### 2.1 Magnetic Materials

#### 2.1.1 Introduction

Magnetic materials are the materials, which get magnetized in a magnetic field. These materials are having the ability to create a self magnetic field in the presence of external magnetic field. There are nearly eleven types of magnetic materials. Some important among them are diamagnetic, paramagnetic, ferromagnetic, antiferromagnetic and ferrimagnetic materials. The magnetism arises from the magnetic moment of the magnetic materials. Whenever a charged particle has an angular momentum, it contributes to the permanent magnetic moment. In general, there are three contributions to the angular momentum of an atom.

#### 1. Orbital angular momentum of the electrons

This corresponds to permanent orbital angular magnetic dipole moments.

### 2. Electron spin angular momentum

This corresponds to electron spin magnetic moments.

### 3. Nuclear spin angular momentum

This corresponds to nuclear magnetic moments.

(**Note**: Since the magnitudes of orbital magnetic moments and nuclear magnetic moments are small, it is assumed that the permanent magnetic dipoles arise due to the electron spin only).

Let us see some of the important terms involved in this chapter.

#### 2.2 Basic Definitions

# Magnetic dipole

Any two opposite magnetic poles separated by a distance 'd' constitute a magnetic dipole.

# Magnetic dipole moment $(\mu_m)$

If 'm' is the magnetic pole strength and 'l' is the length of the magnet, then its dipole moment is given by,

$$\mu_m = m \times 1$$

It can also be defined as follows:

When an electric current of 'i' amperes flows through a circular wire of 1 turn having an area of cross section 'a' m<sup>2</sup>, then it is said to have a magnetic moment of,

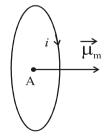


Fig.2.1 Magnetic moment

$$\mu_m = i \times a$$
 Unit: ampere (metre)<sup>2</sup>

Dipole moment is a vector quantity. Its direction is normal to the plane of the loop to the right, if the current is clockwise.

### Magnetic Flux ( $\phi$ )

It is defined as the total number of magnetic lines of force passing perpendicular through a given area. It can also be defined as the total number of lines of force emanated from north pole. Unit: weber.

#### Magnetic flux density or Magnetic Induction (B)

It is defined as the number of magnetic lines of force passing through an unit area of cross section. It is given by,

$$B = \frac{Magnetic \ Flux}{Unit \ Area} = \frac{\varphi}{A} Weber/m^{2} (or) Tesla$$

It is also defined as the magnetic force (F) experienced by an unit north pole placed at the given point in a magnetic field. *i.e.*  $B = \frac{F}{m}$ 

# Magnetic field strength or Magnetic field intensity (H)

Magnetic field intensity or magnetic field strength at any point in a magnetic field is equal to  $\left(\frac{1}{\mu}\right)$  times the force acting on a unit north pole placed at the point. i.e.  $H = \frac{1}{\mu} \times \left(\frac{F}{m}\right) = \frac{B}{\mu}$  ampere .turns / metre where,  $\mu$  = permeability of the medium in which the magnetic field is situated.

### Magnetization or Intensity of Magnetization (M)

The term magnetization is the process of converting a non-magnetic material into a magnetic material. It measures the magnetization of the magnetized specimen. Intensity of magnetization (M) is defined as the magnetic moment per unit volume. It is expressed in ampere/metre.

#### Magnetic susceptibility $(\chi)$

It is the measure of the ease with which the specimen can be magnetized by the magnetizing force. It is defined as the ratio of magnetization produced in a sample to the magnetic field intensity. i.e. magnetization per unit field intensity.  $\chi = \frac{M}{L}(no\ unit)$ 

## Magnetic permeability (µ)

It is the measure of degree at which the lines of force can penetrate through the material.

It is defined as the ratio of magnetic flux density in the sample to the applied magnetic field intensity.

*i.e.* 
$$\mu = \mu_0 \mu_r = \frac{B}{H}$$

### Relative permeability $(\mu_r)$

It is the ratio of permeability of the medium to the permeability of free space. i.e.  $\mu_r = \frac{\mu}{\mu_0}$ 

### Relation between $\mu_r$ and $\chi$

When a magnetic material is kept in a magnetic field (H), then two types of lines of induction passes through the material. One is due to the magnetic field (H) and the other one is due to self-magnetization of the material itself. Therefore, total flux density (B) in a solid can be given as,  $B = \mu_0 \, (H+M)$ 

We know that

$$\mu = \frac{B}{H} (or) \qquad B = \mu H \tag{2}$$

Equating (1) and (2), we get,

$$\begin{array}{lll} \mu H \; = \; \mu_0(H+M) & = \; \mu_0 H + \mu_0 M \\ \\ \mu_0 \mu_r H \; = \; \mu_0 H + \mu_0 M & \left[\because \mu = \mu_0 \mu_r \right] \\ \\ \mu_r = \frac{\mu_0 H}{\mu_0 H} + \frac{\mu_0 M}{\mu_0 H} & = 1 + \frac{M}{H} \quad \textit{i.e.} \quad \mu_r = 1 + \chi \end{array}$$

### Bohr Magneton (µB)

Bohr magneton is the magnetic moment produced by one unpaired electron in an atom. It is the fundamental quantum of magnetic moment.

1 Bohr magneton = 
$$\frac{e}{2m} \cdot \frac{h}{2\pi} = \frac{eh}{4\pi m}$$
;  $1\mu B = 9.27 \times 10^{-24}$  ampere metre <sup>2</sup>.

