
chapter III

Magnetic Properties

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Section A - Magnetic Properties

3A.1 Introduction

Ferrite is a magnetic material. Similar to ferromagnetic substance. Ferrites belong to ferrimagnetic class, consist of self saturated domains and exhibit the phenomena of magnetic saturation and hysteresis. The saturation magnetization, coercivity and remanance are studied with the help of hysteresis. The magnetization is the magnetic moment or dipole moment per unit volume of material. Magnetization occurs even in the absence of external field, called spontaneous magnetization and it is most important property of magnetic material.

In ferrites, the study of hysteresis gives valuable data on saturation magnetization (M_s), coercive force (H_c) and remanance ratio (M_r/M_s). The magnetic properties of ferrites are strongly dependent on chemical composition, sintering temperature, sintering atmosphere, crystal structure, cation distribution, impurity, porosity, grain size and the pressure applied during the formation of final product [1-4].

Ferrites have been classified into two categories on the basis of coercive force (H_c). Ferrites with low coercive forces are called soft ferrites and find application in the manufacture of motors, transformers and generators etc. [5]. Ferrites with high coercive force are called hard ferrites

and find application in the manufacture of permanent magnets [6].

Ferrites exhibit the properties of ferromagnetics in which the spontaneous magnetization is maximum at absolute zero. If the temperature increases, the spontaneous magnetization decreases and at particular temperature the transition from ferromagnetic phase to paramagnetic phase occurs. This temperature is called Curie temperature. According to Neel and Gorter the Curie temperature of ferrites depends on the distance of metallic ions on two sites A and B.

3A.2 Magnetization in Ferrites

Substances get magnetized under the applied magnetic field if they acquire magnetic moment. The magnetization is given by

$$M = \chi H$$

Where χ is the susceptibility of the material. If χ is small and negative, the substance is diamagnetic. If χ is small and positive the substance is paramagnetic.

If χ is large and positive, substance is self saturating and consists of domains which are randomly oriented is called as ferromagnetic.

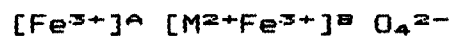
If χ is small and positive at all temperatures and lattice of magnetic ion breaks into A and B sites with stronger tendency towards antiparallelism the substance is called as antiferromagnetic.

If χ is large and positive, lattice magnetic ions breaks into A and B sublattices with their magnetic moments, antiparallel and of different magnitude the substance is called as ferrimagnetic.

The above described magnetic materials are based on the magnetic ordering and spontaneous magnetization. The spontaneous magnetization was first explained by Weiss [7] postulating the existence of molecular field which is the internal field among the atoms or molecules which lines up the magnetic moments parallel to each other. Heisenberg [8] attempted to make up for the limitations of Weiss molecular field theory. With the help of quantum mechanical treatment he explained the alignment of magnetic moments in terms of exchange interaction between electron spins. The coupling between magnetic atoms in a substance may lead to parallel or antiparallel alignment of the spins of neighbouring atoms. When the alignment is parallel, the exchange interaction is positive and it is ferromagnetic when it is antiparallel, the exchange interaction is negative and it is either antiferromagnetic or ferrimagnetic depending upon the complete or incomplete cancellation of magnetic moment within the crystal. The exchange interaction may be positive or negative. In ferrites the magnetic moments may be arranged in antiparallel or some other complex fashion. Gorter [9] and Guillaud [10] gave experimental evidence to Neel's theory. Yafet-Kittel [11] extended Neel's theory assuming the triangular arrangement of spins in which A-A

and B-B interactions are comparable in magnitude to the A-B interaction.

The magnetization in spinel structure can be explained on the basis of Neel's two sublattice model. The normal spinel ferrite is nonmagnetic, while inverse spinels are ferrimagnetic. For the inverse spinel ferrite the magnetization can be expressed as



The net moment is only due to M^{2+} divalent metal ions as the Fe^{3+} ions on A-sites are coupled with their spins antiparallel to those of Fe^{3+} ions on B-sites.

