NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: PHY 407

COURSE TITLE: SOLID STATE PHYSCICS II

COURSE GUIDE

PHY 407
SOLID STATE PHYSICS II

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INTRODUCTION

Solid state physics is a very important branch of physics that has to do with the study of rigid matter, or solids, through methods such as quantum mechanics, crystallography, electromagnetism, and metallurgy. It is known to be the largest branch of condensed matter physics. In this course you will learn how large-scale properties of solid materials result from their atomic-scale properties.

Solid materials are formed from densely-packed atoms, which interact intensely. These interactions produce the mechanical (e.g. hardness and elasticity), thermal, electrical, magnetic and optical properties of solids. Depending on the material involved and the conditions in which it was formed, the atoms may be arranged in a regular, geometric pattern (crystalline solids, which include metals and ordinary water ice) or irregularly (an amorphous solid such as common window glass).

What is the importance of solid state physics? Solid state physics applies everywhere around us. It involves how the macro-scale properties of solid materials result from their micro-scale properties. Most of the solids are arranged in such a way that their atoms are in an orderly repetitive arrays so the solids we see around are the examples of solid state physics e.g. sugar molecules, salt (Nacl), glass, etc. So, it forms the theoretical basis of material science. Its applications are in the technology of transistors and semiconductors. Quantum mechanics, metallurgy, electromagnetism, crystallography, etc. are all part and parcel of solid state physics.

THE COURSE

Solid State Physics II, is a 2-unit course made up of 1 module divided into 3 units.

Unit 1 deals with dielectric properties of solids, unit 2 explains the magnetic properties of solids and unit 3 elucidates the various imperfections in solids.

COURSE AIMS

The aim of this course is to teach you properties of solids and imperfections in solids.

COURSE OBJECTIVES

After studying this course, you should be able to:

- explain the dielectric properties of solid
- explain local electric field
- define dielectric constant, polarisability and susceptibility
- explain magnetisation of materials
- differentiate between diamagnetism and paramagnetism
- differentiate between ferromagnetism and antiferromagnetism
- explain magnetic resonance
- explain the various imperfections in solids.

WORKING THROUGH THE COURSE

Solid state physics is the theoretical foundation of material science. It has applications in the technology of transistors and semiconductors, which are important components in electronics. It is expected that you must have pass the prerequisite which is PHY 307. It is hoped that bearing this in mind, you would find enough motivation to thoroughly work at this course.

THE COURSE MATERIAL

You will be provided with a course guide and study material containing the study units.

At the end of the course, you will find a list of recommended textbooks which are necessary as supplements to the course material. However, note that it is not compulsory for you to acquire or indeed read all of them.

STUDY UNITS

The following units are contained in this course:

Module 1

Unit 1	Dielectric Properties of Solids
Unit 2	Magnetism
Unit 3	Imperfection in Solids

TEXTBOOK

Charles, K. (2005). *Introduction to Solid State Physics*. USA: John Wiley and Sons, Inc.

ASSESSMENT

There are two components of assessment for this course:

i. the self-assessment exercises, and
ii. the tutor-marked assignments.

The assessments are continuous assessment of each component of this course.

SUMMARY

This course is designed to lay a foundation for you for further studies in solid state physics. At the end of this course, you should be able to:

- explain polarisation and depolarisation fields
- discuss dielectrics
- define dipole moment
- define electric susceptibility and polarisability
- explain the relevance of Clausius-Mossotti equation to material sciences
- explain all the symbols in Langevin expression and state their SI units
- explain why the magnetic susceptibility of diamagnetic materials will always be less than zero
- differentiate between diamagnetism and paramagnetism
- list five materials that are diamagnetic and paramagnetic
- differentiate between ferromagnetism and antiferromagnetism.

We wish you all the best as you work through the course.

MAIN COURSE

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MODULE 1

Unit 1	Dielectric Properties of Solids
Unit 2	Magnetism
Unit 3	Imperfection in Solids

UNIT 1 DIELECTRIC PROPERTIES OF SOLIDS

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    3.3 Dielectric Constant and Polarisability
    3.4 Dipole Relaxation and Dielectric Losses
4.0 Conclusion
5.0 Summary
6.0 Tutor-Marked Assignment
7.0 Reference/Further Reading

1.0 INTRODUCTION

In the previous course on solid state physics, you learnt the crystal structure of solids, thermal and elastic properties of the crystal lattice. You will recall that a solid has been defined as a rigid substance in which the average positions of the constituent atoms form a lattice structure. In this course, our discussion is on the properties of solids. We will distinguish between the properties of different materials. Glass flows like liquids at high temperatures and copper exhibits characteristics of a crystal structure.

Solid state physics is the study of crystalline solids, through methods such as quantum mechanics, crystallography, electromagnetism, and metallurgy. It is the largest branch of condensed matter physics. Solid state physics studies how the large-scale properties of solid materials result from their atomic-scale properties. Thus, solid state physics forms the theoretical basis of material science. It has direct applications, for example in the technology of transistors and semiconductors.

Solid materials can be divided into two distinct groups on the basis of their behaviour under the influence of an external electric field.

i. Conductors – those in which there are electrons which are free to move in the presence of a field. Examples of these are metals, carbon, etc.
ii. Insulators or dielectrics – those in which the electrons are strongly bound to the atoms or molecules composing the material and cannot be detached by the application of an electric field to these materials. Examples of these are sulphur, porcelain, mica, etc.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- explain the dielectric properties of solid
- explain local electric field
- define dielectric constant, polarisability and susceptibility.

3.0 MAIN CONTENT

3.1 Dielectric Properties

A dielectric is a non-conducting material, such as glass, rubber, or waxed paper. The following are some of the properties of a dielectric:

i. when a dielectric material is inserted between the plates of a capacitor, the capacitance increases by a factor K, called the dielectric constant of the dielectric

$$C = KC_o \tag{1.1}$$

where C_o is the capacitance in the absence of the dielectric

ii. the dielectric constant K has no unit and it is characteristic of a given material

iii. f ε_o is the permittivity of free space and ε is the permittivity of the dielectric material, thus

$$K = \frac{\varepsilon}{\varepsilon_o} \tag{1.2}$$

iv. with the introduction of the dielectric materials, the energy density becomes

$$u = \frac{1}{2}\varepsilon \mathbf{E}^2 \tag{1.3}$$

i. the potential difference V between the plates when a dielectric material is inserted, provided that the charge remains unchanged, is given as

$$V = \frac{V_o}{K} \qquad (1.4)$$

where V_o is the potential difference when the dielectric is not inserted.

Equation (1.4) states that the potential difference V between the plates decreases by a factor of K.

ii. f the potential difference is kept unchanged when the dielectric material is inserted, then we have,

$$Q = KQ_o \qquad (1.5)$$

thus, the charge on a capacitor with a fixed potential difference between its plates is increased by factor K

iii. f the electric field between the parallel plate capacitor is E_o and it is E after the material with dielectric constant K is inserted into the space between the plates, then

$$E = \frac{E_o}{K} \qquad (1.6)$$

from equation (1.6), we see that the electric field within the dielectric is reduced by a factor equal to the dielectric constant

iv. Net field E within the dielectric is given as

$$E = E_o - E_{ind} \qquad (1.7)$$

where E_o is the original field and E_{ind} is the electric field induced

If you use Equation (1.6), (1.7) becomes,

$$\frac{E_o}{K} = E_o - E_{ind}$$

$$E_{ind} = E_o\left(1 - \frac{1}{K}\right) \qquad (1.8)$$

v. the induced electric field in the dielectric is related to the induced charge density σ_{ind} through the relationship $E_{ind} = \sigma_{ind}/\varepsilon_o$.

vi. from Equation (1.9), you have,

$$\sigma_{ind} = \sigma\left(1 - \frac{1}{K}\right) \qquad (1.9)$$

and

$$Q_{ind} = Q\left(1 - \frac{1}{K}\right) \qquad (1.10)$$

since K is always greater than 1, these expressions [Equations (1.8), (1.9), and (1.10)] show that $E_{ind} > E_o$, $\sigma_{ind} > \sigma$ and $Q_{ind} > Q$.

3.2 Local Electric Field

It should be noted that:

- every material is made up of a very large number of atoms/molecules
- an atom consists of a positively charged nucleus and negatively charged electrons
- a system consisting of two equal and opposite charges *q*, separated by a certain distance *d*, is an electric dipole
- when an atom or a molecule of a dielectric is placed in an electric field, the positive and negative charges feel opposite forces and are separated forming a dipole.

Suppose the charges -*q* and +*q* are placed, respectively, at *d*/2 and –*d*/2 from the origin, as shown in Figure 1. The magnitude of the potential due to this system at a point *X* is given by

$$\Phi(r) = \frac{q}{4\pi\varepsilon_o}\left(\frac{1}{r_1} - \frac{1}{r_2}\right) \qquad 1.11$$

where r_1, r_2 are the distances of *X* from + *q* and – *q* respectively.

