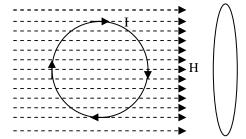
# **Magnetic Properties**

## **Origin of Magnetism:**

If there is current carrying loop of radius 'r' carrying current I in a magnetic field H, then the this loop experiences a torque due to which loop becomes perpendicular to the field. The loop exhibit magnetic moment in magnetic field.

Figure 1: A current carrying loop in magnetic field experience a torque which makes loop plane perpendicular to the field.



Thus the moment per unit field =  $Current \times Area i.e.$ ,

$$M = I A$$
 .....(1)

An orbiting electron with an angular velocity  $\omega$  in a orbit of radius r is having a current associated with its motion given by

I = charge \* turns per second = 
$$-e \omega/2\pi$$
 .....(2)

This orbiting electron is equivalent to a current loop, whose magnetic moment can be written as

As the angular momentum L= n  $\hbar$  (  $\hbar$ = h/2 $\pi$ ), so the magnetic moment can be written as

$$\begin{split} M_{orb} &= - \, e(nh)/4\pi m \\ &= - n \, \left( eh/4\pi m \right) \\ &= - n \, M_B \end{split} \tag{4}$$

i.e.,  $M_{orb}$  can change its value in units of  $M_B$  which is given as

$$M_{B} = eh/4\pi m \qquad ....(5)$$

Thus,  $M_B$  is the smallest unit or fundamental magnetic moment and is usually called Bohr Magneton. Substituting value of constants its value can be estimated by substituting constants,  $e = 1.6 \times 10^{-19}$  C,  $m = 9.1 \times 10^{-31}$  Kg, and  $h=6.62*10^{-34}$  J-s

$$\begin{array}{l} M_B = 1.165 \times 10^{-29} \; Wb \; m \\ = \mu_o \times 1.165 \times 10^{-29} \; A \; m^2 \quad \text{where, } \mu_o = 4\pi \times 10^{-7} H/m \\ = 9.27 \times 10^{-24} \; A \; m^{-2} \; (\text{or J T}^{-1}) \end{array}$$

Similarly spinning electron is also equivalent to a current loop and thus this spin motion of the electron also contributes to magnetic moment, the value of which is double of that due to its orbital motion. So the magnetic moment  $M_S$  arising due to spin motion of the electron can be written as

$$M_{\text{Spin}} = -2 \text{ n (eh/4}\pi\text{m)}$$
 .....(7)

Thus in general,

M=-g neh/4 $\pi$ m, where g is called gyro-magnetic ratio relating angular momentum to magnetic moment and is having value 1 for orbital motion and 2 for spin motion.

These orbital and spin magnetic moments of all the electrons in an atom are added together following vector addition rules giving rise to the total magnetic moment of an atom as below

$$\mathbf{M}_{\text{atom}} = \mathbf{M}_{\text{B}} \ \mathbf{g} \sqrt{\mathbf{J}(\mathbf{J}+1)}$$
 (8)

where, J is total angular momentum quantum number. The 'g' the gyro-magnetic ratio is given by

$$g = [1 + {J(J+1)+S(S+1)-L(L+1)}/2J(J+1)] \qquad ....(9)$$

which, acquires value 1 for S=0, 2 for L=0 and 3/2 for L=S. Here S, L and J are spin, orbital and total angular momentum quantum numbers for the atom, respectively.

#### Hund's Rule:

- 1. The sum of spin quantum number has to be maximum provided Pauli's exclusion principle is not violated.
- In commensurate with rule 1 above, the sum of orbital quantum number has to be maximum.
- The total angular momentum quantum number is
  - J = L S, when the orbit is less than half filled and
    - = L + S, when the orbit is more than half filled,

projection of 's' on **H** is denoted by  $m_s(\pm \frac{1}{2})$  and that of 'l' on **H** is denoted by  $m_1(\pm 1)$ .

#### **Ouantum numbers:**

Principle quantum number : n = 14... (n-1) for each n 2 3 Orbital quantum number : 1 = 1

p

Magnetic quantum number:  $m_1 = 0, \pm 1, \pm 2, \pm 3, \dots \pm l$  (for each l) Spin quantum number :  $m_s = \pm \frac{1}{2}$  (for each  $m_l$ )

For example:  

$$He^2 = 1s^2$$
,  $l_1 = 0, l_2 = 0$  so  $L = l_1 + l_2 = 0$   
 $s_1 = \frac{1}{2}, s_2 = -\frac{1}{2}$  so  $S = s_1 + s_2 = 0$   $J = L + S = 0 \Rightarrow M_{He} = 0$ 

$$Si^{14} = 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^2 \\ l_1 = 1, \ l_2 = 0 \\ s_1 = \frac{1}{2}, \ s_2 = \frac{1}{2} \\ so \ S = s_1 + s_2 = 1 \\ J = L - S = 0 \\ \Rightarrow M_{Si} = 0$$

$$\begin{aligned} Fe^{26} &= 1s^2 \ 2s^2p^6 \ 3s^2p^2d^6 \ 4s^2 \\ &\qquad \qquad I's=2, \ 1, \ 0, -1, \ -2, \ 2 \implies L = 2 \\ &\qquad \qquad s's=\frac{1}{2}, \ \frac{1}{2}, \ \frac{1}{2}, \ \frac{1}{2}, \ \frac{1}{2}, \ -\frac{1}{2}, \implies S = 2 \\ &\qquad \qquad J = 2+2 = 4, \ \text{and} \ g = 3/2 \implies M_{Fe} = M_B \ (3/2)\sqrt{4*5} = 6.7 \ M_B \end{aligned}$$

$$\begin{aligned} Ni^{27} &= 1s^2\ 2s^2p^6\ 3s^2p^2d^7\ 4s^2 \\ &\qquad \qquad I's = 2,\ 1,\ 0,\ -1,\ -2,\ 2,1 \ \Rightarrow \ L = 3 \\ &\qquad \qquad s's = \frac{1}{2},\ \frac{1}{2},\ \frac{1}{2},\ \frac{1}{2},\ \frac{1}{2},\ \frac{1}{2},\ \frac{1}{2} \Rightarrow S = 3/2 \\ &\qquad \qquad J = 3 + 3/2 = 9/2,\ and\ g = 127/99 \Rightarrow M_{Co} = 6.63\ M_B \\ Co^{28} &= 1s^2\ 2s^2p^6\ 3s^2p^2d^8\ 4s^2 \\ &\qquad \qquad I's = 2,\ 1,\ 0,\ -1,\ -2,\ 2,1,0 \ \Rightarrow \ L = 3 \\ &\qquad \qquad s's = \frac{1}{2},\ \frac{1}{2},\ \frac{1}{2},\ \frac{1}{2},\ \frac{1}{2},\ -\frac{1}{2},\ -\frac{1}{2} \Rightarrow S = 1 \end{aligned}$$

