microscopic theory, phonon interactions, cooper-pairs, Bardeen, Cooper and Schrieffer, de Broglie waves, zero electrical resistivity, phonons (lattice waves/vibrations), scattering centres, isotopic effect, Fröhlich, the electron-phonon interaction, virtual phonon, Arrhenius plot, electron-lattice interaction energy, electron density of states, Fermi level, dynamic process, collective state, attenuation, copper oxide perorskites, ceramic oxide, antiferromagnetism, 1-2-3 compounds, YBCO, joule heating, memory element, ductility, Josephson effect, SQUID.

5.1 INTRODUCTION

The electrical resistivity of many metals and alloys at low temperatures is nearly constant. For a perfectly pure metal, where the electron motion is impeded only by the thermal vibrations of the lattice, the resistivity should approach zero as the temperature is reduced to 0 K. Any real specimen of a metal cannot be perfectly pure and will contain some impurities. Therefore the electrons, in addition to being scattered by *thermal vibrations* of the *lattice atoms*, are scattered by the *impurities*, and this *impurity scattering* is more or less independent of temperature. As a result, there is a certain "*residual resistivity*" (ρ_0) which remains even at the lowest temperatures. The more impure the metal, the larger will be its residual resistivity.

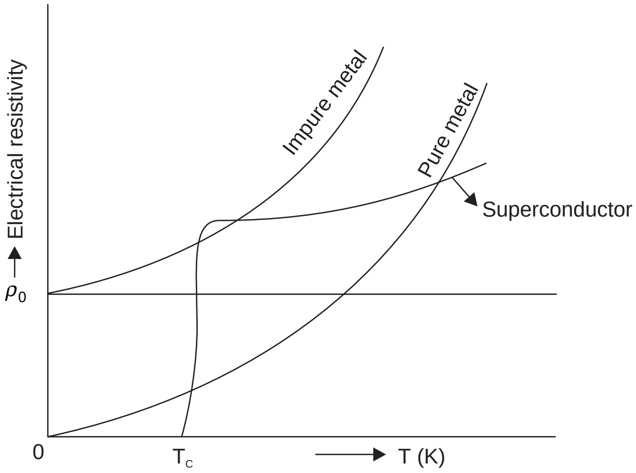


Fig. 5.1.1 *Variation of resistance of a metal and a superconductor with temperature*

However a good number of metals and alloys behave differently at low temperatures near absolute zero. As the temperature decreases, the resistivity at first decreases regularly, like that of any metal. At a particular temperature (*known as critical temperature*), *a phase transition* occurs and the resistivity suddenly drops to zero as shown in Fig. 5.1.1. The transition from normal conductivity occurring over a very narrow range of temperature of the order of 0.05 K (presence of small trace of impurity may be the cause for the range of temperature over which it drops to zero). This phenomenon was first observed by *Kamerlingh Onnes* in 1911 while studying the behaviour of mercury at liquid helium temperature. He observed that at 4.2 K, the resistance of mercury suddenly vanished. This phenomenon of disappearance of *electrical resistance* below a certain temperature is called *superconductivity*. This zero resistivity was observed in other metals such as Al, Pb, Sn, Nb, etc.

Refrigeration is cheap when the difference between the working temperature and that of the *heat sink* is not too great. A domestic refrigerator requires about 0.2 J to remove 1 J of heat from its interior. However, liquid helium boils at 4.2 K and 300 J must be expended to remove 1 J from a body at 4.2 K to be rejected to a heat sink at 300 K, when the *efficiency* of the cooling plant is taken into account. So using liquid helium means keeping down heat leaks as much as possible: usually liquid nitrogen is used to cool radiation shields surrounding the liquid helium, and the *cryostatic apparatus* is bulky and costly- so much so that superconducting magnets are the only large-scale application of superconductivity.

Though some bubble chamber and accelerator magnets are enormous, there are not many of them and the tonnage of superconducting material used word-wide is relatively small. The economic picture will be vastly changed, however, when superconducting materials capable of carrying reasonable current densities are able to operate at 77 K. In such a case large *generators*, *motors*, *transformers* and *transmission lines* will be a practical.

Q 5.1 Give an elementary account of superconductivity.

Certain substances completely lose their electrical resistance below a *certain critical temperature*. This critical *temperature* is different for different substances. When a substance loses its electrical resistance, a current set up in it unaltered for ever. This phenomenon is known as *superconductivity*. The *characteristic transition temperature* T_c varies form 0.15 K to 20 K for pure metals. However *ceramic materials* have transition temperature around 90 K. Superconducting elements have at room temperature, greater electrical resistivity than others. When impurities are added to superconducting elements, the superconducting properties are not lost, but the transition temperature is lowered. The transition temperature of an element differs for different *isotopes*.

Below the transition temperature, when a substance is a superconductor, the superconducting property may be destroyed by the application of a sufficiently strong magnetic field. At any given temperature below T_c, there is a *critical magnetic field* H_c such that the superconducting property is destroyed by the application of a magnetic field of intensity $H \geq H_c$. The value of H_c decreases as the temperature (which is less than T_c) increases. See Fig. Q 5.2.2 (*a*).

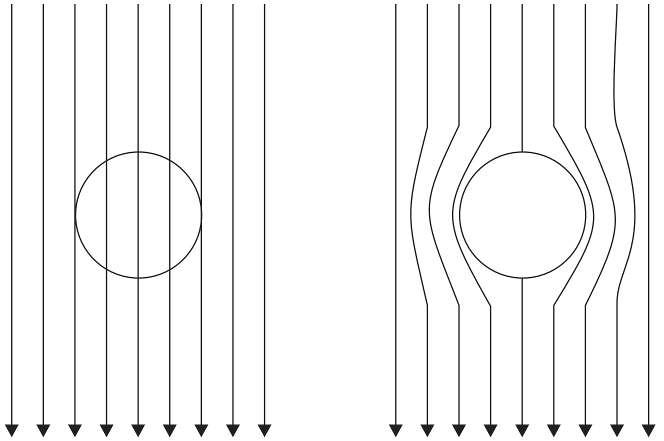


Fig. Q 5.1.1 *The Meissner effect (a) Normal $T > T_c$ or $H > H_c$ (b) Superconducting $T < T_c$ or $H < H_c$*

If a superconducting substance is placed in a magnetic field H_c such that $H < H_c$, at a temperature $T \leq T_c$, it is found that no lines of magnetic induction exist inside the substance. The substance, therefore, pushes out the lines, of *magnetic induction*, so that B = 0 inside the substance. See Fig. Q 5.1.1. This is known as *Meissner effect*. The thermal properties such as *specific heat* and *thermal conductivity* of a substance change abruptly when it passes over into the superconducting state. The phenomenon of superconductivity can be explained satisfactorily on the basis of wave mechanics. In ordinary metal, the electrical resistance is the result of the collisions of the conduction electrons with the vibrating ions in the crystal lattice. In the superconducting state, the electrons tend to scatter in pairs rather than individually. This gives rise to an exchange force (similar to the force between the atoms in a hydrogen molecule and the forces between *nucleans* in a nucleus) between the electrons. The force is attractive, and is very strong if the electrons have opposite spins and momenta.

In the superconducting state, the forces of attraction between the conduction electrons exceed the forces of electrostatic repulsion. The entire system of conduction electrons then becomes a *bound system*. No transfer of energy takes place from this system to the lattice ions. If an electric field is established inside the substance, the electrons gain additional kinetic energy and give rise to a current. But they do not transfer this energy to the lattice, so that they do not get slowed down. As a consequence of this, substance does not possess any electrical resistivity.

Q 5.2 Discuss the important experimental results in the study of superconductivity using simple models and suitable diagrams.

Answer*: 1. *Infinite conductivity

When a superconducting specimen is cooled to a temperature below the transition temperature, the resistivity of the sample becomes zero, and not just small. Experimental measurements conclude that the resistance of a superconductor is about 10^{18} times smaller than that of a metal; or it is zero for all practical purposes. Other conclusions are: there is no change in crystal structure at this temperature; similarly, the transition is not a *magnetic transition*, as can be inferred from *neutron scattering* experiments. The state that is produced is clearly a completely new thermodynamic state associated with an electronic transition. Assuming that the relationship between current and electric field is given by *Ohm's law*,

$$\vec{J} = \sigma \vec{E} \tag{Q 5.2.1}$$

in order that the current density is infinite, the electric field E inside a superconductor must be zero.

2. *Meissner effect*

Although the infinite conductivity characterizes a superconducting state, the truly different nature of the superconducting state is manifested in its magnetic property. Let us first consider a normal metal say aluminium or lead in a uniform magnetic field.

Refer Fig. Q 5.2.1*a*. The given metal is first cooled to a temperature, below the *critical temperature*, making it superconducting. This cooled sample is now placed under the influence of a uniform external field. The flux lines will not penetrate into the specimen or they are excluded. This is because (according to *Faraday's law of induction*), currents induced in the sample will oppose any change of flux through the specimen. Since the sample is a superconductor, such currents, once induced, will persist in the *absence of any resistance* will keep the *magnetic flux* out. The worth mentioning point is that, not only does a superconductor oppose the entry of *flux* into a superconducting specimen, it expels any flux that might be there in the specimen before it became a superconductor. This behaviour is best illustrated in Fig. Q 5.2.1 (b), where a normal metal in a magnetic field is shown. Since the metal is in a normal state, magnetic flux lines will penetrate the sample. When such a sample is cooled to a temperature below its transition temperature, the magnetic flux, which is already inside the specimen, will be expelled. This is contrary to the expectation from *Faraday's law* which would tend to trap the flux which is already inside the specimen. Thus, a superconductor is not just a perfect conductor, it is also a *perfect diamagnetic*

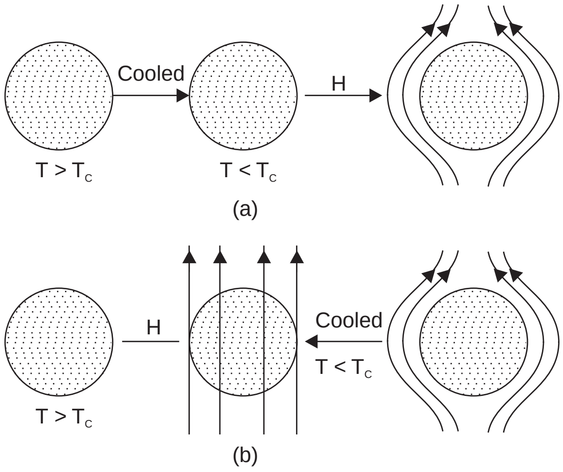


Fig. Q 5.2.1 *Meissner effect. In Fig. Q 5.2.1 (a), the sample is first cooled and then subjected to the field, while in (b) a normal metal is first subjected to a magnetic field and then cooled below critical temperature*

3. *Critical field*

Prof. Onnes important finding is that the application of suitable magnetic fields destroy superconductivity. The minimum magnetic field necessary to destroy superconductivity is called *critical field* (generally denoted as H_c). It is also observed that this critical magnetic field is a function of temperature. Fig. Q 5.2.2 shows that the critical magnetic field H_0 near absolute zero falls to zero at the *superconducting transition temperature*. This figure can also be called *phase diagram* of a superconductor. The metal will be a superconducting one for any combination of the applied magnetic field and temperature. This combination gives a point P. The arrows indicate, the metal can be driven into the normal state by increasing either the field or temperature.

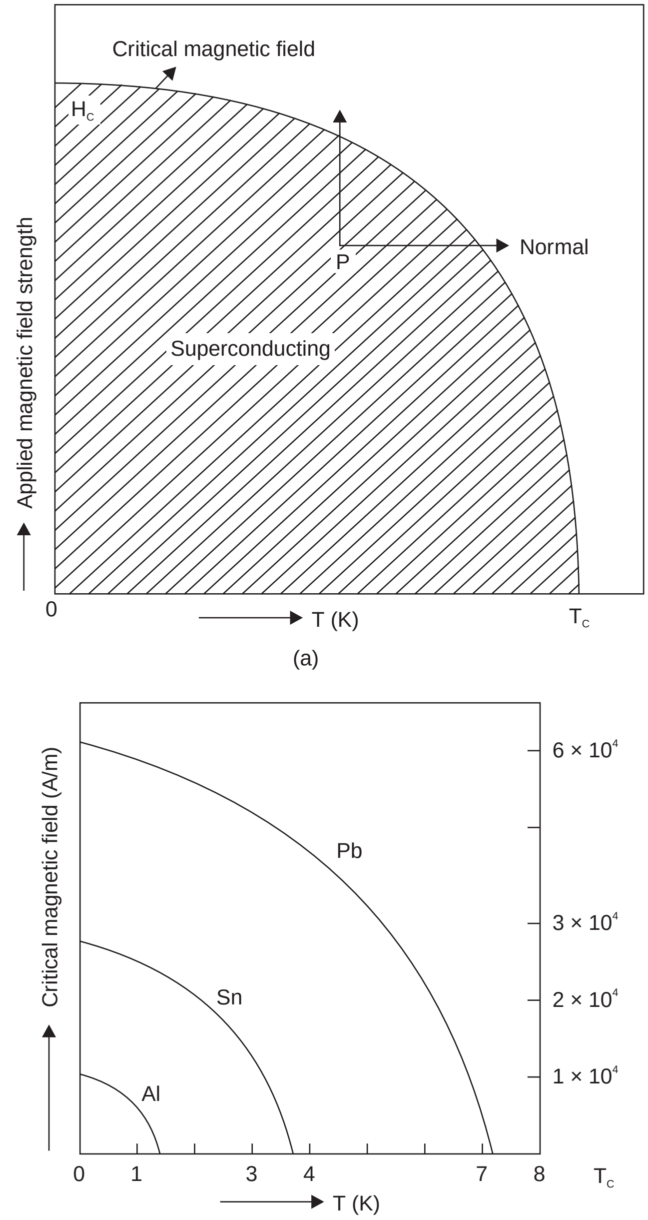
Metallic elements with *low transition temperatures* have low electric fields at zero degree kelvin. Hence every superconductor has a different *Phase diagram.* See Fig. Q 5.2.2 (b). As the magnetic field strength is increased, flux lines start penetrating the sample, destroying superconductivity.

If $H_c(T)$ is the strength of the magnetic field required to destroy the superconductivity in a specimen at a temperature T, the difference in the *free energy* per unit volume between the superconducting state and the normal state at this temperature is given by the energy density of the magnetic field.

$$\boxed{A_n(T) - A_s(T) = \frac{H_c^2(T)}{8\pi}} \qquad \text{(Q 5.2.1)}$$

This energy difference is called the *condensation energy*. Experimental results guide that the critical fields fall almost as the square of the absolute temperature, so the curves can be closely approximated by the parabola of the form:

$$\boxed{H_c = H_0\left[1 - \left(\frac{T}{T_c}\right)^2\right]} \qquad \text{(Q 5.2.2)}$$



(a)

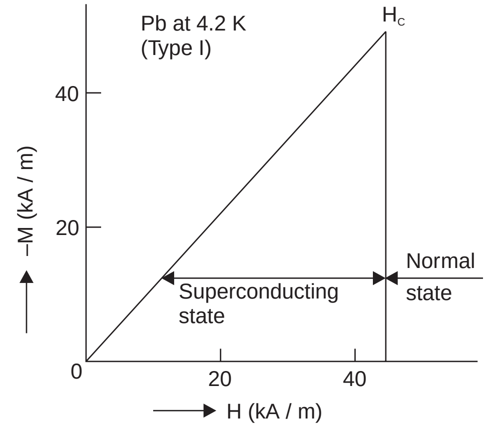
(b)

Fig. Q 5.2.2 *(a) Phase diagram of a superconductor (b) Critical fields of superconductors*

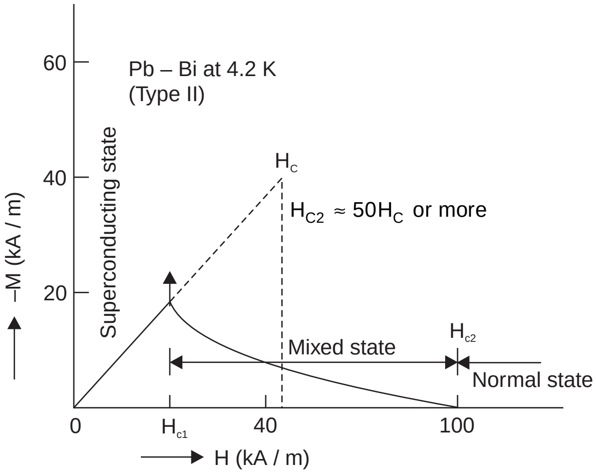
Here H_o and T_c are the critical field at 0 K and the critical temperature respectively for a given specimen. Thus the critical field at any temperature can be computed using this equation.

Q 5.3 Explain Type I and II superconductors. Also briefly discuss the important property changes during the transition.

***Answer*:** Both type I and type II materials up to H_{c1} exhibit *perfect diamagnetism*, since $\mathbf{M} = -\mathbf{H}$, $\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{M}) = 0$, and $\chi = \dfrac{M}{H} = -1$. But on reducing the magnetic field from H_c or H_{c2}, we find that it does not trace the same path in reverse as when we increase the field from zero. In fact, in type II superconductors, the magnetization follows the path shown in Fig. Q 5.3.1 (c) below the field axis, while in type I materials it follows a path a little below the perfectly diamagnetic plot. Thus both samples show hysteresis, but it is much more pronounced for the type II material. Indeed, if a type I superconductor is made from very pure material, and it is well annealed so that it contains very few dislocations, then the *hysteresis* is slight. The hysteresis indicates that the flux which penetrated the sample while the field was increasing is not all expelled when the field is reduced. Cold working a type I material increases the *hysteresis* considerably, so that dislocations and other defects must cause *flux pinning*: this is a clue to making hard superconductors that will keep their magnetic flux in place-make them 'dirty'. Movement of magnetic flux (known as *flux-jumping*) is not desirable in a superconducting wire because it causes heating and reversion of superconducting regions to normal conduction, leading sometimes to a runway condition known as a *quench* in which the whole solenoid may revert suddenly to normal conduction.



(a)



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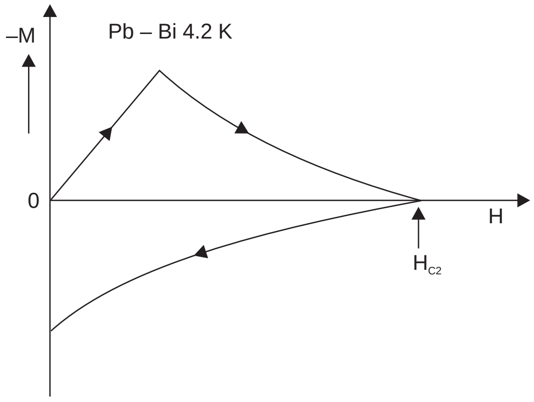


(c)

Fig. Q 5.3.1 *(a) Magnetization curve for type I superconductors*
(b) Magnetization curve for type II superconductors
(c) Hysteresis in a type II superconductors

The critical fields are found to be highly dependent on the temperature, and in type I materials we can write,

$$\boxed{H_c(T) = H_c(0)\left[1 - \left(\frac{T}{T_c}\right)^2\right]} \qquad \text{(Q 5.3.1)}$$

where $H_c(T)$ is the *critical field* at T K and T_c is the *transition temperature*. For lead, H_c (4.2) = 42 kA/m, T_c = 7.2 K, so $H_c(0)$ 64 *kA*/m. This relation is approximately true for upper critical field of type II materials.

It was believed that Maxwell's equations be supplemented in the case of superconductors as per F. London and H. London around the year 1935. This leads to

$$\boxed{\nabla \times \vec{J} = \frac{\vec{H}}{\lambda_L^2}} \qquad \text{(Q 5.3.2)}$$

where λ_L is the *London penetration depth*. Now $\nabla \times \mathbf{H} = \mathbf{J}$ by Maxwell's equations, where **J** is the current density, so $\nabla \times \nabla \times \mathbf{H} = \nabla \times \mathbf{J}$, which is $-\frac{\vec{H}}{\lambda_L^2}$ from Eqn. (Q 5.3.2). It can be shown that $\nabla \times \nabla \times \mathbf{H} = -\nabla^2\ \mathbf{H}$, so that $\nabla^2 \mathbf{H} = \frac{\vec{H}}{\lambda_L^2}$. Considering a superconductor with the field parallel to its surface, whose normal is the x–axis, we can see that

$$\boxed{H(x) = H_0 \exp(-x/\lambda_L)} \qquad \text{(Q 5.3.3)}$$

is a solution for the equation if $x = 0$ is the surface and H_0 is the field at the surface. The applied field thus penetrates into the superconductor with exponential decay and *characteristic length* λ_L. For thin films with thickness, $t << \lambda_L$, the field penetrates uniformly, there is no Meissner effect and the critical field becomes very large. For lead, λ_L = 37 nm, so the films have to be very thin for H_c to be increased much.

Another characteristic length, which arose from the *Ginsberg-Landau theory* is known as the *intrinsic coherence length*, $\in_0$. i.e., $\in_0$ is the distance (apparently) over which the superconducting electron concentration remains constant in a varying applied magnetic field. The B C S theory showed that $\in_0 = \dfrac{\hbar v_F}{\pi \Delta}$, where v_F is the speed of electrons at the Fermi surface and Δ is a difference in superconducting energy states. In type II superconductors, the *coherence length* depends on the *mean free path* of *normal conduction electrons*, l_m, as do the *penetration depth*, λ, and $\in_0$. Within a factor of $\sqrt{2}$:

$$\in = \sqrt{\in_0 l_m} \text{ and } \lambda \approx \lambda_L \left[\sqrt{\frac{\in_0}{l_m}}\right] \tag{Q 5.3.4}$$

Thus $\dfrac{\lambda}{\in} = k = \dfrac{\lambda_L}{l_m}$, and it is found from Ginsberg-Landau theory that $H_{c1} = \dfrac{H_c}{k\sqrt{2}}$ and $H_{c2} = \left(k\sqrt{2}\right) H_c$, so that $H_{c1} H_{c2} = H_c^2$. The superconductor is type I when $k < 1$, while it is type II if $k > 1$.

In a type II superconductor, the magnetic flux penetrates the material so that there are alternate regions of normal and superconducting material. In the normal region the field strength is H_a, the same as the applied field, and in the superconducting layer the field strength falls exponentially. The flux in the normal material is quantized in multiples of ϕ_0 called a *fluxoid*, which is given by:

$\phi_0 = \dfrac{h}{2e} = 2.07 \times 10^{-5}$ T m^2. At the *lower critical field*, H_{c1}, the flux h, from a *fluxiod* penetrates a distance λ into the surrounding superconducting material, so the area normal to the flux is roughly $\pi \lambda^2$, and the flux is $\mu_0 \pi \lambda^2 H_{c1}$ in T m^2, which must be equal to ϕ_0, so

or

$$\boxed{\begin{aligned} \mu_0 \pi \lambda^2 H_{c1} &= \phi_0 = \frac{h}{2e} \\ H_{c1} &= \frac{h}{2\pi e \mu_0 \lambda^2} = \frac{\hbar}{e \mu_0 \lambda^2} \end{aligned}} \tag{Q 5.3.5}$$

Suppose H_{c1} = 10 k A/m, then we find λ =230 *nm*. At the *upper critical field limit*, the *fluxoids* are packed together as closely as possible and $\in$ is the smallest possible depth of penetration of the flux into the surrounding superconducting material, giving

$$\pi \in^2 H_{c2} = \phi_0 = \frac{h}{2e}$$

leading to

$$\boxed{H_{c2} = \frac{\hbar}{e \mu_0 \in^2}} \tag{Q.5.3.6}$$

Given that H_{c2} = 1 MA/m, we find $\in$ = 23 *nm*, *k* = 10 and H_c = 100 kA/m.

Specific Heat

Fig. Q 5.3.2 shows that at temperatures well below the transition temperature the *specific heat* of the superconducting metal falls to a very small value, becoming even less than that of the normal metal. The difference in the values of the specific heats of the superconducting and normal states is the result of a change in the electronic specific heat. In order to understand the difference in specific heats we need, therefore, to be able to deduce the value of the electronic specific heat from the experimentally measured values of the total specific heat. This may be done as follows: for a *normal metal* at low temperatures, the total specific heat has the form:

$$\boxed{C_n = C_{la} + \left(C_{el}\right)_n = A\left(\frac{T}{\theta_D}\right)^3 + \lambda T} \tag{Q 5.3.7}$$

where A is a constant with the same value for all metals. The *Debye temperature* of the lattice θ_D, and the *Sommerfeld constant* γ, which is a measure of the density of the electron states at the *Fermi surface*, both vary from metal to metal. We can evaluate the *lattice contribution*, C_{la} as follows:

$$\frac{C_n}{T} = \left(\frac{A}{\theta_D^3}\right)T^2 + \gamma,$$

so a plot of the experimentally determined values of $\frac{C_n}{T}$ against T^2 should give a straight line whose slope is $\frac{A}{\theta_D^3}$ and whose intercept is γ. Hence, from measurements on the superconductor in the normal state, i.e., by applying a magnetic field greater than H_c, we can determine the *lattice specific* heat, $C_{lat} = A\left(\frac{T}{\theta_D^3}\right)^3$. The lattice specific heat is the same in both the superconducting state and normal states, so, by subtracting the values of C_{la} from the total specific heat C_s of the superconducting state, we can obtain the electronic contribution $(C_{el})_s$.

It is difficult to obtain accurate experimental values of the specific heats of superconductors, because at very low temperatures the specific heats become very small. However, careful measurements have revealed that at temperatures well below the transition temperature the electronic specific heat of a metal in the superconducting state varies with temperature in an exponential way,

$$(C_{el})_s = a\exp(-b/k_BT)$$

where a and b are constants. Such an exponential variation suggests that as the temperature is raised electrons are excited across an energy gap above their ground state. The number of electrons excited across such a gap would vary exponentially as the temperature. BCS theory of superconductivity also predicts such a gap in the energy levels of the electrons. Because, of the energy gap, the number of electrons excited across the gap is given by the Boltzmann factor, exp $(-\Delta/k_BT)$ with 2Δ as the energy gap:

$$\boxed{(C_{el})_s = a\exp(-\Delta/k_BT)} \tag{Q 5.3.8}$$

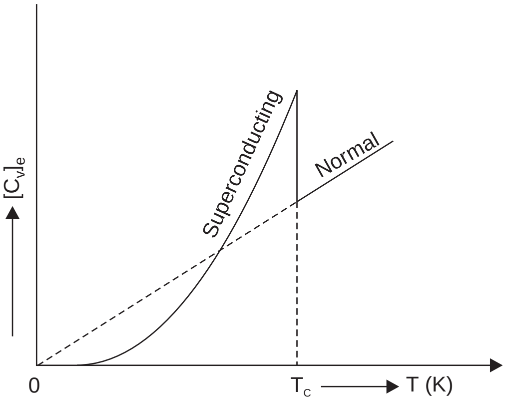


Fig. Q 5.3.2 *Temperature dependence of the electronic specific heat in normal and superconducting states*

Isotope Effect

The other distinct property of the superconductors is the isotopic effect. For the same material, the transition temperature is found to depend on the *ionic mass* by a relationship of the form:

$$\boxed{T_c \propto \frac{1}{M^\beta}}\text{; or } T_c\,M^\beta = \text{ a constant}$$

with $\beta = \dfrac{1}{2}$ for all metals. As an example, for mercury T_c varies from 4.185 K to 4.146 K as the isotopic mass varies from 199.5 to 203.4. The argument was that isotopic mass can enter in the process of the formation of the superconducting phase of the electron states only through the electron-phonon interaction. i.e., the lattice plays an important role in what is basically an electronic process. This provides a sound evidence for the phonon mediated attractive *electron-electron interaction* leading to the formation of *cooper-pairs*.

Q 5.4 Discuss with suitable theory the thermodynamical behaviour of superconductors. List out some of the thermodynamically related properties of superconductors.

***Answer*:** Here we discuss a few *thermodynamic aspects* of superconductors. The transition from the normal to the superconducting state is thermodynamically *reversible transition*. Though the free energy density g_n of a metal in the normal state is independent of the strength of the applied magnetic field say $H_{a,}$ the application of a magnetic field raises the *free energy density* g_s of the metal in the superconducting state by an amount $\frac{\mu_0 H_a^2}{2}$. The critical field H_c is that field strength which would be required to raise the free energy of the superconducting state above that of the normal state. Hence the difference in free energy between the normal and superconducting states, in an applied field of strength H_a is:

$$\boxed{g_n - g_s(H_a) = \frac{1}{2}\mu_0\left(H_c^2 - H_a^2\right)} \qquad \text{(Q 5.4.1)}$$

The *free energy of a magnetic body* can be written,

$$\boxed{G = U - TS + pV - \mu_0 H_a M} \qquad \text{(Q 5.4.2)}$$

where U is the *internal energy*, S the *entropy*, p the *pressure*, V the *volume*, H_a the applied *magnetic field* and M the *magnetic moment.* If the pressure and applied field strength are kept constant but the temperature is varied by an amount dT there will be a change of free energy,

$$dG = dU - T\,dS - S\,dT + dV - \mu_0 H_a\,dM$$

By the *first law of thermodynamics*

$$dU = T\,dS - p\,dV + \mu_0 H_a\,dM$$

Thus $\quad dG = -S\,dT$

or

$$\boxed{S = -\left(\frac{dG}{dT}\right)_{p,H_a}} \qquad \text{(Q 5.4.3)}$$

The general equation for entropy per unit volume is:

$$s = -\left[\frac{\partial g}{\partial T}\right]_{p,H_a}$$

Substituting Q 5.4.1 into this equation assuming H_a does not depend on temperature, one gets

$$\boxed{s_n - s_s = -\mu_0 H_c\left(\frac{dH_c}{dT}\right)} \qquad \text{(Q 5.4.4)}$$

Since the critical magnetic field decreases with increase of temperature, $\frac{dH_c}{dT}$ will be negative and hence the R.H.S of the above equation must be positive. Thus we have been able to deduce that the *entropy* of the superconducting state is less than that of the normal state. i.e. the degree of order in a superconducting state is much higher than that in the normal state. This conclusion is in total agreement with *BCS microscopic theory* of superconductivity where in a superconductor '*condense*' into a highly *correlated system* of electron pairs. The critical field H_c falls to zero as the temperature is raised towards T_c. The entropy difference between the normal and superconducting states vanishes at this transition temperature. Again by the third law of thermodynamics s_n must also be equal to s_s at $T = 0$. From the observation that the entropies of the superconducting and normal states must be the same at $T = 0$, we can deduce from Eqn. Q 5.4.4 that, since the critical field H_c is not zero, $\frac{dH_c}{dT}$ must be zero at 0 K. This is in accordance with the experimental observation that, for all superconductors, the slope of the H_c versus T curve (Fig. Q 5.2.2) appears to become zero as the temperature approaches 0 K.

Specific Heat-Once Again

Many physical properties of superconductors have been understood from a study and the measurement of their specific heat. The solid curve in Fig. Q 5.3.2 shows how the specific heat of a typical type 1 superconductor varies with temperature in the absence of any applied magnetic field. The corresponding curve for the normal state can be obtained by making measurements in an applied field strong enough to derive the superconductor into a normal state. The general expression for entropy is:

$$s = -\left[\frac{\partial g}{\partial T}\right]_{p,H_a}$$

Hence for the superconducting-normal transition at T_c

$$\boxed{\left(\frac{\partial g}{\partial T}\right)_n = \left(\frac{\partial g}{\partial T}\right)_s} \qquad \text{(Q 5.4.5)}$$

as $s_n = s_s$ at T_c

A phase transition which satisfies this condition is known as *second order phase transition.* A second order transition has two important characteristics: at the transition there is no latent heat, and there is a jump in the specific heat. The first characteristic follows immediately from the fact $dQ = Tds$ and we have seen that at the transition temperature $s_n = s_s$. Hence when the transition occurs there is no change in entropy and therefore no latent heat, and there is a jump in the latent heat. The second condition follows from the fact that the specific heat of a material is given by:

$$C = vT\frac{\partial s}{\partial T}$$

with v-the volume per unit mass, so the difference in the specific heats of the superconducting and normal states may be obtained from Eqn. Q 5. 4. 4

$$\boxed{C_s - C_n = vT\mu_0 H_c \frac{d^2 H_c}{dT^2} + vT\mu_0\left(\frac{dH_c}{dT}\right)^2} \qquad \text{(Q 5.4.6)}$$

Since at the transition temperature, $H_c = 0$ and so we have for the transition in the absence of an applied field:

$$\boxed{C_s - C_n = vT_c\,\mu_0\left(\frac{dH_c}{dT}\right)^2_{T_c}} \tag{Q 5.4.7}$$

This is the famous *Rutger's formula*, and it predicts the value of the discontinuity in the specific heat of a superconductor at the transition temperature. If $v = 1$, then equation Q 5.4.7 can be presented as:

$$\boxed{C_s - C_n = T_c\,\mu_0\left(\frac{dH_c}{dT}\right)^2_{T_c}} \tag{Q 5.4.8}$$

Mechanical Pressure

It is experimentally found that both the transition temperature and the critical magnetic field of a superconductor are slightly altered if the material is mechanically stressed. Many of the mechanical properties of the superconducting and normal states are thermodynamically related to the free energies of these states, and we have seen that the critical magnetic field strength depends on the difference in the free energies of the two states. Hence, once it is known that the critical field changes slightly when the material is under stress, thermodynamic arguments show that the *mechanical properties* must be slightly different in the normal and superconducting states. The noted examples are: there is an extremely small change in volume when a normal material becomes superconducting, and the coefficient of thermal expansion and bulk modulus are also slightly different in the superconducting and normal states.

Thermal Conductivity

The changes in the magnitudes of thermal conductivity from normal state to the superconducting state is significant. In a normal metal heat flow in the steady state is totally by the conduction electrons. However, the *superelectrons* in the superconducting state no longer interact with the lattice in such a way that they can *exchange energy*, and so they cannot pick up heat from one part of the specimen and deliver it to another. Or, if a metal goes into the superconducting state, its *thermal conductivity* is reduced. This reduction is very marked at temperatures well below the critical temperature as very few normal electrons are available to transport thermal energy. If, however, the superconductor is driven normal by the application of a magnetic field, the thermal conductivity is restored to the higher value of the normal state. Hence the thermal conductivity of superconductor can be controlled by means of a magnetic field, and this effect has been used in "*thermal switches*" at low temperatures to make and break heat contact between specimens connected by a link of superconducting materials. The thermal conductivity of tin at 2 K is 34 W $\text{cm}^{-1}\,\text{K}^{-1}$ for the normal phase and 60 W $\text{cm}^{-1}\,\text{K}^{-1}$ for the superconducting phase. At 4 K, it is 55 W $\text{cm}^{-1}\text{K}^{-1}$ (at 4 K there is no superconducting phase for tin as $T_c = 3.73$ K).

Thermoelectric Effects

It is found, both from theory and experiment, that thermoelectric effects do not occur in a superconducting metal. For example, no current is set up around a circuit consisting of two superconductors, if the two junctions are held at different temperatures below their transition temperatures. If a thermo e.m.f were produced there would be a strange situation in which the current would increase to the critical value, no matter how small the temperature difference is. It follows from the Thomson relations that, if there is no thermo e.m.f in superconducting circuits, the Peltier and Thomson coefficients must be the same for all superconducting metals, and they are in fact zero. Hence they can be used as a standard to measure that of others.

Q 5.5 Arrive at London's equation and explain coherence length.

***Answer*:** According to *London's theory* it is assumed that there are two types of conduction electrons in a superconductor, namely, the *superelectrons* and the *normal electrons*. At 0 K a superconductor contains only superconducting electrons, but as temperature increases the ratio of normal electrons to superconducting electrons increases, until at the transition temperature all the electrons are normal. At any temperature the sum of the superconducting electrons and the normal electrons is equal to the *conduction electron density* in the *normal state*. The superconducting electrons are not subjected to any *lattice scattering* and therefore are merely accelerated in an electric field.

Expulsion of flux from a superconductor is one of the important features of superconductors (Meissner effect). Actually in a microscopic scale, the flux does not abruptly become zero at the surface of a superconductor. Typically, the flux penetrates a surface layer of thickness 25 nm. The origin of Meissner effect may, therefore, lie in the electronic wave functions of macroscopic extent not getting perturbed in a magnetic field. We shall now discuss the phenomenological theory suggested. Unlike an ordinary conductor, the charge carriers in a perfect conductor or superconductor are not subjected to forces of *scattering* from *lattice vibrations*, *defects*, etc. Thus the acceleration due to the field $\vec{E}$ and hence the force is given by:

$$m\frac{d\vec{v}}{dt} = e\vec{E}\,;\ \frac{d\vec{v}}{dt} = \frac{e\vec{E}}{m}$$

If n_s is the *density of* charge *carriers* in the superconductor, then the current density,

$$\boxed{\vec{J}_s = n_s e\vec{v}} \tag{Q 5.5.1}$$

Thus,

$$\boxed{\frac{d\vec{J}_s}{dt} = n_s e\left(\frac{d\vec{v}}{dt}\right) = \left[\frac{n_s e^2}{m}\right]\vec{E}} \tag{Q 5.5.2}$$

This equation replaces *Ohm's law* and gives the relationship between the *current density* and the electric field applicable for a superconductor. One can obtain a differential equation for the *magnetic induction vector* $\vec{B}$, by using this equation in conjunction with Maxwell's equations of electromagnetism. Taking curl of both sides of Eqn. (Q 5.5.2), one gets

$$\boxed{\frac{d}{dt}\left(curl\,\vec{J}_s\right) = \left[\frac{n_s e^2}{m}\right] curl\,\vec{E}} \tag{Q 5.5.3}$$

Combining this with *Faraday's law of induction*

$$curl\,\vec{E} = -\frac{d\vec{B}}{dt}$$

Eqn. Q 5.3.3 becomes

$$\boxed{\frac{d}{dt}\left[curl\,\vec{J}_s + \left[\frac{n_s\,e^2}{m}\right]\vec{B}\right] = 0} \tag{Q 5.5.4}$$

Assuming the fields to vary slowly, the displacement current can be neglected, so that the current density is given by:

$$\boxed{\vec{J}_s = \frac{curl\,\vec{B}}{\mu_0};\ \mu_0\,\vec{J}_s = curl\,\vec{B}} \tag{Q 5.5.5}$$

Equation (Q 5.5.4) together with (Q 5.5.5) determines the magnetic field and the current density which can exist within a superconductor.

London and London proposed that a special solution for Eqn. (Q 5.5.4) characterizes a superconductor. The solution consists of equating the quantity inside the bracket in this equation to zero, instead of an arbitrary constant. The resulting equation is:

$$\boxed{curl\,\vec{J}_s + \left\{\frac{n_s\,e^2}{m}\right\}\vec{B} = 0} \tag{Q 5.5.6}$$

Equation (Q 5.5.6) is called *London equation*. To see how this yields Meissner effect, substitute Eqn. (Q 5.5.5) in Eqn. (5.5.6) and use the identity,

$$curl\ curl\,\vec{B} = grad\left(div\,\vec{B}\right) - \nabla^2\,\vec{B}$$

together with $\vec{B} = 0$

Thus

$$\boxed{\begin{aligned} &curl\ curl\,\vec{B} = -\nabla^2\,\vec{B} \\ &\mu_0\,curl\,\vec{J}_s = -\nabla^2\,\vec{B}\end{aligned}} \tag{Q 5.5.7}$$

Referring Eqn. (Q 5.5.6), we get

$$-\frac{\mu_0\,n_s\,e^2}{m}\vec{B} = -\nabla^2\vec{B}$$

or

$$\boxed{\nabla^2\,\vec{B} = \left[\frac{\mu_0\,n_s\,e^2}{m}\right]\vec{B}} \tag{Q 5.5.8}$$

The significance of the equation (Q 5.5.8) may be well understood by considering a semifinite perfect conductor bound by the plane $z = 0$ and extending in the positive z-direction. Let the applied field $\vec{B}$ be parallel to the surface. Equation (Q 5.5.8) for a one dimensional case can be written as:

$$\boxed{\frac{d^2B(z)}{dz^2} = \left[\frac{\mu_0\, n_s\, e^2}{m}\right] B(z)} \qquad \text{(Q 5.5.9)}$$

i.e.,

$$\frac{d^2B}{dz^2} = \frac{B(z)}{\lambda_L^2}$$

with

$$\boxed{\lambda_L = \sqrt{\frac{m}{\mu_0\, n_s\, e^2}}} \qquad \text{(Q 5.5.10)}$$

λ_L is called *London's penetration depth*. The physical solution to Eqn. (Q 5.5.10) is:

$$B(z) = B(0)\exp(-z/\lambda_L)$$

Now penetration depth can be defined as the distance at which the field is reduced $\frac{1}{e}$ of its initial value at the surface.

Coherence Length

In deriving London equation, it was assumed that the current density (or electron velocity) varies slowly in space. In the *condensed state*, the velocities of a pair of electron are correlated only if the distance between them is less than a certain coherence length $\in_0$. This is a measure of the size of the cooper-pair. The electrons which participate in the condensation process, have an energy within a range Δ of the Fermi energy. The resulting spread momentum $\Delta p = \frac{2\Delta}{v_F}$ with v_F the velocity at the Fermi level. By *uncertainty principle*

$$\boxed{\frac{\hbar}{\Delta p} = \frac{\hbar v_F}{2\Delta}} \qquad \text{(Q 5.5.11)}$$

where 2Δ is the *energy gap*.

Q 5.6 Briefly outline B C S theory of superconductivity.

***Answer*:** The *microscopic theory of superconductivity* predicts that under certain conditions, the attraction between two conduction electrons due to a succession of *phonon interactions* can slightly exceed the repulsion that they exert directly on one another due to the Coulomb interaction of their like charges. The two electrons are thus weakly bound together forming a so-called *cooper pair*. It is these cooper pairs that are responsible for superconductivity. This was proposed by Bardeen, Cooper and Schrieffer in 1957. B C S theory also showed there are several conditions that have to be met for a sufficient number of cooper pairs to be formed and superconductivity to be achieved.

In normal metals, *plane electron waves*, also called *de Broglie waves*, are assumed to travel or propagate in the direction of the motion of the electrons. Hence the electron gas in a metal can thus be considered as a superposition of several, de Broglie waves. These waves are reflected randomly by the surface of the crystal and there is no net electric current in the absence of an external field. But in the presence of an external electric field, an additional wave component in the direction of the field arises and a finite current starts flowing. For an ideal crystal devoid of any imperfections, there will be *zero electrical resistivity* (or *infinite conductivity*). However, in real metals, *phonons* (*lattice waves*/*vibrations*) and *defects* such as *impurities* and *vacancies* act as *scattering centres* for the de Broglie waves, giving rise to a finite resistance. At high temperatures, phonon scattering plays a major role, while at low temperatures, scattering from static defects predominates.

Bardeen, Cooper and Schriffer showed that the mechanism of superconductivity is entirely different from that of *conductivity* in normal, pure metals in several respects and is associated with the pairing of conduction electrons into what are known as cooper-pairs. To recapitulate, any successful microscopic theory of superconductivity must be able to explain the following:

(i) Superconductivity is essentially bound up with some profound change in the behaviour of the conduction electrons which is marked by the appearance of long range order and a gap in their energy spectrum of the order of 10^{-4} eV.

(ii) The crystal lattice does not show any change of properties, but must nevertheless play a very important part in establishing superconductivity because the *critical temperature* depends on the *atomic mass* (the *isotope effect*).

(iii) The superconducting **-** to normal transition is a phase change of the second order.

The long-range order noted in (i) clearly means that the electrons must interact with each other. It has, of course, been appreciated for a long time that the conduction electrons in a metal interact very strongly through their *coulomb repulsion*, and it is surprising that the ordinary free-electron theory of metals and semiconductors, which neglects this interaction, works as well as it does. It is difficult, however, to believe that the coulomb repulsion is the interaction responsible for superconductivity because there is no known way in which a repulsive interaction can give an energy gap. Furthermore, because the energy gap is very small, the interaction responsible for it must be very weak, much weaker than the coulomb interaction. The apparent lack of any mechanism for a weak attractive interaction was for some time the stumbling block in the way of any microscopic theory of superconductivity.

An early step forward in the search for a microscopic theory came in 1950 when Fröhlich pointed out that the *electron-phonon interaction* was able to couple two electrons together in such a way that they behaved as if there was a direct interaction between them. In the interaction postulated by Fröhlich, one electron emits a phonon which is then immediately absorbed by another, and he was able to show that in certain circumstances this emission and subsequent absorption of a phonon could give rise to a weak attraction between the electrons of the short which might produce an energy gap of the right order of magnitude. We may think of the interaction between the electrons as being transmitted by a phonon.

Normally electrons are scattered by lattice vibrations giving rise to electrical resistance, but in B C S theory an electron of wave vector **k** causes a slight distortion in the neighbouring lattice which forms an attractive potential for an electron of wave vector-**k**. The suggestion is that superconduction might occur through an electron-lattice interaction. In quantum-mechanical terms, the first electron creates a *virtual phonon* and loses momentum, but the second electron then comes along and is colliding with the *virtual phonon* acquires all the momentum lost by the first electron. The overall momentum change is zero and the paired electrons are superconducting. These *Cooper pairs* are bound together by a very small energy, Δ, forming a new ground state which is superconducting and is separated by an energy gap, 2Δ, from the lowest (excited) state above it. The Fermi level is in the middle of the gap. Δ can be found by measuring the specific heat in both superconducting state and normal state (the material is normal below T_c when $H > H_c$) and making an *Arrhenius plot* of the difference [that is, a plot of *ln* (Δ C_v) against $\frac{1}{T}$]. The slope of the plot is $-\frac{\Delta}{k_B}$. Δ is found to be about $2k_BT_c$ at 0 K, so for niobium $\Delta \approx$ 1.5 meV. Though this energy is very small, so that cooper pairs are continuously being split up, many other electrons are available to form fresh ones, and superconductivity is maintained. B C S theory predicts that the $\Delta - T$ graph follows,

$$\delta = \tan\left(\delta/t\right)$$

where $\delta = \frac{\Delta(T)}{\Delta(0)}, t = \frac{T}{T_c}$ and Δ (T) is the gap at T K. Thus Δ disappears at T_c and is roughly Δ (0) for $T < \frac{T_c}{2}$. The experimental data are in complete accord with B C S theory. B C S theory is too complicated for discussion here, but it explains all the phenomena described above and makes quantitative predictions which are borne out by experiment; for example, it predicts that the superconducting transition temperature will be:

$$T_c = 1.14\,\theta_D \exp\left[-1/UD\left(E_f\right)\right]$$

where θ_D is the Debye temperature, U is the *electron-lattice interaction energy* and $D(E_f)$ is the *electron density of states* at the *Fermi level*. U is higher when the electrical resistivity at 300 K is high, so that T_c is higher for the more resistive elements among those of similar electronic structures and Debye temperatures.

Conclusions

B C S theory presses for several conditions that have to be met for the generation of a sufficient number of Cooper pairs and then superconductivity is to be achieved. Though a lengthy discussion is not possible it is clear that the electron-phonon interaction must be strong and that low temperatures favour pair formation, hence high temperature superconductors are not predicted by B C S theory.

Cooper pairs are weakly bound with typical separation of 10^6 pm for the two electrons. They are also constantly breaking up and reforming (usually with other partners). There is thus enormous overlap between different pairs and the pairing is a complicated *dynamic process*. The ground state of a superconductor therefore is a *collective state*, describing the ordered motion of large numbers of Cooper pairs. When an external electric field is applied, the Cooper pairs move through the lattice under its influence. However, they do so in such a way that the ordering of the pairs is maintained. The motion of each pair is locked to the motion of all the others, and none of them can be individually scattered by the lattice. Because the pairs cannot be scattered by the lattice, the resistance is zero and the system is a superconductor.

Q 5.7 List out some of the characteristic features of superconductors comparing with that of normal conductors (where ever possible).

***Answer*:** Some of the common properties observed in superconductors are now summarized as follows:

1. The current in a superconductor once set up continues for a very long time without *attenuation*.
2. The permeability of a superconductor is 0. A superconductor is thus a perfect diamagnetic. Hence the magnetic field does not penetrate the superconductor. This is the *Meissner effect*. However when the magnetic field exceeds a certain critical value H_c the superconductor becomes a normal conductor.
3. When the current through a superconductor is increased beyond a critical value the super conductor becomes normal.
4. At 0 K all conduction electrons, behave like superelectrons, but if the temperature is raised, a few begin to behave as normal electrons, and on further heating the proportion of normal electrons increases. Eventually, at the transition temperature, all the electrons become normal electrons and the metal loses its superconducting properties.
5. Fröhlich suggestion that the interaction responsible for superconductivity is one which involves lattice vibrations (or phonons) enabled him to predict the isotope effect before it had been discovered experimentally. The fact that an electron-phonon interaction is responsible for superconductivity also explains why superconductors are bad normal conductors. For example, lead, which has one of the highest critical temperatures, must have a fairly strong electron-phonon interaction and as a result is a poor conductor at room temperature, whereas the noble metals gold and silver are very good conductors at room temperature, must be characterized by a weak electron-phonon interaction and do not become superconducting even at the lowest temperatures attained.
6. *Specific heat and energy gap*

   The right hand side of Eqns. (Q 5.4.6) and (Q 5.4.7) should be a finite quantity, hence there must be a discontinuity at the transition temperature. This has been experimentally found to be so. Just at the transition there is no latent heat, and there is a jump in the specific heat. At the transition temperature, $s_n = s_s$. Refer Fig. Q 5.3.2. Near absolute zero temperature the specific heat is smaller in the superconducting state compared to that in the normal state. It increases exponentially and at T_c, it is three times the value in a normal state. This behaviour of the specific heat in the superconducting state is the strong indication of the existence of an energy gap in the excitation spectrum of the electrons in the conduction band. At very low temperatures, very few electrons in the conduction band can get excited because of the energy gap 2Δ. As the temperature is increased the magnitude of the energy gap decreases and hence more electrons get excited to the available states above the gap and C_v increases exponentially.
7. *Coherence length*

   The paired electrons are not scattered as they smoothly ride over the lattice imperfections without exchanging energy with them. They can maintain their coupled motion up to a certain distance called *coherence length* and it is found to be of the order of 10^{-6} metre.
8. The B C S theory makes the following predictions which have been compared with experiments for a number of oxides superconductors:
   (a) The transition temperature T_c and energy gap 2Δ are related to the Debye temperature θ_D, the electron-electron attractive potential U and density of electrons at the Fermi level as:

$$T_c = 1.14\ \theta_D\ \exp\left[-1/UD\left(E_f\right)\right]$$

with $D(E_f)$ the electron density of states at the Fermi level, and

$$2\Delta = E_g = 4k_B\,\theta_D \exp\left[-1/UD\left(E_f\right)\right]$$

(b) The energy gap E_g is proportional to the transition temperature through $\dfrac{E_g}{k_B T_c} = 3.5$ except for gapless superconductors.

(c) The London equation is a consequence of the B C S theory and hence one expects the state of perfect diamagnetism to exist below T_c with $\chi = -1$.

(d) The transition temperature depends upon the average isotopic mass M through the relation

$$T_c = \frac{1}{\sqrt{M}}$$

which gives a clear guide to the theory that electron-electron interactions exist via lattice ions.

(e) There is discontinuity in the electronic contribution to the specific heat at the transition temperature given by:

$$\frac{C_s - C_n}{C_n} = 1.43$$

where subscripts s and n denote the superconducting and normal states respectively.

Q 5.8 *Write short notes on*:

(a) Josephson effects

(b) SQUIDs

(c) High temperature superconductors

***Answer*:**

(a) In 1962, Josephson predicted that if two superconducting metals are placed next to each other separated by a thin insulating layer (such as oxide coating) then a current would flow in the absence of any voltage. This effect is indeed observed because if the barrier is not too thick then electron pairs can cross the junction from one superconductor to the other without dissociating. This is known as the d.c Josepson effect. He further predicted that the application of a d.c potential to such a junction would produce a small alternating current, the a.c Josephson. These two properties are of great interest to the electronics and computer industries where they can be exploited for fast-switching purposes.

(b) The persistent of a current in a superconducting loop produces a magnetic field which never decays. This makes it possible to use the loop as a memory element in a computer. Josephson junctions are used in *Superconducting Quantum Interference Devices* (SQUIDs). These consist of a loop of superconductive wire with either one built-in Josephson junction (RF SQUID) or two (DC SQUID). The device is extremely sensitive to changes in a magnetic field, and can measure voltages as small as 10^{-18} V, currents of 10^{-18} A and magnetic fields of 10^{-14} T.

(c) The discovery of high T_c superconductivity in *copper oxide perorskites* by *Bednorz* and *Muller* in 1986 brought greater interests for the workers in this area. The first group of high T_c superconductor discovered were $La_{(2-x)}\ M_{(x)}\ CuO_4$ (where M = Ba, Sr, Ca) with T_c values in the range 25 to 40 K. These crystals possess K_2NiF_4 structure with orthorhombic distortion. The discovery of superconductivity with T_c around 90 K have a general formula:

$L_n\,Ba_2\,Cu_3\,O_{6+x}$ [$x = 0.95$, $L_n = Y$, Nd, Eu, Yb] with orthorhombic structures. These intermediate high T_c superconductors are *ceramic oxides,* not metals have mechanical properties of ceramics. The systems said above are brittle and not ductile as metals. They also exhibit antiferromagnetism. Around 1990 several new non-rare based copper systems involving the elements bismuth and thallium exhibiting superconductivity between 60 K and 125 K were made available. Mostly high temperature superconductors are not metals or inter-metallic compounds, they are oxides. Of the high temperature superconductors, a representative examples is 1 – 2 – 3 compound of YBCO having a formula $Y_1Ba_2\,Cu_3\,O_7$ with the critical temperature around 90 K. A direct consequence of high T_c is that the coherence length $\in$ is very small. A typical value of $\in$ in YBCO is 1 nm which is of the order of unit cell dimensions. $\in$ is the length scale which determines the extent over which cooper-pairs are correlated. A small value of $\in$ therefore indicates that the superconductivity in these materials is much more affected by structural changes than in conventional superconductors. Small coherence length also leads to a high value of the upper critical field.

Q 5.9 Bring out the potential applications of superconductors.

***Answer*:** If the core of an electromagnet is wound with a coil of superconducting material, large currents can be maintained without *joule heating*. Thus very intense magnetic fields can be produced. Magnetic field of the order of 10^5 gauss can be produced by this method. Superconductors are used for amplifying very small direct currents and voltages. If an alternating magnetic field with a mean value of H_c is applied to the superconductor, the substance alternates between its normal and superconducting states. Its electrical resistance varies periodically between zero and a finite value. If a small direct voltage is applied across the superconductor, the current fluctuates periodically with the same frequency as that of the magnetic field. The periodically varying current can then be amplified using ordinary *a.c amplifiers*. An amplified direct voltage can be recovered from the amplified periodically varying current.

Since the superconducting property of a substance can be quickly destroyed by the application of a magnetic field, superconductors are employed in *switching devices*. Since currents can be maintained without change for very long durations in a superconductor, superconductors are used as *storage of* '*memory*' in computers. The persistent current in a superconducting loop produces a magnetic field which never decays. This makes it possible to use the loop as a *memory element in a computer*. Josephson effect has also been used to practical advantage by combining two Josephson junctions in parallel to produce a device known as *superconducting quantum interference device* or SQUID. This can be used as an extremely sensitive magnetometer to detect fluxes smaller than $10^{-15}\ T\,m^2$. Such devices can be used to detect small changes in earth's magnetic field.

Superconductors are used for producing very strong magnetic field of about 20 – 30 tesla, which is much larger than the field obtained from an electromagnet and such high magnetic fields are required in power generators. Magnetic energy can be stored in large superconductors and drawn as required to counter the voltage fluctuations during peak loading. As there is no heat losses in a superconductor (i.e., $I^2R = 0$), so power can be transmitted through the superconducting cables without any losses. In view of the wide applications of superconductors, it is obviously desirable to have higher critical temperatures so that the cost of refrigeration can be cut down drastically. However, this by itself is not the only property which makes a material suitable for practical use. The high temperature superconductors, for instance, have rather low critical current density compared to the conventional superconductors, which is an obvious practical disadvantage. Similarly, the mechanical property like ductility of the material plays an important role in whether the material can be used in the form of coils. Efforts to synthesize HTSCs with improved performance are still underway.

Flash News:

In December 2003, Japan tested the run of the fastest train at 510 km/hour using superconducting magnets. The regular service is expected in May 2004. The distance between Kannya Kumari and Kashmir can be covered in 8 hour–though it is a hypothetical one in India.

Q 5.10 Superconducting state is a collective one, in which all the conduction electrons act co-operatively. Explain

***Answer*:** In a semiconductor there is a separation in energy between the top of the (full) valence band and the bottom of the (empty) conduction band. If the energy of the photon exceeds E_g, an electron may excite from the valence band to the conduction band. It is natural to postulate that some thing similar occurs in the case of a superconductor, and that radiation is heavily absorbed when the photon energy is sufficient to excite electrons across an energy gap of some sort. Since in a superconductor absorption occurs for frequencies greater than 10^{11} Hz, the energy gap must be of the order of 10^{-4} eV. It may be observed that if we express this energy gap in the form of k_BT, then T is about $1K$, which is of the order of magnitude of superconducting critical temperatures.

More evidence for the existence of some sort of energy gap is the electron levels comes from specific heat data. As we have already pointed out, at very low temperatures the contribution to the specific heat due to the conduction electrons in the superconducting state is proportioned to $\exp(-b/T)$. This is precisely the form to be expected if there is a gap in the range of energies available to an electron. As the temperature is raised, electrons are thermally excited across the gap and for each of these electrons an amount of energy equal to the energy E_g is absorbed in the process. It follows from a simple application of statistical mechanics that at a temperature T the number of electrons in energy levels above the gap is proportional to $\exp(-E_g/2k_B T)$ where k_B is the Botzmann constant, and the thermal energy absorbed in exciting these conduction electrons is therefore proportional to $E_g \exp(-E_g/2k_B T)$. The specific heat associated with this process is proportional to the derivative of the energy with respect to temperature, i.e., to $\frac{1}{T^2} \exp(-E_g/2k_B T)$. The T^{-2} term vairies much more slowly with T than the exponential term, so the variation of specific heat with temperature should be very nearly expontential. Tunneling experiments tells the existence of an energy gap. It should be stated, however, that under certain special circumstances a super conducting metal may not posses an energy gap. These *gapless* superconductors are not typical, and under normal circumstances all elemental superconductors and most alloys exhibit a well defined energy gap.

Two electrons usually repel each other because of coulomb interaction. Let for some reasons, the two electrons could then form a bound state. In a bound state, electrons are paired to form a single system, and their motions are correlated. The pairing can be broken only if an amount of energy equal to the binding energy is applied to the system. This pair of electrons is known as a cooper pair. At a temperature $T < T_c$, the lattice-electron interaction is stronger than the electron-electron force of coulomb. At this stage, the cooper pairs of electrons will have a peculiar property of smoothly sailing over the lattice point without any energy exchange (i.e the cooper-pairs are free from scattering by the ions in the lattice points). Hence no transfer of energy takes place from the electron pair to the lattice ions. If an electric field is established inside the substance, the electrons gain additional kinetic energy and give rise to a current. But they do not transfer this energy to the lattice, so that they do not get slowed down. Because of this, the material does not possess any electrical resistivity. Thus B C S theory explains the zero resistivity of a superconductor. The cooper pair of electrons can maintain the coupled motion up to a certain distance among the lattice points in a superconductor called *coherence length* which is found to be of the order of 10^{-8} cm.

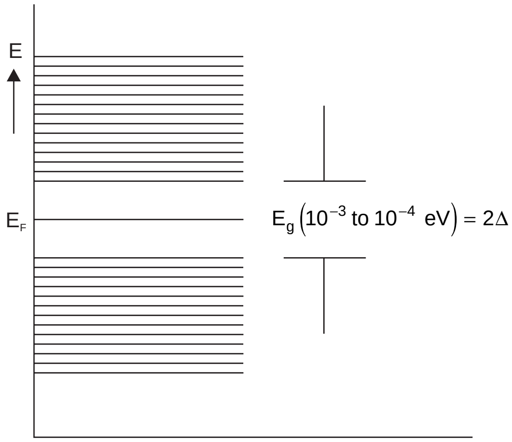


Fig. Q 5.10.1 *Energy bands of a superconductor*

Superconductivity state is a collective state, in which are the conduction electrons act co-operatively. The wave function associated with the superconducting state extends coherently over the entire volume of the superconductor. Thus, the electrons in superconductors display quantum effects on a macroscopic scale, in contrast to the electrons in individual atoms or molecules, which display quantum effects only on a microscopic scale.

Some of the peculiar properties of the superconducting materials such as diamagnetism, zero resistance may be explained in terms of the energy spectrum assuming the conduction electrons in superconductors are condensed into a single "*macromolecule*" which spreads over the whole volume and is capable of motion as a whole. The energy spectrum has a gap of the order of $10^{-3} - 10^{-4}$ eV between the higher occupied state and the first excited state. This gap reminds us the gap in an insulator. The difference is : in insulators the fully occupied band below the gap cannot conduct current, in superconductors this band does conduct. The gap width is proportioned to T_c.

i.e., $E_g = 3.52\, k_B\, T_c$.

Essentially, the gap represents the energy needed to break up one of the cooper pairs.

TABLES

Table 5. A *Critical temperature T_c and critical field H_c (at 0 K) of some superconducting materials*

Material	T_c *(K)*	H_0		*Type*
		(Amp/m)	*(gauss)*	
Hg	4.12	33×10^3	413	I
Sn	3.72	24×10^3	306	I
Al	1.196	7.9×10^3	99	I
Zn	0.79	3.8×10^3	45	I
Pb	7.175	6.4×10^3	803	I
V	5.1	105×10^3	1300	I
Ga	1.09	0.41×10^4	51	I
Ta	4.48	67×10^3	829	II
Nb	9.25	156×10^3	1950	II
Nb – 44% Ti	10.5	9.5×10^3	120	II
Nb_3Al	18	3.2×10^7	400×10^3	II
V_3Ga	16.5	2.8×10^7	350×10^3	II
Nb_3Sn	18.5	1.6×10^7	200×10^3	II

Table 5. B *Superconducting transition temperatures of some alloys and metallic compounds compared with their constituent elements*

	Ta – Nb	Pb – Bi	3 Nb – Zr	Nb_3Sn	Nb_3Ge
T_c (K)	6.3	8	11	18	23

	Nb	Pb	Ta	Sn	Zr	Bi	Ge
T_c (K)	9.3	7.2	4.5	3.7	0.8	not s/c	not s/c

Table 5. C *Energy gap at 0 K for some superconductors*

Element	E_g *(0)* $[2\Delta(0)]$ *in* 10^{-4}*eV*	T_c *(K)*	$\frac{E_g(0)}{k_B T_c}$
Aluminium	3.4×10^{-4}	1.2	3.3
Tin	11.6×10^{-4}	3.72	3.6

Contd

Element	E_g (0) $[2\Delta(0)]$ in 10^{-4}eV	T_c (K)	$\frac{E_g(0)}{k_B T_c}$
Niobium	30.5×10^{-4}	9.5	3.7
Tantalum	14.0×10^{-4}	4.48	3.6
Lead	27.3×10^{-4}	7.18	4.4
Mercury	16.5×10^{-4}	4.16	4.6
Zinc	2.4×10^{-4}	0.9	3.1
Gallium	3.3×10^{-4}	1.09	3.5

Table 5. D *Some properties of 1 2 3 compounds*

	Superconducting Coherence length (T = 0 K)	London penetration depth (T = 0 K)	Lattice constant
In plane	1.2 – 1.6 nm	150 nm	0.4 nm
Along c-axis	0.13 – 0.3 nm	700 nm	1 nm

Table 5. E *Penetration depth λ and the coherence length $\in_0$ of some selected superconductors*

Material	λ (nm)	$\in_0$ (nm)
Sn	34	23
Al	16	1600
Nb	39	38
Pb	37	83
Cd	110	760
Nb – Ti	300	4.0
V_3Ga	90	2.0
Nb_3 Sn	65	3.0
Nb_3Ge	90	3.0

OBJECTIVE QUESTIONS

1. The susceptibility of a superconductor
   - (a) becomes quite small as the temperature approaches the transition temperature
   - (b) has a positive value
   - (c) becomes quite large as the temperature approaches the transition temperature
   - (d) has a negative value
2. A superconducting material on being subjected to the critical field changes to
   - (a) superconducting state which is independent of temperature
   - (b) zero conductivity
   - (c) normal state
   - (d) remains uninfluenced
3. Critical magnetic field
   - (a) does not depend on temperature
   - (b) increases if temperature decreases
   - (c) increases if temperature increases
   - (d) none of these
4. The specific heat of a superconducting material shows an abrupt change at $T = T_c$ jumping to a large value for:
   - (a) $T < T_c$
   - (b) $T > T_c$
   - (c) $T = T_c$
   - (d) $T = T_c \ \theta_D$

   where θ_D is the Debye temperature
5. Superconductivity results due to
   - (a) crystal structure having infinite atomic vibrations at 0 K
   - (b) crystal structure having no atomic vibrations at 0 K
   - (c) all electrons interacting in the superconducting state
   - (d) all electrons having Fermi energy at 0 K
6. The electron density in a superconductor is
   - (a) finite at absolute zero
   - (b) infinite at absolute zero
   - (c) zero at absolute zero
   - (d) none of these
7. In superconducting state
   - (a) entropy and thermal conductivity decrease
   - (b) entropy decreases and thermal conductivity increases
   - (c) entropy and thermal conductivity increase
   - (d) entropy increases and thermal conductivity decreases
8. The transition temperature of most superconducting elements is in the range
   - (a) above 50 K
   - (b) 20 K to 50 K
   - (c) 10 K to 20 K
   - (d) zero to 10 K
9. Pippard coherence length
   - (a) increases by the presence of impurities in a superconductor
   - (b) is independent of mean free path
   - (c) depends on mean free path
   - (d) is independent of penetration depth

10. A superconducting material when placed in a magnetic field will
    - (a) attract the magnetic field toward its centre
    - (b) repel all the magnetic lines of forces passing through it
    - (c) attract the magnetic field but transfer it into a concentrated zone
    - (d) not influence the magnetic field
11. Value of critical density (j_c) in a superconductor depends upon
    - (a) temperature (b) magnetic field strength
    - (c) Silsbee effect (d) both (a) and (b)
12. Which of the following is type II superconductor
    - (a) Hg (b) Pb (c) Al (d) Nb
13. The isotope effect coefficient is
    - (a) zero (b) generally in the range 0.2 – 0.6
    - (c) generally in the range 0.5 – 1 (d) ∞
14. The width of the energy gap of a superconductor is zero at
    - (a) 0 K (b) the room temperature
    - (c) the transition temperature (d) 100°C
15. The critical current in a Josephson junction is in the range
    - (a) $0 - 100\,\mu\text{A}$ (b) $100\,\mu\text{A} - 1\,\text{mA}$
    - (c) 1 mA – 1 A (d) greater than 1 A
16. As the isotopic mass of mercury decreases
    - (a) the critical temperature increases slightly
    - (b) the critical temperature decreases slightly
    - (c) remains constant (d) none of these
17. Cooper pairs are formed
    - (a) at very low temperatures the thermal energy is not sufficient to disrupt the binding
    - (b) at high temperatures as the thermal energy is sufficient to form the cooper-pair
    - (c) none of these
18. The favourable condition both for superconductivity and low resistance is
    - (a) a weak electron-phonon interaction (b) a strong electron-phonon interaction
    - (c) a weak phonon-phonon interaction (d) none of these
19. The coherence length of the paired electrons is
    - (a) 0.001 nm (b) 0.25 nm
    - (c) 0.01 nm (d) 250 nm
20. Superconducting state is more ordered than the normal state for type I superconductors
    - (a) true (b) false
21. The energy gap in a superconductor is of the order of
    - (a) 1 eV (b) 10^{-1} eV (c) 10^{-4} eV (d) 10^{-10} eV

22. Lead which has one of the highest critical temperatures, must have a weak electron-phonon interaction and as a result is a poor conductor at room temperature (compared with silver).
    (a) true (b) false
23. The noble metal gold is a very good conductor at 300°K but not a superconductor at very low temperatures because of strong electron-phonon interaction.
    (a) true (b) false
24. Penetration depth is the distance at which the field is reduced to
    (a) 7% of the initial value (b) 17% of the initial value
    (c) 27% of the initial value (d) 37% of the initial value

PROBLEMS AND SOLUTIONS

5.1 For a specimen of V_3Ga, the critical fields are respectively 1.4×10^5 and 4.2×10^5 A/m for 14 K and 13 K. Calculate the transition temperature and critical fields at 0 K and 4.2 K.