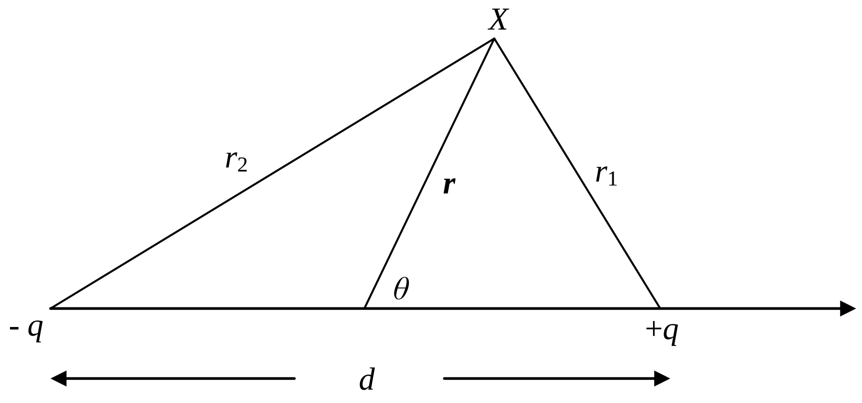

Fig. 1.1: Dipole

If θ is the angle between the axis of the charges and the position vector of X, we can write

$$\frac{1}{r_1} \approx \frac{1}{r} + \frac{d\cos\theta}{2r^2}$$

and

$$\frac{1}{r_2} \approx \frac{1}{r} - \frac{d\cos\theta}{2r^2}$$

Substituting in (11)

$$\Phi(r) = \frac{q}{4\pi\varepsilon_o}\frac{d\cos\theta}{r^2} \qquad 1.12$$

The dipole moment, ***p***, is the vector along the axis of the dipole pointing in the direction – *q* to + *q* and having magnitude *qd*.

In terms of the dipole moment, you can see that Eq. 1.12 becomes

$$\Phi(r) = \frac{p\cos\theta}{4\pi\varepsilon_o r^2} = \frac{\bar{p}.\bar{r}}{4\pi\varepsilon_o|r|^3} \qquad 1.13$$

Using $\nabla\left(\frac{1}{r}\right) = -\frac{\bar{r}}{|r|^3}$, the Eq. (1.13) can be written as

$$\Phi(r) = -\frac{\bar{p}}{4\pi\varepsilon_o r^2}\cdot\nabla\left(\frac{1}{r}\right) = -\bar{p}\cdot\nabla\Phi_o. \qquad 1.14$$

where Φ_o is the potential of a unit charge.

The field of an electric dipole may also be expressed in the following way,

$$\bar{E} = -\nabla\Phi = -\frac{1}{4\pi\varepsilon_o}\nabla\left(\frac{\bar{p}\cdot\bar{r}}{|r|^3}\right)$$

$$= \frac{1}{4\pi\varepsilon_o}\left[\frac{3(\bar{p}\cdot\bar{r})\bar{r} - r^2\bar{p}}{r^5}\right] \qquad 1.15a$$

In Centimetre-Gram-Second (CGS) system of units, Eq. (1.15a) becomes

$$\bar{E} = \frac{3(\bar{p}\cdot\bar{r})\bar{r} - r^2\bar{p}}{r^5} \qquad 1.15b$$

Considering a cubic crystal dielectric Figure 1.2 and assume an electric field of magnitude E_o is applied parallel to one of the axes of the crystal. The field will push the positively charged nucleus of the atoms of the dielectric slightly in the direction of the field and negatively charged electrons in the opposite direction, as shown in Figure 1.2. We say that the atom is polarised under the influence of the applied external field and the charges are called polarisation charges.

The polarisation **P** is defined as the dipole moment **p** per unit volume, averaged over the volume of a cell. The total dipole moment is defined as

$$\overline{P} = \sum q_n \overline{r_n} \qquad 1.16$$

Let us imagine that a small sphere is cut out of the specimen around the reference point; then $\mathbf{E}_1$ is field of the polarisation charges on the inside of the cavity left by the sphere, and $\mathbf{E}_2$ is the field of the atoms within the cavity. The polarisation charges on the outer surface of the specimen produce the depolarisation field, $\mathbf{E}_3$. The depolarisation field is opposite to **P**, that is, the field $\mathbf{E}_3$ is called depolarisation field, because within the body it tends to oppose the applied field $\mathbf{E}_o$ as in Figure 1.2. The dielectric acquires a polarisation due to the applied electric field $\mathbf{E}_o$. This polarisation is the consequence of redistribution of charges inside the dielectric.

The local electric field $\mathbf{E}_{loc}$ at any atom of the dielectric may be written as

$$\mathbf{E}_{loc} = \mathbf{E}_o + \mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3 \qquad 1.17$$

The contribution $\mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3$ is the total effect at one atom of the dipole moments of all the other atoms in the system (in CGS units):

$$E_1 + E_2 + E_3 = \frac{3(\overline{p} \cdot \overline{r})\overline{r} - r^2 p}{r^5} \qquad 1.18a$$

and in SI unit

$$E_1 + E_2 + E_3 = \frac{1}{4\pi\varepsilon_o}\left[\frac{3(\overline{p} \cdot \overline{r})\overline{r} - r^2 p}{r^5}\right] \qquad 1.18b$$

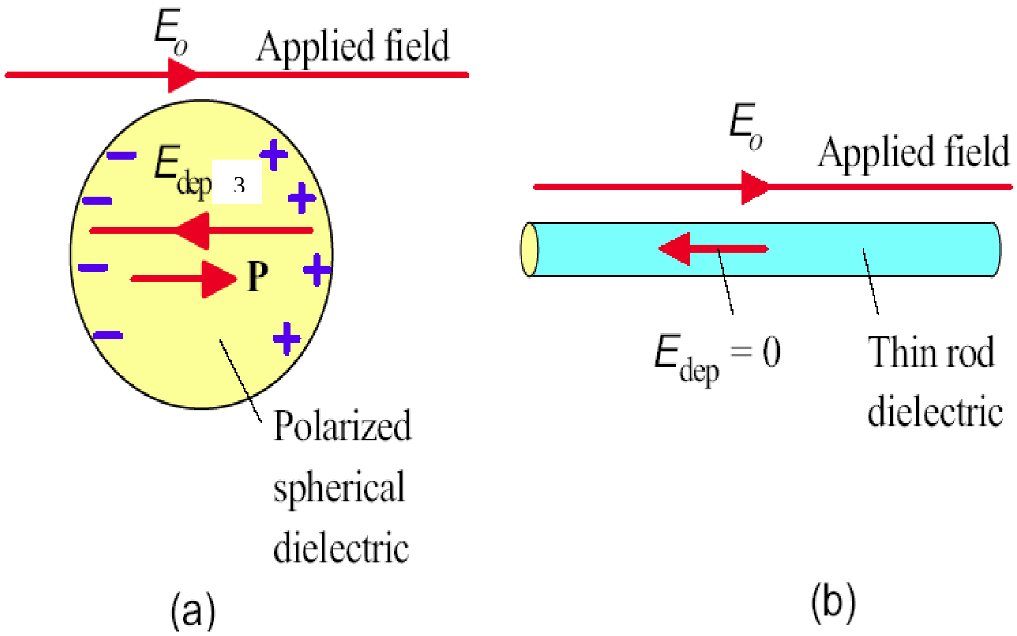

Fig. 1.2: The Depolarisation Field is Opposite to P

Lorentz showed that the field $\mathbf{E}_1$ due to the polarisation charges on the surface formed a continuous distribution. The density of the surface charge is equal to $\mathbf{P}\cos\theta$, where θ is the polar angle along the direction of polarisation in Figure 3.

$$E_1 = \int_0^{\pi} \left(R^{-2}\right)\left(2\pi R\sin\theta\right)\left(\overline{P}\cos\theta\right)\left(\cos\theta\right)\left(Rd\theta\right) = \frac{4\pi\overline{P}}{3} \qquad 1.19$$

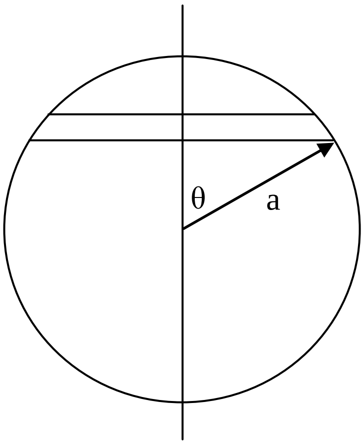

Fig. 3: Calculation of $\mathbf{E}_1$

The field $\mathbf{E}_2$ due to the dipoles within the spherical cavity is the only term that depends on the crystal structure. It can be shown that for a reference site with cubic surroundings in a sphere that $\mathbf{E}_2 = 0$ if all the atoms may be replaced by point dipoles parallel to each other.

For specimens in the shape of ellipsoids oriented with one of the principal axes parallel to the applied field, it can be shown that the depolarisation field will be parallel to the applied field and

$$\bar{E} = -\frac{N\bar{P}}{\varepsilon_o} \qquad 1.20a$$

The constant N is known as the depolarisation factor.

If P_x, P_y, P_z are the components of the polarisation **P** referred to the principal axes of an ellipsoid, then the components of the depolarisation field are written

$$E_{3x} = -\frac{N_x P_x}{\varepsilon_o}; \quad E_{3y} = \frac{-N_y P_y}{\varepsilon_o}; \quad E_{3z} = \frac{-N_z P_z}{\varepsilon_o}; \qquad 1.20b$$

SELF-ASSESSMENT EXERCISE

i. Explain polarisation and depolarisation fields.
ii. What are dielectrics?
iii. Define dipole moment.

3.3 Dielectric Constant and Polarisability

Let us now consider the dielectric behaviour of molecules which have a permanent dipole moment. The dielectric constant ε has been defined for an isotropic or cubic medium relative to vacuum as:

$$\varepsilon = \frac{D}{E} = 1 + \frac{P}{\varepsilon_o E} = 1 + \chi \qquad 1.21a$$

where χ is the electric susceptibility.

The susceptibility (in SI unit) is related to the dielectric constant by

$$\chi = \frac{P}{\varepsilon_o E} = \varepsilon - 1 \qquad 1.21b$$

If the field is not too large, the strength of the induced dipole moment in an atom i is proportional to the local electric field acting on the dielectric. That is

$$p_i \; \alpha \; E_{loc}$$

$$p_i = \alpha_i E_{loc}^{i} \qquad 1.22$$

where α_i is the polarisability and p_i is the dipole moment of atom *i*.