$$\sqrt{2}$$
,  $\sqrt{2}$ ,  $\sqrt{2}$ ,  $\sqrt{2}$ ,  $\sqrt{2}$ ,  $-\sqrt{2}$ ,  $-\sqrt{2}$   $\Rightarrow$  S = 1  
 $J = 4$ , and  $g = 5/4 \Rightarrow M_{Ni} = 5.59 M_B$ 

### **Magnetization:**

Magnetic field due to current in solenoid having n number of turns in free space is given as  $B_0 = \mu_0 n i$ .....(10)







Figure 2: (a) A long solenoid with free space as medium inside, the magnetic field is  $\mathbf{B}_{o}$ .(b) A material medium inserted into the solenoid develops a magnetization M. (c) Elementary current loops result in surface currents. There is no internal current as adjacent currents on neighboring loops are in opposite directions

When a cylindrical shape material medium is placed within the solenoid the magnetic field changed. New magnetic field will be denoted as B. Bo being the magnetic field into which the material medium is placed. Each atom of the material responds to the applied field  $B_0$  and acquires net magnetic moment  $M_{atom}$  along applied field. This can be viewed as a result of precession of each atomic magnetic moment about B<sub>0</sub>. The material therefore develops a net magnetic moment along field and become magnetized. The magnetization vector M, describe the extent of alignment of theses elementary dipoles in the medium. The  $\mathbf{M}$  is defined as the dipole moment per unit volume. If the number of atoms per unit volume is 'n' and Mav is average dipole moment per atom then we can write  $M = n M_{av}$ 

Each of magnetic moment  $M_{\rm av}$  can be viewed as an elementary current loop at the atomic scale. Each elementary current loop arises from both the orbital and spin motions of the electrons. Each current loop has its current plane normal to  $B_o$ . As all atoms has same average magnetic moment there is no net current inside the material because at any point within the material corresponding to each electron moving clockwise there is another electron moving anti-clockwise. However, currents at surface do not cancel thereby leading to net surface currents. These surface currents (also called magnetization currents) are induced by magnetization of the medium by applied magnetic field and therefore depend on the magnetization M of the specimen. From definition of M the total moment of the cylindrical specimen is

Total magnetic moment =  $M \times \text{volume}$ =  $M \times A \times I$ . (1)

'1' being the length and 'A' area of the specimen. If the magnetization current on surface per unit length of specimen is ' $I_m$ ' then total circulating surface current is  $I_m \times I$  and so total magnetic moment of the specimen is

The total magnetic moment = total current  $\times$  area

On comparing the two, we get  $M=I_{\rm m}$ . This magnetization current is not due to flow of free charge carriers as in current carrying wire but due to localized electronic currents within the atom of the solid at the surface. Thus magnetization of the medium is represented by a surface current per unit length i.e. M is equal to  $I_{\rm m}$  i.e., magnetization is nothing but the induced surface currents per unit length on the material.

### Magnetizing field and magnetic field strength:

The magnetized specimen placed inside the solenoid develops magnetization currents on the surface. These circulating currents on the materials surface behaves like a solenoid giving rise to a magnetic field associated with them. The magnetic field within the medium now arise from conduction current 'I' through the coils and the magnetization current ' $I_m$ ' on the surface. Thus the magnetic field 'B' inside the solenoid now is given by usual expression

Thus field inside magnetized material is the sum of the applied field  $B_o$  and a contribution  $\mu_o M$  arising from magnetization M the material.  $B_o$  is due to external conduction current. Thus  $B - \mu_o M$  at any point is the contribution of external conduction current alone to the magnetic field at that point inside the material that we called  $B_o$ . This  $B - \mu_o M$  represents the magnetizing field because it is the field of the external current that magnetized the material. Thus magnetizing field is H is defined as

$$\begin{aligned} &H=B_o/\mu_o=~(B-\mu_o M)/\mu_o=B/\mu_o-M\\ &\text{or} &H=B_o/\mu_o \end{aligned} \tag{14}$$

The magnetizing field is also known as magnetic field intensity (A/m). Reason for dividing by  $\mu_o$  is that the resulting vector field H becomes simply related to external conduction current (through Ampere's law). Since  $B_o$  is  $\mu_o$ ni. H = ni = total conduction current per unit length. H is actually *cause* and B is the *effect*. The cause H depends only on the external conduction current, whereas, the effect B depends on the magnetization M of matter.

### Magnetic permeability and susceptibility:

Let in presence of material the magnetic field is  $\bf B$  and magnetizing field is  $\bf H$ . If in free space  $\bf B_o$  be the magnetic field in absence of any material, the magnetic permeability of the medium is defined as the magnetic field per unit magnetizing field i.e.,

$$\mu = B/H \text{ (wb/A-m or A/m)}$$
 .....(15)

It relates the effect **B** to cause **H** at the same point inside a material. It represents the extent a medium is permeable by the magnetic field. Relative permeability  $\mu_r$  of a medium is the fractional increase in the magnetic field when a material medium is introduced, with respect to the field in free space. For example suppose the field in a solenoid with free space in it is  $B_o$  but with material inserted it is B, then relative permeability is given as

 $\mu_r = B/B_o = \mu H/\mu_o H \quad (A/m) \tag{16}$  From these equations above it clearly means  $\mu = \mu_r \, \mu_o \tag{17}$ 

The magnetization M produced in a material depends on the external applied magnetic field H around it. The extent of magnetization of the material is expressed in terms of magnetic susceptibility as

$$M = \chi H$$

In presence of the material, magnetic field **B** in terms of magnetization is written as

$$\mathbf{B} = \mu_{o} (\mathbf{H} + \mathbf{M}) = \mu_{o} (\mathbf{H} + \chi \mathbf{H}) = \mu_{o} (1 + \chi) \mathbf{H} = \mu \mathbf{H}$$
 (18)

