CHAPTER-III

MAGNETIC PROPERTIES

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3.1 INTRODUCTION :

3.1(A) MAGNETISATION :

Magnetisation is one of the fundamental properties of ferrites. The saturation magnetisation, coercivity and remanance are studied with the help of hysteresis. The magnetic properties related to hysteresis help to decide the scope of application of ferrites. Besides these, ferrites exhibit properties of switching and memory. The origin of magnetism lies in the aligning forces due to an internal magentic field called as Weiss field [1]. However, quantum mechanics relates this to the Heisenberg's exchange force [2]. It has been shown by a number of workers [3,4,5] a the variety of substituted ferrites can be prepared with fairly large range of saturation magnetisation. The saturation magnetisation (Ms) plays an important role in the application of ferrites. The value of Ms depends on the type of cations and their distribution. Ferrimagentics, like ferromagnets, consist of self saturated domains and show the phenomenon of magnetic saturation and hysteresis. These can be divided into two :

i) Magnetically soft, which are easy to magnetise and demagnetise.

ii) Magnetically hard, which are difficult to magnetise and demagnetise

The soft ferrites are used in the manufacture of core of transformer, motors and generators, high frequency inductance. Hard ferrites are generally used as permanent magnets. According to Neel [6], the coercive force (H_c) is related to saturation magnetisation, internal stresses, porosity [7] and anisotropy [8]. Hysteresis property is highly sensitive to crystal structure, heat treatment, chemical composition, porosity and grain size etc [9].

3.1(b) A.C. SUSCEPTIBILITY:

A.C. susceptibility and magnetisation studies explore the existance of Multi-Domain (MD), Single-Domain (SD) and Super-Paramagnetic (SP) particles in the material. The shapes of χ_{ac} -T curves have been corelated with the domain structure by Radhakrishnamurthy et al [10]. In the χ_{ac} -T studies the Curie temperature is estimated to be that at which the curve drops almost to zero. Various workers have used χ_{ac} -T to infer domain states in the system. [11,12]. Stierstadt, et al [13] have made the correlation of Hopkinson peak with statistical distribution of Cu²⁺ ions over A and B sites.

The study on susceptibility is useful in order to invoke the grain size effects like a very fine stable SD particles becoming SP particles on heating to the temperature several degrees below the Curie temperature. This temperature at which SD \rightarrow SP change occurs is known as the blocking temperature(T_b) Magnetic grains which have a few hundred Angstroms dimension are termed as the Single Domain (SD) for which the magnetisation direction is fixed in space. The very small grains, upto about hundred Angstroms are called as Super-Paramagnetic (SP) when the thermal energy of SD particles becomes comparable to effective magnetic anisotropy energy. Under these conditions,

magnetisation direction fluctuates between the easy axes of the grains. In such a state, the grain is said to be exhibiting superparamagnetism (SP).

The volume (V)of the grains, the saturation magnetisation (M_s) and coercive field (H_c) are related by the relation given by Neel [14]

$$VMH_{c} = 2kT_{b}$$
(3.1)

where k is the Boltzmann constant and T_b blocking temperature. Thus the SP can be changed to SD by cooling the ferrites below the T_b . The susceptibility becomes infinite and the spontaneous magnetisation appears at particular temperature called as Curie or Neel temperature. The transition from ferro to para region is not sharp in each case but may give Tailing effect due to spin clusters (i.e. short range spin ordering). The low field a.c. susceptibility plays an important role in the study of spin glass behaviour. Bean [15] has stated that for MD particles, very small values of H_c and M_r/M_s are observed whereas for SD particles these values are larger. High temperature a.c. susceptibility measurements were first carried out on iron by Hopkinson [16]. The results indicate that the susceptibility reaches to a peak value just before T_c and becomes zero rapidly.

3.2 MAGNETIC PROPERTIES OF FERRITES :

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The properties of ferrites can be classified into two groups such as intrinsic and structure sensitive. Saturation magnetisation, anisotropy, magnetostriction and Curie temperature are the intrinsic properties while permeability, hysteresis are structure sensitive.