3A.3 Domain Theory

To explain the spontaneous magnetization Weiss [7] has introduced the concept of magnetic domain. According to him the ferromagnetic substances consist of number of small regions called "domains". According to Weiss, in an unmagnetized material (the material) the domains are oriented randomly resulting in zero magnetization. The magnetic domains are separated by a thin layer called domain wall or Bloch wall [12]. When an external magnetic field is applied these domains displace or rotate and align themselves along the field direction giving rise to net magnetization. The thickness of domain wall is given by

$$\sigma = (A/K)^{1/2}$$

and the wall energy is given by

$$W_p = 4/(A/K)^{1/2}$$

Where A is the exchange energy constant between two domains and K is anisotropy constant.

The origin of domains in ferromagnetic materials can be understood from the thermodynamic principle, that at equilibrium the total energy of the system is minimum.

The total energy is given by

$$E = E_k + E_\lambda + E_x + E_w$$

E_k = Anisotropy energy

E_λ = Magnetoelastic energy

E_m = Magnetic energy

E_x = Exchange energy

and E_w = Domain wall energy.

3A.4 Hysteresis and Coercivity

When an external magnetic field is applied to a ferromagnetic substance its magnetization increases, with increasing applied field, till it reaches a saturation value for certain critical field. Now, if the external field is decreased demagnetization is not recovered completely. Thus magnetization lags behind the applied field. This is known as the phenomenon of hysteresis. Weiss explained the hysteresis phenomenon on the basis of concept of magnetic domains. The entire cycle of magnetization is shown in Fig. (3.1) which is referred as hysteresis loop. Studies on magnetic hysteresis provide the useful information about the parameters such as coercivity, saturation magnetization etc.