Polarisability has the SI units of $\mathrm{C{\cdot}m^2{\cdot}V^{-1}} = \mathrm{A^2{\cdot}s^4{\cdot}kg^{-1}{\cdot}m^{-1}}$ but is more often expressed as polarisability volume with units of $\mathrm{cm^3}$ or in $\mathrm{Å^3} = 10^{-24}\ \mathrm{cm^3}$.

The polarisation of a crystal may be expressed approximately as the product of the polarisabilities of the atoms times the local electric field:

$$P = \sum_i N_i p_i = \sum_i E^i_{loc} N_i \alpha_i \qquad 1.23$$

where N_i is the number per unit volume of atom *i*.

Electric susceptibility can now be defined as

$$\chi = \frac{P}{E} = \frac{\sum E^i_{loc} N_i \alpha_i}{E_{loc} - \frac{4\pi}{3} P}$$

Using Eqs. (1.23) and the Lorentz relation, you will have:

$$\frac{P}{E} = \frac{\sum_i E^i_{loc} N_i \alpha_i}{E^i_{loc} - \frac{4\pi}{3} \sum_i E^i_{loc} N_i \alpha_i} = \frac{\sum_i N_i \alpha_i}{1 - \frac{4\pi}{3} \sum_i N_i \alpha_i} = \frac{\varepsilon - 1}{4\pi} \qquad 1.24$$

Hence (in CGS)

$$\sum_i N_i \alpha_i = \frac{3}{4\pi} \left(\frac{\varepsilon - 1}{\varepsilon + 2} \right) \qquad 1.25$$

Eq. (1.25), known as Clausius-Mossotti equation, expresses the relation between the dielectric constant and the atomic polarisabilities.

You can calculate the dielectric constant of various materials from the polarisability by use of the Clausius-Mossotti equation. This equation holds fairly accurately for non-polar substances but it fails completely in pure polar liquids or solids.

The total polarisability of an atom can be separated into three parts: electronic, ionic, and orientational. The electronic contribution arises from the deformation of the electron shell about a nucleus. The ionic or atomic contribution comes from the displacement and deformation of a charged ion with respect to other ions. The orientational or dipolar polarisability arises when the substance is built up of molecules possessing a permanent electric dipole moment which may be more or less free to change orientation in an applied electric field.

In general, the total polarisability is given by

$$\alpha = \alpha_{dipolar} + \alpha_{ionic} + \alpha_{electronic} \qquad 1.26$$

which is the sum of the dipolar, ionic, and electronic polarisabilities, respectively. The electronic contribution is present in any type of substance, but the presence of the other two terms depends on the material under consideration.

SELF-ASSESSMENT EXERCISE

i. Define electric susceptibility and polarisability.
ii. Explain the relevance of Clausius-Mossotti equation to material sciences.

3.4 Dipole Relaxation and Dielectric Losses

Dipole relaxation time is the time interval characterising the restoration of a disturbed system to its equilibrium configuration; the relaxation frequency is defined as the reciprocal of the relaxation time. The orientational contribution to the dielectric constant is a major cause to the difference between the low frequency dielectric constant and the high frequency dielectric constant. The orientational relaxation frequencies are strongly dependent on the temperature and frequency as:

$$\alpha = \frac{\alpha_o}{1 + i\omega\tau} \qquad 1.27$$

where τ is known as Debye relaxation time, α_0 is the static orientational polarisability and ω is the angular frequency.
In liquids the relaxation time, for a molecule of radius a can be expressed as:

$$\tau = \frac{4\pi\eta a^3}{kT} \qquad 1.28$$

4.0 CONCLUSION

In this unit we have reviewed the dielectric properties of a solid in a capacitor. You have also seen the generation of local electric field, polarisation and depolarisation fields. We also defined dielectric constant, polarisability and susceptibility.

5.0 SUMMARY

- Solid materials can be divided into two distinct groups on the basis of their behaviour under the influence of an external electric field: Conductors and Insulators or dielectrics.
- The dipole moment, ***p***, is the vector along the axis of the dipole pointing in the direction – q to + q and having magnitude qd.
- The polarisation **P** is defined as the dipole moment **p** per unit volume, averaged over the volume of a cell. The total dipole moment is defined as $\overline{P} = \sum q_n \overline{r_n}$
- The polarisation charges on the outer surface of a specimen produce the depolarisation field. The depolarisation field is opposite to **P**.
- The local electric field $\mathbf{E}_{\text{loc}}$ at any atom of the dielectric may be written as

$$\mathbf{E}_{\text{loc}} = \mathbf{E}_{\text{o}} + \frac{3(\overline{p} \cdot \overline{r})\overline{r} - r^2 p}{r^5}$$

and in SI unit

$$\mathbf{E}_{\text{loc}} = \mathbf{E}_{\text{o}} + \frac{1}{4\pi\varepsilon_o}\left[\frac{3(\overline{p} \cdot \overline{r})\overline{r} - r^2 p}{r^5}\right]$$

- For specimens in the shape of ellipsoids oriented with one of the principal axes parallel to the applied field, it can be shown that the depolarisation field will be parallel to the applied field and $\overline{E} = -\frac{N\overline{P}}{\varepsilon_o}$. The constant N is known as the depolarisation factor.
- The dielectric constant ε has been defined for an isotropic or cubic medium relative to vacuum as: $\varepsilon = \frac{D}{E} = 1 + \frac{P}{\varepsilon_o E} = 1 + \chi$

  where χ is the electric susceptibility.
- The susceptibility (in SI unit) is related to the dielectric constant by $\chi = \frac{P}{\varepsilon_o E} = \varepsilon - 1$
- If the field is not too large, the strength of the induced dipole moment in an atom i is proportional to the local electric field acting on the dielectric. That is $p_i = \alpha_i E^i_{loc}$ where α_{i} is the polarisability and p_i is the dipole moment of atom i.

- The polarisation of a crystal may be expressed approximately as the product of the polarisabilities of the atoms times the local electric field: $P = \sum_i N_i p_i = \sum_i E^i_{loc} N_i \alpha_i$ where N_i is the number per unit volume of atom *i*.
- In CGS, $\sum_i N_i \alpha_i = \frac{3}{4\pi}\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)$ known as Clausius-Mossotti equation, expresses the relation between the dielectric constant and the atomic polarisabilities.

6.0 TUTOR-MARKED ASSIGNMENT

1. Two parallel plates have equal and opposite charges. When the space between the plates is evacuated, the electric field is 1.2 x 10^5 V/m, the electric field within the dielectric is 2 x 10^5 V/m. Calculate the induced charge density on the surface of the dielectric.
2. A parallel plate air capacitor is made of 0.2 m square tin plates and 1 cm apart. It is connected to a 50 V battery. What is the charge on each plate?
3. The plates of a parallel-plate capacitor are 2 mm apart and 5 m^2 in area. The plates are in vacuum. A potential difference of 2000 volts is applied across the capacitor. Calculate the magnitude of the electric field between the plates.
4. Find the frequency dependence of the electronic polarisability of an electron having the resonance frequency ω_o, treating the system as a simple harmonic oscillator.
5. Calculate the individual dipole moment p of a molecule of carbon tetrachloride given the following data.

   Relative permittivity $\varepsilon_r = 2.24$
   Density = 1.60 g/cm^3
   Molecular weight = 156
   Field = 10^7 volts/metre
   Find also the average electron displacement.

7.0 REFERENCE/FURTHER READING

Charles, K. (2005). *Introduction to Solid State Physics*. USA: John Wiley and Sons, Inc.

UNIT 2 MAGNETISM

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1.0 INTRODUCTION

You should understand that:

- a bar magnet has its magnetism concentrated mainly at the ends or poles
- these poles are called north (N) and south (S)
- two bar magnets will either attract each other or repel each other when their poles are placed close to each other
- the pole-force law or law of poles states that like magnetic poles repel each other, and unlike magnetic poles attract each other
- magnetic poles always occur in pairs, never singly
- two opposite poles form a *magnetic dipole*, if a magnet is broken in an attempt to separate the poles, one finds two new magnets each having a north and a south pole
- the direction of a magnetic field **B** at any point is the direction that the north pole of a compass at that location would point.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- explain magnetisation of materials
- differentiate between diamagnetism and paramagnetism
- differentiate between ferromagnetism and antiferromagnetism
- explain magnetic resonance.

3.0 MAIN CONTENT

3.1 Magnetisation

In this section we explain the magnetisation of materials and how it relates to magnetic field intensity. A material substance acquires a magnetic polarisation when placed in a magnetic field just as a dielectric medium acquires an electric polarisation in an electric field. The response of the materials to an applied magnetic field depends on the properties of the individual atoms and molecules, and on their interactions. The orbital motion of the electrons in atoms and molecules provide currents which give rise to the magnetic dipoles. In many materials the small electric currents associated with the orbital motion and spin of the electrons average to zero. When such atoms are placed in a magnetic field, minute electron currents are generated by induction in the clouds of electrons, the direction of which is such that the magnetic field associated with them opposes the inducing field **B**. These are known as diamagnetic substances.

There are other materials in which the atoms do have an intrinsic magnetic moment on account of the fact that the currents from the orbital motions and spins of the electrons do not average to zero. Although electron spins tend to pair and cancel one another, there are atoms in which pairing is incomplete. When such materials are placed in a magnetic field, the magnetic moments of the atoms and the induced magnetism enhances the external field. This effect is more pronounced at low temperatures. Such substances are called paramagnetic substances.