***Solution*:**

$$H_c = H_o\,[1 - (T_1/T_c)^2] \tag{1}$$

$$H_c' = H_o\,[1 - (T_2/T_c)^2] \tag{2}$$

i.e.,

$$\frac{H_c}{H_c'} = \frac{\left(T_c^2 - T_1^2\right)}{\left(T_c^2 - T_2^2\right)};\ \frac{1.4}{4.2} = \frac{\left(T_c^2 - T_1^2\right)}{\left(T_c^2 - T_2^2\right)} = \frac{\left(T_c^2 - 14^2\right)}{\left(T_c^2 - 13\right)}$$

or

$$4.2\,T_c^2 - 4.2 \times 14^2 = 1.4 \times T_c^2 - 1.4 \times 13^2$$

$$T_c^2\left(4.2 - 1.4\right) = 4.2 \times 14^2 - 1.4 \times 13^2$$

$$T_c^2 = \frac{586.6}{2.8}$$

$$\boxed{T_c = 14.5\ K}\ \textbf{\textit{Answer (a)}}$$

Substituting $T_c = 14.5$ K and 1.4×10^5 for H_c in equation (1), one gets,

$$H_0 = \frac{H_c}{\left[1 - \left(14/14.5\right)^2\right]}$$

with $H_c = 1.4 \times 10^5$ amp/metre

Thus

$$H_0 = \frac{1.4 \times 10^5}{\left[1 - 0.9322\right]}$$

$$H_0 = 20.7 \times 10^5 \text{ A/m}$$

Now critical fields at 0 K and 4.2 K are calculated as follows:

At 0 K

$$H_c = H_0\left[1-\left(T/T_c\right)^2\right]$$

$$= H_0\ [1 - 0] = H_o$$

$$= 20.7 \times 10^5 \text{ A/m}$$

$$\boxed{H_c = 20.7 \times 10^5 \text{ A/m}}$$ ***Answer (b)***

At 4.2 K

$$H_c = H_0\left[1-\left(T_1/T_c\right)^2\right] = 20.7 \times 10^5\ [1 - (4.2/14.5)^2]$$

$$H_c = 18.9 \times 10^5 \text{ A/m}$$

$$\boxed{H_c = 18.9 \times 10^5 \text{ A/m}}$$ ***Answer (c)***

5.2 Estimate the London penetration depth for tin from the following data at 2.3 K. $T_c = 3.7$ K, density 7.3×10^3 kg/m^3, $M_A = 118.7$ and $m^* = 1.9$ m.

***Solution*:**

London penetration depth,

$$\lambda(0) = \sqrt{\frac{m^*}{\mu_0 ne^2}}$$

$\frac{118.7}{7.3 \times 10^3}$ m^3 will contain $2 \times 6.02 \times 10^{26}$ electron

1 m^3 will have $\frac{7.3 \times 10^3 \times 12.04 \times 10^{26}}{118.7}$

i.e., $n = 7.4 \times 10^{28}$

Thus $$\lambda(0) = \sqrt{\frac{1.9 \times 9.1 \times 10^{-31}}{4\pi \times 10^{-7} \times 7.4 \times 10^{28}\left(1.6 \times 10^{-19}\right)^2}}$$

$$\boxed{\lambda(0) = 27\,\text{nm}}$$ ***Answer (a)***

Also $$\lambda(T) = \frac{\lambda(0)}{\left[1-\left(T/T_c\right)^4\right]^{1/2}}$$

with $T = 2.3$ K and $T_c = 3.7$

or
$$\lambda(T) = \frac{27 \times 10^{-9}}{\left[1 - \left(\frac{2.3}{3.7}\right)^4\right]^{1/2}} = 29.1 \text{ nm}$$

$$\boxed{\lambda(T) = 29.1 \text{ nm}} \quad \textbf{\textit{Answer (b)}}$$

5.3 For a superconducting specimen, the superconducting transition temperature and critical magnetic field at 0 K are 1.18 K and 99 × 10^{-4} T respectively. If the specific heat constant γ is 1.35 × 10^3 J/m^3 K^2, then determine the ratio of the specific heat discontinuity to the normal state specific heat.

***Solution*:**

Formula used:

$$\frac{\Delta C}{C_n} = \frac{4\mu_{c0}^2}{\gamma T_c^2} = \frac{4B_{c0}^2}{\mu_0 \gamma T_c^2}$$

$$= \frac{4 \times 99^2 \times 10^{-8}}{4\pi \times 10^{-7} \times 1.35 \times 10^3 (1.18)^2}$$

$$= 0.17$$

$$\boxed{\frac{\Delta C}{C_n} = 0.17} \quad \textbf{\textit{Answer}}$$

5.4 Using the parabolic temperature dependence of the critical magnetic curve, show that

$$S_n - S_s = \frac{2\mu_0 H_0^2}{T_c}\left[\frac{T}{T_c} - \left(\frac{T}{T_c}\right)^3\right]$$

and
$$C_n - C_s = \frac{2\mu_0 H_0^2}{T_c}\left[\frac{T}{T_c} - 3\left(\frac{T}{T_c}\right)^3\right]$$

for the entropy and heat capacity differences per unit volume; *n* and *s* respectively refer to the normal state and superconducting state.

***Solution*:**

The general equations are

$$S_n - S_s = -\mu_0 \left[H_c \frac{dH_c}{dT}\right] \tag{1}$$

$$C_n - C_s = -\mu_0 T H_c \frac{d^2 H_c}{dT^2} - \left\{\mu_0 T \left[\frac{dH_c}{dT}\right]^2\right\} \tag{2}$$

and
$$H_c = H_0\left[1 - \left(\frac{T}{T_c}\right)^2\right]$$

Now
$$\frac{dH_c}{dT} = -H_0\,\frac{2T}{T_c^2} \quad\text{and}\quad \frac{d^2H_c}{dT^2} = -\frac{2H_0}{T_c^2}$$

Substituting these values in equations (1) and (2) and simplifying we get

$$\boxed{S_n - S_s = \frac{2\mu_0 H_0^2}{T_c}\left\{\frac{T}{T_c}\left[1 - \frac{T^2}{T_c^2}\right]\right\}} \quad \textbf{\textit{Answer (a)}}$$

Similarly,
$$C_n - C_s = -\mu_0 T\left[-\frac{2H_0}{T_c^2}H_c + \frac{4H_0^2T^2}{T_c^4}\right]$$

$$= \mu_0 T\left[\frac{2H_0}{T_c^2}H_0\left\{1 - \frac{T^2}{T_c^2}\right\} - \frac{4H_0^2T^2}{T_c^4}\right]$$

$$= \frac{2\mu_0 H_0^2}{T_c}\left[\frac{T}{T_c} - \frac{T^3}{T_c^3} - \frac{2T^3}{T_c^3}\right]$$

$$\boxed{C_n - C_s = \frac{2\mu_0 H_0^2}{T_c}\left[\frac{T}{T_c} - 3\left(\frac{T}{T_c}\right)^3\right]} \quad \textbf{\textit{Answer (b)}}$$

5.5 The critical temperature, T_c for mercury with isotopic mass 199.5 is 4.18 K. Calculate its critical temperature when its isotopic mass changes to 203.4

***Solution*:**

We know that

$$T_c \propto M_1^{-\beta}$$

and
$$T_c' \propto M_2^{-\beta}$$

$$\frac{T_c}{T_c'} = \left[\frac{M_2}{M_1}\right]^{\beta}$$

$$T_c' = \left[\frac{M_1}{M_2}\right]^{\beta} T_c = 4.18 \times \left[\frac{199.5}{203.4}\right]^{1/2} = 4.139\text{K}$$

$$\boxed{T_c' = 4.139\,\mathrm{K}}\quad \textbf{\textit{Answer}}$$

5.6 The superconducting transition temperature is 7.22 K. The Debye temperature is 96 K. Determine $\mathrm{N}(0)\phi$ from these values and then the energy gap $\Delta(0)$.

***Solution*:**

Formula used:

$$\frac{1}{N(0)\phi} = \ln\frac{1.14\,\theta_D}{T_c} = \ln\frac{1.14 \times 96}{7.22}$$

$$\boxed{N(0)\phi = 0.3678}\quad \textbf{\textit{Answer (a)}}$$

Further

$$\Delta(0) = \frac{k_B\,\theta_D}{\sin\mathrm{h}\left[\dfrac{1}{N(0)\phi}\right]} = \frac{1.38 \times 10^{-23} \times 96}{7.546}\ \text{joule}$$

$$= \frac{96 \times 1.38 \times 10^{-23}}{7.546 \times 1.6 \times 10^{-19}} = 10.97 \times 10^{-4}\ \mathrm{eV}$$

$$\boxed{\Delta(0) = 10.97 \times 10^{-4}\ \mathrm{eV}}\quad \textbf{\textit{Answer (b)}}$$

EXERCISE

5.1 Calculate the critical current density for 1 mm diameter wire of lead at (a) 4.2 K (b) 7 K. Given: T_c for lead = 7.18 K and H_c for lead = 6.5×10^4 A/m.

(***Ans*:** 1.71×10^8 A/m^2, 1.285×10^7 A/m^2)

5.2 Calculate the value of the London penetration depth at 0 K for lead whose density is 11.3×10^3 kg/m^3 and atomic weight 207.19. Given: T_c = 7.22 K. Calculate the increase in penetration depth at 3.61 K from its value at 0 K. (***Ans*:** 1 nm)

5.3 A superconducting Nb solenoid requires a current of 20 A in order to produce a magnetic field of 6×10^4 A/m. If the solenoid is immersed in liquid helium (4.2 K) and H_0 for Nb 1.56×10^5 A/m, estimate the minimum diameter of the wire that may be used. T_c for Nb is 9.5 K. (***Ans*:** 1.16 mm)

5.4 The penetration depth λ of Hg at 3.5 K is about 75 nm. Estimate the values of λ and n as $T \to 0$. T_c = 4.12 K. (***Ans*:** 51.9 nm, 10^{28}/m^3)

5.5 The resitivity of a superconductor becomes zero. Consequently the flux density is zero due to this abrupt change. Prove that the superconductor behaves as perfect diamagnetic.

6

Magnetism and Magnetic Materials

6.1 INTRODUCTION

KEY WORDS

Motion of electrons, atomic orbital states, diamagnetic phenomena, paramagnetism phenomena, paramagnetism, permanent atomic magnet, exchange interaction, principal quantum number, angular momentum quantum number, magnetic quantum number, degeneracy of the energy states, spin angular momentum, total angular momentum, quantum number, total magnetic quantum number, degeneracy of the states, Sommerfeld system, Kennelly system, magnetic flux density, Len's law, frequency of revolution, flux, magnetic moment, orbital electrons, average radius, paramagnetism, Langevin, Langevin function, paramagnetism of free electrons, molecular magnets, Drude-Lorentz, electron gas, Bohr magneton, paramagnetic susceptibility, Fermi-Dirac statistics, wave mechanics, quantum theory of paramagnetism, Brillouin function, paramagnetic salt, entropy, adiabatic transformation, Maxwell's relation, adiabatic demagnetization, ferromagnetism, ferrite inductor, canted spin system, Neel temperature, magnetic susceptibility, degenerate state, magnetic energy, Pauli paramagnetism, isolated spin, paired and unpaired electrons, lanthanides, Fermi level, ferromagnetic materials, ferromagnetic curie temperature, Curie-Weiss law, paramagnetic curie temperature, magnetization, hysteresis, Weiss molecular field, remanence, coercivity, coercive force, exchange field, Curie-Weiss law, Weiss constant, Curie temperature, spontaneous magnetization, dipole-dipole interaction, Heisenberg theory, Heitler-London model, exchange integral, easy and hard directions, closer domains, anisotropy energy, Weiss field, hysteresis, domains, Bitter, Bloch wall energy, magnetic energy, closure domains, easy and hard directions, magnetostriction, magneto-elastic energy, Bitter pattern, hysteresis phenomenon, irreversibility, hysteresis loss, catastrophe, asymptotic curie temperature, antiferromagnetic and paramagnetic behaviour, interpenetrating sub lattice, ferrimagnetism, ferromagnetic Neel temperature, hyperbolic curve, ferrites and garnets, antiferromagnetic exchange interaction, sublattice magnetization, molecular field, ferrimagnets, antiferromagnetic interaction, spontaneous magnetization, magnetite, Faraday effect, interstices, spinel structure, tetrahedral voids, magnetostrictive coefficient, hard and soft magnetic materials.

6.1 INTRODUCTION

Magnetism has a very ancient history: it is one of the topics in which considerable advances have been made, both in theoretical understanding and in experimental work, over the last few decades. It is perhaps that aspect of solid state physics which has been familiar to man as early as 800 BC. Infact, almost every thing known about the magnetic properties has been derived from experimental work and from a few stimulated guesses.

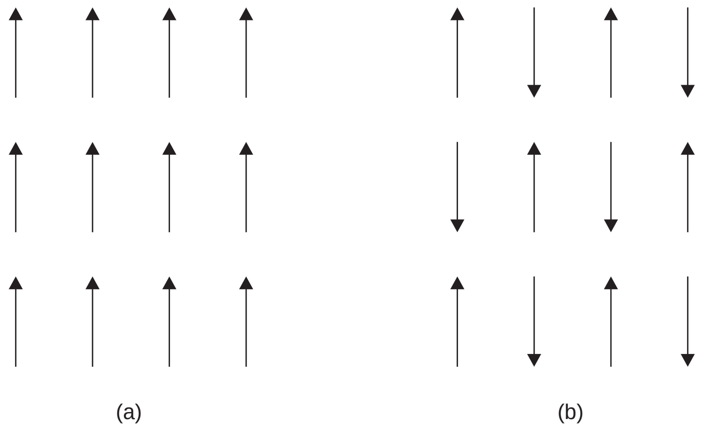
Some of the important features of magnetic materials are listed below:

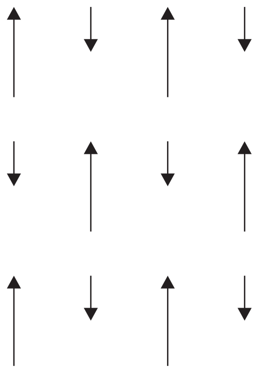
(i) Some materials are magnetic even with out the application of any magnetic field and become more magnetic when a weak magnetic field is applied to such materials.

(ii) Several other materials lose their initially strong magnetism when heated above certain critical temperature and become comparatively weakly magnetized.

(iii) Some materials show a magnetic response in a direction opposite to that of any externally applied field.

The source of magnetism in solids is mainly due to the *motion of the electrons* and in the permanent magnetic moments of the atoms and electrons. The application of a magnetic field induces a change in the *atomic orbital states* causing the *diamagnetic phenomena*, which is quite weak. On the other hand *paramagnetism* is the result of the presence of *permanent atomic* or *electronic magnetic moments*. In this case the magnetic moments line up with the magnetic field to decrease the total energy. In diamagnetism, there is slight repulsion of a material by the magnetic field, where as in paramagnetism, there is a slight attraction of a material by the magnetic field. However *ferromagnetism* occurs when *quantum mechanical exchange interaction* align adjacent magnetic moments in the same direction in the absence of a magnetic field below a *critical temperature*, called the *curie temperature*. Above the curie temperature, the ferromagnetic materials become paramagnetic. If the exchange interaction aligns the moments in opposite directions, cancellation takes place and the material is known as an *antiferromagnetic material*. The total moment over a finite volume is zero. The antiferromagnetism vanishes above a critical temperature, called the *Neel temperature.* In ferromagnetism, the number of atoms with opposite spins are unequal and hence there is a net *magnetic moment.* Fig. 6.1.1 shows the *magnetic ordering* of the different kinds of the said magnetic materials. The interesting information is that ferro and ferrimagnetic materials consist of *domains* of completely magnetized regions, separated by boundaries.





(c)

Fig. 6.1.1 *Various types of magnetic ordering. Each arrow indicates a magnetic moment and its orientation (a) Ferromagnetic (b) Anti Ferromagnetic (c) Ferrimagnetic*

Q 6.1 Discuss the origin of magnetism and also the magnetic quantities and their units.

***Answer*:** In the simplest case, i.e., hydrogen atom, the motion of the electron is governed by three quantum numbers;

(i) *principal quantum number*, *n*, where $n = 1, 2, 3$……..;
(ii) *angular momentum* (or *orbital momentum*) *quantum number*, *l*, where $l = 0, 1, 2 \ldots (n-1)$ and
(iii) *magnetic quantum number* m_l, where $m_l = 0, \pm 1, \pm 2 \ldots \pm l$.

While *n* determines the energy of the electron, *l* denotes the magnitude of the angular momentum vector $\vec{L}$; the magnitude and orientation in space of the vector $\vec{L}$ are determined by *l* and m_l. In other words, for a fixed value of *n*, different values of *l* and m_l describe the same energy state. If an external magnetic field is applied, however, the *degeneracy of the energy states* is lifted and each set of *n*, *l* and *m* quantum numbers corresponds to a different energy state. The magnitude of the orbital angular momentum (*L*) of the electron is quantized in terms of $\hbar$, i.e.,

$$L = \sqrt{l(l+1)}\,(\hbar)$$

For $l = 0, 1, 2, 3$, etc., the electrons are designed s, p, d, f, etc. In the presence of a magnetic field, the z-component of $\vec{L}$ is quantized such that

$$\boxed{L_z = m_l \hbar} \tag{Q 6.1.1}$$

If θ is the angle between $\vec{L}$ and the magnetic field direction, which may be conveniently taken as the z-axis, then

$$\boxed{\cos\theta = \frac{L_z}{L} = \frac{m_l \hbar}{(\hbar)\sqrt{l(l+1)}} = \frac{m_l}{\sqrt{l(l+1)}}} \tag{Q 6.1.2}$$

Eqns (Q 6.1.1) and (Q 6.1.2) indicate that L can have $(2l + 1)$ *orientations in space*, corresponding to the number of permissible values of m_l.

In addition to the orbital motion an electron possesses *spin angular momentum* also, represented by the vector $\vec{S}$, whose magnitude is quantized in terms of $\hbar$ such that:

$$S = \sqrt{s(s+1)}\,(\hbar)$$

where $s = \frac{1}{2}$ is the *spin quantum number*. In the presence of an external magnetic field, z- component of $\vec{S}$ is also quantized such that:

$$S_z = m_s\hbar$$

where $m_s = \pm\frac{1}{2}$ is the *spin magnetic quantum number*.

The orientations in space of $\vec{S}$, with respect to the z-axis (magnetic field direction), are determined by the relation,

$$\cos\theta = \frac{S_z}{S} = \frac{m_s\hbar}{\sqrt{s(s+1)}\,(\hbar)} = \frac{m_s}{\sqrt{s(s+1)}}$$

Since $m_s = \pm\frac{1}{2}$, there are only two permissible values of θ. If $\vec{J}$ is the total angular momentum vector, then

$$\vec{J} = \vec{L} + \vec{S}$$

$$J = \sqrt{j(j+1)}\,(\hbar)$$

where j is the *total angular momentum* quantum number. The z-component of $\vec{J}$ is also quantized such that

$$J_z = m_j\hbar$$

and

$$\cos\alpha = \frac{J_z}{J} = \frac{m_j\hbar}{\sqrt{j(j+1)}\,(\hbar)} = \frac{m_j}{\sqrt{j(j+1)}}$$

Here m_j is the *total magnetic quantum number* and α is the angle between $\vec{J}$ and the magnetic field direction. Further, if β is the angle between the directions of $\vec{L}$ and $\vec{S}$, then

$$\cos\beta = \frac{j(j+1) - l(l+1) - s(s+1)}{2\sqrt{l(l+1)\,s(s+1)}}$$

Magnetic Quantities and Related Units

Magnetism is bedevilled by the different units used for magnetic field strength, *H* (SI unit: A/m) and magnetic induction, *B* (SI unit, *T* for tesla) and by the fact most publications still use the old c.g.s units of oersted (*Oe*) and gauss (*G*) for these respective quantities. In addition, there are two rival subsystems of magnetic units within the SI. One of these, the *Sommerfeld system*, says that when a magnetic field, *H*, is applied to a material may be considered to give rise to a magnetic induction, *B*, which is related to *H* by

$$\boxed{\vec{B} = \mu_0\left(\vec{H} + \vec{M}\right)} \tag{Q 6.1.3}$$

M is the *magnetization* or the magnetic moment per unit volume of the material (and has also units of A/m). *B*, *H* and *M* are all vector quantities. μ_0 is the permeability of vacuum, $4\pi \times 10^{-7}$ H/m, though it is better to call it the magnetic constant. Because $B = \mu_0 H$ in vacuum, a magnetic field is often said to be, say 0.5 *T* instead of $\frac{0.5}{\mu_0}$ (= 39800 A/m). Some say this is incorrect, but it is convenient, because a good many equations then do not require a factor of μ_0, while conversion from tesla to gauss or oersted is simple (1tesla = 10000 G, 1G = 1 *Oe*). In the *Kennelly system*, equation (Q 6.1.3) may be written in terms of the magnetic polarization, $\vec{J}(= \mu_0 M)$:

$$\boxed{\vec{B} = \mu_0\vec{H} + \vec{J}} \tag{Q 6.1.4}$$

$\vec{J}$ is in tesla. Using just magnitudes, dividing Eqn. (Q 6.1.3) by *H*,

$$\frac{B}{H} = \mu_0\left(1 + \frac{M}{H}\right)$$

i.e.,

$$\mu = \mu_0\,(1 + \chi) = \mu_0\,\mu_r$$

or

$$\boxed{\chi = (\mu_r - 1) = \frac{M}{H}} \tag{Q 6.1.5}$$

where μ is the magnetic permeability of the material, χ is its (magnetic) susceptibility and μ_r is its relative permeability. χ and μ_r are dimensionless in the SI system. The permeability of a material is not a constant, except under specific conditions of measurement. B is also referred to as the *magnetic flux density*, $\frac{\phi}{A}$, where ϕ is the magnetic flux in weber (*Wb*) and *A* is the area normal to the flux.

Q 6.2 Discuss the classical theory of diamagnetism bringing out the salient features of Langevin's work on diamagnetism.

***Answer*:** Diamagnetism, paramagnetism, ferromagnetism and antiferromagnetism are the chief types of magnetic ordering in solids. Diamagnetism is a small effect caused by the reaction of the orbiting electrons to an applied magnetic field in accordance with *Len's law*, so that the magnetization and hence the susceptibility are both negative. The magnetic induction is less in the material than it would be in a vacuum with the same field. Typical susceptibilities are about 10^{-5} (for example for water -9×10^{-6}, graphite –8 × 10^{-5}). Most every day materials are diamagnetic, but the phenomenon has few uses. Elements like Bi, Cu, Ag and compounds of Fe and Ni are the other examples. Let us now consider the simplest case.

An electron of charge e is moving in a circular orbit of radium r. The *frequency of revolution* is $(v/2\pi r)$ and hence the electron with a charge e revolving in a circle with the said frequency is equivalent to a current.

$$I = e\frac{v}{2\pi r}$$

This gives rise to the magnetic moment of the orbiting electron as:

$$\boxed{M = \pi r^2 I = \frac{1}{2}evr} \qquad \text{(Q 6.2.1)}$$

Let a magnetic field of induction $\vec{B}$ be applied normal to the orbit. Then the *flux* in the circuit will be $\pi r^2 B$. If the magnetic field varies with time, then an induced e.m.f will be generated in the circuit equal to

$$\boxed{e.m.f. = -\frac{d}{dt}\pi r^2 B = -\pi r^2 \frac{dB}{dt}} \qquad \text{(Q 6.2.2)}$$

This induced e.m.f. is equivalent to an electrostatic field E is given by

$$2\pi rE = -\pi r^2 \frac{dB}{dt}$$

$$\boxed{\vec{E} = -\frac{r}{2}\frac{d\vec{B}}{dt}} \qquad \text{(Q 6.2.3)}$$

This field exerts a force $e\vec{E}$ on the electron and in turn produces change in velocity resulting in,

$$e\vec{E} = m\frac{d\vec{v}}{dt}$$

$$\frac{d\vec{v}}{dt} = \frac{e\vec{E}}{m} = -\left[\frac{er}{2m}\right]\frac{d\vec{B}}{dt}$$

Consequently, in the time that $\vec{B}$ changes by $\Delta\vec{B}$, $\vec{v}$ changes by $\Delta\vec{v}$, where

$$\boxed{\Delta\vec{v} = -\left[\frac{er}{2m}\right]\Delta\vec{B}} \qquad \text{(Q 6.2.4)}$$

According to equation (Q 6.2.1), this produces a corresponding change in the magnetic moment of the orbit:

$$\boxed{\Delta\vec{M} = \left[\frac{er}{2}\right]\Delta\vec{v}} \qquad \text{(Q 6.2.5)}$$

Now equations (Q 6.2.4) and (Q 6.2.5), yield

$$\Delta\vec{M} = \left[\frac{er}{2}\right]\left[-\frac{er}{2m}\right]\Delta\vec{B} = -\frac{e^2r^2}{4m}\Delta\vec{B}$$

Since $\Delta\vec{B} = \mu_0\,\Delta\vec{H}$, the above equation becomes,

$$\boxed{\Delta\vec{M} = -\frac{\mu_0\,e^2r^2}{4m}\Delta\vec{H}}$$

By definition, $$\boxed{\chi = \frac{\Delta\vec{M}}{\Delta\vec{H}} = -\frac{\mu_0\,e^2}{4m}\,r^2} \qquad \text{(Q 6.2.6)}$$

If N is the number of atoms per cubic metre, the volume susceptibility is

$$\chi = -\frac{N\,\mu_0\,e^2\sum r^2}{4m}$$

The summation extends over all the *Z orbital electrons* in the atom. Since the core electrons have different radii, we may write:

$$\sum r^2 = Z < r^2 >$$

where $[< r^2 >]^{1/2}$ is the *average radius* of the electron from the field axis (z-axis). If the orbit lies in the $x\,y$-plane, then

$$< r^2 > = < x^2 > + < y^2 >$$

If the atom has spherical symmetry, then

$$< x^2 > = < y^2 > = < z^2 >$$

Thus $$< r^2 > = 2< x^2 >$$

$$< R^2 > = 3 < x^2 >$$

and $$<r^2> = \frac{2}{3}<R^2>$$

Equation (Q 6.2.6) becomes,

$$\boxed{\chi = -\frac{ZN\,\mu_0\,e^2\left\langle R^2\right\rangle}{6m}} \qquad \text{(Q 6.2.7)}$$

Conclusion: All materials have diamagnetic properly, although it may be superposed by other magnetic effect. Since $\chi_{dia} \propto Z$, the bigger the atom, the larger is the magnitude of the diamagnetism. The negative sign indicates that diamagnetism is an induced opposing effect that disappears as soon as the field is removed. Equation (Q 6.2.7) indicates that the susceptibility is not a function of temperature, but depends on the structure of the atom.

Q 6.3 Discuss the features of paramagnetic materials and obtain the expression for susceptibility of the paramagnetic substance using classical laws.

***Answer*:** *Paramagnetism* is a relatively weak effect akin to diamagnetism, but the susceptibility is small and positive: application of a magnetic field to a paramagnet increases the induction beyond what it would be in a vacuum. Paramagnetism is strongly dependent on the temperature, being reduced as the temperature rises. In certain atoms there is a net magnetic moment arising from a particular combination of the orbital magnetic moments and the spin magnetic moments of the electrons. The interactions between the atoms are ignored, so that the only force on each dipole is that due to the applied magnetic field *H*. The atoms are subject to thermal agitation and Langevin assumed that their energy distribution could be described by classical Maxwell–Boltzmann statistics, so that the number of atoms *dn*, having energies between ϕ and $\phi + d\phi$ is given by:

$$dn \propto \exp\left(-\phi/k_B T\right) d\phi$$

$$\boxed{dn = C \exp\left(-\phi/k_B T\right) d\phi} \tag{Q 6.3.1}$$

The potential energy of a dipole whose axis makes an angle θ with a field or magnetic induction *B* is

$\phi = -\mu_m B \cos\theta$ with μ_m, the dipole moment

$$\boxed{d\phi = \mu_m B \sin\theta \, d\theta} \tag{Q 6.3.2}$$

Substituting the values of ϕ and $d\phi$ in Eqn. (Q 6.3.1), one gets

$$\boxed{dn = C \exp\left(\mu_m B \cos\theta/k_B T\right) \mu_m \sin\theta d\theta \times B} \tag{Q 6.3.3}$$

Now the total number of atoms, *n*, is just $\int dn$ over all angles between 0 and π. The total magnetization may be described as $M = n\overline{\mu}_m$ where $\overline{\mu}_m$ is the average dipole moment per atom in the direction of H is $\mu_m \cos\theta$ and the sum of these, $\int \mu_m \cos\theta \, dn$, will give the total magnetization, thus

$$M = n\overline{\mu}_m = \mu_m \int \cos\theta \, dn$$

i.e.,

$$\overline{\mu}_m \int dn = \mu_m \int \cos\theta \, dn$$

$$\boxed{\frac{\bar{\mu}_m}{\mu_m} = \frac{\int_0^{\pi} \cos\theta \, dn}{\int_0^{\pi} dn}} \tag{Q 6.3.4}$$

Substituting the value of *dn* from Eqn. (Q 6.3.3)

$$\boxed{\frac{\bar{\mu}_m}{\mu_m} = \frac{\int_0^{\pi} \cos\theta \, \exp\left(\mu_m B \cos\theta / k_B T\right) \mu_m B \sin\theta \, d\theta}{\int_0^{\pi} \exp\left(\mu_m B \cos\theta / k_B T\right) \mu_m B \sin\theta \, d\theta}} \tag{Q 6.3.4 a}$$

Let $$a = \frac{\mu_m B}{k_B T} \text{ and } x = \cos\theta$$

Thus $$\frac{\bar{\mu}_m}{\mu_m} = \frac{\int_{-1}^{+1} x \exp(ax)\, dx}{\int_{-1}^{+1} \exp(ax)\, dx} = \left(\coth a - \frac{1}{a}\right)$$

i.e., $$\boxed{\frac{\bar{\mu}_m}{\mu_m} = \left(\coth a - \frac{1}{a}\right) = L(a)} \tag{Q 6.3.5}$$

$L(a)$ is known as the *Langevin function* and is plotted as a function of a as in Fig. Q 6.3.1. When a is large the value of $L(a)$ tends to unity, which corresponds to $\bar{\mu}_m = \mu_m$ and all the dipoles are aligned with the field. For μ_m equal to 10^{-28} weber-metre (60000 oersted), T = 300K and $H = 10^{7}$A/m, a is only of the order of 0.25, from which it may be seen that it is impossible to magnetize the assembly to saturation at room temperature in fields normally available. More usually a may be treated so small so that the Langevin function approximates to $\frac{a}{3}$ and

$$\frac{\bar{\mu}_m}{\mu_m} = \frac{a}{3} = \frac{\mu_m B}{3k_B T} = \frac{\mu_0 \mu_m H}{3k_B T}$$

from which the susceptibility is given by

$$\chi = \frac{M}{H} = \frac{n\bar{\mu}_m}{H}$$

$$\boxed{\chi = \frac{n\mu_0\,\mu_m^2}{3k_B\,T} = \frac{C}{T}} \tag{Q 6.3.6}$$

where n is the number of atoms per m^3 and C is curie constant.

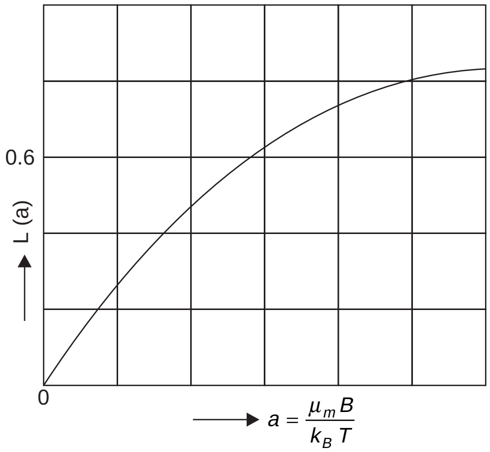


Fig. Q 6.3.1 *Langevin function*

Paramagnetism of free electrons: The Langevin theory discussed earlier is found to have fair applicability in the case of gases where the interaction between neighbouring *molecular magnets* is negligible. It is well known that several metallic conductors exhibit paramagnetism. This paramagnetism is attributed to the spins of free electrons. According to *Drude-Lorentz theory* of metals, the free electrons in a metal behave exactly like gas molecules and hence the magnetic contribution of the spins of the free electrons can be calculated in the same way as is done for paramagnetic gases. Of course there is this difference, that the paramagnetic gas molecules can orient in any direction, where as the paramagnetic free electrons can orient only in two directions, either along the magnetic field or against the field. Here also the interactions of the neighbouring spin magnets is neglected and the assembly of free electrons in a metal is called the *electron gas*.

The intrinsic magnetic moment of each electron due to spin is one *Bohr magneton* $(\beta$ or $\mu_B)$. Suppose the electron gas in a metal is subjected to a magnetic field H or magnetic induction B. Out of n electrons per unit volume of the electron gas, let n_1 electrons have their spins oriented parallel to the field and n_2 electrons have their spins oriented antiparallel to the field. Since the orientation effect of the applied field is opposed by the randomizing effect of the thermal energy, the number of electrons n_1 and n_2 aligned parallel and anti-parallel is proportional to the Boltzmann factor,

$\exp(\beta\mu_0 H)$ and $\exp(-\beta\mu_0 H)$ respectively.

Thus

$$n_1 = C\,n\exp(\beta\mu_0\,H/k_BT) \text{ and } n_2 = C\,n\,(-\beta\mu_0\,H/k_BT)$$

The net magnetization per unit volume M is given by:

$$M = \beta(n_1 - n_2) = \beta\,C\,n\left[\exp\left(\beta\mu_0\,H/k_BT\right) - \exp\left(-\beta\mu_0\,H/k_BT\right)\right]$$

The mean magnetic moment per dipole is equal to the net magnetization divided by the number of moments per unit volume.

i.e.,
$$\bar{\mu} = \frac{M}{n} = \frac{M}{(n_1 + n_2)}$$

or
$$\mu = \frac{\beta\, C\, n\left[\exp\left(\beta\mu_0\, H/k_B T\right) - \exp\left(-\beta\mu_0\, H/k_B T\right)\right]}{C\, n\left[\exp\left(\beta\mu_0\, H/k_B T\right) + \exp\left(-\beta\mu_0\, H/k_B T\right)\right]}$$

$$\bar{\mu} = \beta \tanh\left(\frac{\mu_0\, \beta H}{k_B T}\right)$$

Since $\beta H << k_B T$ at all temperatures, we get

$$\boxed{\bar{\mu} = \frac{\mu_0\, H\beta^2}{k_B T}} \qquad \text{(Q 6.3.7)}$$

The paramagnetic susceptibility χ for free electrons works out to be

$$\boxed{\chi = \frac{M}{H} = \frac{n\bar{\mu}}{H} = \frac{n\mu_0\beta^2}{k_B T}} \qquad \text{(Q 6.3.8)}$$

Conclusions: The only difference from the Langevin's expression for the *Paramagnetic Susceptibility* for a gas is that the factor 3 is missing in the expression (Q 6.3.8). The value of χ calculated from the above formula is approximately 100 times greater than the experimental value. Further the experiments show that the paramagnetic susceptibility of free electrons is practically independent of temperature, whereas the above expression gives an inversion temperature dependence. Obviously the electron gas is not that much free as the molecules of a gas. It is clear that the application of classical statistics to the electron gas leads to contradictory experimental results. This discrepancy represents an outstanding failure of the classical free electron model of a metal. This difficulty is solved by applying *Fermi-Dirac* statistics and *wave mechanics* to the free electrons. The corresponding quantum expression for the paramagnetic susceptibility is,

$$\chi = \left[\frac{\mu_0\, n\beta^2}{k_B T}\right]\frac{T}{T_F}$$

where T_F is the Fermi temperature of the metal.

i.e,
$$\boxed{\chi = \left[\frac{n\mu_0\beta^2}{k_B\ T_F}\right]} \qquad \text{(Q 6.3.9)}$$

The value of χ calculated from the above equation is of the order of 10^{-3} to 10^{-5}, which is of the same order as obtained from experiments. Because T_F is of the order of 10^4 K, the value χ is very small. Equation (Q 6.3.9) also shows the temperature independence of χ. However a more rigorous treatment of this proposition gives

$$\boxed{\chi = \frac{3}{2}\left[\frac{n\mu_0\beta^2}{k_B\ T_F}\right]} \tag{Q 6.3.9 a}$$

Quantum Theory of Paramagnetism

According to quantum theory, the permanent magnetic moment of a given atom, ion or molecule is not freely rotating but limited to a finite set of orientations with respect to the applied field. The quantum mechanics gives that the magnetic moment associated with a particular vector $\bar{J}$ [angular momentum = $\hbar\sqrt{J(J+1)}$] cannot have just any projection upon the direction of the magnetic field. The magnetic dipole moment quantum number of each atom J is $[-g\ \beta\sqrt{J(J+1)}]$ where g is known as *Lande 'g-factor'* and β is *Bohr magneton*. *Quantum theory* suggests that the magnet has only (2*J* +1) allowed orientations relative to the magnetic field. These orientations are those in which the component of the magnetic moment parallel to the magnetic field is given by

$$\boxed{M_J = -g\ \beta J,\ -g\ \beta(J-1)\ .....\ 0\ .....\ +g\ \beta(J-1),\ g\ \beta J} \tag{Q 6.3.9 b}$$

The corresponding (2*J* + 1) energy values are:

$$\boxed{-M_J\ B = g\ \beta JB,\ g\ \beta B(J-1)\ .....\ 0\ .....\ -g\ \beta(J-1)B,\ -g\beta\ JB} \tag{Q 6.3.10}$$

Since the atomic dipole moments of a substance are distributed in (2*J* + 1) directions, one may use statistical mechanics to obtain the net magnetic moment of the system. Assuming the magnetic system to be in thermal equilibrium with the crystal lattice at a temperature T, the average magnetic moment can be calculated by assigning a statistical weight of Maxwell Boltzmann statistics to obtain the magnetization as

$$\boxed{M = N\ \frac{\sum\limits_{-J}^{J} M_J\ \exp(-M_J\ B/k_BT)}{\sum\limits_{-J}^{J} \exp(-M_J\ B/k_BT)}} \tag{Q 6.3.11}$$

The coefficients N (the number of atoms per unit volume) on the R.H.S of Eqn. (Q 6.3.11) is the statistical average of the magnetic moment component per atom along B. Using Eqns. (Q 6.3.9 b and Q 6.3.10) and some consequent algebraic manipulation, one obtains the expression

$$\boxed{M = Ng\ \mu_B\ B_j\ (x)} \tag{Q 6.3.12}$$

where $x = \dfrac{g\,\mu_B\ J\ B}{k_BT}$ and $B_j\ (x)$ the *Brillowin function* defined by

$$\boxed{B_J\ (x) = \left(\frac{2J+1}{2J}\right)coth\left[\frac{(2J+1)x}{2J}\right] - \frac{1}{2J}coth\left(\frac{x}{2J}\right)} \tag{Q 6.3.13}$$

When J becomes very large, it approaches as a limit the Langevin function

$$\boxed{L(x) = \left(\coth x - \frac{1}{x}\right)} \tag{Q 6.3.14}$$

as we should expect from the fact that a summation over a large number of terms can be replaced by an integration.

At ordinary field strengths and normal temperatures, the value of x is very small, say 0.002. In this limit, Eqn. (Q 6.3.11), becomes

$$\boxed{M = N \frac{\sum_{-J}^{J} - g\mu_B J \; exp(-g\mu_B \; JB/k_B T)}{\sum_{-J}^{J} exp(-g\mu_B \; JB/k_B T)}}$$

$$\boxed{M = N \frac{\sum_{-J}^{J} - g\mu_B J \; exp(-x)}{\sum_{-J}^{J} exp(-x)}}$$

when $e^{-x} = (1 - x)$,

$$M = Ng\mu_B \frac{\sum_{-J}^{J} \left(-J + J^2 y\right)}{\sum_{-J}^{J} \left(1 - J \; y\right)}$$

where $$y = \frac{x}{J} = \frac{g\mu_B B}{k_B T}$$

The summation over J is zero, because the values run from + J to – J, and since the sum of the squares of the first J natural numbers is (1/6) J (J + 1) (2J + 1) [which becomes (1/3) J (J + 1) (2J + 1) for summation from – J to J].

Thus

$$M = \frac{N \; g\mu_B \, y \, J\,(J + 1)\,(2J + 1)}{3(2J + 1)}$$

$$\boxed{M = \frac{N \; g^2 \, \mu_B^2 \, J\,(J + 1)\,(2J + 1)B}{3(2J + 1) \; k_B T}} \tag{Q 6.3.15}$$

The susceptibility per unit volume is thus given by *Curie law* i.e.,

$$\boxed{\begin{aligned}\chi &= \frac{M}{H} = \frac{\mu_0 N\, g^2\, \mu_B^2\, J(J+1)}{3k_B T} \\ \chi &= \frac{C}{T}\end{aligned}} \tag{Q 6.3.16}$$

with $$C = \frac{N\, g^2\, \mu_0\, \mu_B^2\, J(J+1)}{3k_B}$$

Conclusion: The magnetic susceptibility of a paramagnetic substance is inversely proportional to the absolute temperature. We can understand the *Curie law* by observing that the thermal agitation, which tends to give a random orientation to dipoles is less at low temperatures resulting in a bigger proportion of the dipoles to be able to align themselves parallel to the field. Hence, at low temperatures, for a given field, the magnetization and, therefore, the susceptibility is greater.

Q 6.4 Write a note on adiabatic demagnetization.

***Answer*:** Temperature below 1 degree kelvin can be obtained with the help of *Paramagnetic salts*. Fig. Q 6.4.1 gives the *entropy* of the working substance as a function of temperature.

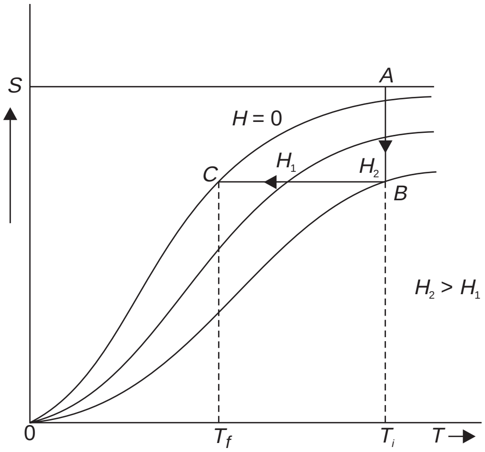


Fig. Q 6.4.1 *Variation of entropy with temperature without and with magnetic field*

The first line OCA represents the variation of entropy with temperature in the absence of a field. Let at an initial temperature T_i, the magnetic field be applied isothermally, then the magnetic dipoles will tend to line along the direction of the field. The spin system will become more orderly decreasing the entropy of the system from A to B. If now the paramagnetic specimen is isolated from its surroundings and the magnetic field is removed, then we go from B to C along an *adiabatic transformation* with no change in entropy. By successive steps of this kind, temperatures of the order of 0.001 K have been obtained. Thermodynamically with the help of *Maxwell's relations*, one obtains the entropy as

$$\boxed{S = S_0 + \int_0^H \left[\frac{\partial M}{\partial T}\right]_H dH} \qquad \text{(Q 6.4.1)}$$

where S_0 is the *entropy* without magnetic field. According to Cureie's law, from equation (Q 6.3.16),

$$\boxed{M = \frac{\mu_0 \, N \, \beta^2 \, g^2 \, J(J+1)}{3k_B T} H} \quad \text{or;} \quad \frac{\partial M}{\partial T} = -\frac{M\mu_0 N\beta^2 g^2 J(J+1)}{2k_B T^2}$$

equation (Q 6.4.1) becomes

$$\boxed{S = S_0 - \frac{N \, \mu_0 \, \beta^2 \, g^2 \, J(J+1) H^2}{6k_B T^2}} \qquad \text{(Q 6.4.2)}$$

This shows that entropy with magnetic field at $T = T_i$ will be lower than S_0 at $T = T_i$ and will actually correspond to S_0 at $T = T_f$ where T_f is a lower temperature than T_i. The last step is obtained by adiabatically moving along *BC* ($dS = 0$) removing the magnetic field, thus the name *adiabatic demagnetization* bringing the temperature below 1K by successive steps of the kind described above.

Q 6.5 Give an account of the different theories of ferromagnetism with a brief introduction.

***Answer*:** *Ferromagnetism*, ferrimagnetism and antiferromagnetism are all properties of materials possessing magnetic order, even in the absence of an applied field. If we think of each atom acting like a tiny bar magnet, then in a ferromagnet they are all aligned parallel to each other as in Fig. Q 6.5.1 (*a*). In an antiferromagnet alternate atoms align their magnetic moments antiparallel, so that the net magnetization is zero, as in Fig. Q 6.5.1 (b).

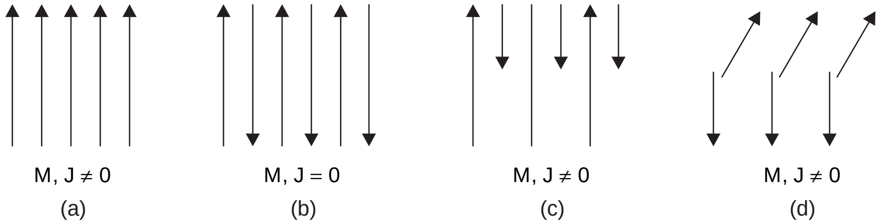


Fig. Q 6.5.1 *Alignment of atomic moments in (a) a ferromagnet, (b) an antiferromagnet, (c) a ferrimagnet and (d) a canted spin ferrimagnet.*

In a ferrimagnet the magnetic moments on some atoms is less than on others, so that when the two moments align antiparallel, as in an antiferromagnet, there is incomplete cancellation and a net magnetization results as in Fig. Q 6.5.1 (c). A ferrimagnet behaves much like a ferromagnet, and the commonest and cheapest magnets are made from ferromagnetic materials such as the hexaferrite ceramics Ba O.6 Fe_2 O_3 and Sr Fe_{12} O_{19}. *Ferrite inductor* and transformer cores are also made from ferrimagnets, such as nickel ferrite, $NiFe_2O_4$ (which can be written as $NiO.Fe_2O_3$). The alignment of magnetic moments need not be so simple as in Figs. 6.5.1 (*a*), 6.5.1 (*b*), 6.5.1 (*c*) but can be at other, constant angles as in Fig. Q 6.5.1 (d), which shows a *canted spin system*. The magnetic order in ferrimagnetic compounds disappears above their Curie points and the magnetic order in antiferromagnets disappears above a characteristic temperature called the *Neel temperature* (T_N): in both cases the material then becomes paramagnetic. Little use is made of antiferromagnetism. Nearly all the technically important magnetic materials are ferromagnetic or ferromagnetic.

The core electrons contribute a diamagnetic term to the *magnetic susceptibility*, but the valence electrons can give rise to paramagnetism or other cooperative effects. In filling the conduction band, we have implicitly put electrons into energy levels with paired spins. Even in the ground state of simple molecules such as O_2, however; it can be more favourable to have electrons in different orbitals with parallel spins than in the same orbital with paired spins. This occurs when there are *degenerate* or nearly *degenerate levels*. In an energy band, there are many degenerate levels and many levels very close in energy to the highest occupied level. It might well be favourable then to reduce electron repulsion by having electrons with parallel spin singly occupying levels near the Fermi level. To obtain a measurable effect, however, the number of parallel spins would have to be comparable with the number of atoms; 10^3 unpaired spins would not be noticed in a sample of 10^{23} atoms. Unless the density of states is very high near the Fermi level, a large number of electrons would have to be promoted to high energy levels in the band in order to achieve a measurable number of unpaired spins. The resulting promotion energy would be too great to be compensated for by the loss in electron repulsion. In the wide bands of the simple metals, the density of states is comparatively low, so that in the absence of a magnetic field, few electrons are promoted.

When a magnetic field is applied, the electrons will acquire an extra energy term due to interaction of their spins with the field. If the spin is parallel to the field, then its magnetic energy is negative, i.e. the electrons are at lower energy than they were in the absence of a field. For an electron with spin antiparallel to the field, it is now worthwhile to go to a higher energy state and change spin so long as the promotion energy is not more than the gain in *magnetic* energy. This will produce a measurable imbalance of electron spins aligned with and against the field and hence the solid will exhibit paramagnetism. This type of paramagnetism is known as *Pauli paramagnetism* and is a very weak effect giving a *magnetic susceptibility* much less than that due to *isolated spins* and comparable in magnitude to diamagnetism.

For a very few metals, however, the unpaired electrons in the conduction band can lead to ferromagnetism. In the whole of the periodic table, only iron, cobalt, nickel and a few of the *lanthanides* (Gd, Tb) posses this property. So, what is so special about these elements that confers this uniqueness on them? It is not their crystal structure; they each have different structures and the structures are similar to those of other non-ferromagnetic metals. Iron, cobalt and nickel, however, do all have a nearly full, narrow 3*d* band.

The 3d orbitals are less diffuse than the 4s and 4p, i.e. they are concentrated nearer the atomic nuclei. This leads to less overlap so that the 3d band is a lot narrower than the 4s/4p band. Further more, there are five 3d orbitals so that for a crystal of N atoms, 5N levels must be accommodated. With more electrons and a narrower band, the average density of states must be much higher than that in other bands. In particular the density of states near the Fermi level is high. In this case it is energetically favourable to have substantial numbers of *unpaired electrons* at the cost of populating higher energy levels. Thus these elements have large number of unpaired electrons even in the absence of a magnetic field. For iron, for example, in a crystal of N atoms there are up to 2.2 N unpaired electrons all with their spins aligned parallel. Note the contrast with a paramagnetic solid containing transition metal complex ions where each ion may have as many as five unpaired electrons but in the absence of a magnetic field, electrons on different ions are aligned randomly.

Ferromagnetism thus arises from the alignment of electron spins throughout the solid, and this occurs for partially filled bands with a high density of states near the *Fermi level.* 4d and 5d orbitals are more diffuse than 3d and produce wider bands so that ferromagnetism is not observed in the second and third row transition elements. The 3d orbitals themselves become less diffuse across the transition series and lower in energy. In titanium the valence electrons are in the 4s/4p band with low density of states and, at the other end of the row in copper, the 3d band has dropped in energy so that the Fermi level is in the 4s/4p band. Thus it is only at the middle of the series that the Fermi level is in a region by high density of states.

Many ferromagnetic alloys were produced for special uses. Some of these contain one or more ferromagnetic elements and among these alloys of iron, cobalt and nickel with the lanthanides, e.g. $SmCo_5$, $Nd_2Fe_{14}B$, have produced some of the most powerful permanent magnets known. In the lanthanide alloys, *f* electrons contribute to the magnetism. Potentially this could lead to a very high magnetization because there are seven *f* orbitals and so a maximum possible magnetization corresponding to seven electrons per atom. The theoretical maximum magnetization for the transition metals is five electrons per atom, as there are only five *d* orbitals. In practice this maximum is never reached. In the pure lanthanide metals, the overlap of *f* orbitals is so small that they can be regarded as localized. In the ferromagnetic lanthanides, the magnetism is produced by delocalized *d* electrons. The interaction between these *d* electrons and the localized *f* electrons causes alignment of the *d* and *f* electrons in order to reduce electron repulsion. Thus *f* electrons on different atoms are aligned through the intermediary of the *d* electrons. In alloys, the *f* electrons can align via the transition metal *d* electrons and although not all the *d* and *f* electrons are aligned, it can be seen that high values of the magnetization could be achieved. It is not surprising, then, that it is these transition metal/lanthanide alloys that are the most powerful magnets. Other alloys can be made from non-magnetic elements such as manganese and in these the overlap of *d* orbitals is brought into the range necessary for ferromagnetism by altering the interatomic distance from that in the element. The usefulness of a particular ferromagnetic substance depends on factors such as the size of the magnetization produced, how easily the solid can be magnetized and demagnetized and how readily it responds to an applied field. The number of unpaired electrons will determine the maximum field, but the other factors depend on the structure of the solid and the impurities it contains.

Ferromagnetic materials have their properties divided into two distinct and separate temperature ranges in such a way that the properties above a particular temperature are quite different from the properties below that temperature. This temperature is called the *ferromagnetic curie temperature* θ_c. Both the cases are discussed below:

***Case* 1** $T > \theta_c$. At a temperature above θ_c, a ferromagnetic material has properties similar to those of paramagnetic materials. Thus above θ_c, a ferromagnetic material has very small susceptibility and hence very small magnetization. In this temperature region, the susceptibility depends upon temperature according to a law called *Curie-Weiss* law and the susceptibility is expected to decrease with increase of temperature. This law states

$$\boxed{\chi = (\mu_r - 1) = \frac{C}{T - \theta} \text{ for } T > \theta_c} \qquad \text{(Q 6.5.1)}$$

where C is the *Curie constant* of the material and θ is the *paramagnetic Curie temperature*. The interesting information is that Eqn. (Q 6.5.1) is untrue for temperatures T very close to θ_c as $(T - \theta)$ *may* become negative which is not possible in the case of ferromagnetic materials.

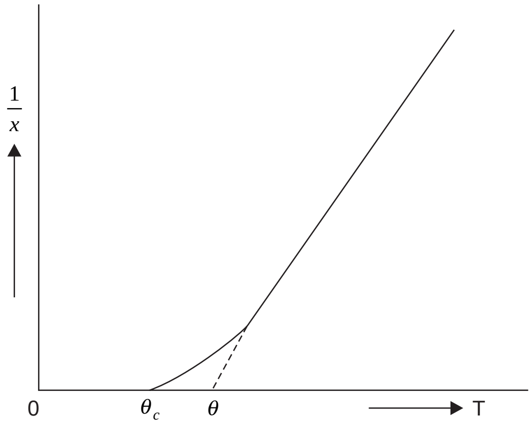
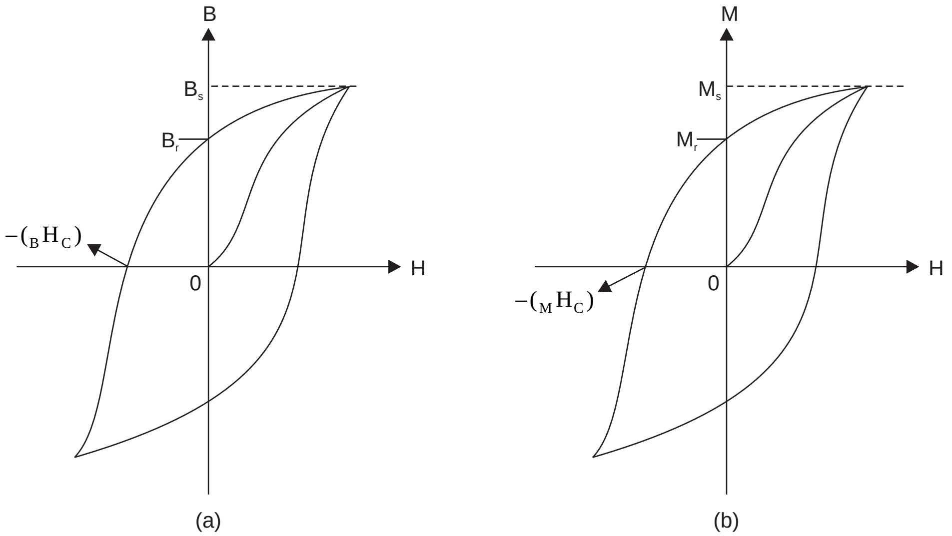


Fig. Q 6.5.2 *Inverse susceptibility versus temperature curve for a ferromagnetic material (θ_c or θ_f is used)*

In Fig. Q 6.5.2, the plot between $\frac{1}{\chi}$ and T is a straight line, starting from θ_c on the temperature axis. In the vicinity of θ_c, the variation of $\frac{1}{\chi}$ is non-linear. The *paramagnetic curie temperature* θ of the material may be got by extrapolation. A ferromagnetic material differs from a paramagnetic material in the fact that for the latter $\theta = 0$. Also we see that $\theta > \theta_c$. However $(\theta - \theta_c)$ is small. For example $\theta = 1093$ and $\theta_c = 1043\,\text{K}$ for iron.

***Case* 2** $T < \theta_c$. The most important technological property of a ferromagnet (or ferrimagnet) is hysteresis. In Fig. (Q 6.5.3) plotted a typical B – H diagram for a ferromagnet as the applied field is increased to a large positive value good enough to saturate the polarization (*magnetization*) of the material, B then reduced to a negative value large enough to produce saturation in the reverse direction, then increased back to zero once more. A symmetrical closed loop known as a *hysteresis* loop is formed. The magnetic induction remaining when the applied field is reduced from saturation to zero is called the *remanence*, B_r. The magnitude of the negative field required to reduce the induction to zero is known as the *coercivity* or *coercive force*, H_c. Remanence and coercivity are some of the properties with highest practical significance.



(a)

(b)

Fig. Q 6.5.3 *Hysteresis curve for ferromagnetic material*

Weiss Molecular Field Theory of Ferromagnetism

P. Weiss assumed phenomenologically that the strong interaction, which tends to align the atomic or ionic moments parallel in ferromagnets, could be assumed as equivalent to some magnetic field, H_i – called *Weiss field*, *molecular field* or *exchange field*. The strength of the field may be estimated as follows:

Beyond the curie temperature, a ferromagnet becomes a paramagnet and follows the *Curie-Weiss law*. Hence the thermal energy just balances the magnetic potential energy at $T = \theta_c$. i.e.,

$$\mu_0 H_i \mu_B = k_B \theta_c, \text{ or } B \mu_B = k_B \theta_c \text{ (with } \mu_B = \beta)$$

For iron $\theta_c = 1000$ K

$$H_i = \frac{k_B \theta_c}{\mu_B \mu_0} = \frac{1.38 \times 10^{-23} \times 1000}{9.27 \times 10^{-24} \times 4\pi \times 10^{-7}}$$

$$H_i = 10^9 \text{ A/m } (1\ Oe = 79.6 \text{ A/m})$$

As mentioned earlier transition metals Fe, Co, Ni; rare earth metals Gd and oxides CrO_2, ErO exhibit very large magnetizations; their magnetization is not reversible and remains even if the magnetic field is recovered. In order to explain the sources of this large magnetization, Weiss in 1907, postulated the existence of an internal field proportional to the magnetization in the material. Here the field seen by an atomic dipole is the sum of the applied field B_0 and the internal field B_i, i.e.,

and

$$\boxed{\begin{aligned} B &= B_0 + B_i \\ B_i &= \lambda M \end{aligned}} \qquad \text{(Q 6.5.2)}$$

Where λ is known as *Weiss constant*. If B is such that $\frac{g\beta B}{k_B T}$ is small, then equation (6.3.15) can be used to give

or

$$\boxed{\begin{aligned} \chi_f &= \frac{\mu_0 M}{B_0} = \frac{\mu_0 N g^2 \beta^2 J(J+1)}{3k_B T}\left[1+\frac{\lambda M}{B_0}\right] \\ \chi_f &= \frac{C}{T}\left[1+\frac{\lambda \chi_f}{\mu_0}\right] \text{ as } \chi_f = \frac{\mu_0 M}{B_0} \\ \chi_f &= \frac{C}{(T-\theta)}, \theta = \frac{C\lambda}{\mu_0} \end{aligned}} \tag{Q 6.5.3}$$

θ is the *curie temperature* at which the susceptibility tends to infinity from equation (Q 6.5.3). This means that *M* has a finite value when B_0 is zero which is an evidence of spontaneous magnetization. From equation (Q 6.3.12), we get

$$\boxed{\begin{aligned} M &= N_g \beta J B_J\left[\frac{N_g \beta J}{N k_B T}(B_0 + \lambda M)\right] \\ M &= M_s(0) B_J\left[\frac{M_s(0)}{N k_B T}(B_0 + \lambda M)\right] \end{aligned}} \tag{Q 6.5.4}$$

where $M_s(0) = Ng\beta J$ represents the maximum value of magnetization at 0 K. When there is no magnetic field, $B_0 = 0$.

$$\boxed{M = M_s(0) B_J\left[\frac{M_s(0)}{N k_B T}\lambda M\right] = M_s(0) B_J(y)} \tag{Q 6.5.5}$$

where *y* is given by Eqn. (Q 6.3.16); in case of ferromagnetic materials, as

$$\boxed{y = \frac{g\beta J}{k_B T} B = \frac{g\beta J}{k_B T}(B_0 + \lambda M)} \tag{Q 6.5.6}$$

In case of no magnetic field, $B_0 = 0$ and hence

$$\boxed{M = \frac{k_B T y}{g\beta J\lambda}} \tag{Q 6.5.7}$$

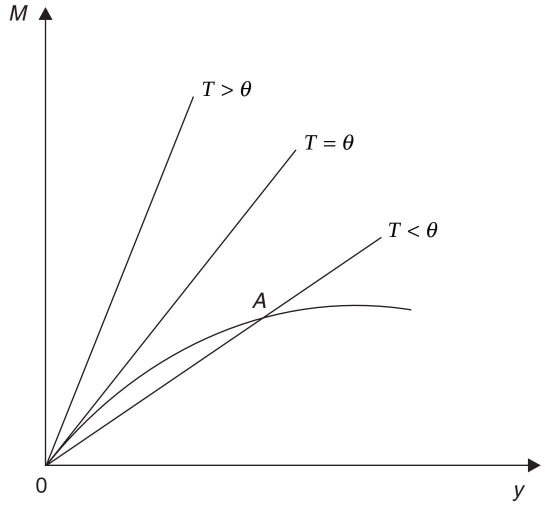


Fig. Q 6.5.4 *Graphical solution of equations Q 6.5.5 and Q 6.5.7*

Since M must satisfy both Eqns. (Q 6.5.5) and (Q 6.5.7), the two M versus y curves are plotted in Fig. Q 6.5.4. Equation (Q 6.5.7) is a straight line between M and y and for various temperatures. i.e $T < \theta$, $T = \theta$ and $T > \theta$ are shown in Fig (Q 6.5.4). The equation (Q 6.5.5) represents a curve which intersects the straight line for $T < \theta$ at point A. This gives a nonvanishing value of M even if the external field B_0 is zero. *This spontaneous magnetization* below the curie temperature is shown in Fig. (Q 6.5.5) where the magnetization decreases from a saturated value M_s at $T = 0$ to zero at $T = \theta$. At $T = \theta$, the straight line given by equation (Q 6.5.7) is the tangent to the curve (Q 6.5.5) at the origin. Thus, there is no spontaneous magnetization for $T \geq \theta$.

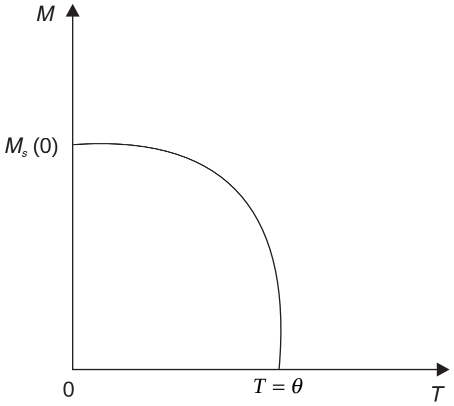


Fig. Q 6.5.5 *Spontaneous magnetization below the curie temperature*

A rough estimate of the internal field B_i is made as follows. The energy of a given atomic dipole in its field should be of the order of $k_B\ \theta$. i.e.

$$\beta B_i = k_B \theta$$

For say θ = 1500 K, B_i needs to be about 10^3 tesla. This value is enormously larger than 0.1 tesla due to the *dipole – dipole interaction*, which therefore, can not be the origin of the internal field.