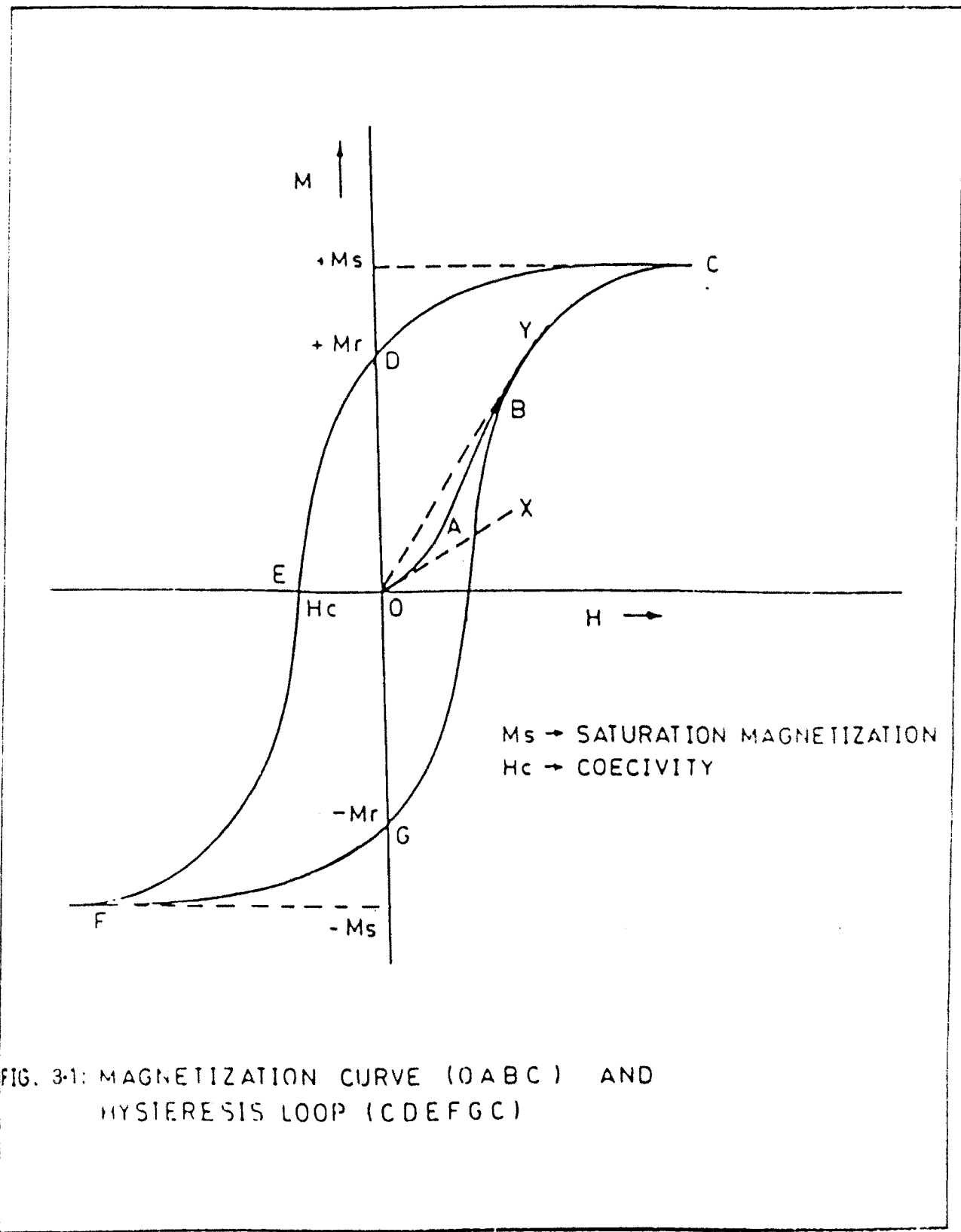


FIG. 3-1: MAGNETIZATION CURVE (OABC) AND HYSIERESIS LOOP (CDEFGC)

The process of magnetization takes place by domain growth. The magnetization is reversible at low applied fields and is temperature dependent. At high fields the magnetization takes place due to domain wall rotation. This process of magnetization is irreversible and is temperature dependent. The rotation of domains have been observed by Barkhausen [13].

Saturation magnetization is independent of particle size but coercivity appreciably dependent on it. As shown in Fig. (3.2) with the reduction of particle size, the coercivity increases, reaches a certain maximum value and then approaches to zero. The different regions of the graph corresponds following types of magnetic particles.

(1) Multi domain particles (MD)

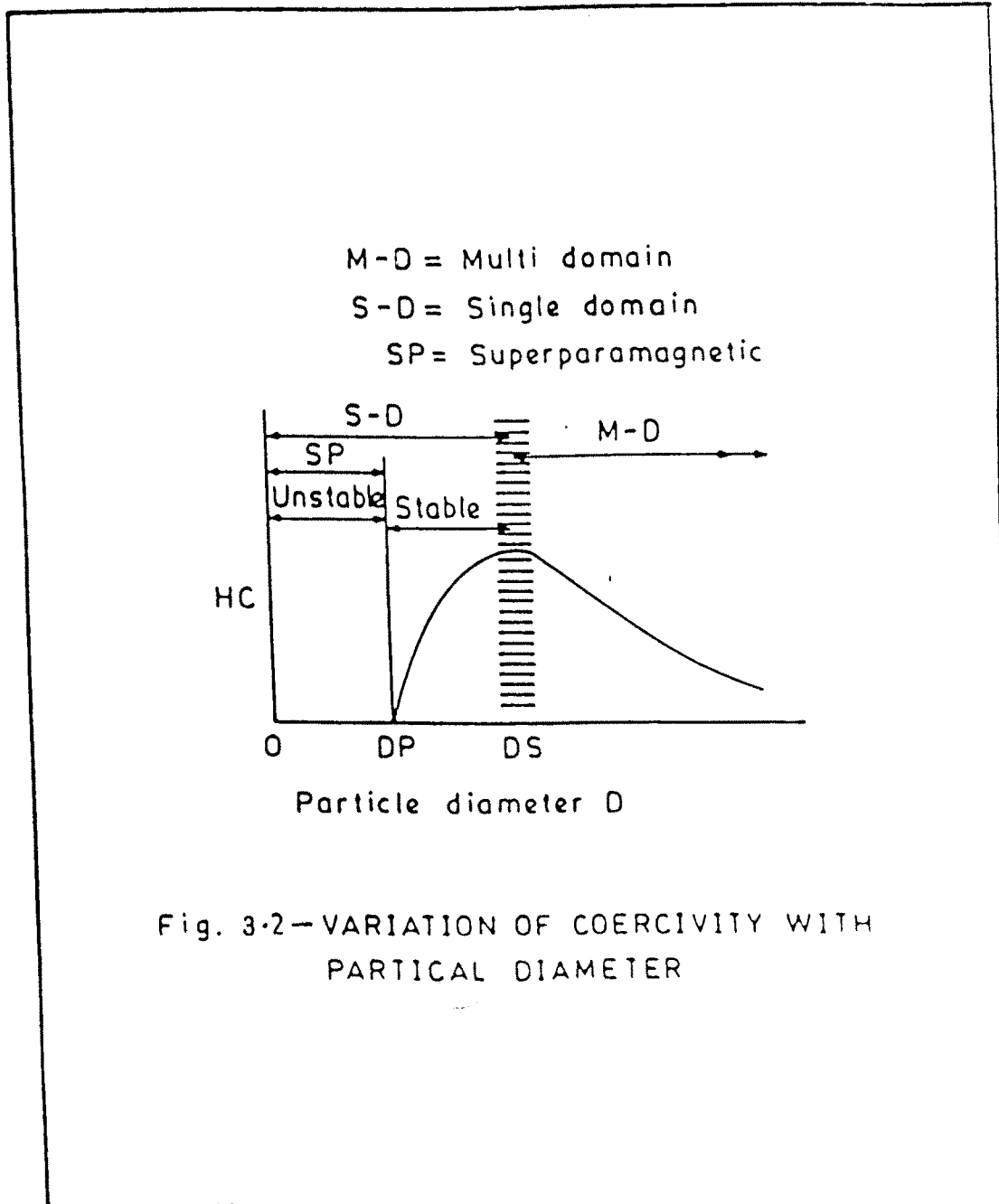
Particles of very large size have multi domain structure and magnetization is due to the motion of the domain walls.