Thus,  $\mu = \mu_o(1 + \chi)$  or  $\mu/\mu_o = (1 + \chi)$  or  $\mu_r = (1 + \chi)$ , ......(19) which is the relation between magnetic permeability and susceptibility. The presence of magnetic material is conveniently accounted for by using the relative permeability  $\mu_r$  or  $(1+\chi)$  to simply multiply  $\mu_o$ 

Physical quantity Magnetic induction	Symbol B	Si units Tesla (wb/m²)
(flux density)		,
Magnetic field strength	Н	A/m
Magnetization	M	A/m
Permeability of free space	$\mu_{ m o}$	H/m
Relative permeability	$\mu_{ m r}$	_
Susceptibility	χ	_
Magnetic moment	M	$A-m^2$

### Types of magnetism or magnetic materials:

On the basis of their response to external applied magnetic field the materials are classified into five distinct groups, namely,

1. Diamagnetic, 2. Paramagnetic, 3. Ferromagnetic, 4. Anti-ferromagnetic, 5. Ferri-magnetic

#### Diamagnetism:

Typical diamagnetic materials have a magnetic susceptibility that is negative and very small. The relative permeability of the diamagnetic materials is slightly less than unity. When a diamagnetic material is placed in a magnetic field the induced magnetization M in the material is in a direction opposite to that of the applied magnetizing field and the resulting magnetic field B within the material is less than that in free space. Negative  $\chi$  can be interpreted as the substance trying to expel the applied field out from the material.

Diamagnetism is a very week form of magnetism i.e., non-permanent and persist only while external field is being applied. Atoms of a diamagnetic material have no net magnetic moment associated with them because of completely filled shell or sub-shell electrons. Covalent crystals and many ionic solids are typical diamagnetic materials because the constituent atoms have no unfilled shells. The magnetic field, however, induces a change in the orbital motion of electrons in such a way that atom possess net magnetic moment. The magnitude of induced magnetic moment is extremely small and in a direction opposite to that of the applied field. Thus the relative permeability  $\mu_r$  is less than unity. The susceptibility  $\chi$  of diamagnetic solid material is of the order of  $\sim 10^{-5}$ . These are attracted towards region where the field is week. The variation of B with H in diamagnetic materials is shown in Figure 4.



Figure 3: (a) Atoms of the diamagnetic material having no net magnetic moment in absence of applied magnetic field. In applied magnetic field induces a magnetic moment in each atom in the opposite direction.

Diamagn		<u>Paramagnetic</u>		
Materials	$\chi(\times 10^{-5})$	Materials	χ	
Al oxide	-1.81	Al 2.	07×10 <sup>-5</sup>	
Copper	-0.96	Mn sulphate 3.	$70 \times 10^{-3}$	
Au	-3.44	Mo 1.1	19×10 <sup>-4</sup>	
Hg	-2.85	Na 8.4	18×10 <sup>-6</sup>	
Si	-0.41	Ti 1.8	31×10 <sup>-4</sup>	
Ag	-2.38	Zr 1.0	)9×10 <sup>-4</sup>	
NaCl	-1.41			
Zn	-1.56			

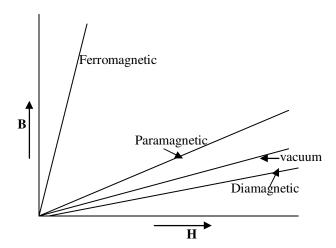


Table 1: Typical diamagnetic and paramagnetic materials with their susceptibility values.

Figure 4: Magnetization behavior of different type of magnetic materials.

### **Paramagnetism:**

For these materials each atom possesses a permanent dipole moment by virtue of incomplete cancellation of their spin and/ or orbital magnetic moments. It is observed in materials in which atoms are having incomplete s- and p- shell electrons. In the absence of external magnetic field the orientation of these magnetic moments are random, such that a piece of material possess no net macroscopic magnetization. These atomic magnetic moments are free to rotate and paramagnetism results when they preferentially align by rotation with an external field.

These magnetic dipoles are acted on individually with no mutual interaction between adjacent dipoles as shown in Figure 5(a). In presence of applied magnetic field, the dipoles align little along the field, Figure 5(b). With increasing field they enhance it giving rise to a relative permeability,  $\mu_r$  that is greater than unity and to a relatively small but positive magnetic susceptibility,  $\chi$ , having values varying from  $10^{-5}$  to  $10^{-2}$ . The variation of B with H in these materials is shown in Figure 4.



Figure 5: (a) In paramagnetic material each individual atom possesses a permanent magnetic moment, due to thermal agitation these elementary dipole are randomly oriented in space thereby giving rise to no net magnetization in the material. (b) In the presence of an applied field these dipoles are aligned along the field resulting in finite **M**, along **H**.

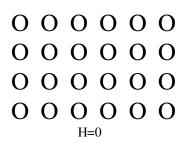
Both diamagnetic and paramagnetic materials are considered to be non-magnetic because they exhibit magnetization only in presence of external magnetic field. Moreover, for both the materials the flux density  $\bf B$  within them is almost the same as it would be in vacuum (free space). Some examples of these types of materials are as given in the table 1.

### **Ferromagnetism:**

Certain metallic materials possess a large magnetic moment even in the absence of an external magnetic field. The succeptibility  $\chi$  is typically +ve and very large ~  $10^6$  (even infinite) and further depends on the applied field intensity. These characteristics of the ferromagnetism are displayed by the transition metal iron, cobalt nickel and some of the rare earth's metals like Gd.

The permanent magnetic moments in ferromagnetic materials results from atomic dipoles arising due to the electron spin (uncancelled electron spins as a consequence of the electronic structure). There is also contribution from orbital magnetic moment that is small in comparison to spin moments. Further more in these materials coupling interactions cause net spin magnetic moments of adjacent atoms to align with one another even in absence of external field. The origin of ferromagnetism is quantum mechanical exchange interaction between the constituent atoms that result in regions of material possessing permanent magnetization. These small regions having net magnetization M due to the spin alignment of the magnetic moments of all atomic dipoles in the material are called magnetic domains. These domains has magnetic ordering as the atomic magnetic moments have been aligned parallel to each other. This ferromagnetism occurs below a critical temperature called Curie temperature T<sub>c</sub>. At temperature above T<sub>c</sub> the ferromagnetism vanishes and the material become paramagnetic.