**Table 2.1 Classification of Magnetic materials – A comparative chart** 

Туре		Special Remarks	Magnitude of susceptibility	Temperature dependence of susceptibility	Spin alignment	Examples
Diamagnetic materials	*	They repel magnetic lines of force	Small negative	Independent		Organic materials, light elements like H <sub>2</sub> , germanium and silicon.
	*	Permanent dipole moment is absent.	Intermediate, negative	Varies with magnetic field and temperature below 20 K	, ·	Alkali earths, Bismuth, Cu, Ag and Au.
	*	Magnetic effects are very small	Large, negative	Exists only below a critical temperature		Superconducting materials like Niobium and its compounds
Paramagnetic materials	*	They weakly attract magnetic lines of force	Small positive	Independent	NA TOP TO THE TOP TO T	Alkali Metals and Transition metals FeSO <sub>4</sub> , MnSO <sub>4</sub> , NiSO <sub>4</sub> , etc.,
	*	Permanent dipole moment is present	Large Positive	$\chi = \frac{C}{T - \theta}$ (Curie-Weiss Law) where, $C - Curie constant$ $\theta - Ferromagnetic Curie$ Temp.		Rare earths like chromium, yttrium, etc.,
Ferromagnetic materials	* *	They strongly attract magnetic lines of force  Due to the large internal field, the permanent dipoles are strongly aligned in the same direction and as a consequence, a large spontaneous magnetization is produced even in the absence of an external applied field.  They exhibit magnetization even when the magnetizing field is removed. i.e they exhibit magnetic hysteresis.  During heating, they lose their magnetization slowly.	Very Large Positive	$\chi = \frac{C}{T - \theta}$ 1.) For $T > \theta_f$ paramagnetic behaviour 2.) For $T < \theta_f$ ferromagnetic behaviour	<del>111111</del>	Some transition and rare earth metals.  Iron, nickel, cobalt and gadolinium

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Туре	Special Remarks	Magnitude of susceptibility	Temperature dependence of susceptibility	Spin alignment	Examples
Antiferro magnetic materials	* The opposite alignment of adjacent magnetic moments in a solid is produced by an exchange interaction.  * The dipoles are anti parallel and equal in magnitude. So the resultant magnetization is zero.		$\chi = \frac{C}{T + \theta}, \text{ for } T \!\!>\!\! T_N$ $\chi \propto T, \text{ for } T \!\!<\! T_N$ where $T_N - \text{Neel Temp.}$		Salts of transition elements like, ferrous oxide, manganese oxide, chromium oxide, etc.,
Ferrimagnetic materials	* Permanent dipole moment present  * These materials are a special case of anti ferromagnetics in which the magnetic dipoles align themselves anti parallely but with unequal magnitudes. Therefore a large magnetization arises.  *They are composed of two or more sets of different transition metals.		$\chi = \frac{C}{T \pm \theta} \text{, for } T \!\!>\!\! T_N$ when $T < T_N,$ they become ferrimagnetic.		Ferrous ferrite and Nickel ferrite.

The following Fig. 2.2 illustrates the variation of susceptibility with temperature in different magnetic materials

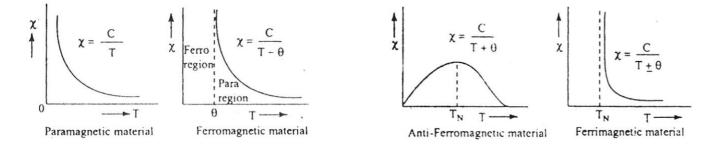


Fig. 2.2 Variation of susceptibility with temperature

# 2.3 Classification of Magnetic Materials

It has been seen earlier that the permanent magnetic moment is mainly due to the spin magnetic moment of the electrons. Generally, every two electrons in an energy state of an atom will form a pair with opposite spins. If all the electrons are paired, their spin magnetic moments will be cancelled and so their net magnetic moment is zero. Whereas if there are unpaired electrons in an atom, the spin magnetic moment of these unpaired electrons interact with the spin magnetic moment of the unpaired electrons of the adjacent atom, in a parallel manner resulting in enormous permanent magnetic moment.

So, magnetic materials are broadly classified into two categories, as follows.

- a) Those not having any permanent magnetic moment diamagnetic materials, and
- b) Those having permanent magnetic moment, para, ferro, antiferro and ferrimagnetic materials.

The properties of the different types of magnetic materials are summarized in the Table 2.1.

# 2.4 Hard and Soft Magnetic Materials

The magnetic materials are classified into two types, namely, hard and soft magnetic materials, depending upon the direction of magnetization by an applied magnetic field.

# 2.4.1 Soft magnetic materials

The materials, which are easily magnetized and demagnetized, are said to be soft magnetic materials. In soft materials, the domain walls move easily and reversibly so that magnetization changes by large amounts for small changes in the magnetic field.

The soft magnetic material is prepared by heating the pure materials to a temperature at which sufficient movement of the atoms is possible for them to settle into an ordered lattice, followed by slow cooling.

## **Properties**

The soft magnetic materials have the following properties

- The nature of the hysteresis loop of a soft magnetic materials is very steep as shown in Fig 2.3.
- The hysteresis area is very small and hence the hysteresis loss is also small.
- The materials have a large value of susceptibility and permeability.
- The resistivities of these materials are very high and hence they have low eddy current loss.
- These materials are free from irregularities like strain or impurities.
- The magnetostatic energy of a soft magnetic material is very small.

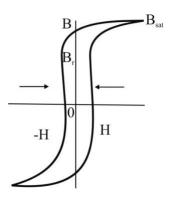


Fig 2.3 Hysteresis loop of a soft magnetic material

# **Examples**

- (i) Iron and silicon alloys( silicon steel)
- (ii) Nickel-Iron alloy, and
- (iii) Iron-cobalt alloy

## **Applications**

- (i) Iron-silicon alloy are used in electrical equipment and magnetic cores of transformers operating at power line frequencies. Silicon steel is also extensively used in large alternators and high frequency rotating machines.
- (ii) Nickel alloys are used in high frequency devices such as high —speed relays, wide band transformers and inductors. They are also used to manufacture small motors and synchros. They are also used for precision current and voltage transformers, and inductive potentiometers.

## 2.4.2 Hard Magnetic Materials

The materials, which are very difficult to magnetize, are said to be hard magnetic materials. In hard magnetic materials, the rotation of domain wall is very difficult.

The hard magnetic materials are prepared by heating magnetic materials to the required temperature and then suddenly cooling them by dipping in a cold liquid. In a hard magnetic material, the impurities are purposely introduced, to make them hard.