(2) Single domain particles (SD)

Particles become single domain below the critical diameter D_s and the coercivity (H_c) becomes maximum.

(3) Super paramagnetic particles

Below a certain critical diameter D_p , the thermal vibrations are sufficiently strong enough to distribute the particles in random fashion. Accordingly the material gets spontaneously demagnetized and coercivity (H_c) becomes zero.



3A.5 EXPERIMENTAL

The measurement of the saturation magnetization of the samples were carried out by using the high field hysteresis loop tracer. The photograph of the experimental setup of hysteresis loop tracer is shown in Fig 3.3 and the block diagram of hysteresis loop tracer is shown in Fig (3.4).

The loop tracer consists of an AC electromagnet operating on 50 Hz main supply with the help of which a sinusoidal magnetic field of maximum peak value 3500 oersted is produced in an air gap of about 1 cm. A special balancing coil is used to measure the saturation magnetisation of the sample in air gap. Depending upon the magnetic induction in the specimen, pick up coil produces a field proportional to the magnetic induction of the specimen. A supporting coil produces a signal which is equivalent to the strength of the magnetic field. When the respective signals are supplied to the vertical and horizontal plates of the oscilloscope, it displays a hysteresis loop on the screen. The vertical deflection is calibrated in emu and horizontal in terms of oersted per division. For the purpose of calibration standard nickel sample having magnetization of about 53.34 emu/gm is used.

The saturation magnetization $\sigma's$ (emu/gm) is calculated using the formula

$$\sigma's = \sigma_s / \text{mass of pellet}$$

where σ_s = vertical displacement x calibration factor (emu)