Origin of Weiss Field on the Basis of Heisenberg's Theory

Gyromagnetic experiments conducted by Einstein de Hass and Barnett have conclusively established that the magnetization in ferromagnetics is due to the spin moments and not orbital moments. In 1928 Heisenberg showed that this large Weiss field can be explained in terms of the so called *exchange interaction* between the electron spins. He developed his theory on the analogy of the *Heitler-London* model of the hydrogen molecule. Exchange interaction between electrons in different quantum states can be shown to lead to a decrease in energy when the spins are parallel. When two atoms approach each other the spins of unpaired electrons in each atom assume parallel orientations. Exchange interaction is purely a quantum mechanical phenomenon. The interaction energy between such spins is derived from quantum mechanics as

$$V_{ij} = -k\, J_{ij}\, \bar{S}_i \cdot \bar{S}_j$$

where k is a constant, J_{ij} is called the *exchange integral*, S_i and S_j are the spin angular momenta associated with the i^{th} and the j^{th} state and V_{ij} the corresponding interaction energy. In general this exchange integral is negative and it is a function of the interatomic distance. The Fig. Q 6.5.6 shows the plot of the exchange integral value versus the interatomic distance. It appears that in a few cases it becomes positive. The positive value of J is found to be obtained when the ratio $\frac{r_{ab}}{r_0}$ for the atom is greater than 3 but not very much larger, where r_{ab} is the interatomic distance and r_0 is the 3d orbital radius. Incidentally it is the 3d orbit which contains unbalanced spins due to incomplete filling. The values of the ratio $\frac{r_{ab}}{r_0}$ for different atoms are

Fe	Co	Ni	Cr	Mn	Gd
3.26	3.64	3.94	2.6	2.9	3.1

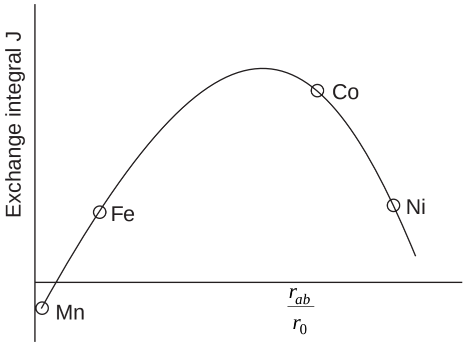


Fig. Q 6.5.6 *Variation of exchange integral with* $\frac{r_{ab}}{r_0}$

When the *J* value is positive the exchange energy is negative and hence becomes a minimum for parallel orientation and so that the atom is found to exhibit ferromagnetic properties. From the above criteria we find that Fe, Co, Ni and Gd are ferromagnetic. It is found that Cr and Mn are not ferromagnetic since the ratio $\frac{r_{ab}}{r_0}$ is less than 3. Thus we get the criteria for ferromagnetism as, that the atom must have unbalanced spins and the exchange integral J_{ij} should be positive. J_{ij} is found to be positive when the ratio $\frac{r_{ab}}{r_0}$ is slightly greater than 3. The question arises whether an element with unpaired spins but with unfavourable $\frac{r_{ab}}{r_0}$ ratio can be combined with another nonferrmagnetic element to form a compound for which the ratio $\frac{r_{ab}}{r_0}$ becomes greater than 3 will be suitable for ferromagnetism. In fact this is so and is amply proved by the fact that Mn – As, Cu – Mn and Mn – Sb alloys become ferromagnetic because of the favourable $\frac{r_{ab}}{r_0}$ ratio obtainable. This is the greatest triumph of the solid state theory, which enables us to find the criteria for a certain phenomenon from the microscopic point of view. Once the criteria is known it is only a matter of proper cooking of the molecules to fabricate materials of any desired characteristics.

Q 6.6 Explain the different contributions for the formation of domains in a ferromagnetic material and show how the hysteresis curve is explained.

***Answer*:** The concept of internal magnetic field to explain the spontaneous magnetization in *ferromagnetic materials* was first introduced by Weiss. Though the origin of this *Weiss field* was not clear at that time when Weiss proposed in 1907, the modern quantum theory has clearly established that the so called exchange interaction is responsible for this large internal molecular field in ferromagnetic materials. Again when he was confronted with the problem of explaining the phenomenon *hysteresis*, exhibited by the ferromagnetic materials he made a bold and noval suggestion that a ferromagnetic solid is divided into a large number of small regions called *domains* each of which is spontaneously magnetized to saturation. The *domain* size may vary 10^{-6} to the entire volume of the crystal. The spin magnetic moments of all the atoms in each domain are all aligned in a particular direction, but the direction of magnetization of the different domain are so oriented, as to make the net magnetization of the specimen zero. The process of magnetization consists in rotating the different domains in the direction of the applied external field so that the specimen exhibits a net magnetization externally. The existence of domains was not very much clear until Bitter successfully demonstrated the *domain structure* 25 years later. The present quantum mechanical explanation of the phenomenon also confirms domain structure idea. It is indeed a very ingenious guess which Weiss made at so early a period. We will follow the present day reasoning about the formation of domains and their roles in ferromagnetic materials.

The first question we must set ourselves is, why the entire crystal of iron does not organize itself as a single domain? In that case the specimen will be spontaneously magnetized even without any external magnetic field. But this does not happen. We know from thermodynamics that every solid structure will take up that configuration for which the free energy ($E – TS$) is a minimum. Due to high degree of order in magnetic system we can neglect the entropy term and concentrate only on the internal energy term.

The total internal energy of domain structure in a ferromagnetic material is made up from the contributions summarized below:

(a) magnetostatic energy or the magnetic field energy or the exchange energy
(b) crystalline energy or anisotropy energy
(c) domain wall energy or the Bloch wall energy
(d) magnetostriction energy

The domain structure is usually determined by the minimization of the different types of energy mentioned above. We have to now discuss how these different energies arise and what are the essential conditions to be satisfied for minimizing them.

Magnetostatic Energy

The interaction energy which makes the adjacent dipoles align themselves is the exchange energy or the magnetic field energy. Let us consider the case when all the dipoles in the crystal are aligned so as to form a single domain as shown in Fig. Q 6.6.1(*a*). Because of the free magnetic poles formed on the surface of the crystal, this configuration will have high magnetic energy $(1/8\pi)\int H^2\, dv$. In fact this is the energy required in assembling the atomic magnets into a single domain and this work done is stored as potential energy in the field outside. In Fig. Q 6.6.1 (*b*), the magnetic energy has been reduced by one half as a result of dividing the crystal into two domains magnetized in opposite directions. The sub division can be continued until the reduction in magnetic energy is less than the increase in energy to form another domain and its boundary called *Bloch wall*. A domain structure as in Fig. Q 6.6.1(c) and Fig. Q 6.6.1(d) has *zero magnetic energy*. Here the boundaries of triangular prism domains as *closure domains* near the end faces of the crystal, make equal angles of 45^0 with the magnetization direction. Hence the normal component of the magnetization in crossing such a wall is continuous, i.e., there are no free poles and there is no *field energy*. The energy required to produce a closure domain is essentially determined by the *anisotropy* of the crystal, i.e., by the fact that ferromagnetic materials have '*easy*' and '*hard*' directions of magnetization. Summarizing the ideas discussed above we may say that domain structure will depend to a large extent on the shape and size of the crystal under consideration. The size of the domains for a particular domain structure may also be obtained form the principle of minimum energy. The volume of the domains may vary between say, 10^{-2} to 10^{-6} cm^3.

Anisotropy Energy

It is found that the ferromagnetic crystals have easy and hard directions of magnetization i.e., higher fields are required to magnetize a crystal in a particular direction than others. For e.g., in *bcc* iron the *easy direction* is (1 0 0), the *medium direction* is (1 1 0) and the *hard direction* is (1 1 1). In nickel the easy direction is (1 1 1), the medium direction is (1 1 0) and the hard direction is (1 0 0). In cobalt the hexagonal axis is the only direction and all other directions are hard directions. The difference between the easy and the hard directions is, that for producing the same saturation magnetization, stronger fields are required in the hard direction than in the easy direction. The excess of energy required to magnetize a specimen in a particular direction over that required to magnetize it along the easy direction is called the *crystalline anisotropy energy*. It can be enormous if Fe, Co and Ni are magnetized in hard directions. The exact origin of this crystalline energy is not quite clear.

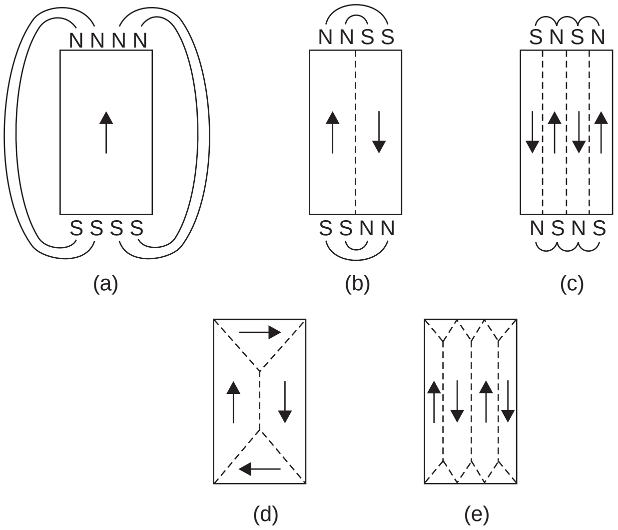


Fig. Q 6.6.1 *The origin of domains*

Magnetostrictive Energy

When a specimen is magnetized it is found that it suffers a change of dimensions and this phenomenon in known as *magnetostriction*. This deformation is different along different crystal directions. So if the domains are magnetized in different directions they will either expand or shrink. This means that work must be done against the elastic restoring forces. The work done by the magnetic field against these elastic restoring forces is the energy due to magnetostriction or the *magneto-elastic energy* is zero. But usually the lattice is strained along the different directions of magnetization of the domains.

Bloch Wall or the Domain Wall Energy

We know that the spin moments in any two adjacent domains are differently oriented so as to create the boundary between two such domains some energy, like the surface tension energy in liquids, must be spent. The boundary between two adjacent domains is called the *domain wall* or *Bloch wall* and the construction of the Bloch wall involves expenditure of energy. Work has to be done against exchange interaction (E_1) which has a tendency to align the spins in the same direction. Creation of *Bloch walls* demarcates regions with misaligned spins. Again some spins may have to point along hard directions as well. So the anisotropy energy also increases (E_2). E_1 is less if the spins change directions gradually. i.e., if the Bloch wall is thick. But E_2 is less if the spins change directions abruptly. i.e., if the Bloch wall is thin. So the thickness of the Bloch walls is a compromise. Usually Bloch walls are about 200 to 300 lattice constant thickness. In summary we can say that the equilibrium domain structure is that which gives the lowest total energy due to all the above four contributions.

Bitter in 1931 gave a visual demonstration of the *domain structure* by depositing colloidal iron oxide particles of very small size into an etched surface of a ferromagnetic solid. The iron particles concentrate at the places where the domain walls intersect since there is a strong local magnetic field in these places. The pattern is known as the *Bitter Pattern.*

Explanation of Hysteresis

The domain concept is very well suited to explain the phenomenon of hysteresis. In the absence of an external applied field the domains are oriented such as to form closed magnetic paths some what as shown in Fig. Q 6.6.2.

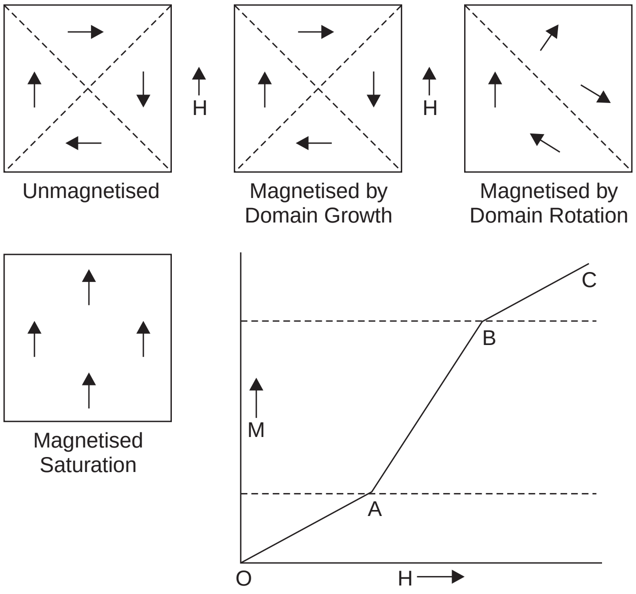


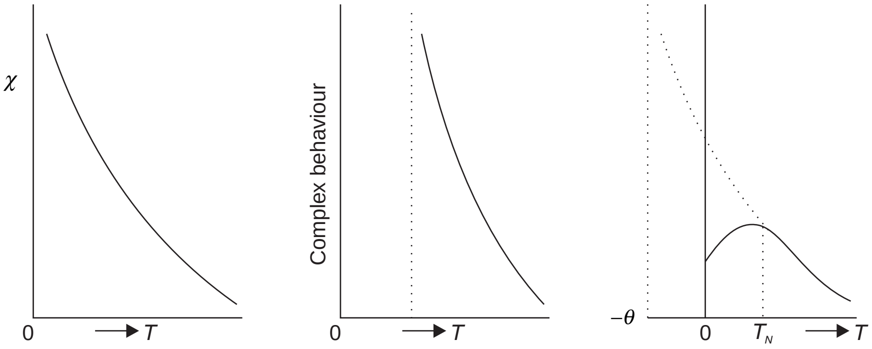
Fig. Q 6.6.2 *Hysteresis loop of a ferromagnetic material*

There are two ways by which the specimen can be magnetized, one by rotating the domains in the direction of the applied magnetizing field and other is to permit the growth of the domain which is initially in the direction of the field. In fact the magnetization takes place by both the processes. When a weak magnetic field is applied it is found that the domains which are oriented parallel to the field and in the easy direction of magnetization grows in size at the expense of less favorably oriented ones. This means less energy is required for the domain growth in the early stages than is required for the domain rotation. The domain growth requires the Bloch wall movement which involves expenditure of energy. The wall movements have been actually observed by *Bitter patterns*. This movement of the domain walls are mostly reversible and is indicated by the portion of OA of the magnetization curve in the Fig. Q 6.6.2. When the field becomes stronger the Bloch wall movement continues rather sharply and they are mostly irreversible movements. This is indicated by the portion AB of the magnetization curve. This *irreversibility* explains the existence of the *hysteresis phenomenon.* At B each domain is magnetized along their easy directions. Application of still higher fields rotates the domains into the field direction and this may be away from the easy direction, thereby storing *anisotropy energy*. Fig. Q 6.6.2 shows the position of the domains at the position C of the magnetization curve. At C the specimen is saturated when all the domains are aligned in the field direction. On removing the magnetizing field the specimen tends to attain the original configuration. This requires the movement of the Bloch walls. But this movement is impeded by impurities, lattice defects, etc., and so more energy must be supplied to over come the opposing forces. This means that a coercive field is required to bring the specimen to zero magnetization. The energy which is spent in over coming the forces opposing the Bloch wall motion is not recoverable and it is this loss of energy which is identified as the *hysteresis* loss.

Q 6.7 Give an account of Neel's theory of antiferromagnetism with a brief introduction.

***Answer*:** A ferromagnetic material is distinguished by a large, positive exchange energy between neighbouring dipoles, such that the lowest energy state is that in which the dipoles are aligned with their magnetic moments parallel. In the antiferromagnetic material the exchange energy is large and negative so that the lowest energy state is that in which neighbouring dipoles have antiparallel alignment. This means that the material would not show any spontaneous magnetization. The actual spin arrangement can be deduced from neutron diffraction experiments. The neutron, having no charge, is not affected by the electrostatic charge on ions in the lattice, but since it has a magnetic moment it can be scattered by the electron spins. By using a beam of polarized neutrons, i.e., with their magnetic moments all lying in one direction, and studying their diffraction by the crystal lattice, the spin directions of the atoms from which they are scattered can be deduced. This technique was pioneered by Shull and Smart in 1949 and has since been applied to a wide range of materials. The distinguishing features of the temperature dependence of the magnetic susceptibility in para, ferro and antiferromagnetic substances are shown in Fig. Q 6.7.1.

In the case of ferromagnetic materials there is what is called magnetization *catastrophe* at the curie temperature. Below the curie temperature the material exhibits ferromagnetism and above the curie temperature the material behaves like a paramagnetic. Similarly in the case of antiferromagnetic materials there is a pronounced kink in the susceptibility versus temperature curve. χ increases at first with temperature and reaches a maximum at a certain temperature called the Neel temperature (T_N) and then decreases as for any other paramagnetic materials as shown in Fig. Q 6.7.1. The Neel temperature plays the same part in antiferromagnetics as curie temperature in ferromagnetic materials. The susceptibility is found to follow the relation $\chi = \dfrac{C}{T+\theta}$ where C is the curie constant and θ is the paramagnetic curie temperature, or the *asymptotic curietemperature*. It must be noted that the transition from *antiferromagnetic to paramagnetic behaviour* occurs at a different temperature (T_N) and not at the curie temperature (θ).



$\chi = \dfrac{C}{T}$ (a)

$\chi = \dfrac{C}{T-\theta}$ (b)

$\chi = \dfrac{C}{T+\theta}$ (c)

Fig. Q 6.7.1 *Temperature dependence of χ in para, ferro and antiferromagnetic materials*

The interpretation of this behaviour was suggested by Neel, Bitter and van V lack as given below:

Antiferromagnetism arises when the lattice of paramagnetic ions are distributed in two *interpenetrating sub lattices* A and B where all the nearest neighbours of an ion in the sub lattice A lie in the sub lattice B and vice versa.

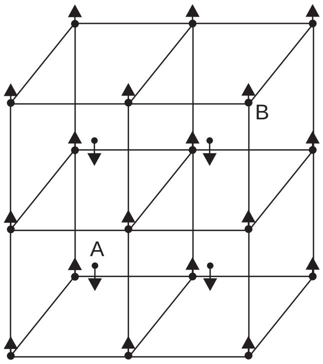


Fig. Q 6.7.2 *Distribution of ions*

Let us consider a bcc lattice where we distinguish two sites A and B as shown in Fig. Q 6.7.2. Each A site is surrounded by eight B sites and each B site is surrounded by eight A sites. Let us assume that all sites are occupied by identical atoms and that the atom in the A site tends to align its spin opposite to the spin of the neighbouring atoms in the B sites. Let H_a and H_b be the internal fields on the two sites respectively. Following the same lines as adopted for writing the Eqn. (Q 6.5.2) we have

$$H_a = H - \gamma M_b$$

and

$$H_b = H - \gamma M_a$$

where M_a and M_b represent the magnetizations of the A and B sub lattices respectively. The negative signs follow from the assumption that the atoms in A sites have their moments antiparallel to the atoms in the B sites. γ is a constant which determines the strength of the exchange interaction. If there are N atoms per unit volume in each of the two lattices sites we can write for the high temperature region,

$$M_a = \frac{N \mu_B^2}{3k_B T}(H - \gamma M_b)$$

and

$$M_b = \frac{N \mu_B^2}{3k_B T}(H - \gamma M_a)$$

Total magnetism $M = M_a + M_b$

$$M = \frac{N \mu_B^2}{3k_B T}(2H - \gamma M)$$

The above equation is similar to Eqn. (Q 6.5.4)

$$\chi = \frac{M}{H} = \frac{N\mu_B^2}{3k_B T}\left(2 - \frac{\gamma M}{H}\right)$$

$$\frac{M}{H}\left(1+\frac{\gamma N \mu_B^2}{3k_B T}\right) = \frac{2N\mu_B^2}{3k_B T}$$

or

$$\boxed{\chi = \frac{M}{H} = \frac{\dfrac{2N\mu_B^2}{3k_B T}}{\left(1+\dfrac{\gamma N\mu_B^2}{3k_B T}\right)}} \qquad \text{(Q 6.7.1)}$$

Let $$C = \frac{N\mu_B^2}{3k_B}$$

$$\chi = \frac{2C}{(T+\gamma C)} = \frac{2C}{(T+\theta)} \qquad \text{(Q 6.7.2)}$$

The above equation gives the susceptibility variation acquired by the experimental curve. It is observed that the antiferromagnetic case contains $(T+\theta)$ instead of $(T-\theta)$ and the curie constant is twice that in the ferromagnetic case. The variation of χ with T is shown in Fig. Q 6.7.1 for the three classes of magnetic materials.

Q 6.8 Explain Neel's model of ferrimagnetism. Write a note on ferrites.

***Answer*:** A ferrimagnetic material may be defined as an antiferromagnetic in which the sub-lattice moments are unequal. This means that there will be a net spontaneous magnetization in the direction of the larger sub-lattice moment, for the case of a simple *antiferromagnetic material* with strictly antiparallel sub-lattice moments. The word *ferrimagnetism* was coined by L. Neel to describe those materials which exhibit spontaneous magnetization due to antiparallel alignment between two magnetic sub-lattices. The non-vanishing, net magnetization could arise due to several reasons; however, the two principal reasons are: (a) the two sub-lattice are occupied by different types and numbers of magnetic ions and (b) the two sub-lattices correspond to two different crystallographic sites, which may also be occupied either by the same type or different types and number of magnetic ions. Above a certain critical temperature called the *ferromagnetic Neel temperature*, T_{FN} – a ferrimagnet becomes a paramagnet. The paramagnetic susceptibility follows a *hyperbolic curve*, which becomes linear at higher temperatures, stimulating the Curie-Weiss behavior exhibited by antiferromagnets.

In the ordered region,

$$M_a = M_a(0)\, B_Z(a'')$$

and

$$M_b = M_b(0)\, B_Z(b'')$$

where $$B_z = \left(a''\right) = \frac{J\, g\, \mu_B\, H_{ia}}{k_B\, T}\ \underline{\Omega}\ \frac{S\, g\, \mu_B\, H_{ib}}{k_B\, T}$$

with $$H_{ia} = -\frac{\lambda\, M_b}{\mu_0} \text{ and } H_{ib} = -\frac{\lambda\, M_a}{\mu_0} \quad \text{[Refer Eqn. 6.5.2]}$$

In many of the ferromagnetic compounds such as the *ferrites* and the *garnets*, the crystal field quenches the orbital contribution to magnetization and, therefore, J can be replaced by S. Further, in the simplest case, the presence of only one *antiferromagnetic exchange interaction* operating between the two *sub-lattice magnetization* could be assumed to exist which might be represented by the molecular field constant λ. Strictly speaking, the sub-lattice magnetizations should be represented by,

$$\boxed{\begin{aligned} M_a &= \sum_i N_i\, g_i\, \mu_B\, J_i\, B\left(a_i''\right) \\ M_b &= \sum_j N_j\, g_j\, \mu_B\, J_j\, B_z\left(b_j''\right) \end{aligned}} \tag{Q6.8.1}$$

where, $$a_i'' = \frac{J_i\, g_i\, \mu_B\, H_{ia}}{k_B\, T}$$

and $$b_j'' = \frac{J_j\, g_j\, \mu_B\, H_{ib}}{k_B\, T}$$

since each sub-lattice may be occupied by different types and numbers of magnetic ions. Moreover, the orbital contribution may not be negligible and, in addition, exchange interactions may exist within each of the two sublattices, necessitating the introduction of more than one *molecular field constants*.

Ferrites

One special class of antiferromagnetic substances which merit attention are the *ferrites* or the *ferrimagnets*. Generally the net magnetization due to the *antiferromagnetic interaction* will be zero since the spins in the A sites and B sites are equal and antiparallel. Sometimes the spins in the two sites may not neutralize exactly in which case we get a class of substances called *ferrimagnets or ferrites* which exhibit *spontaneous magnetization* below Neel temperature. These ferrimagnetic materials are of great industrial importance because ferrimagnetism has been found to occur is materials with chemical formula MO. Fe_2O_3, M corresponds to divalent cations like Mn, Fe, Co, Ni, Cu or Zn. The particular material with M = Fe; i.e., Fe O. $Fe_2\,O_3$ occurs naturally as the *iron ore magnetite*. Two kinds of iron are in this material, doubly charged ferrous ions and triply charged ferric ions i.e. ($Fe^{++}\,O^{--}$) and ($Fe_2^{+++}\,O_3^{--}$). The unit cell of magnetite contains altogether 32 oxygen atoms and 24 iron atoms. Out of these 24 iron atoms, 8 are Fe^{++} and 16 are Fe^{+++}. X – ray studies further inform that the iron ions occupy two types of positions in the unit cell. In one type, the iron ion has 4 oxygen ions about it in tetrahedral coordination, whereas in the other type, the iron ion has 6 oxygen atoms arranged about it in octahedral symmetry. Out of the 16 Fe^{+++} ions, 8 are in the tetrahedral sites whereas the rest 8 Fe^{+++} ions are in the octahedral sites.

Let us now concentrate on the spins of these iron ions. The spin moments of the 8 Fe^{+++} ions on the tetrahedral sites are directed opposite to the 8 Fe^{+++} ions on the octahedral sites. Hence these moments cancel each other, thus 16 Fe^{+++} ions contribute no net moment to the solid. The contribution to the net magnetic moment comes from 8 Fe^{++} ions, which are all aligned in the same directions for their spins. This contribution to the magnetic moment is 4β per molecule, in good agreement with the experimental measurement of 4.1β per FeO. Fe_2O_3 molecule. Extending the same argument for other ferrites, MO. Fe_2 O_3, the total magnetic moment will correspond to the magnetic moment of the M^{++} ion. Hence, the magnetic moment per molecule will be 5β for Mn, 3β for Co, β for Cu and zero for Zn. Another important characteristic of ferrites is that in addition to their ferrimagnetic property, they are insulators with very high resistivity (10^{10} Ω *m*) and hence do not have eddy-current loss problems as in iron, specially at high frequencies. Another application of ferrites is microwave devices based on Faraday effect in a ferromagnetic medium. i.e. the rotation of the plane of polarization of a linearly polarized electromagnetic wave propagating through the ferromagnet. One important application of ferrites is as core computer memories because these have a low *coercive field*, and a short switching time. The *gyromagnetic properties* of ferrites are used in developing devices like isolators and *circulators* which have applications in radar communication.

Q 6.9 Describe the structure of ferrites. How is the magnetic moment of ferrite molecule calculated?

***Answer*:** Ferrites are said to have a *spinel structure*, the same as the structure exhibited by the natural mineral Mg Al_2 O_4. In this spinel structure the oxygen atoms are closely packed in face centred lattices, *into the interstices* of which the metal ions are distributed. A unit cell of magnetite, which is a natural ferrite contains 8 molecules. There are 32 divalent oxygen ions, 16 trivalent iron ions and 8 divalent iron ions per unit cell. When the oxygen atoms arrange themselves in fcc structures there are formed 8 *tetrahedral voids* called the A sites and 16 octahedral voids called the B sites. In the normal *spinel structure* as exhibited by Mg Al_2 O_4, the divalent ions occupy the A sites and the trivalent ions occupy the B sites. Magnetite is said to exhibit an inverse spinel structure. In this structure the 8 Fe^{+++} ions occupy all the A sites and the other 8 Fe^{+++} ions occupy half the number of B sites. The remaining B sites are occupied by the Fe^{++} ions. In the case of nickel ferrite the divalent nickel ions occupy half of the B sites. The remaining B sites and the A sites are occupied by the trivalent iron ions. There are infinitely many possible ferrites, since there are several ion combinations possible in A and B sites. A wide range of ions may be used, such as Ni, Co, Mg, Mn, Cu, etc. A combination of two or more can also be used in which case we get mixed ferrites.

The magnetic moment of a ferrite material is found to be equal to the difference in the moments of ions in A and B sites. For example in the case of magnetite if we attribute 5 Bohr magneton to Fe^{+++} and 4 Bohr magneton to Fe^{++} the net moment between the A and the B sites works out to be 4 Bohr magneton ($5 + 4 - 5 = 4$). The experimental value is 4.1 Bohr magneton. If we assume 2 Bohr magneton per Ni^{++} ion, we get 2 Bohr magneton per formula weight of nickel ferrite. The experimental value is 2.3 Bohr magneton. The difference is attributed to the difference in the ‘g’ factors for the free electron.

Q 6.10 Explain the classification of magnetic materials into hard and soft. What are the chief magnetic characteristics and mention their applications?

Answer*:** ***Hard Magnetic Materials

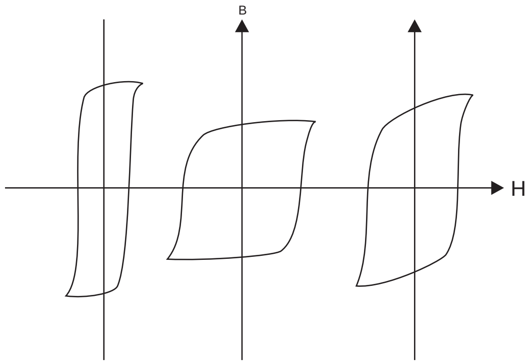
The description *hard* as applied to magnetic materials is an indication that the cohersive force is high-generally above 10^4 A/m. If, in addition the remanent flux density is high the material is suitable as a permanent magnet. In a polycrystalline material the grains are randomly oriented. In a randomly array only few grains will be favourably oriented in the direction of easy magnetization and so the process of magnetization is slowed down. Further magnetostriction effects prevent the easy movement of the grains thereby affecting magnetization in a complicated way. When a permanent magnet is required you must look for materials with the highest possible saturation magnetization, remnance and coercive force. This means that the hysteresis loop must have a large area. When the area of the hysteresis loop is large there is little loss of induced magnetism when the applied field is removed. Again you must look for a material of large magnetostrictive coefficient, since large magnetostriction gives rise to large coercive force. When magnetostriction is large, it is more difficult to change the direction of magnetization once it has reached saturation in a particular direction, since any further rotation involves expenditure of work against elastic restoring forces. Another useful criterion is the energy product given by BH, since the useful energy which a permanent magnet can deliver is determined by the BH product. Larger area for the hysteresis loop takes care of this criterion. The most important commercial hard materials are the Alnico type alloys. A steady improvement in fabrication has been achieved in Alnico alloys and Alnico V introduced in the year 1940 has very many interesting properties. Its composition is 8% Al, 14% Ni, 24% Co, 51% Fe and 3% Cu. It has a coercive field 50000 ampere turn and a BH product of 45000 J/m^2. The alloy is cast and solidified directionally along the direction of easy magnetization (100). The alloy is annealed at an elevated temperature of 1300^{0}C for a prolonged period during which a new phase precipitates out of the grains and the material is mechanically hardened. This process is called *precipitation hardening* and it increases the coercive force.

Soft Magnetic Materials

For transformer cores a ferromagnetic material having a small hysteresis loop is required. This means that the material must have very low magnetostrictive coefficient so that the material is practically stress free. The following materials are found to be suitable for the different frequencies.

1. Fe – Si alloys for low frequency high power applications.
2. Fe – Ni alloys for high quality audio transformers.
3. Ferrites for high frequency low power applications.

The addition of Si to Fe improves its magnetic quality in two ways (1) by increasing the resistivity and thereby reducing the *eddy current* losses and (2) by decreasing the hysteresis losses. An alloy with 2% Si is used for ordinary quality induction motors. Another alloy with high quality performance contains 4% Si. The rolling and annealing are carefully controlled so that the crystallites get oriented in the preferred direction. In that case the domains are large and regular in shape. The direction of easy magnetization also lies in the direction of rolling. The Ni–Fe alloy which goes under the commercial name *Hypernik* is made of two different compositions. One grade contains 50% Ni and 50% Fe. Another grade called the *permalloy* contains 78% Ni and 32% Fe. Both have high permeabilities and low hysteresis losses. The 78% permalloy has in addition zero *magnetostrictive coefficient*. *Suppermalloy* is made of 78% Ni, 5% Mo and 17% Fe. This alloy has higher resistivity and hence lower eddy current losses.



(a) Soft (b) Hard (c) Hard

Fig. Q 6.10.1 *Typical hysteresis (a) small coercive force and large B (b) large coercive force and small B, and (c) large coercive force and large B.*

TABLES

Table 6.A *Characteristics of the types of magnetism*

Type	*Sign of χ*	*Typical χ value (calculated using SI units)*	*Dependence of χ on H*	*Change of χ with increasing temperature*	*Origin*
Diamagnetism	–	$-(1-600)\times10^{-5}$	Independent	No change	Electron charge
Paramagnetism	+	$(0-0.1)$	Independent	Decreases	Spin and orbital motion of electrons on individual atoms
Ferromagnetism	+	$0.1-10^{7}$	Dependent	Decreases	Cooperative interaction between magnetic moments of individual atoms
Antiferromagnetism	+	$0-0.1$	May be dependent	Increases	
Pauli paramagnetism	+	10^{-5}	Independent	No change	Spin and orbital motion of delocalized electrons

Table 6.B *Diamagnetic volume susceptibilities of some materials*

Material	χ
Cu	-0.95×10^{-5}
Si	-0.4×10^{-5}
He	-0.5×10^{-9}
A	-11×10^{-9}
Kr	-16×10^{-9}
Xe	-25×10^{-9}
Au	-3.7×10^{-5}
Ge	-0.8×10^{-5}

Table 6.C *The susceptibility of some paramagnetic materials at room temperature*

Material	$\chi = (\mu_r - 1)$
Oxygen	0.19×10^{-5}
Platinum	35.5×10^{-5}
Air	0.035×10^{-5}
Nitrogen	0.0012×10^{-5}
Tungsten	7.5×10^{-5}
Co O	585×10^{-5}
$MnSO_4$	360×10^{-5}
Fe_2O_2	142×10^{-5}
$FeCl_2$	372×10^{-5}
$NiSO_4$	122×10^{-5}

Table 6.D *Saturation magnetization and paramagnetic* (θ_p) *and ferromagnetic* (θ_f) *curie temperatures for ferromagnetic materials*

Material	M_{sat} *at 300 K (amp/m)*	M_{sat} *at 0K (amp/m)*	θ_p *(K)*	θ_f *(K)*	*Bohr magneton per atom*
Nickel	0.475×10^6	0.5×10^6	630	646	0.612
Iron	1.710×10^6	1.763×10^6	1044	1047	2.21
Cobalt	1.45×10^6	1.446×10^6	1400	1503	1.70
Gadolinium	1.0×10^6	1.970×10^6	228	–	7.10

Table 6.E *Classification of magnetic materials*

Classification	*Permanent dipoles*	*Interaction between neighboring dipoles*
Diamagnetic	No	–
Paramagnetic	Yes	Negligible
Ferromagnetic	Yes	Parallel orientation
Antiferromagnetic	Yes	Antiparallel orientation of equal moments
Ferrimagnetic	Yes	Antiparallel orientation of unequal moments

Table 6.F *Neel and curie temperatures for anti-ferromagnetic materials*

Crystal	*Paramagnetic ion lattice*	T_N *(K)*	T_c *(K)*	$\frac{T_N}{T_c}$	$\frac{\chi(T_c)}{\chi(T_0)}$
MnO	fcc	610	122	5.0	2/3
$FeCl_2$	hcp	48	23.5	2.0	< 0.2
Fe O	fcc	570	198	2.9	0.7
Co O	fcc	–	291	–	–
Ni O	fcc	–	523	–	–

Table 6.G *Saturation magnetization and the curie temperature of some selected ferrites*

Material	*Maximum magnetization*	*Curie temperature*
Fe	1750	1043
$MnO Fe_2O_3$	358	783
$NiO Fe_2O_3$	240	893
$CuO Fe_2O_3$	290	728
$MgO Fe_2O_3$	143	523

Table 6.H *Magnetic characteristics of some typical hard materials*

Name and composition	*Coercive field (ampereturn/m)*	*Remnance (weber/m^2)*	*BH (J/m^3)*
Fe	75	1.5	100
Tungsten Steel (6% W, 1%C and 93% Fe)	5000	1.0	3000
Remalloy (12% Co, 17% Mo and 71% Fe)	20000	1.0	12000
Alnico 11 (10% Al, 17% Ni, 12% Co, 6% Cu and 55% F)	50000	1.7	17000

Contd

Name and composition	*Coercive field (ampereturn/m)*	*Resistivity (weber/m^2)*	*BH (J/m^3)*
Alnico V (8% Al, 14% Ni, 24% Co, 3% Cu and 51% Fe)	50000	1.2	45000
Index 1 (Ba $Fe_{12}O_{19}$)	140000	0.22	8000

Table 6.I *The magnetic characteristics of some of the soft materials*

Name and Composition	*Saturation magnetization in 10^5 (Ampere (turn/m)*	μ_r	ρ *in* 10^{-8} Ω *m*	*Hysteresis loss J/kg/cycle*	*Uses*
Fe	17.5	5000	10	0.03	Motors, High Quality Transformers and Audio transformers
98% Fe and 2% Si	16.7	7500	35	0.02	
98% Fe and 4% Si	15.5	30000	55	0.005	
Hipernik (50% Ni and 50% Fe)	12.7	60000	45	0.003	
78 – Permalloy (78% Ni and 32% Fe)	8.7	100000	16	0.0005	
Supermalloy (79% Ni, 5% Mo and 16% Fe)	7.0	1000000	60	0.0001	
Mn – Zn Ferrite ($Mn_{0.5}$ $Zn_{0.5}$ Fe_2 O_4)	3.1	2500	20×10^{-6}	0.001	

Table 6.J *Carbon free non – machinable alloys (Alnico)*

Alnico 2	Alnico 5	Alnico 6	Alnico 7
10 Al 17 Ni 12.5 Co 6 Cu	8 Al 14 Ni 24 Co 3 Cu	8 Al 15 Ni 24 Co 3 Cu	8.5 Al 18 Ni 24 Co 3.25 Cu

OBJECTIVE QUESTIONS

1. All materials have
   (a) paramagnetic property (b) ferrimagnetic property
   (c) ferromagnetic property (d) diamagnetic property

2. The susceptibility of a diamagnetic material is essentially independent of temperature
   (a) under all circumstances
   (b) as long as the electronic structure is independent of temperature
   (c) at very low temperatures of the order of 10 K
   (d) at very high temperature
3. Bohrmagneton is
   (a) magnetic moment of an electron spin
   (b) magnetic moment of a nucleus spin
   (c) magnetic moment of an electron orbital motion
   (d) none of these
4. The magnetic material in which permanent magnet dipoles (due to electron spin) are already aligned due to bonding forces are known as
   (a) paramagnetic materials (b) diamagnetic materials
   (c) ferromagnetic materials (d) ferromagnetic materials
5. In ferrimagnetism
   (a) the number of atoms with opposite spins are equal
   (b) the number of atoms with opposite spins are unequal
   (c) the number of atoms with opposite spins are zero
   (d) there is zero magnetic moment
6. In a ferromagnetic material, susceptibility is
   (a) very small and positive (b) very small and negative
   (c) very large and positive (d) very large and negative
7. For paramagnetic materials, relative permeability at room temperature is nearly
   (a) 0 (b) 0.1 (c) 1 (d) 10
8. Interaction between the neighbouring dipoles is negligible in the case of
   (a) diamagnetic material (b) paramagnetic material
   (c) antiferromagnetic material (d) ferrimagnetic material
9. Curie's law predicts that
   (a) the susceptibility depends on the applied field
   (b) the susceptibility is linearly proportional to the absolute temperature
   (c) the susceptibility is unversely proportional to the absolute temperature
   (d) none of these
10. Which of the following materials is used for making permanent magnet
    (a) platinum cobalt (b) alnico V
    (c) carbon steel (d) all the above
11. Ferromagnetic materials or ferrites are obtained from
    (a) copper (b) zinc
    (c) aluminium (d) mercury

12. Magnetically saturated ferrites can
    - (a) cause large hysteresius (b) produce low eddy current
    - (c) interact with ultrasonic heat radiation (d) interact with electromagnetic waves
13. At Neel temperature
    - (a) susceptibility is maximum (b) susceptibility is minimum
    - (c) permeability is minimum (d) permeability is maximum
14. Bloch walls are an example of
    - (a) magnon (b) polaron
    - (c) soliton (d) exciton
15. The diamagnetic susceptibility is
    - (a) positive always (b) negative always
    - (c) zero always (d) all are false
16. If θ_f is the curie temperature and θ is the paramagnetic temperature. Then the relation relating susceptibility χ with curie constant C and for $T > \theta_f$ is
    - (a) $\frac{C}{(\theta - T)} = \chi$ (b) $\chi = C(\theta - T)$
    - (c) $\chi = \frac{C}{(T - \theta)}$ (d) $\chi = C(\theta + T)$
17. The susceptibility of a diamagnetic material is about
    - (a) 10^5 (b) 10^{-5} (c) 10^7 (d) 0.1
18. The ferromagnetic curie temperature of iron is
    - (a) 630 K (b) 926 K (c) 1428 K (d) 1043 K
19. The magnetization of a solid is related to its magnetic induction B and the field strength H by the equation
    - (a) $M = (B/\mu_0) - H$ (b) $B = \mu_0 H + M$
    - (c) $B = H + \mu_0 M$ (d) $B = \mu_0 (H - M)$
20. The relative permeability for iron is
    - (a) 1000 (b) 3000 (c) 5000 (d) 7000
21. Below 300 K, $\chi_m(\text{dia}) > \chi_m$ (para)
    - (a) true (b) false
22. Permanent dipole moment consists of the following angular momentum
    - (a) orbital angular momentum (b) electron spin angular momentum
    - (c) nuclear spin angular momentum (d) all the above
23. Chemical formula of a simple ferrite is
    - (a) $Me^{2+} Fe_2^{3+} O_4^{2+}$ (b) $Me^{3+} Fe^{4+} O_4^{2+}$
    - (c) $Me^{4+} Fe^{2+} O_4^{3+}$ (d) None of these

24. In antiferromagnetic materials, the susceptibility
    (a) increases with increase in temperature (b) decreases with increase in temperature
    (c) is independent of temperature (d) all are true

PROBLEMS AND SOLUTIONS

6.1 A magnetic material has a magnetization of 3200 A/m and flux density 0.005 weber/m^2. Calculate the magnetizing force and the relative permeability of the material

***Solution*:**

$$B = \mu_0 (M + H)$$

Substituting the values,

$$0.005 = 4\pi \times 10^{-7} (3200 + H)$$

$$H = \frac{0.005}{4\pi \times 10^{-7}} - 3200$$

$$\boxed{H = 780.9 \ A/m} \quad \textbf{\textit{Answer}}$$

But

$$M = H(\mu_r - 1) = 3200$$

$$3200 = 780.9(\mu_r - 1)$$

$$\mu_r - 1 = \frac{3200}{780.9} = 4.1$$

$$\boxed{\mu_r = 5.5} \quad \textbf{\textit{Answer}}$$

6.2 Although manganese is not ferromagnetic, certain alloys such as Cu$_2$ Mn Al are ferromagnetic. The Mn – Mn distance in these alloys is greater than in manganese metal. What effect would this have on the 3*d* band of manganese? Why would this cause the alloy to be ferromagnetic?

***Answer*:** Because the manganese atoms are further apart, the overlap of the 3*d* orbits will be less. The 3*d* band will therefore be narrower than in manganese metal. With a narrower band, there is a larger inter electron repulsion and a state with a number of unpaired spins comparable to the number of atoms becomes favourable. The alloy is thus ferromagnetic.

6.3 The curie temperature of ferromagnetic europium oxide is 70 K. The europium ion has $g = 2$ and $J = \frac{7}{2}$. Assume molecular field model. Determine the ratio of magnetization at 300 K in a field at 0.01 T to that at 0 K.

***Solution*:**

$$\frac{M}{H} = \frac{\mu_0 M}{B_0} = \frac{C}{T - \theta} = \frac{\mu_0 N g^2 \beta^2 J(J+1)}{3k_B (T - \theta)}$$

or
$$M = \frac{Ng^2\beta^2 J(J+1)B_0}{3k_B(T-\theta)}$$

At very low temperatures, the saturation magnetization is equal to that with all the dipoles aligned parallel

$$M(0) = Ng\beta J$$

Hence

$$\frac{M(300)}{M(0)} = \frac{g\beta(J+1)B_0}{3k_B(T-\theta)}$$

$$\frac{2\times 9.27\times 10^{-24}\times 4.5\times 0.01}{3\times 1.38\times 10^{-23}\times(300-70)}$$

$$\frac{2\times 9.27\times 4.5\times 0.01}{3\times 1.38\times 2300} = 8.76\times 10^{-5}$$

$$\boxed{\frac{M(300)}{M(0)} = 8.76\times 10^{-5}}$$ ***Answer***

This indicates that paramagnetism is quite small as compared to ferromagnetism.

6.4 Consider an atom with L = 2 and 0 spin angular momentum placed in a uniform magnetic field of induction 2 weber/m^2. Calculate the rate of precession of the resultant magnetic moment.

***Solution*:**

$$S = 0,\ L = 2,\ B = 2\ \text{wb/m}^2$$

The rate of precession in given by Larmor frequency,

$$\omega_L = g_L\left(\frac{eB}{2m_e}\right)$$

and
$$g_J = \left(\frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)}\right)+1$$

Because $L = 2$ and $S = 0$, $J = L + S = 2$

Therefore
$$g_J = g_L = \frac{2\times 3+0-2\times 3}{2\times 2\times 3}+1 = 1$$

Thus
$$\omega_L = \frac{1\times 1.6\times 10^{-19}\times 2}{2\times 9.1\times 10^{-31}} = 1.76\times 10^{11}\ \text{rad/s}$$

The linear frequency is given by

$$\upsilon_L = \frac{\omega_L}{2\pi} = \frac{1.76 \times 10^{11}}{2 \times 3.14} = 2.8 \times 10^{10}$$

$$\boxed{\upsilon_L = 2.8 \times 10^{10} \text{ rev/s}}$$ ***Answer***

6.5 Zn Fe_2 O_4 has the inverse spinel structure at low temperatures. What type of magnetism would you expect it to exhibit?

Answer**:** The Zn^{2+} and half the Fe^{3+} ions are on octahedral sites with spins aligned antiparallel. The net moment of the Fe^{3+} ions is zero. As all the electron spins are paired in Zn^{2+} ions, there is no over all magnetic moment and hence the compound is antiferromagnetic.

6.6 A paramagnetic system of electronic spin magnetic dipole moment is placed in an external field of 10^5 ampre/metre. Calculate the average magnetic moment per dipole at 300 K. Also calculate the fractional number of spins which are parallel to the field.

Solution**:**

$$\bar{\mu}_m = \frac{M}{N} = \frac{\mu_0 H \beta^2}{k_B T}$$

$$\bar{\mu}_m = \frac{M}{N} = \frac{4\pi \times 10^{-7} \times 10^5 \times \left(9.27 \times 10^{-24}\right)^2}{1.38 \times 10^{-23} \times 300}$$

i.e.,

$$\boxed{\bar{\mu}_m = 2.6 \times 10^{-27}\ Am^2}$$ ***Answer***

$$\frac{N_p}{N} = \frac{\exp\left[(\mu_0 \beta H)/k_B T\right]}{\left[\left\{\exp(\mu_0 \beta H)/k_B T + \exp(-\mu_0 \beta H/k_B T)\right\}\right]}$$

$$\frac{N_p}{N} = \frac{\exp\left(2.8 \times 10^{-4}\right)}{\left[\exp\left(2.8 \times 10^{-4}\right) + \exp\left(-2.8 \times 10^{-4}\right)\right]} = 0.5$$

$$\boxed{\frac{N_p}{N} = 50\%}$$ ***Answer***

6.7 For iron the temperature θ_c at which the mutual interaction of the dipoles is just strong enough to overcome the thermal agitation, is about 1000 K. Assuming that each dipole has a strength of 1 Bohr magneton, calculate the internal field at the curie temperature.

Solution**:**

Equating the magnetic and thermal energies, one gets

$$\mu_B B_i = k_B \theta_c$$

i.e., the corresponding field at the curie temperature is

$$B_i = \frac{k_B\,\theta_c}{\mu_B} = \frac{1.38\times10^{-23}\times10^3}{9.27\times10^{-24}} = 1488 \text{ weber/m}^2$$

$$\boxed{B_i = 1488 \text{ weber/m}^2} \quad \textbf{\textit{Answer}}$$

This is a fantastic field; a large electromagnet can only produce fields of the order 10 weber/m^3. Hence we see that the internal field due to domains will have a profound effect of magnetic properties of the material, by affecting the domain structure, has such as enormous effect on the total polarization.

6.8 Derive the relation between the 'internal field' of a ferromagnet and curie temperature. Calculate this field for iron which has a curie temperature of 1043 K and an effective moment of 2.2 Bohr magneton.

***Solution*:**

The proportionality of the internal field B_i to the magnetization M is of the form

$$B_i = \lambda M$$

$$M = N\,\mu_m$$

$$\text{with} \quad \lambda = \frac{\mu_0\,\theta_c}{C}$$

where θ_c is curie temperature and C is curie constant

Also $$C = \frac{\mu_0\,g^2\,N\,\beta^2\,S(S+1)}{3k_B}$$

with $g = 2$

Since the average magnetic moment of an iron atom is given by $2.2\,\mu_B$ and hence the magnetic moment,

$$\mu_m = g\,\mu_B\left[S(S+1)\right]^{1/2}$$

$$2.2\,\mu_B = g\,\mu_B\left[S(S+1)\right]^{1/2}$$

$$1.1 = [S\,(S+1)]^{1/2}$$

$$S\,(S+1) = 1.1^2$$

Thus

$$B_i = \frac{\mu_0\,\theta_c\,M}{C} = \frac{\mu_0\,\theta_c\,M\times 3k_B}{\mu_0\,g^2\,N\,\beta^2\,S(S+1)}$$

Substituting $M = N\mu_m$,

$$B_i = \frac{\mu_m \theta_c 3k_B}{g^2 \beta^2 S(S+1)} = \frac{3k_B \theta_c 2.2\beta}{g^2 S(S+1)\beta^2}$$

$$B_i = \frac{3 \times 1.38 \times 10^{-23} \times 2.2 \times 9.27 \times 10^{-24}}{4 \times \left(9.27 \times 10^{-24}\right)^2 \times 1.1^2}$$

$$\boxed{B_i = 2117 \text{ tesla}} \quad \textbf{\textit{Answer}}$$

6.9 At what initial temperature should gadolinium sulphate be in order that an adiabatic demagnetization from an initial field of 6200 gauss to zero field should yield a final temperature of 0.346 K? Curie constant and specific heat constant for gadolinium sulphate are 7.85cm^2 deg/(gm ion) and 0.32 R$_u$ respectively.

***Solution*:**

For adiabatic magnetization,

$$\left[\frac{T_i}{T_f}\right]^2 = 1 + \frac{H_i^2 \times \text{ Curie constant}}{\text{Specific Constant}} = 1 + \frac{6200^2 \times 7.85}{1.38 \times 10^{-16} \times 6.02 \times 10^{23} \times 0.32}$$

$$= 1 + \frac{6200^2 \times 7.82}{1.38 \times 6.02 \times 0.32 \times 10^7} = 1 + \frac{6200^2 \times 7.85}{2.65 \times 10^7} = 11.3 + 1$$

$$\frac{T_i^2}{0.346^2} = 12.3$$

$$T_i^2 = 12.3 \times 0.346^2$$

$$T_i = 1.213 \text{ K}$$

$$\boxed{T_i = 1.213 \text{ K}} \quad \textbf{\textit{Answer}}$$

6.10 Domains are pinned in a material by inhomogeneities having an average spacing of $1\mu m$. If the domain wall energy, γ is 1*m* J/m^2 and saturation polarization field J_s is 2 tesla at 300 K, what will be the initial susceptibility, χ_i ?. The curie temperature of the material, T_c is 700 K and γ –proportional to $\sqrt{T_c - T}$; what will be χ_i at 600 K. If the interactomic spacing is 0.15 *nm*, estimate the first magneto crystalline anisotropy constant and the wall thickness at 300 K. Given: $\frac{J_s}{J_0} = 0.6$ at 600 K and $\frac{J_s}{J_0} = 0.98$ at 300 K.

***Solution*:**

Formula used,

$$\chi_i = \frac{J_s^2 \, y}{\gamma \, \mu_0}$$

with

(i) $J_s = 2$ tesla
(ii) $y = 10^{-6}\ m$
(iii) $\mu_0 = 4\pi \times 10^{-7}$ H/m
(iv) $\gamma = 1 \times 10^{-3}$ J/m^3

Now $$\chi_i = \frac{J_s^2\, y}{\gamma\, \mu_0}$$

$$= \frac{4^2 \times 10^{-6}}{10^{-3} \times 4\pi \times 10^{-7}}$$

$$\boxed{\chi_i = 3185} \quad \textbf{\textit{Answer}}$$

Again $$\gamma \propto \sqrt{T_c - T}$$

$$\frac{\gamma_{600}}{\gamma_{300}} = \frac{\sqrt{T_c - 600}}{\sqrt{T_c - 300}} = \sqrt{\frac{(700 - 600)}{(700 - 300)}}$$

$$\gamma_{600} = \gamma_{300}\left[\sqrt{\frac{100}{400}}\right] = 10^{-3} \times \sqrt{0.25}$$

$$\gamma_{600} = 0.5 \times 10^{-3}\ \text{J/m}^3$$

At 600 K $$\frac{T}{T_c} = \frac{600}{700} = 0.86$$

and $$\frac{J_s}{J_0} = 0.6\text{, or } J_s = 0.6\, J_0$$

At 300 K $$\frac{T}{T_c} = \frac{300}{700} = 0.43$$

$$\frac{J_s}{J_0} = 0.98;\ J_0 = \frac{J_s}{0.98} = \frac{2}{0.98} = 2.041$$

At 600 K $J_S = 0.6\ J_0 = 0.6 \times 2.041$
$J_S = 1.22$

$$\chi_i = \frac{J_s^2\, y}{\mu_0\, \gamma} = \frac{1.22^2 \times 10^{-6}}{0.5 \times 10^{-3} \times 4\pi \times 10^{-7}}$$

$$\boxed{\chi_i = 2370} \quad \textbf{\textit{Answer}}$$

Again $$\gamma = \sqrt{\frac{2k_B T_c K_i}{a}}$$

Now K_1 is the first anisotropy constant

i.e., $$K_1 = \frac{\gamma^2 a}{2k_B T_c}$$

$$K_1 = \frac{10^{-6}\left(0.15 \times 10^{-9}\right)}{2 \times 1.38 \times 10^{-23} \times 700} = 7.8 \times 10^3 \text{ J/m}^3$$

$$K_1 = 7.8 \times 10^3 \text{ J/m}^3$$

Wall thickness is

$$\delta = \frac{\gamma}{2K_1} = \frac{10^{-3}}{2 \times 7.8 \times 10^3} = 64.4 \times 10^{-9} \text{ m}$$

$$\delta = 64.4 \text{ nm} \quad \textbf{\textit{Answer}}$$

EXERCISE

6.1 Estimate the paramagnetic contribution to the magnetic susceptibility per m^3 of potassium, for which the Fermi energy is 2.1 eV. Given: $n = 1.33 \times 10^{28}/m^3$. (***Ans*****:** 6.4×10^{-6})

6.2 Given that

$$\mu_0 = 4\pi \times 10^{-7} \text{ H/m}$$
$$e = 1.6 \times 10^{-19}\ C$$
$$h = 6.625 \times 10^{-34} \text{ J s}$$
$$m_e = 9.1 \times 10^{-31} \text{ C}$$

Compute Bohr magneton (***Ans*****:** 9.27×10^{-24} amp m^2)

6.3 Determine the magnetization in a magnetic field B in terms of Bohr magneton β and the number of ions per unit volume N. A paramagnetic material is subjected to a homogeneous field of 10^6 A/m at 310 K. Determine the average magnetic moment along the direction per spin in Bohr magneton.

(***Ans*****:** 2.72×10^{-3} Bohr magneton/spin)

6.4 The ions in the molecule of magnetite are Fe^{+2}, F_{e2}^{+3} and O_4^{-3}, the subscripts, giving the number of ions per molecule. In the conventional unit cell, which is cubic one with $a = 0.837$ nm, there are eight molecules. The Fe^{+3} magnetic moments cancel and the magnetization is that produced by the Fe^{+2} ions alone. If the saturation magnetite is 5.2×10^5 A/m, calculate the moment per Fe^{+2} ion is Bohrmagneton.

(***Ans*****:** 4 Bohr magneton)

6.5 The curie temperature of iron is 1043 K. Assume that iron atoms have moments of two Bohr magneton per atom. Determine the saturation magnetization. Curie constant, Weiss field constant, and the magnitude of internal field. The radius of iron atom is 0.123 nm.

(***Ans*****:** 15.8×10^5 A/m, 0.699, 1559, 3.1 weber/m^2)

6.6 Consider an atom, placed in a magnetic field of 1 weber/m^2, with $l = 2$. Calculate (*a*) rate of precession (*b*) the torque on the atom, given that the magnetic moment makes an angle 45^0.

(***Ans*****:** 8.8×10^{10} revolution/s, 1.3×10^{-23} J)

6.7 A typical magnetic field achievable with an electromagnet with iron core is about 1 tesla. Compare the magnetic interaction energy, $\mu_B B$ of an electron spin magnetic dipole moment with $k_B T$ at room temperature and show that at ordinary temperatures the approximation $\frac{k_B T}{\mu_B B} >> 1$ is valued.

6.8 The saturation magnetic induction of nickel is 0.65 Wb/m^2. If the density of nickel is 8906 kg/m^3 and its atomic weight 58.7, calculate the magnetic moment of nickel in Bohr magneton.

(***Ans*****:** 0.61 μ_B)

6.9 Calculate the frequency of the radiation which must be incident on a substance placed in a magnetic field of strength $\left[5 \times 10^5/\pi\right]$ amp/m, so that the electron can absorb energy.

(***Ans*****:** 5.6×10^{-9} s^{-1})

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7

Theory of Semiconductors

7.1 INTRODUCTION

Q 7.1 Energy band model of a semiconductor
Q 7.2 Role of a hole in semiconductors
Q 7.3 Electron density and statistics of an intrinsic semiconductor
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KEY WORDS

semiconductors, resistivity, scattering of electrons by phonons, mobility, operating temperature, positive temperature coefficient, negative temperature coefficient, thermistors, photoelectric device, electronic configuration of silicon, cross over point, equilibrium distance, conduction band, valence band, forbidden energy gap (or band gap), thermal activation, intrinsic semiconductors, charge carriers, chemical impurities, extrinsic semiconductors, dopants, hole, vacancy, probability of missing an electron, effective mass of electron and hole, position of Fermi level, intrinsic semiconductor and charge carriers, intrinsic density of charge carriers and intrinsic conductivity, graphical evaluation of energy gap, extrinsic semiconductor, intrinsic conduction and extrinsic conduction, valency, ionized atoms, concentration of ionized donor and acceptor atoms, shift of Fermi level, its variation with temperature and concentration of impurities, theory of *n*-type and *p*-type semiconductors, ionization energy, immobile positive ions, current flow in a biased semiconductor, variation of conductivity with temperature, mobility variation, lattice scattering, drift current, diffusion current, gradient of the electron density, concentration gradient, diffusion coefficient, Einstein diffusion equation, life time and diffusion length, thermal equilibrium, life time of carriers, thermal agitation, recombination, thermal generation rate, recombination rate, recombination coefficient, density of minority carriers, Hall effect, Hall coefficient, Hall voltage, Hall angle, applications of Hall effect, thermistors, sensitiveness, temperature coefficient of resistance, thermal sensitiveness, junction diode, p-n junction, barrier potential, charge density gradient, uncovered negative and positive ions, theory of p-n junction, depletion region, redistribution of energy, temperature coefficient of resistance, diffused charge carriers, up hill, junction diode, theory of p-n junction, reverse bias, forward bias, effective rectifier, avalanche break down, junction transistor, emitter, collector.

7.1 INTRODUCTION

At room temperature (say 300 K), the materials classified as *semiconductors* have *resistivity* some where between that of a good conductor such as a metal and that of a typical insulator. This becomes obvious from the study of Table 7.1.

Table 7.1 *Electrical resistivity of typical materials at 300 K in ohm-metre*

Metal	*Resistivity*	*Semiconductor*	*Resistivity*	*Insulator*	*Resistivity*
Cu	1.7×10^{-8}	Pure Ge	0.47	Glass	10^{10} to 10^{11}
Al	2.8×10^{-8}	Pure Si	3000	Diamond	10^{14}
Fe	10×10^{-8}	FeO_4	0.01	Mica	9×10^{14}
Constantan	49×10^{-8}	Sn (Gray)	2×10^{-6}		
Nichrome	100×10^{-8}				

The fundamental difference between these three classes of materials can be easily explained on the basis of energy band theory.

The *resistivity* of semiconductors greatly depends on the following factors, remembering

$$\rho = \frac{1}{n e \mu}$$

(i) As the temperature (in metals) increases, the *scattering of electrons* by phonons increases and hence the *mobility* decreases. Hence in copper the resistivity increases as the temperature increases assuming *n* (concentration or density of free electrons) remains fairly constant over normal range of *operating temperatures*. Thus metals have a *positive temperature coefficient*.

(ii) But the temperature coefficient of resistance is negative in semiconductors. Here as the temperature increases the number of charge carriers increases exponentially which masks the decreasing effect of mobility. Hence in semiconductors *resistivity* decreases as temperature increases. i.e. they have a *negative temperature coefficient*.

(iii) Resistivity in semiconductors decreases in brighter surroundings.

(iv) Current in semiconductors does not obey Ohm's law and increases rapidly than voltage. i.e. semiconductors are non-linear resistors.

(v) Even a small trace of suitable *chemical impurity* added into pure semiconductors may change the electrical properties many fold; even a change of mechanism of conduction is possible.

The elemental semiconductors are germanium (Ge), silicon (Si), selenium (Se), grey (crystalline) tin, tellurium (Te), boron, etc. A large number of compounds are also semiconductors, like cuprous oxide (Cu_2O), indium antimonide, bismuth telluride, etc. Semiconductor materials and fabiricated devices are used in many vital areas mainly because of their small size and low operating voltage. They are used as *rectifiers* and *transistors*. Semiconductors, whose resistance is temperature dependent are employed as *thermistors*; if it is voltage dependent, the semiconductors may be used as a *varistor*, and if light dependent, as a *photoelectric device*. Semiconductors are used in heating appliances, photo cells, refrigerators, measuring instruments, automatic and remote control systems, etc. Devices made out of *p-n* junction helped to replace the bulky valves operated at high voltages. New devices coming up every year using semiconductors make significant contributions right from animation work in computer engineering to reduction of weight in space ships.

Q 7.1 Discuss the energy band model of a semiconductor with a diagram connecting energy values and spacing between atoms of the semiconductor.

***Answer*:** When two atoms of the same element are very far apart their electronic levels do not influence each other. The two atoms may be considered to be isolated. If the atoms are of sodium the 3s electron of each atom will have a single energy level with respect to its respective nucleus. If the two atoms approach each other the wave functions of the two 3s electrons will start overlapping. As a result of the interaction of the two atoms two different 3s levels will be formed. But our present interest is to study this problem by considering a semiconductor.

The electronic configuration of silicon (14) is $1s^2$, $2s^2 2p^6$, $3s^2 3p^2 3d^0$. The outermost shell contains 4 electrons of which 2 in the 3s level and the other 2 in the 3p though it can accommodate 6 in total. When the silicon atoms come close together strong interaction starts and the sharp 3s and 3p levels widen into bands. At one particular distance of separation (called *cross over point*), the bands merge and split again. What is actually happening at the *equilibrium distance* r_0 where stability is reached? The *unoccupied states* put together form the upper *conduction band* is separated by the occupied states put together form the lower *valence band*, by a *forbidden energy* gap. This *band gap* (E_g) is 0.67 *eV* for *Ge* and 1.106 *eV* for *Si* at 300 K.

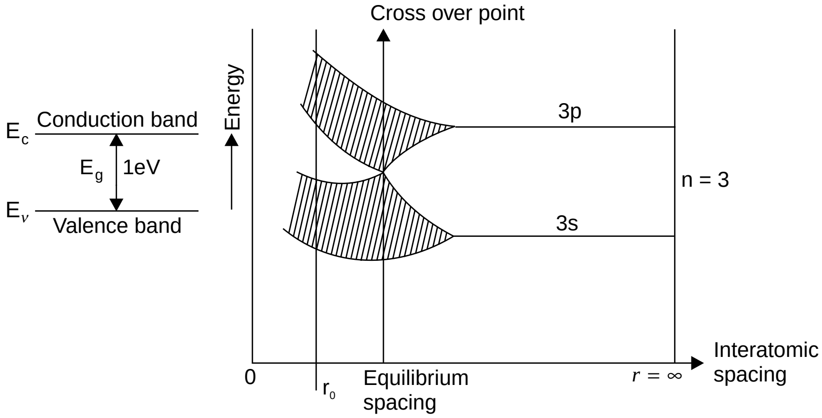


Fig. Q 7.1.1 *The bands arising for the 3s and 3p states of silicon as a function of interatomic distance*

This band gap is 0 for metals (over lapping of conduction band and valence band) and it is 6 *eV* for the insulator carbon in the diamond structure. Pure germanium and pure silicon where electrons and holes are produced by phonons (thermal activation) or by photons of suitable frequency are called *intrinsic semiconductors*. In the other type the *charge carriers* are produced by the addition of suitable *chemical impurities*. Such semiconductors are called *extrinsic semiconductors* or *impurity semiconductors*. The impurities injected are called *dopants*.

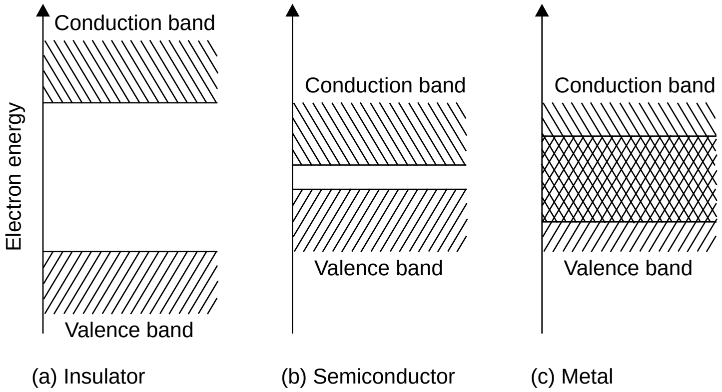


Fig. Q 7.1.2 *Typical energy bands*

Q 7.2 What is meant by a 'hole' in a semiconductor? How does the existence of a hole lead to electrical conductivity?

***Answer*:** The valence band and the conduction band in a semiconductor are separated by a small energy gap of the order of 1 eV. At 0 K the valence band is completely filled and the conduction band is empty provided the semiconductor is pure and free from defects or imperfections. Even if an electric field is established at this low temperature (0 K), the electrons in the valence band cannot acquire additional energy as there are no unoccupied energy states in the valence band to which the electrons can be raised. Thus there will be no electric current and the solid will be an insulator.

At high temperatures (can be even lower than 300 K), a reasonable number of electrons in the valence band may acquire sufficient energy and get excited into the conduction band (as the energy gap is small). They may also acquire additional energy in an applied electric field. This gives rise to an electric current and such solids are intrinsic semiconductors. If an electron in the completely filled valence band of a semiconductor is removed from that band, a vacancy is left behind in that band which is called a 'hole'. Removal of electrons from the valence band is possible either by *thermal excitation* (*intrinsic one*) or by adding *dopants* (impurity semiconductor).