# **Properties**

The properties of hard magnetic materials are listed as follows:

- The nature of the hysteresis curve is shown in Fig 2.4. It is very broad and has a large area.
- Since the area of the hysteresis curve is large, the hysteresis loss is also large.
- These materials have low value of susceptibility and permeability.
- The coercivity and retentivity are large.
- The eddy current loss is very large.

• These materials have large amount of impurities and lattice defects the magneto static energy is very large.

# **Examples**

Carbon steels, tungsten steel, chromium steel, alnico, etc.,

## **Applications**

- (i) The carbon steel is used as magnets for toys, compass needle, latching relays and certain types of meters.
- (ii) The tungsten steel finds use in d.c meter magnets and in other devices where comparatively large size is permissible.
- (iii) Chromium steel is the best permanent magnet.

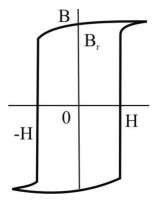


Fig 2.4 Hysteresis loop of a hard magnetic material

The following table gives the comparison of hard and soft magnetic materials.

Table 2.2 Comparison between soft and hard magnetic materials

Sl.No	Soft Magnetic Materials	Hard Magnetic Materials		
1.	<b>Definition:</b> Materials, which are easy to	<b>Definition:</b> Materials, which are difficult		
	magnetize and demagnetize are called	to magnetize and demagnetize are called		
	soft magnetic materials.	soft magnetic materials.		
2.	The nature of the hysteresis loop is very	The nature of the hysteresis loop is very		
	steep, as shown in Fig 2.3	broad, as shown in Fig 2.4		
3.	These materials have small hysteresis	These materials have large hysteresis loss		
	loss due to small hysteresis loop area.	due to large hysteresis loop area.		
4.	These materials have a large value of	These materials have low value of		
	susceptibility and permeability.	susceptibility and permeability.		
5.	The coercivity and retentivity are small.	The coercivity and retentivity are large.		
6.	The eddy current loss is small due to	The eddy current loss is more due to their		
	their high resistivity.	small resistivity.		
7.	These materials are free from	These materials have large amount of		
	irregularities like strain or impurities.	impurities and lattice defects.		

8.	Its magneto static energy is very small.	Its magneto static energy is very large.		
9.	Examples: Iron and silicon alloys( silicon steel), Nickel-Iron alloy and	Examples: Carbon steels, tungsten steel, chromium steel, alnico, etc.		
	Iron-cobalt alloy,etc.			

# 2.5 Ferrimagnetic Materials (Ferrites)

- Ferrimagnetic materials are also called as Ferrites. Ferrites are the modified structures of iron with no carbon and are composed of two or more sets of different transition metals.
- These materials have anti parallel magnetic moments of different magnitudes, giving rise to large magnetic moment in the presence of external magnetic field.

#### **Properties**

- The susceptibility  $(\chi)$  is very large and positive. It is represented by,  $\chi = C / (T \pm \theta)$ , when  $T > T_N$
- When  $T < T_N$ , they behave as ferrimagnetic materials.
- Mechanically, they have pure iron character. They have low tensile strength and are brittle and soft
- In these, all valence electrons are tied up by ironic bonding and they are bad conductors with high resistivity of  $10^{11} \Omega$  m.
- Ferrites are manufactured by powder metallurgical process by mixing, compacting and then sintering at high temperatures followed by age hardening in magnetic fields.
- They are soft magnetic materials and so they have low eddy current losses and hysteresis losses.

### 2.5.1 Structure of Ferrites

- The general chemical formula of a ferrite molecule is M<sup>2+</sup>Fe<sub>2</sub><sup>3+</sup>O<sub>4</sub><sup>2-</sup>, where M<sup>2+</sup> represents a divalent metal ion such as Zn<sup>2+</sup>, Fe<sup>2+</sup>, Mg<sup>2+</sup>, Mn<sup>2+</sup>, Cd<sup>2+</sup> etc.,
- Ferrites crystallize in the form of a cubic structure. Each corner of a ferrite unit cell consists of a ferrite molecule.
- Therefore, in a ferrite unit cell there are eight molecules. Therefore in a ferrite unit cell, there are eight divalent metal ions, 16 ferric ions and 32 Oxygen ions.
- If only the oxygen ions in ferrite crystal are considered, it is found that they constitute a close packed face centered cubic structure.
- In these arrangement it is found that for every four O<sup>2-</sup>ions there are 2 octahedral sites (surrounded by 6 O<sup>2-</sup>ions) and one tetrahedral site (surrounded by 4 O<sup>2-</sup>ions).
- The metal ions are distributed over these tetrahedral sites (A sites) and octahedral sites (B sites). Thus in ferrites the number of octahedral sites is twice the number of tetrahedral sites.
- Normally there are two types of structures in ferrites.
  - i) Regular spinel and

### ii) Inverse spinel

#### i) Regular spinel structure

- In this type, each divalent metal ion occupies 1 tetrahedral site and each trivalent metal ion occupies 1 octahedral site. Totally in an unit cell, there will be 8 tetrahedral (8 A) sites and 16 octahedral (16B) sites.
- Hence, the sites A and B combined to form a regular spinel ferrite structures as shown in Fig.2.5.
- The schematic representation of zinc ferrite molecule as shown in Fig.2.6.

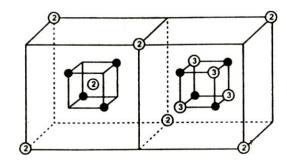


Fig. 2.5 Regular spinel structure

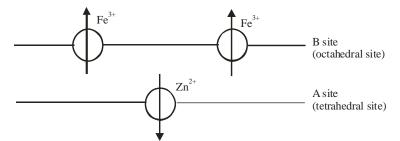
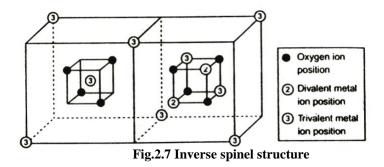


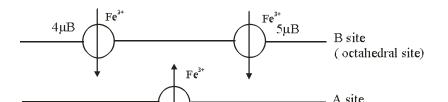
Fig. 2.6 Schematic representation of Zn<sup>2+</sup>Fe <sub>2</sub><sup>3+</sup>O<sub>4</sub><sup>2-</sup>

#### ii) Inverse spinel structure

• In this type half of the B sites (8sites) are occupied by divalent metal ions and the remaining half of the B sites (8 sites) and all the A sites are occupied by the trivalent metal ions, as shown in Fig. 2.7.