Figure 6 shows the schematic illustration of the mutual alignment of atomic dipoles in a ferromagnetic material, which will exist even in the absence of external magnetic field.



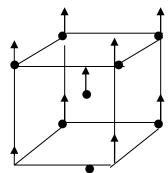


Figure 6: (a) Schematic arrangement showing alignment of dipoles in a ferromagnetic substance.(b) The iron atoms in bcc cubic unit cell having spins mutually aligned even in absence of applied field

This quantum-mechanical exchange interaction of spins leads to exchange energy like shown in Figure 7 for some of transition metals as a function of ratio of radius of d-orbital (or f-orbital) to the interatomic distance for transition (or rare-earth) metals. Higher is this value, more is the overlap of d- or f- orbital more is the interaction favoring alignment of spins. Lesser is the overlap less is the interaction less is the alignment of spins of neighboring atoms.

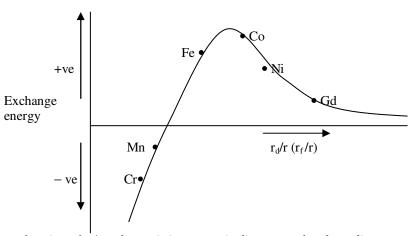


Figure 7: The exchange interaction energy as a function of  $r_d/r$ , where r is inter-atomic distance and  $r_d$  the radius of the d orbital for transition metals from chromium to nickel. For rare earth gadolinium, Gd the x axis is  $r_f/r$ , with  $r_f$  the radius of the f orbital.

The maximum possible magnetization or saturation magnetization  $M_S$  of a ferromagnetic material represents magnetization that results when all the magnetic dipoles mutually aligned with the external field. There is a corresponding saturation flux density  $B_s$ . The saturation magnetization is equal to the product of the net magnetic moment for each atom and the number of atoms present. For each of iron, cobalt and nickel the net magnetic moment per atom is 2.22, 1.72 and 0.60  $M_B$ , respectively.

### **Antiferromagnetism:**

The phenomenon of magnetic moment coupling between adjacent atoms or ions occurs in materials other than that are ferromagnetic. In one such group, spin coupling results in an antiparallel alignment i.e. alignment of spin moments of adjacent atom or ions in opposite directions is termed as anti-ferromagnetism.

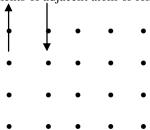
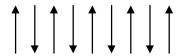


Figure 8: Shows anti-ferromagnetic materials with atoms at alternate positions have their spins aligned in opposite directions resulting in complete cancellation of the magnetic moments hence net zero magnetization.



The schematic arrangement of atoms in solid and alignment of their magnetic moments is shown in Figure 8. In elemental form phenomenon of anti-ferromagnetism is observed in pure chromium having body centered cubic structure, where atoms at corner positions have their spins up while those at body centers have their spins aligned downward as shown in Figure 10.

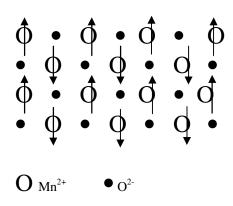


Figure 9: MnO having NaCl type structure, Mn<sup>2+</sup> ions at corners have spin up while those at face centers have spins down.

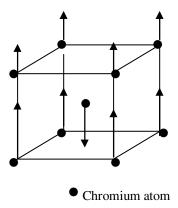


Figure 10: Chromium metal with bcc lattice, having spins of neighboring atoms aligned in opposite directions.

MnO is another compound crystal, which exhibit anti-ferromagnetic behavior as shown in Figure 9. MnO is ceramic material that is ionic in character having both  $Mn^{2+}$  and  $O^{2-}$  ions forming two, interpenetrating fcc lattices (NaCl–type). Another way to imagine its crystal structure is as if  $Mn^{2+}$  ions making fcc with  $O^{2-}$  ions occupying octahedral sites (i.e. edge centers and body center). Now the magnetic moment of  $Mn^{2+}$  ions at corners of cubic unit cell are aligned in one directions while those at face centers is in opposite directions thereby leading to complete cancellation of magnetic moments resulting in net zero magnetic moment of the crystal. The  $O^{2-}$  ions having no magnetic moments associated with them.Other examples of anti-ferromagnetic materials are Mn, TiH $_2$ , CuO , CrV, MnCr, MnBr $_2$ , MnCr etc

### **Ferrimagnetism:**

The phenomenon of ferrimagnetism is similar to anti-ferromagnetism but there is no complete cancellation of spin of adjacent atoms because of different type of atoms/ions occupying these positions. For example all A atoms in one position have their spins aligned in one direction and all B atoms at other neighboring sites have their spins aligned in opposite directions. However, the magnetic moment of A atoms is different from that of the B atom there is no complete cancellation of the magnetic moments and crystal possess net magnetization even in the absence of an applied field.

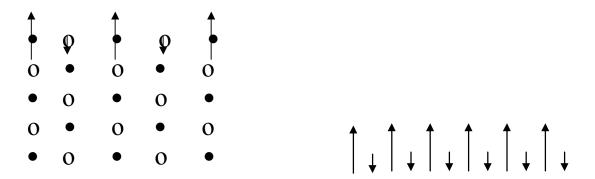


Figure 11: Here, **O** and • shows two atoms A and B, with different magnetic moment aligned in opposite directions. as there is no complete cancellation of magnetic moments, material possesses net magnetization even in absence of the magnetic field.

The macroscopic magnetic characteristics of ferromagnets and ferrimagnets materials are similar; distinction lies in the source of magnetic moments. The most common materials showing ferrimagnetic behavior are cubic ferrites, the metal oxides having chemical formula  $AFe_2O_4$  in which A represents any one of several metallic elements. The one such oxide is a natural magnet, namely, magnetite (formerly ore lodestone).  $Fe_3O_4$  is basically  $FeOFe_2O_3$  [ $Fe^{2+}O^{2-}$  ( $Fe^{3+}$ )<sub>2</sub>( $O^{2-}$ )<sub>3</sub>] in which Fe ions exists in both +2 and +3 valence states in the ratio of 1:2. A net spin magnetic moment exists for each  $Fe^{2+}$  and  $Fe^{3+}$  ions, which correspond to 4 and 5  $M_B$  units respectively for the two ion types. The  $O^{2-}$  ions are magnetically neutral. There are anti-parallel spin-coupling interactions between the Fe ions, similar in character to anti-ferromagnetism. The net magnetic moment arises from the incomplete cancellation of spin moments of the Fe ions at different sites.