3.2(a) MAGNETISATION :

Spontaneous magnetisation is characteristic of ferromagnetic material, which arises if the magnetic atoms are sufficiently close to each other. Then the electrons can undergo an exchange between neighbouring magnetic atoms. The exchange interaction between neighbouring atoms may be indirect and may take place via an intermediate non-magnetic atom such as oxygen or sulphur [17]. The coupling between magnetic atoms in a substance may either be due to parallel or antiparallel alignment of the spins of the neighbouring atoms. When the alignment is parallel ferromagnetism results and when it is antiparallel antiferromagnetism or ferrimagnetism results, depending on the complete or incomplete cancellation of the atomic magnetic moments within the crystal.

The saturation magnetisation in ferrites is determined by its physico chemical constitution and also by the cation distribution and other attendant aspects of thermo-physical history. In case of ferrites the solid solubility affords to prepare mixed ferrites, crystallising in the spinel structure either of normal or of inverse type. The normal spinels are non-magnetic while inverse spinels are ferrimagnetic. The ferrites with inverse structure can be represented as

 $[Fe^{3+}]^{A} [M^{2+} Fe^{3+}]^{B}O^{2-4}$ (3.1)

The Fe^{3+} ions on A site are coupled with their spins antiparallel to those Fe^{3+} ions on B site, so that the net moment is only due to divalent M^{2+} metallic ions.

 $[Fe_A \uparrow] Fe_B \downarrow 5 \mu_B M_B \downarrow] \qquad \dots (3.2)$

Suppose that M is a transition element with n electron in d-shell, the magnetic moment μ_B per formula unit is μ_B or (10-n) μ_B depending on d-shell which is filled less than half or more than half respectively. The degree of inversion is a fraction x of the divalent metal ions that are on B site. The arrangement of moments could be written as,

 $[(1-x)M_{A} \uparrow X Fe_{A} \uparrow] [2-x)Fe_{B} \downarrow X M_{B} \downarrow] \qquad (3.3)$

The net magnetic moment is written as,

= M [(1-x)-x]-5 (1+(1-x)-x]

= M [1-2x] -5 [2 - 2x]

For normal spinel x = 0 and for invese spinel x = 1.

The indirect exchange coupling between metallic ions acting through oxygen ions is maximum for those ions A and B, for which the angle AOB is close to 180° . For the perfect spinel lattice the major angles between the ions are AOB is 125° 9' or 154° 34', BOB 90° or 125° 2' and AOA 79° 38' as shown in Fig.3.1. The nearest to perfect alignment are Fe_A and Fe_B ions making an angle of 154° 34'. giving strong antiferromagnetic coupling [18].

3.2(b) HYSTERESIS AND DOMAINS:

Hysteresis properties are mainly dependent on chemical composition, crystal structure, cation distribution, heat treatment, sintering atmosphere and final fabrication. Experimental techniques for the measurement of magnetic properties are described by Maxwell [19]. A demagnetised ferromagnetic material exhibits a state of zero magnetisation. This was first explained by Weiss [1]. He postulated that the magnetic material comprises large number of regions



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or domains, in each of which the spins are aligned. The domains are arranged in such a way that the net magentisation is zero. The existance of domains is a consequence of the process which minimises the free energy of the system.

The magnetisation increases slowly by reversible wall motion at low fields and by irreversible wall motion above critical field and by irriversible rotation at very high field . Rotation of domains have been observed by Barkhahusen [20]. The wall energy is maximum at very high fields. This leads to irreversible increase in magnetoeleastic and magneto-static energies of the material under the action of external magnetic field. When the magnetic field is reduced to zero a residual magnetisation remains . An opposite field need be applied for the reversal of domains to their original state of zero magnetisation. This gives rise to the hysteresis of the magentisation cycle signifying the energy loss during the cycle. The hysteresis loop of micropowers can be classified into three types, namely [21].