When a *vacancy* is created in the valence band, a lower energy electron in the band may be excited to the higher energy vacant level by an applied electric field. The hole then moves down to the lower energy level. Since the hole moves in a direction opposite to that of the electron, we can treat the hole as a positively charged particle. The energy of the hole increases when it moves from a higher electronic level to a lower electronic level. Thus we conclude that the hole gains energy in an applied electric field and to cause a current.

Q 7.3 Deduce the expression for electron density in the conduction band of an intrinsic semiconductor at T K by applying Fermi-Dirac distribution law. What will be the density of holes in the valence band at that temperature?

***Answer*:** We may write the general expression for the number of electrons (in a volume a^3) in the conduction band having energy values lying between E and ($E + dE$) [referring Eqn. (Q 4.6.1)] as

$$\boxed{N(E)\,dE = \frac{\pi}{2}\left[\frac{8ma^2}{h^2}\right]^{3/2}(E - E_c)^{1/2}\,dE\;F(E)} \qquad \text{(Q 7.3.1)}$$

Integrating

$$N = \frac{\pi}{2}\left[\frac{8ma^2}{h^2}\right]^{3/2} \int (E - E_c)^{1/2}\, dE \,\frac{1}{\left[1 + e^{\frac{E - E_F}{k_B T}}\right]}$$

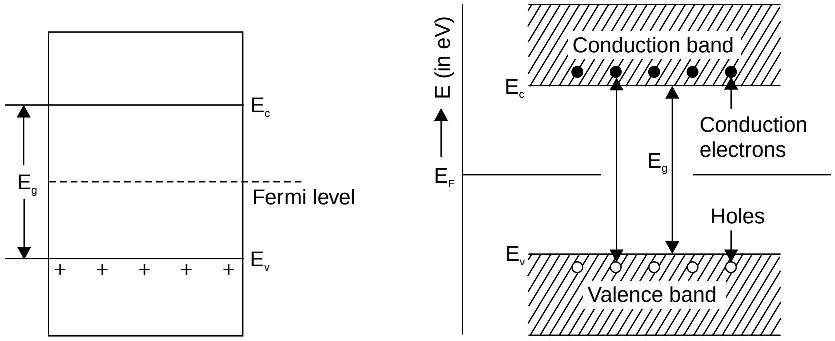


Fig. Q 7.3.1 *Thermal excitation of electrons*

Even at 300 K, $(E - E_F) >> k_B T$, hence

$$N = \frac{\pi}{2}\left[\frac{8ma^2}{h^2}\right]^{3/2} \int_{E}^{\infty} (E - E_c)^{1/2}\, e^{\frac{E_F - E}{k_B T}}\, dE$$

Let $x = (E - E_c)$

$$N = \frac{\pi}{2}\left[\frac{8ma^2}{h^2}\right]^{3/2} e^{\frac{E_F - E_c}{k_B T}} \int_{0}^{\infty} x^{1/2}\, e^{-\frac{x}{k_B T}}\, dx$$

The solution of the integral using gamma function is

$$\int_{0}^{\infty} x^{1/2}\, e^{-\alpha x}\, dx = \frac{\sqrt{\pi}}{2}\,\frac{1}{\alpha^{3/2}} \text{ with } \alpha = \frac{1}{k_B T}$$

For unit volume and using effective mass m_e^* in place of m, we get

$$n = \frac{N}{a^3} = \frac{\pi}{2}\left[\frac{8m_e^*}{h^2}\right]^{3/2} \left[\frac{\sqrt{\pi}}{2}(k_B T)^{3/2}\right] e^{\frac{E_F - E_c}{k_B T}}$$

Thus

$$\boxed{\begin{aligned} n &= 2\left[\frac{2\pi m_e^* k_B T}{h^2}\right]^{3/2} e^{\frac{(E_F - E_c)}{k_B T}} \\ n &= N_e\, e^{\frac{(E_F - E_c)}{k_B T}} \end{aligned}} \tag{Q 7.3.2}$$

Calculation of Holes

[1– F (E)] is the probability of missing the electron in the valence band which gives the probability of finding a hole there.

$$1 - F(E) = 1 - \frac{1}{1 + e^{\frac{E_F - E_F}{k_B T}}} = \frac{e^{\frac{(E - E_F)}{k_B T}}}{1 + e^{-\frac{(E_F - E)}{k_B T}}}$$

Since $-\dfrac{(E_F - E)}{k_B T}$ is a large negative quantity,

$$1 - F(E) = e^{\frac{E - E_F}{k_B T}}$$

Refer equation (Q 7.3.1): proceeding in the same way, one will get,

$$P(E)dE = \frac{\pi}{2}\left[\frac{8m_p^* a^2}{h^2}\right]^{3/2} (E_v - E)^{1/2}\, dE\left[1 - F(E)\right]$$

A simplification on the same line yields [Refer Eqn. Q 7.3.2]

$$\boxed{\begin{aligned} p &= 2\left[\frac{2\pi m_p^* k_B T}{h^2}\right]^{3/2} e^{\frac{(E_v - E_F)}{k_B T}} \\ p &= N_p\, e^{\frac{(E_v - E_F)}{k_B T}} \end{aligned}} \tag{Q 7.3.3}$$

Q 7.4 Discuss the special features of the above two equations for electrons and holes bringing out their important uses and then the conclusions.

***Answer*:** In an intrinsic semiconductor both the electrons and holes are equal in a given volume. Their charges are also having the same value though the *effective mass* of hole is usually greater than that of electron. These important physical properties help one to arrive at the following conclusions.

(i) *Position of Fermi level*: Since n and p are the same in an intrinsic semiconductor, we may write,

$$\left(m_e^*\right)^{3/2} e^{\frac{(E_F - E_c)}{k_B T}} = \left(m_p^*\right)^{3/2} e^{\frac{(E_v - E_F)}{k_B T}}$$

$$e^{\frac{2E_F}{k_B T}} = e^{\frac{(E_c + E_v)}{k_B T}} \left[\frac{m_p^*}{m_c^*}\right]^{3/2}$$

$$\frac{2E_F}{k_B T} = \frac{(E_c + E_v)}{k_B T} + \frac{3}{2} \ln\left[\frac{m_p^*}{m_e^*}\right]$$

$$E_F = \frac{(E_c + E_v)}{2} + \frac{3k_B T}{4} \ln\left[\frac{m_p^*}{m_e^*}\right]$$

If $m_p^* = m_e^*$

$E_F = \dfrac{(E_c - E_v)}{2}$, or Fermi level lies mid-way between the conduction band and valence band. If $m_p^* > m_e^*$, it will be slightly shifted from this position towards conduction band.

(ii) *Calculation of intrinsic charge carriers*: The density of electrons equals that of holes, and they are both called the *intrinsic density*, n_i, where

$$n_i^2 = np = (N_e N_p) e^{\frac{E_V - E_C}{k_B T}}$$

Substituting for $N_e N_p$ and introducing $-(E_c - E_v) = -E_g$, one gets,

$$n_i^2 = (N_e N_p) e^{-\frac{E_g}{k_B T}}$$

$$= 4\left[\frac{2\pi k_B T}{h^2}\right]^3 \left(m_e^* m_p^*\right)^{3/2} e^{-\frac{E_g}{k_B T}}$$

$$n_i = 2\left[\frac{2\pi k_B T}{h^2}\right]^{3/2} \left(m_e^* m_p^*\right)^{3/4} e^{-\frac{E_g}{2k_B T}}$$

If $m_e^* = m_p^*$ is equal to the rest mass, then

$$\boxed{n_i = 2\left[\frac{2\pi k_B T}{h^2}\right]^{3/2} \left(m^{3/2}\right) e^{-\frac{E_g}{2k_B T}} = 2\left[\frac{2\pi k_B T}{h^2}\right]^{3/2} e^{-\frac{E_g}{2k_B T}}} \qquad \text{(Q 7.4.1)}$$

i.e.,

$$\boxed{n_i = 2\left[\frac{2\pi \times 1.38 \times 9.1 \times 10^{-31}}{\left(6.62 \times 10^{-34}\right)^2}\right]^{3/2} \times T^{3/2} e^{-\frac{E_g}{2k_B T}}} \qquad \text{(Q 7.4.2)}$$

or
$$\boxed{\begin{aligned} n_i &= 4.83 \times 10^{21} \times T^{3/2}\, e^{-\frac{E_g}{2k_B T}} \\ n_i &= C T^{3/2}\, e^{-\frac{E_g}{2k_B T}} \end{aligned}} \tag{Q 7.4.3}$$

(iii) *Electrical conductivity of intrinsic semiconductors*: The conductivity of a semiconductor is different from a metal in the respect that in a semiconductor the *charge carriers* are electrons as well as holes. On the basis of free electron theory the conductivity σ of a metal is

$$\sigma = n e \mu_e$$

In the case of the semiconductor it is,

$$\sigma_i = \sigma_n + \sigma_p = n e \mu_e + p e \mu_p$$

i.e.,
$$\boxed{\sigma_i = n_i e(\mu_p + \mu_e)} \tag{Q 7.4.4}$$

(iv) *Evaluation of the energy gap* (E_g): The mobility of charge carriers is proportional to $\frac{1}{T^{3/2}}$

i.e.,
$$\mu_e \propto \frac{1}{T^{3/2}} = \frac{\alpha}{T^{3/2}} \text{ and } \mu_p = \frac{\beta}{T^{3/2}}$$

Hence
$$\sigma_i = n_i e \frac{(\alpha + \beta)}{T^{3/2}}$$

Substituting the value of n_i from Eqn. (Q 7.4.3), one gets

$$\sigma_i = C e\, T^{3/2} \frac{(\alpha + \beta)}{T^{3/2}} e^{-\frac{E_g}{2k_B T}}$$

i.e.,
$$\boxed{\begin{aligned} \sigma_i &= B e^{-\frac{E_g}{2k_B T}} \\ \rho_i &= A e^{\frac{E_g}{2k_B T}} \end{aligned}} \tag{Q 7.4.5}$$

$$\boxed{\ln \rho_i = \frac{E_g}{2k_B T} + \ln A} \tag{Q 7.4.6}$$

Now measure the resistivity of the intrinsic semiconductor at various temperatures; draw a graph between $\ln \rho_i$ and $\frac{1}{T}$. The slope of the graph will be $\frac{E_g}{2k_B}$ from which E_g can be estimated.

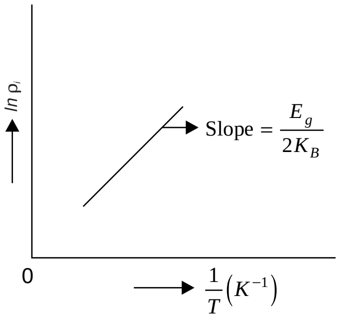


Fig. Q 7.4.1 $ln\,\rho_i$ *versus* $\frac{1}{T}$

(v) *Illustration and conclusion*: For silicon E_g = 1 eV. Let the operating temperature be 27°C

$$n_i = 4.83 \times 10^{21} \times 300^{3/2} \times e^{-\frac{E_g}{2 \times 0.025}}$$

$$n_i = 5.02 \times 10^{17}$$

i.e., the number of free charge carriers in a semiconductor like Si is about 10^{11} times smaller than that of Si atoms. Because of this, the conductivity of intrinsic semiconductors is low. Hence for an appreciable current to flow, the applied field must be large and therefore this type of semiconductors is usually of interest only from a theoretical point of view.

Q 7.5 What is meant by extrinsic (or impurity) semiconductor? In what way does it differ from an intrinsic semiconductor? Discuss the effect of doping arsenic atoms in germanium.

***Answer*:** In crystalline semiconductors such as germanium or silicon the valence band is completely filled and the conduction band is fully empty at zero degree kelvin assuming the energy gap is small. If a trace of suitable foreign atoms from selected elements, having a *valency* different from Ge (or Si) is incorporated as impurity in the crystal lattice of the given semiconductor, the impurity atoms either add electrons to the conduction band or remove electrons from the valence band (or add 'holes' to the valence band). The presence of electrons in the conduction band, or the presence of holes in the valence band, makes the solid a conductor. This type of germanium is called *extrinsic semiconductor* or *impurity semiconductor*. The presence of *impurities* causes electrical conduction even at low temperatures. At higher temperatures some electrons in the *valence band* are excited to the *conduction band*, causing electrical conduction. This is due to *intrinsic charge carriers*. At very low temperatures the intrinsic conductivity will be absent, but there will be extrinsic conductivity due to impurities. At higher temperatures, the conductivity is due both to *intrinsic activity* and to extrinsic activity. Here the intrinsic conductivity varies more rapidly with temperature than extrinsic conductivity.

An impurity semiconductor is said to be donor type or *n*-type, if the impurity material or dopant has valency of five, i.e. one more than the *valency* of germanium or silicon. Typical donor materials used are *phosphorus, antimony, arsenic* and *bismuth.* These impurity atoms have size of the order of as that of germanium atoms and, therefore, dislodge some of the germanium atoms in the crystal lattice as shown in Fig. Q 7.5.1.

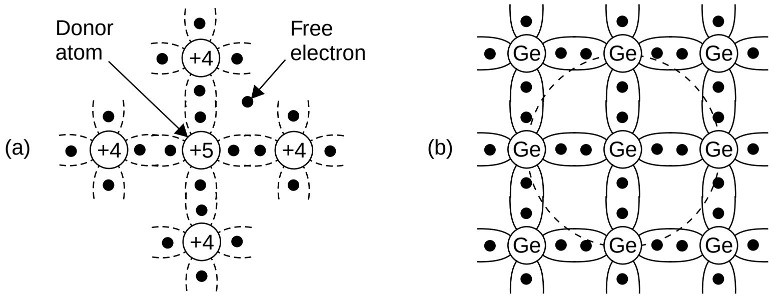


Fig. Q 7.5.1 *Crystal lattice with one germanium atom replaced by arsenic atom*

Since the percentage of impurity atoms is very small, normally every impurity atom is surrounded by Ge atoms. There are thus four germanium atoms at equal distances from the impurity atom. Out of five valence electrons of the donor atom, four electrons form regular covalent bonds with the valence electrons of the four adjoining germanium atoms and are tied down by covalent bonds. The remaining fifth valence electron remains loosely bound to the parent impurity atom and is available as a carrier current. The amount of energy needed to detach this fifth valence electron from the impurity is of the order 0.01 eV for Ge when arsenic is used. This *ionization energy* is small in comparison with 0.75 eV needed to break a regular covalent bond.

Q 7.6 Point out the standard symbols used in the discussion of impurity semiconductors. Also get the required information of the position of Fermi level in n-type and p-type semiconductors

***Answer*:** The following symbols are used in the theory of impurity semiconductors.

(i) N_d is density of donor atoms

(ii) N_d^+ is density of donor atoms ionized

(iii) N_a is density of acceptor atoms

(iv) N_a^- is density of ionized acceptor atoms

(v) n is the general symbol for the electrons in the conduction band

(vi) p is the general symbol for the holes in the valence band

(vii) n_i density of intrinsic holes and electrons or intrinsic charge carriers

Let p_n represent the concentration of holes in an n-type material; since all the holes present in the n-type material are as a result of the *break of covalent bonds*, we have

$$n' = p_n$$

If N_d and N_d^+ be the concentrations of donor impurities and ionized donor atoms. n-represents the free electron density due to impurity atoms.

i.e., $$n = N_d^+$$

Thus $$\left(n + n'\right) p_n = n_i^2$$

$$\left(p_n + N_d^+\right) p_n = n_i^2$$

or
$$p_n^2 + p_n N_d^+ = n_i^2$$

$$p_n^2 = n_i^2 - p_n N_d^+$$

$$\boxed{p_n < n_i} \tag{Q 7.6.1}$$

This tells that as a result of the doping, the hole concentration has decreased from its intrinsic value; the net effect of doping a semiconductor with a *n*-type impurity is to increase the free electron concentration and to decrease the hole concentration. Similarly in a *p*-type semiconductor

$$\boxed{n_p < n_i} \tag{Q 7.6.2}$$

Fermi Level in Impurity Semiconductors

The general equations for the concentrations of electrons and holes in an extrinsic semiconductor are given by

$$n = CT^{3/2} e^{\frac{E_f - E_c}{k_B T}}$$

and
$$p = CT^{3/2} e^{\frac{E_v - E_f}{k_B T}}$$

where E_f is the Fermi level in the extrinsic semiconductor.

For *n*-type material, $n > p$

Hence
$$-\left(E_c - E_f\right) > -\left(E_f - E_v\right)$$

$$\boxed{\left(E_c - E_f\right) < \left(E_f - E_v\right)} \tag{Q 7.6.3}$$

This shows that the Fermi level shifts upward, closer to the conduction band in a *n*-type semiconductor. The magnitude of the shift is proportional to the doping level. Similarly in the case *p*-type semiconductor, the Fermi level shifts downward, closer to the valence band. Hence

$$\boxed{\left(E_c - E_f\right) > \left(E_f - E_v\right)} \tag{Q 7.6.4}$$

Q 7.7 Derive the general expression to speak of a semiconductor doped with donor and acceptor types of impurities. What are the teachings that can be made with the expressions?

***Answer*:** Let us consider unit volume of a semiconductor. This is doped with N_d donor impurities and N_a acceptor impurities. Let *n* and *p* be the density of electrons and holes respectively. N_a^- and N_d^+ are the ionized atoms.

For charge neutrality,

$$\left(ne + N_a^- e\right) = \left(pe + N_d^+ e\right)$$

or
$$\boxed{n + N_a^- = p + N_a^+} \tag{Q 7.7.1}$$

Referring Eqns. (Q 7.3.2 and Q 7.3.3) and using common sense we write

(i) $n = N_e e^{\frac{(E_f - E_c)}{k_B T}}$

(ii) $N_a^- = N_a F(E_a) = \dfrac{N_a}{1 + e^{\frac{(E_a - E_f)}{k_B T}}}$

(iii) $p = N_p e^{\frac{(E_v - E_f)}{k_B T}}$

(iv) $N_d^+ = N_d [1 - F(E_d)]$

$$1 - F(E_d) = \left\{1 - \frac{1}{1 + e^{\frac{(E_d - E_f)}{k_B T}}}\right\} = \left\{\frac{e^{\frac{E_d - E_f}{k_B T}}}{1 + e^{\frac{(E_d - E_f)}{k_B T}}}\right\}$$

$$[1 - F(E_d)] = \frac{1}{\left[1 + e^{\frac{(E_f - E_d)}{k_B T}}\right]}$$

Substituting these values in Eqn. (Q 7.7.1), we get

$$\boxed{N_e e^{\frac{(E_f - E_c)}{k_B T}} + \frac{N_a}{\left[1 + e^{\frac{(E_a - E_f)}{k_B T}}\right]} = N_p e^{\frac{(E_v - E_f)}{k_B T}} + \frac{N_d}{\left[1 + e^{\frac{(E_f - E_d)}{k_B T}}\right]}} \qquad \text{(Q 7.7.2)}$$

E_f is used instead of E_F as this is the case of an impurity semiconductor and the Fermi level in this case may not coincide with that in an intrinsic semiconductor for a wide range of temperature.

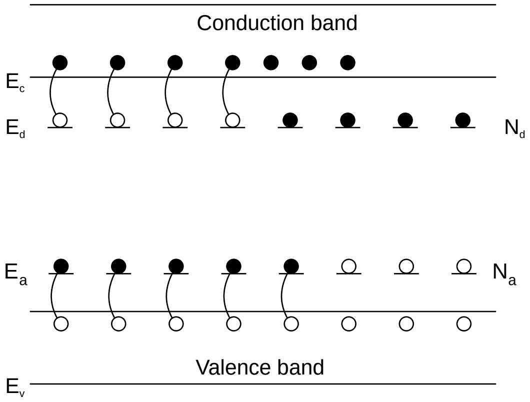


Fig. Q 7.7.1 *A semiconductor with both type of impurities*

(i) *Fermi level in an n-type semiconductor at very low temperatures:* Let us consider N_d donor levels/m^3 having energy E_d as shown in Fig. Q 7.7.2. At 0 K all the donor levels are filled and the number of electrons in the conduction band is zero. When the temperature is slightly increased such that only a small fraction of *donors is ionized*, we expect the Fermi level to lie only half way between the donor level and the bottom of the conduction band. At very low temperatures,

$$n = N_d F(E_c)$$

$$n = \frac{N_d}{1 + e^{\frac{(E_c - E_f)}{k_B T}}} = N_d \exp\left[(E - E)/k_B T\right]$$

$1 - F(E_d)$ means an electron missing E_d state

$$1 - F(E_d) = 1 - \frac{1}{\left[1 + e^{\frac{(E_d - E_f)}{k_B T}}\right]} = \frac{e^{\frac{(E_d - E_f)}{k_B T}}}{\left[1 + e^{\frac{(E_d - E_f)}{k_B T}}\right]} = \frac{e^{\frac{(E_d - E_f)}{k_B T}}}{\left[1 + e^{1 - \frac{E_f - E_d}{k_g T}}\right]}$$

At very low temperatures

$$1 - F(E_d) = e^{\frac{(E_d - E_f)}{k_B T}}$$

Now $$N_d^+ = N_d\left[1 - F(E_d)\right] = N_d\, e^{\frac{(E_d - E_f)}{k_B T}}$$

But $$n = N_d^+ \text{ with } n = N_d \exp\left[(E_f - E_c)/k_B T\right]$$

$$N_d \exp\left[(E_f - E_c)/k_B T\right] = N_d\, e^{\frac{(E_d - E_f)}{k_B T}}$$

$$(E_f - E_c) = (E_d - E_f)$$

$$\boxed{E_f = \frac{E_c + E_d}{2}} \qquad \text{(Q 7.7.3)}$$

i.e., at very low temperatures E_f lies mid way between E_c and E_d. As the temperature increases E_f begins to fall and coincide with E_F.

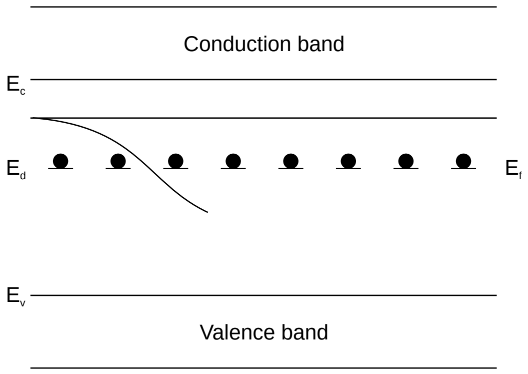


Fig. Q 7.7.2 *Fermi level in an n-type semiconductor at very low temperatures and its variation with temperature*

(ii) *Theory of n-type semiconductors*: Rewrite the general equation (Q 7.7.2) by assuming that $n >> p$ and N_a is absent: i.e.,

$$N_e \, e^{\frac{(E_f - E_c)}{k_B T}} = \frac{N_d}{\left[1 + e^{\frac{(E_f - E_d)}{k_B T}}\right]}$$

or
$$N_e \, e^{\frac{(E_f - E_c)}{k_B T}} + N_e \, e^{\frac{2E_f}{k_B T}} \, e^{\frac{-(E_c - E_d)}{k_B T}} - N_d = 0$$

i.e.,
$$e^{\frac{2E_f}{k_B T}} \left[N_e \, e^{\frac{-(E_c - E_d)}{k_B T}} \right] + e^{\frac{E_f}{k_B T}} \left[N_e \, e^{\frac{-E_c}{k_B T}} \right] - N_d = 0$$

This is of the form $ax^2 + bx + c = 0$. A final simplification gives

$$\boxed{e^{\frac{E_f}{k_B T}} = \frac{-1 + \left\{1 + \frac{4N_d}{N_e} \exp\left[(E_c - E_d)/k_B T\right]\right\}^{1/2}}{2\, e^{\frac{-E_d}{k_B T}}}} \qquad \text{(Q 7.7.4)}$$

The two possible limiting cases are now discussed:

***Case* 1:**

$$\frac{4N_d}{N_e} \exp\left[(E_c - E_d)/k_B T\right] << 1$$

This means N_d is small and T is high. This is a bad approximation; because if N_d is too small and T is too high the fact hole suppression becomes untrue. However if the said quantities are kept with in the limit, then Eqn. (Q 7.7.4) becomes $\left[\text{using } (1 + x)^{1/2} = 1 + \frac{x}{2}\right]$

$$\boxed{e^{\frac{E_f}{k_BT}} = \frac{-1+\left\{1+\frac{4N_d}{2N_e}\,e^{\frac{(E_c-E_d)}{k_BT}}\right\}}{2\,e^{\frac{-E_d}{k_BT}}} = \frac{N_d}{N_e}\,e^{\frac{E_c}{k_BT}}} \qquad \text{(Q 7.7.5)}$$

or

$$N_d = N_e\,e^{\frac{(E_f\ -\ E_c)}{k_BT}}$$

$$\boxed{N_d = n} \qquad \text{(Q 7.7.6)}$$

(since $N_e\,e^{\frac{(E_f - E_c)}{k_BT}}$ is the general expression for n).

Table Q 7.7.1 *Ionization energy from donor and acceptor states in silicon and germanium (in eV)*

Doping Element	*Silicon (14)*		*Germanium (32)*	
	Donor $(E_c - E_d)$	*Acceptor* $(E_a - E_v)$	*Donor* $(E_c - E_d)$	*Acceptor* $(E_a - E_v)$
Phosphorus (15)	0.045	–	0.0120	
Arsenic (33)	0.049 – 0.056	–	0.0127	
Antimony (51)	0.039	–	0.0096	
Boron (5)	–	0.045	–	0.0104
Aluminium (13)	–	0.057 – 0.067	–	0.0102
Gallium (31)	–	0.065 – 0.071	–	0.0108
Indium (49)	–	0.16	–	0.0112

Illustration

(i) Temperature 20°C

(ii) $N_d = 10^{23}/m^3$

(iii) Donor level lies at 0.015 eV below the conduction band

(iv) $k_B T = 1.38 \times 10^{-23} \times 293 / 1.6 \times 10^{-19}$ eV
or $k_B T = 0.0253$ eV

Refer Eqn. (Q 7.7.5)

$$e^{\frac{(E_c - E_f)}{k_BT}} = \frac{N_e}{N_d}$$

$$\left(E_c - E_f\right) = 0.0253 \times ln\left(\frac{N_e}{N_d}\right)$$

$$= 0.0253 \times ln\left[\frac{4.83 \times 10^{21} \times 4.5 \times 10^{3}}{10^{23}}\right]$$

$$\left(E_c - E_f\right) = 0.136 \text{ eV}$$

Now $\left(E_d - E_f\right) = \left(E_c - E_f\right) - \left(E_c - E_d\right) = 10.136 - 0.015 = 0.121 \text{ eV}$

If N_d^+ and N_d' are the ionized and unionized donor atoms, then

$$N_d' = \left(N_d - N_d^+\right) = N_d\, F\left(E_d\right) \text{ with } N_d^+ = n$$

Thus $$N_d' = \frac{10^{23}}{1 + e^{\frac{\left(E_d - E_f\right)}{k_B T}}} = \frac{10^{23}}{\left[1 + e^{\frac{0.121}{0.0253}}\right]}$$

$$N_d' = 8.3 \times 10^{20}$$

But $$N_d^+ + N_d' = N_d$$

$$N_d^+ = N_d - N_d' = n$$

i.e., $$n = 10^{23} - \frac{8.3 \times 10^{20} \times 10^{3}}{10^{3}}$$

$$= 10^{23}\left\{1 - 8.3 \times 10^{-3}\right\}$$

$$n = 10^{23}$$

But at 293 K, n_i in an intrinsic semiconductor is only 10^{17} charge carriers. i.e., 10^{6} times smaller than the extrinsic value.

***Case* 2:**

Let $$\left[\frac{4N_d}{N_e}\right] e^{\frac{\left(E_c - E_d\right)}{k_B T}} >> 1$$

This implies large N_d and low T. As this conduction has no limiting problem as in case 1, it is more important than the first case. The general equation (Q 7.7.4) becomes

$$\boxed{e^{\frac{E_f}{k_B T}} = \frac{2\left(N_d / N_e\right)^{1/2} e^{\frac{\left(E_c - E_d\right)}{k_B T}}}{2\, e^{\frac{-E_d}{k_B T}}} = \frac{\left(N_d / N_e\right)^{1/2} e^{\frac{\left(E_c + E_d\right)}{k_B T}}}{1}} \qquad \text{(Q 7.7.7)}$$

i e.,

$$\boxed{\frac{E_f}{k_B T} = \frac{(E_c + E_d)}{2k_B T} + (1/2)\, ln \left[\frac{N_d}{N_e}\right]} \quad \text{(Q 7.7.8)}$$

$$\boxed{E_f = \frac{(E_c + E_d)}{2} - \frac{k_B T}{2}\, ln \left[\frac{N_e}{N_d}\right]} \quad \text{(Q 7.7.9)}$$

At 0 K, E_f lies half way between the donor level and bottom of the conduction band. As T increases, Fermi level drops. Also for a given temperature the Fermi level shifts upward as the concentration increases. This is shown in Fig. Q (7.7.3).

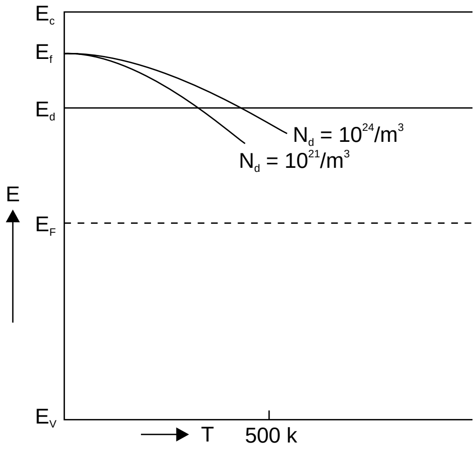


Fig. Q 7.7.3 *Variation of Fermi level with temperature for different concentrations in an n-type semiconductor*

The general equation for density of electrons is

$$n = N_e\, e^{\frac{(E_f - E_c)}{k_B T}}$$

Substituting for $e^{\frac{E_f}{k_B T}}$ from Eqn. Q (7.7.7),

$$n = N_e\, e^{\frac{-E_c}{k_B T}} \left[\left(\frac{N_d}{N_e}\right)^{1/2} e^{\frac{(E_c - E_d)}{2k_B T}}\right]$$

i.e.,

$$n = (N_e\, N_d)^{1/2}\, e^{\frac{-(E_c - E_d)}{2k_B T}} \quad \text{(Q 7.7.10)}$$

Conclusions

Equation (Q 7.7.10) says that the density of electrons in the conduction band is proportional to square root of the donor concentration. Another important conclusion is that as the temperature increases, the

Fermi level falls below the donor level and it approaches the centre of the forbidden gap which makes the semiconductor an intrinsic one.

Q 7.8 Give the required guide lines to discuss *p*-type semiconductors. The important results may be summarized.

***Answer*:** Assuming n is small and N_d is absent, Eqn. (Q 7.7.2) for *p*-type semiconductor becomes

$$N_p \, e^{\frac{(E_v - E_f)}{k_B T}} = \frac{N_a}{\left[1 + e^{\frac{(E_a - E_f)}{k_B T}}\right]}$$

A simplification of this equation as in the case of *n*-type, yields many interesting conclusions summarized below:

(i) The number holes and the number acceptor atoms are equal at higher temperature and at lower concentration, i.e.,

$$N_a = p$$

(ii) The expression for Fermi level is

$$E_f = E_v + k_B T \, ln \frac{N_p}{N_a}$$

i.e., At 0 K, this is not valid as it is obtained by assuming T is large. $T \longrightarrow \infty$ is also untrue as *electron suppression* may become untrue. The only fact is E_f moves upward as T increases.

(iii) The other interesting conclusion is the general expression for E_f at low temperature and high concentration of N_a is

$$E_f = \frac{E_a + E_v}{2} + \left[\frac{k_B T}{2}\right] ln \frac{N_p}{N_a}$$

i.e., at $T = 0$, E_f lies exactly half way between E_c and E_a. As the temperature increases, E_f moves upwards. How the variation of N_a affects the Fermi curve is also shown in the Fig. (Q 7.8.1).

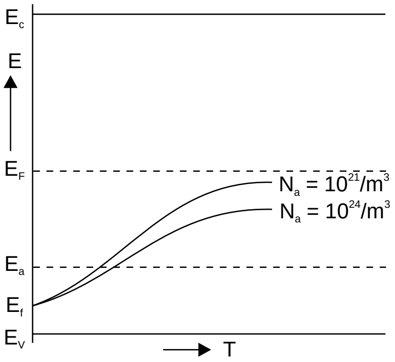


Fig. Q 7.8.1 *The variation of Fermi level with temperature for different concentrations in p-type semiconductors*

(iv) The equation for the density of holes in the valence band is proportional to the square root of the acceptor concentration. The corresponding equation is,

$$p = \left(N_a\, N_p\right)^{1/2} \exp\left[-\left(E_a - E_v\right)/2k_B\, T\right]$$

An interesting illustration:

(a) Sample used: *n*-type germanium
(b) Donor impurities used: 10^{22} germanium atoms /m^3
(b) Temperature: 27°C
(d) Forbidden energy gap: $E_g = 0.67$ eV

Discussion

The number of electrons reaching the conduction band from the donor level is,

$$n = N_d^{+} = N_d - N_d'$$

$$n = N_d - N_d\, F\left(E_d\right)$$

The general expression for *n* is,

$$C\,T^{3/2}\, e^{\frac{\left(E_f - E_c\right)}{k_B T}}$$

i.e.,

$$C\,T^{3/2}\, e^{\frac{\left(E_f - E_c\right)}{k_B T}} = N_d - N_d\, F\left(N_d\right)$$

$$\boxed{n = 4.8 \times 10^{21} \times 300^{3/2}\, e^{-\frac{\left(E_c - E_f\right)}{k_B T}} = 10^{22}\left[1 - \frac{1}{1 + e^{\frac{\left(E_d - E_f\right)}{k_B T}}}\right] = 10^{22}}$$

i.e.,

$$\exp\left[\left(E_c - E_f\right)/k_B\, T\right] = 24.96 \times 10^2$$

$$\left(E_c - E_f\right) = 0.196 \text{ eV}$$

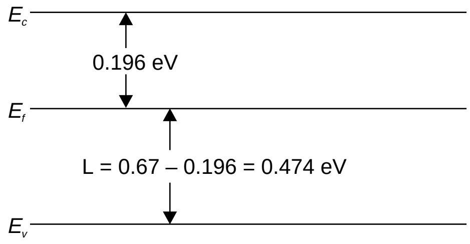


Fig. Q 7.8.2 *Impurity and intrinsic carriers in an n-type semiconductor*

Now the number of electrons coming from the valence band to the conduction band is

$$n' = p_n = N_e\, e^{(-0.474/0.025)} = \left\{25 \times 10^{24}/e^{18.96}\right\}$$

$$n' = p_n = 1.5 \times 10^{17}$$

Hence

$$n' p_n = 1.5 \times 10^{17} \times 10^{22} \text{ with } n = N_d = 10^{22}$$

$$n' p_n = 1.5 \times 10^{39} \qquad \text{(A)}$$

The density of charge carriers if it is an intrinsic semiconductor will be

$$n_i = 24.96 \times 10^{24}\, e^{-\frac{0.67}{2 \times 0.025}}$$

$$n \times p = n_i^2 = 1.43 \times 10^{39} \qquad \text{(B)}$$

Equations (A) and (B) are the same with $n_i = 3.8 \times 10^{19}$

***N.B.*:** Now the interesting question is that when A and B are the same, why the conductivity of an *n*-type semiconductor is much higher than that of an intrinsic one. This question is now answered:

In an intrinsic semiconductor,

$$\sigma_i = n_i\, e\left(\mu_e + \mu_p\right)$$

$$\sigma_i = 3.7 \times 10^{19} \times 1.6 \times 10^{-19} \times (0.39 + 0.19)$$

$$\boxed{\sigma_i = 3.7 \times 1.6 \times 0.58 = 3.4 \text{ ohm}^{-1}\,\text{m}^{-1}}$$

In an *n*-type semiconductor, $\sigma_{ex} = e\left\{n\mu_e + p_n\,\mu_p\right\}$

$$\sigma_{ex} = e\left\{0.39 \times 10^{22} + 0.19 \times 1.5 \times 10^{17}\right\}$$

$$= e \times 10^{22}\left[0.39 + \frac{0.19 \times 1.5}{10^5}\right]$$

$$= 0.39 \times 1.6 \times 10^{-19} \times 10^{22}$$

$$\boxed{\sigma_{ex} = 6.2 \times 10^{2} = 620 \text{ ohm}^{-1}\,\text{m}^{-1}}$$

i.e., the conductivity in an *n*-type semiconductor is about 200 times greater than that of an intrinsic one at a given temperature. This result tells that any device with extrinsic semiconductors can be operated at low voltages over a wide range of temperatures. i.e., large flow of current density at low *p .d* is easily possible unlike valves-an astonishing character of impurity semiconductors with greater applications.

Q 7.9 Discuss briefly the current flow in a biased *n*-type semiconductor. Also discuss the variation of electric conductivity with temperature using a suitable graph.

***Answer*:** An *n*-type semiconductor has (i) electrons as majority carriers, (ii) an (almost) equal number of *immobile positive* ions, and (iii) holes as minority carriers. Assume hole contribution is negligible.

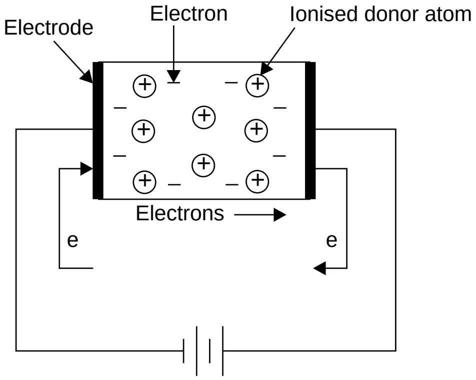


Fig. Q 7.9.1 *Biased n-type semiconductor*

Let us now consider an *n*-type semiconductor placed between a pair of electrodes across which a voltage is applied. Due to the field produced by the voltage, there will be a steady drift of the free electrons towards the positive electrode. The electrons reaching the positive terminal disappear at the *metal electrode* and the *immobile positive ions* in the vicinity of the negative electrode remain *unneutralised* due to the drift of the free electrons. These ions immediately attract electrons. Thus a continuous flow of electrons from one terminal of the voltage source to the other terminal via the semiconductor takes place. The rate of flow of electrons from the negative electrode to the semiconductor and from the semiconductor to the positive electrodes is determined by the applied voltage and the conductivity of the semiconductor which accounts for the current flow.

Variation of Conductivity with Temperature

In a metal, the density of charge carriers is essentially electrons. This number remains constant for a wide range of operating temperatures; consequently any variation of resistivity in a metal with temperature is due to mobility variation. In most metals, the main type of scattering is lattice scattering which increases with increasing temperature and hence mobility decreases and hence resistivity of metal increases with increasing temperature.

However a semiconductor is characterized by the activation of current carriers, either intrinsically or from impurities, or both. This activation is an exponential function of temperature. As the temperature increases, lattice scattering becomes more effective and it reduces the mobility of charge carriers in a semiconductor; but its effect is masked by the exponential addition of new carriers to the conduction process. Consequently, even though the mobility decreases, the many fold increase of charge carries decrease the resistivity on the whole.

The general expression for electrical conductivity is

$$\sigma = ne\mu$$

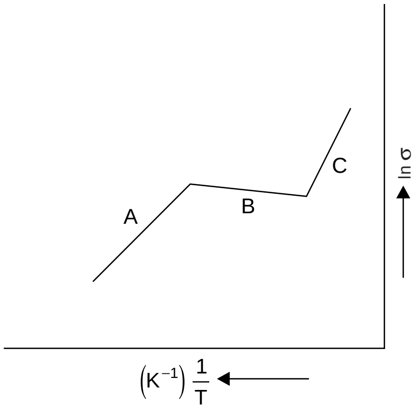


Fig. Q 7.9.2 *Variation of conductivity in an n-type semiconductor with the reciprocal of the absolute temperature*

In a metal, *n* is constant and σ decreases with increase of temperature because of the reduction of the value of μ; while in a semiconductor, however, *n* increases with *T* faster than μ decreases, hence ρ decreases with increasing temperature. The graph shows qualitatively the temperature dependence of the conductivity σ of a semiconducting crystal containing a moderate number of impurities. In the region A, the impurity atoms alone are ionized and hence σ is low. As the temperature is increasing the number of atoms ionized will be increasing and σ increases. The slow increase in σ is due to large *impurity scattering* and small amount of carriers. Usually the impurities are completely ionized at 200 K. The slope of $ln\ \sigma\ vs\ \frac{1}{T}$ in the region A is related to the ionization energy of the impurity.

In the region B, there is no increase in σ due to impurity conduction and the temperature is not high enough to allow very many electrons to jump directly from the valence band to the conduction band; here σ remains relatively constant. In fact σ shows a slight downward trend in this region. (since the mobility decreases slightly due to the predominance of *lattice scattering* when all the impurities are ionized). In the region C, the temperature is high enough to allow carriers arising from the valance band to the conduction band generation to dominate. Now the semiconductor behaves as an intrinsic material. The slope of the curve of the portion C can be related to the energy gap E_g. The on set of C in Ge is at 100 K while for a Si it is about 200 K.

Q 7.10 Discuss the various relations used to study carrier transport in semiconductors.

***Answer*:** The net current that flows across a semiconducting crystal has two components. (1) *Drift current* (2) *Diffusion current.*

1. *Drift Current*: When an electric field is applied across a semiconductor, the charge carriers, such as free electrons and holes attain a certain drift velocity which is the product of μ (mobility of charge carriers) and the applied electric field *E* or E_x. This movement of the charge carriers constitutes a current which is called *drift current.* Thus the drift current density for holes is given by

$$\boxed{J_{pd} = pev_p = pe\mu_p E} \qquad \text{(Q 7.10.1)}$$

Similarly the *drift current* density for electrons,

$$\boxed{J_{nd} = nev_n = ne\mu_e E} \qquad \text{(Q 7.10.2)}$$

Thus the total drift current is:

$$J_d = J_{nd} + J_{pd} = ne\mu_n E + pe\mu_p E$$

or

$$\boxed{\sigma = \frac{J_d}{E} = ne\mu_e + pe\mu_p} \qquad \text{(Q 7.10.3)}$$

and

$$\boxed{\sigma_i = n_i \left(\mu_e + \mu_p\right) e}$$

for intrinsic semiconductors.

For extrinsic semiconductors with typical dopant levels, the minority carrier component is negligible at normal operating temperatures.

2. *Diffusion Current*: The phenomenon of *diffusion* plays an important role in transistor operation. An electron current may flow in a semiconductor even in the absence of an electric field, if there exist a *gradient of the electron density.* Although the mobility of the charge carriers in a semiconductor is greater than that of the electrons in a metal, the conductivity in the former is much less than that in the latter because of the too few current carriers. The conductivity is so less that the random movements of the carriers due to unequal carrier densities plays a greater part in conduction than the drift due to the applied field. Diffusion arises essentially from density differences and the resulting current is called *diffusion current*.

Since diffusion process is analogous to the heat conduction in a rod, we can write the diffusion of electrons in semiconductors by the equation,

$$N \propto \frac{dn}{dx}$$

$$N = -D_n \frac{dn}{dx}$$

where N is the number of electrons diffusing through unit area in unit time. $\frac{dn}{dx}$ is *concentration gradient*. D_n is *diffusion coefficient*. The diffusion current density,

$$J_{nD} = eD_n \frac{dn}{dx}$$

Similarly the diffusion current density due to holes is:

$$J_{pD} = -eD_p \frac{dp}{dx}$$

Thus total current density due to holes is:

$$J_p = J_{pd} + J_{pD} = pe\mu_p E - eD_p \frac{dp}{dx}$$

Similarly the total current density due to electrons is:

$$J_e = J_{nd} + J_{nD} = ne\mu_n E + eD_n \frac{dn}{dx}$$

Thus the total current density is

$$\boxed{J = J_e + J_p = e\left\{\left(n\mu_e E + D_n \frac{dn}{dx}\right) + \left(p\mu_p E - D_p \frac{dp}{dx}\right)\right\}} \qquad \text{(Q 7.10.4)}$$

Einstein Relation

There exists a definite relationship between the mobility and the *diffusion constant* of a particular type of charge carrier. The higher the value of the mobility of the charge carrier, the greater will be its tendency to diffuse. The electron current density due to diffusion is $eD_n \frac{dn}{dx}$. Such diffusion will result in an electronic field E. When the steady state is reached the conduction current J_c must be equal and opposite to the diffusion current. i.e.,

$$J_c = -J_{nD}$$

$$\sigma E = -eD_n \frac{dn}{dx}$$

or $$\boxed{ne\mu_n E = -eD_n \frac{dn}{dx}} \qquad \text{(Q 7.10.5)}$$

The presence of the electric field produces a potential difference $V(x)$ over a distance say x. The variation of n with x is given by the Boltzmann relation,

$$n = Ce^{-\frac{eV}{k_B T}} = Ce^{-\frac{eEx}{k_B T}}$$

$$\frac{dn}{dx} = Ce^{-\frac{eEx}{k_B T}}\left(-eE/k_B T\right) = -\frac{neE}{k_B T}$$

or $$\frac{dn}{dx} = -\frac{neE}{k_B T} \qquad \text{(Q 7.10.6)}$$

Substituting this value of $\frac{dn}{dx}$ in Eqn. (Q 7.10.5), we get

$$ne\mu_n E = \left\{\frac{eD_n}{k_B T}\right\}(neE)$$

$$\boxed{D_n = \frac{\mu_n k_B T}{e}} \qquad \text{(Q 7.10.7)}$$

Equation (Q 7.10.7) is known as *Einstein's diffusion equation.* The corresponding equation for holes is

$$\boxed{D_p = \frac{\mu_p k_B T}{e}} \tag{Q 7.10.8}$$

Life Time and Diffusion Length

In a semiconductor which is in *thermal equilibrium*, though the concentration of electrons and holes are steady, the equilibrium is a dynamic one. That means the generation of the electron hole pairs is exactly equal to the recombination of such electron hole pairs at any instant. It is possible to change such equilibrium concentration of electrons and holes by several processes. These carriers do not remain indefinitely and take part in the diffusion process but recombine to form neutral particles. It is found that the excess carrier density decreases exponentially with time and the carrier density at any time 'τ' is found to be proportional to $\exp(-t/\tau)$ where τ is the *life time of the carriers*. The life time τ can be defined as the time taken for the carrier density to fall to $\frac{1}{e}$ of its initial value. The average distance L of a carrier diffuses before recombination, is related to the diffusion coefficient and the life time by the equations.

$$\boxed{\begin{aligned} L_n &= \sqrt{D_n \tau_n} \\ L_p &= \sqrt{D_p \tau_p} \end{aligned}} \tag{Q 7.10.9}$$

Q 7.11 Discuss the theory of generation and recombination of charge carriers bringing out the related equations.

***Answer*:** In a semiconductor, thermal agitation produces charge carriers. The addition of impurity atoms will increase one type of charge carriers at a given temperature keeping an equilibrium concentration of charges.

It is therefore clear that the addition of donor impurities increase the density of electrons could lead to a reduction of hole density unless some mechanisms exist for the removal of holes, as well as for their generation.

Indeed the fact the product *np* is a constant of the material and independent of added impurities even though the generation is occurring implies that both holes and electrons must be removed also. This process is called *recombination.* This means an electron which escapes from a bond might also be capable of falling back in it again. Such a process is called *direct recombination*. The direct transition can be explained as follows:

We assume that for a particular semiconductor (in the absence of the field) the *thermal generation rate* g_T is a function of temperature alone (the value of g_T is an empirical quantity of the material and varies with impurity density, imperfection in the crystal, deformation, etc). In other words, it is not a unique property of germanium, but is only a unique quantity for a particular sample of germanium.

But the *recombination rate R* depends upon how frequently an electron in the conduction band encounters a vacant state (hole) in the valence band. i.e., the rate is $\propto$ to the concentration of holes and electrons. The more holes there are, the sooner an electron will encounter. Similarly, the more electrons there are, the sooner will encounter an electron.

Thus $$R \propto np$$

i.e., $$R = r\,np$$

where *r* is the *recombination coefficient*. In equilibrium state the two processes must be precisely equal.

i.e., $$\boxed{\begin{aligned} &g = R = r\,n_o\,p_o = r\,n_i^2 \\ &\frac{g}{r} = n_o p_o = n_i^2 \end{aligned}} \qquad \text{(Q 7.11.1)}$$

If the electron density, say is increased by doping with donors, this enhances the recombination rate, but does not alter the generation rate, so that the net *density of minority carriers* falls. If now the crystal slightly disturbed from equilibrium by a few excess holes Δp (by light falling on it) an equal number of electrons, Δn are generated, then the rate of excess of hole-carrier recombination at any instant is given by

$$-\frac{d(\Delta p)}{dt} = g_T - R$$

$$= r\left[(n_o + \Delta n)(p_o + \Delta p)\right] - r\,n_o\,p_o$$

$$= r\left[(n_o\,p_o + n_o\,\Delta p + p_o\,\Delta n + \Delta n\,\Delta p)\right] - r\,n_o\,p_o$$

$$= r\,\Delta p(n_o + p_o)$$

i.e., $$\frac{d(\Delta p)}{dt} = -r(n_o + p_o)\Delta p$$

$$\frac{d(\Delta p)}{dt} = -\left(\frac{\Delta p}{\tau}\right) \text{ with } \tau = \frac{1}{(n_o + p_o)r}$$

Thus $$\frac{d(\Delta p)}{\Delta p} = -\frac{dt}{\tau}$$

Integrating $$ln\,\Delta p = -\frac{t}{\tau} + ln\,C$$

i.e., $$\boxed{\Delta p = C\,e^{-\frac{t}{\tau}}} \qquad \text{(Q 7.11.2)}$$

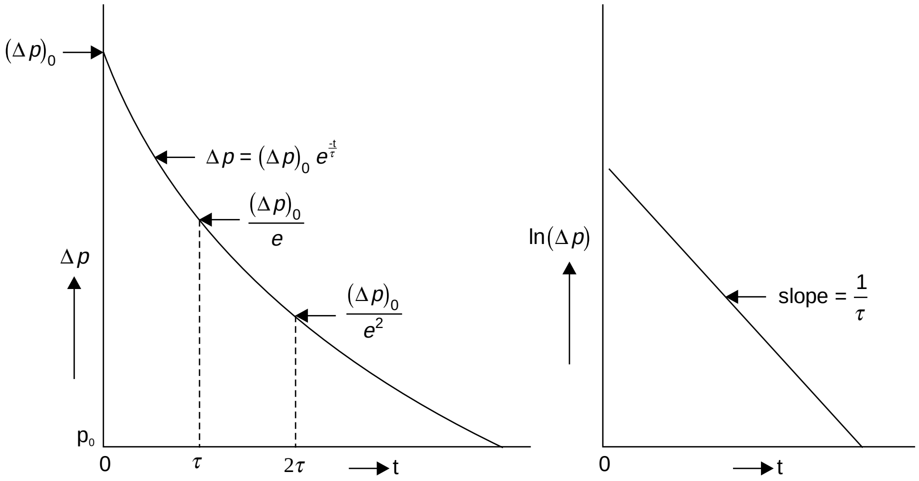


Fig. Q 7.11.1 *The decay of excess hole concentration with time*

When $t = 0$, $(\Delta p) = (\Delta p)_0 = C$

i.e.,
$$(\Delta p) = (\Delta p)_0 \, e^{-\frac{t}{\tau}}$$

where $(\Delta p)_0$ is the initially injected number of holes at $t = 0$ and Δp is the number of injected holes left at the instant t. It is apparent that the excess of holes injected decay exponentially with time.

When $t = \tau$,
$$\Delta p = \frac{(\Delta p)_0}{e}$$

Therefore the mean life time of the carrier can be defined as the time in which carrier value falls to $\frac{1}{e}$ or 37% of its initial value.

Q 7.12 What is Hall effect? Show that for a p-type semiconductor the Hall coefficient R_H is given by $R_H = \frac{1}{pe}$. Describe an experimental set-up for the measurement of Hall effect. Arrive at the important uses of the study of Hall effect.

***Answer*:** When a semiconductor is placed in a magnetic field $\vec{B}$ (along the z-direction) and a current density $\vec{J}$ (along x-direction) passed through it, a transverse electric field $\vec{E}$ (along y-direction) is set up given by

$\vec{E} = R_H \vec{B} \vec{J}$ where R_H is the Hall *coefficient or Hall constant.*

The Hall effect may be explained with the help of Fig. Q 7.12.1

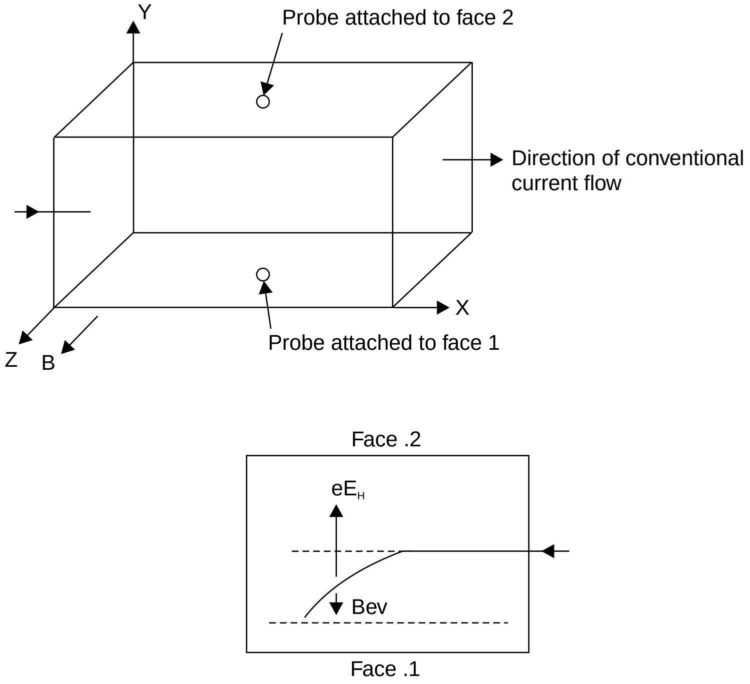


Fig. Q 7.12.1 *Hall effect and motion of electrons in an n-type semiconductor*

Assuming that the material is an *n*-type semiconductor, the current flow consists almost entirely of electrons moving from right to left just opposite to the conventional flow of current . If *v* is the velocity of electrons at right angles to the magnetic field, there is downward force on each electron of magnitude Bev. This causes the electron to be deflected in a downward direction and causes a negative charge to accumulate on the bottom face of the slab. A potential difference is therefore established from top to bottom of the specimen with bottom face negative. This potential difference causes a field E_H in the negative of *y*-direction, and so there is a force of e E_H acting in the upward direction on the electron. Equilibrium occurs when

$$e\,E_H = e\,Bv$$

$$E_H = Bv$$

If J_x is the current density in the *x*-direction, then

$$J_x = nev$$

where *n* is the concentration of current carriers. Thus

$$E_H = \frac{B\,J_x}{ne};\ \frac{E_H}{B\,J_x} = \frac{1}{ne}$$

The *Hall effect* is described by means of the Hall coefficient R_H, defined in terms of the current density J_x by the relation

or
$$\boxed{\begin{aligned} E_H &= R_H\, J_x\, B \\ R_H &= \frac{E_H}{J_x\, B} \\ R_H &= \frac{1}{ne} \end{aligned}} \tag{Q 7.12.1}$$

In this case
$$R_H = \frac{1}{ne}$$

Negative sign is used because the electronic field developed is in the negative *y*-direction

i.e.,
$$\boxed{R_H = \frac{E_H}{J_x\, B} = -\frac{1}{ne}} \tag{Q 7.12.2}$$

All the quantities E_H, B and J_x can be measured, and so the Hall coefficient and carrier density n can be found out.

Fig. Q 7.12.2 shows the conditions that exist in a *p*-type semiconductor under identical conditions as that of *n*-type specimen described above.

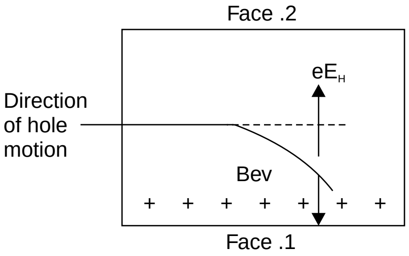


Fig. Q 7.12.2 *Hall effect in p-type semiconductor*

Experiment

Theory: The Hall coefficient is determined by measuring the Hall voltage that generates the Hall field. If V_H is the Hall voltage across the sample of thickness t, then

$$V_H = E_H\, t$$

Substituting for E_H for Eqn. (7.12.1),

$$\boxed{V_H = B\,t\,R_H\, J_x} \tag{Q 7.12.3}$$

If b-is the width of the sample, then its cross-section will be ($b \times t$) and the current density,

$$J_x = \frac{I_x}{bt}$$

$$\boxed{\begin{aligned} V_H &= \frac{B t R_H I_x}{bt} \\ R_H &= \frac{V_H b}{I_x B} \end{aligned}} \qquad \text{(Q 7.12.4)}$$

Note the polarity of V_H will be opposite for *n* and *p*-type

A rectangular slab of the given material having a thickness *t* and width *b* is taken and a current I_x ampere is allowed to pass through this sample by connecting it to a battery. The slab is then placed between two pole pieces of an electromagnet such that if the current direction coincides with the x-axis, the magnetic flux density *B* coincides with the *z*-axis, as shown in Fig. Q 7.12.3.

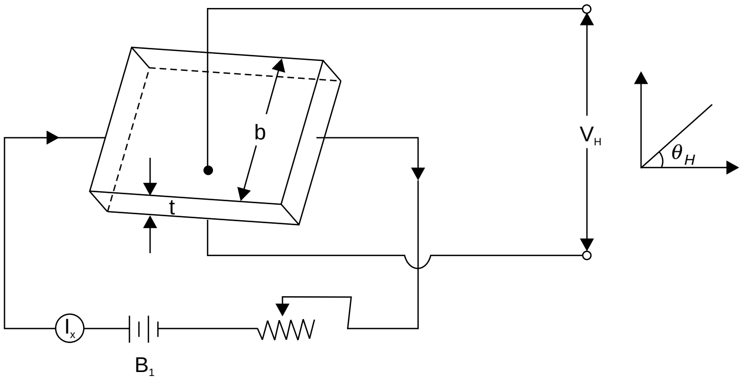


Fig. Q 7.12.3 *Set up for the measurement of Hall voltage*

The Hall voltage V_H is then measured by placing two probes at the centres of the bottom and top faces of the sample. If the magnetic flux density is *B* weber/m^2 and the Hall voltage is V_H volt, then R_H is obtained from Eqn. Q 7.12.4 in m^3/coulomb. The analysis is given above applies only when the charge carriers are free of attractive forces in the energy bands and when they move with a steady drift velocity v_d. This is not the case in a semiconductor, and a computation of the average speed leads to the conclusion that

$$R_H = \frac{3\pi}{8ne} = -\frac{1.18}{ne} \text{ instead of } -\frac{1}{ne} \text{ as seen in Eqn. (Q 7.12.2)}$$

For *n*-type of material, the conductivity is given by

$$\sigma_n = n e \mu_n$$

For *p*-type material

$$\boxed{\begin{aligned} \mu_n &= \frac{\sigma_n}{ne} = -\frac{\sigma_n R_H}{1.18} \\ \mu_p &= \frac{\sigma_p}{pe} = \frac{\sigma_p R_H}{1.18} \end{aligned}} \qquad \text{(Q 7.12.5)}$$

There is another interesting quantity called the *Hall angle* (θ_H) defined by the equation,

$$\tan\theta_H = \frac{E_H}{E_x}$$

But (Refer Eqn. 7.12.2) $$\boxed{E_H = \frac{J_x B}{ne} = \frac{nev_x B}{ne}} \qquad \text{(Q 7.12.6)}$$

i.e., $$\boxed{E_H = \frac{v_x B E_x}{E_x}}$$

Hence $$\boxed{\frac{E_H}{E_x} = \tan\theta_H = \frac{v_x B}{E_x} = \mu B} \qquad \text{(Q 7.12.7)}$$

where μ is the mobility of the charge carriers.

Thus $$\boxed{\tan\theta_H = \frac{E_H}{E_x}} \qquad \text{(Q 7.12.8)}$$

Applications of Hall Effect

(i) *Determination of type of semiconductor*: For an *n*-type semiconductor the Hall coefficient is negative where as for a *p*-type semiconductor it is positive. Thus, the sign of the Hall coefficient can be used to determine whether a given semiconductor is *n*-type or *p*-type.

(ii) *Calculation of carrier concentration*: *The Hall voltage* V_H is measured as usual by placing the two probes at the centres of the top and bottom faces of the sample. If the magnetic flux density is B wb/m^2, then

$$n = \frac{1}{eR_H}$$

where $$R_H = \frac{1}{ne}$$

(iii) *Determination of mobility*: If the *conduction* is due to one type of carriers, e g., electrons, we have

$$\sigma = ne\mu_n$$

$$\mu_n = \frac{\sigma}{ne} = \sigma R_H$$

$$\mu_n = \sigma(V_H b/I_x B)$$

i.e., knowing σ, the mobility μ_n can be determined.

(iv) *Measurement of magnetic flux density*: Since Hall voltage V_H is proportional to the magnetic flux density B for a given current I_x through a sample, the Hall effect can be used as the basis for the design of a magnetic flux density meter.

(v) *Measurement of power in an electromagnetic wave*: In an *electromagnetic* wave in free space the magnetic field H and the electric field E are at right angles. Thus, if a semiconductor sample is placed parallel to E, it will derive a current I in the semiconductor. The semiconductor is subjected simultaneously to a transverse magnetic field H producing a Hall voltage across the sample. The Hall voltage will be proportional to the product E and H. i.e., to the magnitude of the *poynting vector* of the electromagnetic wave. Thus, the Hall effect can be used to determine the power flow in the electromagnetic wave.

(vi) *Hall effect multiplier*: If the magnetic flux density B is produced by passing a current I' through an air core coil, B will be proportional to I'. The Hall voltage is thus proportional to the product of I and I'. This forms the basis of multiplier.

Q 7.13 Write a note on thermistors. What are the advantages of semiconductor devices?

***Answer*:** The word *thermistors* is the abbreviation of 'thermally *sensitive resistors*. They are intrinsic semi-conductors prepared by embedding the oxides of manganese, iron, cobalt and nickel in ceramic binders and then heating them to a high temperature. The resulting hard mass is in the form of beads, discs or rods. A pair of platinum wires is attached to the thermistor to enable electrical connections to be made. The electrical conductivity of thermistor varies almost linearly with temperature over a wide range of temperatures. They can, therefore, be used as thermometers. The rate of change of conductivity with temperature is very high. Thus the *sensitiveness of a thermistor is very high* and it can be used to measure temperature changes of the order of 10^{-6} °C. A thermistor, whose electrical conductivity increases with temperature, may be connected in series with metallic conductors, whose electrical conductivity decreases with temperature, such that the resistance of an electrical circuit remains unaffected by temperature changes.

The electrical resistance of a thermistor varies with temperature in a manner similar to a semiconductor. The resistance R of a thermistor at the kelvin temperature T is given by

$$R = a \exp\left(\frac{b}{T}\right) \qquad \text{(Q 7.13.1)}$$

where a and b are constants for a given *thermistor*. Differentiating the above equation with respect to T we have,

$$\frac{dR}{dT} = a \exp\left(\frac{b}{T}\right)\left(-\frac{b}{T^2}\right)$$

$$\frac{1}{R}\frac{dR}{dT} = -\frac{b}{T^2} = \alpha$$, the *temperature coefficient of resistance*.

Thus the *temperature coefficient of resistance* of a thermistor is negative. Its value is dependent on temperature. Its numerical value is large compared to that of a metal.

Consider two temperatures T_1 and T_2 which are close to each other. Thus we have from Eqn. (Q 7.13.1),

$$ln\ R_1 = ln\ a + \frac{b}{T_1}$$

and
$$\ln R_2 = \ln a + \frac{b}{T_2}$$

$$\ln R_1 - \ln R_2 = b\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = b\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

If T_1 and T_2 are close to each other we can write $T_1 T_2 = T^2$ where T is the mean of T_1 and T_2. Hence we get

i.e.,
$$\boxed{\begin{aligned} \alpha &= -\frac{b}{T^2} \\ \alpha &= \frac{(\ln R_1 - \ln R_2)}{(T_1 - T_2)} \end{aligned}} \qquad \text{(Q 7.13.2)}$$

Thus if the resistance of a thermistor is measured at two close temperatures its temperature coefficient can be calculated using Eqn. (Q 7.13.2). It must be noted that the temperature coefficient is not a constant. It varies with temperature. The important features of a thermistor are its high *thermal sensitiveness* and *compactness*. Thermistors find a number of uses. Here are some of them. They are used:

(i) to measure low temperatures of the order of 10 K or less,
(ii) to protect electronic circuits against *surges of current*,
(iii) to measure varying temperatures,
(iv) in voltage stabilizers,
(v) in temperature control units,
(vi) to protect the windings in transformers, motors and generators from surges of heavy currents and
(vii) to measure wind velocity and altitude

Most of the devices in the field of electronics today are built from semiconductors. The vacuum devices like diode, triode, etc. have been replaced by semiconductor devices like *p-n* junction diodes, transistors, etc. The advantages of semiconductor devices over vacuum tubes are the following:

(a) As the name indicates, vacuum tubes require vacuum, but semiconductors do not require vacuum.
(b) Vacuum tubes have filaments, and so require supply for heating the filament. Semiconductors do not have filaments.
(c) Semiconductor devices are smaller in size, lighter in weight, and are mechanically very rugged.
(d) Operation of semiconductor devices requires low-voltage power supply, the power consumption is also smaller than that of the corresponding vacuum tubes.
(e) The semiconductor devices require very small warm-up time and, therefore, operate immediately after the supply voltages are switched on.
(f) The performance of semiconductor devices is more reliable than that of vacuum devices.

(g) The operating life of a semiconductor device is appreciably longer than that of its equivalent vacuum tube.

Q. 7.14 Draw the energy-band diagram of an unbiased *p*-*n* junction. Explain the terms: barrier potential and depletion region as applied to a *p*-*n* junction.

***Answer*:** A *junction diode* is a combination of an *n*-type and a *p*-type semiconductor in intimate contact. For example, if a small pellet of indium (having valency three) is placed on an *n*-type germanium piece, and if they are allowed to melt, the molten indium diffuses into the molten germanium. If the germanium is now allowed to cool, it recrystallises, with a large concentration of indium in its upper parts. The lower part continues to be of the *n*-type. But the larger concentration of the *p*-type imputity, namely indium, makes the upper part of the germanium a *p*-type semiconductor. Thus the *n*-type germanium and *p*-type germanium have been brought into intimate contact, forming *p*-*n* junction. See Fig. Q 7.14.1.