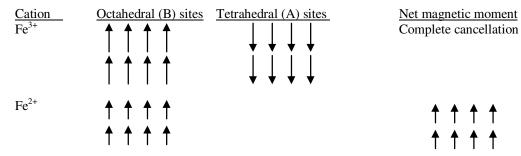
The cubic ferrites have spinel structures. Spinel is the name of the ore magnesium aluminate  $MgOAl_2O_3$ . In spinel structure oxygen ions forms fcc lattice. Now in one cube of such fcc cell there are 8 tetrahedral voids (A- or 4-f sites) with coordination number four and 4 octahedral voids (B- or 6-f sites) with coordination number six. In one formula unit the four oxygen ions forms fcc lattice.  $Mg^{2+}$  ion occupies one of the 8 4-f sites, whereas  $Al^{3+}$  ions occupy two of the 6-f sites. This way  $1/8^{th}$  of the 4-f and 1/2 of the 6-f sites are filled with metal ions. This resulting structure is called *normal spinel structure*. Thus, in this normal spinel structures

Oxygen ions form f.c.c. lattice Doubly ionized Mg occupies tetrahedral (A-) sites Triply ionized Al occupies octahedral (B-) sites

There is another different arrangement of metal ions in fcc oxygen lattice possible, resulting into a structure called an *inverse spinel* structure. Natural ore magnetite  $(Fe_3O_4)$  is an example of this type where

 $O^2$ - ions form f.c.c. lattice Doubly ionized (Fe<sup>2+</sup>) iron ions occupy octahedral (B-) sites Half of triply ionized (Fe<sup>3+</sup>) atoms occupy octahedral (B-) sites Half of triply ionized (Fe<sup>3+</sup>) atoms occupy tetrahedral (A-) sites

The alignment of magnetic moments of the ions at tetrahedral sites is in one direction while of those at octahedral sites is in opposite direction. The distribution of spin magnetic moments of  $Fe^{2+}$  and  $Fe^{3+}$  ions in a unit cell (containing 8 formula units  $Fe_3O_4$ ,) of magnetite which is given below.



In these spinel structures oxygen ions have no magnetic moment associated with them. The magnetic moment of the metal ions at A- sites is in a direction opposite to that of the atoms at B- sites. The  $FeOFe_2O_3$  is inverse spinel type structure. Half of ferric ions are in octahedral sites and other half in the tetrahedral sites. The spin moments of ferric ions in octahedral sites are aligned to one another; however they are directed oppositely to the ferric ions at tetrahedral sites which are also aligned mutually. Thus the spin moments of all ferric ions cancel one another and make no net contribution to magnetization of the solid. All ferrous ions have their spin moments aligned in the same direction, which is responsible for net magnetization. Thus the saturation magnetization of a ferrimagnetic solid may be computed from the product of net spin magnetic moment of ferrous ions and the number of these ions in the unit volume. The oxides having inverse spinel structures with resulting net magnetic moments are called *ferrites*. So the net magnetic moment of the one cubic cell will be

$$M = 5M_B (Fe^{3+} at 6-f) + 4M_B (Fe^{2+} at 6-f) - 5M_B (Fe^{3+} at 6-f) = 4M_B$$

The one unit cell of spinel structure contains 8 such formula units one each in 8 cubic cells. So one unit cell will have magnetic moment of  $8\times4M_B=32M_B$ . The unit cell dimension is 0.839 nm. Thus the saturation magnetization of such a ferrite will be  $M_S=32\times9.27\times10^{-24}/\left(8.39\times10^{-10}\right)^3$  A/m =  $5.0\times10^5$  A/m. The magnetic moments of various metal ions are as given below.

$Fe^{3+}$ 5 $Co^{2+}$ 3	
$\begin{array}{c c} \underline{Cation} & \underline{Net\ mag.\ mom\ (\ M_B\ )} & \underline{Cation} & \underline{Net\ mag.\ mom\ (} \\ Fe^{3+} & 5 & Co^{2+} & 3 \\ Fe^{2+} & 4 & Ni^{2+} & 2 \end{array}$	
$Mn^{2+}$ 5 $Cu^{2+}$ 1	

Cubic ferrites having other composition may be produced by adding metallic ions that substitute some of the ferrous ions in the structure like listed above in the table. Each of these possesses a net magnetic moment different from four units of  $Fe^{2^+}$ . Thus by adjustment of composition, ferrites compounds having a range of magnetic properties may be produced. For example,  $NiFe_2O_4$ ,  $MgFe_2O_4$ , and  $MnFe_2O_4$ . Other compounds may be produced containing mixture of two divalent metal ions such as  $(Mn_xFe_{1-x})$   $Fe_2O_4$  in which Mn to Fe ratio may be varied, giving rise to *mixed ferrites*.

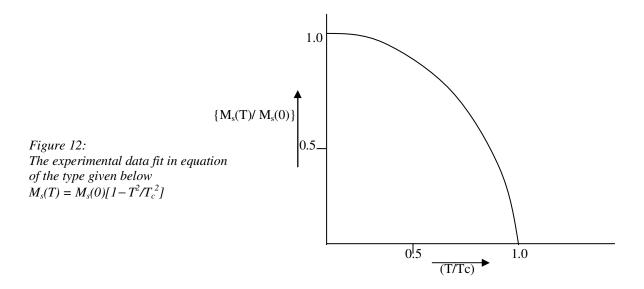
Ceramic materials other than cubic ferrites are also ferrimagnetic; these include hexagonal ferriters and garnets. Hexagonal ferrites have a crystal structure similar to inverse spinel with hexagonal symmetry rather than cubic. The chemical formula of these materials is given as  $AB_{12}O_{19}$  or  $AO6(B_2O_3)$ , where A is divalent metal ion like  $Ba^{2+}$ ,  $Ca^{2+}$ ,  $Pb^{2+}$ ,  $Sr^{2+}$  etc. and B is a trivalent metal ion like  $Al^{3+}$ ,  $Ga^{3+}$ ,  $Cr^{3+}$ ,  $Fe^{3+}$  etc. The two most common such hexagonal ferrites are lead ferrite (PbO6Fe<sub>2</sub>O<sub>3</sub>) and barium ferrite (BaO6Fe<sub>2</sub>O<sub>3</sub>).