I) Multidomain

ii) Superparamagnetic

iii) Single Domain

3.2(c) CURIE TEMPERATURE:

In ferromagnetics the domain ordering is due to the presence of internal molecular field and is found to be maximum at 0 K. Therefore, the spontaneous magnetisation is found to be maximum at absolute zero. The spontaneous magnetisation decreases with increase in temperature. At Curie temperature, the spontaneous magnetisation is lost by the substance and paramagnetic phase results. Thus, on one side of Curie temperature we have disordered paramagnetic phase while on the other the ordered ferromagnetic phase. Curie temperatures of ferrites have been found to be closely related to Fe³⁺ - O-Fe³⁺ and other magnetic linkages via the interaction energy per linkage [22]. Substitution of non magnetic ion reduces the Curie temperature. The relation between Curie temperature and cation distribution is given by Gilleo [23].

3.3 EXPERIMENTAL :

3.3(a) MAGNETISATION MEASUREMENTS:

The saturation magnetisation of the ferrite sample was determined by using an alternating current electro-magnetic type hysteresis loop tracer. It mainly consists of an electromagnet, a pick-up coil system, balancing and intergrating circuits and a pre-amplifier. The details of this method are given elesewhere [24]. The schematic diagram of hysteresis loop tracer is shown in Fig.3.2.

The multicoil was slid into the pole gap and the current in the emerging coil was increased to produce the required magnetic field. The potentiometers and the resistances in the balancing network were adjusted such that, the scope tracer show horizontal line when there was no specimen in the multicoil. The current was then reduced to zero and the coil was pulled out and reintroduced in the pole gap with the sample placed in its center. The current in the emerging coil was raised to a value sufficient to saturate the sample. The hysteresis loop produced by the sample was obtained on the screen. For the measurement of Ms a digital voltmeter was connected across the vertical deflection of C.R.O.

and corresponding readings in milivolts were noted for each sample and also for a standard Ni-sample.

CALCULATION OF M_{s} AND n_{B} :

The vertical displacement on C.R.O and corresponding readings in milivolt (390 mV) were taken for pure Ni sample of mass 1.0611 gms. As the standard magnetisation for Ni sample is 53.34 emu/gm, the total magnetisation of the Ni sample is

Hence, the calibration factor is

The vertical readings with the help of milivoltmeter were taken at room temperature . By using the reading of the samples the magnetisation per gram of the sample is,

Where R is the reading of the sample. The saturation magnetisation is calculated using the relation,

 $Ms = \sigma s'x$ density of the pellet.

The magnetic moment per formula unit in Bohr magneton (n_B) is given by,

Molecular weight of the sample X σs' n_B = ------5585

3.3(b) A.C. SUSCEPTIBILITY :

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The low field a.c. susceptibility measurements of the powdered sample were taken in the temperature range 300 K to 760 K using the apparatus developed by Likhite, et al [25] as shown in Fig.3.3, operating at frequency of 263 Hz and in r.m.s. field of 7 Oe. It consists of Helmholtz coils two pick-up coils, furnace and a sample holder.

The set up consists of two Helmholtz coils to produce a uniform field at the pick-up coil. A furnace was fabricated by winding a platinum wire on a silica tube to heat the sample. To avoid overheating of coil, a glass jacket with water circulation was used. The furnace was placed at the center of the pick-up coil. Sample holder was a quartz tube fused at one end. The height of the sample holder was maintained at the center of the coils. The current to the Helmholtz coil was supplied by an oscillator and a high quality power amplifier. The signal induced in the double coil, when the sample is placed in the sample holder was amplified, rectified and read out on a digital voltmeter. The digital voltmeter was pre-calibrated in terms of magnetic moments. The temperature of the furnace was maintained by a power supply and was measured by using platinum-irridium



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Fig. 3-1- Schematic diagram of hysteresis loop tracer



EXPERIMENTAL SETUP OF HYSTERESIS LOOP TRACER



EXPERIMENTAL SETUP OF SUSCEPTIBILITY MEASUREMENT

thermocouple. The powder sample was gradually heated and at various temperatures the signals corresponding to the magnetic moment were recorded. The heating was continued till the signal reduces to zero.

RESULTS AND DISCUSSION:

COMPOSITIONAL VARIATION OF MAGNETIC MOMENT :

The magnetisation data obtained from hysteresis study is given in Table 3.1. The magnetic moment n_B for $Cu_{0.5}Co_{0.5}$ Fe₂O₄ is about 2.52 which agrees with the reported values [26]. In Cr substituted samples the n_B value increases slightly with $x \le 0.2$ Cr and slowly decreases with x > 0.2 Cr. However, the decrease in n_B is fast for the samples x > 0.6.