• The schematic representation of a ferrous ferrite molecule is shown in Fig. 2.8.



# Fig.2.8 Schematic representation of a ferrous ferrite molecule $Fe^{2+} Fe_2^{3+} O_4^{2-}$ .

- The anti parallel alignment of a ferrous ferrite molecule in inverse spinel structure is explained by the calculation of its magnetic moment. In a ferrous ferrite molecule, there are one ferrous ion and 2 ferric ions. To determine the net magnetic moment for each of the ferrous ferrite molecule, we must know the 3d inner electronic configuration of the ferrite ions.
- When the Fe atom is ionized to form the Fe<sup>2+</sup> ions, there are 4 unpaired 3d electrons left after the loss of two 4s electrons.
- When the Fe atom is ionized to form the Fe<sup>3+</sup> ions, there are 5 unpaired 3d electrons left after the loss of two 4s electrons and one 3d electron. It is shown in the following electronic configuration

Ion	No. of electrons	3d electronic configuration					Ionic magnetic moment	
Fe <sup>2+</sup>	24	$\uparrow\downarrow$	<b>↑</b>	<b>↑</b>	<b>↑</b>	<b>↑</b>		4μΒ
Fe <sup>3+</sup>	23	<b>↑</b>	<b>↑</b>	$\uparrow$	$\uparrow$	$\uparrow$		5μΒ

Table 2.3 3d electronic configuration of Fe<sup>2+</sup> and Fe<sup>3+</sup>

- Since each unpaired 3d electron has a magnetic moment of one  $\mu B$ , the Fe <sup>2+</sup> ion has a moment of  $4\mu B$ , and Fe<sup>3+</sup> ion has a moment of  $5\mu B$ .
- If parallel alignments of ferrous and ferric ions are considered, the total dipole moment  $= 4 + (2 \times 5) = 14 \mu B$ . This observed value doesn't coincide with the experimental value.
- Consider anti parallel alignment of ferrous and ferric ions in inverse spinel structure.
- If one ferrous ion and one ferric ion are in one direction and another ferric ion is in opposite direction then the dipole moment is,  $\{[(5\times1)+4]-(5\times1)\}=4\mu B$
- This observed value is in good agreement with the experimental value and hence this confirms the anti parallel alignment of dipoles in ferrites.

#### 2.5.3 Applications of Ferrites

- Ferrite is used in radio receivers to increase the sensitivity and selectivity of the receiver.
- Ferrites are used as cores in audio and TV transformers.
- Ferrites are used in digital computers and data processing circuits. Ferrites are used to produce low frequency ultra sonic waves by magnetostriction principle.
- Ferrites are widely used in non-reciprocal microwave devices. Examples for non-reciprocal microwave devices are Gyrator, Isolator and Circulator.

- Ferrites are also used in power limiting and harmonic gyration devices.
- Ferrites can also be used in the design of ferromagnetic amplifiers of microwave signals.
- Ferrite core can be used as a bitable element.
- The rectangular shape ferrite cores can be used as a magnetic shift register.
- Hard ferrites are used to make permanent magnets.
- The permanent magnets (hard ferrites) are used in instruments like galvanometers, ammeter, voltmeter, flex meters, speedometers, wattmeter, compasses and recorders.

#### 2.6 Garnets

Garnet is a group of minerals that have been used since the <u>Bronze Age</u> as gemstones and abrasives. Garnets species are found in many colors including red, orange, yellow, green, blue, purple, brown, black, pink and colorless.

Garnets are <u>nesosilicates</u> having the general formula  $X_3Y_2(SiO_4)_3$ . The X site is usually occupied by divalent cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Fe^{2+}$ ,  $Mn^{2+}$ ) and the Y site by trivalent cations ( $Al^{3+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ ,  $Mn^{3+}$ ,  $V^{3+}$ ) in an <u>octahedral/tetrahedral</u> framework with  $[SiO_4]^{4-}$  providing the tetrahedra.

They crystallize in the <u>isometric</u> system, having three axes that are all of equal length and perpendicular to each other.

Garnets do not show <u>cleavage</u>, so when they fracture under stress, sharp irregular pieces are formed.

Because the chemical composition of garnet varies, the atomic bonds in some species are stronger than in others. As a result, this mineral group shows a range of hardness on the <u>Mohs Scale</u> of about 6.5 to 7.5.

Garnets can be made in the lab by powdering MgO,  $Al_2O_3$ , and  $SiO_2$ . The powder is then placed inside gold or platinum tubes which are welded shut. (Gold and platinum are used since they do not melt and corrode at high temperatures and do not suffer oxidation). The capsule in then placed in a hydraulic press and brought to a pressure of 80 - 50,000 atm. An electrical current is run through the sample to attain temperatures of 1200 to 1400 °C.