The garnet have very complicated crystal structure, having general formula  $A_3B_5O_{12}$ , where A is a rare earth ion such as samarium, europium, gadolinium or yttrium and B is a trivalent metal ions.  $Y_3Fe_5O_{12}$  (YIG; yttrium iron garnet) is most common material of this type.

The saturation magnetization of ferrimagnetic materials is not as high as that for ferromagnetic. One the other hand ferrites, being ceramics are good electrical insulator. For some magnetic applications, such as in high frequency transformers, a low electrical conductivity is mostly desirable where use of ferrites become of importance.

### **Saturation Magnetization and Curie Temperature:**

The maximum magnetization in a ferromagnetic material when all the atomic dipoles have been aligned as much as possible is called saturation magnetization  $M_{sat}$ . As temperature of the material is increased the thermal vibrations of the lattice atoms become more energetic which leads to a frequent disruption of the alignment of the spins. The spins can not align perfectly with each other as the temperature increases since the lattice vibrations randomly agitating the individual spins. These vibrations disorientate the spins of atoms. This way we see that the alignment of spins decreases as the temperature increases and the ferromagnetic behavior disappears at certain temperature. This temperature at which the vibrations of the lattice atoms completely randomize the atomic dipoles, the net magnetic moment due to spins totally vanishes, is called as *Curie temperature* ( $T_c$ ). At this temperature thermal energy of lattice vibrations in crystal overcome the potential energy of the exchange interaction and hence destroy the spin alignments. Above the Curie temperature the crystal behaves as if it were paramagnetic (as each atom possessing dipole moment, which are randomly oriented in space). The saturation magnetization ( $M_{sat}$ ) therefore decreases from its maximum value at absolute zero Kelvin to zero at  $T_c$ . The variation of saturation magnetization  $M_{sat}$  with temperature is shown in the figure below.



This type behavior is shown by iron, Nickel and cobalt. For iron with  $T_c$  = 1043K, at room temperature (300K, when  $T/T_c$  = 0.29)  $M_s$  is very close to its value at 0 K i.e.  $M_{sat}(0)$ . The Table 2 below gives summary of some of the important magnetic parameters of ferromagnetic materials.

Property	Iron (Fe)	Cobalt (Co)	Nickel (Ni)	Gadolinium (Gd)	$Fe_3O_4$
Structure	B.C.C	H.C.P.	F.C.C.	H.C.P.	
Magnetic moment	2.22	1.72	0.60	7.1	
per atom (M <sub>B</sub> )					
$M_{sat}(0) (\times 10^6 \text{ A/m})$	1.75	1.45	0.50	2.0	
$B_{sat}(0)$ (Tesla or wb/m <sup>2</sup> )	2.20	1.82	0.64	2.5	
T <sub>c</sub> (in Kelvin)	1043	1400	631	289	
(in °C)	770	1127	358	16	585
, ,					

Table 2: Properties of ferromagnets Fe, Co, Ni, Gd and magnetite Fe<sub>3</sub>O<sub>4</sub>

**Question:** Calculate the (a) saturation magnetization and (b) saturation flux density for nickel. The density of nickel is 8.9 gm/cc.

**Question:** Find composition of a mixed-ferrite having saturation magnetization of 5.25×10<sup>5</sup> A/m.

Solution.: As seen above for the case of  $Fe_3O_4$ , it is having saturation magnetization of  $5.25 \times 10^5$  A/m which correspond to 32 Bohr magneton per unit cell. Now to increase saturation magnetization from this value we require addition of some Mn ions as they have higher magnetic moment. Then corresponding to new value of magnetization we can compute magnetic moment per unit cell under the assumption that addition of Mn does not alter the unit cell dimension, as

Magnetic Moment =  $32 \times 5.25 \times 10^5 / 5 \times 10^5 = 33.45$  Bohr magneton per unit cell.

If y is the fraction of  $Mn^{2+}$  ions replacing ferrous (Fe<sup>2+</sup>) ions in the crystal then magnetic moment per unit cell will be =  $8[y \times magnetic moment of Mn^{2+} + (1-y) \times magnetic moment of Fe^{2+}]$ 

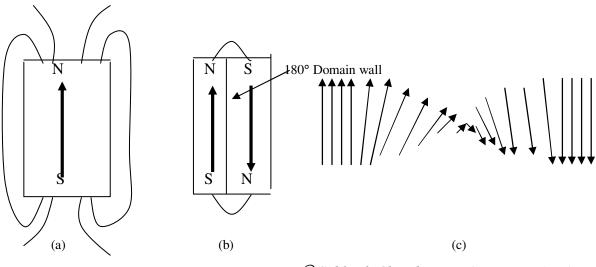
Thus equating the two we have

 $8[y.5+(1-y).4]=33.45 \implies y = 0.181$ 

Thus, 18.1 atomic percent Mn<sup>2+</sup> atoms replacing Fe<sup>2+</sup> in Fe<sub>3</sub>O<sub>4</sub> will yield the required magnetization in the material.

## **Magnetic Domains:**

A magnetic domain is the region of the crystal in which all the spin magnetic moments are aligned to produce a magnetic moment in one direction only. Figure (a) below shows a single crystal of iron that has a permanent magnetization as a result of ferromagnetism. There is potential energy called magneto-static energy stored in a magnetic field and we can reduce this energy in the external field by the crystal into two domains where magnetization are in opposite directions as shown in figure (b). The external magnetic field lines are reduced and there is now less potential energy associated with the magnetic field. There are only field lines at the end. This arrangement is energetically favourable because the magneto-static energy has been reduced, by decreasing the external field lines. However, there is now a boundary called as *domain wall or Bloch wall*, separating the two domains wherein magnetization **M** changes from one direction to an opposite direction and hence the atomic spins do also. It requires energy to rotate the atomic spins through 180° with respect to its neighbour because the exchange energy favour alignment of the neighbouring spins. This domain wall is not simply an atomic spacing thin but has a finite thickness, which for iron is about 0.1µm, several hundred atomic spacing. Domains wall have high potential energy (P.E.) then in the bulk of domain where all spins are aligned.