The magnetisation behaviour in ferrites is generally explained on the basis of Neel's molecular field model [6]. According to this model AB interaction is stronger than BB and AA interactions. The net magnetisation is a vector sum of magnetisations of octahedral (B) and tetrahedral (A) sites, $(Mo= M_B-M_A)$. In this model collinear arrangement of magnetic moments of individual sites is presumed, i.e., the magnetic ions on each sublattice are ferromagnetically aligned.

Miller [22] has given the site preference energies of cations in ferrites. According to his observations, the Fe³⁺ ions are statistically distributed in B and A sites. Whereas Co and Cr ions have a strong preference of B site. It is also observed that, Cu has strong preference to B site although it can migrate from B site to A site depending on quenching or the substituting element [27]. Considering these facts the cation distribution for the present system can be written as $\delta = (n_B - 1.5 + 2x)/10$. Using this cation distribution and magnetic moments of cations Fe,Co,Cr we have calculated the cation distribution for present system. Here, Cu ion is considered as diamagnetic and its magnetic moment is taken as zero. From this cation distribution it is observed that the concentration of Cu ions at A site increases with x up to $x \le 0.6$ and then decreases for x > 0.6. The reverse behaviour is observed for Fe ions. This behaviour can be seen clearly in Fig.3.4.

THEORETICAL MODEL (GILEO'S MODEL) :

To check whether the Neel's model explains the magnetisation behaviourof the present system, we have calculated the Curie temperatures by applying the Gilleo's model. Gilleo's [23] model has been used with the assumption that, a magnetic ion actively participate in ferrimagnetism only when it interacts with two or more magnetic ions in different coordination (i.e. sites or opposing sub-lattices). Gilleo has proposed a statistical model which neglects the intrasublattice interaction. Thus, no canted spin is considered [28]. The theoretical calculations to estimate the Curie temperatures of substituted ferrites are given by this model. Accordingly, the Curie temperature (T_c) is proportional to the number of active magnetic linkages per magnetic ion per formula unit and is given by,

$$T_{c}(K_{o},K_{1}) = \frac{3}{---} \frac{n(k_{o},k_{1})}{----} T_{o}(0,0)$$
24 N(k_{o},k_{1})

Here $T_o(0,0)$ is Curie temperature of unsubstituted ferrite, $n(k_o,k_1)$ denotes active magnetic interaction per formula unit, $N(k_o,k_1)$ denotes number of magnetic ions

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Sample	ós	u B B B	л M S	cation distribution
Cu _{0.5} Co _{0.5} Fe ₂ O ₄	116.08	2.5254	3096	(Cu _{0.1} Fe _{0.9}) ^A (Cu _{0.4} Co _{0.5} Fe _{1.1}) ^B 0 ⁻ / ₄
Cu _{0.5} Co _{0.4} Cr _{0.2} Fe _{1.8} O ₄	112.45	2.9352	3613	$(cu_{0.8} Fe_{0.82})^{A} (cu_{0.32} Co_{0.5} Cr_{0.2} Fe_{0.98})^{B_{0}}$
^{2u} 0.5 ^{Co} 0.5 ^{Cr} 0.4 ^{Fe} 1.6 ^O 4	101.57	2.8731	3539	$(Cu_{0.22} F_{0.78})^{A} (Cu_{0.28} Co_{0.5} Cr_{0.4} F_{0.82})^{B} O_{4}$
u0.5 ^{C0} 0.5 ^{Cr} 0.6 ^{Fe} 1.4 ^O 4	58.04	2.5665	3243	$(Cu_{0.23}Fe_{0.77})^{A}(Cu_{0.25}Co_{0.5}Cr_{0.6}Fe_{0.63}^{B}O_{4}^{-})$
3u _{0.5} Co _{0.5} Cr _{0.8} Fe _{1.2} O ₄	60.94	2.0092	2553	$(Cu_{21} Fe_{0.79}^{A} (Cu_{29} Co_{5} Cr_{8} Fe_{41})^{B} O_{4}^{2}$
$u_{0.5} c_{0.5} c_{rFeO_4}$	55.14	1.3616	1738	$(Cu.15e.81^{A} (Cu.31Co.5 Cr.1^{Fe}.19)^{B} O_{4}^{-2}$