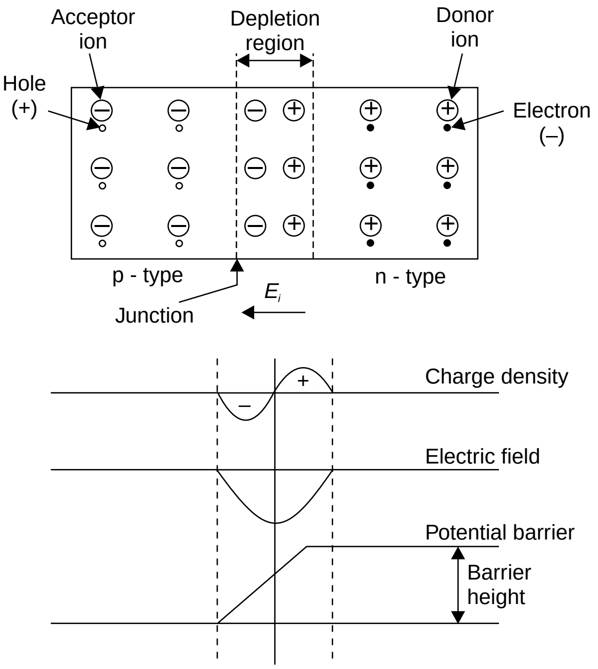


Fig. Q 7.14.1 *Barrier potential*

The *p-type region* has (positive) holes as majority charge-carriers, and an equal number of fixed negatively-charged acceptor ions to keep the material as a whole in neutral. Similarly, the *n*-type region has electrons as majority charge carriers, and an equal number of fixed positively-charged donor ions. In addition to these majority charge carriers, there are a few minority charge-carriers in each region. The *p*-region contains a few electrons while the *n*-type contains a few holes.

Thus, when the junction is formed, there is a *charge-density gradient*. This causes diffusion of charge-carriers across the junction. Holes diffuse from the *p*-region into the *n*-region, and electrons from the *n*-region into the *p*-region. The *diffused charge carriers* combine with their counter parts in the vicinity of the junction and neutralize each other. The diffusion of holes leaves *uncovered negative* *acceptor ions* on the left of the junction and the diffusion of electrons leaves *uncovered (positive) donor ions* on the right. Thus, there is net negative charge on the *p*-side of the junction and net positive charge on the *n*-side. This sets up a potential difference across the junction, and hence an internal electrical field E_i directed from the (positive) *n*-side to the (negative) *p*-side. Equilibrium is established when the field becomes large enough to stop further diffusion of the *majority charge carriers.* The field E_i, however helps the *minority carriers.* (electrons in the *p*-region and holes in the *n*-region) to move across the junction.

The region on either side of the junction which becomes depleted (free) of the mobile charge carriers is called the *depletion region* (or *transition region*). The thickness of this region is of the order of $10^{-6}m$. The potential difference across the depletion region is called the *potential barrier*. It is of the order of 0.1 to 0.5 volt depending on the temperature. The general shapes of the charge distribution, the internal electric field and the potential barrier in the depletion-region are shown in Fig. Q 7.14.1.

Theory of p-n Junction

It has already been established that the Fermi level will be different in the two types of semiconductor, and yet the Fermi energy was originally defined as a chemical potential and hence must be constant through out the specimen. In two separate pieces of semiconductor it is acceptable that the electrons in one should have higher energy than in the other. When the two are joined this is no longer possible since the high energy electrons will move to the region with lower energy and hence equalize the Fermi level. The number of electrons required to move is rather small but *re-distribution of energy* is important.

As all the energies we measure in the semiconductor are relative to the Fermi level the re-adjustment when two different types of semiconductor are joined is equivalent to moving the whole band structure of one relative to the other, to equalize the Fermi level. See Fig. Q 7.14.2.

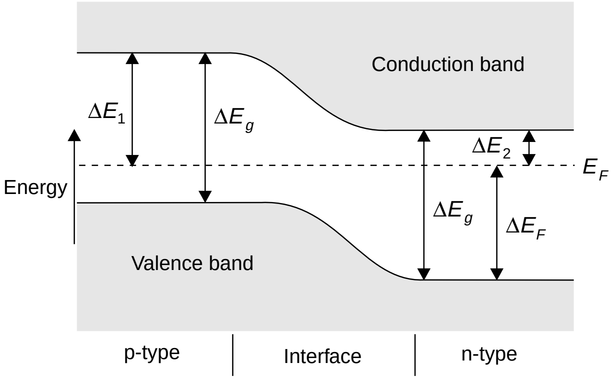


Fig. Q 7.14.2 *The band gap at the p-n junction*

This bodily movement of band structure up or down the energy scale is just a matter of changing the potential and a re-distribution of electrons does just that. In the region where the material goes from *n*-type to *p*-type the band gap changes position as shown in Fig. Q 7.14.2 and in constructing a *p-n* junction, one of the aims is to get this interface as narrow as possible. It is the properties of the junction which govern those of the device.

We now calculate the equilibrium flow, i.e., after the initial redistribution of electrons from one side of the junction to the other has taken place. The number of electrons in the conduction band of the *p*-

type material is proportional to exp $\{-\Delta E_1/k_B T\}$ as usual, where ΔE_1 is the difference between the *Fermi level* and the bottom of the conduction band in the *p*-type. Similarly the number of electrons in the conduction band in the *n*-type is proportional to exp $(-\Delta E_2/k_B T)$ where ΔE_2 in the energy difference between E_F and the bottom of the conduction band in the *n*-type. It is clear from the figure that

$$\Delta E_2 = \Delta E_g - \Delta E_F$$

where ΔE_g is the width of the gap and ΔE_F is the energy difference between the Fermi energy and bottom of the energy gap on the *n*-type side.

Now any electron in the conduction band in the *p*-type will simply flow down hill into the conduction band of the *n*-type giving an electron current to the right.

$$\boxed{I_d \propto \exp\left\{-\frac{\Delta E_1}{k_B T}\right\}} \tag{Q 7.14.1}$$

(This electron current is of course equivalent to the reverse conventional current flow).

There is a finite probability that electrons will flow uphill in the conduction band to the *p*-type side by thermal fluctuations. The probability that such a fluctuation will occur is just:

$$\boxed{\exp\left\{-\left(\Delta E_1 - \Delta E_g + \Delta E_F\right)/k_B T\right\}} \tag{Q 7.14.2}$$

The energy term in the exponent here is the energy difference between the bottom of the band on the *n*-type side and that on the *p*-type side. However to obtain the number of electrons flowing in this direction, we need to know the number in the conduction band on the *n*-side. As usual this is proportioned to

$$\boxed{\exp\{-\Delta E_2/k_B T\} = \exp\{-(\Delta E_g - \Delta E_F)/k_B T\}} \tag{Q 7.14.3}$$

The electron flow is proportional to the number of electrons moving uphill, which is equal to the number in the conduction band multiplied by the probability of a thermal fluctuation lifting them up. The uphill electron flow is then:

$$I_u \propto \exp\left\{-\left(\Delta E_1 - \Delta E_g + \Delta E_F\right)/k_B T\right\} \exp\left\{-\left(\Delta E_g - \Delta E_F\right)/k_B T\right\}$$

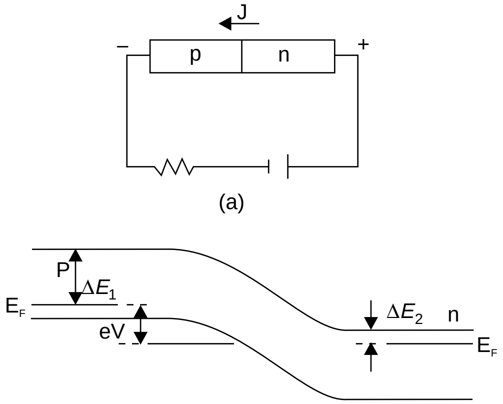
i.e.,

$$\boxed{I_u \propto \exp\{-\Delta E_1/k_B T\}} \tag{Q 7.14.4}$$

From Eqn. (Q 7.14.1), we then have $I_u = I_d$, so that zero electron current flows at equilibrium when the Fermi level is equalized on both sides. All this analysis can be repeated for positive holes and a similar result obtained for hole conduction.

Q 7.15 Explain the working of a *p*-*n* junction diode under forward and reverse biasing.

***Answer*:** In an unbiased junction, the net current is zero. Let us now consider the simple circuit shown in Fig. Q 7.15.1 in which an external potential is applied so that *n*-side is positive. Recalling that conventional current flow is in the reverse direction to electron movement, this implies a *removal of electrons* from the *n*-side and so the Fermi level is decreased there by an amount eV (Fig. Q 7.15.1b) where *V* is the external potential. Application of an external potential in this way is called *reverse bias*.



(a)

(b)

Fig. Q 7.15.1 *(a) A reverse bias p-n junction and (b) the resulting band gap*

The electron flow uphill is reduced by this procedure since the energy which has to be overcome by thermal fluctuation has been increased by eV. The probability that an electron will in fact overcome it, is reduced from Eqn. (Q 7.14.2) to give a current flow:

$$\boxed{I_u \propto \exp\left\{-(\Delta E_1 + eV)/k_B T\right\}} \qquad \text{(Q 7.15.1)}$$

instead of Eqn. (Q 7.14.4). The opposing, current flow [Eqn. (Q 7.14.1)] is unchanged since it depends only on the number of electrons in the band and as the energy difference ΔE_1 has not been changed, it remains constant.

Therefore

$$I_d \propto \exp\left(-\Delta E_1 / k_B T\right)$$

The net current flow *I* is then

$$\boxed{I = \left(I_u - I_d\right) \propto \exp\left[-\left(\Delta E_1 + eV\right)/k_B T\right] - \exp\left(-\Delta E_1 / k_B T\right)} \qquad \text{(Q 7.15.2)}$$

Therefore
$$\boxed{I \propto \exp\left\{-\Delta E_1 / k_B T\right\}\left\{\exp\left(-eV/k_B T\right) - 1\right\}} \qquad \text{(Q 7.15.3)}$$

which constitutes an electron flow from left to right in Fig. Q 7.15.1(b) and a conventional current from right to left, i.e., from high to low applied potential. However, it is very small current. The applied voltage occurs in the term in parentheses in a negative exponential which approaches zero asymptotically. This long flat exponential tail gives little variation of current with applied potential. The small current in *reverse bias* therefore stays almost constant even for large applied voltages so that the resistance (or more properly, the impedance) is large in this mode.

If the circuit is altered so that the positive potential is applied to the *p*-side we have *forward bias* (Fig. Q 7.15.2). The effect is to reduce the height of the energy hill which the electrons traverse by an amount *eV* (Fig. Q 7.15.2 b).

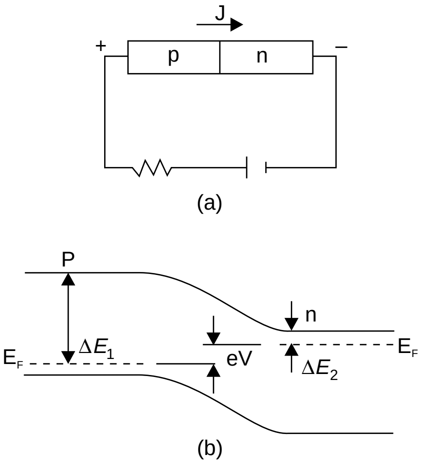


Fig. Q 7.15.2 *(a) A forward bias p-n junction and (b) the resulting band gap*

Once again the flow downhill from left to right is unchanged, depending only on ΔE_1 (Eqn. Q 7.14.4). The electron flow uphill is now strongly affected because the height of the energy step has been reduced.

Therefore
$$\boxed{I_u \propto \exp\left\{-(\Delta E_1 - eV)/k_B T\right\}} \tag{Q 7.15.4}$$

which combines with Eqn. (Q 7.14.4) to give a net electron flow to the left:

$$I = \left(I_u - I_d\right) \propto \exp\left\{-(\Delta E_1 - eV)/k_B T\right\} - \exp\left(-\Delta E_1/k_B T\right)$$

Therefore
$$\boxed{I \propto \exp\left[-\Delta E_1/k_B T\right]\left\{\exp\left(eV/k_B T\right) - 1\right\}} \tag{Q 7.15.5}$$

which is equivalent to a conventional current to the right. Since the function e^{+x} increases dramatically with x, the electron flow increases strongly with applied voltage. In other words the forward biased junction has a low impedance.

Now these current characteristics in both modes are plotted in Fig. (Q 7.15.3). The total effect is to produce an *effective rectifier* which can often resist reverse voltages up to several hundred volt. The device has low impedance in forward bias so that such voltages produce high currents as required in a rectifier. The uses of *p*-*n* junctions as rectifiers is now general.

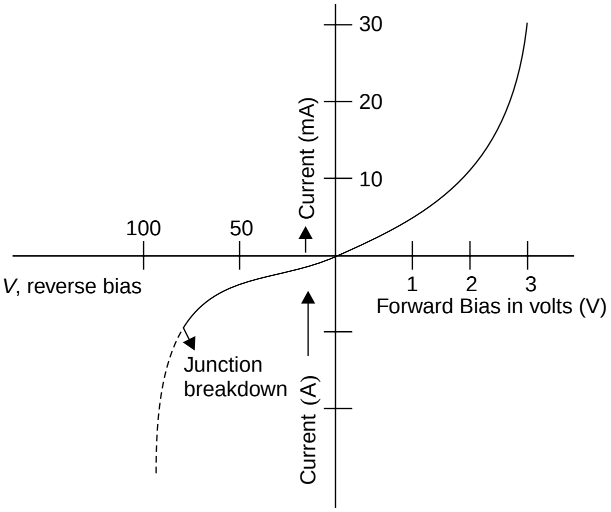


Fig. Q 7.15.3 *The current-voltage characteristics of a p-n junction*

Avalanche Breakdown

If the reverse bias is made very high (20 volt), the covalent bonds near the junction break down and a large number of electron-hole pairs are liberated. The reverse current then increases abruptly to a relatively large value. This is known as '*avalanche breakdown*', and may damage the junction by the excessive heat generated unless the current is limited by external circuit.

Q 7.16 What is a junction transistor? Describe the action of *p*-*n*-*p* and *n*-*p*-*n* transistors.

***Answer*:** A thin layer of an *n*-type semi-conductor sandwiched between two *p*-type semi-conductors or a thin layer of *p*-type semiconductor sandwiched between two *n*-type semiconductors, is called a *transistor.* The transistor is by far the best known semiconductor device. It is freely used for three main reasons: cheap to make and reliable compared with vacuum tubes, it is small, and it is extremely efficient, demanding very small power for its operation.

In the transistor we enter a stage of further complication for it consists of two *p*-*n* junctions back-to-back. The arrangement is therefore either a *p*-*n*-*p* or an *n*-*p*-*n* transistor: we shall consider the latter.

The arrangement of the energy levels in the unbiased condition is obvious by extension of the ideas of the last section. The conduction band in the central *p*-type region is now an *energy hill* with lower energy conduction bands on either side. See Fig. (Q 7.16.1). We have already noted that zero current flows when no bias is applied to a junction and the uniting of two junctions does not change this.

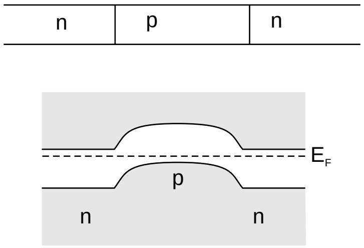


Fig. Q 7.16.1 *An n-p-n transistor-un biased*

In order to bias the two junctions independently we have two biasing circuits both connected to the central *p*-type part which is called the *base*. We shall consider the left-hand junction to be forward biased and the right-hand junction to be reverse biased as shown in Fig. Q 7.16.2 and the bias voltage is made larger for the reverse bias side.

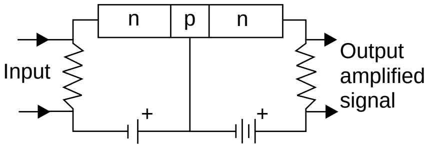


Fig. Q 7.16.2 *The circuit for using an n-p-n transistor as an amplifier*

The resulting displacement of the energy gap is shown in Fig. Q 7.16.3 which should be familiar since it is merely a back-to back combination of Figs. Q 7.15.1b and Q 7.15.2b. The electron flow through the forward biased junction on the left is the same as in the rectifier diode of the last section. A substantial flow occurs which is strongly dependent upon the biasing voltage.

Now suppose that some varying signal voltage is applied across the terminals labelled '*input*' in Fig. Q 7.16.2. The strong dependence of the electron flow upon the applied voltage will give corresponding variations in the former and the left hand *n*-type portion is naturally called the *emitter* of this signal flow.

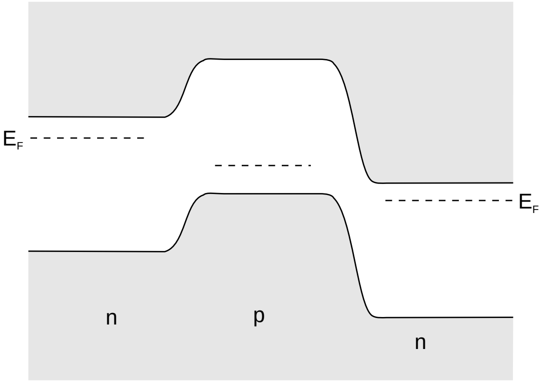


Fig. Q 7.16.3 *The effect on the band gap of the potential in Fig. Q 7.16.2*

In the manufacture of the transistor it is essential that the base is very thin, it should be a *p*-type material about a tenth of a millimetre thick. We can now see why this is important, for if the base were, say, a few millimetre thick the current in the forward bias side would flow without influence on the much smaller current on the reverse bias side.

However if the base is thin, electrons flowing into the base from the emitter are caught up in the flow through the reverse bias side. Although this flow is small the biasing voltage is large and it is this which constrains a large proportion of the electrons to continue through the second junction to the right hand *n*-type region (called the collector). For a suitably thin base, well over nine tenths of the electrons travel this way rather than going back to the emitter via its external circuit. The efficiency of the whole operation is therefore dependent upon the thinness of the base.

Now this extra flow of electrons through the reverse bias, *p-n*, junction is equivalent to a large extra voltage across it, since even a small current flows in the reverse bias mode correspond to large applied voltages {re-call Fig. (Q 7.15.3)}. The result is that relatively, small changes in electron flow through the emitter caused by the signal voltage changes create large voltage changes across the output terminals in Fig. Q. 7.16.2. In other words the signal has been amplified; the gain can be quickly calculated. Suppose that the signal V_s generated across the signal resistor R_s produces a forward current I_s; as R_s is much larger than the impedance of the forward biased junction we have a signal current flowing through this:

$$I_s = \frac{V_s}{R_s}$$

Suppose that all the electrons in this current flow pass through the base towards the collector then the voltage across the output resistor R_o is

$$\begin{aligned} V_o &= R_o I_s \\ &= \frac{V_s R_o}{R_s} \end{aligned}$$

Therefore $$\frac{V_o}{V_s} = \frac{R_o}{R_s}$$

Note that this gain does not include the large resistance of the reverse bias junction and that the signal current flow is superimposed upon the steady flow which occurs for zero signal.

Note also the key place occupied by the collector applied voltage, it is this which forces the extra electron flow toward the collector and hence supplies the power for the applied signal. The gain is dependent upon the efficiency with which the electrons in the base are persuaded to pass from the emitter circuit to the collector circuit.

All the discussion above could have been developed using positive holes as charge carriers. These flow in the opposite direction to the electrons, i.e., the conventional current direction. Since we measure energies for holes in the reverse direction they flow up the energy barrier and require thermal activation to diffuse down. The final results are similar to those for electrons and in reality both types of carriers are flowing at once. This presents a possibility that holes and electrons may unite, annihilating both (i.e., the electron is scattered back into the valence band). The extra energy is absorbed by the lattice. This is far more likely in regions where the potential is low and random thermal motion is dominant. In a transistor this situation is present in the base except close to the collector junction. It is therefore very important that scattering centres, such as point defects and dislocations, should be avoided in the base. The acceptor atoms also act as scattering centres which promote annihilation and hence these are minimsed by making the base less *p*-type and increasing the *n*-type nature of the collector and emitter. The surface of the base is also treated to reduce scattering and recombination there. All this gives a longer mean scattering time and hence an increased average time before an electron recombines with a hole. The base thickness must be much smaller than the mean distance travelled by an electron or hole in this *recombination time*. If it is, almost all electrons and holes will pass out of the base without recombination and the efficiency will remain high.

Q 7.17 ***The author is on the hope that at least a few readers will go through this chapter in depth and derive some inspiration as a large number of devices made from semiconductors such as transistors, photo cells, light emitting diodes, solid state lasers, solar cells, thermistors, photovoltac cells in space ships are widely used in electronic industries. The present question is whether you can prepare a review report of 2 to 4 pages on the principle, design, working mechanism and uses and applications of important semiconductor-devices?***

Answer: *The author will be greatly disappointed if your answer is No. If it is yes, you are suggested to read selected standard text-books on semiconductor devices and prepare a short essay on the said topic. The best contribution will be incorporated in the next edition under Q 7.17 and will be gratefully acknowledged.*

TABLES

Table 7.A *Electrical and mechanical characteristics of Ge, Si and Ga As*

S.No	*Property*	*Ge*	*Si*	*Ga As*	*Units*
1	Melting point	937	1415	1240	$^\circ$C
2	Density at 25 $^\circ$C	5320	2330	5310	kg/m^3
3	Thermal expansion	6.1×10^{-6}	4.2×10^{-4}	5.9×10^{-4}	/kelvin
4	Thermal conductivity	630	840	520	W m^{-1} K^{-1}
5	Specific heat	310	760	361	J kg^{-1} K^{-1}
6	Atomic weight	72.66	28.09	144.6	number
7	Lattice constant	0.5657	0.5431	0.5654	nm
8	Atoms/m^3	4.42×10^{28}	4.99×10^{28}	4.34×10^{28}	number
9	Dielectric constant	16	11.8	11.1	number
10	Band gap energy	0.67	1.106	1.4	eV
11	Intrinsic resistivity (300 K)	46	2300	3.7×10^{6}	Ω m
12	Electron mobility	0.39	0.15	1	m^2 V^{-1} s^{-1}
13	Hole mobility	0.19	0.05	0.045	m^2 V^{-1} s^{-1}
14	Intrinsic charge density	2.4×10^{19}	1.5×10^{16}	1.4×10^{9}	/m^3
15	Electron diffusion constant at 300 K	0.01	0.0038	0.031	m^2 s^{-1}
16	Hole diffusion constant at 300 K	0.0049	0.0013	0.00115	m^2 s^{-1}

Table 7.B *Room temperature resistivity and energy gap of elements of the fourth group*

Element	*C (diamond)*	*Si*	*Ge*	*Sn (gray)*	*Pb*
ρ (Ω m)	10^{14}	3000	0.47	2×10^{-6}	2×10^{-7}
E_g (in eV)	5.2	1.21	0.75	0.08	0

Table 7.C *Classes of semiconductors*

Material	*Crystal structure*	*Lattice spacing (nm)*	*Fundamental energy gap, E_g (in eV)*
Si	Diamond	0.542	1.08
Ge	Diamond	0.562	0.65
Sn (gray)	Diamond	0.646	–
Ga P	Zinc blende	0.545	2.24
Ga As	Zinc blende	0.565	1.38
Si C	Wurtzite	0.435	2.86
Cd S	Zinc blende	0.583	2.40
Zn S	Zinc blende	0.541	3.70
Pb Te	Rock salt	0.645	0.32

Table 7.D *Dopants ionization energy*

Semiconductor	*Dopant (type)*	*Ionisation energy (in eV)*
Ge	B (*p*)	0.010
	Al (*p*)	0.010
	Ga (*p*)	0.011
	P (*n*)	0.012
	As (*n*)	0.013
	Sb (*n*)	0.0096
Si	B (*p*)	0.045
	Al (*p*)	0.057
	Ga (*p*)	0.065
	P (*n*)	0.044
	As (*n*)	0.055
	Sb (*n*)	0.039

Table 7.E *Majority and minority concentrations for n-type and p-type samples of germanium*

Given: $\mu_n = 0.36\,\text{m}^2\,\text{V}^{-1}\,\text{s}^{-1}$, $\mu_p = 0.17\,\text{m}^2\,\text{V}^{-1}\,\text{s}^{-1}$ and $n_i = 2.5 \times 10^{19}/\text{m}^3$

p-type samples			*n-type samples*		
σ *ohm*$^{-1}$ *m*$^{-1}$	$n\ (m^{-3})$	$p\ (m^{-3})$	σ *ohm*$^{-1}$ *m*$^{-1}$	$n\ (m^{-3})$	$p\ (m^{-3})$
10^4	1.70×10^{15}	3.68×10^{23}	10^4	1.75×10^{23}	3.57×10^{15}
10^2	1.70×10^{17}	3.68×10^{21}	10^2	1.75×10^{21}	3.57×10^{17}
10	1.70×10^{18}	3.68×10^{20}	10	1.75×10^{20}	3.57×10^{18}

Table 7.F *Physical properties of Si and Ge and some compounds*

Material	*Lattice constant (nm)*	E_g *at 300 K (eV)*	*Electron mobility at 300 K* $(m^2\,V^{-1}\,s^{-1})$	*Hole mobility at 300 K* $(m^2\,V^{-1}\,s^{-1})$	*Dielectric constant* $\in_r$	$\dfrac{m_e^*}{m_p^*}$	$\dfrac{m_p^*}{m_e^*}$
In Sb	0.648	0.168	7.8	0.074	17	0.0115	0.5
Ge	0.566	0.660	0.39	0.181	16	–	–
Si	0.543	1.120	0.15	0.062	11.8	–	–
Al Sb	0.614	1.6	0.02	0.042	11.4	0.39	0.8
Ga P	0.545	2.24	0.01	7.5×10^{-3}	10	0.34	0.5
Ga As	0.565	1.35	0.85	0.044	12.4	0.070	0.5
Ga Sb	0.610	0.67	0.41	0.140	15	0.048	0.38

OBJECTIVE QUESTIONS

1. Semiconductors have positive temperature of coefficient while it is the other way in metals
   (a) true (b) false
2. The mobility of charge carriers in an intrinsic semiconductor is proportional to
   (a) $T^{3/2}$ (b) $T^{1/2}$ (c) $\dfrac{1}{T^2}$ (d) $\dfrac{1}{T^{3/2}}$
3. The constant of proportionality in the calculation of intrinsic charge carriers is of the order
   (a) 10^{21} (b) 10^{19} (c) 10^{10} (d) 10^{28}
4. The Fermi level lies exactly at the middle of the forbidden gap if $m_p^* > m_e^*$
   (a) true (b) false

5. The intrinsic charge carriers per m^3 at 27°C in silicon is about 10^2 times greater than that of *Si* atoms in a volume of 1 m^3.

   (a) true (b) false

6. In an impurity semiconductor, donor impurity atoms

   (a) add electrons to the valence band (b) remove electrons from the valence band

   (c) add holes to the valence band (d) add electrons to the conduction band

7. The energy needed to ionize the indium impurity atoms in germanium is approximately

   (a) 0.001 eV (b) 0.02 eV

   (c) 0.01 eV (d) 0.1 eV

8. In a *p*-type semiconductor, the concentration of holes is proportional to the square root of

   (a) the concentration of donor impurities

   (b) the concentration of acceptor impurities

   (c) the concentration of intrinsic impurities

   (d) none of these

9. The energy gap of germainium is 0.67 eV and at 300 K the Fermi level lies at 0.195 eV below the conduction band. The concentration of electrons due to intrinsic semiconduction is

   (a) $C\,e^{0.861/0.025}$ (b) $C\,e^{-0.861/0.05}$

   (c) $C\,e^{0.672/0.05}$ (d) $C\,e^{-0.475/0.025}$

10. The incremental temperature ΔT, necessary to double the conductivity or more accurately to double the number of carriers is $\dfrac{\Delta T}{T}$ and it is

    (a) $\dfrac{k_B T}{E_g}$ (b) $(k_B T)\ ln\ 2$

    (c) $\dfrac{(2k_B T)\ ln 2}{E_g}$ (d) $\dfrac{E_g}{2k_B T}$

11. When a trace of indium is added to germanium, one gets *p*-type semiconductor

    (a) true (b) false

12. In a *p*-type semiconductor at 0 K, the Fermi level lies midway between the acceptor level and top level of the valence band

    (a) true (b) false

13. If the concentration of the donor impurities is increased, the Fermi level shifts towards the conduction band

    (a) true (b) false

14. At low temperature and higher concentration of acceptor impurities, the density of holes *p* varies as

    (a) $p \propto N_a$ (b) $p \propto \dfrac{1}{N_a}$

(c) $p \propto \sqrt{N_a}$ (d) $p \propto N_a^2$

15. Even though in the donor exhaustion range the charge carriers remain the same, we find a small fall in conductivity as the temperature increases, because

(a) mobility increases (b) mobility decreases

(c) charge of the carriers affect the scattering

(d) lattice scattering decreases

16. An electron current can flow in a semiconductor even in the absence of an electric field, if there exist a gradient of the electron density

(a) true (b) false

17. Since diffusion process in a semiconductor is analogous to the heat conduction in a rod, the number of electrons diffusing through unit area for unit time is proportional to carrier density gradient

(a) true (b) false

18. The average distance an electron diffuses before recombination is related to the diffusion coefficient and the life time by the equation

(a) $L_n = D_n \tau_n$ (b) $L_n = \sqrt{D_n \tau_n}$

(c) $L_n = \dfrac{1}{D_n \tau_n}$ (d) none of these

19. The mean life time of the carrier injected in to a semiconductor is the time in which the carrier value falls to

(a) 17 % of its initial value (b) 27 % of its initial value

(c) 37 % of its initial value (d) none of these

20. The voltage developed across a current carrying conductor in the absence of any magnetic field is called Hall voltage

(a) true (b) false

21. The diffusion current is proportional to

(a) square of the applied electric field (b) applied electric field

(c) concentration gradient of charge carriers

22. The ratio of the diffusion constant for hole to the mobility for hole is proportional to

(a) temperature T (b) T^2

(c) $\dfrac{1}{T}$ (d) independent of temperature

23. The depletion region in an open circuited *p-n* junction contains

(a) electrons (b) holes

(c) uncovered immobile impurity ions (d) neutralized impurity atoms

24. The reverse saturation current in a *p-n* diode

(a) increases (b) decreases

(c) remain constant (d) when the reverse bias increases

25. The Einstein relationship between the diffusion constant *D* and mobility μ for electron is

(a) $\dfrac{D_n}{\mu_n} = \dfrac{2k_B T}{e}$ (b) $\dfrac{D_n}{\mu_n} = \dfrac{e}{k_B T}$

(c) $\dfrac{D_n}{\mu_n} = \dfrac{k_B T}{e}$ (d) $\dfrac{D_n}{\mu_n} = k_B T - E$

PROBLEMS AND SOLUTIONS

7.1 Calculate the current produced in a small germanium crystal of area 1cm^2 and of thickness 0.3 mm when a potential difference of 2 volt is applied across the faces. Given: concentration of free electrons in *Ge* is $2 \times 10^{19}/m^3$. $\mu_e = 0.36\ m^2\ V^{-1}\ s^{-1}$ and $\mu_p = 0.17\ m^2\ V^{-1}\ s^{-1}$.

***Solution*:**

The basic formula is,

$$\sigma_i = \frac{J}{E};\ J = \sigma_i E$$

$$I = JA = \sigma_i EA = n_i e(\mu_e + \mu_p)\frac{AV}{l}$$

i.e.,

$$I = 2 \times 10^{19} \times 1.6 \times 10^{-19}(0.36 + 0.17)\left(\frac{10^{-4} \times 2}{0.3 \times 10^{-3}}\right)$$

$\boxed{I = 1.13A}$ ***Answer***

7.2 Show that the ratio of maximum resistivity to intrinsic resistivity is expressed as

$$\frac{\rho_{\max}}{\rho_i} = \frac{(\mu_e + \mu_p)}{2\sqrt{\mu_e \mu_p}}$$

***Solution*:**

Intrinsic conductivity,

$$\sigma_i = n_i e(\mu_e + \mu_p)$$

The conductivity at any other doping level is expressed as

$$\sigma = e(n_e \mu_e + n_p \mu_p)$$

Since $n_e n_p = n_i^2$

$$\sigma = e\left(n_e \mu_e + \frac{n_i^2 \mu_p}{n_e}\right)$$

For resistivity to be maximum, conductivity has to be minimum for which

$$\frac{d\sigma}{d\,n_e} = 0 = e\left[\mu_e - \frac{n_i^2\,\mu_p}{n_e^2}\right]$$

i.e.,

$$\mu_e = \frac{n_i^2\,\mu_p}{n_e^2}; \text{ or } n_e = n_i\sqrt{\frac{\mu_p}{\mu_e}}$$

and

$$n_p = n_i\sqrt{\frac{\mu_e}{\mu_p}}$$

Hence

$$\sigma_{\max} = e\left[n_i\left(\mu_e\,\mu_p\right)^{1/2} + \frac{n_i^2\,\mu_p}{n_i}\sqrt{\frac{\mu_e}{\mu_p}}\right]$$

$$= n_i\,e\left\{\left(\mu_e\,\mu_p\right)^{1/2} + \left(\mu_e\,\mu_p\right)^{1/2}\right\}$$

$$\sigma_{\max} = n_i\,e\left\{2\left(\mu_e\,\mu_p\right)^{1/2}\right\}$$

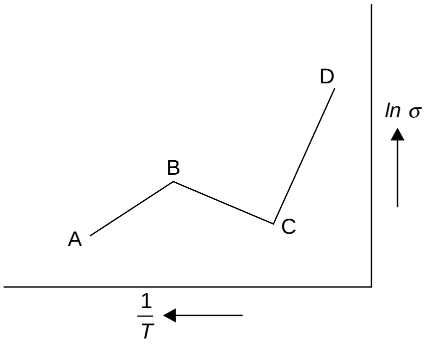
$$\frac{\sigma_i}{\sigma_{\max}} = \frac{\rho_{\max}}{\rho_i} = \frac{n_i\,e\left(\mu_e + \mu_p\right)}{2n_i\,e\left(\mu_e\,\mu_p\right)^{1/2}}$$

i.e.,

$$\boxed{\frac{\sigma_i}{\sigma_{\max}} = \frac{\left(\mu_e + \mu_p\right)}{2\sqrt{\mu_e\,\mu_p}}}\quad \textbf{\textit{Answer}}$$

7.3 All the 10^{20} donor impurities is an *n*-type semiconductor are ionized at 200 K. If the conductivity at 300 K is 26 Ω^{-1} m^{-1}, find the conductivity at 200 K. Mobility of electrons at 300 K and 200 K are respectively 0.39 and 0.41 $m^2\,V^{-1}\,s^{-1}$.

***Solution*:**



$$\sigma_{200} = N_d\, e\, \mu_e$$

$$\sigma_{300} = N_d\, e\, \mu_e'$$

$$\frac{\sigma_{200}}{\sigma_{300}} = \frac{\mu_e}{\mu_e'} = \frac{0.39}{0.41}$$

$$\sigma_{200} = \sigma_{300} \times 0.95$$

$$= 26 \times 0.95 = 24.7$$

For 26 Ω^{-1} m^{-1} the decrease in conductivity is 1.3; for 100 unit, it is

$$\frac{1.3 \times 100}{26} = 5\%$$

$\boxed{5\%}$ ***Answer***

7.4 The resistivity of pure silicon is 2300 Ω *m* and the mobilities of electrons and holes in it are 0.135 and 0.048 $m^2/V\text{–}s$ respectively. Find the electron and hole concentrations, and the resistivity of a specimen of silicon doped with 10^{19} atoms of phosphorus / m^3.

***Solution*:**

$$\rho_i = \frac{1}{n_i\, e\left(\mu_e + \mu_p\right)}$$

$$n_i = \frac{1}{\rho_i\, e\left(\mu_e + \mu_p\right)} = \frac{1}{2300 \times 1.6 \times 10^{-19}\left(0.048 + 0.135\right)}$$

$$n_i = \frac{10^{19}}{0.183 \times 2300 \times 1.6} = 1.48 \times 10^{16}\ /\text{m}^3$$

If n_e is the electron from donor level, then

$$n_e\, n_p = n_i^2$$

$$N_d\, n_p = n_i^2\ ;\ n_p = \frac{n_i^2}{N_d} = \frac{1.48^2 \times 10^{32}}{10^{19}} = 2.2 \times 10^{13}$$

The conductivity of doped semiconductor is

$$\sigma_d = e\left(n_e\, \mu_e + n_p\, \mu_p\right)$$

As $n_e >> n_p$

$$\sigma_d = e\, \mu_e\, n_e$$

The resistivity

$$\rho_d = \frac{1}{e\mu_e n_e} = \frac{1}{1.6 \times 10^{-19} \times 0.135 \times 10^{19}} = 4.63$$

$$\boxed{\rho_d = 4.63\ \Omega\,\mathrm{m}} \quad \textbf{\textit{Answer}}$$

7.5 At 0 sec, holes were injected in a bar of germanium. 12 micro second later, the density decreased to $10^{18}/\mathrm{m}^3$. The lifetime of the hole in the bar is 4.5 μs. Compute the density of holes injected at $t = 0$ sec.

***Solution*:**

$$\Delta p = (\Delta p)_0\, e^{\frac{-t}{\tau}}$$

$$10^{18} = (\Delta p)_0\, e^{-\frac{12}{4.5}} = (\Delta p)_0\, e^{-2.7}$$

$$(\Delta p)_0 = 10^{18} \times e^{2.7} = 1.4 \times 10^{19}$$

$$\boxed{(\Delta p)_0 = 1.4 \times 10^{19}} \quad \textbf{\textit{Answer}}$$

7.6 Get the equation for Hall coefficient when both holes and electrons are present. If $b = 10$, show that the Hall coefficient has its maximum value when $p = 18.1\, n_i$ and its minimum value when $p = 1.75\, n_i$, where n_i is the intrinsic carrier concentration. $b = \frac{\mu_n}{\mu_p}$. Show that $R_H(\max) = \frac{0.036}{n_i e}$ and $R_H(\min) = \frac{0.966}{n_i e}$.

***Solution*:**

Formula used:

$$R'_H = -\frac{\mu_n}{\sigma}$$

$$R''_H = \frac{\mu_p}{\sigma}$$

$$R_H = \frac{(\mu_p - \mu_n)}{\sigma} = \frac{(\mu_p - \mu_n)}{e(n\mu_n + p\mu_p)}$$

$$R_H = \frac{(\mu_p - b\mu_p)}{e(n\mu_n + p\mu_p)} = \frac{(\mu_p - b\mu_p)}{e(bn\mu_p + p\mu_p)}$$

$$R_H = \frac{(1-b)}{e(nb+p)} = \frac{(1-b)(nb+p)}{e(nb+p)^2}$$

$$R_H = \frac{nb+p-nb^2-bp}{e(nb+p)^2} = \frac{(p-nb^2)}{e(p+nb)^2}$$

assuming in a compensated material $nb = bp$ and $n = \frac{n_i^2}{p}$. In this case $p = 18.1\ n_i$ and hence

$$n = \frac{n_i^2}{p} = \frac{n_i}{18.1 n_i} = 0.0552\, n_i$$

Thus

$$R_H\,(\max) = \frac{1}{e}\left\{\frac{(18.1 \times n_i - 100 \times 0.0552\, n_i)}{(18.1 \times n_i + 10 \times 0.0552\, n_i)^2}\right\} = \left\{\frac{1}{n_i\, e}\right\}\left[\frac{12.58}{347.9}\right] = 0.036$$

Similarly R_H (min) can be calculated in a similar way

$$\boxed{\begin{aligned} R_H\,(\min) &= \frac{0.966}{n_i\, e} \\ R_H\,(\max) &= \frac{0.036}{n_i\, e} \end{aligned}}$$

Answer

7.7 A germanium rod 10 mm long by 1 mm square in cross-section has been doped with a total of 5 × 10^{13} donor atoms at room temperature. Calculate the electron and hole densities and the conductivity. Also calculate the resistance between the square ends of the rod. The intrinsic carrier density in Ge is 2.4 × 10^{19}/m^3 and electron mobility is 0.39 m^2 / V–sec.

***Solution*:**

(i) $l = 10^{-2}\, m$

(ii) $a = 10^{-6}\, m^2$

(iii) $V = 10^{-8}\, m^3$

$$N_d = \frac{5 \times 10^{13}}{10^{-8}} = 5 \times 10^{21}\ \text{atom/m}^3$$

The intrinsic concentration is

$n_i = 2.4 \times 10^{19}$ atom / m^3

$n = N_d = 5 \times 10^{21}$/ m^3

Now

$$n\,p = n_i^2$$

$$p = \frac{n_i^2}{n} = \frac{n_i^2}{N_d} = \frac{\left(2.4 \times 10^{19}\right)^2}{5 \times 10^{21}}$$

$$p = 1.15 \times 10^{17}\ /\mathrm{m}^3$$

$$\sigma_{ex} = ne\mu_e + pe\mu_p$$

$$= ne\mu_e = 5 \times 10^{21} \times 1.6 \times 10^{-19} \times 0.39 \text{ neglecting the second term}$$

$$\sigma_{ex} = 312 \text{ ohm}^{-1}\,\mathrm{m}^{-1}$$

$$\rho_{ex} = \frac{1}{312} = 3.2 \times 10^{-3} \text{ ohm metre}$$

$$R = \rho_{ex}\frac{l}{A} = 3.2 \times 10^{-3} \times 10^{-2}/10^{-6}$$

$$= 32 \text{ ohm}$$

$$\boxed{\begin{aligned} n &= 5 \times 10^{21}/\mathrm{m}^3 \\ p &= 1.15 \times 10^{17}/\mathrm{m}^3 \\ \sigma_{ex} &= 312 \text{ ohm}^{-1}\,\mathrm{m}^{-1} \\ R &= 32 \text{ ohm} \end{aligned}}$$

Answer

7.8 The constant α of a transistor is 0.95. What would be the charge in the collector-current corresponding to a change of 0.4 *m* A in the base-current in a common-emitter arrangement?

***Solution*:** The current-gain of a transistor in common-emitter arrangement is β, which is related to its current-gain α in common-base arrangement by

$$\beta = \frac{\alpha}{(1-\alpha)}$$

Here $\alpha = 0.95$

i.e., $$\beta = \frac{0.95}{1 - 0.95} = 19$$

Now β is the ratio of change in collector-current to the change in base-current, that is

$$\beta = \frac{\Delta i_c}{\Delta i_b}$$

$$\Delta i_c = \beta \times \Delta i_b = 19 \times 0.4$$

$$\boxed{\Delta i_c = 7.6 \text{ mA}} \quad \textbf{\textit{Answer}}$$

EXERCISE

7.1 Calculate the energy gap in silicon: given that it is transparent to radiation up to a wave length of 1100 nm. (***Ans*:** 1.1 eV)

7.2 The energy gap in germanium is 0.47 eV. Compare the intrinsic conductivities of germanium at 27°C and at 47°C. (***Ans*:** 2.27)

7.3 The density of atoms in pure silicon is 5×10^{28}. If the density of charge carriers at 47^0C is about 10^{12} times smaller than that of the atoms, compute the energy gap. Given $m_e^* = m_p^* = m$.

(***Ans*:** 0.72 eV)

7.4 The band gap of some materials are given below. Which substance would be photoconductors over the entire range of visible wave length?

Substance	Si	Ge	CdS
Band gap	1.9×10^{-19} J	1.3×10^{-19} J	3.8×10^{-19} J

(***Ans*:** Si and Ge)

7.5 Determine the position of Fermi energy level in an *n*-type germanium at 300 K if the impurity atom content in one part is 10^6. The forbidden gap is 0.72 eV and ionization energy of donor atom is 0.01 eV. There are 4.4×10^{28} germanium atom/m^3. (***Ans*:** $(E_c - E_f) = 1.6$ eV)

7.6 Get the ratio of diffusion coefficient of electrons and holes of a silicon single crystal at 27^0C. Given: mobilities of electrons and holes at 27^0C are 0.17 $m^2\ V^{-1}\ s^{-1}$ and 0.025 $m^2\ V^{-1}\ s^{-1}$ respectively.

(***Ans*:** $D_n = 0.68\ D_p$)

7.7 A rod of semiconductor 2 cm long, 2 mm wide and 1mm thick has contacts at each end to which 20 volt d.c is supplied. The rod is exposed to a uniform beam of radiation, the absorption of which increases the current by 2.5 m A. When the beam of radiation is suddenly cut off, the current decreases initially at the rate of 21.5 A/s. If $\mu_n = 0.39$ and $\mu_p = 0.19\ m^2\ V^{-1}\ s^{-1}$, find (a) the minimum frequency of the electromagnetic radiation (b) the equilibrium density of electron-hole pairs due to exposure to radiation (c) the minority carrier life time and (d) the excess density of electrons and holes remaining 0.5 millisecond after the radiation is cut off. E_g. for the semiconductor is 0.72 eV.

(***Ans*:** 1.74×10^{14} s^{-1}, 1.34×10^{19}/m^3, 116×10^{-6} s, 1.73×10^{17}/m^3)

7.8 The alternating current-gain of a transistor in a common base arrangement is 0.98. Find the change in collector-current corresponding to a change of 5.0 *m* A in emitter-current. What would be the change in the base-current? (***Ans*:** 0.1 m A)

8

Dielectrics

8.1 INTRODUCTION

Q 8.1 Fundamental equations and relations
Q 8.2 Dipoles and electric polarization
Q 8.3 Langevin theory of polarization in polar dielectrics
Q 8.4 Interaction of atoms in solid dielectrics and internal field
Q 8.5 Clausis–Mosotti relation and Debye equation and evaluation of permanent dipole moment
Q 8.6 Frequency dependence of polarization and energy dissipation in capacitors
Q 8.7 Ferroelectric materials and their uses
Q 8.8 Dielectrics and their dependence on temperature, permittivity....

KEY WORDS

insulating materials and dielectrics, specific resistance, leakage of current, negative temperature coefficient of resistance, dielectric constant (or specific inductive capacitance), flux density, (or electric displacement or electric induction), Gauss theorem, unit vector, total electric flux, polarization, induced dipoles, dipole moment, electric susceptibility, electronic polarization, molar or ionic polarization, orientation polarization, polar and non–polar molecules, centre of gravity of the electron cloud and that of protons, induced dipoles, restoring force, charge configuration, monoatomic gas, Lorentz force and coulomb force, electronic polarization and polarizability, Langevin function, molecular polarization, local or internal field, Lorentz proposal, polarizing field, Clausius–Mosotti equation, Debye's equation, refractive index, Lorentz–Lorentz relation, frequency dependence of polarization, frequency domain, complex permittivity, resonant frequency, relaxation time, frequency domain, Fourier transform, static permittivity, complex permittivity, imaginary part of permittivity, relaxation processes, absorption peak, micro wave frequencies, loss tangent, Maxwell's equations, dissipation factor, power factor, loss tangent, power dissipation, dielectric break down, avalanche effect, ferroelectric material, spontaneous polarization, perovskite, saturation polarization, catastrophe, resting forces, paraelectric state, coefficient of linear thermal expansion, remannet polarization, coercive field, ferroelectric and piezoelectric, pyroelectric materials, pyroelectric coefficient, surface density, pyroelectric devices, thermal-imaging devices. Temperature coefficient of permittivity.

8.1 INTRODUCTION

Insulating materials are also termed as *insulators* or *dielectrics* in the wider sense. They are non–metallic materials with high *specific resistance*. They are used to prevent the *leakage of current* from one conductor to another or to earth. Almost all insulating materials have a *negative temperature coefficient of resistance*. i.e., their resistivity is reduced as the temperature increases. The function of any insulator is to prevent the flow of electricity through it when a difference of potential is applied across its ends. Insulating materials obstruct the flow of current without any appreciable power loss.

Dielectric materials are those which are used in condensers to store electrical energy. e.g for power factor correction in single phase motors, in tube lights, etc. Dielectric materials are essentially insulating materials. The function of an insulating material is to obstruct the flow of electric current while that of a dielectric material is to store electrical energy. Thus, insulating materials and dielectric materials differ in their functions. The theory of dielectric was begun by *Faraday* and subsequently developed by Maxwell. From Farady's experiment we see that if in a charged condenser the air space between the plates is filled with a solid or liquid insulator the potential difference between the plates is lowered and thus the capacitance of the condenser is increased by a factor $\in_r$ which is greater than one. This factor is known as *dielectric constant or specific inductive capacitance* and is independent of the shape or size of the capacitor, but varies widely for different materials (or medium). The value of $\in_r$ for some selected materials is given in the following table.

Material	$\in_r$	*Material*	$\in_r$
Vaccum	1	Germanium at 20°C	16
Air (1 atm) at 20°C	1.006	Glycerin at 20°C	42.5
Air (100 atm) at 20°C	1.0548	Mica at 25°C	3–6
Benzene at 20°C	2.284	Backelite at 27°C and at 88°C	5–10
Polystyrene at 20°C	2.6		
Paraffin at 20°C	2.1	Liquid ammonia (–78°C)	25
Petroleum oil at 20°C	2.2	Water at 25°C	78.5
Ice at – 5°C	2.9	Metal	∞
Rubber at 27°C	2.94		
Paper at 25°C	3.5		

The comparatively high value of $\in_r$ of water suggests that water is a poor insulator; water is in fact a semiconductor.

Q 8.1 List out the formulae, equations and relations that are used in the study of electrical properties of dielectric materials.

***Answer*:** 1. *Flux density*

In the rationalized *mks* system of units, one line of force or flux line originate on each unit charge. Hence a charge q_1 will send q_1 lines of forces and this will be received by an area

$4\pi r^2$. The number of lines of forces received by unit area is called *flux density* or *electric displacement,* $\vec{D}$. D is also known as *electric induction.*

Thus
$$\vec{D} = \frac{q_1}{4\pi \vec{r}^{\,2}}$$

We know that the force experienced by a charge q_2 in a field $\vec{E}$ created by a charge q_1 is
$$\vec{F} = q_2\,\vec{E}$$

or
$$\vec{E} = \frac{\vec{F}}{q_2}$$

Substituting for $\vec{F} = \dfrac{q_1\,q_2}{4\pi \in \vec{r}^{\,2}}$, we get
$$\vec{E} = \frac{q_1\,q_2}{4\pi \in \vec{r}^{\,2}}$$

i.e.,
$$\vec{E} = \frac{q_1}{4\pi \in \vec{r}^{\,2}}$$

or
$$\boxed{\begin{aligned} &\vec{E} \in = \frac{q_1}{4\pi r^2} = \vec{D} \\ &\vec{E} \in_0 \in_r = \vec{D} \\ &\vec{D} = \vec{E} \in_0 \text{ with } \in_r = 1 \end{aligned}} \qquad \text{(Q 8.1.1)}$$

The unit of electric flux density is coulomb/m^2.

2. *Gauss theorem*

Gauss theorem states that the *total normal electric induction* through a closed surface is equal to the charge enclosed by the surface. The electric flux passing through a differential area is:

$$\boxed{d\phi = \vec{D} \bullet d\vec{A}} \qquad \text{(Q 8.1.2)}$$

$$= \frac{q}{4\pi r^2}\,\vec{i}_r\,d\vec{A}$$

The *unit vector* $\vec{i}_r$ may be written as the vector $\vec{r}$ divided by its magnitude; or $\dfrac{\vec{r}}{r}$.

Thus
$$d\phi = \frac{q}{4\pi}\left[\frac{\vec{r} \bullet d\vec{A}}{r^3}\right]$$

The term in the parenthesis is the differential solid angle, $d\omega$, subtended at the charge q by the differential area $d\vec{A}$.

Thus
$$d\phi = \frac{q}{4\pi} d\omega$$

Thus the *total electric flux* that emanates from the charge q is found by integrating over the enclosed surface, A

$$\phi = \frac{q}{4\pi}\int_0^{4\pi} d\omega = q$$

Comparing this equation with Eqn. (Q 8.1.2), one gets

$$\boxed{\phi = \int \vec{D} \bullet d\vec{A} = q} \qquad \text{(Q 8.1.3)}$$

Equation (Q 8.1.3) is often referred to as *Gauss law*. Knowing $D = E \in$, Eqn. (Q 8.1.3) becomes

$$\boxed{\in \int \vec{E} \bullet d\vec{A} = q} \qquad \text{(Q 8.1.3 } a\text{)}$$

3. *Dielectrics and Gauss theorem*

Let us apply Gauss theorem to a parallel plate condenser without a dielectric and then with a dielectric. In the first case, when no dielectric present, the electric field E_o at any point on the gaussian surface is given by

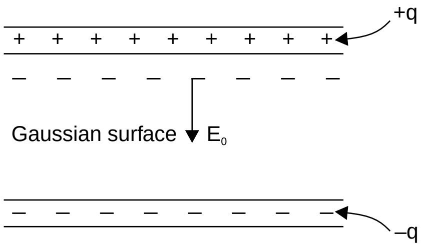


Fig. Q 8.1.1 *A parallel plate condenser with no dielectric*

$$\int E_0 \bullet dA = \frac{q}{\in_0}$$

i.e.,
$$\boxed{E_0 = \frac{q}{A \in_0}} \qquad \text{(Q 8.1.4)}$$

In the second case, when dielectric is present, the net charge within the guassian surface is $q - q'$, where q' is the induced surface charge, and the field $\vec{E}$ is given by

$$\boxed{\begin{aligned} \int \vec{E} \bullet d\vec{A} &= \frac{(q - q')}{\in_0} \\ E\,A &= \frac{q}{\in_0} - \frac{q'}{\in_0} \\ E &= \frac{q}{A\in_0} - \frac{q'}{A\in_0} \end{aligned}} \qquad \text{(Q 8.1.5)}$$

Equation (Q 1.8.5) indicates that the induced charge q' tends to weaken the original field (i.e., $E < E_0$) which reveals itself a reduction in the potential difference when dielectric is present and not present respectively, then

$$\boxed{\frac{E_0}{E} = \frac{V_0}{V_d}} \qquad \text{(Q 8.1.6)}$$

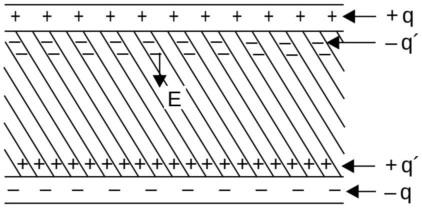


Fig. Q 8.1.2 *A parallel plate condenser with dielectric*

The corresponding expressions for capacitances are:

$$C_0 = \frac{A\in_0}{d} = \frac{Q}{V_0}$$

$$C = \frac{A\in_0\in_r}{d} = \frac{Q}{V_d}$$

$$\frac{C}{C_0} = \in_r = \frac{V_0}{V_d}$$

Thus Eqn. (Q 8.1.6) becomes

$$\frac{E_0}{E} = \in_r$$

$$E = \frac{E_0}{\in_r}$$

Substituting for E_0 from Eqn. (Q 8.1.4), one gets

$$\boxed{E = \frac{E_0}{\in_r} = \frac{q}{A \in_0 \in_r}} \qquad \text{(Q 8.1.7)}$$

Comparing equation (Q 8.1.7) with (Q 8.1.5), we get

$$\boxed{\begin{array}{l} \dfrac{q}{A \in_0 \in_r} = \dfrac{q}{A \in_0} - \dfrac{q'}{A \in_0} \\ q - q' = \dfrac{q}{\in_r} \end{array}} \qquad \text{(Q 8.1.8)}$$

or

This shows that the induced charge q' is less than the free charge q and is zero when $\in_r = 1$ or the dielectric is absent.

Thus Eqn. (Q 8.1.5) is

$$\int \vec{E} \bullet d\vec{A} = \frac{q - q'}{\in_0} = \frac{q}{\in_0 \in_r} \quad \text{[see Eqn. Q 8.1.8]}$$

$$\boxed{\in_0 \in_r \int \vec{E} \bullet d\vec{A} = q} \qquad \text{(Q 8.1.9)}$$

This is nothing but the Gauss law in the presence of the dielectric

4. *Electric flux density and polarization*

Owing to the *polarization* of the medium, charges are induced at the surfaces of the dielectric, the charge due to electric polarization at the boundary near the positive plate of the capacitor being negative and vice-verse. If q is the charge on the plate and q' is the induced charge on the boundary of the dielectric, then we can write Eqn. (Q 8.1.8) as

$$\frac{q}{A} = \frac{q}{A \in_r} + \frac{q'}{A}$$

$$\boxed{\frac{q}{A} = \in_0 \left[\frac{q}{A \in_0 \in_r} \right] + \frac{q'}{A}} \qquad \text{(Q 8.1.10)}$$

The last term of this equation gives induced surface charge per unit area, called *electric polarization*, *P*. It is also equal to the *induced dipolement for unit volume*.

Substituting $E = \dfrac{q}{A \in_0 \in_r}$ from Eqn. (Q 8.1.7) in to Eqn. (Q 8.1.10), one gets

$$\frac{q}{\vec{A}} = \vec{E} \in_0 + \vec{P} \text{ with } \frac{q}{\vec{A}} = \vec{D}$$

i.e.,

$$\boxed{\vec{D} = \vec{E} \in_0 + \vec{P}} \qquad \text{(Q 8.1.11)}$$

In free space, where there is no dielectric and thus $\vec{P} = 0$, we have

$$\vec{D} = \vec{E} \in_0 \text{ with } D = \frac{q}{A}$$

Thus $$D = \frac{q}{A} = \frac{q \in_0 \in_r}{A \in_0 \in_r} = E \in_0 \in_r = E \in \qquad \text{\{Refer Eqn. (Q 8.1.7)\}}$$

Thus equation Q 8.1.11 becomes,

$$E \in = E \in_0 + P$$

$$P = E \in_0 \in_r - E \in_0 = E \in_0 (\in_r - 1)$$

i.e., $$(\in_r - 1) = \frac{P}{E \in_0}$$

$$\boxed{(\in_r - 1) = \frac{\vec{P}}{\vec{E} \in_0} = \chi} \qquad \text{(Q 8.1.12)}$$

where χ is *electric susceptibility* of the *dielectric medium*.

Q 8.2 What is meant by dipole and dipolemoment in dielectrics? Discuss the phenomenon of electric polarization. Write a note on electronic polarization.

Answer: An ideal insulator contains no free electrons so that an electric field applied to it there is no macroscopic movement of charge; instead, it suffers displacement of its electrons with respect to their parental nuclei, creating thus *electric dipoles*. The electric field is said to polarize the material electrically. See Fig. Q 8.2.1.

The dipolemoment of the polarized atom is given by $\mu = qd$, where d is the displacement of the charge cloud. μ is directed from negative charge centre to positive charge centre. The units of dipole moment are thus coulomb-metre in SI units, but frequently used is the more conveniently sized unit, the Debye (D), which is 3.33×10^{-30} C m. The *polarization, P*, is the dipole moment per unit volume (C/m^2) or the induced charge for unit area:

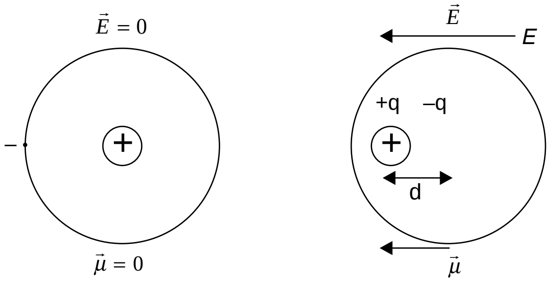


Fig. Q 8.2.1 *The electric dipole moment induced on an atom by an applied electric field*

$$P = N\mu$$

where N is the number of dipoles/m^3.

There are three principal classes of polarization in materials.

1. *Electronic polarization*: the displacement of orbiting electrons about an atom by an electric field.
2. *Molecular or ionic polarization*: the displacement of ions by the electric field.
3. *Orientational polarization*: the partial alignment of polar molecules free to rotate in the electric field.

The molecules of a dielectric are classified as *polar* and *non-polar*. In any molecule there will be a distribution of protons and a distribution of electrons. The protons can be considered to act as the equivalent positive electric charge at some specific point in the molecule, the *centre of gravity of the protons*. Similarly there is a point, at which a negative charge is equivalent to the distributed electrons, the *centre of gravity of electrons*. If these two points coincide then the molecule is *non polar* and if they are separated by short distance then the molecule is *polar molecule*. Symmetrical molecules such as H_2, N_2, and O_2 are non polar. On the other hand molecules H_2O, N_2O, etc., are polar, as both hydrogen atoms or both nitrogen atoms lie on the same side of the oxygen atom. Thus the polar molecules work as dipoles and have dipole moments. If the dielectric is placed in an electric field, the charges of a non-polar molecule become displaced. The molecules are then said to become *polarized* by the field and are called *induced dipoles*. The *displacement* is however limited by strong *restoring force produced* by the charge configuration in the molecule. When a dielectric consists of polar molecules (permanent dipoles), these dipoles are oriented at random in the absence of an external electric field. When an electric field is applied, the forces on a dipole give rise to a couple, whose effect is to orient the dipole along the direction of the electric field. The stronger the field, the greater is the aligning effect. Thus non-polar molecules become induced dipoles, where as polar molecules are orientated by the field and therefore have their dipole moments increased. The orientation of the induced dipoles or of the permanent dipoles in an external electrostatic field is such as to set the axis of the dipole along the field. This is electric polarization as stated earlier.

Electronic Polarization

Consider a monoatomic gas such as helium or argon in an electric field. Since the spacing between the gas molecules is much greater than the size of the molecule, the interaction between the molecules may be neglected. Hence the effect of the field on any molecule is essentially uninfluenced by the presence of other molecules. A simple discussion equating the *Lorentz force* with *coulomb force* and as simplification gives an expression for the displacement of the electron cloud as

$$\boxed{x = \frac{4\pi \in_0 R^3 E}{Ze}} \qquad \text{(Q 8.2.1)}$$

i.e., the displacement is proportional to the field. Thus the *electric dipole moment* is

$$\mu_e = Ze\,x = 4\pi \in_0 R^3 E$$

$$\mu_e \propto E$$

or

$$\boxed{\mu_e = \alpha_e E} \qquad \text{(Q 8.2.2)}$$

where $\alpha_e = 4\pi \in_0 R^3$ is called *electronic polarizability*

Thus $$P_e = N\mu_e = N\alpha_e E$$

Referring Eqn. Q 8.1.12, we get

$$\vec{P}_e = \vec{E} \in_0 (\in_r - 1) = N\alpha_e \vec{E}$$

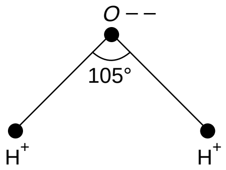
$$\boxed{(\in_r - 1) = \frac{N\alpha_e}{\in_0}} \qquad \text{(Q 8.2.3)}$$

In a similar way the theory of ionic polarization may be discussed. However ionic polarization is much less for many materials.

Example: In hydrogen atom, $r = 0.05\ nm$, so that $\alpha_H = 4\pi \in_0 R^3 = 1.4 \times 10^{-41}\ F m^2$. Thus for a field of 1 mV/m, $\mu_e = \alpha_H E = 1.4 \times 10^{-35}\ C m$. In solid, the density of hydrogen atoms might be about $10^{29}/m^3$, giving a (relatively small) polarization of 1.4×10^{-6} C/m^2. Eqn. Q 8.2.2 indicates that larger atoms are polarized much more than the smaller ones.

Q 8.2 Give an analytical discussion of Langevin's theory of polarization in polar dielectrics.

Answer: *Debye* in 1927 conceived the idea that *polar molecules* in liquids or gases such as H_2O, CH_3Cl or NH_3, have a permanent dipole moment which can be partially aligned with an applied field. The measurement of the dipole moment of a molecule, allied with knowledge of its size, gives a measure of the charge separation in it which can be related to the atomic electro negativities (an index of how readily atoms will donate or accept electrons). Alignment of polar molecules in an electric field is upset by random thermal motion, so that Maxwell-Boltzman statistics can be used to find the average polarization, just as for a paramagnet. The expression for the polarization can be obtained from Langevin-Debye theory, which is as under:



Consider a dipole whose moment, μ, makes an angle θ with the applied field *E*. Its potential energy is given by

$$\boxed{W = -\mu \bullet E = -\mu E \cos\theta} \qquad \text{(Q 8.3.1)}$$

In a solid angle, $d\omega$, there are $N\,d\omega$ dipoles, where N is the number of dipoles/m^3, given by

$$\boxed{N = A \exp(-W/k_B T)} \qquad \text{(Q 8.3.2)}$$

where A is a constant. The component of the dipole moment aligned with the field is $\mu \cos\theta$ so that the net dipole moment due to solid angle, $d\omega$, is $N\mu \cos\theta\, d\omega$

$$\langle \mu \rangle = \frac{\int_0^\pi N\mu \cos\theta \, d\omega}{\int_0^\pi N d\omega} = \frac{\int_0^\pi \mu \, N \cos\theta \; 2\pi \sin\theta \, d\theta}{\int_0^\pi N \; 2\pi \, \sin\theta \, d\theta}$$

with $d\omega = 2\pi \, \sin\theta \, d\theta$. Substituting for *N* and making use of $a = \frac{\mu E}{k_B T}$ and $x = \cos\theta$ leads to

$$\langle \mu \rangle = \frac{\mu \int_{-}^{+} x \, \exp(ax) \, dx}{\int_{-}^{+} \exp(ax) \, dx} = \mu \left[\coth(a) - \frac{1}{a} \right]$$

The integrals are standard forms: $\left[\coth(a) - \frac{1}{a} \right]$ is the *Langevin function*, *L* (*a*), which has been widely used in the chapter on Magnetic Properties of Materials.

When the argument, *a*, of *L* (*a*) is small, $L(a) = \frac{a}{3}$ and then $<\mu> = \frac{1}{3} \frac{\mu^2 E}{k_B T}$ and the polarization is:

$$\boxed{P = N \, \langle \mu \rangle = \frac{1}{3} \left\{ \frac{N \mu^2 E}{k_B T} \right\}} \qquad \text{(Q 8.3.3)}$$

To check if $\frac{\mu E}{k_B T}$ is small, consider water, which has a dipole moment of 1.8 Debye unit or 6 × 10^{-20} *C m*, to which a field of 1 *M V/m* is applied at 300 K. Then $\mu \; E = 6 \times 10^{-24}$ *J* and $k_B T = 4 \times 10^{-21}$ *J*, so Eqn. (Q 8.3.3) holds under normal circumstances.