Every atom or molecule may be regarded as a tiny magnetic dipole with the magnetic moment

$$Q_m l = \hat{e}_n \, IdS \qquad 2.1$$

where Q_m is the magnetic pole strength, l is the pole separation, I is the current and dS is the area of the loop. The effect of atomic magnets is described by a quantity called magnetisation **M** which is defined as the magnetic dipole moment per unit volume.

In many materials it is found that the magnetisation **M** is linearly proportional to magnetic field intensity **H**, that is

$$\overline{M} = \chi_m \overline{H} \qquad 2.2$$

where χ_m is a dimensionless constant called the magnetic susceptibility of the material. The susceptibility is a function of temperature.

3.2 Diamagnetism

Substances with a negative magnetic susceptibility are called *diamagnetic*. Diamagnetism, to a greater or lesser degree, is a property of all materials and will always make a weak contribution to the material's response to a magnetic field. However, for materials that show some other form of magnetism (such as ferromagnetism or paramagnetism), the diamagnetic contribution becomes negligible. Substances that mostly display diamagnetic behaviour are termed diamagnetic materials, or diamagnets. Materials that are said to be diamagnetic are those that are usually considered by non-physicists to be *non-magnetic*, and include water, wood, most organic compounds such as petroleum and some plastics, and many metals including copper, particularly the heavy ones with many core electrons, such as mercury, gold and bismuth. The magnetic susceptibility of various molecular fragments is called *Pascal's Constants*.

Diamagnetic materials have a relative magnetic permeability that is less than or equal to 1, and therefore a magnetic susceptibility which is less than 0. This means that diamagnetic materials are repelled by magnetic fields. However, since diamagnetism is such a weak property its effects are not observable in everyday life. For example, the magnetic susceptibility of diamagnets such as water is $\chi = -9.05\times10^{-6}$. The most strongly diamagnetic material is bismuth, $\chi = -1.66\times10^{-4}$, although pyrolytic carbon may have a susceptibility of $\chi = -4.00\times10^{-4}$ in one plane. Nevertheless, these values are orders of magnitudes smaller than the magnetism exhibited by paramagnets and ferromagnets.

All conductors exhibit an effective diamagnetism when they experience a changing magnetic field. The Lorentz force on electrons causes them to circulate around forming eddy currents. The eddy currents then produce an induced magnetic field which opposes the applied field, resisting the conductor's motion.

The magnetic susceptibility per unit volume is defined as

$$\chi_m = \frac{M}{H} \qquad 2.3,$$

where *M* is the magnetic moment per unit volume, or *magnetisation,* and *H* is the magnetic field intensity. Diamagnetism explains the tendency of electrical charges to partially shield the interior of a body from applied magnetic field. For an atom in a magnetic field the motion of the electrons is the same as a possible motion in the absence of H except for the superposition of a common precession of angular frequency

$$\omega_L = -\frac{eH}{2mc} \qquad 2.4$$

The precession of the electron distribution is equivalent to diamagnetic current

$$I = \frac{(Ze)(eH/2mc)}{2\pi c} \qquad 2.5$$

As the magnetic moment μ of a current loop is given by the product of the current by the area of the loop, we have

$$\frac{\mu}{H} = -\left(\frac{Ze^2}{4mc^2}\right)\overline{\rho^2} \qquad 2.6$$

for Z electrons, where $\overline{\rho^2} = \overline{x^2} + \overline{y^2}$ is the average of the square of the perpendicular distance of the electron from the field axis. In terms of the mean square distance $\overline{r^2} = \overline{x^2} + \overline{y^2} + \overline{z^2}$ from the nucleus, we have

$$\overline{r^2} = \frac{3}{2}\overline{\rho^2} \qquad 2.7$$

for a distribution of charge which on the average is spherically symmetrical, so that $\overline{x^2} = \overline{y^2} = \overline{z^2}$. Then the diamagnetic susceptibility per unit volume is, if *N* is the number of atoms per unit volume,

$$\chi = -\frac{Ze^2 N}{6mc^2}\overline{r^2} \qquad 2.8$$

Equation (2.8) is the Langevin expression that be used to calculate diamagnetic susceptibility.

SELF-ASSESSMENT EXERCISE

i. Explain all the symbols in Langevin expression and state their SI units.
ii. Explain why the magnetic susceptibility of diamagnetic materials will always be less than zero.

3.3 Paramagnetism

We have discussed diamagnetism in the previous section. Now we will discuss paramagnetism. Substances with a positive susceptibility are called *paramagnetic.* Positive susceptibility can be found in:

- all atoms and molecules that has odd number of electrons. Examples of such atoms and molecules include: sodium atoms; nitrogen II oxide (NO)
- all free atoms and ions with a partly filled inner shell: transition elements; ions isoelectronic with transition elements; rare earth and actinide elements. Examples include Mn^{2+}, Gd^{3+}, U^{4+}
- metals.

Paramagnetism is a form of magnetism whereby the paramagnetic material is only attracted when in the presence of an externally applied magnetic field. In contrast with this behaviour, diamagnetic materials are repelled by magnetic fields. Paramagnetic materials have a relative magnetic permeability greater or equal to unity (i.e., a positive magnetic susceptibility) and hence, are attracted to magnetic fields. The magnetic moment induced by the applied field is linear in the field strength and rather weak. Paramagnetic materials have a small, positive susceptibility to magnetic fields. These materials are slightly attracted by a magnetic field and the material does not retain the magnetic properties when the external field is removed. Paramagnetic properties are due to the presence of some unpaired electrons, and from the realignment of the electron paths caused by the external magnetic field. Paramagnetic materials include magnesium, molybdenum, lithium, and tantalum.

Unlike ferromagnets, paramagnets do not retain any magnetisation in the absence of an externally applied magnetic field, because thermal motion randomises the spin orientations. Some paramagnetic materials retain spin disorder at absolute zero, meaning they are paramagnetic in the ground state. Thus the total magnetisation drops to zero when the applied field is removed. Even in the presence of the field there is only a small induced magnetisation because only a small fraction of the spins will be oriented by the field. This fraction is proportional to the field strength and this explains the linear dependency. The attraction experienced by ferromagnetic materials is non-linear and much stronger, so that it is easily observed, for instance, by the attraction between a refrigerator magnet and the iron of the refrigerator itself.

Consider a paramagnetic material containing N atoms per unit volume, each having a magnetic moment μ. If a magnetic field **H** is applied to the material magnetisation occurs from the orientation of the magnetic moments and thermal disorder resists the tendency of the applied field to orient the moments. The energy of interaction with the applied magnetic field is

$$V = -\mu \cdot H \qquad 2.9$$

For thermal equilibrium, the magnetisation can be derived as

$$M = N\mu L(a) \qquad 2.10$$

where $a = \mu H / kT$, and the Langevin function $L(a)$ is

$$L(a) = ctnh\ a - \frac{1}{a}$$

For $a << 1$, $L(a)$ = a/3, and

$$M \cong N\mu^2 H / 3kT. \qquad 2.11$$

In the limit $\mu H / kT << 1$, the magnetic susceptibility is

$$\chi = M/H = N\mu^2 / 3kT = C/T\,, \qquad 2.12$$

where $C = N\mu^2 / 3k$ is known as Curie constant. The $1/T$ temperature dependence is known as the Curie law. Equation (2.12) is known as Langevin equation.

SELF-ASSESSMENT EXERCISE

i. Differentiate between diamagnetism and paramagnetism.
ii. List five materials that are diamagnetic and paramagnetic.

3.4 Ferromagnetism

In the previous sections we differentiated between diamagnetism and paramagnetism. Now, we will explain ferromagnetism and antiferromagnetism. Ferromagnetism is the basic mechanism by which certain materials (such as iron) form permanent magnets, or are attracted to magnets. In physics, several different types of magnetism are distinguished. Ferromagnetism (including ferrimagnetism) is the strongest type; it is the only type that creates forces strong enough to be felt, and is responsible for the common phenomena of magnetism encountered in everyday life. Other substances respond weakly to magnetic fields with two other types of magnetism, paramagnetism and diamagnetism, but the forces are so weak that they can only be detected by sensitive instruments in a laboratory. An everyday example of ferromagnetism is a refrigerator magnet used to hold notes on a refrigerator door.

Permanent magnets (materials that can be magnetised by an external magnetic field and remain magnetised after the external field is removed) are either ferromagnetic or ferrimagnetic, as are other materials that are noticeably attracted to them. Only a few substances are ferromagnetic. The common ones are iron, nickel, cobalt and most of their alloys, some compounds of rare earth metals, and a few naturally-occurring minerals such as lodestone.

Ferromagnetism is very important in industry and modern technology, and is the basis for many electrical and electromechanical devices such as electromagnets, electric motors, generators, transformers, and magnetic storage such as tape recorders, and hard disks.

We now derive the Curie-Weiss law. We discuss the physical origin and properties of the saturation magnetisation in ferromagnetic. The properties of ferromagnetic materials of interest in technical applications are closely related to the domain structure. Iron, nickel and cobalt are known as transition elements; they and their alloys react very strongly in a magnetic field. They are ferromagnetic and have very high values of magnetic susceptibility. In ferromagnetic materials, the mutual coupling forces between neighboring molecular dipole moments are sufficiently stronger than the randomising effect of thermal agitation and the dipoles are all aligned parallel within a small region known as domain.

3.4.1 Curie-Weiss Law

Ferromagnetic materials are substance that possesses a magnetic moment even in the absence of an applied magnetic field. The saturation magnetisation M_s is defined as the spontaneous magnetic moment per unit volume. The Curie point T_c is the temperature above which the magnetic moment vanishes.