## Examples:

Pyralspite garnets - Aluminium in Y site

• Almandine : Fe<sub>3</sub>Al<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub>

• Pyrope :  $Mg_3Al_2(SiO_4)_3$ 

• Spessartine : Mn<sub>3</sub>Al<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub>

Ugrandite group - calcium in X site

• Andradite : Ca<sub>3</sub>Fe<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub>

• Grossular :  $Ca_3Al_2(SiO_4)_3$ 

• Uvarovite : Ca<sub>3</sub>Cr<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub>

#### Less common species

#### Calcium in X site

• Goldmanite : Ca<sub>3</sub>V<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub>

• Kimzeyite :  $Ca_3(Zr,Ti)_2[(Si,Al,Fe^{3+})O_4]_3$ 

• Morimotoite : Ca<sub>3</sub>Ti<sup>4+</sup>Fe<sup>2+</sup>(SiO<sub>4</sub>)<sub>3</sub>

• Schorlomite :  $Ca_3(Ti^{4+}, Fe^{3+})_2[(Si, Ti)O_4]_3$ 

# Hydroxide bearing - calcium in X site

• Hydrogrossular: Ca<sub>3</sub>Al<sub>2</sub>(SiO<sub>4</sub>)<sub>3-x</sub>(OH)<sub>4x</sub>

• Hibschite :  $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$  (where x is between 0.2 and 1.5)

• Katoite :  $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$  (where x is greater than 1.5)

#### Magnesium or manganese in X site

• Knorringite : Mg<sub>3</sub>Cr<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub>

• Majorite : Mg<sub>3</sub>(Fe,Al,Si)<sub>2</sub>(SiO<sub>4</sub>)<sub>3</sub>

• Calderite :  $Mn_3Fe_2^{3+}$  (SiO<sub>4</sub>)<sub>3</sub>

Yttrium iron garnet (YIG), Y<sub>3</sub>Fe<sub>2</sub>(FeO<sub>4</sub>)<sub>3</sub>, another important garnet, the five iron(III) ions occupy two octahedral and three tetrahedral sites, with the yttrium(III) ions coordinated by eight oxygen ions in an irregular cube. The iron ions in the two coordination sites exhibit different spins, resulting in magnetic behaviour. YIG is a ferrimagnetic material having a Curie temperature of 550 K. By substituting specific sites with rare earth elements, for example, Gadolinium, interesting magnetic properties can be obtained.

### **Applications of Garnets:**

- Gadolinium gallium garnet, Gd<sub>3</sub>Ga<sub>2</sub>(GaO<sub>4</sub>)<sub>3</sub>, which is synthesized for use in magnetic bubble memory.
- Yttrium aluminium garnet (YAG), Y<sub>3</sub>Al<sub>2</sub>(AlO<sub>4</sub>)<sub>3</sub>, is used for synthetic gemstone. When doped with neodymium (Nd<sup>3+</sup>), these YAl-garnets are useful as the lasing medium in lasers.
- The Garnet group is a key mineral in interpreting the genesis of many igneous and metamorphic rocks.
- Garnets are also useful in defining metamorphic facies of rocks.
- Pure crystals of garnet are used as gemstones.
- Garnet sand is a good abrasive, and a common replacement for silica sand in sand blasting.
- Mixed with very high pressure water, garnet is used to cut steel and other materials in water jets.
- Garnet sand is also used for water filtration media.

## 2.7 Magnetoplumbites

Magnetoplumbites belong to a family of ferrites (barium, strontium or calcium hexaferrites) that is important in at least four areas of modern technologies like permanent magnets, high density magnetic recording, microwave and magnetic-optic applications.

Magnetoplumbites are hexagonal ferrites having the general formula  $MFe_{12}O_{19}$ , where M is usually Barium (Ba), Strontium (Sr), Calcium (Ca) or Lead (Pb). The structure can be described as a hexagonal structure with stack of oxygen and lead ions, with the iron sites coordinated only by oxygen. There are three octahedral sites, a tetrahedral site and a five-coordinated trigonal bipyramidal site.

The most important hexagonal ferrites are barium ferrite (BaFe<sub>12</sub>O<sub>19</sub>) and Strontium ferrite (SrFe<sub>12</sub>O<sub>19</sub>). The barium ferrite structure containing ten oxygen layers in its elementary unit cell, and it is constructed from four building blocks, labeled as S,S\*, R and R\* in the Fig. 2.9. The S and S\* blocks are spinels with two oxygen layers and six Fe<sup>3+</sup> ions. Four of the Fe<sup>3+</sup> ions are in octahedral sites and having their spins aligned parallel to each other and the other two are in tetrahedral sites with the opposite spin direction to the octahedral ions. The S and S\* blocks are equivalent but rotated 180° with respect to each other. The R and R\* block consists of three oxygen layers, with one of the oxygen anions in the middle layer replaced by a barium ion. Each R block contains six Fe<sup>3+</sup> ions, five of which are in octahedral sites with three up - spin and two down - spin, and one of which is coordinated by five O<sup>2+</sup> anions and has upspin. The net magnetic moment per unit cell is  $20\mu_{\rm B}$ .

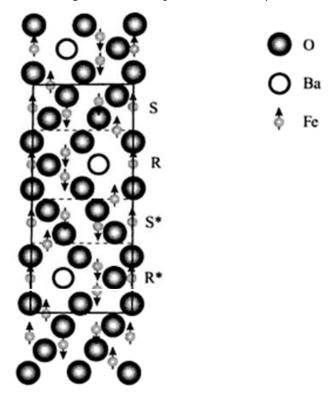


Fig.2.9 Structure of barium ferrite

Magnetoplumbites are magnetically hard unlike the cubic ferrites with typical coercivities of around 200KA/m. Also, they are easy to produce by ceramic processing methods, and can be powered and formed easily into any required shape.

They are subclassified into six subclasses namely; M, W, Y, Z, X and U type according to their crystal structure and arrangement of respective S, R and T blocks. Table 2.4 shows the subclasses of magnetoplumbites with their chemical formulae. Where, A represents Ba, Pb or Sr and M is a divalent transition metal ion.

**Table 2.4 Subclasses of Magnetoplumbites** 

Sl. No.	Magnetoplumbites	Chemical formula		
1.	M-type	AFe <sub>12</sub> O <sub>19</sub>		
2.	Y-type	$A_2M_2Fe_{12}O_{22}$		
3.	W-type	$AM_2Fe_{16}O_{27}$		
4.	X-type	$A_2M_2Fe_{28}O_{46}$		
5.	U-type	$A_4M_2Fe_{36}O_{60}$		
6.	Z-type	$A_3M_2Fe_{24}O_{41}$		

# **Applications of Magnetoplumbites**

- Barium hexaferrite is used in hybrid microwave devices, monolithic microwave integrated circuits
  and future replacement for yttrium iron garnet due to its high uniaxial anisotropy and large
  resistivity.
- Magnetoplumbites are used in magnetic recording media due to their high quality magnetic behavior.
- M-type compound of these system are used in developing glass ceramic.
- Magnetoplumbites can be used as a substrate material for catalyst support.
- After doping with proper ions like Eu<sup>2+</sup>, it can be used as luminescent materials in lighting tubes.
- Magnetoplumbites can also be used as interface coating on high temperature ceramic matrix composites.