The total polarization of a material is the sum of electronic, molecular and orientational polarizations:

$$P_T = P_{\text{el}} + P_{\text{mol}} + P_{\text{diploe}}$$

The first two terms are almost independent of temperature. Using $P = N\mu$ and $\mu = \alpha E_L$

$$P_T = N \, E_L \left(\alpha_e + \alpha_{\text{mole}} + P_{\text{dip}} \right)$$

$$P_T = N \, E_L \left\{ \alpha_e + \alpha_{\text{mole}} + \frac{\mu^2}{3 k_B T} \right\}$$

E_L is the field acting locally on the dipole, and is in general different from the applied field, E mostly in solids.

Again taking water as an example, the dipolar polarizability is about 3×10^{-39} $F\,m^2$ at 300 K and the electronic polarizability $\left(4\pi \in_0 r^3\right)$ is about 10^{-40} $F\,m^2$, taking $r = 0.1$ nm. The dipolar term dominates and there is no molecular polarizability.

Q 8.4 Discuss the nature of interaction between atoms in solids and obtain the expression for internal field is solid dielectrics.

Answer: Solids and liquids have same types of polarizing phenomenon as that of gases but the main difference lies in the fact, that in solids and liquids the interaction between the atoms cannot be neglected as the density of atoms is very high in solids. Hence the field experienced by a given atom is determined in part by the dipoles possessed by the surrounding particles; in general, therefore E_i or E_L, the internal field is not equal to the applied field. Hence a study of the polarization in such materials becomes more complicated as the calculations of interaction are difficult, and can generally be taken into account only approximately.

Lorentz suggested a method to calculate the *Local field* as given below:

The dipole is imagined to be surrounded by a spherical cavity of radius r and centre A, such that radius r is large compared with the intermolecular distance so that the sphere contains many molecules but small compared with the dimensions of the whole dielectric. If this dielectric is placed between two charged plates, the electric field experienced by a molecule of the dielectric, if assumed to be placed at the centre of the cavity, is given by

$$\vec{E}_L = \vec{E}_1 + \vec{E}_2 + \vec{E}_3 + \vec{E}_4$$

where

(i) $\vec{E}_1$ is the field intensity due to charge density on the plates of the capacitor (i.e., with no dielectric)

(ii) $\vec{E}_2$ is the field at the atom due to the polarized charges (induced charge on the plane surfaces of the dielectric (i.e., depolarizing field))

(iii) $\vec{E}_4$ is the field due to the polarized charges on the surface of the spherical cavity.

(iv) $\vec{E}_3$ is the field due to all the dipoles inside the spherical cavity.

Now

$$\boxed{\begin{aligned} \vec{D} &= \vec{E}_1 \in_0 = \vec{E} \in_0 + \vec{P} \\ \vec{E} &= \frac{\vec{D}}{\in_0} = \vec{E} + \frac{\vec{P}}{\in_0} \end{aligned}} \qquad \text{(Q 8.4.1)}$$

$$\boxed{\vec{E}_2 = -\frac{\vec{D}}{\in_0} = -\frac{\vec{P}}{\in_0}} \qquad \text{(Q 8.4.2)}$$

taking $\vec{E} = 0$ in Eqn. Q 8.4.1

$\vec{E}_3$ is the field intensity at *A* due to other atoms contained in the cavity. We are assuming a cubic structure, so $E_3 = 0$ because of symmetry

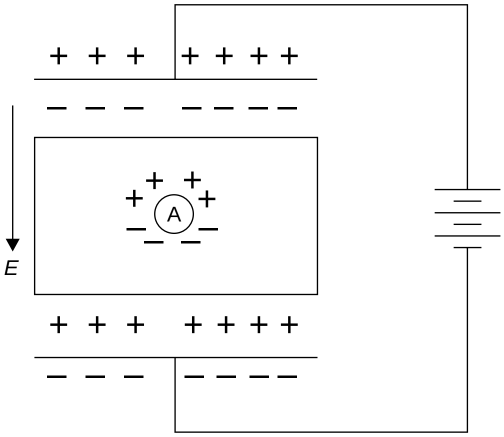


Fig. Q 8.4.1 *Calculation of Local field*

Computation of E_4

The magnified view of the cavity is shown in Fig. Q 8.4.2

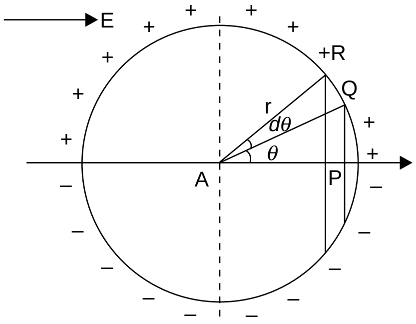


Fig. Q 8.4.2 *Cavity magnified*

The enlarged view of the cavity is shown in Fig. Q 8.4.2. If *dA* is the surface area of the sphere of radius *r* lying between θ and $\theta + d\theta$, where θ is the direction with reference to the direction of the applied field, then

$$dA = 2\pi\,(PQ)\,(QR)$$

and
$$\theta = \frac{pQ}{r} \text{ and } d\theta = \frac{QR}{r}$$

or
$$dA = 2\pi r^2 \sin\theta\, d\theta$$

The charge *dq* on the surface *dA* is equal to the normal component of the polarization multiplied by the surface area

Therefore,

$$dq = \vec{P}\cos\theta \, dA = \vec{P}\, 2\pi r^2 \sin\theta \, \cos\theta \, d\theta$$

The field due to this charge at *A* denoted by $d\vec{E}_4$ in the direction $\theta = 0$ is:

$$d\vec{E}_4 = \frac{dq \times 1 \times \cos\theta}{4\pi \in_0 r^2} = \frac{\vec{P}\, 2\pi r^2 \sin\theta \, \cos^2\theta \, d\theta}{4\pi \in_0 r^2}$$

Thus the total field $\vec{E}_4$ due to charges on the surface of the entire cavity is obtained by integrating

$$\int d\vec{E}_4 = \frac{\vec{P}}{2\in_0}\int_0^{\pi}\cos^2\theta \, \sin\theta \, d\theta = \frac{\vec{P}}{2\in_0}\int_0^{\pi}\cos^2\theta \, d\left(-\cos\theta\right)$$

$$= -\frac{\vec{P}}{2\in_0}\left[\frac{\cos^3\theta}{3}\right]_0^{\pi} = -\frac{\vec{P}}{6\in_0}\left[-1-1\right] = \frac{\vec{P}}{3\in_0}$$

Now $$\vec{E}_L = \vec{E}_1 + \vec{E}_2 + \vec{E}_3 + \vec{E}_4 = \vec{E} + \frac{\vec{P}}{\in_0} - \frac{\vec{P}}{\in_0} + 0 + \frac{\vec{P}}{3\in_0}$$

i.e., $$\boxed{\vec{E}_L = \vec{E} + \frac{\vec{P}}{3\in_0}} \qquad \text{(Q 8.4.3)}$$

Q 8.5 Using the equation for local field, obtain Clausius-Mosotti relation and hence suggest a method to evaluate permanent dipole moment

Answer: If there are *N* atoms in a cubic metre of the dielectric, then the electric moment for unit volume is:

$$P = N\alpha E_L$$

or $$P = E \in_0 \left(\in_r - 1\right) = N\alpha E_L$$

$$\boxed{\in_r = 1 + \frac{N\alpha E_L}{\in_0 E}} \qquad \text{(Q 8.5.1)}$$

Also electric susceptibility, $\chi = \left(\in_r - 1\right) = \dfrac{N\alpha E_L}{\in_0 E} = \dfrac{N\alpha}{\in_0 E}\left(E + \dfrac{P}{3\in_0}\right)$

If $$\beta = \frac{N\alpha}{3\in_0}, \text{ then } \chi = 3\beta + \frac{\beta P}{E \in_0} = 3\beta + \beta\chi$$

i.e.,
$$\chi(\beta - 1) = 3\beta$$

i.e.,
$$\chi = \frac{3\beta}{(\beta - 1)} \tag{Q 8.5.1a}$$

Referring Eqns. 8.4.3 and 8.5.1, one can write

$$\vec{E}_L = \vec{E} + \frac{N\alpha \vec{E}_L}{3\in_0}, \text{ or } E_L\left[1 - \frac{N\alpha}{3\in_0}\right] = E$$

or
$$\boxed{\frac{E_L}{E} = \frac{1}{\left(1 - \frac{N\alpha}{3\in_0}\right)}} \tag{Q 8.5.2}$$

Substituting this value in Eqn. (Q 8.5.1),

$$\in_r = 1 + \frac{N\alpha}{\in_0}\left[\frac{1}{\left(1 - \frac{N\alpha}{3\in_0}\right)}\right]$$

$$\boxed{\in_r = 1 + \frac{N\alpha}{\in_0}\left[\frac{1}{\left(1 - \frac{N\alpha}{3\in_0}\right)}\right]} \tag{Q 8.5.3}$$

$$= \frac{\in_0\left(1 - \frac{N\alpha}{3\in_0}\right) + \frac{N\alpha\in_0}{\in_0}}{\in_0\left[1 - \frac{N\alpha}{3\in_0}\right]}$$

or

$$\in_r = \frac{1 + \frac{2}{3}\left(\frac{N\alpha}{\in_0}\right)}{1 - \frac{1}{3}\left(\frac{N\alpha}{\in_0}\right)}$$

A calculation and simplification will yield

$$\boxed{\left[\frac{\in_r - 1}{\in_r + 2}\right] = \frac{N\alpha}{3\in_0}} \tag{Q 8.5.4}$$

This is *Clausius-Mosotti relation* connecting macroscopic dielectric constant with the microscopic polarizabilities. If $\frac{M_A}{\rho}$ is the molar volume, then the molar polarization is:

$$\left[\frac{\in_r - 1}{\in_r + 2}\right]\frac{M_A}{\rho} = \frac{N\alpha}{3\in_0}\left(\frac{M_A}{\rho}\right)$$

i.e.,

$$\left[\frac{\in_r - 1}{\in_r + 2}\right]\frac{M_A}{\rho} = \frac{N_A}{3\in_0}(\alpha_e + \alpha_i + \alpha_0)$$

in the presence of orientational polarization.

i.e.,

$$\boxed{\left[\frac{\in_r - 1}{\in_r + 2}\right]\frac{M_A}{\rho} = \frac{N_A}{3\in_0}(\alpha' + \alpha_0)} \tag{Q 8.5.7}$$

This equation is called *Debye's equation* which suggests a method to determine the permanent dipole moment:

$$\left[\frac{\in_r - 1}{\in_r + 2}\right]\frac{M_A}{\rho} = \frac{N_A\alpha'}{3\in_0} + \frac{\mu_m^2 N_A}{9\in_0 k_B T} = a + \frac{m}{T}$$

Conduct an experiment using a dipolemeter and determine the dielectric constant at different temperatures. Draw a graph between $\left[\frac{\in_r - 1}{\in_r + 2}\right]\frac{M_A}{\rho}$ and $\frac{1}{T}$ and get the slope *m*.

Thus

$$m = \frac{N_A\mu_m^2}{9\in_0 k_B}$$

$$\boxed{\mu_m = 3\left[\sqrt{\frac{m k_B \in_0}{N_A}}\right]} \tag{Q 8.5.8}$$

Thus the magnitude of the slope *m* helps to determine μ_m.

Refractive Index

The refractive index of a material (*n*) is the ratio of the speed of light (*c*) to the speed of light in the material.

We know that $c = \frac{1}{\sqrt{\mu_0 \in_0}}$ and $v = \frac{1}{\sqrt{\mu \in}}$

i.e.,
$$v = \frac{1}{\sqrt{\mu_r \, \mu_0 \in_r \in_0}};\ n = \frac{c}{v} = \sqrt{\mu_r \in_r}$$

$n = \sqrt{\in_r}$ as in most optical materials and dielectrics, $\mu_r = 1$.

Now referring Eqn. 8.5.4,
$$\boxed{\frac{n^2 - 1}{n^2 + 2} = \frac{N\alpha}{3\in_0}} \qquad \text{(Q 8.5.9)}$$

This is knows as *Lorentz-Lorentz relation.*

Q 8.6 Discuss frequency dependence of polarization with suitable graphs. Write a note on loss tangent and energy dissipation in capacitors.

Answer: At low frequencies, in the radio-frequency region of the *electromagnetic spectrum*, the dipolar molecules in some media may be capable of rotation in response to the oscillations of an alternating electric field. This rotation will be opposed by damping forces, such as viscous drag, which results in a characteristic relaxation time for the dipoles, which is given by

$$\tau = \frac{1}{\omega_0}$$

where ω_0 is the frequency of maximum power absorption, the resonant frequency. When $\omega << \omega_0$, the dipoles are in phase with the field and no energy is absorbed and when $\omega >> \omega_0$, the dipoles cannot respond to the field at all and again no energy is absorbed. At low frequencies the dipoles make maximum contribution to the permittivity and at high frequencies they make no contribution.

We can write the time dependence of the polarization as $P(t) = P_0 \exp\left(-t/\tau\right)$

where τ is the *relaxation time*. To obtain the corresponding function, $P(\omega)$, in the *frequency domain*, we perform a *Fourier transform* in the positive frequency domain only:

$$P(\omega) = \int_0^\infty P_0 \exp\left(-t/\tau\right) \exp\left(-i\omega t\right) dt$$

i.e.,
$$\boxed{P(\omega) = \frac{P_0}{\left(\omega_0 + i\omega\right)}} \qquad \text{(Q 8.6.1)}$$

where we have substituted ω_0, the resonant frequency of the relaxation process, for $\frac{1}{\tau}$. Now P depends directly on the permittivity, so instead of a complex polarization we shall use a complex permittivity of the same form:

$$\boxed{\in(\omega) = \frac{A}{(\omega_0 + i\omega)} + B = \frac{A}{\omega_0\{1 + i(\omega/\omega_0)\}} + B} \qquad \text{(Q 8.6.2)}$$

A and B are constants which can be found by considering what happens at $\omega = 0$ and $\omega = \infty$. The permittivity at zero frequency is the static permittivity, $\in_s$, so putting $\omega = 0$ in Eqn. (Q 8.6.2) leads to

$$\boxed{\in(0) = \in_s = \frac{A}{\omega_0} + B} \qquad \text{(Q 8.6.3)}$$

At frequencies for above resonance, the permittivity is $\in_\infty$ which is less than the static permittivity. Substituting $\omega = \infty$ in Eqn. (Q 8.6.2) gives $B = \in_\infty$, so that {Refer Eqn. Q 8.6.3}

$$\in_s = \frac{A}{\omega_0} + \in_\infty$$

i.e.,

$$A = \omega_0(\in_s - \in_\infty)$$

and Eqn. (Q 8.6.2) becomes

$$\boxed{\in(\omega) = \frac{(\in_s - \in_\infty)}{1 + i(\omega/\omega_0)} + \in_\infty} \qquad \text{(Q 8.6.4)}$$

$$\boxed{\in(\omega) = \frac{(\in_s - \in_\infty)\{1 - (\omega/\omega_0)\}}{\{1 + (\omega/\omega_0)^2\}} + \in_\infty} \qquad \text{(Q 8.6.5)}$$

The complex permittivity can be expressed as

$$\in = \in' - i\in''$$

which can be compared to Eqn. Q 8.6.4 and Q 8.6.5, yielding

$$\boxed{\in' = \in_\infty + \frac{(\in_s - \in_\infty)}{\{1 + (\omega/\omega_0)^2\}}} \qquad \text{(Q 8.6.6)}$$

and

$$\boxed{\in'' = \frac{(\omega/\omega_0)(\in_s - \in_\infty)}{\{1 + (\omega/\omega_0)^2\}}} \qquad \text{(Q 8.6.7)}$$

The imaginary part of the permittivity, $\in''$, causes energy to be absorbed and is a maximum at the resonant frequency, ω_0, and zero far above and below it. The real part of the permittivity starts off at low frequencies at the static value, falls as the resonant frequency is approached to reach halfway between $\in_s$ and $\in_\infty$ at $\omega = \omega_0$, then drops to $\in_\infty$ as the frequency increases further.

Fig. Q 8.6.1 shows the graphs of $\in'$ and $\in''$ against $\log \omega$.

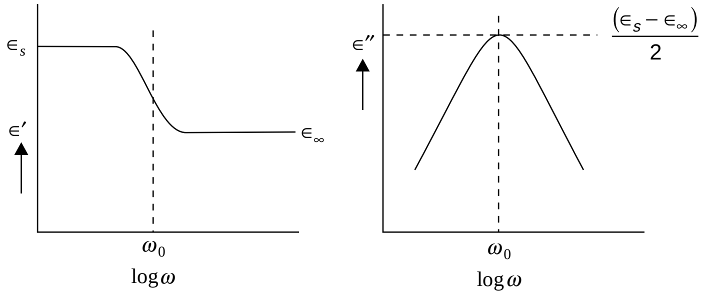


Fig. Q 8.6.1 $\in'$ *and* $\in''$ *against* $\log\omega$

If there are several absorption mechanisms in the material, such as orientational molecular and electronic relaxation processes, then there are corresponding peaks in $\in''$ and reductions in $\in'$ as the frequency goes up. As electrons can respond very quickly to electric field changes, the absorption peak for electronic polarization occurs at very high frequencies – in the ultra – violet or optical region. Ionic motion is several thousand times slower and so ionic polarization leads to peaks in the infra–red region, while orientational polarization gives rise to peaks at UHF and microwave frequencies. Fig. Q 8.6.2 shows a plot of $\in''$ and $\in'$ against ω for a hypothetical solid exhibiting all three types of absorption.

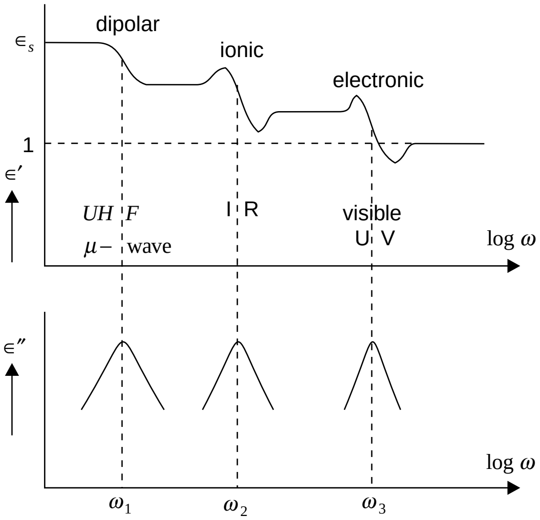


Fig. Q 8.6.2 $\in'$ *and* $\in''$ *against* $\log\omega$ *for a material with three absorption peaks*

The Loss Tangent

The *loss tangent,* $\tan\delta$, is equal to $\frac{\in''}{\in'}$. Maxwell's equations were used to find the energy absorbed from electromagnetic waves by conducting media and a dispersion relation was derived and the important equation obtained for wave vector k is:

$$k^2 = \mu \in \omega^2 + i\,\mu\sigma\omega$$

In this equation, $\in$ is real $(= \in_0 \in_r)$. The phase of k^2 is identical so that

$$\boxed{\tan\delta = \frac{\sigma}{\in\omega} = \frac{\in''}{\in'}} \qquad \text{(Q 8.6.8)}$$

Since this $\in$ is real, we can identify it with $\in$ and then $\in'' = \frac{\sigma}{\omega}$. Now power losses per unit volume in a conducting medium are given by

$$W_v = \sigma E^2$$

Since $\in'' = \frac{\sigma}{\omega}$, we get

$$W_v = \in''\omega E^2$$

Since $\in'' = \in' \tan\delta$ so the power losses/m^3 are

$$\boxed{W_v = \omega E^2 \in' \tan\delta} \qquad \text{(Q 8.6.9)}$$

The *dissipation factor* is the same as $\tan\delta$, the *loss tangent*. The loss factor is $\in''$ and is therefore equal to $\in' \tan\delta$. *The power factor* is $\sin\delta = \tan\delta$, a very good approximation for capacitor materials. Because dielectric losses are proportional to E^2, they are an important consideration in the design of capacitors and high-voltage cables. Though the frequency of the National Grid is only 50Hz, the fields in the dielectric of a 300 kV cable may be 15 MV/m, so if $\tan\delta$ is 0.01, the losses will be $W_v = 2.3 \times 8.85 \times 10^{-12} \times (15 \times 16)^2 \times 2\pi \times 50 \times 0.01 = 14$ kW/m^3. The loss is significant, though much less than the conductor losses. In practice, solid dielectrics cannot be used above 33 kV because of the large thickness required and consequent problems in dissipating heat. The field in solid dielectrics for power cables is limited to about 5 MV/m to lessen the risk of breakdown. One advantage of dielectric heating is that heat is produced uniformly through out the material, rather than just within skin depth as in RF-heated, metallic bodies.

An example of capacitor losses

The following table gives some relative permitivities and loss tangents for a variety of dielectrics used in making capacitors. The properties of dielectrics, especially $\tan\delta$, are very dependent on the preparation of the material, as well as temperature ($\tan\delta$ tends to increase with temperature rise) and frequency, so the values given in the table should be treated as guide lines only.

Table 8.5.1 *Properties of dielectrics at 300 K and at 1 M Hz*

Material	ϵ_r	$\tan\delta$ *in* 10^{-4}
Alumina	10	5 – 20
Porcelain	5	75
Ba TiO_3	500	150
Nylon 610	3.1	220
Polycarbonate	3.1	10
Silica (Quartz)	3.8	150
PZT4	1000	40
Perspex	2.6	145
Polyethylene	2.3	2
Polystyrene	2.6	0.7
PTFE	2.1	2
PVC	3	160

PZ T4 Lead Zirconate – titanate, $Pb(ZrTi)O_3$

Suppose we want to make a capacitor with a capacitance, *C*, of $1\mu F$ working at an *rms* voltage of 50 volt at 1 MHz with a dielectric of thickness, *d*, of $50\ \mu m$. The electric field is therefore 1 MV/m and if we choose polycarbonate as the dielectric its area can be found from

$$C = \frac{A\epsilon}{d} \text{ with } \epsilon = 3.1\epsilon_0$$

$$A = \frac{Cd}{\epsilon} = \frac{Cd}{3.1\,\epsilon_0}$$

$$= \frac{1 \times 10^{-6} \times 50 \times 10^{-6}}{8.85 \times 10^{-12} \times 3.1}$$

i.e., $A = 1.8\ m^2$

Now the volume of the *polycarbonate* ($A \times d$) is $9 \times 10^{-5}\ m^3$. Use Eqn. Q 8.6.9 to calculate power loss.

i.e., $$W_v = \omega E^2 \epsilon' \tan\delta$$

$$= 2\pi \times 10^6 \times 10^{12} \times 3.1 \times 8.85 \times 10^{-12} \times 10 \times 10^{-4}$$

$$W_v = 172\ kW$$

Power dissipation, W_v × volume of the dielectric

$$P = 172 \times 10^3 \times 9 \times 10^{-5}$$

$$P = 15 \text{ watt}$$

Repeating the calculation using *PZT* 4 leads to a volume of 2.8×10^{-7} m^3 and a power dissipation of 62 *W*. The power dissipation is proportional only to $\tan\delta$, as the product of capacitor volume and power loss per unit volume is independent of $\in$. *PZT*4 is therefore useless for high frequency capacitors, while polycarbonate will just do at 1 MHz. Polystyrene would be a better choice.

Dielectric Breakdown

The breakdown of dielectrics in high fields is bedevilled by particular circumstances rather than being illuminated by general scientific principles-though these have their place-because breakdown often accompanies a flow in the material rather than being dependent on its inherent properties. Three types of dielectric breakdown are distinguishable.

- Intrinsic
- Thermal
- Discharge

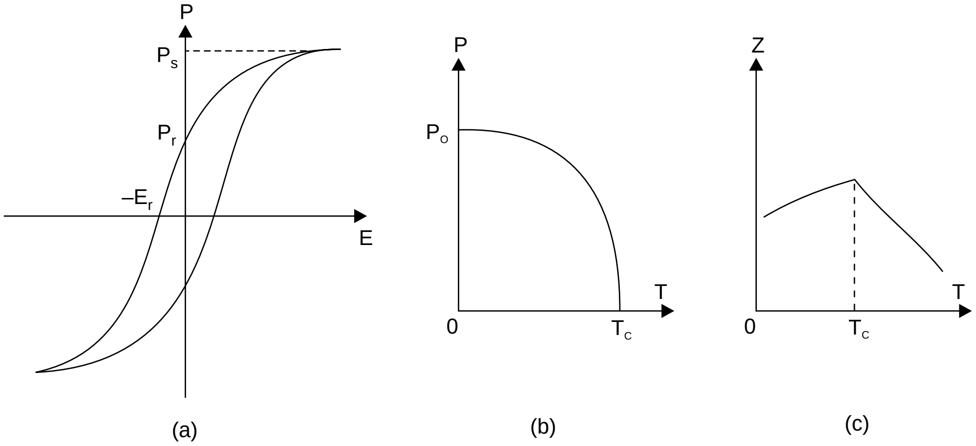
Intrinsic breakdown: It is caused by the acceleration of free electrons in high fields which can ionize other atoms to cause an *avalanche effect*. The original electron must acquire roughly the band-gap energy in order to promote electrons from valence band to conduction band. Now the electron has to gain energy between collisions, so that if its mean free path l_m, this energy is $E\,e\,l_m$, while the energy required is $e\,E_g$, where E_g is the band gap in *eV*. Equating the two energies, gives $E = \dfrac{E_g}{l_m}$. Now E_g will be about 5 *eV*, while l_m = 50 nm, giving the intrinsic breakdown field as 100 MV/m. In some cases, such as amorphous silicon nitride films, where l_m is small, this figure can be exceeded by a factor of five, giving intrinsic breakdown fields as high as 500 MV/m or $500\ \text{V}/\mu\text{m}$. Breakdown fields of this magnitude cannot be achieved in practical components because of imperfections in the dielectric.

Thermal breakdown: This occurs when $\tan\delta$ losses cause heating which lowers the breakdown field. Each dielectric will have a temperature limit which cannot be exceeded without risking thermal break down.

Discharge breakdown: This occurs when the gas is small pockets in the dielectric becomes ionized by the field. The gaseous ions are accelerated by the field and impact the side of the cavity causing damage and more ionization. Because gases are more readily ionized than solids, voids in dielectrics must be avoided at all costs. In high-voltage power cables the problem can be reduced by permeating the insulation with a difficult-to-ionize, high pressure gas.

Q 8.7 Describe the behaviour of ferroelectric materials bringing out their important uses.

Answer: A *ferroelectric material* possesses a *spontaneous polarization* which can be aligned by an external field. Hysteresis occurs so that a *P* – *E* loop may be drawn for a ferroelectric as in Fig. Q 8.7.1*a*, exactly like the *M* – *H* loop of a ferromagnet. The spontaneous polarization – temperature graph is like a ferromagnet's one [Fig. Q 8.7.1b] and the spontaneous polarization vanishes at the Curie temperature also, above which the material is said to be *paraelectric* [Fig. Q 8.7.1c]. These are two classes of ferroelectric; the order – disorder type involving the movement of hydrogen atoms, for example KH_2PO_4, and the displacive type such as the *perovskites*, typified by $BaTiO_3$. Only the latter will be discussed as they are by far the most important. These materials or derivatives from them have been found to be superconductive at extraordinarily high temperatures.



(a) (b) (c)

Fig. Q 8.7.1 *(a) Polarization against E for a ferroelectric (b) spontaneous polarization against T for a ferroelectric (c) electric susceptibility against T for a ferroelectric*

Perovskite is a mineral with the formula $CaTiO_3$, whose structure is shown in Fig. Q 8.7.2. Essentially the structure consists of a close-packed anion lattice in which every fourth anion is replaced by a divalent cation (the face centres in Fig. Q 8.7.2), with a quadravalent cation in the octahedral site at the centre of the unit cell. The first important *perovskite ferroelectric* was $BaTiO_3$, but its relatively low curie temperature (400 K) led to the development of superior materials, especially $Pb(Zr,Ti)O_3$, which has T_c = 650 K. The magnitude of the ionic displacements in the unit cell can be calculated from the saturation polarization, P_s (which is the dipole moment/m^3). The unit cell of $BaTiO_3$ is cubic above the curie temperature and the lattice parameter is about 0.4 nm. At 300 K the saturation polarization is 0.26 C/m^2, so the dipole moment per unit cell, μ_m, is $0.2 \times (4 \times 10^{-10})^3$, which is 1.7×10^{-29} C m. The charge on the Ti^{4+} and Ba^{2+} ions is 6*e* (= 9.6×10^{-19} coulomb) per unit cell, so their displacement with respect to the O^{2-} ions, $d\left(=\dfrac{\mu_m}{q}\right)$ must be $\dfrac{1.7 \times 10^{-29}}{9.6 \times 10^{-19}}$, or 1.8×10^{-11}m (0.018 nm). This displacement causes the structure to become tetragonal below T_c though the axial ratio is close to unity.

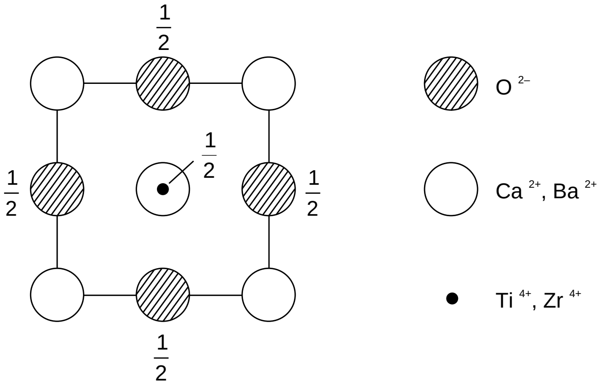


Fig. Q 8.7.2 *The Perovskite unit cell*

The Catastrophe Theory

Displacive ferroelectircs can be interpreted in terms of a polarization catastrophe in which the local field produced by the displacement of the ions is larger than the *restoring forces*, so that displacement, and hence the polarization, tends to infinity. The non-linearity of the restoring forces results in a finite, though very large polarization. While deriving the Clausius-Mosotti equation, we found that

$$\in_r = \frac{(1+2\beta)}{(1-\beta)}$$

where $\beta = \frac{\alpha N}{3\in_0}$, the sum of the contribution of all the ions in the structure to the polarization. Thus when $\beta = 1$, the relative permittivity becomes infinite. Since the derivation of Eqn. (Q 8.5.1*a*) relies on an isotropic or cubic, ionic environment, the structural distortion as β approaches unity restricts the value of $\in_r$. Nevertheless, the relative permittivity reaches extraordinarily high values (over 10000) is some perovaskites.

It may be shown that in the *paraelectic state* ($T > T_c$), the relative permittivity is given by

$$\in_r = \frac{1}{\gamma(T - T_c)}$$

where γ -is the *coefficient of linear thermal expansion*. Thus the susceptibility sufferes a rapid fall just above the curie temperature as in Fig. Q 8.7.1c.

Uses and Applications of Ferroelectric Materials

Ferroelectrics, some what surprisingly, find wide use as sound transducers (1 kHz to 10 MHz, for both sonar and ultrasonic applications), accelerometers, delay lines, positional transducers, strain gauges, in spark ignition (domestic gas appliances) and pressure gauges, besides the more obvious application as a capacitor material. Most of these applications are the consequence of their large electrosctrictive coefficients.

When an electric field is applied to an electrostrictive material it contracts or expands, depending on the sign of the coefficient, along the polarization direction. The polarity of the field is immaterial, unlike a piezoelectric material such as quartz (once used in sound transducers, until superseded by magnetostrictive nickel transducers and then by ferroelectrics). Thus, if an alternating field is applied to an electrostrictor, it responds well, there is frequency-doubling, which can be removed by applying a bias field. The advantage of ferroelectric materials lies in the possibility of their having a built-in biasing field, which can be produced by a process called *poling*. The ceramics is heated to a little below T_c and large field (1 – 5 *MV*/*m*) is applied for a few minutes. The ferroelectric then has a *remanent polarization* which can only be destroyed by heating near T_c or employing fields in excess of the *coercive field* (about 1 *MV*/*m*). After poling, the *ferroelectric material* behaves just like a *piezoelectric material,* though strictly it is a polarized, electrostrictive material.

Ferroelectric materials are also good *pyroelectic materials*. The *pyroelectric coefficient* is defined by

$$\lambda = \frac{dP}{dt}$$

A change in temperature of the material causes a change in polarization and hence a change in *surface charge*. In a good material, such as barium niobate, $\lambda = 3 \times 10^{-3}$ C/m^2/K, and as a charge of 10^{-6}C is detectable, it can be seen that *pyroelectric* devices can register temperature changes of the order of $1\mu\text{K}$. Extensive use is made of this in military hardware responding to infrared radiation (heat). *Thermal–imaging* devices are also made from pyroelectic materials.

Q 8.8 Discuss the dependence of permittivity of dielectrics on different well known factors.

Answer: *Dependence of permittivity on frequency*: As we know from the theory of polarization that time of setting of electronic polarization and ionic polarization is very little in comparison with the time of variation of the sign of voltage that is one half period of alternating voltage even for the highest frequency which are used practically in electrical and communication engineering. Therefore the polarization of dielectrics having only deformational mechanism of polarization is completely set for the time, which is very little in comparison with half period of voltage and permittivity will be independent of frequency. We may say that neutral dielectrics have the permittivity independent of frequency with in a very wide range of frequency see Fig. Q 8.8.1.

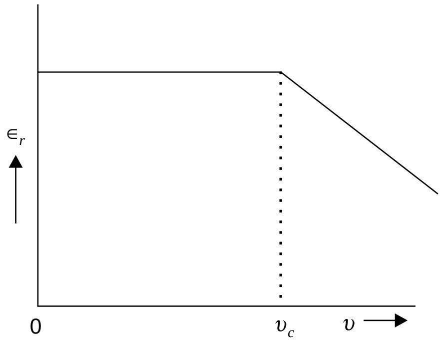


Fig. Q 8.8.1 *Frequency dependence of permittivity*

The case is somewhat different with dipole polarization. If we increase the frequency of *a. c* voltage the permittivity of a dipole material at first is constant but decreases with the increase of frequency starting from critical frequency υ_c, when the polarization already does not have time completely set for one half period. The critical frequency υ_c is given by the relation,

$$\upsilon_c = \frac{k_B T}{8\pi f R^3}; \frac{1}{2\tau_0} = \frac{k_B T}{8\pi f R^3}$$

i.e., $\tau_0 = \dfrac{4\pi f R^3}{k_B T} = \dfrac{3 f V}{k_B T}$ where f = restoring force constant and V = molecule volume. The phenomenon of dependence of permittivity on frequency is called some times '*dispersion of permittivity*' which is analogous to the dispersion of light. τ_0 is time of relaxation and R is the radius of the molecule.

Dependence of permittivity on temperature: Temperature does not affect the electronic polarization. Hence electronic polarization in separate molecules is independent of temperature. But thanks to thermal expansion of the material, the quantity of molecules which can be polarized per unit of dielectric volume decreases if temperature increases and therefore the value of $\in$ decreases. If liquids are heated they will form gas and $\in$ will be nearer to unity. Solid ionic dielectrics have different dependence of permittivity on temperature. Generally ionic polarization increases the permittivity, like *inorganic glasses* and in *ceramic materials*. Permittivity decreases with increase of temperature for ruitle (TiO_3) and *perovskite* ($CaTiO_3$).

In *polar dielectrics* in the range of low temperatures, molecular orientation is impossible in majority of cases. With the increase of temperatures at high value, dipole orientation is possible that rises permittivity, but further rise of temperatures reduces their orientation and after a peak value of $\in$, it will be down.

Let us assume that $T_{(c\in)}$ as *temperature coefficient of permittivity*

Thus
$$\boxed{T_{(c\in)} = \frac{1}{\in}\frac{d\in}{dT}} \tag{Q 8.8.1}$$

If $T_{(c\in)}$ is *temperature coefficient of capacity*, then

$$\boxed{T_{(ce)} = \frac{1}{C}\frac{dC}{dT}} \tag{Q 8.8.2}$$

and
$$\boxed{T_{(c\rho)} = \frac{1}{\rho}\frac{d\rho}{dT}} \tag{Q 8.8.3}$$

where $T_{(c\rho)}$ is *temperature coefficient of resistivity*. Similarly the temperature coefficient of linear expansion,

$$T_{(cL)} = \frac{1}{L}\frac{dL}{dT}$$

Now
$$T_{(c\in)} = T_{(c\in)} + T_{(cL)} = T_{(c\in)} + \alpha_L$$

and
$$T_{(c\in)} = \frac{1}{\in}\frac{d\in}{dT} = \frac{1}{\in}\frac{(\in_2 - \in_1)}{(T_2 - T_1)}$$

Hence
$$\frac{d\in}{dT} = \frac{(\in_2 - \in_1)}{(T_2 - T_1)}$$

For highly *polar liquids* the temperature coefficient of permittivity is given by

$$T_{(c\in)} = \frac{1}{T}$$

Dependence of permittivity on pressure: In certain dielectrics the permittivity increases with increase of pressure. For the case of gases we have

$$\in = 1 + AP$$

where A is a constant and P is pressure.

Thus $\frac{d\in}{dP} = A$ and hence $\frac{(\in - 1)}{P} = \frac{d\in}{dP}$.

In non-polar gases the permittivity increases linerarly with the increase of pressure

$$P_{(c\in)} = \frac{1}{\in}\frac{d\in}{dP}$$

Thus $$P_{(c\in)} = \frac{(\in - 1)}{P\in}$$

For the normal conditions of pressure, temperature and humidity, permittivity of air is:

$$\in_{air} = 1.00053$$

and $$P_{(c\in)} = 0.00058 \text{ /atmosphere}$$

For pressures the variation of permittivity is given by *A. R. Volpert's formula*

$\in = 1 + (688 - 93\ \mathrm{H}) \times 10^{-6}$ (summer seasons)

$\in = 1 + (648 - 81\ \mathrm{H}) \times 10^{-6}$ (winter seasons)

H = sea level of H km

Dependence of permittivity on humidity: Hygroscopic dielectrics have higher permittivity. At any rate as we are considering dielectric permittivity which is smaller than water. The permittivity grows considerably with humidification, and

1. Resistivity decreases
2. Losses increases
3. Electric strength is lowered

However in a great majority of important cases, it is difficult to calculate the value of permittivity of humidified dielectric. Water has permittivity of about, $\in_r = 80$ greater than other materials.

Dependence of permittivity on voltage: Clearly expressed dependence of permittivity upon voltage applied to dielectrics is the character of ferroelectrics. For linear dielectrics the permittivity is independent of voltage.

For polar dielectric is especially liquids and gases one may expect effect of saturation. For example, water, the ratio is

$$\frac{\Delta\in}{\in} = 0.0011$$

$$\Delta\in = \in \times 0.0011$$

Due to saturation the dielectric constant falls down. In some cases effect of saturation may increase permittivity called the positive effect by B. Piekara, and permittivity increases in strong fields.

TABLES

Table 8.A *Dipole moment of some selected molecules*

Molecule	*Dipole moment (Debye unit)*	*Molecule*	*Dipole moment (Debye unit)*
NO	0.1	CO_2	0
HCl	1.04	CS_2	0
CO	0.11	H_2O	1.84
HBr	0.79	H_2S	0.93
HI	0.38	CH_4	0
NO_2	0.40	CH_2Cl	1.15

Table 8.B *Dielectric constant of gas molecules at 0 °C*

Gas	$(\in_r - 1) \times 10^3$	*Dipole moment (Debye unit)*	*Gas*	$(\in_r - 1) \times 10^3$	*Dipole moment (Debye unit)*
He	0.071	0	C_2H_4	1.38	0
H_2	0.270	0	CO	0.692	0.10
O_2	0.531	0	N_2O	1.08	0.17
N_2	0.588	0	NH_2	8.34	1.45
CO_2	0.998	0	SO_2	9.93	1.50
CH_2	0.948	0			

Table 8.C *Properties of some widely used dielectrics*

Material	*Dielectric constant* $\in_r$	*Dielectric strength (kV / mm)*	*Density* (kg / m^3)	*Resistivity (ohm metre)*
Glass	4 – 10	20 – 32	2200 – 4000	$10^{13} - 10^{16}$
Mica	4 – 5.6	60 – 125	2500 – 2700	$10^{14} - 10^{19}$
Asbestos	–	2	2300 – 2600	2×10^7
Bakelite	4 – 4.5	10 – 40	1.2	–
Ebonite	4 – 4.6	25	1.3	1×10^{20}
Polystyrene	2.2 – 2.8	25 – 50	1.05 – 1.65	$5 \times 10^{13} - 5 \times 10^{19}$
Polyvinyl chloride (PVC) (resin)	3.1 – 3.5	50	1.38	–
Rubber (soft)	2.6 – 3.0	15 – 25	1.7 – 2.9	4×10^{15}

Table 8.D *Insulating materials for different applications*

Application	*Insulating material used*
Heating element of an oven	Nichrome
Fuse holder	Porcelain
Switch for domestic purpose	Bakelite
Commutator	Mica
Cable joint box	Bitumen compound
Electric iron	Mica
Low voltage cable	Rubber
Flexible wire	Plastic
Distribution board	Wood
Laminated insulating boards	Epoxy Resins

Table 8.E *Relative permittivity of some selected substances*

Dielectric	$\in_r$
Vacuum / Air	1 (by definition) 1.0006
Benzene	2.284
Glass	5–10
Paraffin	2.2
ice at – 5°C	2.9
Quartz	3.8
Bakelite	5
Mica	3–6
Marble	10–15
Porcelain	5.6
Polyethylene	2.25
Polyvinyl chloride (PVC)	6
Epoxy resign	3.5–11
Water	81
Calcite	6.1
Bee wax	2.7
Barium titanate	1200
Transformer oil	2.2
Viscous Vaseline	2.4
Polystyrene	2.6
Toluene	2.39

Table 8.F *Physical properties of important dielectrics*

Material	*Dielectric constant*	*Dielectric strength (kV/mm)*	*Maximum working temperature °C*	*Density kg/m³*	*Thermal conductivity (milli watt/m K)*	Tan δ
Air	1	3	–	1.4	0.25	–
Alcohol	2.6	–	–	794	180	–
Asbestos	2	2	400	3000	80	–
Paraffin wax	2.2	12	35	882	270	0.0003
Dry paper	2.2	5	90	822	132	0.007
(Impregnated paper)	3.2	15	90	1100	142	0.060
Porcelain	5.7	15	1000	2400	1000	0.008
Mica	6	40	750	2880	600	0.02
Quartz fused	3.5	13	1000	2200	1200	0.002
Ebonite	2.8	50	80	1402	155	0.005
Rubber (vulcanized)	4	10	70	1520	260	0.01
Flint glass	6.6	6	–	4555	1100	–
Grown glass	4.8	6	–	2200	602	0.02
Resin	3.0	–	–	1100	–	–

Table 8.G *Properties of some ferroelectric materials*

Material	*Chemical formula*	*Curie temperature °C*	*Spontaneous polarization in 10^{-2} C/m²*
Rochelle salt	$NaKC_4H_4O_4 . 4H_2O$	Upper + 23 lower – 18	0.25
KDP (dihydrogen phosphate)	KH_2PO_4	–150	4.95
Barium titanate	$BaTiO_3$	+ 120	26.0
Trighylene sulphate	$(NH_2CH_2COOH_2). H_2SO_4$	+ 4	2.8
Sodium nitrate	$NaNO_2$	+ 160	7.0

Table 8.H $\in_r$ *and* $\tan\delta$ *of some dielectrics at 300 K*

Material	$\in_r$	$\tan\delta$
Alumina	10	$(5-20)\times 10^{-4}$
Porcelain	5	75×10^{-4}

Contd

Material	$\in_r$	$\tan\delta$ *in* 10^{-4}
Silica (Quartz)	3.8	2
Mica	5.4	3
$BaTiO_3$	500	150
PZT	1000	40
Nylon	3.1	220
Perspex	2.6	145
Polyethylene	2.3	2
Polystyrene	2.6	0.8
PTFE	2.1	2.0
Polycarbonate	3.1	10
PVC	3	162

Table 8.1 *Dielectric properties of* $Ba\,Ti\,O_3$

Temperature	*Permittivity,* $\in_r$ *at 1.5 MHz*	*Frequency*	*Permittivity* $\in_r$	*Temperature °C*	$\tan\delta$
20 °C	400	1000 Hz	1500	0	0.24
60 °C	500	1 Hz	1490	40	0.20
100 °C	600	10^7 Hz	1375	80	0.16
115 °C	2000	10^9 Hz	1000	120	0.06
120 °C (Curie point)	4900	10^{11} Hz	200	160	0.04
140 °C	2800				
145 °C	2000				
180 °C	1500				

OBJECTIVE QUESTIONS

1. The function of a dielectric material is to obstruct the flow of electric current while the function of an insulating material is to store electric energy.
   (a) true (b) false
2. The electronic polarizability, at moderate temperature is
   (a) linearly depending on absolute temperature
   (b) independent of temperature
   (c) inversely depending on temperature
   (d) linearly depending on square of temperature
3. Line integral of electric field around a closed path is zero
   (a) true (b) false

4. The induced dipole moment for unit volume is called
   (a) Debye's temperature (b) flux density
   (c) electric polarization (d) none of these
5. The high value of the dielectric constant of water indicates that water is infact a semiconductor than a dielectric
   (a) true (b) false
6. At low frequencies
   (a) a crystal is unpolarized (b) the crystal is less polarizable
   (c) the crystal is more polarizable (d) none of these
7. The unit of dipole moment per unit volume is
   (a) coulomb (b) coulomb-metre
   (c) metre/coulomb (d) coulomb/metre^2
8. When a monoatomic gas atom is placed is a uniform electric field E, the displacement of the nucleus is proportional to
   (a) E (b) E^2 (c) $\frac{1}{E}$ (d) independent of E
9. When a monoatomic gas atom is placed in a uniform electric field E, the induced dipole moment is proportional to
   (a) R^4 (b) R^3 (c) R^2 (d) R
   where R is the radius of the atom
10. At optical frequencies, the dielectric constant is
    (a) linearly proportional to the refractive index
    (b) linearly proportional to the square of the refractive index
    (c) inversely proportional to the refractive index
    (d) inversely proportional to the square of the refractive index
11. The electronic polarizability α_e of a monoatomic gas is related to the radius as
    (a) $4\pi \in_0 R^2$ (b) $4\pi\ R^2$
    (c) $4\pi \in_0 /R$ (d) $4\pi \in_0 R^3$
12. For fixed number of atoms per unit volume, the dielectric constant of monoatomic gas is essentially independent of temperature.
    (a) true (b) false
13. The orientational polarizability per molecule in a polyatomic gas is given by
    (a) $\frac{\mu_0}{3k_B T}$ (b) $\frac{\mu_0^2}{3k_B T}$
    (c) $\frac{\mu_0}{3k_B T^2}$ (d) $\frac{3k_B T}{\mu_0}$

14. In a solid, with the external applied electric field, as the electronic polarizability α_e increases, the internal field E_i,

    (a) increases (b) reduces (c) remains unaltered

15. For given dielectric, as the temperature increases, the ionic polarizability

    (a) increases (b) decreases
    (c) remains unaltered (d) may increase or decrease with temperature

16. In a dielectric, the dipoles aligned in the absence of a field

    (a) true (b) false

17. $\frac{N\alpha}{3\in_0} = \frac{(\in_r - 1)}{(\in_r + 2)}$ is

    (a) Lorentz relation (b) Clausius-Mosotti relation
    (c) Einstein relation (d) none of these

18. Fibrous insulating materials have high hygroscopicity

    (a) true (b) false

19. Condition under which spontaneous polarization in a dielectric occurs is

    (a) $\frac{N\alpha\beta^2}{\in_0} = 1$ (b) $\frac{N\alpha^2\beta}{\in_0} = 1$
    (c) $\frac{N^2\alpha\beta}{\in_0} = 1$ (d) $\frac{N\alpha\beta}{\in_0} = 1$

20. In a ferroelectric material, as the applied field is gradually reduced to zero, the polarization still left is knows as:

    (a) coercive polarization (b) remanent polarization
    (c) zero polarization (d) positive polarization

21. The factor responsible for spontaneous polarization is

    (a) free electrons (b) atoms
    (c) permanent dipoles (d) none of these

22. The losses in a dielectric subjected to an alternating field are determined by

    (a) real part of the complex dielectric constant
    (b) imaginary part of the complex dielectric constant
    (c) both real and imaginary parts of the complex dielectric constant

23. In a dielectric power loss is proportional to

    (a) ω (b) $\frac{1}{\omega}$ (c) ω^2 (d) $\frac{1}{\omega^2}$

PROBLEMS AND SOLUTIONS

8.1 NaCl is a cube with lattice parameter 0.564 *nm* and four formula units per unit cell. The polarizabilities of Na and Cl are 0.16×10^{-40} and 3.30×10^{-40} F/m^2. Calculate the refractive index of NaCl.

Solution:

The number of formula ions per m^3 is

$$\frac{4}{\left(0.564 \times 10^{-9}\right)^3} = 2.2 \times 10^{28}/\text{m}^3$$

Now

$$\sum \alpha N = (3.3 + 0.16) \times 10^{-40} \times 2.2 \times 10^{28}$$

$$= 7.7 \times 10^{-12} \text{ F/m}$$

$$\frac{\sum \alpha N}{3 \in_0} = \frac{\in_r - 1}{\in_r + 2}$$

$$\frac{\in_r - 1}{\in_r + 2} = \frac{7.7 \times 10^{-12}}{3 \times 8.8 \times 10^{-12}} = 0.29$$

$$0.29(\in_r + 2) = (\in_r - 1)$$

$$0.29 \in_r + 0.58 = \in_r - 1$$

$$1.58 = 0.71 \in_r$$

$$\in_r = 2.23$$

But $$n = \sqrt{\in_r} = \sqrt{2.23} = 1.49$$

$$\boxed{n = 1.49}$$ ***Answer***

8.2 Determine the percentage of ionic polarizability in the sodium chloride crystal which has the optical index of refraction and the static dielectric constant 1.5 and 5.6 respectively.

Solution:

According to Clausius – Mosotti equation,

$$\frac{\in_r - 1}{\in_r + 1} = \frac{N(\alpha_e + \alpha_i)}{3 \in_0} \qquad (1)$$

At optical frequencies,

$$\frac{n^2 - 1}{n^2 + 2} = \frac{N\alpha_e}{3 \in_0} \qquad (2)$$

where n is the refractive index

Hence $$\boxed{\left[\frac{\alpha_i}{\alpha_e+\alpha_i}\right]100 = \left[1-\frac{\alpha_e}{\alpha_e+\alpha_i}\right]\times 100} \tag{3}$$

Dividing equation (2) by equation (1)

$$\left[\frac{\alpha_e}{\alpha_e+\alpha_i}\right] = \left[\frac{n^2-1}{n^2+2}\right]\left[\frac{\in_r+2}{\in_r-1}\right]$$

Now equation (3) becomes

$$\left[\frac{\alpha_i}{\alpha_e+\alpha_i}\right]100 = \left[1-\frac{(n^2-1)}{(n^2+2)}\left\{\frac{\in_r+2}{\in_r-1}\right\}\right]100$$

$$\left[1-\frac{1.25}{4.25}\left\{\frac{7.6}{4.6}\right\}\right]100 \;=51.4\ \%$$

$\boxed{51.4\%}$ ***Answer***

8.3 The polarizability of ammonia molecule is found approximately by the measurement of dielectric constant as 2.42×10^{-39} C^2 m / N and 1.74×10^{-39} C^2 m / N at 309 K and 448 K respectively. Calculate for each temperature the orientation polarizability.

Solution:

The total molecular polarizability of a polar gas is

$$\alpha = \alpha_e + \alpha_i + \alpha_0 \quad \text{where} \quad \alpha_0 = \mu_m^2/3k_B T$$

$$2.42\times 10^{-39} = \alpha_e + \alpha_i + \frac{\mu_m^2}{3\times 1.38\times 10^{-23}\times 309}$$

$$1.74\times 10^{-39} = \alpha_e + \alpha_i + \frac{\mu_m^2}{3\times 1.38\times 10^{-23}\times 448}$$

$$\frac{2.42\times 10^{-39}-(\alpha_e+\alpha_i)}{1.74\times 10^{-39}-(\alpha_e+\alpha_i)} = \frac{448}{309}$$

or $$\boxed{\alpha_e+\alpha_i \;= 0.228\times 10^{-39}\, C^2 \text{ m/N}}$$ ***Answer***

Now orientational polarizability at 309 K is $2.42 \times 10^{-39} - 0.228 \times 10^{-39} = 2.192 \times 10^{-39}$ C^2 m/N Similarly the orientational polarizability at 448 K is $1.74 \times 10^{-39} - 0.228 \times 10^{-39} = 1.512 \times 10^{-39}$ C^2 m/N

Thus $$\boxed{\begin{aligned}\alpha_0(309) &= 2.192\times10^{-39}\,C^2\text{ m/N}\\ \alpha_0(448) &= 1.512\times10^{-39}\,C^2\text{ m/N}\end{aligned}}$$ ***Answer***

8.4 Make a capacitor with a capacitance of $1\mu F$ working at *rms* voltage of 50 volt at 1 MHz with a dielectric of thickness $50\,\mu\text{m}$. The electric field therefore is 10^6 volt/*m*. Given: $\in = 3.1\in_0$ and $\tan\delta = 10^3$. Calculate power loss and dissipation.

Solution:

$$C = \frac{A\in}{d}$$

$$A = \frac{Cd}{\in} = \frac{10^{-6}\times 50\times10^{-6}}{3.1\times 8.85\times10^{-12}}$$

$$A = 1.82\,\text{m}^2$$

Volume, $v = 1.82 \times 50 \times 10^{-6} = 9.1 \times 10^{-5}\ \text{m}^3$

Power loss, $P = W = \omega E^2 \in' \tan\delta = \omega E^2 \in_0 \in_r \tan\delta$

$P = 2\pi \times 10^6 \times 10^{12} \times 8.85 \times 10^{-12} \times 3.1 \times 10^{-3}$ k watt

$$\boxed{P = 172\text{ kW}}$$ ***Answer***

Power dissipation,

$P_d = \text{P} \times v = 172 \times 9.1 \times 10^{-5} \times 10^3$ watt

$$\boxed{P_d = 15.7\text{ W}}$$ ***Answer***

8.5 If a dielectric is introduced between the plates of a parallel plate capacitor, show that the induced charge varies with the dielectric as $\in_r = \left(1 - \dfrac{\sigma^1}{\sigma}\right)^{-1}$. Also show that $\in_r \to \infty$ for a metal dielectric

Solution:

The induced charge

$$q' = q - \frac{q}{\in_r} = q\left(1 - \frac{1}{\in_r}\right)$$

$$\frac{q'}{A} = \frac{q}{A}\left(1 - \frac{1}{\in_r}\right)$$

$$\sigma' = \sigma\left(1 - \frac{1}{\in_r}\right)$$

$$\frac{\sigma'}{\sigma} = 1 - \frac{1}{\in_r};\ \frac{1}{\in_r} = 1 - \frac{\sigma'}{\sigma}$$

$$\boxed{\in_r = \left\{1 - \frac{\sigma'}{\sigma}\right\}^{-1}}$$ ***Answer***

In the metal dielectric, the induced charge is same as that of the free charge, but opposite in sign. i.e., $\sigma' = \sigma$ or $\in_r = \infty$.

8.6 What is the temperature coefficient of permittivity? How will you determine the temperature coefficient of permittivity for highly polar liquid insulating materials?

Find the temperature coefficient of permittivity of a highly polar liquid at 25°C.

Solution:

The general formula for temperature coefficient of permittivity,

$$T_{cp} = \frac{1}{\in} \frac{d\in}{dT} \tag{1}$$

Here $\in$ means $\in_r$

Clausius – Mosotti relation is

$$\frac{\in - 1}{\in + 2} = \frac{N\alpha}{3\in_0}$$

Differentiating this equation assuming that $\in$ and N are depending on temperature.

Thus

$$\frac{3}{(\in + 2)^2}\left(\frac{d\in}{dT}\right) = \frac{\alpha}{3\in_0}\left(\frac{dN}{dT}\right) \tag{2}$$

We know that

$$T_{cp} = \frac{1}{\in} \frac{d\in}{d\,T}$$

and $$\frac{1}{N}\frac{dN}{dT} = -\beta_v = -3\alpha_t$$

where α_t and β_v are the coefficient of linear expansion and volume expansion and linear expansion respectively.

Eqn. (2) can be written as

$$\frac{3\in}{(\in + 2)^2}\frac{1}{\in}\frac{d\in}{dT} = \frac{N\alpha}{3\in_0}\frac{1}{N}\frac{dN}{dT} \tag{3}$$

Here $\frac{1}{\in}\frac{d\in}{dT}$ is T_{cp}, the temperature coefficient of permittivity and $\frac{1}{N}\frac{dN}{dT} = -\beta_v$ the volume coefficient. Also $\frac{N\alpha}{3\in_0} = \frac{\in - 1}{\in + 2}$

Thus referring Eqn. (3)

$$\frac{3\in_r}{(\in_r + 2)^2} T_{cp} = \left(\frac{\in_r - 1}{\in_r + 2}\right)(-\beta_v) = 3\alpha_l \frac{(1 - \in_r)}{(2 + \in_r)}$$ with α_l is coefficient of linear expansion.

Now $$\boxed{T_{cp} = \frac{(\in_r + 2)(\in_r - 1)\alpha_l}{\in_r}}$$ ***Answer***

For highly polar liquid

$$T_{cp} = -\frac{1}{T} = -\frac{1}{25 + 273}$$

$$\boxed{T_{cp} = 0.0034}$$ ***Answer***

EXERCISE

8.1 The polarizability of NH_3 molecule in gaseous state, from the measurement of dielectric constant, is found to be 2.5×10^{-39} coulomb^2 m / N and 2×10^{-39} coulomb^2 m /N at temperatures 300 K and 400 K respectively. Calculate the contribution to the polarizability because of deformation of molecules and the contribution because of permanent dipole moment at each temperatures.

(***Ans***: 0.5×10^{-39} C^2 m / N, 1.5×10^{-39} C^2 m / N)

8.2 The dielectric constant of helium, measured at 0^0 C and at one atmosphere is 1.0000684; under these conditions the gas contains 2.7×10^{25} atom /m^3. Calculate the radius of the electron clould (atomic radius). Also calculate the displacement x when a helium atom is subjected to a field of 10^6 volt /*m* (0.0587 nm, 7.03×10^{-17}m).

8.3 The energy stored in a capacitor per unit volume is given by

$$U = \frac{1}{2}\in_0 \in_r E^2$$

where $E = \frac{V}{d}$. If the maximum permissible field is 5 MV / m, what volume of capacitor with $\in_r = 1000$ is required to store one kW? (***Ans***: 33 m^3)

8.4 Draw a graph for a ferroelectric material from the following readings obtained by J. Halbutzel.

Absolute temperature	225	270	280	290	298
Spontaneous polarization (coulomb/m^2)	0	1200	2600	2400	0

Mark on it the curie temperature

8.5 The bakelite is found to have the real part of its complex relative dielectric constant as 4.36 with a loss tangent of 2.8×10^{-2} at frequency 1 MHz. Calculate the complex polarizability of the material assuming Lorentz field Given: $N = 4 \times 10^{28}/m^3$. [***Ans***: $(3.5 - i\ 0.06) \times 10^{-40}$]

8.6 The electronic polarizability of helium is $0.18 \times 10^{-40}\ F\ m^2$. Calculate the value of the radius of electron orbit and hence the permittivity for 2.7×10^{25} atoms in one cubic metre.

(***Ans***: 5.46×10^{-11}m , 1.000057776)

9

Optoelectronics and Lasers

9.1 INTRODUCTION

KEY WORDS

dielectric constant, conductivity, reflection coefficient and absorption coefficient, optical properties, optoelectronics, light amplification, stimulated emission, discreteness/quantization, quantum electronics, optical devices, signal processing and image analyzing, quantum electronics, optical frequency amplifier, reflectors, selection rules, photonics, forbidden level, forbidden transition, spontaneous emission, induced or vibrational energy, non-radiative transition, amplification and stimulated emission, positive feed back oscillator, natural resonator frequencies, spatial and temporal coherence, High peak power, radiative transition, transmittance, host, amplification, feed back, excitation potential, resonance potential, elastic collisions and inelastic collisions, metastable state, incoherent radiation, broad spectrum, spatial coherence, temporal, population inversion, high intensity coherent radiation, spontaneous and stimulated probabilities, inversed population, negative temperature states, active system, optical pumping, pumping transition, ruby laser, Helium-neon laser, four level laser, semi conductor lasers, coherent light and laser cavity, welding, cutting directionality, line width, beam coherence, brightness, focusing, tuning, material processing.

9.1 INTRODUCTION

Here we are concerned with the propagation of electromagnetic waves into and through solids. While some solids are transparent, others are opaque. Some solid surfaces are strongly reflecting, while others tend to absorb the radiation that falls on them. These effects depend on the frequency of radiation that falls on them. This necessiates the inclusion of the whole electromagnetic spectrum for studying the response of the solid surfaces to the incident radiation.

The difference between wave propagation in free space and the propagation in the solid is expressed by the two coefficients–the *dielectric constant* $\in$ and *conductivity* σ. These in turn may be correlated with the real (n) and imaginary (n_i) parts of the refractive index. A calculation of n and n_i would lead to the determination of *reflection and absorption coefficients*. In fact, the *optical properties* are concerned with absorption, reflection, emission or anything that one can do to a solid to influence optical behaviour. Imperfect crystals contain many types of lattice defects, which trap electrons forming colour centres giving rise to electronic energy levels spaced at optical frequencies. Typical experiments that yield information about colour centres are optical absorption experiments, which tell us about the transition energies and other properties of transitions.

Q 9.1 Write a note on optoelectronics, quantum electronics and interaction of light with atoms.

***Answer*:** Optical electronics will embrace devices which convert electrical signals into optical ones and vice versa, as well as the medium of transmission. Though it can be argued convincingly that *optoelectronics* has existed in practice for some considerable time, it was the remarkable advances in materials for optical fibers-especially for telecommunications-occurring in the 1970s that led to the current wealth of activity in the field. Of course, significant developments in solid-state devices for the production and detection of light would have taken place without the advent of the near-lossless fiber, but not to the same degree. Here λ refers to the wave length of light in vacuum only. In any other medium it will be $\frac{\lambda}{n}$ where n is the refractive index (RI). Vissible light has wave length from 800 *nm* to 400 *nm*, or about an octave in frequency.

A laser is an oscillator that operates at very high frequencies range to values several orders of magnitude higher than that can be achieved by the conventional approaches of *solid-state electronics* or *electron tube technology*. In common with electronic circuit oscillators, a laser is constructed from an amplifier with an appropriate amount of positive feed back. The acronym LASER, which stands for *light amplification by stimulated emission* of radiation, is in reality therefore a slight misnomer.

It is essential to consider the fundamental process whereby amplification at optical properties is obtained. These processes involve the fundamental atomic nature of matter. At the atomic level, matter is not a continuum, it is composed of discrete particles-atoms, molecules or ions. These particles have energies that can have only certain discrete values. This *discreteness* or *quantization*, of energy is intimately connected with the duality that exists in nature. Light some times behaves as if it were a wave and in other circumstances it behaves as if it were composed of particles. These particles, called photons, carry the discrete packets of energy associated with the wave. For light of wave frequency υ the energy of each photon is $h\upsilon$. At the microscopic level the amplification of light within a laser involves the emission of these quanta. Thus the term *quantum electronics* is often used to describe the branch of science that has grown from the development of the maser in 1954 and the laser in 1960.

The wide spread practical use of lasers and *optical devices* in applications such as communications, and increasingly in areas such as *signal processing* and *image analyzing* has lead to the use of the term *photonics*. Whereas, electronics uses electrons in various devices to perform analog and digital functions, photonics aims to replace the electrons with photons. Because photons have zero mass, do not interact with each other to any significant extent, and travel at the speed of light, photonic devices promise small size and high speed.

In *conventional electronics*, where by the word conventional for the present proposes we mean frequencies where solid-state devices such as *transistors* or *diodes* will operate, say below 10^{11} Hz, an oscillator is conveniently constructed by applying an appropriate amount of positive feedback to an amplifier.

A laser (or maser) is an optical (microwave) frequency oscillator constructed from an *optical (microwave) frequency amplifier* with positive feedback. Light waves which become amplified on traversing the amplifier are returned through the amplifier by the *reflectors* and grow in intensity, but this intensity growth does not continue indefinitely because the amplifier saturates. The arrangement of mirrors (and some times other components) that provides the feed back is generally referred to as the laser cavity or resonator.

When an atom absorbs a photon of light of the correct wave length, it undergoes a transition to a higher energy level. To a first approximation in many cases, we can think of one electron in the atom absorbing the photon and being excited. The electron will only absorb the photon if the photon's energy matches that of the energy difference between the initial and final electronic energy level, and if certain rules, known as *selection rules*, are obeyed. In light atoms, the electron cannot change its spin and its orbital angular momentum must change by one unit; in terms of quantum numbers $\Delta s = 0$, $\Delta l = \pm 1$. (One way of thinking about this is that the photon has zero spin and one unit of angular momentum. Conservation of spin and angular momentum then produces these rules). For a sodium atom, for example, the 3s electron can absorb one photon and go to the 3p level (there is no restriction on changes of the principal quantum number). The 3s electron will not, however, go to the 3d or 4s level. However, the spin and orbital angular momenta are not entirely independent and coupling between them allows *forbidden transition* to occur; however, the probability of an electron absorbing a photon and being excited to a *forbidden level* is much smaller than the probability of it being excited to an allowed level. Consequently spectral lines corresponding to *forbidden transitions* are less intense than those corresponding to allowed transitions.

An electron that has been excited to a higher energy level will sooner or later return to the ground state. It can do this in several ways. The electron may simply emit a photon of the correct wave length at random some time after it has been excited. This is known as *spontaneous emission*. Alternatively a second photon may come along and instead of being absorbed may induce the electron to emit. This is known as *induced or stimulated emission* and plays an important role in the action of lasers. The emitted photon in this case is in phase with and travelling in the same direction as the photon inducing the emission; the resulting beam of light is said to be coherent. Finally the atom may collide with another atom, losing energy in the process, or give energy to its surroundings in the form of *vibrational energy*. These are examples of *non-radiative transitions*. Spontaneous and stimulated emission obey the same selection rules as absorption. Non-radiative transitions have different rules. In a crystal (or of course a molecule), the atomic energy levels and the selection rules are modified.