© Subhash Chand, NIT HAMIRPUR (HP)

Figure showing the formation of closure domains

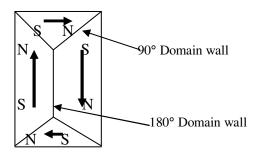


Figure 13 (a) Magnetized bar of ferromagnetic in which there is only one domain and hence an external field.

- (b) Formation of two domains with opposite magnetization reduces the external field. There are, however, field lines at the ends.
- (c) In domain wall the neighboring spin magnetic moments rotate gradually and it extends over several hundred atomic spacings to rotate the magnetic moments in two domains by 180°.
- (d) Formation of the closure domains at the ends eliminate the external fields at the ends.

The magneto-static energy associated with field lines at the end can be further reduced by eliminating the external field lines by closing the ends with side way domain with 90° rotation. These domains at end are called *closure domains* 

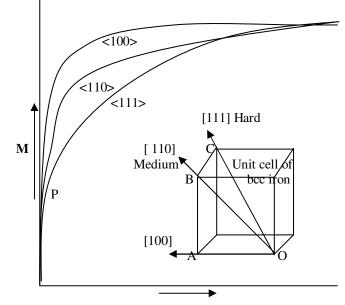
#### **Easy Directions:**

The magnetization of each domain is normally along one of preferred direction in which the atomic dipoles are easily aligned (the exchange interaction being strongest). For iron magnetization is easiest along one of the six <100> directions i.e., along unit cell edges. Such directions along which atomic dipoles moments in solid are easily aligned are called *easy directions*. The domains have magnetization along easy directions. The magnetization of the crystal along an applied field occurs in principle by growth of domains with magnetization (or component of **M**) along **H** (applied field). For simplicity the magnetizing field is taken along easy direction.

#### **Magnetic Anisotropy:**

Ferromagnetic crystals characteristically exhibit magnetic anisotropy, which means that the magnetic properties are different along different directions. For example in case of bcc iron atomic spin in domains are almost easily aligned in any of six <100> directions which corresponds to the six edges of the cubic unit cell. The exchange interactions are such that spin magnetic moments are most easily aligned with each other if they all point in one of these six directions. Thus <100> directions in iron crystal continue the easy directions of magnetization.

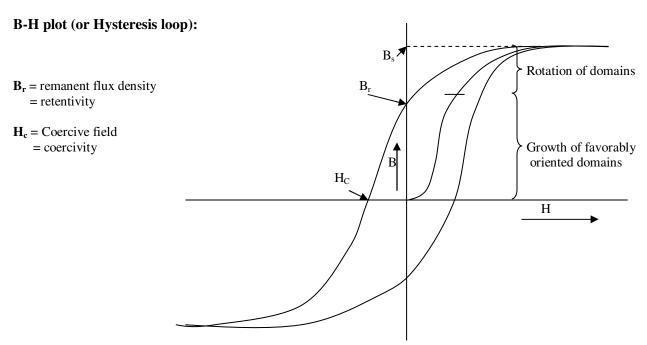
Figure 14: Magnetocrystalline anisotropy in a single crystal of iron. Magnetization depends on the crystal direction and is easiest along [100] and hardest along [111]. Inset figure shows these directions in unit of iron.



© Subhash Chand, NIT HAMIRPUR (HP)

When a magnetizing field **H** is applied along [100] direction, domain walls migrate to allow those domains with magnetization along H to grow at the expense of those domains with magnetization opposite to **H**. The observed **M** vs **H** plot is shown in the Figure 14. On the other hand if we want to magnetize the crystal along the [111] direction by applying field along this direction, then we have to apply a stronger field than that along [100] direction. It is shown in Figure 14, where resulting magnetization along [111] is smaller than that along [100] for same magnitude of applied field. In fact saturation is reached at an applied field that is about a factor of 4 greater than that along [100] which is easy direction of magnetization.

When field is applied along OD, the diagonal [111], initially, all those domains with their **M** along OA, OB or OC i.e., with **M** having component along **H** grows by consuming those domains with **M** in opposite directions. This is an easy process similar to the process along [100] and requires small fields and consequent rise in **M** is shown in figure from point O to P on magnetization curve. From P onward the magnetization in the domain have to rotated away from their easy directions i.e., from OA, OB, OC towards OD. This process consumes substantial energy and hence need much stronger fields. Thus magnetization of the crystal requires the least energy along [100] direction whereas that along [111] consumes greatest energy. This extra energy required, to magnetize unit volume of a crystal in a particular direction with respect to that along easy direction is called *anisotropy energy*. Thus for iron anisotropy energy is zero along [100] and largest along [111] direction. For cobalt, having hcp structure, the anisotropy energy is an order of magnitude greater than that for iron.



Figre 15: A typical **B** (**M**) versus **H** Hysteresis curve of a ferromagnetic material.

# **Classification of Magnetic Materials:**

Materials are classified into two groups on the basis of their magnetization behavior. They are, namely, (i) Soft magnetic materials and (ii) Hard magnetic materials.

#### **Soft Magnetic Materials:**

These are easy to magnetize and demagnetize and they require relatively low magnetic field intensities. For these materials B-H loop is having small area so that hysterisis loss per cycle of magnetization and demagnetization is small. These materials are typically suitable for applications where repeated cycle of magnetization and demagnetization are involved as in electric motors, transformers and inductors where the magnetic field varies cyclically. These applications also require low hysterisis losses or small hysterisis loop area. Electromagnetic relays

that have to be turned on and off require relay iron to be magnetized and demagnetized and therefore need soft magnetic materials.

An ideal soft magnetic material would have zero  $H_c$ , a very large  $B_s$  zero  $B_r$  zero hysterisis loss and very large permeability  $\mu$ .