# 2.8 Magnetic bubbles

#### **Definition**

It is a tiny movable <u>magnetized</u> cylindrical volume in a thin <u>magnetic</u> material that along with other like volumes can be used to represent a bit of information (as in a computer).

A thin wafer of Ferromagnetic Garnet reveals its magnetic domain alignment as light and dark serpentine patterns when viewed between crossed polarizer. These domains can be flipped by an external magnetic field, changing the pattern structure.

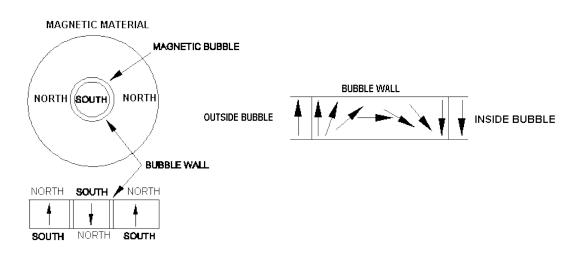


Fig. 2.10 Formation of Magnetic bubbles



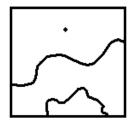


Fig. 2.11 Serpentine patterns of magnetic bubbles

#### Working

The magnetic bubble apparatus consists of a thin (8-12µm) single crystal film of Ferromagnetic Garnet (FMG) sandwiched between a pair of crossed Polaroids. The FMG crystals are magnetically anisotropic, that is, they have a strong tendency to orient themselves in fixed directions under the influence of an external magnetic field. The preferred or "easy" axis of orientation is perpendicular to (in or out of) the crystal surface. With no external magnetic field, the domains in the crystal orient up or down in roughly equal amounts. Polarized light passing through the crystal will have its plane of polarization rotated by due to interaction with the magnetic field of the domains (an effect called Faraday rotation). For the 'up' domains, the light will be crossed with respect to the exiting Polaroid therefore appearing dark, and for 'down' domains uncrossed (or vice versa) so appearing bright. The domains appear as serpentine patterns [Fig. 2.11] of alternating bright and dark. Application of an external magnetic field (provided by a built-in electromagnet) flips the domains to one preferred orientation. As the field is increased, the serpentine patterns gradually disappear and isolated magnetic bubble may be available.

#### **Applications and Advantages of Magnetic bubbles**

#### **Applications**

A memory device is formed by lining up tiny electromagnets at one end with detectors at the other end. Bubbles written in would be slowly pushed to the other, forming a sheet of Twisters lined up beside each other. Attaching the output from the detector back to the electromagnets turns the sheet into a series of loops, which can hold the information over long duration.

Bubble memory is a non-volatile memory. Even when power was removed, the bubbles remained, just as the patterns do on the surface of a disk drive. Better yet, bubble memory devices needed no moving parts: the field that pushed the bubbles along the surface was generated electrically, whereas media like tape and disk drives required mechanical movement.

Finally, because of the small size of the bubbles, the density was theoretically much higher than existing magnetic storage devices. The only downside was speed; the bubbles had to cycle to the far end of the sheet before they could be read.

#### **Advantages of bubble memories**

The future growth of distributed process systems will be greatly impacted by magnetic-bubble memories. These microprocessor-based systems demand high-density mass storage at low cost. Magnetic-bubble memories satisfy all of these requirements with definite advantages over the existing magnetic storage technologies. MBM's advantages over moving-head disks or floppy disks are low access time (the time necessary to retrieve the desired data), small physical size, low user entry cost, no maintenance, and higher reliability.

The advantages of MBM's over random-access memories (RAM's) are nonvolatility, potentially lower price per bit, and more bits per chip. The RAM has the advantage of much better access time, higher transfer rate, and simpler interfacing.

In summary, the main MBM advantages are the low price, nonvolatility, and high-density storage in a small physical space. Because magnetic bubble memories are a solid-state, nonvolatile technology, they are ideally suited for portable applications as well as providing memory for traditional processing systems. Industrial applications include memory for numerical control machines and various types of process control. Solid-state bubble memories are more reliable in harsh environments; they are affected much less by shock, vibration, dirt, and dust than electromechanical magnetic memories. Innovative new products include data terminals, calculators, word processing, voice storage, and measurement equipment.

#### 2.9 Magnetic Thin Film

Magnetic thin films are a sheet of magnetic material with thicknesses of a few micrometers or less, used in the electronics industry. Magnetic films can be single-crystal, polycrystalline, amorphous, or multilayered in the arrangement of their atoms. Both ferro and ferrimagnetic films are used. The ferromagnetic films are usually transition-metal-based alloys. For example, permalloy is a nickel-iron alloy, the ferri magnetic films, such as garnets or the amorphous films, contain transition metals such as iron or cobalt and rare earths.

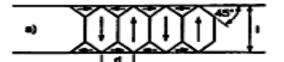
#### **Properties**

Thin films have different magnetic properties from their bulk counterparts. This is due to the artificial confinement of the electrons realized in the two-dimensional film geometry. The magnetic thin films are having the following properties compare to the bulk.

- Much lower resistivity
- High magnetic saturation induction
- Optical absorption of the thin films is much higher.
- Much higher saturation flux density, and
- Can have much lower hysteresis loss

### Magnetism of thin films

The thickness of a thin film is usually on the order of magnitude of a typical domain wall in the bulk material, up to 100 nm. In principle, there are three possibilities for establishing a domain structure. If the film is thick enough, the domain structure in Fig. 2.12a is possible. In the case of only two easy



directions perpendicular to the film plan, the structure of Fig. 2.12b could be established. This domain structure is important for magneto-optical applications.