Q 9.2 Give a clearer and more cohesive description of the requirements for laser action, working and the unique properties.

***Answer*:** Electromagnetic radiation anywhere in the spectrum from the ultraviolet region through the infrared, which includes wave lengths from roughly 0.1 to $1000\ \mu m$ plays a vital role in laser optics. The term MASER was originally coined to describe a similar device (using ammonia molecular transitions and a microwave cavity) that operates in the microwave region of the electromagnetic spectrum at say a wavelength 1.25 cm.

The key words used are *amplification and stimulated emission*. It is the ability of light to stimulate the emission of light that creates the situation in which light can be amplified. It may not be helpful to point out at this time that a very important feature of most lasers is an optical resonator, usually consisting of two precisely aligned mirrors, one of which is partially transmitting, to allow an output. This mirror arrangement provides positive feedback. So the laser is basically a *positive feedback oscillator*. As such, it is analogous to electrical positive feedback oscillators where a certain amount of the output is fed back in phase with the input, resulting in oscillation at some frequency characteristic of the circuit. In effect, the oscillator selects a frequency component from the noise always present from biasing, amplifies it, and oscillates at that frequency. The laser does essentially the same thing except that an optical oscillator can operate in many allowed modes (*natural resonator frequencies*).

Unique Properties of Laser Light

The laser is basically a light source. The radiation that it emits is not fundamentally different than any other form of electromagnetic radiation. The nature of the device, however, is such that some remarkable properties of light are realized. These unique properties, taken as a whole, are not available from any other light source to the extent that they are obtained from a laser. The unique properties referred to are

1. High monochromaticity (small wave length spread)
2. High degree of both *spatial and temporal coherence* (strong correlation in phase)
3. High brightness (primarily due to small beam divergence)
4. Capability of very low (microwatt) to very high (kilowatt) continuous power output for different types of lasers
5. *High peak power* (terawatt) and large energy (hundreds of joule) per pulse in pulsed output lasers
6. Capability of being focused to a small diffraction limited spot size (of the order of the wave length of light).

These properties are by no means independent of each other and, in fact, some may be inferred directly from others.

Requirements for Laser Action

A number of conditions must be satisfied to achieve lasing action. They are listed below:

1. Population inversion
2. Optical resonator, except in extremely high gain systems.
3. Lasing medium
4. Means of excitation
5. Host medium

The notion of a population inversion refers to a condition in which a certain ensemble of atoms or molecules is in a non equilibrium situation where more of these atoms or molecules are in some specified excited energy state (electronic or vibrational) than are in a lower energy state. These atoms or molecules undergo a transition to a lower state in which the probability of emission of a photon is extremely high, so-called *radiative transition*. The optical resonator refers to the technique for providing positive feed back into the system to produce oscillation. This process usually consists of two parallel mirrors placed some distance apart; one is as nearly totally reflecting as possible and the other is partially transmitting to obtain a useful output from the system. The *transmittance* of the output mirror, which is the ratio of transmitted power to incident power, ranges roughly from 1 to 60%, depending on the power level and type of laser. The lasing medium (called the *lasant*) refers to the atoms or molecules that actually emit the light, such as Ne atoms in a He–Ne laser or Cr^{3+} ions is a ruby laser.

Some means of excitation is required to achieve the population inversion. This step is usually accomplished by the electric discharge or high intensity light from gas–discharge lamps, such as xenon or krypton gas–discharge lamps. Many other important techniques for excitation exist, such as chemical reaction, electron beam preionisation and nuclear. A host medium is one in which the lasant is dispersed. In the ruby laser Al_2O_3 is the *host* and serves a matrix to hold the Cr^{+3} ions. Helium is the host in the He–Ne laser and is essential to the process of exciting the lasant, Ne. Some laser types have no host; examples are the semiconductor diode laser and ion lasers like argon and krypton.

How the Laser Works

All laser action begins with the establishment of a population inversion by the excitation process. Photons are spontaneously emitted in all directions. Photons travelling through the active medium can stimulate excited atoms or molecules to undergo radiative transitions when the photons pass near the atoms or molecules. This factor in itself is unimportant except that the stimulated and stimulating photons are in phase, travel in the same direction, and have the same polarization. This phenomenon provides for the possibility of *gain* or *amplification*. Only those photons travelling nearly parallel to the axis of the resonator will pass through a substantial portion of the active medium. A percentage of these photons will be *fed back* (reflected) into the active region, thus ensuring a large build of stimulated radiation, much more than the spontaneous radiation a the same frequency. Lasing will continue as long as the population inversion is maintained above some *threshold level*.

Q 9.3 Discuss spontaneous and stimulated (induced) emission with suitable transition figures.

***Answer*:** An atom has a number of quantized energy states characterized by integral numbers. Electromagnetic radiation can interact with atomic energy levels in three different ways. There are two methods to excite an atom. The first method is the collision of the atom with certain energetic particles. During this process part of the kinetic energy of the incident particle is absorbed by the atom. The atom excited by this method will return to its ground state in 10^{-8}s with the emission of a photon. The energy in electron volt necessary to raise an atom from its normal state to the excited is called *excitation potential* for the state.

However the excitation process differs when an atom absorbs a photon of energy equal to the energy required to raise the atom to higher energy level called *resonance potential*. It is also a well known fact that discrete amounts of energy are required to excite the atom to its different quantized states. The existence of discrete energy states within an atom was confirmed by experiments of Franck, Hertz and others on critical potentials. The critical potential is defined as the accelerating potential:

(i) Below which the colliding electron cannot excite the atom. i.e., the internal energy of the atom remains unchanged. Such collisions of the electrons with atoms are called *elastic collisions*.

(ii) Above which the colliding electron can excite or even ionize the atom. i.e., the atom suffers change in its internal energy. Such collisions of the electrons with atoms are called *inelastic collision*.

Spontaneous and Stimulated Emission

We know that light is absorbed or emitted by particles (atoms, molecules or ions) during their transition from one energy state to another. The process of particle transfer from normal state corresponding to minimum energy of the system to a higher energy state is termed as excitation and the particle itself is excited as shown in Fig. Q 9.3.1. In this process the absorption of energy from the external field takes place. Usually the number of excited particles in a system is smaller than the non-excited particles. The time during which the particle can exist in the ground state is unlimited. On the other hand, the particle can remain in the excited state for a limited time known as *life time*. The life time of the excited atom is of the order of 10^{-8}s. However, there exist such excited states in which the life time is greater than 10^{-8}s. The states are called *metastable state*. The two points to be considered are:

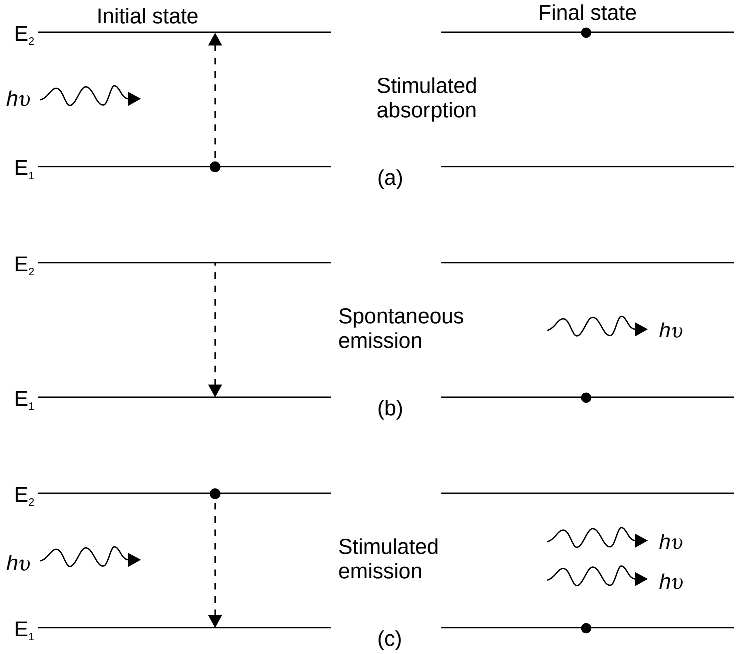


Fig. Q 9.3.1 *Excitation and emission of a particle*

(1) only certain transition are possible which are allowed by selection rules (2) the transition of a particle from one energy to another can be non-radiative. In such cases the energy is transmitted to other particles which is converted into heat now.

After being in the excited state, the particle returns to the ground state. The probability of transition to the ground state with emission of radiation is made up of two factors, one constant and the other variable. The constant factor of probability is knows as *spontaneous emission*. Fig. Q 9.3.1 (b). In this process a particle passes from higher energy state to lower energy state spontaneously emitting a photon $h\upsilon$. The spontaneous emission depends on the type of the particle and type of transition but is independent of outside circumstances. The spontaneous emission is random in character. The radiation in this case is a random mixture of quanta having various wave lengths. The waves coincide neither in wavelength nor in phase. Thus the radiative is *incoherent* and has a *broad spectrum*.

We should also know that the variable factor of probability of transition from a higher to a lower energy state with emission of radiation depends on the presence of the radiation of the same frequency. This implies that a particle can pass from an excited state to a normal state emitting a light photon not only spontaneously but also when forced to it, under the effect of another external quantum photon. This means that the incidence of a radiation on the particle which is in excited state, stimulates the emission of a similar radiation by the particle by transition to lower energy state. This type of emission is called stimulated emission as shown in Fig. Q 9.3.1 (c). The remarkable feature of the stimulated emission is that it is coherent with the stimulated incident radiation. Amazingly enough this stimulated photon has exactly the same frequency, direction and polarization as the primary incident photon (*spatial coherence*) and exactly the same phase and speed (*temporal coherence*).

Both of these photons may now be considered primary waves and, upon passing close to other atoms in their metastable states, they stimulate them to emit photons in the same direction with the same phase. However, transitions from the ground state to the excited state can also be stimulated, thereby absorbing the primary wave. An excess of stimulated emission, therefore, requires a *population inversion.* This means more atoms in the metastable state than the ground state. Thus if the conditions in the laser material are right, a chain reaction can be developed, resulting in *high-intensity coherent radiation.*

Spontaneous and Stimulated Emission Probabilities

Let us consider an assembly of atoms in thermal equilibrium at temperature T with radiation of frequency υ and energy density $E(\upsilon)$. This energy density indicates the total energy in the radiation field per unit volume and per unit frequency due to photons with energy $h\upsilon$, i.e., energy difference between excited and unexcited states. Let N_1 and N_2 be the number of atoms in the lower energy state 1 and higher energy state 2 respectively at any instant. The probability that the number of atoms in state 1 absorb a photon and rise to state 2 per unit time is

$$\boxed{N_1 P_{12} = N_1 B_{12}\ E(\upsilon)} \tag{Q 9.3.1}$$

because the probability P_{12} is directly proportional to energy density $E(\upsilon)$. Here B_{12} is called the *Einstein's coefficient of absorption*. The probability of emission is sum of two parts, one which is independent of the radiation density and the other proportional to it. The probability that the number of atoms in state 2 that drop to state 1, either spontaneously or under stimulation, emitting a photon per unit time is

$$\boxed{N_2 P_{21} = N_2\left[A_{21} + B_{21}\ E(\upsilon)\right]} \tag{Q 9.3.2}$$

where A_{21} is the *Einstein's coefficient of spontaneous emission* and B_{21} is the *Einstein's coefficient of induced emission* and $A_{21} N_2$ is the rate of spontaneous emission and $N_2 B_{21}\ E(\upsilon)$ is the rate of stimulated emission. In thermal equilibrium, emission and absorption must balance,

i.e.,
$$N_1 B_{12} E(\upsilon) = N_2\left[A_{21} + B_{21} E(\upsilon)\right]$$

or $$E(\upsilon)\left[N_1 B_{12} - N_2 B_{21}\right] = N_2 A_{21}$$

or $$E(\upsilon) = \frac{N_2 A_{21}}{\{N_1 B_{12} - N_2 B_{21}\}}$$

i.e., $$\boxed{E(\upsilon) = \frac{(A_{21}/B_{21})}{\left\{\left(\frac{N_1}{N_2}\right)(B_{12}/B_{21})\right\} - 1}} \tag{Q 9.3.3}$$

Thermodynamically, it was proved by Einstein that the *probability of stimulated absorption* must be equal to the *probability of stimulated emission*

i.e., $$B_{12} = B_{21}$$

Thus Eqn. (Q 9.3.3) becomes

$$\boxed{E(\upsilon) = \frac{A_{21}/B_{21}}{\{(N_1/N_2) - 1\}}} \tag{Q 9.3.4}$$

The equilibrium distribution of atoms among different energy states is given by Boltzmann's law. According to this law

$$N_1 = N_2 \exp\left[\,(E_2 - E_1)/k_B T\,\right]$$

$$\boxed{\frac{N_1}{N_2} = \exp(h\upsilon/k_B T)} \tag{Q 9.3.5}$$

where E_1 and E_2 are the lower and higher energy states and k_B is the Boltzmann constant.

$$\boxed{E(\upsilon) = \frac{A_{21}/B_{21}}{\{\exp(h\upsilon/k_B T) - 1\}}} \tag{Q 9.3.6}$$

which relates energy density of photons of frequency υ in equilibrium with atoms in energy states 1 and 2 at temperature T degree kelvin. If we relate this relation with Planck's radiation law, then

$$\boxed{E(\upsilon) = \left[\frac{8\pi h\upsilon^3}{c^3}\right]\frac{1}{\{\exp(h\upsilon/k_B T) - 1\}}} \tag{Q 9.3.7}$$

Comparing this equation with (Q 9.3.6), we find that

$$\boxed{A_{21}/B_{21} = \frac{8\pi h\upsilon^3}{c^3}} \tag{Q 9.3.8}$$

where *c* is the velocity of light.

This is the relation for the ratio between the spontaneous emission and induced emission coefficients and shows that probability of spontaneous emission increases rapidly with the energy difference between the two states. It is instructive to calculate the value of the ratio of spontaneous emission and stimulated emission

namely $\dfrac{N_2 A_{21}}{N_2 B_{21} E(\upsilon)}$

Now putting $B_{12} = B_{21}$ in Eqn. (Q 9.3.3)

$$E(\upsilon) = \frac{A_{21}}{B_{21}\left\{\dfrac{N_1}{N_2} - 1\right\}}$$

or (Refer Eqn. Q 3.9.5)

$$\boxed{\frac{A_{21}}{B_{21} E(\upsilon)} = \left\{\exp\left(h\upsilon / k_B T\right) - 1\right\}} \qquad \text{(Q 9.3.8 } a\text{)}$$

Population Inversion

Usually the number of particles N_2 i.e.; population of higher energy level is less than the population N_1 of lower energy level. Making $N_2 > N_1$. i.e.; the number of particles N_2 more in higher level than the number of particles N_1 in lower energy level is called *population inversion or inversed population*. The states of system, in which the population of higher energy state is more in comparison of the population of lower energy state are called *negative temperature states*. Here it should be clearly understood that the negative temperature is not a physical quantity but it is a convenient mathematical expression, signifying the equilibrium state of the system. When the system has a number of states, then one of them may have a negative temperature with respect to other states. A system in which population inversion is achieved is called an *active system*. The method of raising a particle from lower energy states to higher energy state is called *pumping*. This can be done by a number of waves. Let us consider the pumping of ammonia gas. It has two states with separation corresponding to λ = 1.27 cm. Ammonia is first heated and then passed through a non-uniform electric field. The field deflects the excited and unexcited molecules to different regions. This causes $N_2 > N_1$ in one region. A more common method of pumping is *optical pumping*, which is discussed below:

Consider a three level system as in Fig. Q 9.3.2. Let us allow all transitions between these levels. If υ is the frequency of the external source on the system, then

$$h\upsilon = E_2 - E_1 \text{ or } \upsilon = \frac{E_2 - E_1}{h}$$

corresponding to the transition from level 1 to 3, some of the particles will pass to the level 3. If the life time of particles in level 3 is sufficiently long, their number in this level will exceed that in level 2. In this way level 3 will be inversely populated with respect to level 2. Thus by pumping, the condition $N_3 > N_2$ is obtained. Now for a light of frequency υ_{23} the system acts as laser. The stimulated radiation, together with the original incident radiation, both coherent, can stimulate the emission of more coherent radiation of other particles in the higher energy state. This process can go on, steadily amplifying as it proceeds, provided enough molecules are in higher energy state. Fig. Q 9.3.2 (b) shows that population inversion $N_2 > N_1$ is achieved. The main condition for this is that the state 2 must be a metastable state.

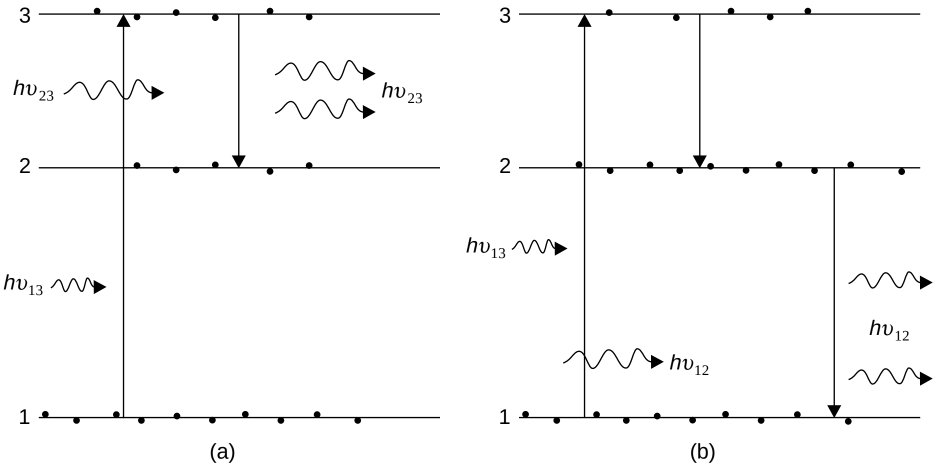


Fig. Q 9.3.2 *Energy levels in a three-level laser system*

Optical pumping rises the particles to level 3, from where most of them return to state 1 but some go to state 2. The probability of transition from state 2 to state 1 is very low, hence in due course of time N_2 exceeds N_1, if pumping power is sufficient to keep level 2 fed at faster level than depletion by $2 \to 1$ transition.

Similar to the three-level laser system, there exists a four-level laser system as shown in Fig. Q 9.3.3. Level 1 is ground level and levels 2, 3 and 4 are excited levels of the system. Atoms from level 1 are excited by a pump light to level 4, from which the atoms decay very rapidly through some non radiative transition to level 3. Level 3 is a meta stable level having a long life time (10^{-3}s). This level forms the upper laser level and level 2 forms the lower laser level. The lower laser level must have a very short life time so that the incoming atoms from level 3 relax down immediately from level 2 to level 1, ready for being pumped to level 4. If the rate of relaxation of atoms from level 2 to level 1 is faster than the rate of arrival of atoms into level 2. One can obtain population inversion between levels 3 and 2 even for very small pump powers.

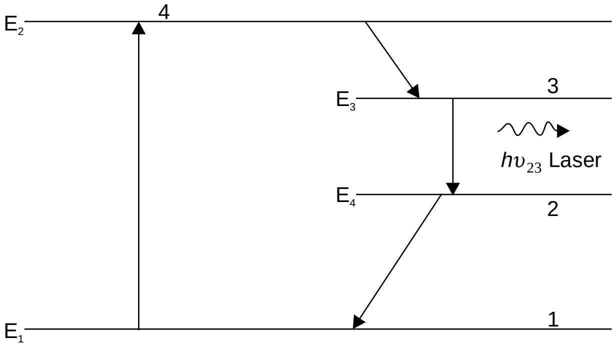


Fig. Q 9.3.3 *The energy levels in a four level laser system*

Q 9.4 Describe the construction and working of a ruby laser (three-level laser) with necessary diagrams.

***Answer*:** Laser action was first reported in ruby by Maimam in 1960, and both technique and theory have since been extensively developed. Ruby laser rods are grown from *sapphire* (Al_2O_3) doped with 0.01 to 0.05 % chromium (by weight) to form a synthetic ruby crystal coloured red or pink. Rods are up to 20 cm long 3 to 2.5 mm in diameter. Ruby resists optical damage at normal power level if its surface is clean, and conducts heat better than glass. The ends of the ruby rod are optically flat and parallel. The rod is surrounded by a glass tube. Upon the rod is wound a coiled flash lamp filled with xenon gas which acts as the optical pumping system.

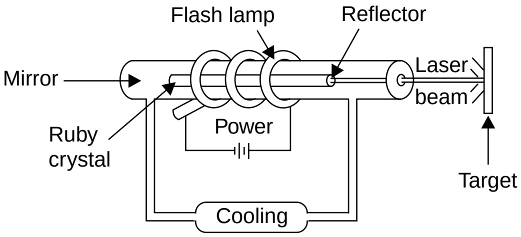


Fig. Q 9.4.1 *Sketch of ruby laser*

Working: As mentioned earlier the ruby rod is a crystal of aluminium oxide (Al_2O_3), so that some of the Al^{+++} ions are replaced by Cr^{+++} ions. These impurity chromium ions give pink colour to the ruby and give rise to the laser action. The energy-level diagram of chromium ions is shown in Fig. Q 9.4.2.

It consists of upper short-lived energy level (rather energy band) E_3 above its ground state energy level E_1, the energy difference $(E_3 - E_1) = h\upsilon$ corresponding to a wave length of 550 nm. There is an intermediate excited state level E_2 which is *metastable* (a state relatively long – lived one) having a life time of 10^{-3}s about 10^5 times greater than the life time of E_3.

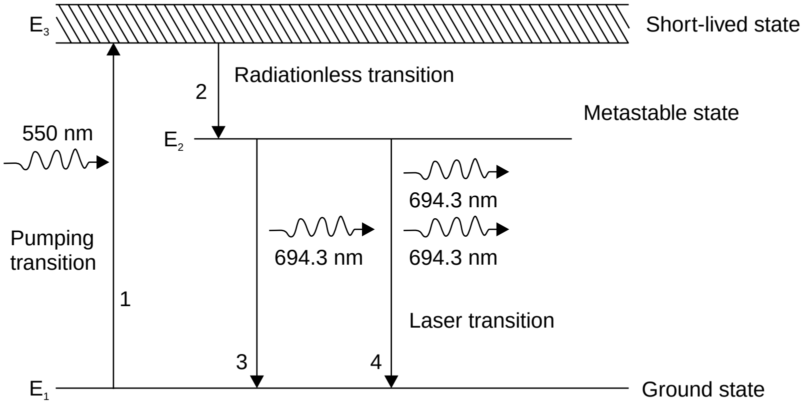


Fig. Q 9.4.2 *Energy level diagram of chromium ion*

Usually, most of the chromium ions are in the ground state E_1. When the flash of light (which lasts only for about a milli second) falls upon the *ruby rod*, the 550 nm radiation photons are absorbed by the chromium ions which are pumped (raised) to the excited state E_3. The transition 1 is the (optical) *pumping transition*. The excited ions give up, by collision, part of their energy to the crystal lattice and makes a transition or decay to the metastable state E_2. The transition from E_3 to E_2 (transition 2) is thus a radiation less transition. As the life time of the state E_2 is much longer, the number of ions in this state goes on increasing while that in the ground state E_1 goes on decreasing. By this *population inversion* is achieved between the excited metastable state E_2 and the ground state E_1.

When an excited ion passes spontaneously from the meta stable state E_2 to the ground state (transition 3), it emits a photon of wave length 694.3 nm. This photon travels through the ruby rod and, if it is moving parallel to the axis of the crystal, is reflected back and forth by the silvered ends until it stimulates an excited ion and causes it to emit a fresh photon in phase with the stimulated photon. This stimulated transition 4 is the laser transition. (The photons emitted spontaneously which do not move axially escape through the side of the crystal). The process is repeated again and again because the photons repeatedly move along the crystal being reflected from its ends. The photons thus multiply. When the photon-beam becomes sufficiently intense, part of it emerges through the partially-silvered end of the crystal. The drawbacks of the ruby laser are:

The laser requires high pumping power because the laser transition terminates at the ground state and more than one- half of the ground state atoms must be pumped up to the higher state to achieve population inversion. Moreover, ions which happens to be in their ground state absorbs the 649.3 nm photons from the beam as it builds up. The ruby laser is pulsed laser. The active medium (Cr^{+++} ions) is excited in pulses, and it emits laser light in pulses. While the xenon pulse is of several millisecond duration; the laser pulse is much shorter, less than a millisecond duration. It means enhanced instantaneous power.

Helium-Neon Laser

In gas lasers, the atoms are characterized by sharp energy levels compared with that is solids, the electric discharge method is usually employed to pump the atoms to the higher energy states. He – Ne laser was the first one to be operated successfully. It is a four level laser and population inversion is achieved by electric discharge. The laser tube is approximately 5 mm in diameter and 0.5 m long. It contains a helium-neon mixture, in the radio 5:1 at a total pressure of about 1 torr (=1mm of mercury). The ends of the tube are plane and parallel. One end of the tube is heavily silvered. The other end is partially silvered.

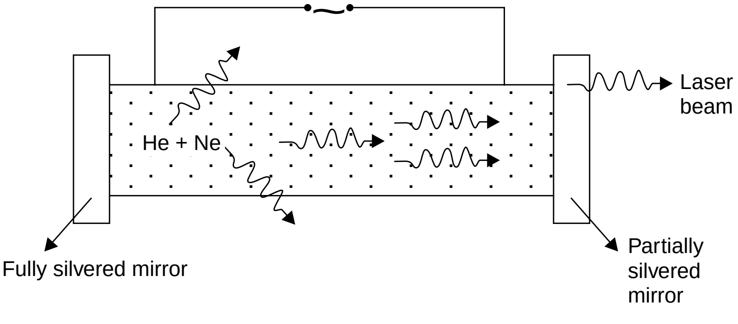


Fig. Q 9.4.3 *Helium-Neon Laser*

An electric discharge is produced in the gas mixture by electrodes connected to a high frequency electric source. The collision of the helium and neon atoms with the electrons from the discharge excite (or pump) the helium and neon atoms to metastable states. The metastable state in helium is 20.61 eV above the ground state. That in neon is 20.66 eV above the ground state. Some of the excited He atoms transfer their energy to ground state. Ne atoms by collisions, with the 0.05eV of additional energy being provided by the kinetic energy of atoms [the advantage of this collision process is that the lighter He atoms can easily be pumped up to their excited states; the much heavier neon atoms could not be raised efficiently without them]. Thus He atoms help in achieving a population inversion in the Ne atoms. When a Ne atom passes spontaneously from the metastable state at 20.66 eV to state at 18.70 eV, it emits 632.8 nm photon. This photon travels through the gas mixture, and if it is moving parallel to the axis of the tube, is reflected back and forth by the mirror ends until it stimulates an excited Ne atom and causes it to emit a fresh 632.8 nm photon in phase with the stimulating photon. This stimulated transition from 20.66 eV level to 18.70 eV level is the laser transition. This process is continued and a beam of coherent radiation builds up in the tube. When the beam becomes sufficiently intense, a portion of it escapes through the partially-silvered end.

From the 18.7 eV level the Ne atom passes down spontaneously to a lower metastable state emitting incoherent light, and finally to the ground state through collision with the tube walls. The final transition is thus radiation less. Obviously, the Ne atom in its ground state cannot absorb 632.8 nm photons from the laser beam, as happens in the three level ruby laser. Also, because the electron impacts that excite the He and Ne atoms occur all the time, unlike the pulsed excitation from the xenon flash lamp in the ruby laser; the He – Ne laser operates continuously. Further, since the laser transition does not terminate at the ground state, the power needed for excitation is less than that in a three-level laser.

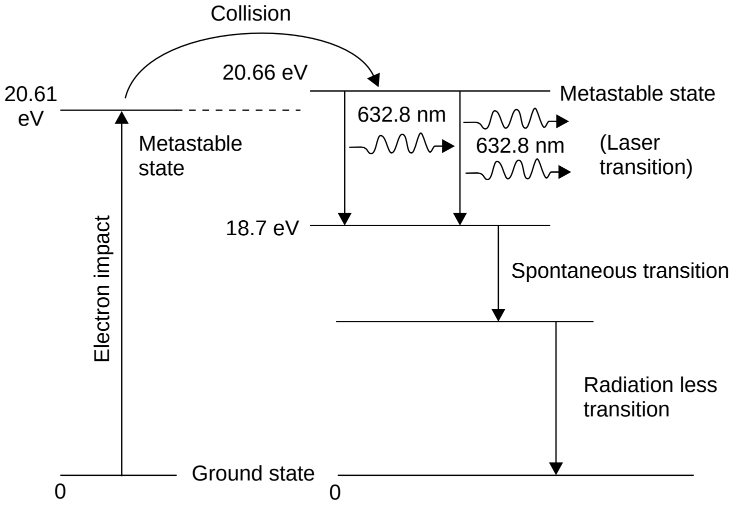


Fig. Q 9.4.4 *A four-level laser*

Semiconductor Lasers

A semiconductor laser consists of a flat junction of two pieces of semiconductors materials, each of which has been treated with a different type of impurity. On passing an electrical current through such a device, laser light emerges from the junction region. Low cost, small size and relatively high efficiency make these lasers well suited for *microelectronic adaptation*, and applications are almost unlimited in high-technological uses, for example, fiber optics communication though power output is limited. These lasers are similar in construction to a transistor or a semiconductor diode. They are usually infra red pulses with power on the order of watts and can be produced with good efficiency, especially at low temperatures, liquid nitrogen or lower. The activation mechanism can be voice or television current signal, there by producing laser beams modulated with these signals. Silicon and germanium conduct electricity better than insulators but not so well as true conductors. These semiconductor materials allow construction of complex *microelectronic circuits* by carefully controlling the composition making possible to build many useful structures to accommodate the desired use. Advances made in this field since 1975 have resulted at room temperature life time of 100 years for continuously emitting semiconductor lasers. It is now possible producing beams of high quality and low diversion angles with millions of years of useful time. Using of materials such as indium and phosphorus in addition to the standard gallium, arsenic and aluminium (which emit wave lengths $0.8 - 0.9\ \mu\text{m}$ in the infrared region), has resulted in longer wavelengths $1.1 - 1.6\ \mu\text{m}$, which increases efficiency of light transmission in optical fibers. Also being developed are shorter wave lengths, such as in the visible (red, particularly) and, even in the ultraviolet $(0.4\ \mu\text{m})$ region.

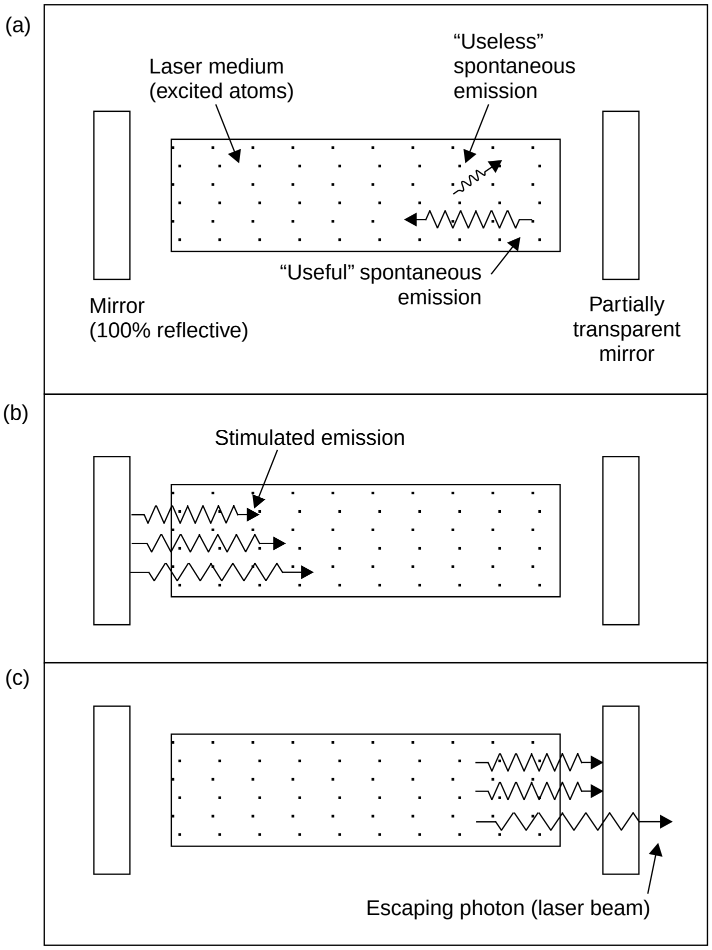


Fig. Q 9.4.5 *Diagrammatic sketch showing (a) excitation of gaseous laser medium (i.e., electrical discharge), (b) reflection of photons during stimulated emission, and (c) exiting photons in a laser beam*

Gas Lasers

Gas lasers produce *coherent light* beams by an electric discharge in the *laser cavity* or gas chamber. Several types of gas laser have gained popularity because of (a) the simplicity of the lasing function, (b) the wide variety of wave lengths available (c) they are less expensive, (d) some, for example the CO_2, are very efficient (30 %), and (e) very high power outputs are available from relatively small units. Gas lasers can be explained by the following parts: the gas cavity, excitation of the gas by electrical charge and stimulated emission of the laser light on discharge of the electric pulse. A variety of pumping methods are used in gas laser technology where by the atoms or molecules of the lasing gas are excited. In some gas mixtures, such as the most popular of all, helium – neon, the electrical discharge excites the helium atoms which transfer the energy to the neon atoms which emits red light: other gas mixtures, such as carbon dioxide, nitrogen, and argon, are energized by the CO_2 molecules absorbing the electrical energy and vibrating at high energy level. The helium – neon laser cannot produce much power, typically only a few miliwatt, but this versatile laser can emit laser continuously for many thousands of hours and has a *plethora* of uses.

The CO_2 laser can be used to produce tetra watt (10^{-7} W) in pulses of ultra short pulse widths (10^{-12} s). Amplification is possible by making multiple passes of the beam through the huge cavities developed to produce clusters of beams of several feet is diameter. Continuous beams of CO_2 lasers of high intensity are also available in such applications as *welding* or *cutting* metals. Other popular gas lasers are the argon and krypton lasers which emit in the green and red portions of the spectrum respectively. Mixed together, the resulting emissions can be controlled to provide for individual and separate wavelengths in the visible range. One application popular with this combination is in the entertainment field-light shows, movies, etc.

Q 9.5 Discuss the important properties of laser light. Also bring out some of the industrial applications of lasers.

***Answer*:**

Properties

One must know that not all of the different types of lasers exhibit the following properties to the same degree and, this may generally restrict the choice of laser for a given application.

1. *Directionality*: Apart from semiconductor junction lasers, lasers emit radiation in a highly directional, collimated beam with a low angle of divergence. This is important because it means that the energy carried by laser beam can be collected easily and focused onto a small area.
2. *Line width*: Laser beam is potentially extremely monochromatic but the spectral content of the laser radiation may extend over almost as wide a range as the florescent line width of the laser medium. In other words, although the line width of an individual cavity mode may be extremely small there may be many modes present in the laser output.
3. *Beam coherence*: One of the characteristics of stimulated emission in that the stimulated wave is in phase with the stimulating wave, i.e., *spatial* and *temporal variation* of the electric field of the two waves are the same. Thus for a perfect laser we would expect the electric field to vary with time in an identical fashion for every point on the beam cross-section.
4. *Brightness*: The primary characteristic of laser radiation is that lasers have a higher brightness than any other light source. We define brightness as the power emitted per unit area per unit solid angle.

5. *Focusing*: The minimum spot size to which a laser beam can be focused is determined by diffraction. A single mode beam can be focused into a spot which has dimensions of the order of the wavelength of the light, though the imperfections in the optical system may mean that we cannot achieve this in practice.
6. *Tuning*: Some lasers can be tuned to emit radiation over a range of wavelengths. Laser tunability leads to applications in *photochemistry*, high resolution Raman spectroscopy.

Applications

Lasers are being used in many areas because of the two special features which are not available in light from ordinary sources

(i) *Narrow band width*: Which is the same thing as high *monochromacity* or high *temporal coherence*.

(ii) *Narrow angular spread*: Which is the same thing as high directionality (hence high intensity) or large spatial coherence.

Where lasers are used?

1. *Communication*: Modulated laser beams are being used for transmitting messages. Due to high degree of coherence, the loss of transmitted energy is comparatively much less. The narrow band width of laser beam has increased the simultaneous transmission of large number of channels. In computers, the storage capacity for information similarly improves with the narrowness of the band width. In any information processing system, which uses radiation signals, the capacity to distinguish between smaller difference increases the quality of performance. Lasers provide this through high monochromaticity of their beam.
2. *Surgery*: Laser has also bean used extensively for bloodless surgery. e.g. lasers can be used to weld the detached retinas. The laser beams can be used for drilling the teeth, removal of tumors and removal of infected cells, etc. It can also be used for preventing the tooth decay by depositing hard materials on the surface of the tooth.
3. *Measurement of long distances*: It enabled us to determine the distance of the moon from the earth with an error within 0.6 m.
4. *Nuclear fusion*: The laser beams can be used to induce the nuclear fusion. By concentrating the laser beam to a very very narrow spot, temperature may rise to about 10^8 K and nuclear fussion can occur at this temperature.
5. *Scientific research*: A modified version of the Michelson Morley experiment was conducted to test for the ether drift. Here the beams of two infrared lasers of slightly different frequencies were combined by means of a beam splitter and the beam frequency was determined. Lasers can be focused into a very very fine beam, resulting in rising the temperature to about 1000 K and can be used for drilling holes and fusing or melting of metals.
6. *Weather forecasting*: Pictures of the clouds, wind movements, etc., can be obtained with laser beam and the data so obtained can be used in weather forecasting.
7. *National defence*: Lasers can be used for guiding in missiles and satellites.
8. *Other uses*: The other uses of lasers are: in holography, the production of three dimensional images, cutting of *microelectronic circuits,* cutting and sealing nerves and to raise the temperature of the localized area of tissue, i.e., physiotherapy. Laser can be used for unblocking the heart valves, breaking kidney stones, etc.

Industrial Applications

Material Processing

For mechanical and metallurgical engineers, a knowledge of laser technology relating to metal working techniques is a pre requisite. Laser can cut, drill, weld, remove metal from surfaces, and perform these operations ever at surfaces in accessible by mechanical methods. It is not necessary that users of lasers for these operations understand all the technical details of the laser system, but knowledge of the beam characteristics and material absorption qualities is essential in proper adaptation of the beam to obtain the desired result.

Cutting and Drilling

Because of CO_2 lasers, which produce $10.6\ \mu m$ wave length beam, can be manufactured with extremely high continuous wave power densities, this laser system is the most commonly used one in industrial cutting and drilling operations not only with metals but also such non metals as ceramics, plastics, cloth, paper, glass and so on. Gas jetting is usually associated with industrial metal cutting either to enhance removal with a reactive gas, such as oxygen, or with a protective (inert) gas to protect flammables. Typical metals that are efficiently cut or drilled with the CO_2 systems are steel, aluminium and titanium; cutting speeds reach rates from 20 inch per minute for one-inch carbon steel sheets to 100 inch per minute for one-half inch aluminium alloys. Laser energy supplies all the energy needed to cut or drill non-metals, but often coaxial gas sets serve to protect the treated surfaces and coaxial vacuum can be included to direct toxic fumes away from the operation.

Welding

Several advantages over gas or arc welding are possible with laser-welding techniques; (a) purity of the materials involved is not altered, (b) localized heating by the small spot size can be accurately controlled, even programmed, by computers to reproduce exact characteristics, and the laser beam can be transmitted through windows of a closed container to permit welding (or other operations) in a controlled atmosphere.

Heat Treatment

Although induction heating has served the metal processing operations for many years in providing surface treatments, for hardening steel particularly, the versatility of the laser beam has proven very useful in the treatment of many metal surfaces. Cost saving is one consideration, because less energy is required, heat losses are reduced, and the time involved is considerably lessend. Steel and aluminium surfaces can be hardened or alloyed by methods established for production line applications. A less expensive substrate can be used in some applications so that metal powder layers can be coated and then processed thermally by the laser beam is precise locations.

Astronomer's Measurements

By bouncing light from a newly developed laser off reflectors left by astronomers on the moon, astronomers have taken new measurements of the constantly changing distance between earth and moon. It is believed that the measurements made across 230000 miles of space, were accurate to within an inch, ten times more accurate than by the other methods in the past. The new measures provide detailed records of day-to-day changes in the rotation of the earth and slight wobbles it makes as it spins on its axis. They are also recording lunar motions caused by *subtle gravitational* effects arising from the influences of relativity. Analysis of the new data helped the scientists to have a better understanding of the forces deep within the earth that set off great earthquakes, as well as the variations in the earth's rotation that have been linked with the effect that causes of cyclic warm-water ocean current that is believed to cause weather anomalies.

PROBLEMS AND SOLUTIONS

9.1 Get the units of energy density $E(\upsilon)$ and Einstein's coefficients A and B.

***Answer*:** Since energy density is the energy of the radiation field per unit volume and per unit frequency, therefore, unit of energy density $E(\upsilon)$ must be J/m^3 s^{-1}. Again, the quantity $N_2 A$ represents the rate of spontaneous emission, therefore, unit of A will be s^{-1}. Also, $N_2\, B\ E(\upsilon)$ represents the rate of induced emission, therefore, unit of B is m^3 J^{-1} s^{-2}.

9.2 A laser beam has a power of 50 mW. It has an aperature of 5×10^{-3} m and wave length 700 nm. A beam is focused with the lens of focal length 0.2 m. Calculate the areal spread and intensity of the image.

***Solution*:**

$$\text{Angular spread, } d\theta = \frac{\lambda}{d} = \frac{700 \times 10^{-9}}{5 \times 10^{-3}} = 1.4 \times 10^{-4} \text{ radian}$$

$$\text{Area spread } = (d\theta \times f)^2 = \left(1.4 \times 10^{-4} \times 0.2\right)^2 = 0.4 \times 10^{-8}$$

$$\boxed{A_{sp} = 0.48 \times 10^{-8} \text{ m}^2} \ \textit{\textbf{Answer}}$$

Also

$$\text{Intensity } = \frac{power}{area} = \frac{50 \times 10^{-3}}{0.48 \times 10^{-8}} = 125 \times 10^5 \text{ watt/m}^2$$

$$\boxed{125 \times 10^5 \text{ W/m}^2} \ \textit{\textbf{Answer}}$$

9.3 A laser beam of wave length 740 *nm* has coherence time 4×10^{-5}s. Deduce the order of magnitude of its coherence length and spectral half-width.

***Solution*:**

(i) the coherence length

$$l = \tau c = 4 \times 10^{-5} \times 3 \times 10^8 = 12 \times 10^3 \text{ m}$$

$l = 12$ km ***Answer (a)***

(ii) The spectral half width

$$\Delta\lambda = \frac{\lambda^2}{l}$$

$$\Delta\lambda = (740 \times 10^{-9})^2 / 12 \times 10^3 \text{ m}$$

$\Delta\lambda = 0.45 \times 10^{-16}$ m ***Answer (b)***

(iii) The purity factor,

$$Q = \frac{\lambda}{\Delta\lambda} = \frac{740 \times 10^{-9}}{0.45 \times 10^{-16}} = 1.6 \times 10^{10}$$

$\boxed{Q = 1.6 \times 10^{10}}$ ***Answer (c)***

9.4 A laser source of wave length 6×10^{-7} m, coherence width 8×10^{-3} m and power 10 mW shines on a surface 100 m away. Deduce the illumination. Compare it with that due to a collimated beam from a torch filament of diameter 0.1 cm, lens of focal length 10 cm and power 10 W.

***Solution*:**

The semi angle of cone of laser beams,

$$\theta = \frac{\lambda}{a} = \frac{6 \times 10^{-7}}{8 \times 10^{-3}} = 7.5 \times 10^{-5} \text{ radian}$$

Solid angle, $\Delta\omega = \dfrac{\Delta s}{r^2} = \dfrac{\pi (r\theta)^2}{r^2} = \pi \theta^2$

$= \pi \times (7.5 \times 10^{-5})^2 = 176.6 \times 10^{-10}$

Areal spread, $\Delta A = r^2 (\Delta\omega) = 100^2 \times 176.6 \times 10^{-10} = 176.6 \times 10^{-6}$

Illumination,

$$I_1 = \frac{P}{\Delta A} = 10 \times \frac{10^{-3}}{176.6 \times 10^{6}} = 56.6$$

$\boxed{I_1 = 56.6 \text{ W/m}^2}$ ***Answer (a)***

For the torch, the angle subtended by the filament size at the lens

$$\theta' = \frac{0.1}{10} = 10^{-2} \text{ radian}$$

Areal spread, $\Delta A' = \pi (r\theta')^2 = 3.14 \times 100^2 \times 10^{-4} = 3.14$

Illumination,

$$I_2 = \frac{P'}{\Delta A'} = \frac{10}{3.14} = 3.2 \text{ W/m}^2$$

$$I_2 = 3.2 \text{ W/m}^2$$

$\boxed{\dfrac{I_1}{I_2} = 17.7}$ ***Answer (b)***

9.5 Calculate the ratio of spontaneous emission to stimulated emission by an incandescent bulb at 2500 K. The frequency in the optical region is 5.9×10^{14} Hz

***Solution*:**

The ratio R is

$$R = \frac{A_{21}}{B_{21} E(\upsilon)} = \left\{\exp(h\upsilon / k_B T) - 1\right\}$$

i.e., $$R = \exp\left[\frac{6.6\times10^{-34}\times5.9\times10^{14}}{1.38\times10^{-23}\times2500}\right] - 1 = \exp\left[\frac{6.6\times5.9\times10^{3}}{1.38\times2500}\right] - 1$$

$$\boxed{R = 7.9\times10^{4}}$$ ***Answer***

9.6 If a laser is pulsed for one nanosecond, and contains 40 kJ energy, do the power calculation. Also compute the intensity of the beam.

***Solution*:**

$$W = \frac{J}{s} = \frac{40000}{10^{-9}} = 40\times10^{12}\text{ watt}$$

or $$\boxed{W = 40\text{ tara watt}}$$ ***Answer***

For the simple calculation of the length of light ‘bullet’ for a 10^{-9} sec pulse, use the formula,

$$l = \frac{\text{speed of light}}{\text{time}} = \frac{3\times10^{8}}{10^{9}} = 0.3\,\text{m} = 1\text{ foot}$$

so that all the energy of that pulse would be considered in one foot of the laser radiation. If all that energy (40 kJ) could be focused on a 100 μm spot, the spot will receive (per m^2), an energy (or intensity) as

$$\text{Intensity} = \frac{\text{energy}}{\text{space area}} = \frac{40\times10^{3}}{4\pi\left(100\times10^{-6}\right)} = 5.09\times10^{12}\text{ J/m}^2$$

$$\boxed{\text{Intensity} = 5\text{ tera joule/m}^2}$$ ***Answer***

9.7 (a) What is the diffraction-limited beam divergence of a *Q*-switched *Nd*: glass laser $(\lambda = 1.06\ \mu m)$ having an output aperture d = 1” ?

***Solution*:**

The calculation would be

$$\theta_{diff} = \frac{2.44\times\lambda}{d} = \frac{2.44\times1.06\times10^{-6}}{2.54\times10^{-2}}$$

$$\theta_{diff} = 1.02\times10^{-4}\text{ radian}$$ ***Answer***

9.7 (b) What is the diffraction-limited spot-size diameter if the beam is focused by a lens of focal length, f = 1.5?

***Solution*:**

$$d_{diff} = 2.44\,\frac{f\,\lambda}{d} = 2.44\,\frac{1.5\times2.5\times10^{-2}\times1.06\times10^{-6}}{2.5\times10^{-2}}$$

$$d_{diff} = 3.9\times10^{-6}\text{ m}$$

$$\boxed{d_{diff} = 3.9\ \mu\text{m}}$$ ***Answer***

EXERCISE

9.1 In a material at 300 K two energy levels have a wave length separate of 1 μm. Compute

(i) the ratio of upper to lower level occupation densities when the material is in thermal equilibrium
(ii) the effective temperature when the levels are equally populated
(iii) the effective temperature when the upper level is twice as densely populated as the lower (Assume unit degeneracy for each level).

$$\left(\textbf{\textit{Ans}}\text{: } \frac{N_2}{N_1} = 10^{-21}, T \to \pm\infty \text{ and } T = -2100 \text{ K}\right)$$

9.2 Calculate the coherent length of He – Ne line $(1.15\ \mu m)$ if coherence time is 26.7 *ns*).

(***Ans*****:** 8 metre)

9.3 What is the critical angle for a ray in a step – index fribre for which n_1 = 1.53 and which has a cladding whose *R* 1 is 2.5 % less.

(***Ans*****:** 77.2^0)

9.4 At what temperature are the rates of spontaneous and stimulated emission equal? λ = 500 nm.

(***Ans*****:** 41532 K)

10

Miscellaneous Topics

Q 10.1 Discuss the properties of a few important insulating/dielectric materials with their special features

***Answer*:** *Gaseous insulating materials*: Air, nitrogen, hydrogen, neon and argon are some important insulating materials available in nature. Electro-negative gases such as freon and sulphur hexafluoride are also used. They are cheap and are easily available. Nonflammable and non-explosive. Air is the most commonly used dielectric and is used as insulator in the following applications:

(i) Overhead transmission lines
(ii) Air condensers
(iii) Plugs, switches and various electrical machines and apparatus

Liquid insulating materials: *Insulating liquids* are generally used as an insulating and heat transfer medium or purely dielectric purpose in order to eliminate air or other gases and there by obtaining improved dielectric strength. Generally, insulating liquids are used in conjunction with solid insulation. Broadly, the liquid insulating materials may be classified as

1. Mineral oils (petroleum oils)
2. Askarels
3. Silicon liquids
4. Fluorinated liquids
5. Synthetic Hydrocarbon Liquids
6. Organic esters
7. Vegetable oils

–20° C to 150° C is the temperature range under which the above liquids are used as insulating materials.

Mineral oils are derived from crude petroleum. After distilling off the lighter fractions (gasolin, petroleum, naptha, kerosene) in the process of crude oil distillation '*masult*', a petroleum residue is obtained, which renders various oils after further distillation. Thus mineral oil is the final product of refining a certain oil fraction. Among the important electrical insulating products derived from the crude petroleum are the insulating oils (used in cables, capacitor, transformer and switch-gear application), electrical grade *impregnating* waxes and *petroleum* and *asphaltic compounds*, varnishes and sealing compounds. The said oil in transformers is some times known as *transformer oil*.

Transformer oil: The transformer oil in the transformer has a vital role in the performance and life of the unit. Some requirements of the oil are as follows:

(i) to provide high dielectric strength
(ii) to permit good transfer of heat i.e., heat dissipating media
(iii) to be of low viscosity
(iv) to have high flash point
(v) to prevent corrosion of insulating material of the transformer
(vi) to ensure long life and chemical stability

Transformer oil is a special mineral oil with high dielectric strength. This oil is used for insulation and cooling of transformer. The oil should be perfectly free from moisture because presence of even a trace of water in it reduces its insulation strength considerably. The oil is undergone the process of dehydration periodically to remove moisture contents from it. *Sludge formation* takes place in the oil due to moisture, dirt or some foreign matter in the oil which is harmful. So the oil is to be tested at regular intervals to know its qualities.

The transformer oil serves the following two main purposes:

(a) It transfers heat by convection from the windings and core to the cooling surfaces.
(b) It maintains the insulation of the windings

While the oil is in service in the transformer, a *sludge* is formed which is an oxidation product. Sludge formation is accelerated by the contact with air and temperature. Sludge is also caused by the presence of acids and alcohols. Sludge formation produces the following effects:

(a) Rate of heat transfer is reduced
(b) Ducts are clogged
(c) Operating temperature increases

Properties of transformer oil

(i) Dielectric strength 40 kV per mm when applied for one minute
(ii) Flash point 160°C
(iii) Sludge value percent 1.2 (the percentage of insoluble matter formed when the oil is heated and oxidized)
(iv) Pour point 40°C
(v) Specific gravity 0.88
(vi) Dielectric constant 2.2
(vii) Acidity after oxidation 0.5

The transformer oil should possess the following properties:

(i) Non-inflammable
(ii) Non-sludging
(iii) High insulation resistance
(iv) Low evaporation
(v) Better mobility and penetrating quality
(vi) Easily available in sufficient quantity
(vii) Low cost
(viii) High thermal conductivity

The following laboratory tests may be carried out on the transformer oil for determination of its properties

(i) Moisture test
(ii) Acidity test
(iii) Dielectric strength test
(iv) Sludge resistance test

When insulating oil is in circuit breakers it serves two purposes. i.e., it provides *insulating property* and helps in *quenching* the arc produced when the contacts are opened or closed. i.e. it acts as a fire extinguishing media. Now a days synthetic oil is used as an insulator in transformers in place of transformer oil (mineral oil) because synthetic oils are very much resistant to *oxidation* and *fire hazards*.

Fibrous insulating materials: These materials are having alongated particles called fibers in their structure. They are mechanically very strong and cheap. They are textile materials. They are having high hygroscopicity and this is the drawback. Some examples are: wood, papers, card boards, cotton, jute, silk, rayon, nylon, adhesive tapes, asbestos, fiber glass. Some of them are discussed here.

Wood: Density of wood is 10^3 kg/m^3 and its tensile strength is 800 to 1300 × 10^4 kg/m^2. It is frequently used for low voltage installation. It is very hygroscopic and after absorbing moisture tends to lose markedly its mechanical properties. Because of the above limitations wood in rarely used as such. Whenever it has to be used as an insulating material it is impregnated in oil. Because the wood is cheap, easily available and easily fabricated, it is used as structural material for transmission and distribution poles. It is also used for switch boards, round blocks, casing and capping and handles of tools.

Paper and card-board: The paper is manufactured from coniferous wood. The organic contamination like lignin and pantosans must be properly removed. Some alkaline reagents are added in the crushed wood which is then boiled. The material is then formed in to papers. The process is called *sulphate process*. Unimpregnated paper is used in telephone cables and capacitors. Cardboards are sheets of short fibers. They are either resilient or stiff. They are used for slot liners in electrical machines, coil frames and as insulation in oil immersed transformers.

Asbestos: It is a mineral (naturally occurring) material of fiberous structure. The larger the fiber, the higher is the grade of asbestos and greater is its cost. These fibers are strong and flexible and some varieties are even suited for spinning into different textiles. Asbestos finds extensive use in electrical machines because of its ability to withstand very high temperature. It can bear a temperature of about 400 °C without any considerable change. Asbestos is also used for making cloth types, paper boards for insulation purposes. Asbestos materials are impregnated because it absorbs moisture. Its dielectric strength is 3 – 5 kV/*mm*. The main applications of asbestos:

(i) In low voltage work as insulation in the form of rope, tape, cloth and board. For these purposes asbestos is properly impregnated with a liquid or solid like resin. Proper impregnation improves the mechanical and electric properties.

(ii) It is used as insulation in wires and cables under high temperature conditions, in coil winding and in end-turn insulation in motors and generators, as conductor insulation and layer insulation in transformers.

(iii) It is used as arcing barrier in switches and circuit breakers, etc.

(iv) It is used for covering wire for electric heating devices, ovens, electric iron, etc.

Cotton and silk: Cotton is combustible and chars when heated, even without the presence of sufficient air or oxygen. It is a porous material and soaks water rapidly. Moisture or humid air can also make it moist. Hence it is not a good insulator. However it is used where flexibility is an important factor, very high temperature are not reached and the atmosphere is not humid. Cotton covered wire is extensively used for winding of small magnet coils, armature windings of small and medium sized machined, chokes.

Silk is more expensive then cotton but takes up less space and is, therefore, used for covering windings in fractional horse power machines. Silk is less hygroscopic and has a higher dielectric strength than cotton, but like cotton it requires impregnation.

Fiber glass: Fiber glass products are less hygroscopic, possess good electrical and mechanical properties and sufficient flexibility to get moulded into required shapes. For many applications fiber glass is impregnated with materials like synthetic resin.

Adhesive tapes: These tapes are widely used in wiring systems to cover the conductor where its original insulation is cut out. They must bear a temperature of 75°C for 24 hours. They should not have sulphur content otherwise it will react with the copper conductor.

Impregnated fiberous insulating materials: Almost all the fibrous materials used insulation are impregnated. Impregnation reduces hygrosocopicity, chemical and thermal degradation by which the fiberous materials become more useful for insulation. Usually oils are used for the purpose of impregnation. Resins, drying oils, varnishes are also used for impregnation of insulating materials. Oils used for this purpose are selected carefully depending on requirements.

Insulating resins or plastic insulating materials: Plastic is an organic material and is found in many varieties. It can be easily moulded into any shape through application of heat and pressure. Resin is the substitute word normally used in insulation technology in place of plastic. The most common definition for plastics is that they are natural or synthetic resins or their compounds. Most of the plastics are of organic nature composed of hydrogen, oxygen, carbon and nitrogen. Natural resins are derived from plant and animal sources. The use of plastic insulating materials is so common that probably it amounts to more than that of the use of all other insulating materials combined together. Standard forms in which plastics are available include moulding powers, sheets, rods, tubes, films and liquids. The properties common to most of the plastics are: low price, a wide range of colours, toughness, water resistance, low thermal conductivity, low electrical conductivity, light weight.

Plastics or resins can be of two types:

1. Natural resins
2. Synthetic resins

Natural resins: They are available in nature and are derived from plant and animal sources. Simple purification or sometimes a little chemical modification is all that is required to make use of natural resins in electrical insulations. Examples of natural resins are lac, cosein, amber, shellac, wood resin, etc.

Synthetic resins: The resins which are prepared artificially by the *recurring chemical reaction* of a simple organic compound are called synthetic resins. During the reaction the molecules of the simple organic compound combine together to form a high molecular weight composition. This reaction is called *polymerisation*.

Classification of synthetic resins (Plastics): Resins are divided into two main groups:

1. *Thermosetting resins* (it is hard, rigid and does not soften when heated)
2. *Thermoplastic resins* (it is soft and melts easily when heated)

1. *Thermosetting resins*

The thermosetting resins are formed by the intermedia products which under the influence of heat, pressure, etc. undergo chemical changes of *condensation* and *polymerization* to form a rigid final shape. They require heat and pressure to mould them into shape. When heat is applied, they first become soft and plastic and on further heating they undergo change and set hard. The process is called *thermosetting* or *thermohardening*, when a material is thermoset, it is permanently set and does not soften to any appreciable extent when being heated. However, intense heating will being about the breakdown of the material by burning.

The thermosetting materials under a chemical change when moulded and cannot be resoftened by heating to reshape them. Compared to thermoplastics, thermosetting materials are harder, mechanically stronger and are suitable for use at higher temperatures. These materials are less flexible and have heat resisting properties. The moulding temperature for the thermosetting are usually considerably higher than for thermoplastics. They are widely used for telephone receivers, radio and television cabinets, switch boxes and electrical outlets. Proper fillers and reinforcing materials are added to thermosetting to improve various properties. Commonly used fillers and reinforcing materials are wood, flour, rag fibres, chopped glass fibre, mica, clay, magnesium oxide, aluminium oxide, etc.

2. *Thermoplastic resins*

These materials are those resins or plastics which soften on the application of heat, with or without pressure but they require cooling to set them to shape. When heated thermoplastics begin to soften at temperatures as low at 140^0 F and then can be moulded without any change in chemical structure.

Plastic materials which soften and melt retain certain flexibility and are called thermoplasts. They are produced artificially from organic substances like oil and coal products. Fillers like soot, mica, textile, wood, glass fibres are often added to achieve certain desired properties. They are widely used for floor tiles, walls, fluorescent light reflection, lenses, etc.

Q 10.2 Write a note on the special properties of laser beams comparing with that of the radiation from sodium lamp. Discuss briefly the medical applications of lasers.

***Answer*:** Laser is a device for the generation of coherent, nearly monochromatic and *highly directional electromagnetic radiation* emitted somewhere in the range from submillimetere through ultraviolet and x-ray wavelengths. More than hundred types of lasers have been fabricated which range in power, size, performance, use and cost.

A laser differs from ordinary radiations in several aspects. Laser is highly intense as compared to radiations from conventional sources. This makes laser a valuable tool in coherent applications such as welding cutting and drilling operations. A laser beam is highly coherent. The *coherence length* for sodium light is about a few centimetre, where as it is of the order of kilometre for laser. This makes laser an ideal source for *holographic applications*, *inter ferometric measurements*, spectroscopic applications, etc. High coherence of laser leads to narrow line width. Hence laser beam is highly monochromatic. Light from a conventional source is inferior in this respect because it is not sharply peaked at a wavelength. A laser beam is highly directional. It is therefore possible to focus a laser beam to a very fine spot. Hence it is liberally used by *ophthalmic surgeons* to focus the laser to a narrow part of the *retina* without affecting the neighbour hood unlike other radiations.

Medical Applications

The developments of the free-electron laser by John M.J. Madey in 1971 excited research groups throughout the world who have recognized the potential of the concept especially with respect to medical applications. The free-electron laser is considered to be the most exciting medical machine of the next several years. It was considered as a major break through in the treatment of diseases such as cancer, without the liability of harming healing tissue. The *free electron-electron laser* is relatively young device that differs sharply from any other laser type. It requires access to a high-energy electron accelerator. Indeed, medicine is just one of a gaggle of applications cited as promising fields for the free electron laser; others include spectroscopy, IR imaging, chemical processing, welding and metal working, laser fusion, communications, and directed energy weapons. The medical applications of lasers in some of the important areas are now discussed briefly.

Surgery

In medicine as in science fiction, lasers are mostly regarded for their ability to vapourize matter with a concentrated blast of energy. Surgeons use them to burn up brain tumors and remove tattoos. Experiments with lasers to weld tissue, hoping to bring a new delicacy to surgical techniques were successful. Rejoining blood vessels with severed nerves by *laser-welding* is much quicker for the surgeons than using traditional *sutures*. The key difference between using a laser to blast away tissue and using it to rejoin or mould it lies in the amount of energy used. Laser welding will result in fewer post operative infections than sutures because the laser introduces no foreign materials into the body.

Another technique involving the use of lasers is the treatment of paralysis where an He – Ne laser is used to stimulate the nerves in the wrists and ankles. Apparently this procedure has the unique ability to stimulate the part of the brain that controls *motor response* and cause dramatic changes in nerve reactions. Success has been achieved in restoring hand movement after spinal cord injury, reduction of stiffness and spasms in paralyzed limbs, and a major recovery of body movement in some patients previously classified as permanently paralyzed. Relief of pain by this technique has also been reported.

Laser *coronary angioplasty*, the term for removal of unwanted plaque in coronary arteries, is a technique that is available but needs to be modified for clinical applications. Those patients have had their blood flow rerouted around original clogged *arteries*, but in most cases, artery disease continues and may narrow the *replacement artery* in a good percentage of cases. Repeat by-pass surgery is not feasible. Such patients could be helped by *laser angioplasty*, which could be probably be repeated as needed. Such patients could be helped by laser angioplasty, which could probably repeated as needed. The laser that offers a wave length of ultraviolet light that may be just right for the delicate work of clearing our arteries. Called an *excimer laser*, the energy comes from halide gases made from krypton and fluoride or from xenon and chloride. An advantage of the energy beam produced by the excimer appears to be its ability to break apart all materials clogging arteries without producing heat. The term excimer comes from "*excited dimer*" and refers to atomic particles formed by a pulsed electrical discharge, which emit ultraviolet radiation as the excited particles relax.

Ophthalmology

The four most common sight-destroying diseases among people over the age of 45 are; *macular degeneration*, *glaucoma*, *diabetic retinopathy*, and *cataract*, and states that new therapies have simplified much eye surgery so that many operations can be performed on an out patient basis. Millions of people suffer from *glaucoma*, a potentially blinding disease in which pressure builds up inside the eye and pinches the optic nerve. The pressure comes from a backup in the flow of fluid. Watery fluid normally enters and exists the eye at all times, but it gets backed up when something clogs up the "drains" called the *trabecular meshwork*. With too much inflow and too little out flow, pressure mounts. A good percentage of glaucoma patients can control this pressure with special eye drops. For others, an opthamologist might suggest 80 to 100 burst of *argon laser*. There is a rare form of glaucoma, called *angle-closure glaucoma*, for which the laser has also been used. While open angle glaucoma progresses without symptoms, angle-closure glaucoma causes blurry vision, red eyes and pain. To treat it, ophthalmologists use the laser to puncture the iris-the coloured part of the eye-so that fluid flows freely between two chambers in the front of the eye and pressure drops.

Dermatology

Dr Leon Goldman, a dermatologist, was a pioneer in developing removal of skin irregularities at the University of Cincinnati Medical School Laser Laboratory. The treatment of portwine stains and deep-red birthmarks on *Caucasian skin* has become a clinical procedure. Also, removal of unwanted growths, including carcinomas (skin cancerous cells), have become routine laser treatments. *Laser acupuncture* is becoming a popular treatment for some disorders and for the relief of pain. Being painless, fast and hygienic, laser treatment is becoming more popular in China and Western Europe than needle techniques.

Conclusion

About from its inception the laser has found applications in medicine. Sometimes the laser has emerged as a means for carrying out a new surgical procedure, in other cases the laser presents an alternative means for carrying out an existing procedure. Perhaps the best known of these surgical applications of the laser has been in the reattachment of detached retinas. If the detached retina will settle back into the coherent position it can literally be welded back into place by focusing a CW (continuous wave propagation) argon ion or a pulsed or CW Nd: YAG laser through the lens of the eye onto the back of the eye. Bleeding inside the eye can also be stopped by laser heating the site of bleeding-a process called *photocoagulation*. The same lasers that present a serious eye-hazard, because they can penetrate to the back of the eye, can be used for these surgical procedures inside the eye. The ability of lasers to burn or cut, the outer surfaces of the cornea has led to new, and still controversial, procedures in which a laser is used sculpt the *cornea* to correct the vision defects. This procedure is called *radialkeratotomy* and is generally carried out with excimer lasers.

Ultraviolet, visible and infrared lasers are readily absorbed by body tissue so they have an ability to act as scalpels in specialized treatments. For treatment of certain skin conditions including some cancers, the ability of the laser to burn and selectively remove thin layers near the surface without damaging underlying tissue is very valuable. Much of the ability of the laser to burn locally, and selectively, is based on the absorption of the laser wavelength by water. Consequently CO_2 lasers are more effective than argon ion or Nd: YAG lasers in these scalpel-like applications. However, the absorption of water in the body is largest near $3\,\mu m$, so lasers near this wave length such as erbium: YAG, are attracting great interest.