If the ionic and atomic magnetic moments of a paramagnetic substance can be made to line up the same way by the addition of an interaction then a ferromagnetic substance will be formed. This interaction is called Weiss field or the molecular field or the exchange field. Weiss was the first to imagine such a field. The motion of thermal agitation of the elementary particles opposes the orienting effect of the Weiss field.

Pierre Weiss assumes that the Weiss field B_E is proportional to the magnetisation:

$$B_E = \lambda M \tag{2.13}$$

where λ is the Weiss field constant, independent of temperature. The susceptibility above the Curie point can be deduced from the Curie law (Eq. 2.12). That is:

$$\frac{M}{B_E + \lambda M} = \frac{C}{T} \tag{2.14}$$

Note that we have taken the magnetic field as the sum of the applied field B and the Weiss field B_E.

You can easily see that Eq. (2.14) can be rewritten as

$$\chi = \frac{M}{H} = \frac{C}{T - C\lambda} \tag{2.15}$$

This gives a non-zero magnetisation for zero applied field at the Curies point expressed by

$$T_c = C\lambda, \tag{2.16}$$

Therefore,

$$\chi = \frac{C}{T - T_c}. \tag{2.17}$$

Eq. (2.17) is known as the *Curie-Weiss law*. This law describes the observed susceptibility variation in the paramagnetic region above the Curie point.

Let us now determine the value of the mean field constant λ. An atom with angular momentum quantum number J has $2J + 1$ equally spaced energy levels in a magnetic field and the magnetisation is given by

$$M = NgJ\mu_B B_J(x), \tag{2.18}$$

where $x = gJ\mu_B H/kT$, and the Brillouin function B_J is given by

$$B_J = \frac{2J+1}{2J} ctnh\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J} ctnh\left(\frac{x}{2J}\right) \qquad 2.19$$

For $x << 1$, the susceptibility is

$$\chi = NJ(J+1)g^2\mu_B^2/3kT = Np^2\mu_B^2/3kT, \qquad 2.20$$

where the effective number of Bohr magnetons is defined as

$$p = g[J(J+1)]^{1/2}. \qquad 2.21$$

The value of Weiss field constant can be determined as follows:

$$\lambda^{-1} = \frac{C}{T_c} = NS(S+1)g^2\mu_B^2/3kT_c, \qquad 2.22$$

where *S* is spin angular momentum quantum number.

3.4.2 Spontaneous Magnetisation

In this section you will see how we can determine the spontaneous magnetisation of a ferromagnetic substance. A ferromagnetic substance is said to have a spontaneous magnetic moment if it possesses a magnetic moment even in the absence of an applied magnetic field. In order to calculate the spontaneous magnetisation as a function of temperature we must use Eq. (2.18).

We have

$$M_s = NSg\mu_B B_s(x), \qquad 2.23$$

In the absence of an applied magnetic field

$$x = Sg\mu_B\lambda M_s / kT \qquad 2.24$$

Please note that at a temperature $T < T_c$ we obtain M_s by plotting M_s vs. x as given by both (2.23) and (2.24) and the intercept of the two curves gives M_s.

3.4.3 Domain Theory of Ferromagnetism

Every piece of a ferromagnetic material does not have a strong magnetic field, despite the fact that all the spins are aligned. Iron and other ferromagnets are often found in an "unmagnetised" state. At temperatures well below the Curie point the electronic magnetic moments of a ferromagnetic specimen are essentially all lined up.

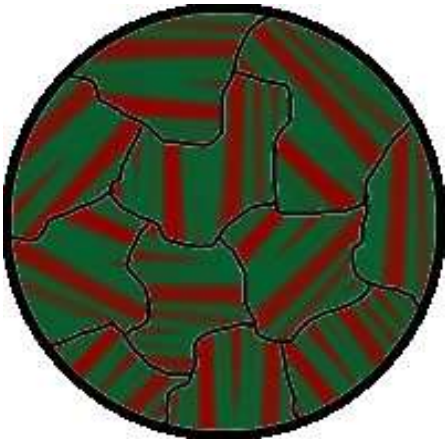

Fig. 2.1: Weiss Domains Microstructure

Weiss explained this phenomenon by assuming that actual specimens are divided into tiny magnetic domains (also known as Weiss domains). Within each domain, the spins are aligned, but (if the bulk material is in its lowest energy configuration, i.e. unmagnetised), the spins of separate domains point in different directions and their magnetic fields cancel out, so the object has no net large scale magnetic field. This implies that within each domain the local magnetisation is saturated and the directions of magnetisation of different domains need not necessarily be parallel.

Ferromagnetic materials spontaneously divide into magnetic domains because the exchange interaction keeps nearby spins aligned with each other. This is a short-range force, so rotations can occur over hundreds of times the distance between atoms. To keep the magnetostatic energy low, this rotation is concentrated in the boundary between domains, or domain wall. The direction that the magnetisation rotates within a domain wall varies. In a Bloch wall, the magnetisation direction stays in the plane of the wall; in a Néel wall, it rotates perpendicular to the plane.

Thus, an ordinary piece of iron generally has little or no net magnetic moment. However, if it is placed in a strong enough external magnetic field, the domains will re-orient in parallel with that field, and will remain re-oriented when the field is turned off, thus creating a "permanent" magnet. The domains do not go back to their original minimum energy configuration when the field is turned off because the domain walls tend to become 'pinned' or 'snagged' on defects in the crystal lattice, preserving their parallel orientation. This is shown by the Barkhausen effect: as the magnetising field is changed, the magnetisation changes in thousands of tiny discontinuous jumps as the domain walls suddenly "snap" past defects.

This magnetisation as a function of the external field is described by a hysteresis curve. Although this state of aligned domains is not a minimal-energy configuration, it is extremely stable and has been observed to persist for millions of years in seafloor magnetite aligned by the Earth's magnetic field (whose poles can thereby be seen to flip at long intervals).

Alloys used for the strongest permanent magnets are "hard" alloys made with many defects in their crystal structure where the domain walls "catch" and stabilise. The net magnetisation can be destroyed by heating and then cooling (annealing) the material without an external field, however. The thermal motion allows the domain boundaries to move, releasing them from any defects, to return to their low-energy unaligned state.

3.4.4 The Bloch Wall

The term Bloch wall denotes the transition layer which separates adjacent domains magnetised in different directions. The essential idea of the Bloch wall is that the entire change in spin direction between domains magnetised in different directions occurs in a gradual way over many atomic planes as shown in Figure 2.2.

This gradual change in direction is due to the fact that for a given total change of spin direction the exchange energy is lower when the change is distributed over many spins than when the change occurs suddenly.
Let us attempt to explain this behaviour. The exchange energy between two spins making a small angle φ with each other is given as:

$$w_{ex} = JS^2\phi^2 \qquad 2.25$$

here *J* is the exchange integral and *S* is the spin quantum number.
Let the total desired change of angle be φ_o; if the change occurs in N equal steps, the angle change between neighboring spins is φ_o/N, and the exchange energy between each pair of neighboring atoms is

$$w_{ex} = JS^2(\phi_o/N)^2. \qquad 2.26$$

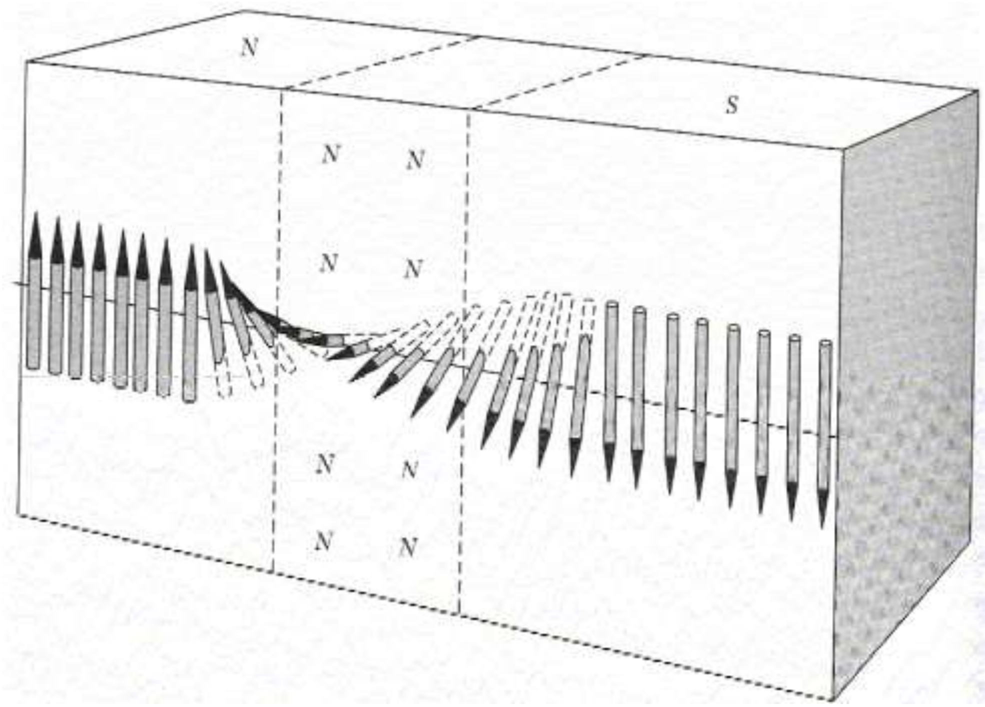

Fig. 2.2: The Structure of the Bloch Wall Separating Domains

The total exchange energy of the line of $N + 1$ atoms is thus

$$E_{ex} = JS^2 \phi_o^2 / N \qquad 2.27$$

Since the exchange energy of a wall is inversely proportional to the thickness, the wall might spread out until it filled a sizable proportion of the crystal, were it not for the restraining effect of the anisotropy energy, which acts to limit the width of the transition layer.