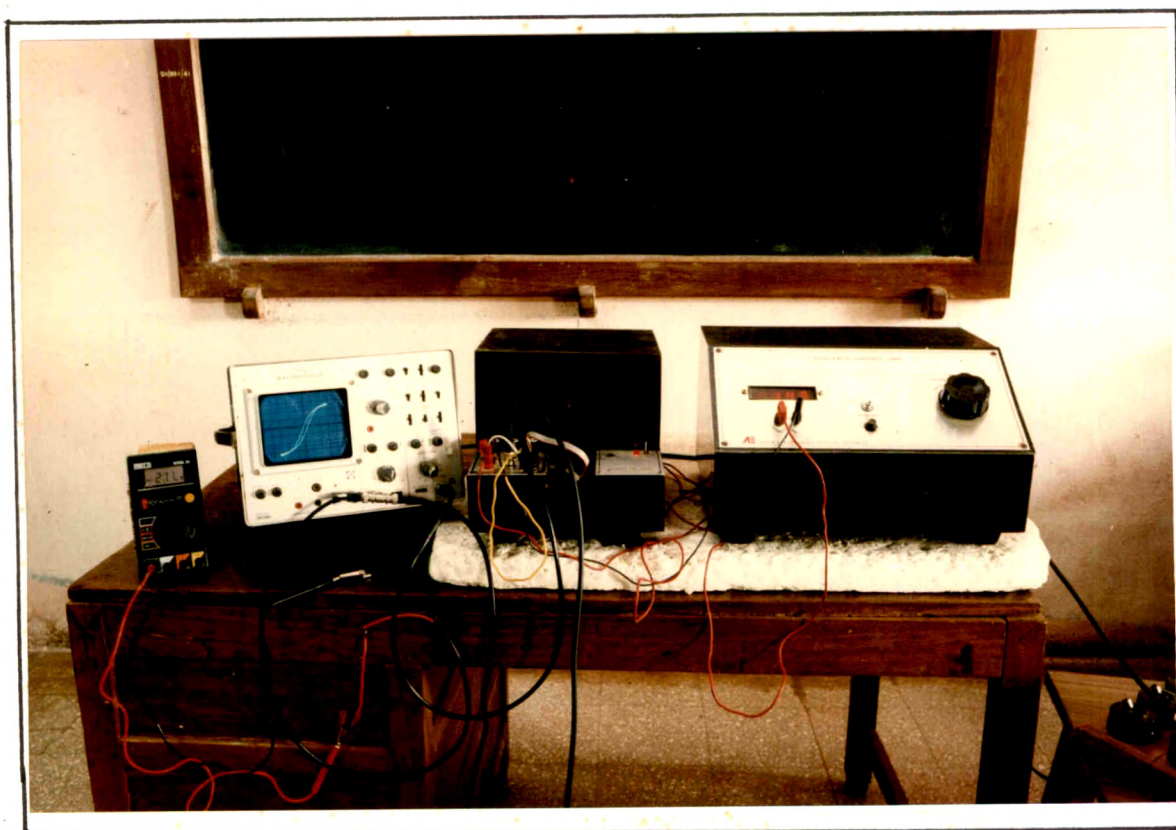


Fig.3.3 : Experimental set up of Hyst eresis loop tracer

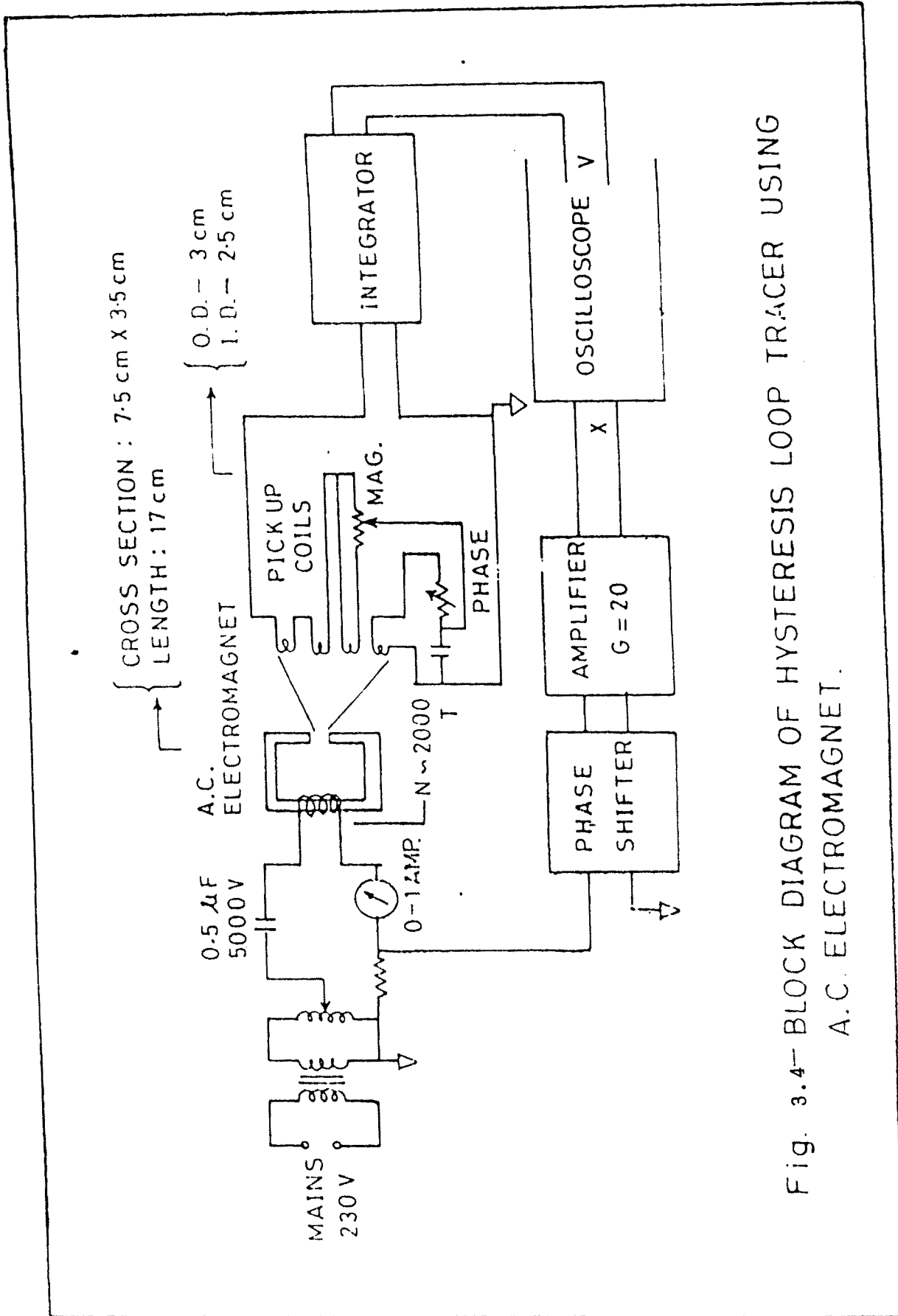


Fig. 3.4- BLOCK DIAGRAM OF HYSTERESIS LOOP TRACER USING A.C. ELECTROMAGNET.

The magnetic moment n_B per formula unit is calculated by the formula

$$n_B = \text{molecular weight of sample} \times \sigma_s / 5585$$

The saturation magnetization M_s (emu/cm³) is given by

$$M_s = \sigma_s \times \text{density of pellet.}$$

3A.6 RESULT AND DISCUSSIONS

The hysteresis loop is obtained for the ferrite system $\text{Cu}_x\text{Co}_{1-x}\text{Al}_{0.5}\text{Fe}_{1.5}\text{O}_4$ at room temperature. From the hysteresis loop the values of magnetic moment (nB) per formula unit and saturation magnetization (M_s) are calculated and given in the Table 3.1. From the Table it is observed that the values of n_B and M_s decrease with increase in Cu content due to the replacement of Co^{2+} by Cu^{2+} cations at B site and magnetic coupling becomes stronger with increase of Cu content which has lower magnetic moment (14). It is expected that the addition of Cu will affect the factors which are governing the irreversible magnetization in the present system.

In the present system the values of magnetic moment obtained are lower than the values of magnetic moment that have been reported earlier the copper and cobalt ferrites without Al [15, 16, 17, 18]. This is due to the change in the molecular formulae and is also due to the structural sensitivity on account of factors like porosity, defects, conditions and atmosphere of firing and cation

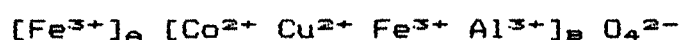
distribution. For aluminium doped samples magnetic moment and corresponding magnetization reduces [17].

While discussing the results obtained for magnetic moment and saturation magnetization we have to take into account following things,

1. Cobalt ferrite is more inverse than the copper ferrite.
2. Co^{2+} ion has got three unpaired spins corresponding to three Bohr magneton where as Cu^{2+} has got one or single unpaired electron corresponding to one Bohr magneton
3. In our samples we have $\text{Al}_{0.5}$ substituted for Fe which has got 5 unpaired spins corresponding to 5 Bohr magneton (μ_B).

Taking into account all these things when cobalt substituted by copper in $\text{Cu}_x\text{Co}_{1-x}\text{Al}_{0.5}\text{Fe}_{1.5}\text{O}_4$ the magnetic moment per formula unit is bound to decrease which is observed in our results.