Magnetic materials	μ <sub>o</sub> <b>H</b> <sub>c</sub> (T)	B <sub>sat</sub> (T)	<b>B</b> <sub>r</sub> (T)	$\mu_{\rm r}$	Typical applications
Ideal soft	0	Large	0	Large	Transformers & em cores, relays, recording devices, electrical machines
Iron commercial Grade (0.2% imp)	<10 <sup>-4</sup>	2.2	<0.1	10 <sup>4</sup>	Large eddy current losses, Generally not only preferred in electrical machinery except in some applications as relays and electromagnets.
Silicon-iron [Fe+(2-4)%Si]	<10 <sup>-4</sup>	2.0	0.5 – 1	~10 <sup>5</sup>	High resistivity and so low eddy current losses used in wide range of electrical machinery (e.g., in transformers)
Supermalloy [79Ni+15Fe+ 5Mo+0.5Mn]	~2×10 <sup>-7</sup>	0.7-0.8	<0.1	~106	High permeability, low loss electrical devices e.g.,transformers and magnetic amplifiers.
78 Permalloy [78.5% Ni +21.8%Fe]	~5×10 <sup>-6</sup>	0.86	<0.1	~10 <sup>5</sup>	Low loss electrical devices, audio transformers, HF transformers, recording heads, filters.
Glassy metals [Fe+Si+B]	~2×10 <sup>-6</sup>	1.6	<10 <sup>-6</sup>	~10 <sup>5</sup>	Low loss transformer cores
Ferrites [Mn-Zn ferrite]	~10 <sup>-5</sup>	0.4	<0.01	~5×10 <sup>3</sup>	HF low loss applications, HF transformers inductors (e.g., E and U cores), recording head

Pure iron although soft is normally not used in electrical machines except in few relay type applications because its good conductivity allows large eddy currents to be induced under varying fields. Induced eddy currents lead to Joule  $(I^2R)$  losses, which are undesirable. Addition of few percent silicon (typically 2 to 4%) to Fe (siliconiron) known typically as silicon steel increase the resistivity and hence reduce the eddy current losses. Silicon-iron is widely used in power transformers and electrical machinery.

Ni-iron alloys, which contain 77Ni+23Fe constitute an important class of soft magnetic materials with low  $H_c$ , low hysteresis losses and high permeabilities. High permeability makes them useful in low magnetic field applications like in audio and wide-band transformers and relays. They found many engineering applications in sensitive relays, pulse transformers, current transformers, magnetic recording heads and magnetic shielding. Alloying iron with nickel increases resistivity and hence reduces eddy current losses. The anisotropy energy is least at these nickel compositions, which lead to easier domain wall motions and hence smaller hysteresis losses.

Ferrites and ferrimagnetic metal oxide of mixed transition metals one of which is iron. For example Mn ferrite is  $MnFe_2O_4$  and Mn-Zn ferrite is  $Mn_{1-x}Zn_xFe_2O_4$ . They are insulators and therefore do not suffer from eddy current losses. They are ideal as magnetic materials for high frequency applications where eddy current losses would prevent the use of any material with reasonable conductivity. Many commercial ferrites are available depending on the application, tolerable losses and required upper frequency of operation. Mn-Zn ferrites are useful only up to 1MHz frequencies. Ni-Zn ferrite is another example, which can be used up to 200MHz frequencies.

Garnets are ferrimagnetic materials that are typically used at highest operating frequencies that cover the microwave range (1-300 GHz). The yttrium iron garnet (YIG, which is of the type  $Y_3Fe_5O_{12}$ ) is one of the simplest garnet with very low hysteresis loss at microwave frequencies. Garnets have excellent dielectric properties with high

resistivities and hence the low losses. The main disadvantages are the low saturation magnetization and low Curie temperature, which are 0.18T and 280°C, respectively for YIG.

#### **Hard Magnetic Materials:**

An ideal hard magnetic material has very large  $H_c$ ,  $B_r$  (or  $M_r$ ) having thereby broad area hysteresis loop. Contrary to soft magnetic materials, hard magnetic materials are difficult to magnetize and demagnetize and hence require large magnetic field intensities. Their B-H curve are broad area and almost rectangular. They possess relatively large coercivity which mean that they need large reverse field for demagnetization. The coercive fields for hard magnetic materials can be millions times greater than those of the soft magnetic materials. Their characteristics make them suitable as permanent magnets for variety of applications. The magnetization can be switched one very persistent direction to another very persistent direction from  $+B_r$  to  $-B_r$  by a suitably large H intensity. As the coercivity is large both the states  $+B_r$  to  $-B_r$  persists until a suitable large H intensity switch the field from one direction to another. Due to this behavior hard magnetic materials find use in magnetic storage of digital data where states  $+B_r$  and  $-B_r$  can be made to represent 1 or 0 bits or vice versa.

Magnetic materials	$\mu_{\rm o}\mathbf{H}_{\rm c}$ (T)	<b>B</b> <sub>r</sub> (T)	Typical applications
Ideal soft	Large	Large	Permanent magnets in various applications.
Alnico (Fe+Al+Ni+Co)	0.19	0.9	Wide range of permanent magnet applications
Strontium ferrite	0.30-0.4	0.4	Starter motors, d.c. motors, loudspeakers, telephones receivers, various toys etc.
Rare earth cobalts $(Sm_2Co_{17})$	0.62-1.1	1.1	Servo motors, stepper motors, clutches, couplings, TWT's Klystrons, gyroscopes, and quality audio headphones.
Amorphous metal magnets (NdFeB)	0.9-1.0	1-1.2	Small motors (hand tools), walkman equipments, CD motors, MRI body scanners, computer applications
Hard ferrite $(\gamma - Fe_2O_3)$	0.03	0.2	Audio and video tapes, floppy disks

Alnico is a popular permanent magnetic material that is an alloy of Al, Fe, Ni and Co. It is consist of elongated Fe-Co rich particles, dispersed in Ni-Al rich phase. These are powdered solid permanent magnets.

An important class of permanent magnetic materials consists of hexagonal ferrites having high  $H_c$ . They are namely, barium (BaFe<sub>12</sub>O<sub>19</sub>) and strontium (SrFe<sub>12</sub>O<sub>19</sub>) ferrites.

Permanent magnet rare earth cobalt  $(Sm_2Co_{17})$  have high BH product used in d.c. motors, servo and stepper motors. TWT's, Klystrons and gyroscopes.

The inter-metallic compound SmCo<sub>5</sub> with hexagonal structure have very high  $H_c$ . The more recent Nd-iron-boron powdered solid magnet have high BH product (loop area) only drawback being that it has low  $T_c$  (~300°C) whereas for AlNiCo and SmCo alloys  $T_c$  is > 700°C.