We now consider a wall parallel to the cube face of a simple cubic lattice and separating domains magnetised in opposite directions. The energy per unit surface area, σ_w may be represented to a good approximation as the sum of contributions from exchange and anisotropy energies:

$$\sigma_w = \sigma_{ex} + \sigma_{anis}$$
2.28

The exchange energy is given approximately by Eq. (2.27) for each line of atoms through the wall and normal to the plane of the wall. There are $1/a^2$ such lines per unit area, where a is the lattice constant; therefore

$$\sigma_{ex} = \pi^2 J S^2 / Na^2 . \qquad 2.29$$

The anisotropy energy is of the order of the anisotropy constant times the volume, or

$$\sigma_{anis} \approx KNa \qquad 2.30$$

therefore

$$\sigma_w = \left(\pi^2 J\, S^2 / Na^2\right) + KNa \qquad 2.31$$

which is a minimum with respect to *N* when

$$N = \left(\pi^2 J\, S^2 / Ka^3\right)^{1/2}. \qquad 2.32$$

The total wall energy per unit area is

$$\sigma_w = 2\pi\left(J\, KS^2/a\right)^{1/2} \qquad 2.33$$

3.5 Domain Dimensions

Let us now calculate the domain width for a flux-closure arrangement of domains in Figure 2.3 in a uniaxial crystal.

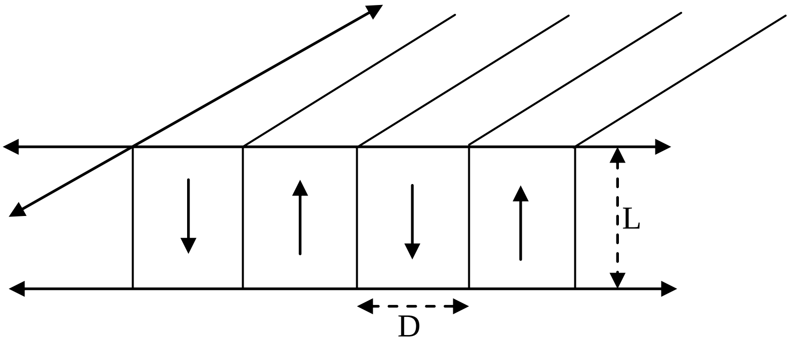

Fig.2.3: Domain Width

The wall energy per unit area of the crystal surface is approximately

$$w_{wall} = \sigma_w\, L/D \qquad 2.34$$

The volume contained within the domains of closure is oriented in a direction of hard magnetisation and involves an energy *K* per unit volume, where *K* is the anisotropy constant. Per unit area of crystal surface on one side, the volume in the domains of closure on both sides is *D*/2, and so the anisotropy energy per unit area is

$$w_{anis} = KD/2. \qquad 2.35$$

Hence, the total energy per unit area is

$$w = \sigma_w L/D + KD/2 \qquad 2.36$$

The condition for the minimum of w with respect to the domain width D is

$$D = (2\sigma_w L/K)^{1/2}, \qquad 2.37$$

and the corresponding energy per unit area is

$$w = (2\sigma_w LK)^{1/2}. \qquad 2.38$$

The energy per unit volume is

$$f_{domain} = (2\sigma_w K/L)^{1/2} \qquad 2.39$$

3.6 Antiferromagnetism

The physical origin of the Weiss field is in the quantum-mechanical exchange integral. It can be shown that the energy of interaction of atoms i, j bearing spins S_i, S_j contains a term

$$E_{ex} = -2J\overline{S}_i \cdot \overline{S}_j \qquad 2.40$$

where J is the exchange integral and is related to the overlap of the charge distributions i, j.

When the exchange integral J in Eq. (2.40) is positive, we have ferromagnetism; when J is negative, we have antiferromagnetism.
In materials that exhibit antiferromagnetism, the magnetic moments of atoms or molecules, usually related to the spins of electrons, align in a regular pattern with neighboring spins pointing in opposite directions as in Figure 2. 4.

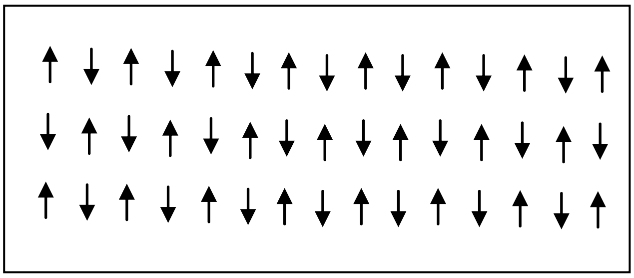

Fig. 2.4: Antiferromagnetic Ordering

SELF-ASSESSMENT EXERCISE

i. Differentiate between ferromagnetism and antiferromagnetism.
ii. Explain ferromagnetism in terms of the exchange integral *J*.

3.7 Ferrites

Ferrites of magnetic interest belong to the group of compounds represented by the chemical formula $MOFe_2O_3$, where M is a divelent metal ion such as Mn, Co, Ni, Cu, Mg, Zn, Cd, Fe^{2+}, or a mixture of these ions.

3.8 Magnetic Resonance

In this section we discuss dynamical magnetic effects associated with the spin angular momentum of nuclei and of electrons. The information that can be obtained about solids by resonance studies may be categorised:

- electronic structure of single defects, as revealed by the fine structure of the absorption
- motion of the spin or of the surroundings, as revealed by changes in the line width
- internal magnetic fields sampled by the spin, as revealed by the position of the resonance line
- collective spin excitations.

3.8.1 Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) is a physical phenomenon in which magnetic nuclei in a magnetic field absorb and re-emit electromagnetic radiation. This energy is at a specific resonance frequency which depends on the strength of the magnetic field and the magnetic properties of the isotope of the atoms; in practical applications, the frequency is similar to VHF and UHF television broadcasts (60–1000 MHz). NMR allows the observation of specific quantum mechanical magnetic properties of the atomic nucleus. Many scientific techniques exploit NMR phenomena to study molecular physics, crystals, and non-crystalline materials through NMR spectroscopy. NMR is also routinely used in advanced medical imaging techniques, such as in magnetic resonance imaging (MRI).

All isotopes that contain an odd number of protons and/or of neutrons have an intrinsic magnetic moment and angular momentum, in other words a nonzero spin, while all nuclides with even numbers of both have a total spin of zero. The most commonly studied nuclei are ^1H and ^{13}C, although nuclei from isotopes of many other elements (e.g. ^{2}H, ^{6}Li, ^{10}B, ^{11}B, ^{14}N, ^{15}N, ^{17}O, ^{19}F, ^{23}Na, ^{29}Si, ^{31}P, ^{35}Cl, ^{113}Cd, ^{129}Xe, ^{195}Pt) have been studied by high-field NMR spectroscopy as well.

A key feature of NMR is that the resonance frequency of a particular substance is directly proportional to the strength of the applied magnetic field. It is this feature that is exploited in imaging techniques; if a sample is placed in a non-uniform magnetic field then the resonance frequencies of the sample's nuclei depend on where in the field they are located. Since the resolution of the imaging technique depends on the magnitude of magnetic field gradient, many efforts are made to develop increased field strength, often using superconductors. The effectiveness of NMR can also be improved using hyperpolarisation, and/or using two-dimensional, three-dimensional and higher-dimensional multi-frequency techniques.

The principle of NMR usually involves two sequential steps:

- The alignment (polarisation) of the magnetic nuclear spins in an applied, constant magnetic field H_0.
- The perturbation of this alignment of the nuclear spins by employing an electro-magnetic, usually radio frequency (RF) pulse. The required perturbing frequency is dependent upon the static magnetic field (H_0) and the nuclei of observation.

The two fields are usually chosen to be perpendicular to each other as this maximises the NMR signal strength. The resulting response by the total magnetisation (M) of the nuclear spins is the phenomenon that is exploited in NMR spectroscopy and magnetic resonance imaging. Both use intense applied magnetic fields (H_0) in order to achieve dispersion and very high stability to deliver spectral resolution, the details of which are described by chemical shifts, the Zeeman effect, and Knight shifts (in metals).

NMR phenomena are also utilised in low-field NMR, NMR spectroscopy and MRI in the Earth's magnetic field (referred to as Earth's field NMR), and in several types of magnetometers.

Let us consider a nucleus that possesses a magnetic moment $\boldsymbol{\mu}$ and an angular momentum $\hbar\mathbf{I}$. The magnetic moment is related to angular momentum as:

$$\boldsymbol{\mu} = \gamma\hbar\mathbf{I} \qquad 2.41$$

where γ is a constant known as magnetogyric ratio. By convention $\mathbf{I}$ denotes the nuclear angular momentum measures in units of $\hbar$.

The energy of interaction with the applied magnetic field is

$$U = -\overline{\mu} \cdot \overline{B}_a \qquad 2.42$$

if $\overline{B}_a = B_o \hat{z}$, then

$$U = -\mu_z B_o = -\gamma\hbar B_o I_z \qquad 2.43$$

The allowed values of I_z are $m_I = I, I - 1$, and $U = -m_I \gamma\hbar B_o$.

In a magnetic field a nucleus with $I = ½$ has two energy levels corresponding to $m_I = \pm½$. If $\hbar\omega_o$ denotes the energy difference between the two levels, then $\hbar\omega_o = \gamma\hbar B_o$ or

$$\omega_o = \gamma B_o \qquad 2.44$$

This is the fundamental condition for the magnetic resonance absorption.