Magnetization in ferrites results from the distribution and alignment of magnetic ions on the tetrahedral and octahedral cation sites, Copper ferrite and cobalt ferrite both has a structure of inverse spinel. $\text{Cu}_x\text{Co}_{1-x}\text{Al}_{0.5}\text{Fe}_{1.5}\text{O}_4$ is considered also as an inverse ferrite where each of the Co^{2+} and Cu^{2+} cations is still occupying a B-site. The cation distribution of this ferrite could be written as [19]



In ferrites, there are three magnetic interactions such as A-B, A-A and B-B out which A-B interaction is the strongest one. For the present system, the possible

Table 3.1

I. Compositional Variation of n_B and M_s for
 $Cu_x Co_{1-x} Al_{0.5} Fe_{1.5} O_4$ samples

Composition	Mag. Moment (n_B)	Saturation Magnetization (M_s)
$CoAl_{0.5}Fe_{1.5}O_4$	1.49	119.8
$Cu_{0.2}Co_{0.8}Al_{0.5}Fe_{1.5}O_4$	1.23	103.2
$Cu_{0.4}Co_{0.6}Al_{0.5}Fe_{1.5}O_4$	1.09	92.8
$Cu_{0.6}Co_{0.4}Al_{0.5}Fe_{1.5}O_4$	0.97	83.1
$Cu_{0.8}Co_{0.2}Al_{0.5}Fe_{1.5}O_4$	0.83	72.1
$CuAl_{0.5}Fe_{1.5}O_4$	0.79	67.9

Magnetic moments of samples without Al.

Samples	n_B	Ref.
$CoFe_2O_4$	3.47	17
"	3.12	18
$Cu_{0.2}Co_{0.8}Fe_2O_4$	2.27	15
$Cu_{0.4}Co_{0.6}Fe_2O_4$	1.60	15
$Cu_{0.6}Co_{0.4}Fe_2O_4$	1.53	15
$Cu_{0.8}Co_{0.2}Fe_2O_4$	0.72	15
$CuFe_2O_4$	1.03	16
"	1.10	18

interaction may be Fe_A-Cu_B , Fe_A-Co_B , Fe_A-Al_B , Fe_A-Fe_B , Fe_B-Cu_B , Fe_B-Co_B , Fe_B-Al_B . Out of these Fe_A-Fe_B is the strongest due to higher magnetic moment. In the present system Fe_B and Co is replaced by copper which has lower value of magnetic moment, and hence decreasing the value of magnetic moment of the system.

Section B - A.C. Susceptibility Studies

3B.1 Introduction

The susceptibility is the ratio of the magnetization (M) produced in the substance to the applied magnetic field (H) as

$$\chi = \frac{M}{H}$$

Where M is the magnetic moment per cm^3 .

In paramagnetic substances susceptibility is temperature dependent and is given by

$$\chi = \frac{C}{T}$$

Where 'C' is the Curie constant

Ferromagnetic and ferrimagnetic substances exhibit spontaneous magnetization below Curie temperature. Since in antiferromagnetic substances the magnetic moments compensates each other. These materials do not possess resultant spontaneous magnetization.

The variation of susceptibility with temperature for ferromagnetic and ferrimagnetic substance is given by

$$\chi = \frac{C}{T - T_c}$$

This is Curie-Weiss law. T_c is the Curie temperature.

For antiferromagnetic materials the relation is given by

$$\chi = \frac{C}{T + T_c}$$

Positive sign in the above expression represents antiparallel coupling of magnetic spins.

A.C. susceptibility studies explore the existence of multi domains (MD), single domain (SP) and super paramagnetic particles (SP) in the material. For ferrimagnetic materials the variation of normalized a.c. susceptibility versus temperature have been reported by many workers [20 to 22]. From these curves the Curie temperature and domain structure have been inferred.

Below Curie temperature ferrites have ferrimagnetic nature. Above Curie temperature magnetic transition occurs from ferrimagnetic to paramagnetic. It has been found that the transition from ferro to paramagnetic region is not sharp in each case but gives tailing effect due to spin clusters (i.e. short range spin ordering).

The variation of normalized susceptibility (χ_T/χ_{RT}) versus temperature (T) curve show Hopkin's peak just below the Curie temperature. Single domain peak occurs at Curie temperature and isotropic peak corresponds to multi domain

state. A.C. susceptibility study can describe the magnetic behaviour of the material that is ferrimagnetic to paramagnetic transition and single domain to super paramagnetic transition. Bean [23] has reported that for single domain SD particles coercive force is large where as it tends to zero for super paramagnetic SP particles. Naik et al. [24] have shown that particles with SD state are easily formed in pure copper ferrite. Kulkarni et al (25) have reported a.c. susceptibility studies on Co-Ca ferrites. The a.c. susceptibility studies for mixed ferrites have been carried out by number of researchers to study the effect of temperature and identify multi domain (MD), single domain (SD) and super paramagnetic (SP) particles [26, 27].