3.4 Variation of Concentration of Cations on A and B Sites with x.

actively participating in the ferrimagnetism, k_o, k_1 are fractions of ions substituted 61 on octahedral (B) and tetrahedral (A) sites respectively; 3/24 is the number of interactions per magnetic ions per formula unit. Using this formula and cation distribution determined from magnetisation, the T_c values are computed and are listed in Table 3.2 along with T_c measured by a.c. susceptibility method.

From the table it is observed that, the Curie temperature nearly agreed with 10% for lower concentration of Cr i.e. $x \le 0.2$ whereas the difference in T_c values is more and more for higher contents of Cr Goodenough et al [30] have concluded that, the Y-K type ordering takes place for higher content of Cr. The calculated T_c values and observed T_c values differ. This may be because of canting spin arrangement due to Cr ions.

A.C SUSCEPTIBILITY WITH TEMPERATURE :

The thermal variation of low field a.c. susceptibility is shown in Fig.3.5 a,b) for all the samples. The following observations are made from these figures. 1) Samples with x =0 and 0.2, show a slow increase in susceptibility and suddenly drops to zero near Curie temperature. The maxima are observed near Curie temperature and its value is about 9 for x = 0 and about 5 for x = 0.2.

For remaining samples the peak height decreases with increase in Cr.
 However, the curves broaden.

3) The peak temperature/blocking temperature (T_b) decreases with Cr content and the difference of T_b-T_c is more for the samples x = 0.8 and 1 Cr.

4) The tailing effect is more for the samples with x = 0.8 and x = 1.

5) The Curie temperatures (Table 3.2) decrease with increase in x. Curie temperature of a ferrite has been found to be closely related to its $Fe^{3+} - O-Fe^{3+}$ linkages, strength and angle between cations [23]. In the present system Fe is replaced by Cr. Therefore it reduces the total no of Fe ions, hence Curie temperatures decrease.

The shapes of the χ_{ac} -T curves give an idea of the type of domains in the material. There are three types of domains, such as Multi Domain(MD) Single Domain (SD) and Super Paramagnetic (SP) domain. Bean [15] has suggested that for MD particles the χ_{ac} is independent of temperature. Whereas for SD and SP types of behaviour χ_{ac} slowly increases and maxima is observed at T_b and then slowly decreases to zero at Curie temperature.

It is noted that the SP particles behave like SD particles below the blocking temperature. C Radhakrishnamurthy, et al [29] have studied the hysteresis and susceptibility at various temperatures. They have stated that, the humps/cusps in χ_{ac} -T curve indicate the presence of SD particles.

Invoking the above ideas, incoordination with domain structures for the present system, we found that the compositions with x = 0 and 0.2 contain MD + SD particles, whereas, the remaining samples contain the SD particles. Therefore it can reasonably be concluded that the Cr ions substitution enhances the formation of more and more SD particles with diminishing size.

L. Madhavrao [30] has given neutron diffraction survey of perturbed magnetic ordering in disordered spinels. A.C. susceptibility measurement of Zn,Co, Fe,CrO₄ and CoFeCrO₄ were made and they have concluded that, the

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X	Tc by susceptibility K	Tc by Gilleo's method K	Tb by susceptibility K
0.0	752	760	727
0.2	696	733	677
0.4	635	714	595
0.6	568	702	510
0.8	510	695	375
1.0	488	686	363

Table 3.2 : The Compositional variation of Tc by susceptiobility Tc by gilleosFormula and blocking temperature by susceptibility of $Cu_{0.5} Co_{0.5} Cr_x Fe_{2-x} O_4 System$

shapes of plots suggest that there is a broad distribution of particle shapes. According to their analysis, the system does not behave as normal ferrimagnet. Also the tailling effect in χ_{ac} -T plot near Curie temperature indicates the Y-K type of ordering in ferrimagnetic system.

The samples with x = 0.8 and x = 1 show tailing effect in χ_{ac} -T plot which indicates that Y-K type of ordering is present.

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