3.8.2 Ferromagnetic Resonance

Let us summarise the unusual characteristics of ferromagnetic resonance:

- The transverse susceptibility components χ' and χ'' are very large because the magnetisation of a ferromagnet in a given static field is very much larger than the magnetisation of electronic or nuclear paramagnets in the same field.
- The shape of the specimen plays an important role. Because the magnetisation is large, the demagnetisation field is large.
- The strong exchange coupling between the ferromagnetic electrons tends to suppress the dipolar contribution to the line width, so that the ferromagnetic resonance lines can be quite sharp (<1 G) under favourable conditions.
- Saturation effects occur at low rf power levels.

Consider a specimen of a cubic ferromagnetic insulator in the form of an ellipsoid with principal axes parallel to x, y, z axes of a Cartesian coordinate system. The components of the internal magnetic field $\mathbf{B}_i$, in the ellipsoid are related to the applied field by

$$B_x^i = B_x^o - N_x M_x; \qquad B_y^i = B_y^o - N_y M_y; \qquad B_z^i = B_z^o - N_z M_z.$$

The Lorentz field and the exchange field do not contribute to the torque. The components of the spin equation of motion $\mathbf{M} = \gamma(\mathbf{M} \times \mathbf{B}^i)$ for an applied static field $B_o \hat{z}$,

$$\frac{dM_x}{dt} = \gamma\left(M_y B_z^i - M_z B_y^i\right) = \gamma\left[B_o + \left(N_y - N_z\right)M\right]M_y$$

$$\frac{dM_y}{dt} = \gamma\left[M\left(-N_x M_x\right) - M_x\left(B_o - N_z M\right)\right] = -\gamma\left[B_o + \left(N_x - N_z\right)M\right]M_x. \qquad 2.45$$

To first order we may set dM_z/dt = 0 and $M_z = M$.
Solving (44) with time dependence exp(-$i\omega t$) and assuming

$$\begin{vmatrix} i\omega & \gamma\left[B_o + \left(N_y - N_z\right)M\right] \\ -\gamma\left[B_o + \left(N_x - N_z\right)M\right] i\omega & \end{vmatrix} = 0,$$

we have that the ferromagnetic resonance frequency in applied field B_o is

$$\omega_o^2 = \gamma^2\left[B_o + \left(N_y - N_z\right)\mu_o M\right]\left[B_o + \left(N_x - N_z\right)\mu_o M\right] \qquad 2.46$$

The frequency ω_o is called the frequency of the uniform mode.
For a sphere $N_x = N_y = N_z$ so that $\omega_o = \gamma B_o$. For a flat plate with B_o perpendicular to the plate $N_x = N_y = 0$; $N_z = 4\pi$, whence the ferromagnetic resonance frequency is

$$\omega_o = \gamma\left(B_o - \mu_o M\right) \qquad 2.47$$

If B_o is parallel to the plane of the plate, the xz plane, then $N_x = N_z = 0$; $N_y = 4\pi$, and

$$\omega_o = \gamma\left[B_o\left(B_o + \mu_o M\right)\right]^{1/2} \qquad 2.48$$

The explanation above showed the effects of specimen shape on the resonance frequency.

3.8.3 Antiferromagnetic Resonance

Let us consider a uniaxial antiferromagnet with spins on two sublattices, 1 and 2. Assume that the magnetisation $\mathbf{M}_1$ on sublattice 1 is directed along the +z direction by an anisotropy field $B_A \hat{z}$. Anisotropy energy is the energy in a ferromagnetic crystal which directs the magnetisation along certain crystallographic axes called directions of easy magnetisation. The anisotropy field is a consequence of anisotropy energy density. The magnetisation $\mathbf{M}_2$ is directed along the –z direction by an anisotropy field $-B_A \hat{z}$. If one sublattice is directed along +z, the other will be directed along –z.

The exchange fields of $\mathbf{M}_1$ and $\mathbf{M}_2$ are

$$\mathbf{B}_1(ex) = -\lambda\mathbf{M}_2; \quad \mathbf{B}_2(ex) = -\lambda\mathbf{M}_1$$
2.49

where λ is positive; $\mathbf{B}_1$ is the field that acts on the spins of sublattice 1, and $\mathbf{B}_2$ acts on sublattice 2. As shown in figure 5, the total field acting on $\mathbf{M}_1$ is $\overline{B}_1 = -\lambda\overline{M}_2 + B_A\hat{z}$; the total field acting on $\mathbf{M}_2$ is $\overline{B}_2 = -\lambda\overline{M}_1 - B_A\hat{z}$. Note that we have assumed that no external field is acting on the antiferromagnet.

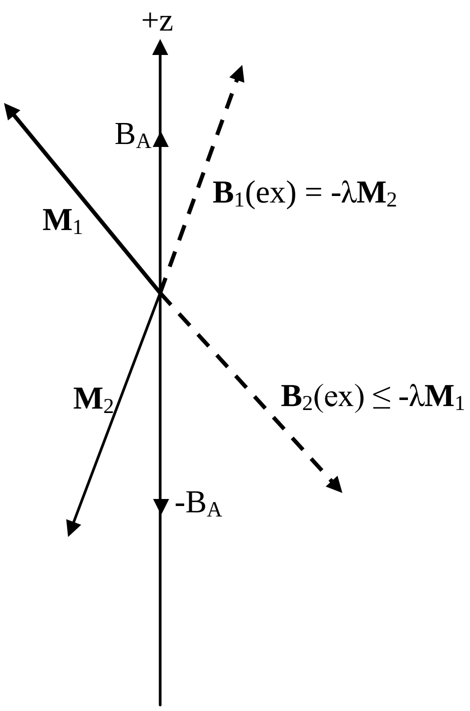

Fig.2. 5: Effective Fields in Antiferromagnetic Resonance

The linearised equations of motion are

$$\frac{dM_1^x}{dt} = \gamma\left[M_1^y(\lambda M + B_A) - M\left(-\lambda M_2^y\right)\right];$$
$$\frac{dM_1^y}{dt} = \gamma\left[M\left(-\lambda M_2^x\right) - M_1^x(\lambda M + B_A)\right]; \qquad 2.50$$

$$\frac{dM_2^x}{dt} = \gamma\left[M_2^y(-\lambda M - B_A) - (-M)\left(-\lambda M_1^y\right)\right];$$
$$\frac{dM_2^y}{dt} = \gamma\left[(-M)\left(-\lambda M_1^x\right) - M_2^x(-\lambda M - B_A)\right]; \qquad 2.51$$

We have set $M_1^z = M; M_2^z = -M$.

If we can define $M_1^+ = M_1^x + iM_1^y; M_2^+ = M_2^x + iM_2^y$, then (2.50) and (2.51) become

$$-i\omega M_1^+ = -i\gamma\left[M_1^+(B_A + \lambda M) + M_2^+(\lambda M)\right];$$
$$-i\omega M_2^+ = i\gamma\left[M_2^+(B_A + \lambda M) + M_1^+(\lambda M)\right].$$

These equations have a solution if, with exchange field $B_E \equiv \lambda M$,

$$\begin{vmatrix} \gamma(B_A + B_E) - \omega & \gamma B_E \\ \gamma B_E & \gamma(B_A + B_E) + \omega \end{vmatrix} = 0.$$

Thus, the antiferromagnetic resonance frequency is given by

$$\omega_o^2 = \gamma^2 B_A (B_A + 2B_E). \qquad 2.52$$

SELF-ASSESSMENT EXERCISE

Explain nuclear magnetic resonance.

4.0 CONCLUSION

You have seen the basic idea of magnetisation of materials in this unit. The differences between diamagnetism and paramagnetism have been highlighted to you and you should be able to differentiate between ferromagnetism and antiferromagnetism. We concluded this unit with explanation on magnetic resonance.

5.0 SUMMARY

- A material substance acquires a magnetic polarisation when placed in a magnetic field just as a dielectric medium acquires an electric polarisation in an electric field. The response of the materials to an applied magnetic field depends on the properties of the individual atoms and molecules, and on their interactions. The orbital motion of the electrons in atoms and molecules provide currents which give rise to the magnetic dipoles. In many materials the small electric currents associated with the orbital motion and spin of the electrons average to zero. When such atoms are placed in a magnetic field, minute electron currents are generated by induction in the clouds of electrons, the direction of which is such that the magnetic field associated with them opposes the inducing field **B**. These are known as diamagnetic substances.

- There are other materials in which the atoms do have an intrinsic magnetic moment on account of the fact that the currents from the orbital motions and spins of the electrons do not average to zero. Although electron spins tend to pair and cancel one another, there are atoms in which pairing is incomplete. When such materials are placed in a magnetic field, the magnetic moments of the atoms and the induced magnetism enhances the external field. This effect is more pronounced at low temperatures. Such substances are called paramagnetic substances.
- $\chi = \frac{C}{T - T_c}$ is known as the Curie-Weiss law. This law describes the observed susceptibility variation in the paramagnetic region above the Curie point.
- The value of Weiss field constant can be determined as follows: $\lambda^{-1} = \frac{C}{T_c} = NS(S+1)g^2\mu_B^2 / 3kT_c$, where S is spin angular momentum quantum number.
- The physical origin of the Weiss field is in the quantum-mechanical exchange integral. It can be shown that the energy of interaction of atoms i, j bearing spins S_i, S_j contains a term $E_{ex} = -2J\overline{S}_i \cdot \overline{S}_j$, where J is the exchange integral and is related to the overlap of the charge distributions i, j. When the exchange integral J is positive, we have ferromagnetism; when J is negative, we have antiferromagnetism.
- For a sphere $N_x = N_y = N_z$ so that $\omega_o = \gamma B_o$. For a flat plate with B_o perpendicular to the plate $N_x = N_y = 0$; $N_z = 4\pi$, whence the ferromagnetic resonance frequency is $\omega_o = \gamma(B_o - \mu_o M)$. If B_o is parallel to the plane of the plate, the xz plane, then $N_x = N_z = 0$; $N_y = 4\pi$, and $\omega_o = \gamma[B_o(B_o + \mu_o M)]^{1/2}$. The explanation above showed the effects of specimen shape on the resonance frequency.
- Antiferromagnetic resonance frequency is given by $\omega_o^2 = \gamma^2 B_A(B_A + 2B_E)$

6.0 TUTOR-MARKED ASSIGNMENT

1. Describe different methods of measurement of susceptibilities.
2. Explain Langevin theory of paramagnetism.
3. The molecular weight of a compound is 400, its density is 2 x 10^3kg/m^3 and its magnetic susceptibility at 293 K is 2.56 x 10^{-4}. Calculate the permanent magnetic dipole moment associated with each molecule.