A clearly beneficial application of pulsed blue-green dye lasers is in the fragmentation of kidney stones that have left the kidney and become trapped in the urinary tract. Pulses of intense visible light directed along an optical fiber at the kidney stone successively break the stone into several pieces that are then able to leave the body. It is preferable to use a *tunable dye laser* for this treatment so as to maximize the energy absorption by the offending stones while at the same time not heating up any blood that is in the vicinity of the stone. For general applications as scalpels lasers are attractive when used to cut very *vascular tissue*, which bleeds a great deal when cut. The laser cuts and cauterizes at the same time, the result being an incision with a layer of burnt tissue on both sides of the cut. Lasers are even finding application in '*painless*' dentistry. Lasers have many additional non-surgical uses in diagnostics and monitoring, for example in analytical procedures, and as optical sources in various types of sensors for temperature and pressure, and blood flow.

For performing surgery inside the body the laser beam must be directed inside an optical fiber system that at the same time provides the surgeon with a TV image of the region at the end of the fiber. An exciting application of lasers in this way involves the burning away or *ablation*, of the plaque inside blocked arteries, thereby opening them up once again to blood flow. This procedure is called laser *angioplasty* and is worthy of further discussion.

Laser Angioplasty: Arteriosclerosis is the constriction, or blocking, of blood flow through arteries. The material that leads to this problem is called plaque, a composite material containing layers of fat, fiberous tissue, muscle tissue, and varying amounts of calcium { as $Ca_3 (P O_4)_2$}. There has been great interest, and some success, in using both CW and pulsed lasers to ablate plaque away. A laser beam is directed at the blockage in an artery along an optical fiber inserted through a catheter into the artery. The *catheter* is threaded over a previously placed guide wire. The use of lasers in this away is called laser angioplasty, in contrast with the earlier (and still more widely used and successfully) technique of balloon angioplasty. In this technique a small balloon is threaded into the occluded region of the artery and then filled with fluid, thereby compressing the plaque against the wall of the artery. The problems that have been faced in the use of lasers to remove plaque have involved:

(i) Avoidance of damage to the wall of the artery, which is only about 1 *mm* thick. This problem has been alleviated to a large extent by placing a ball lens on the end of the fiber.

(ii) The opened region can reocclude within a few months.

(iii) Thermal damage to healthy tissue can occur. The use of pulsed lasers seams to avoid the thermal damage problem while short intense pulses are effective in photoablating the plaque. Sub-microsecond ultraviolet pulses from Xe*Cl* lasers at 308*nm* are being investigated in this application as is the use of holmium lasers operating at 2.1 μm. These lasers are used in a long pulse mode delivering a few joule per pulse in 1/4th sec long pulses at 1 – 10 pulses per second. Their wave length of 2.1 μm is strongly absorbed by water. Both these ultraviolet and near-infrared wavelengths can be delivered to the occluded site along silica fibers. The treatment of the occluded artery is frequently followed up by an application of balloon angioplasty.

Q 10.3 Discuss briefly light-emitting diodes and also one or two photon devices.

***Answer*:** *Light-emitting diodes* (LEDs)

They are effectively the reverse of photovoltaic cells. In photovoltaic cells, light is used to produce an electric voltage; in LEDs, a voltage is applied across a *p-n* junction to produce light. A *p-n* junction diode when forward biased can be made to emit visible light and is known as a LED, which is extensively used in *pocket calculators*. The radiation has a broad spectrum and is spontaneous and non-coherent. It is due to the recombination of electrons and holes which occur when conduction band electrons are captured by valence band holes. By using suitable materials such as GaAs or GaP, the emission of red, green or yellow light can occur at low current densities. The phenomenon is therefore different from that of the laser diode, which requires much higher current densities and emits stimulated, coherent radiation.

LED operates by the emission of photons produced by the transition of electrons from conduction band to valence band. This transition occurs in the material near a *p-n* junction which is supplied with an excess of minority carriers by a forward-biasing current. The material for a visible LED must have a band gap of at least 1.7 eV so that the transition causes the emission of visible light. A glance of the table:

Table 10.3.1 *Some band energies at 300 K*

Material	*Energy gap (eV)*	*Group in periodic table*	$\lambda_g\,(nm)$
C	5.4	IV	230
Si	1.11	IV	1110
Ge	0.66	IV	1880
Al Sb	1.60	III – V	776
Al As	2.17	III – V	573
Ga P	2.24	III – V	555
Ga Sb	0.70	III – V	1775
Ga As	1.42	III – V	875
In P	1.35	III – V	978
Cd Se	1.74	II – VI	714
Cd S	2.42	II – VI	513

Table 10.3.1 shows that III–V compounds such as GAP and II–VI compounds such as CdS are suitable materials, and in fact the majority of LEDs for displays are made from III–V compounds which can cover the band gap 1.42 to 2.24 eV (880 – 558nm), that is, red to yellow green. Some devices made from SiC have been made which *emit* blue light, but at low efficiency II–VI compounds do not find favour as they are hard to drop *p*-type. However, as can be seen from table 10.3.1, while GaAs has a direct gap, both AlAs and GaP have indirect gaps. Because the emission of photon in an indirect-gap material also requires a phonon to participate during the electron's interband transition, the photon probability (or quantum efficiency) is low and the light intensity is low too. This fall in efficiency is compensated to some extent by the increase in the human eye's response at wavelength around 555nm. Doping the material with nitrogen introduces an electron-trapping level about 10 *m*eV below the conduction band, which enhances the efficiency.

Photon Devices

Three important devices using the photoelectric effect are the photomultiplier, photoconductive cell and solar cell.

Photomultiplier

When light falls on a photocathode, the emitted electrons may be only few in number. To increase the number several times, each primary electron is made to emit several secondary electrons by impact on another electrode at a higher potential.

In Fig. Q 10.3.1, K is a photocathode coated with a material such as Cs_3Sb. Photons falling on K emit one or more electrons which are accelerated in turn to a series of dynodes A_1, A_2, etc…held at successively higher potentials. Each dynode is coated with a low work function material emits as many as secondary electrons for every primary electron. The dynodes are suitably positioned and typically ten may be employed, giving an overall amplification factor of 10^{10} electron per primary electron. The emitted electrons are collected at the final anode C to produce a large photoelectric current through an external circuit. An important application of such a device is the scintillation counter which is used for recording radioactive particles.

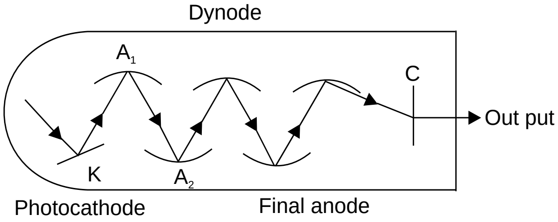


Fig. Q 10.3.1 *Photomultiplier*

Photoconductive Cell

The photoconductive cell is a device for detecting the amount of light radiation present. Typical applications are in photography and as infra-red detectors. For photographic purposes, the conductive cell consists of a pair of electrodes embedded in a CdS surface and connected externally to a small voltage. The spectral response of CdS corresponds to that of the normal eye and so it records the amount of daylight falling on it. It can be calibrated to indicate the amount of exposure required for a certain film. As an infra-red detector CdS has too slow a response and so a commonly used material is PbS, which is very sensitive to infra-red radiation and can be usefully employed in military applications such as missiles for destroying jet aircraft.

A semiconductor *p-n* junction when exposed to light can also be made to change its conductivity. Such a device is known as a *photodiode* and consists of a *p-n* junction which is reverse biased. Photo detection occurs in the *depletion region* where the high electric field separates the electron-hole pairs which are excited on the absorption of radiation. For sufficiently high fields, secondary electron-hole pairs are produced by impact ionization, resulting in internal gain, as in the case of avalanche photodiode. Such a silicon photodiode is best suited to use as a detector in an optical fiber system, employing wave lengths up to 1 μm.

Solar Cell

The direct conversion of solar energy into electrical energy has been of considerable interest, especially in *satellite communications* for recharging conventional batteries. Hence, in recent years, much research and development has been done to produce a cheaper and more efficient device generally known as a *solar cell*.

The solar cell is basically a *p-n* junction diode that converts sunlight directly to electricity with large conversion efficiency. The action of the solar cell is explained as follows:

When *p-n* junction diode is exposed to light, photons are absorbed and electron-hole pairs are generated in both the *p*-side and *n*–side of the junction, as shown in Fig Q.10.3.2. The electrons and the holes that are produced over a small distance from the function reach the space-charge region X by diffusion. See Fig. Q 10.5.2 (b).

The electron-hole pairs are then separated by the strong barrier field that exists across the region X. The electrons in the *p*–side slide down the barrier potential to move to the *n*–side while the holes in the *n*–side move towards the *p*–side Fig. Q 10.3.2 (c).

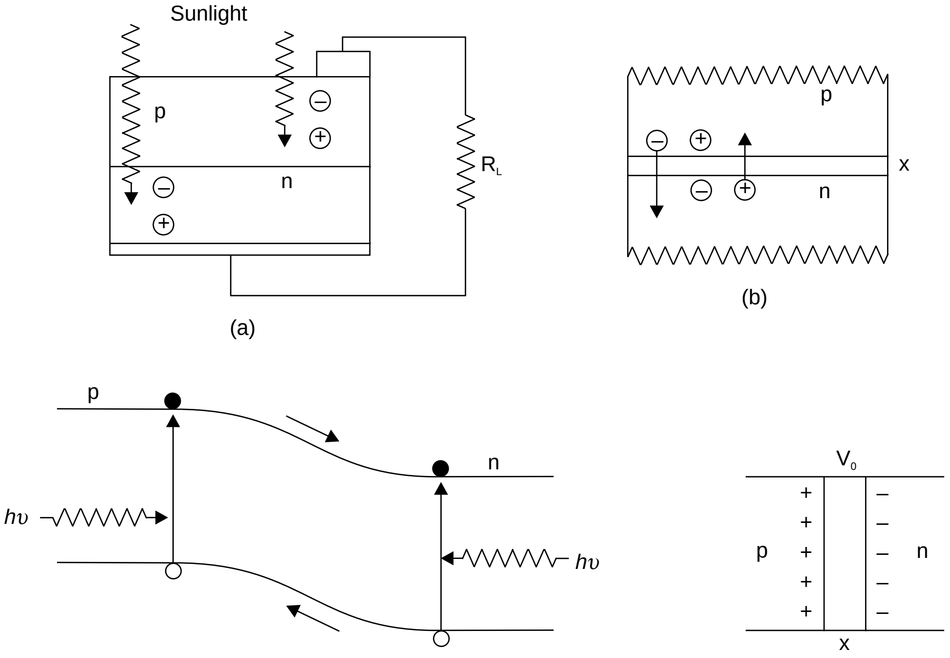


Fig. Q.10.3.2 *(a) p-n junction with load resistance, R_L (b) Diffusion of lectrons and holes (c) Energy band diagram corresponding to (b) (d) Formation of the open circuit voltage, V_O*

When the *p–n* junction diode is open circuited, the accumulation of electrons and holes on the two sides of the junction gives rise to an open-circuit voltage V_0. If a load resistance is connected across the diode, a current will flow in the circuit [Fig. Q 10.3.2 a]. The maximum current, called the short circuit current is obtained when an electric short is connected across the diode terminals. Note that the current flows as long as the diode is exposed to sun light and the magnitude of the current is proportional to the light intensity.

Solar cells are used extensively in satellites and space vehicles as most important long-duration power supply. Solar cells are constructed with silicon, gallium, cadmium sulphide and with many other semiconductors, and in various device configurations.

Q 10.4 Write notes on Fiber optics and Holography.

***Answer*:** 1. *Fiber optics*: Alexander Graham Bell, the inventor of telephone was the pioneer in this field. He successfully transmitted a telephone signal over a distance greater than 200 *m* using light as the signal carrier (1880). The field became active after the invention of lasers (1960), highly monochromatic, intense coherent and directional beam. In 1966 it was proposed that fibers with high purity core surrounded by a *cladding* of lower refractive index could be used for transmitting light over long distances: Robert Maurer was able to produce a fiber with a loss of 20 *dB*/km. To day we have fibers having a fraction of *dB*/km for *attenuation*. Tremendous information carrying capacity is the special feature of fiber optic cables. Fiber optic cables are light weight, inexpensive and they are immune to electromagnetic interference. Reliability is very high. It is believed that *photonics system* may replace electronic system of communications cent percent in another decade.

Optical fibers may be either glass or plastic. When low losses are important, glass fibers are superior, having losses less than 1 dB/km. The operation of simple optical fibers is based on the phenomenon of total internal reflection. If a fiber core is clad with a material of lower refractive index than the core, there will always be a critical angle such that rays striking the interface of core and cladding at an angle greater than this angle will be totally reflected. Thus the fiber becomes a light guide or dielectric wave guide. This phenomenon is illustrated in Fig. Q 10.4.1

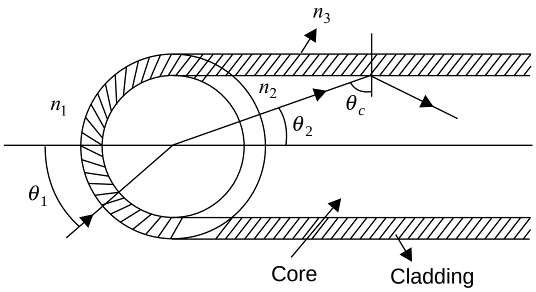


Fig. Q 10.4.1 *Optical fiber showing entering ray striking cladding at critical angle*

In this Fig. Q 10.4.1, a ray shown entering the face of the fiber at the maximum possible angle that will result in total internal reflection of the ray inside the fiber. Applying Snell's law at the fiber face assuming the ray strikes the core-cladding interface at the critical angle we can show that the numerical aperature,

$$\boxed{NA = n_1 \sin\theta_1 = \left\{n_2^2 - n_3^2\right\}^2} \qquad \text{(Q 10.4.1)}$$

Here n_1, n_2 and n_3 are the refractive indices of the external medium, core and cladding, respectively; θ_1 is the half angle of the entrance cone, and *NA* stands for numerical aperature. The cladding in glass fibers is also glass but doped differently than the core to give it a slightly lower refractive index. For example, if the core and cladding indices are 1.55 and 1.50 respectively, for a fiber in air, *NA* = 0.39 and $\theta_1 = 23°$. The type of fiber just discussed is a step index fiber. Another type commonly used is the graded index fiber. Here the refractive index decreases radially from the centre in a parabolic fashion. Rays launched at some angles to the axis of the fiber continuously change direction toward the axis without ever striking cladding. The path is a zig-zag combination of straight-line segments between reflections in a *step index fiber* whereas the path in a graded index fiber is essentially sinusoidal. Losses in glass fibers are primarily due to scattering by impurities and defects. Losses in plastic fibers are chiefly due to absorption.

Short delay times in optical communications are described to minimize pulse spreading and the resultant degradation of information. There are two causes of delay in optical fibers, referred to as *model dispersion* and *wavelength dispersion*. Model delay is caused by the different distances traveled by different rays within the fiber. The maximum value for this type of delay in a step index fiber can be deduced by considering a ray travelling parallel to the axis and a ray reflecting from the cladding at the critical angle. The time delay per unit of fiber length is then given by

$$\boxed{\Delta t = \frac{n_2}{c}\left\{\frac{1}{\sin\theta_c} - 1\right\} = \frac{n_2}{c}\left\{\frac{n_2}{n_3} - 1\right\}} \qquad \text{(Q 10.4.2)}$$

This amounts to 0.17 *ns/m* for many fibers. Actual delay times are less because the losses are higher for the rays traveling grater distances.

Optical fibers are waveguides and, as such, not every imaginable geometrical path for a ray is an allowable mode. In fact, if the fiber is made sufficiently thin, typically a few micrometers in diameter, only one allowed mode exists. Such single-mode fibers effectively eliminate model delay, and picosecond delay times are possible. Graded index fibers minimize modal dispersion because the farther a ray wanders from the axis, the more time it spends in a region of lower refractive index (higher speed). Thus the time delay between axial an non axial rays is reduced. Wave length, is minimized by proper material design to reduce this variation and by the use of narrow band width light emitters, chiefly diode lasers.

It must be recognized that losses also occur due to reflection at entrance and exist surfaces and coupling of light from emitters into fibers and the coupling of light out of fibers to detectors. Highly efficient techniques and devices have been developed, however, for coupling light in and out of fibers and for coupling light from one fiber or several other fibers.

Features of Fiber Optics Communication Systems

Very large information transmission capacity and large repeater spacing are the main features of fiber optic communication systems. They also offer many advantages compared with the usual metallic transmission process. Since the fibers are composed of dielectric materials they are totally immune to extraneous interfering electromagnetic signals. There is virtually no signal leakage from the fibers and therefore cross – talks between neighbouring fibers are almost absent while this is very common in the conventional systems. Since signals do not leak away from the fibers they are resistant to intrusion and are accordingly highly suited to secure good results in defence communication networks. Since these fibers are immune to electromagnetic interference and do not pick up line currents, they can be safely used in a power station, and can be laid along side metallic power cables. They are also much smaller in size than an electric line of equivalent band width and thus would occupy much less *duct space*. Also the raw material used in the fabrication of low loss fibers is silica, which is abundantly available in nature (of course in an impure form), where as copper or aluminium constitutes the basic raw material in co axial cables. Cost surveys indicate that *coaxial cable* price will continue to rise due to an almost continuous increase in the price of copper or aluminium but the prices of fibers will come down as the production volume increases.

Holography

Holography is lensless three-dimensional photography. A conventional photograph is only a flat record of real image projected on to a photographic film. Information about the three-dimensional character of the object is almost entirely lost during the photographic recording process. Only the blurring of the images of objects that are not within the depth of field of the camera preserves any record of the location of the object relative to the camera. *A hologram* on the other hand is a special *photograph* of an object that retains information about the phase of waves coming from the object. Holography has a much longer history than that of the laser, although it was the invention of the laser that made the production of high quality holograms a reality.

In 1947, Denis Gabor was looking for a way to improve the quality of images that could be obtained with an *electron microscope*. Although the electron microscope of that day should have been capable of resolving down to the atomic scale, aberrations of the electron optics prevented them from doing so. Gabor conceived the idea of recording an electron hologram, which would contain amplitude and phase information, and then reconstructing a corrected image of the object by optical means. He did succeed in producing holograms and performing image reconstruction, but the optical sources available to him were not sufficiently temporally coherent allow high quality images to be achieved. For his pioneering work he was awarded the 1971 Nobel prize for physics. The high degree of coherence obtainable with a laser has made the production of holograms and applications of holography into a large subject in its own right. The principles underlying holography share much is common with the phenomena of interference and diffraction.

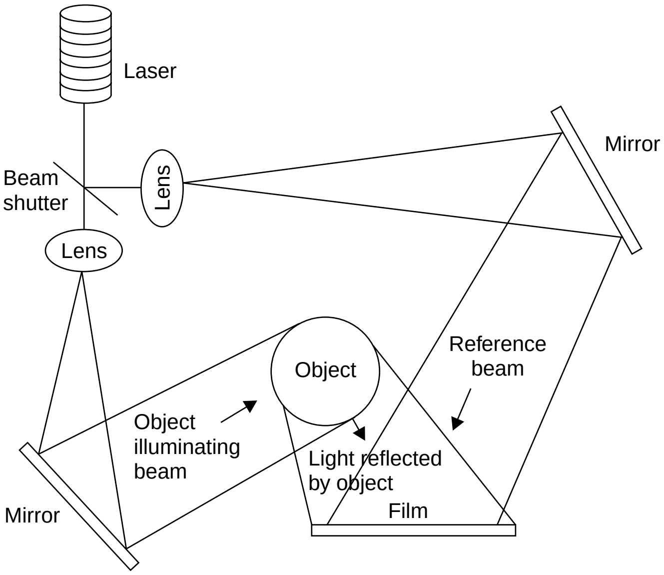


Fig. Q 10.4.2 *Diagramatic sketch illustrating technique with a laser to produce a hologram on film*

In conventional photography the photographic emulsion becomes dark according to the local intensity of the real image falling on it. The emulsion is a mixture of silver halide crystals of different sizes, predominantly silver bromide, in a gelatin matrix. Incident light frees electrons from the halide, but the electrons become trapped. Addition of developer reduces the silver ions in an exposed crystal to silver atoms, leading to a strongly absorbing region where exposure levels were high. This is how a photographic negative is produced. We make a hologram, and preserve phase information in the photographic record, by allowing temporally and spatially coherent light to illuminate the object. Light reflected and scattered from the object falls on a photographic film together with a reference wave supplied directly to the film with the same laser as is used to illuminate the object. The schematic way in which this is done is shown in Fig. Q 10.4.2.

Light emitted by a laser splits into two paths, one to create an object beam and the other to serve as a reference beam. It is intersecting, or interference, of the two beams and the resultant beam projected on a photographic film that forms the *holographic image*. Because every location on the object is illuminated by the object beam, the reflection of these waves intersects the reference pattern and the resulting image appears suspended in space so that as the viewer around the image a three dimensional object is visualized. The developed hologram does not contain a recognizable image of the object as a conventional photograph does. The hologram generally appears as a collection of bright and dark lines with bright and dark patterns of concentric circles. The stored image can be regarded as a representation of the diffraction pattern of the object. The hologram formed by exposure of a film and the production of a complex pattern of transmission is called *amplitude hologram*. However, it is possible to process the film chemically by *bleaching* so that the dark silver atoms are converted into silver salts that are transparent but have a different refractive index than the surrounding film. This converts the recorded hologram into pattern of phase information and is called a *phase hologram*.

Volume Holograms

The holograms that we have been considering so far are called *plane holograms* because we have been tacitly assuming that interference of object and reference waves writes the hologram in a particular plane. We are neglecting the thickness of the photographic emulsion. However, since actual emulsions can be up to $20\ \mu m$ thick it is possible, and in many cases desirable, to write a volume hologram in which interference fringes are written through out the emulsion. The hologram can be thought of as a continuous distribution of plane holograms at different values of z through the *emulsion thickness*. Just as the sample plane hologram produced by the interference of two plane waves was a planar diffraction grating the volume hologram produced in this way will have a structure where the regions of bright and dark are distributed in a series of parallel planes is the recording medium.

Industrial applications of holography include *nondestructive testing* (NDT) techniques to find flaws in structural parts. Called holographic interferometry, this method of examining materials for flaws, dimensional exactness, effect of heat or vibration, or other physical aspects has revolutionized NDT, replacing *radiography* in many instances and supporting other methods of quality control to accuracies not available until the laser was adapted to holography and developed to its present state of the art.

Other applications include data storage, whereby written information can be reduced to small dimension that one source claims that all the material in a library could be stored on a medium about the size of a regular–sugar cube. In the operation of a robot, recognition of patterns stored in a memory bank could help in a robotic decision-making. Holographic logos are being used to foil credit card counterfeits. Holography gives doctors a 3D view of the inner working of the body organs without side effects. The beating heart, the *fetus* of a pregnant woman, flowing blood are now available from *motion holography*.

An instrument called an *ophthalmic laser interferometer* has been developed by eye researches so that the results of certain eye surgery can be predicted. “The pre-surgical prediction of the potential *retinal visual acuity* allows the clinician to make a more confident qualitative and quantitative determination as to the cost/benefit ratio for the patient” as reported in the journal “Laser Optics”. This instrument is therefore valuable for patients with optical media problems such as *lenticular cataract* or *aberration*, or *cloudy vitreous* which cloud or degrade images. The laser interferometer can also serve as a predictor of multiple *sclerosis* by determining if the eye being examined maintains the same decimal acuity through out constant monitoring during a five minute period as a healthy eye wound. A suspected acuity would decrease with time. Holography helps to visualize subatomic particles. It is reported that scientists are looking with holograms to find the elusive fundamental particle of matter, *the quark*.

Laser Plasma

Short pulse, high energy laser pulses when focused produce extremely high energy flux, electric and magnetic fields. For example, a 1kJ 1*ns* rectangular laser pulse focused to spot size of $1\,\mu m$ produces an energy flux of 6.4×10^{23} $W\,m^{-2}$, an electric field of 2.2×10^{13} $V\,m^{-2}$, and a magnetic flux density in free space of 73 kT. Fields substantially smaller than this can strip outer and inner shell electrons from the atoms of a target material. Consequently, intense focused lasers have found wide spread use in the production of plasmas from the surface of target materials. These laser produced plasmas can be copious producers of x-rays, which can be relatively coherent. Such x-rays have significant potential for high resolution *holography* and *lithography*. Because diffraction limits resolvable feature size in a microscopic or lithographic system, the shorter the wave length being used the finer the resolution. Most laser – induced generated x-radiation is coherent because of amplitude spontaneous emission (ASE) effects. The rapid ionization of a target material, frequently a thin metal foil, irradiated with an intense laser pulse, can lead to a short lived population inversion on energy levels of the resultant multiply ionized ions. In many ways the process is an energetic analog of the excitation process is self-terminating pulsed gas lasers such as copper vapour and nitrogen.

The irradiation of various materials at very high laser fluences ($J\,m^{-2}$) has, in and of itself, provided a fruitful means for studying matter at very high temperatures and pressures. However, much of the *impetus* for such studies has been provided by the desire to demonstrate laser – driven, inertial confinement, nuclear fusion. *Nuclear fusion* occurs in stars and hydrogen bomb explosions, and there has been work for several decades on the controlled production of such *thermonuclear reactions* on a laboratory scale for *nuclear power generation*.

Q.10.5 Write short notes on

(i) Ceramic materials
(ii) Polymers

***Answer*:** (i) *Ceramic materials*

The word ceramic is derived from the Greek word “Keramos” which means *Potter’s earth* or *clay*. The word ceramics, to-day, includes not only clay but also a wide variety of substances. In short, ceramics are inorganic, non metallic materials. Since there are many possible combinations of metallic and non-metallic atoms, there may be several structural arrangements of each combination, a wide range of ceramic materials are found to occur and used as very useful engineering materials. Generally ceramic materials can be in three groups: Glays, Glasses and Refractories.

Glays: The mixtures of various minerals which posses kaolinite ($Al_2O_3.2SiO_2.2H_2O$) or similar hydrous-alumino silicates as their basic constituents are known as clays. The important clay products are *bricks*, *terro-cotta ware*, *roofing tiles*, *wall tiles*, *sewer pipes* and *sanitary wares*, etc.

Glasses: A product formed by the fusion of one or more of the oxides of silicon, boron or phosphorus with certain basic oxides (e.g sodium, magnesium, calcium, potassium) which normally is hard, brittle and amorphous is called glass.

Refractories: Those non-metallic materials which are used to with stand high temperature in different industrial processes and operations, are known as *refractories*. The main properties of refractories are refractoriness, low porosity, ability to resist chemical action of environment to thermal shocks, low shrinkage and expansion. Fire clay bricks and silica bricks are some examples.

Electrical Properties of Ceramic Materials

Ceramics do not have high electric conductivity like metals because they generally do not have free electrons. There are ceramic materials with some ionic conductivity. The conductivity in them is because of ionic bonds. But ionic conductivity requires the diffusion of ions and hence is quite low. However, ionic diffusion is very much increased at higher temperatures. Glass is commercially used as an insulator in ordinary electrical applications, but in the glass melting furnace the conductivity is very high because of higher mobility of ions at the high temperature.

Dielectric Properties

Many ceramic materials possess the dielectric property. Not only does a dielectric material act as an insulator, but it also interacts with the electric field. The dielectric constant is an electric property which is direct consequence of electrical dipoles in the internal structure of a material. When the ions, or electrons with in the atoms, or both can align themselves with the external field, more electrons can be collected on the negative electrode and more electrons can be removed from the positive electrode. As most capacitors (and hence dielectric materials) are used with alternating currents, the dielectric constant of a material depends mainly upon the ability of the electric dipoles to reverse their alignment with the reversal of the current. This reversal can take place very quickly for the dipoles resulting from the dispersion effects of electron distribution around the atom. The electrons are accelerated to the side of the atom which is adjacent to the positive electrode and can be shifted quickly (frequency 10^{15} Hz) to the other side of the atom when the polarity of the electrode is reversed.

Clay: Clay possesses a very high dielectric constant under static conditions, but its dipoles cannot change direction with alternating currents. Consequently, in clay the dielectric constant for alternating current arises totally because of ion and electron movements. Some crystals within their unit cell possesses two or more positions when an ion can exist with equal energy. In these crystals high dielectric constants are developed because of the shifting to and fro of the ions as the electric field is reversed. The capability of shifting of the ions because of such crystal arrangement makes the dielectric constant higher. Maximum frequency in such cases is limited to a few billions per second. This value of frequency is of course much lower than the frequencies mentioned earlier. This value of frequency is amply high for many engineering applications, such as television and radio. These materials may be nearly permanently polarized. Permanent polarization is advantageous in engineering applications of the type of memory unit in an electronic calculator. Such dielectric materials are named as *ferroelectric materials*. (e.g) barium titanate ($BaTiO_3$). Of the many different compositions of ceramics, those suitable for electric use are made from the combination involving silica (SiO_2); alumina (Al_2O_3), magnesia (MgO); boron oxide (B_2O_3); titania (TiO_2); or zirconia (ZrO_2). Ceramic materials are commonly classified into two ways and the details are presented in the following table:

Table 10. 5.A *Functional classification of ceramics*

	Group	*Examples*
1.	Abrasives	Alumina, carborundum
2.	Pure oxide ceramics	MgO, Al_2O, SiO_2
3.	Fired-clay products	Bricks, tiles, porcelain, etc.
4.	Inorganic glasses	Window glass, lead glass, etc.

Contd

	Group	*Examples*
5.	Cementing materials	Portland cement, lime, etc.
6.	Rocks	Granites, sand stone, etc.
7.	Minerals	Quartz, calcite, etc.
8.	Refractories	Silica, bricks, magnesite, etc.

Table 10.5.B *Structural classification of ceramics*

	Group	*Examples*
1.	Crystalline ceramics	Single-phase like MgO or multi- phase from the MgO to Al_2O_3 binary system
2.	Non crystalline ceramics	Natural and synthetic inorganic glasses (e.g. window glass)
3.	Glass–bonded ceramics	Fired clay products–crystalline phases are held in glassy matrix
4.	Cements	Crystalline or crystalline and non crystalline phases

(ii) *Polymers*: The term polymer is derived from the Greek words poly, meaning "many", and meros, meaning "parts" or "units". Thus polymers are composed of large number of repeating units (small molecules) called *monomers*. The monomers are joined together end–to–end in a polarization reaction. A polymer is, therefore, made up of thousands of monomers joined together to form a large molecule of collidal dimension, called *macromolecule*. The unique feature of a polymer is that each molecule is either a long chain or a net work of repeating units all covalently bonded together. In some cases, molecules are held together by *secondary bonds* such as van der Waals or hydrogen bond. Polymers, however, are molecular materials and are generally non crystalline solids at ordinary temperatures, but pass through a viscous stage in course of their formation when shaping is readily carried out.

The most common polymers are those made from compounds of carbon, but polymers can also be made from inorganic chemicals such as silicates, and silicates and silicons. The naturally occurring polymers include protein, cellulose, resins, starch, shellac and ligmin. There are also synthetic polymers such as *polyethylene*, *polystyrene*, *nylon*, *terylene*, *decron*, etc. termed under plastics, fibers and *elastomers* which possess properties superior to those found in their naturally-occurring counterparts.

Size of a Polymer

A very important parameter that is to designate the size of a molecule is the *degree of polymerization* or D.P. It refers to the number of repeat units in the chain. At D.P values of about 10–20 per molecule, the substance formed is a light oil-a paraffin if formed from ethylene. As the D.P increases the substance becomes greasy, then waxy, and finally at a value of D.P of about 1000 the substance becomes a solid and is then a true polymer. Naturally the D.P is almost unlimited–it may increase around 100,000 or so. In commercial plastics the D.P normally falls in the range of 75 to 750 per molecule. The molecular weight is another measure of chain length and is equal to the D.P multiplied by the molecular weight of the monomers. In fact, it represents the cumulative weight of all elements forming the gaint molecule.

This may range between 10000 and 1000000. *Polyethylene* with a D.P of 1000 has a molecular weight of 280,000.

Mechanism of Polymerization

The process of linking together of *monomers* is called *polymerization*. The need to start with the process of polymerization lies on the necessity of breaking the double bonds (C = C) of monomers. This requires considerable energy and is equal to 612 kJ/6.02×10^{23} bonds. However, 348 kJ/6.02×10^{23} bonds are released every time a single C — C is formed. Since two new single C — C bonds are formed from each former double C = C bond, external energy is required to start the polymerization reaction rather than to continue it.

Theoretically, it might be possible to link all the monomers into a long continuous chain, but in practice this does not take place. The reason is that the molecules must be available in the immediate ends of the chains, and if they are not found available there, it is necessary to diffuse them to the ends of the chains. The diffusion process by which the molecules of the monomer move to the ends of the growing long-chain molecules or macro molecules being a very slow one, the chain formation must ultimately cease due to non availability of further simple molecules as soon as they are required to continue polymerization.

Elastomers

Natural rubber is an *elastomer*-a polymer whose limit of elastic extension is very much greater than that of other solids. We have described earlier in the chapter how this property depends upon the fact that contorted molecular chains may be uncoiled by a tensile stress. From the discussion of thermo plastic materials it should be obvious that a small degree of cross-linking is necessary to prevent plastic flow. In natural rubber this is achieved by the process known as *vulcanization*. The raw material is latex, a viscous fluid which contains a linear polymer of *isoprene*. The double C — C bond prevents rotation of the monomer units and does not allow the cis form to turn into the transform or vice - versa. Trans-polyisoprene (*known as-gutta-percha*) exhibits a very limited extension under stress because the CH side groups lying on both sides of the chain interfere with one another more than if they were all on the same side. The liquid form of cis-polyisoprene is cross-linked by heating in the presence of sulphur atoms to form a vulcanized rubber with a sulphur content of about 1–2% by weight. If more sulphur is used, a rigid plastic called ebonite is made.

Electrical Behaviour

Polymers do not display marked magnetic properties, nor do they conduct electricity unless combined with a conducting filler. Indeed, some of the polymers are very good insulators. This is due to the fact that all the electrons are strongly bound in the covalent bonds and none is free to conduct electricity. But to select a good insulator one should know which polymers do not absorb water since this can conduct electricity. *Polyvinyl chloride*, *polyethylene*, and *polytetra fluorethylene* (PTFE), are all notable examples of flexible insulators. *Perspex* (Lucite) and *tufnol* are much used where a rigid insulator is required.

Some polymers which contain polar groups such as chloride atoms, hydroxyl groups, or sulphur atoms readily become electrically polarized when subjected to an electric field. This results in a high *dielectric constant* or *permittivity*. Since many plastics contain fillers or *plasticzers*, their *permittivity* is artificially increased by what is called interfacial polarization.

Q 10.6 Explain electro-chemical corrosion with the help of an electro-chemical cell. Briefly discuss the common types of corrosion that are encounted on metals in different situations and indicate the nature of mechanism involved in each case.

***Answer*:** Metals usually occur in nature in combination with the elements oxygen or sulphur as oxides, carbonates, sulphides, etc. They are reduced to the metallic state by the expenditure of energy during melting operations which involve the removal of the bulk of the combining elements. Such extracted metals are inherently unstable and show a general tendency to revert to the natural or oxidized condition by combining with the constitutents of their environment. This reverse process requires no supply of energy so it occurs readily and spontaneously; the results are seen as *corrosion.* Unfortunately, the more corrodible metal include those of the greatest importance to industry, namely the ferrous metals. The extent to which the corrosion of iron and steel takes place can be realized by the fact that in India alone the cost to industry of corrosion including means adopted for its prevention, has been estimated at millions of rupees per year. Corrosion of metals is liable to disfigure the finished products, lose their strength, ductility and other physical properties.

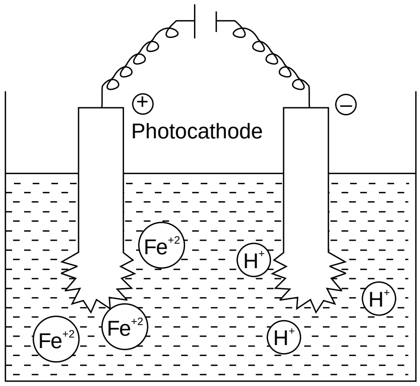


Fig. Q 10.6.1 *Electro-chemical cell*

In a nut-shell, the deterioration of metals by chemical or electrochemical reactions. It converts useful structures, machines and vehicles into scrap. The common types of corrosion reactions involve either direct chemical reaction or electrochemical reaction involving an electrolyte. Dissolution of steel in dilute hydrochloric acid is a good example of chemical reaction. Electro chemical reactions are of great importance in corrosion. In this case, we have to identify an anodic reaction at the positive pole or anode, and the cathodic reaction at the cathode. The anodic reaction leads to dissolution of the anode which is the part undergoing corrosion e.g. ($Fe^{2++} + 2e^-$). The cathodic reaction involves liberation of hydrogen gas at the cathode, or if oxygen is present in the electrolyte, the formation of (OH^-) ions:

$$2H^+ + 2e^- \longrightarrow H_2\ (gas)$$

$$O_2\ (gas) + 2H_2\ O + 4e^- \longrightarrow 4\ (OH)^-$$

In the case of iron, corroding in the presence of aerated water $Fe\ (OH)_2$ may form, i.e. rusting takes place. From this discussion it follows that corrosion can be prevented by deaeration of water.

Although corrosion is commonly an undesirable process, there are also commercial processes which utilize corrosion in a beneficial manner such as electroplating, electrochemical machining, etc. Note that the anodic and cathodic areas for electrochemical corrosion may be found in the same metal piece, in contact with an electrolyte. For example, a highly stressed region of the same component. The cold headed part of a nail corrodes faster than the rest of the nail. Similarly, the grain boundary regions of a metal are anodic to the grain interiors. Therefore corrosion along the boundaries occurs in certain media. The third case would be the oxygen starved regions of a metal which are anodic to oxygen rich regions.

Corrosion occurs in many ways depending on the corrosive environment and as such there may be different types of corrosion. They may be broadly be classified as *dry corrosion* in which a metal or non-metal is chemically attacked by a corrosive liquid or a gas, and *wet corrosion* which occurs in moist conditions and is primarily *electrochemical* in nature. Almost all corrosions fall under these two broad groups. It is customary, however, to classify the multitudes of possible corrosion reaction into many general types and they are:

uniform corrosive attack, galvanic corrosive attack, crevice corrosion, pitting, integranular corrosion, selective leaching, erosion corrosion and stress corrosion.

1. *Uniform attack*: This is a form of corrosion which is easier to control because the average rate of corrosion can be determined and a corrective step can be taken. Usually the rate of corrosion after exposure to certain atmospheres is expressed as loss of thickness, e.g., inch per year or the loss in milligram per decimeter per day. The usual methods of prevention include painting, enamelling and metallic coatings.

2. *Galvanic corrosion*: This form depends on contact between two different metals in an electrolyte such as sea water. Of the two metals, the less noble one becomes the anode and undergoes corrosion. The electrochemical series or galvanic series lists the metals in the order of electro chemical potential or galvanic potential in the electrolytic medium. The galvanic series in sea water is given in the following table:

Less noble: Magnesium, zinc, steel, lead, tin, nickel, copper, silver, titanium and gold

More noble: platinum

If we consider zinc with respect to steel, zinc is more anodic to steel and thus protects steel parts. Note that zinc undergoes dissolution. This is the principle behind galvanizing of steel. As another example, ship hulls made of steel are protected from corrosion in sea water by attacking magnesium or zinc plates to the hull. Galvanic action can be used beneficially by a method called *cathodic protection*. Magnesium cathodes are buried near steel pipes and connected to the pipes electrically.

3. *Crevice corrosion*: This form of corrosion results from oxygen starved areas undergoing dissolution. This may happen under crevices, for example, under bolts or rivets attached to plates. Protection can be afforded by better design and by deaeration of water.

4. *Pitting corrosion*: This is considered a serious form since formation of pits or holes results in leakage from pipes or vessels. Certain alloys are prone to pitting form of corrosion. Pits may form due to presence of inclusions or intermetallic compounds in the microstructure. Generally, pitting can be reduced by alloy additions, for example, addition of 2% molybdenum to stainless steels. Anodising and reduction of inclusions can reduce pitting of aluminium.

5. *Intergranular corrosion*: This results from grain boundaries acting as anodic areas. A specific example is "*sensitisation*" of *austenitic stainless steels* due to formation of chromium carbides near the grain boundaries. This occurs when the steels are heated in the range 500 – 800^0C in service or during welding. This can be avoided by choosing stainless steels with titanium or niobium additions called "stabilized" stainless steels or stainless steels with low carbon (less than 0.03%).

6. *Selective leasing*: This form of corrosion is due to the dissolution of one of the alloying elements from the alloy, leaving the material spongy and weak. For example, in "*dezincification*" of brass, zinc leaves the material, resulting in failure of brass components.

7. *Erosion corrosion*: This type occurs mainly due to mechanical action or impingement attack, particularly in rotating parts in liquids. For example, pump impellers are subjected to erosion corrosion due to solid particles or formation of bubbles and cavitation. The attack can also occur at the corners of bent pipes where a change in velocity occurs. Proper design and selection of alloys, filtering of liquids, deaeration, etc., can reduce erosion corrosion.

8. *Stress corrosion*: This is a form of corrosion due to the presence of stress (residual or applied tensile stress) in combination with specific environment. The classic example is the *season cracking* of brass in ammoniacal atmosphere or humid atmosphere. The other important example is the caustic embrittlement of steel due to sodium carbonate and hydroxide. Another well known example is the stress corrosion cracking of Al–Zn–Mg alloys in chloride temperature. The most important method of preventing stress corrosion is to remove the stress. Therefore the components are stress relief annealed after fabrication to prevent this. In many cases, addition of certain chemicals called "inhibitors" can control stress corrosion.

To summarise, corrosion can be controlled by the following means and methods

(a) Coatings (oils, grease, tar, bitumin, paints, electrodeposited platings, enamels)
(b) Treatment of medium by addition of inhibitors (e.g potassium dichromatic for aluminium alloys); deaeration of water
(c) Use of sacrificial anodes (galvanising, protecting ship hulls, etc.)
(d) Better design to avoid crevices, bimetal contacts, stagnant water, etc.

Oxidation of Metals

Deterioration of metals by oxidation (i.e formation of scales) can be severe at high temperatures. A list of common metals arranged in the order of increasing resistance for oxidation is as follows;

Mg, *Al*, *Ti*, *Cr*, *Fe*, *Co*, *Ni*, *Cu*, *Ag*, *Au*. The noble metals (*Cu*, *Ag* and *Au*) are most resistant to oxidation. The rate of oxidation can be reduced after sometime if the oxide formed is non-porous and protective enough. This can be examined from the following criterion

The ratio of volume of oxide and volume of metal (called Pilling – Bed worth ratio) should be close to one.

***Problem*:** Compute the P. B ratio for the oxidation of magnesium?

Specific gravity of magnesium = 1.74×10^3 kg/m^3

Specific gravity of magnesium oxide is 3.58×10^3 kg/m^3

***Solution*:**

Assume that 100gm of magnesium alone is available

Molecular weight of Mg O = 40.32

Molecular weight of Mg = 24.32

24.3 kg is oxidized as 40.32 Mg O

100×10^{-3} kg will be oxidized as $\dfrac{40.32 \times 100}{24.3} = 167 \times 10^{-3}$ kg

$$\text{Volume of Mg} = \frac{100 \times 10^{-3}}{1.74 \times 10^{-3}} = 57.5 \times 10^{6}\ m^{3} = V_1$$

$$\text{Volume of Mg O} = \frac{167 \times 10^{-3}}{3.58 \times 10^{-3}} = 46.6 \times 10^{6}\, m^{3} = V_2$$

$$\text{P.B ratio} = \frac{V_2}{V_1} = \frac{46.6 \times 10^{6}}{57.5 \times 10^{6}} = 0.81 \quad \textbf{\textit{Answer}}$$

Q 10.7 Write a note on composite materials.

***Answer*:** A composite is an admixture of two or more materials to achieve a combination of properties not otherwise possible by using any of the materials alone. For example the properties needed in most structural materials are high strength or high modulus and low weight along with good toughness. High strength or high modulus and light weight are attained in glass, silica, carbon, boron, etc., in the form of fibers. But they may not possess high toughness or ductility. They easily undergo fracture which is caused by a rapid progress of a small crack. If, however, high quality fibers of these materials are produced and embedded in a ductile matrix (like a metal or plastic matrix) the composite has a combination of high toughness with high strength and low weight. The soft and ductile matrix protects the surface of the fibers from acquiring cracks and also arrests the propagation of cracks already present. Such composite materials are called fiber reinforced composites. In addition, composites can be developed by dispersing particles in a matrix (particulate composites) or by constructing a structure with layers or sheets of different materials (lamellar composites or laminates). There are many natural or organic materials which can be classified as composites. Wood, bamboo, bone and tooth are typical examples.

Fiber Reinforced Composites

In these, fibers usually of length, 1 to $10\,\mu m$, are the load bearing component. The matrix mainly transmits the load to fibers. It further protects the fibers from formation of cracks on the surface. The matrix being soft prevents the spreading of the crack from one fiber to the next. The interfacial bond between fiber and matrix must be strong.

The volume fraction of the fibers can be as high as 90%. The strength σ_c and Young's modulus E_e of a composite can be calculated from the following formulae:

$$\boxed{\begin{aligned} \sigma_c &= \sigma_f V_f + \sigma_m V_m \\ E_c &= E_f V_f + E_m V_m \\ V_m &= 1 - V_f \end{aligned}}$$

where the subscripts f and m refer to fiber and matrix respectively. It is assumed that the fibers are aligned in the direction of loading.

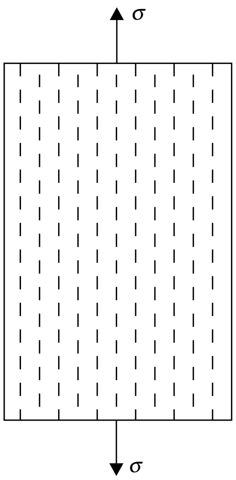


Fig. Q 10.7.1 *Alignment of fibers in a Composite*

Fibrous composites can retain their strength up to very high temperatures, usually 0.9 times the melting point of the matrix in degree kelvin. The combinations of fiber and matrix are: glass and epoxy; boron and epoxy, carbon and aluminium, boron and aluminium. Important applications of glass fiber reinforced plastics (GFRP) are used in boats, helmets, rifle tubes and helicopter rotor blades.

Particulate Composites

Here the matrix is the load bearing constituent. The hard or stiff phase that is dispersed strengthens the matrix and makes plastic deformation difficult. Typically the particle size would be 0.01 to $0.05\ \mu m$. The volume fraction of the hard particles is low, usually about 2 to 5%. The dispersion increases the recrystallisation temperature of the matrix. Particulate composites or dispersion hardened materials can withstand very high temperatures (0.7 – 0.8 times the melting point of the matrix). Typical examples of such composites are sintered aluminium powder (SAP) with dispersion of Al_2O_3 particles in aluminium and thoria – dispersed nickel (T D nickel).

***Problem*:** Calculate the Young's modulus of a composite with glass fibers reinforced in phenol formaldehyde plastics. The volume fraction of fraction of plastics is 33.3%. The modulus of glass fibers is 6.9×10^4 M P*a* and that of polymers 6.9×10^2 M P*a*

***Solution*:**

$$E_c = V_f\, E_f + V_m\, E_m$$

$$= \frac{2}{3} \times 6.9 \times 10^4 + \frac{1}{3} \times 6.9 \times 10^2 \approx 4.6 \times 10^4\ M\ Pa$$

Laminated Composites

Laminates are thin sheets of one material bonded to a second material to form a layer composite. Such composites have good mechanical properties in all directions of the plane. For instance in plywood layers of wood are stacked so that grain direction of one layer is at right angles to the directions in adjacent layers. The layers are then bonded with *epoxy resin*. Since wood has greater strength along the grain compared to the strength across the grain, wood does not have uniform properties in a plane. By forming plywood we are able to achieve a product of uniform or non directional strength. Another example is laminated plastics where woven mats of fiber glass are bonded by a resin.

Undirectionally Solidified Eutectics

Certain alloys of eutectic composition on solidification in a slow manner can develop a structure in which one of the phases get aligned in a direction in the form of rods or plates. For instance it is possible to produce rods with particles of a phase aligned along the length of the rod. Such composites can attain high strength in certain directions. A typical example is an alloy of aluminium with 33% copper in which $CuAl_2$ particle is aligned in a particular direction.

Wood

Wood is a natural composite. It consists of numerous cells with cell sap and cell walls. The cell walls contain basically cellulose and lignin. Both cellulose and lignin are organic polymers with high molecular weight. During the growth process, the cells are elongated in the longitudinal direction of the wood.

Further wood can absorb moisture. The important characteristics of wood are the *anisotropy* or directional nature of its properties such as Young's modules and dimensional change due to absorption of moisture and tensile strength. The properties are usually measured in the directions: longitudinal, radial and tangential. As an example, Young's modulus along these directions are approximately as follows:

$$E_{long} = 7000 - 14000\ MPa$$
$$E_{rad} = 550 - 1000\ MPa$$
$$E_{tan} = 400 - 700\ MPa$$

The result is wood undergoes wraping and splitting due to absorption of moisture or drying, or during cutting.

The properties of wood can be improved by several methods. One method is the formation of plywood. Another method is to fill the pores in cells with a polymer resulting in impregnated wood.

TABLES

Table 10.A *Temperature coefficient of Permittivity of some substances*

Material	*Temperature of permittivity,* $T_{c\in}$
Methylalcohol	$-0.0059/K$
Ethylalcohol	$-0.0057/K$
Chloroform	$-0.0041/K$
Na Cl	$+8.4 \times 10^{-4}/K$
Ka Cl	$+3.03 \times 10^{-5}/K$

Table 10.B *Electronic polarizability of some selected atoms*

Sl. No.	*Material*	*Electronic polarizability, α_e in 10^{-40}*
1.	He	0.12
2.	Ne	0.35
3.	A	1.43
4.	K*r*	2.12
5.	X*e*	3.54

Table 10.C *The electric strength of some materials*

Material	*Electric strength k V/metre*
Air	3000
Mineral oil	15000
Impregnated paper	15000
Polysterene	20000
Hard rubber	21000
Bakelite	25000
Glass	30000
Fused quartz	30000
Mica	200000

Table 10.D *Properties of some ferroelectric materials*

Sl. No.	*Material*	*Curie temperature (C/m^2)*	*Spontaneous polarization (K)*
1.	$NaK(C_4H_4O_6).4H_2O$	290	8000
2.	KH_2PO_4	123	16000
3.	BaT_iO_3	380	78000
4.	$KNbO_3$	708	80000
5.	WO_3	220	–
6.	$CdNb_2O_7$	185	5400

Table 10.E *General properties of mineral insulating oils*

Property	*Oils used in paper insulated cables*	*Oil used in capacitors*	*Oil used in transformers switches circuit breakers*
Specific gravity	0.93	0.885	0.885
Flash point	235 °C	165 °C	135 °C
Pour point	– 5 °C	– 45 °C	– 45 °C
Resistivity (Ω cm)	(1 to 10) × 10^{12}	(50 to 100) × 10^{12}	(1 – 10) × 10^{12}
Dielectric strength (kV/mm)	30 kV	30 kV	30 kV
Power factor at 100 °C at 50 Hz	0.001	0.001	0.001
Specific heat	–	0.412	0.4252

Table 10.F *Properties of polyethylene*

Properties	*Low density polyethylene*	*High density polyethylene*
Dielectric constant (at 10 Hz)	2.28 – 2.32	2.25 – 2.32
Dielectric strength (kV/mm)	20 – 160	20 – 160
Power factor (at 60 Hz)	(1 to 5) × 10^{-4}	(2 to 6) × 10^{-4}
Tensile strength (kg /cm^2 × 10^{-3})	0.09 – 0.16	0.16 – 0.365
Surface strength (Ω)	10^{14} – 10^{17}	10^{14} – 10^{15}
Volume resistivity (Ω cm)	10^{17} – 10^{19}	10^{15} – 10^{16}
Water absorption (%)	Less than 0.01	Less than 0.01
Elongation (%)	110 – 160	40 – 300
Softening temperature (°C)	94 – 110	–
Specific heat	0.55	–
Relative density	0.91 – 0.925	0.95 – 0.97
Crystalline melting point (°C)	110 – 1160	126 – 136

Table 10.G *Properties of polystyrene resin*

Properties	*Value*
Dielectric strength (kV/mm)	20 – 28
Power factor (60 Hz)	10 to 30 × 10^{-5}
Dielectric constant (60 Hz)	2.55
Insulation resistance	$10^{17} – 10^{19}$
Tensile strength (kg /cm^2 × 10^{-2})	0.35 – 0.65
Compressive strength (kg /cm^2 × 10^{-2})	0.78 – 1.12
Elongation %	1 – 3.5
Maximum temperature for continuous use (°C)	65 – 80
Molecular weight	6 × 10^4 – 50 × 10^4
Water absorption %	0.03 – 0.06
Specific heat	0.32
Specific gravity	1.06

Table 10.H *Properties of polyvinyl chloride*

Properties	*Value*
Specific gravity	1.03
Temperature of use (°C)	60 – 90
Insulation resistance (Ω cm)	$10^{12} – 10^{13}$
Britlle temperature (°C)	30
Softening temperature (°C)	12.0
Dielectric constant	5 – 6
Dielectric strength (kV/m)	30

Table 10.I *Properties of polyamide resins*

Properties	*Value*
Tensile strength (kg /cm^2)	0.5 × 10^{-3}
Dielectric strength (kV/mm)	20
Dielectric constant (60 Hz)	4 – 6
Maximum continuous strength	132 – 150
Melting point (°C)	200 – 255
Specific gravity	1.09

Table 10.J *General properties of two main types of mica*

Property	*Muscovity mica*	*Phylogopite mica*
Specific gravity	2.7 – 3.2	2.6 – 2.8
Tensile strength (kg /cm^2 × 10^{-3})	0.35 – 0.7	–
Maximum operating temperature	500 – 600	800 – 900
Moisture absorption	Low	Low
Resistivity at 25 °C (Ω – cm)	$10^{15} – 10^{16}$	$10^{12} – 10^{14}$
Dielectric strength (kV /mm at 25 °C)	80	60
Power factor at 27 °C	$1 \times 10^{-4} – 3 \times 10^{-4}$	$10 \times 10^{-4} – 50 \times 10^{-4}$

Table 10.K *Insulating materials for different applications*

Application	*Insulating material used*
1. Heating element of an oven	Nichrome
2. Fuse holder	Porcelains
3. Switch for domestic purpose	Backelite
4. Commutator	Mica
5. Cable joint box	Bitumen compound
6. Electric iron	Mica
7. Low voltage cable	Rubber
8. Flexible wire	Plastic
9. Distribution board	Wood
10. Laminating insulating boards	Epoxy Resins

Table 10.L *Questions with answers in Yes or No*

Question	*Answer*
1. Brass can stand more mechanical abuse than copper and is used for making flexible wire	No
2. Steel is not used as conducting materials in domestic switches	Yes
3. Nichrome is preferred for winding chokes in tube lights	No
4. P.V.C. insulation does not absorb moisture	Yes
5. Hydrogen is used mainly as a coolant	No
6. Mumetal is an alloy of iron and copper used as magnetic material for small electric motors	No
7. Lead is an alloy used as filament in bulbs	No
8. Aluminium can be soldered more easily than copper	No
9. A fuse material should have low melting point	No

Table 10.M *Properties of some types rubbers*

Property	*Natural rubber*	*Hard rubber*	*Butyl rubber*	*Neoprene*	*Nitrile Butadiene*	*Silicon*	*Hypalon*
1. Maximum service temperature (°C)	75	60	80 – 90	90	–	175 – 200	150
2. Water absorption %	1 – 2	0.2 – 1.0	0.3 – 0.5	3 – 4	–	0.5 – 2.4	–
3. Specific gravity	0.93–1.6	1.1 – 1.4	0.9 – 1.3	1.09 – 1.6	1	0.5 – 2.4	–
4. Tensile strength	0.21– 0.32	0.28 – 1.12	0.05 – 0.21	0.14 – 0.26	0.19 – 0.32	0.09 – 0.12	0.11 – 0.26
5. Dielectric strength (kV/mm)	18 – 24	12 – 28	16 – 32	4 – 20	16 – 20	12 – 28	16 – 24
6. Dielectric constant	2.7 – 5	2 – 16	2.1 – 4	7.5 – 14	3.9 – 10	2.8 – 7.0	5 – 11
7. Power factor	$0.05 - 2 \times 10^{-2}$	$0.5 - 2 \times 10^{-2}$	$0.3 - 8 \times 10^{-2}$	$1.0 - 6 \times 10^{-2}$	$3 - 5 \times 10^{-2}$	$0.1 - 1 \times 10^{-2}$	$2 - 9 \times 10^{-2}$
8. Volume resistance (Ω cm)	$10^{15} - 10^{17}$	10^{14}	$10^{14} - 10^{16}$	$10^{11} - 10^{12}$	$10^{12} - 10^{15}$	$10^{13} - 10^{17}$	$10^{13} - 10^{15}$
9. Surface resistance (Ω)	$10^{14} - 10^{15}$	–	$10^{13} - 10^{14}$	$10^{11} - 10^{12}$	$10^{12} - 10^{15}$	10^{13}	10^{14}

Table 10.N *Properties of important Ceramics*

	Property	*Alumina*	*High voltage porcelain*	*Low voltage porcelain*	*Steatite*	*Ziroon*
1.	Specific gravity	3.1 – 3.9	2.35 – 5.1	2.7 – 2.4	2.5 – 2.9	3.1 – 3.8
2.	Water absorption	0.0 – 0.2	0.0 – 0.5	0.5 – 2.7	0.0 – 0.03	0.0 – 0.02
3.	Dielectric constant (60 Hz, 25^{o}C)	8 – 9.5	5.7	5.5 – 7.0	5.7 – 6.5	7.1 – 9.1
4.	Power factor (× 10^3, 25^{o}C, 60 Hz)	0.5 – 1.5	8 – 25	7 – 20	1.2 – 2.0	1.5 – 36.0
5.	Tensile strength (kg/cm^2 × 10^3)	0.56 – 3.5	0.2 – 0.56	–	0.52 – 1.05	0.49 – 1.04
6.	Compressive strength (kg/cm^2×10^2)	5.6 – 3.0	1.75 – 5.6	1.75 – 4.2	4.2 – 30.5	5.6 – 7.0
7.	Volume resistivity (Ω cm, at 25^{0}C)	$10^{14} – 10^{16}$	$10^{12} – 10^{14}$	$10^{11} – 10^{14}$	$10^{12} – 10^{15}$	$10^{13} – 10^{15}$
8.	Softening temperature, ^{o}C	1450 – 2000	1300 – 1335	1300 – 1335	1300 – 1450	1390 – 1550
9.	Structure limiting temperature, ^{o}C	1400 – 1802	1000 – 1200	1000 – 1100	1000 – 1180	1000 – 1300
10.	Heat conductivity	7 – 50	2 – 8	3.4 – 4	5 – 8	1 – 15

Answers to Objective Questions

CHAPTER 1

1. (b)	**2.** (c)	**3.** (b)	**4.** (a)	**5.** (a)
6. (b)	**7.** (b)	**8.** (d)	**9.** (d)	**10.** (a)
11. (d)	**12.** (a)	**13.** (b)	**14.** (c)	**15.** (d)
16. (a)	**17.** (c)	**18.** (a)	**19.** (a)	**20.** (b)
21. (a)	**22.** (c)	**23.** (d)	**24.** (c)	

CHAPTER 2

1. (b)	**2.** (d)	**3.** (b)	**4.** (a)	**5.** (c)
6. (d)	**7.** (c)	**8.** (d)	**9.** (c)	**10.** (d)
11. (a)	**12.** (b)	**13.** (a)	**14.** (c)	**15.** (a)
16. (d)	**17.** (a)			

CHAPTER 3

1. (b)	**2.** (c)	**3.** (c)	**4.** (c)	**5.** (c)
6. (b)	**7.** (a)	**8.** (b)	**9.** (c)	**10.** (a)
11. (d)	**12.** (d)	**13.** (d)	**14.** (c)	**15.** (c)
16. (a)	**17.** (d)	**18.** (b)		

CHAPTER 4

1. (a)	**2.** (b)	**3.** (c)	**4.** (b)	**5.** (d)
6. (b)	**7.** (b)	**8.** (a)	**9.** (b)	**10.** (a)

11. (a) **12.** (a) **13.** (a) **14.** (d) **15.** (d)
16. (a) **17.** (b) **18.** (d) **19.** (a) **20.** (b)
21. (c) **22.** (b) **23.** (d) **24.** (a) **25.** (a)
26. (b) **27.** (a) **28.** (d) **29.** (a) **30.** (b)
31. (c) **32.** (d) **33.** (a) **34.** (d) **35.** (b)
36. (a) **37.** (a) **38.** (c) **39.** (b)

CHAPTER 5

1. (d) **2.** (c) **3.** (b) **4.** (a) **5.** (b)
6. (a) **7.** (a) **8.** (d) **9.** (c) **10.** (b)
11. (d) **12.** (d) **13.** (b) **14.** (c) **15.** (b)
16. (a) **17.** (a) **18.** (b) **19.** (a) **20.** (a)
21. (c) **22.** (a) **23.** (b) **24.** (d)

CHAPTER 6

1. (d) **2.** (b) **3.** (a) **4.** (d) **5.** (b)
6. (c) **7.** (c) **8.** (b) **9.** (c) **10.** (d)
11. (c) **12.** (d) **13.** (a) **14.** (c) **15.** (b)
16. (c) **17.** (b) **18.** (d) **19.** (a) **20.** (c)
21. (b) **22.** (d) **23.** (a) **24.** (a)

CHAPTER 7

1. (b) **2.** (d) **3.** (a) **4.** (b) **5.** (b)
6. (d) **7.** (c) **8.** (b) **9.** (d) **10.** (c)
11. (a) **12.** (a) **13.** (a) **14.** (c) **15.** (b)
16. (a) **17.** (a) **18.** (b) **19.** (c) **20.** (b)
21. (c) **22.** (a) **23.** (c) **24.** (c) **25.** (c)

CHAPTER 8

1. (b) **2.** (b) **3.** (a) **4.** (c) **5.** (a)
6. (c) **7.** (d) **8.** (a) **9.** (c) **10.** (b)
11. (d) **12.** (a) **13.** (b) **14.** (a) **15.** (c)
16. (b) **17.** (b) **18.** (a) **19.** (d) **20.** (b)
21. (c) **22.** (b) **23.** (a)

Appendices

APPENDIX A1

Fundamental Constants

Constant	*Symbol*	*Value*
Speed of light in a vacuum	c	2.997925×10^{8} m s^{-1}
Charge of proton	e	1.602189×10^{-19} C
Charge of electron	$-e$	
Avogadro constant	N_A	6.022045×10^{23} gmol^{-1}
Boltzmann constant	k_B	1.380662×10^{-23} J K^{-1}
Gas constant	$R = N_A k$	8.31441 J K^{-1} gmol^{-1}
Faraday constant	$F = N_A e$	9.648456×10^{4} C gmol^{-1}
Planck constant	h	6.626176×10^{-34} J s
	$\hbar = \dfrac{h}{2\pi}$	1.05457×10^{-34} J s
Vacuum permittivity	ϵ_0	8.854×10^{-12} Fm^{-1}
Vacuum permeability	μ_0	4p $\times 10^{-7}$ J s^{2} C^{-2} m^{-1}
Bohr magneton	μ_B	9.27402×10^{-24} J T^{-1}
Electron g value	g_e	2.00232

APPENDIX A2

Metric Prefixes

Prefix	*Symbol*	*Factor*
ultra	*u*	10^{15}
tetra	*T*	10^{12}
giga	*G*	10^{9}
mega	*M*	10^{6}
kilo	*k*	10^{3}
hecto	*h*	10^{2}
deka	*d*	10^{1}
–	–	10^{0}
deci	*d*	10^{-1}
centi	*c*	10^{-2}
milli	*m*	10^{-3}
micro	*μ*	10^{-6}
nano	*n*	10^{-9}
pico	*p*	10^{-12}
femto	*f*	10^{-15}
atto	*a*	10^{-8}

APPENDIX A3

Derived SI Units Having Special Names and Symbols

Physical quantity (and symbol)	*Name of SI unit*	*Symbol for SI derived unit and definition of unit*
Frequency (υ)	Hertz	Hz (= s^{-1})
Energy (U) Enthalpy (H)	Joule	J (= kg m^2 s^{-2})
Force	newton	N (=kg m s^{-2}=J m^{-1})
Power	watt	W (=kg m^2 s^{-3}= Js $^{-1}$)
Pressure (P)	pascal	Pa (= kg m^{-1} s^{-2}) = N m^{-2} = J m^{-3})
Electric charge (Q)	coulomb	C (=A s)
Electric potential difference (V)	volt	V (= kg m^2 s^{-3} A^{-1}= J A^{-1} s^{-1})
Capacitance (C)	farad	F (= A^2 s^4 kg^{-1} m^{-2} = A s V^{-1} = A^2 s^2 J^{-1})
Resistance (R)	ohm	Ω (= VA^{-1})
Conductance (G)	siemen	S (= A V^{-1})
Magnetic flux density (B)	tesla	T (= V s m^{-2} = J C^{-1} s m^{-2})

APPENDIX A4

Commercial Laser Types

Wave length (μ m)	*Type*	*Out put type and power*
0.192	Ar F excimer	Pulsed, tens of watt
0.266	Quadrupled Nd	Pulsed, watt
0.275 – 0.31	Argon ion	Continuous – wave (CW)
0.32 – 1.0	Pulsed dye	Pulsed, tens of watt
0.325	He – Cd	CW, tens of milli watt
0.33 – 0.36	Ar or Kr ion	CW, several watt
0.33 – 0.38	Neon	CW, 1-watt range
0.337	Nitrogen	Pulsed, under 1 watt
0.347	Doubled ruby	Pulsed, under 1 watt
0.442	He – Cd	CW, over 0.1 watt
0.5435	He – Ne	Cw, 1mW
0.48 – 0.54	Xenon ion	Pulsed, low power

APPENDIX A5

Advantages of SI Units

(i) It is comprehensive in the sense that its seven base cover all disciplines of science and technology.
(ii) The system is coherent as the unit of a derived quantity can be obtained as the product or quotient of two or more fundamentals.
(iii) It is internationally accepted.

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