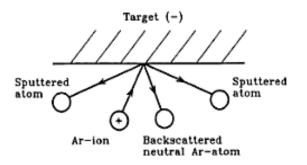
Fig 2.12 Possible domain structures in magnetic thin film

In many cases we have to deal with in-plane magnetization as represented in Fig 2.12. The spontaneous magnetization of metallic ferromagnets is so larger than the magnetocrystaline anisotropy energy. If the thickness of the film is below the domain wall width, the rotation of the magnetic moments from one domain to the neighbor domain direction will be occur in-plane as a Neel-type domain wall. Because of the comparatively high wall energy, thin films often appear uniformly magnetized in the film plane, and magnetization reversal can be achieved by coherent rotation.

#### Magnetic thin film processing

Various techniques are used for the fabrication of thin films, depending on the material and the specific applications. These techniques can be divided into physical vapor deposition (PVD), chemical vapor deposition (CVD), electrochemical deposition, thermal spraying and electro-surfacing. Among these various methods, sputtering (PVD) is the most important deposition technique for magnetic thin films. For example, magnetic films like FeAlSi, CoNbZr, CoCr, FeNiMo, FeSi, CoNiCr and CoNiSi for recording process can be fabricated with this technique.

In common sputtering system positive ions are accelerated from a plasma to a target that is a negative potential with respect to the plasma as shown in Fig 2.13. The ions reach the target surface with than energy given by the potential drop between the target and the plasma. The target surface is considered as the source of material from which films are grown. In addition to the sputtered materials liberated from the bombarded surface, which eventually condenses as a film, there are numerous other events that can occur at the target surface that may influence the growth of films profoundly. These includes secondary electron emission, secondary positive and negative ion emission, emission of radiation, reflection of incident particles, heating, chemical dissociation or reaction and others.



### Fig 2.13 Principle of sputtering

# **Applications of magnetic thin films**

- The ferrimagnetic properties of the thin films are advantageous in magneto optic applications where a low overall magnetic moment can be achieved without a significant change in the Curie temperature.
- The change in electrical properties, such as the electrical resistance, with a magnetic field is used in sensor elements.
- Magnetic thin film transducers have a wide range of applications, both in the area of sensors as well as actuators.
- It can be used in audio, video and computer memories.
- The most important usage of these films is magnetic read and writes heads.
- Magnetic materials thin films have long been used in data recording and storage media.
- Magnetic thin film materials are used extensively in insulators.

## 2.10 Spintronics and Devices

A revolutionary new class of semiconductor electronics based on the spin degree of freedom of an electron (as opposed to the charge degree of freedom) to process electronic data.

Spintronics refers to devices that utilize the spin properties of electrons for their functionality. Because spins can be manipulated faster and at lower energy cost than charges, spintronics has the potential advantages of increasing data processing speed and decreasing electric power consumption. One of the major technological breakthroughs of spintronics is in data storage industry. The discovery of giant magnetoresistance (GMR) effect, used in read-head sensors in hard drives has allowed increasing the storage density to ~ 1 Tbyte/inch² and more. This field received a special recognition with a Nobel prize for Physics in 2007. Currently, there is an increased activity from materials research perspective to understand and develop spintronics devices using new interesting materials like, carbon nanotubes, graphene, topological insulators and also organic semiconductors (OSs) for technological applications.

# Advantages of spintronic devices

- Spintronic devices offer the possibility of enhanced functionality, higher speed, and reduced power consumption.
- Information is stored into spin as one of two possible orientations.
- Spin lifetime is relatively long, on the order of nanoseconds.
- Spin currents can be manipulated.
- Spin devices may combine logic and storage functionality eliminating the need for separate components.
- Magnetic storage is nonvolatile
- Binary spin polarization offers the possibility of applications as qubits in quantum computers.

#### 2.10.1 Magnetoresistance

**Magnetoresistance** is the property of a material to change the value of its <u>electrical resistance</u> when an external <u>magnetic field</u> is applied to it. The effect was first discovered by <u>William Thomson</u> (more commonly known as Lord Kelvin) in <u>1856</u>, but he was unable to lower the electrical resistance of anything by more than 5%. This effect was later called ordinary magnetoresistance (OMR).

The magnetoresistance has been known for many years in ordinary metals and is due to the conduction electrons being forced of move in helical trajectories about an applied magnetic field. The effect becomes evident only when the magnetic field is strong enough to curve the path of the electron within a length equal to its mean free path. The magnetoreisitance effect occurs in metals only at very high magnetic fields and low temperatures. For example, in pure copper at 4 K a field of 10 T produces a factor of 10 change in the resistance. Because of the large fields and low temperatures, magnetoresistance in metals originally had few potential application possibilities.

The magnetoresistance of conventional materials is quite small; but materials with large magnetoresistance have been synthesized now. Depending on the magnitude, it is called either as Giant magnetoresistance (GMR), Tunnel magnetoresistance (TMR) or Colossal magnetoresistance (CMR).

### 2.10.2 Giant magnetoresistance (GMR)

It is a quantum mechanical effect, a type of magnetoresistance effect, observed in thin film structures composed of alternating ferromagnetic and nonmagnetic metal layers. The effect manifests itself as a significant decrease in electrical resistance in the presence of a magnetic field. In the absence of an applied magnetic field, the direction of magnetization of adjacent ferromagnetic layers is antiparallel due to a weak anti-ferromagnetic coupling between layers, and it decreases to a lower level of resistance when the magnetization of the adjacent layers align due to an applied external field. The spins of the electrons of the nonmagnetic metal align parallel or antiparallel with an applied magnetic field in equal numbers, and therefore suffer less magnetic scattering when the magnetizations of the ferromagnetic layers are parallel. The effect is exploited commercially by manufacturers of hard disk drives. The 2007 Nobel Prize in physics was awarded to the European Albert Fert and Peter Grünberg for the discovery of GMR.