7.0 REFERENCE/FURTHER READING

Charles, K. (2005). *Introduction to Solid State Physics*. USA: John Wiley and Sons, Inc.

UNIT 3 IMPERFECTION IN SOLIDS

CONTENTS

1.0 Introduction
2.0 Objective
3.0 Main Content
    3.1 Crystalline Defects
        3.1.1 Point Defects
        3.1.2 Linear Defects (Dislocations)
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1.0 INTRODUCTION

The crystalline structures that we have looked at all have imperfections. We will quantify these imperfections here. The common point imperfections in crystals are chemical impurities, vacant lattice sites, and extra atoms not in regular lattice positions. Linear imperfections are treated under dislocations. The crystal surface is a planar imperfection, with electron, phonon, and magnon surface states.

2.0 OBJECTIVE

At the end of this unit, you should be able to:

- explain the various imperfections in solids.

3.0 MAIN CONTENT

3.1 Crystalline Defects

A crystalline defect is a lattice irregularity having one or more of its dimensions on the order of an atomic dimension. There are five major categories of crystalline defects:

- Zero dimensional: Point defects
- One dimensional: Linear defects (dislocations)
- Two dimensional: Planar (surface) defects
- Three dimensional: Volume (bulk) defects
- Vibrations.

SELF-ASSESSMENT EXERCISE

i. Explain the crystalline defects.
ii. List five major categories of crystalline defects.

3.1.1 Point Defects

There are two main types of geometrical defects in a crystal. There are those which are *very localised and are of atomic dimensions*. These are called **point defects.** An example of this is an impurity atom which can be either a *substitutional* or an *interstitial* impurity.

(a) When some atoms are not exactly in their right place, the lattice is said to contain *imperfections or defects.*
(b) Many properties of solids e.g. the electrical resistance and mechanical strength are governed by the presence of certain types of defects in the lattice.

Point defects allow for diffusion to occur in the solid state.
There are different categories of point defects:

- **Vacancy**

  These are produced by thermal vibrations of the crystal lattice and/or from need to maintain charge neutrality.

- **Self-interstitial or interstitialcy**

  A position on the crystal lattice that is not normally occupied is called an interstitial site. If it is occupied by the same atomic species it is a self-interstitial or self-interstitialcy. It creates large distortions in the crystal lattice and so the concentrations are small.

- **Impurities**

- solid solutions–homogeneous single phase materials that are completely analogous to a liquid solution (alcohol and water)
- solute/solvent/solubility – miscibility
- random solid solution vs. ordered solid solution
- substitutional solid solution (Cu/Ni) vs. interstitial solid solution (Fe/C - α Iron has 0.025% C and γ iron has 2.08% C)
- nonstoichiometric compounds ($Fe_{1-x}O$)

- second phases – completely analogous to a liquid mixture (oil and water)
- Hume-Rothery Rules – used to predict solubility (miscibility):

1. less than 15% difference in atomic radii
2. same crystal structure
3. similar electronegativities
4. same valence.

- **Schottky defect -** a pair of oppositely charged ion vacancies.
- **Frenkel defect -** a vacancy-interstitialcy combination.

3.1.2 Linear Defects (Dislocations)

Unlike point defects, these are types of disorder which extend beyond the volume of one or two atoms. It is a line defect which can extend right through a crystal or it can form closed loops.

A line defect is a lattice distortion created about a line formed by the solidification process, plastic deformation, vacancy condensation or atomic mismatch in solid solutions.

Dislocations explain the observation of plastic deformation at lower stress than would be required in a perfect lattice. They also explain the phenomenon of work hardening. There are two basic types of dislocations, *edge* dislocation and *screw* dislocation.

- **Edge dislocation**

These are caused by the termination of a plane of atoms in the middle of a crystal. In such a case, the adjacent planes are not straight, but instead bend around the edge of the terminating plane so that the crystal structure is perfectly ordered on either side. The analogy with a stack of paper is apt: if a half a piece of paper is inserted in a stack of paper, the defect in the stack is only noticeable at the edge of the half sheet. See figure 1.

- **Screw dislocation**

This is more difficult to visualise, but basically comprises a structure in which a helical path is traced around the linear defect (dislocation line) by the atomic planes of atoms in the crystal lattice. See Figure 3.1.

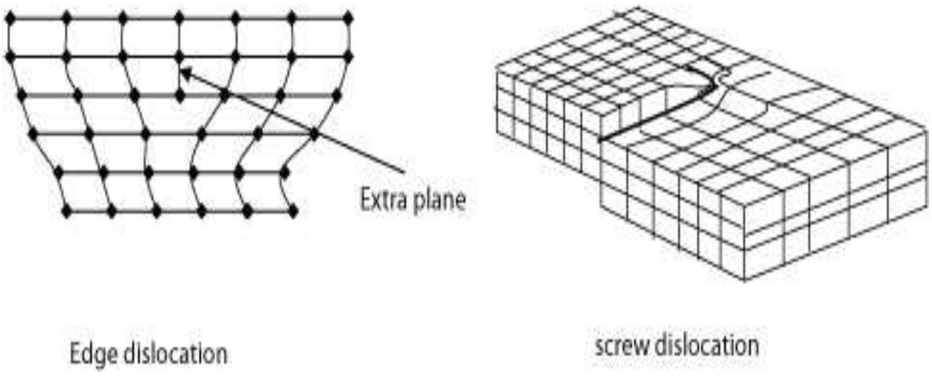

Fig. 3.1: Linear Dislocations in Solids

3.1.3 Planar (Interfacial) Defects

- **External surfaces**

  Atoms at any surface are not in their perfect crystal positions because they will have decrease number neighbors than the atoms inside the volume of the material. Hence, these atoms will be at higher energies. During solidification, materials try to minimise this.

- **Grain boundaries**

  Grains are formed during the solidification process. A grain boundary is the area of mismatch between volumes of material that have a common orientation of the crystallographic axes. The atoms at grain boundaries are not in their perfect crystal positions and hence, the grain boundary is less dense. These atoms are at higher energies than the atoms inside the volume of a grain.
  The thickness is of the order of 2-5 atoms wide.

There are different categories of grain boundaries:

- low angle tilt boundary – a few isolated edge dislocations
- high angle tilt boundary – more complex.

At ambient temperatures, grain boundaries give strength to a material. So in general, fine grained materials are stronger than coarse grained ones because they have more grain boundaries per unit volume. However, at higher temperatures, grain boundaries act to weaken a material due to corrosion and other factors.

Grain size can be quantified by:

- grain size number

- average grain diameter
- grain density.

The size and shape of grains are determined by a number of factors during solidification:

- lots of nucleation sites ⇒ fine grains
- fewer nucleation sites ⇒ coarse grains
- equal growth in all directions ⇒ equiaxed grains
- thermal gradients ⇒ elongated or columnar grains
- slow growth ⇒ coarse grains
- rapid growth ⇒ fine grains.

Most materials are polycrystalline (or polygranular). There are some applications where the expense and time to produce single crystal materials (and hence no grain boundaries) is justified:

- turbine blades
- silicon wafer chips.
- **Twin boundaries** – a special type of grain boundary across which there exists a mirror image of the crystal lattice. It is produced by mechanical shear stresses and/or annealing some materials.
- **Stacking faults** – the interruption of the stacking sequence of close packed planes.
- **Phase boundaries -** the surface area between the grains in multiphase materials.
- **Ferromagnetic domain walls –** the boundary between regions that have a different orientation of magnetic dipoles.

3.1.4 Volume (Bulk) Defects

These are introduced during processing and fabrication.

- Pores
- Cracks
- Foreign inclusions.

4.0 CONCLUSION

In this unit, we have examined the properties of dielectric materials. In addition, we differentiated between paramagnetism and diamagnetism; ferromagnetism and anti-ferromagnetism. We also explained magnetic resonance. We ended the unit with a brief explanation on the various imperfections in solids.

5.0 SUMMARY

- A crystalline defect is a lattice irregularity having one or more of its dimensions on the order of an atomic dimension. There are five major categories of crystalline defects:
- Zero dimensional: Point defects
- One dimensional: Linear defects (dislocations)
- Two dimensional: Planar (surface) defects
- Three dimensional: Volume (bulk) defects
- Vibrations.

6.0 TUTOR-MARKED ASSIGNMENT

1. Distinguish between *point defects* and d*islocations.*
2. Explain the meaning of the followings: *electronic, orientational and ionic polarization*
3. List the different categories of defects.

7.0 REFERENCES/FURTHER READING

Charles, K. (2005). *Introduction to Solid State Physics*. USA: John Wiley and Sons, Inc.

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