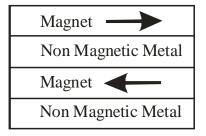


Fig. 2.14. Schematic representation of layered structure for GMR

A schematic of the layered structure and the alternating orientation of the magnetization in the ferromagnetic layer is shown in the Fig.2.14. The effect was first observed in films made of alternating layers of iron and chromium, but since then other layered materials composed of alternating layers of cobalt and copper have been made that display much higher magnetoresistive effects. The magnitude of the change in the resistance depends on the thickness of the iron layer and it reaches a maximum at a thickness of 7 nm.

## 2.10.3 Tunnel magnetoresistance (TMR)

Tunnel magnetoresistance is a quantum mechanical effect which occurs when two ferromagnets are separated by a few atomic layers of insulator. The conductance of such a tunneling junction can vary dramatically depending on whether the ferromagnets are aligned in parrallel or antiparallel. The effect is termed "tunnel magnetoresistance" (TMR) and the relative change in the resistance of the junction, is called 'optimistic' magnetoresistance ratio.

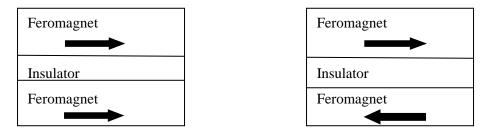


Fig.2.15 Schematic representation of layered structure for Tunnel Magneto resistance (a) Parallel state (b) Antiparallel State

TMR is a consequence of <u>spin-dependent tunneling</u>. TMR can be understood in terms of Julliere's model, which is based on two assumptions. First, it is assumed that spin of electrons is conserved in the

tunneling process. It follows that tunneling of up- and down-spin electrons are two independent processes, so the conductance occurs in the two independent spin channels. According to this assumption, electrons originating from one spin state of the first ferromagnetic film are accepted by unfilled states of the same spin of the second film. If the two ferromagnetic films are magnetized parallel, the minority spins tunnel to the minority states and the majority spins tunnel to the majority states.

In this parallel state the possibility of electron tunneling between the two ferromagnetic electrodes through the insulator layer becomes larger, resulting in larger tunneling current. However, the two films are magnetized antiparallel the identity of the majority- and minority-spin electrons is reversed, so the majority spins of the first film tunnel to the minority states in the second film and vice versa. In this antiparallel state the electron with opposite spin orientation with respect to the magnetization of the ferromagnetic electrode cannot be tunneled successfully. Then the tunneling electron current become smaller compared to the case for the same directions of the magnetizations. Second, it is assumed that the conductance for a particular spin orientation is proportional to the product of the effective density of states of the two ferromagnetic electrodes.

The schematic representation of TMR with parallel state of ferromagnetic films and antiparallel state of ferromagnetic films are shown in Fig 2.15. By sputter depositing ferromagnetic film on top of antiferromagnetic layer, the orientation of the magnetization of thin films can be "pinned" by the exchange coupling between the moment of the antiferromagnetic layer and the thin ferromagnetic layer. The thickness of the ferromagnetic layer must be thinner than the exchange length of the material. The magnetization of the other ferromagnetic layer can be easily changed by applying external field if the film is made of soft magnetic thin film. By this configuration, the magnetic resistance changes sensitively depending on the external magnetic field, thus can be used as high sensitive magnetoresistive devices such as magnetic random memory (MRAM).

# 2.10.4 Colossal magnetoresistance (CMR)

It is a property of some materials, mostly manganese-based perovskite oxides, that enables them to dramatically change their electrical resistance in the presence of a magnetic field. The magnetoresistance of conventional materials enables changes in resistance of up to 5%, but materials featuring CMR may demonstrate resistance changes by orders of magnitude. CMR was discovered in 1993 by von Helmolt et al.

Colossal Magnetoresistance has been predominantly discovered in manganese-based perovskite oxides. This arises because of strong mutual coupling of spin, charge and lattice degrees of freedom. Hence not only high temperature superconductivity, but also new magnetoelectronic properties are increasingly discovered in materials with perovskite structures.

The perovskite like material LaMnO<sub>3</sub> has manganese in the Mn<sup>3+</sup> valence state. If the La<sup>3+</sup> is partially replaced with ions having a valence of 2+, such as Ca, Ba, Sr, Pd or Cd, some Mn<sup>3+</sup> ions transform to Mn<sup>4+</sup> to preserve the electrical neutality. The result is a mixed valence system has been shown to exhibit very large magnetoresistive effects. The unit cell of the crystal is shown in Fig. 2.16.

The particular system  $La_{0.67}Ca_{0.33}MnO_x$  displays more than a thousand fold change in the resistance with the application of a 6 T DC magnetic field.

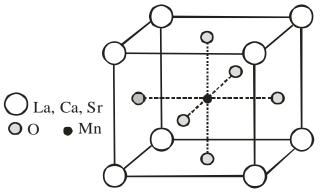


Fig. 2.16 Crystal structure of  $LaMnO_3$  which displays colossal magnetoresistance when the La site is doped with Ca or Sr.

### **Applications of CMR and GMR materials**

- The understanding and application of CMR offers tremendous opportunities for the development of new technologies such as read/write heads for high-capacity magnetic storage, sensing elements in magnetometers and spintronics.
- The largest technological application of GMR is in the data storage industry.
- On-chip GMR sensors are available commercially from Non-Volatile Electronics.
- Other applications are as diverse as solid-state compasses, automotive sensors, non-volatile magnetic memory and the detection of landmines.
- Read sensors that employ the GMR effect available for detecting the fields from tiny regions of magnetization. These tiny sensors can be made in such a way that a very small magnetic field causes a detectable change in their resistivity; such changes in the resistivity produce electrical signals corresponding to the data on the disk.
- It is expected that the GMR effect will allow disk drive manufacturers to continue increasing density at least until disk capacity reaches 10 Gb per square inch. At this density, 120 billion bits could be stored on a typical 3.5-inch disk drive, or the equivalent of about a thousand 30-volume encyclopedias.