3B.2 Experimental

The low field a.c. susceptibility measurements of powdered samples were taken in temperature region 300 to 800 °K using the susceptibility apparatus. The photograph of the a.c. susceptibility apparatus is depicted in Fig.(3.5) and the block diagram of the apparatus is shown in Fig.(3.6). The apparatus essentially consists of Helmholtz coil, two pick-up coils, furnace and a sample holder.

The Helmholtz coil produces uniform magnetic field. A furnace is fabricated by winding the platinum wire on silica tube is used to heat the sample. To avoid over heat of the coils a glass jacket with water circulation is used. The

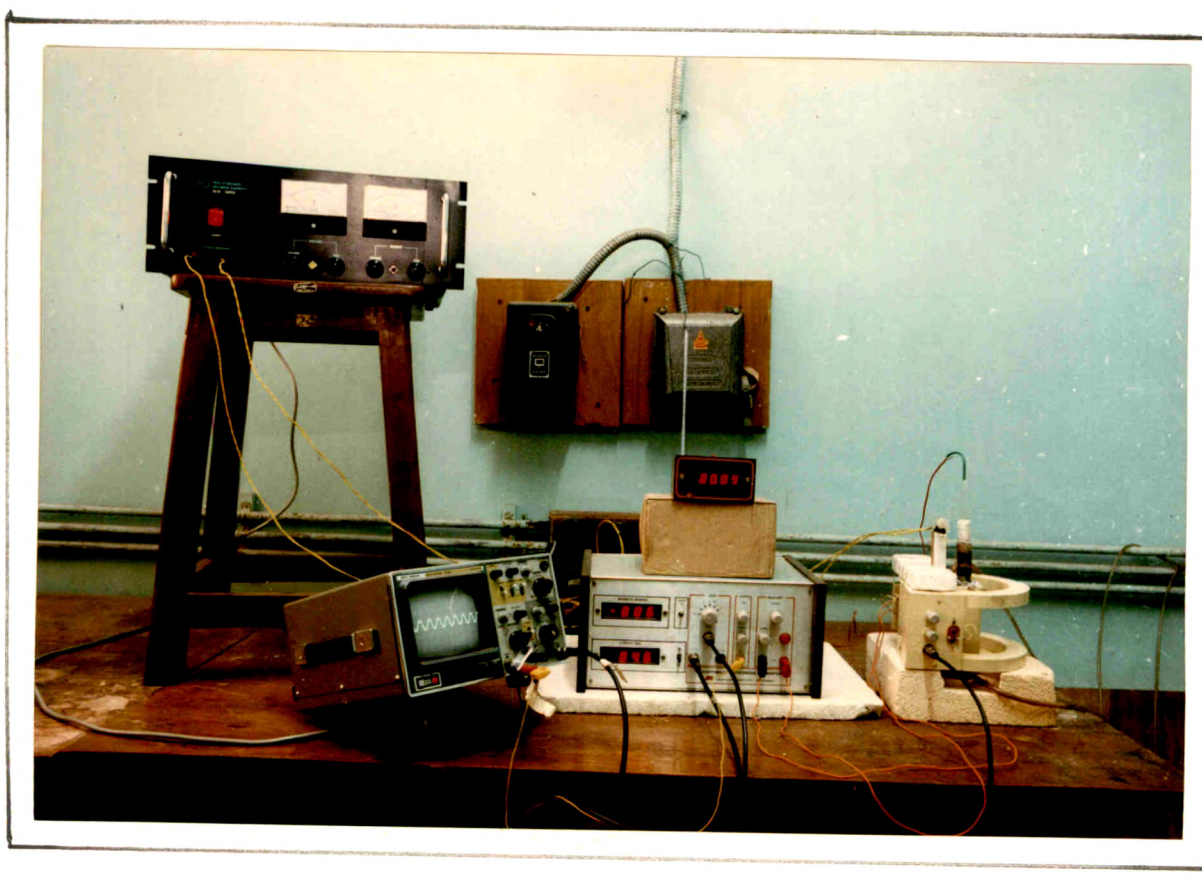


Fig.3.5 : Experimental set up of A.C.Susceptibility measurement.

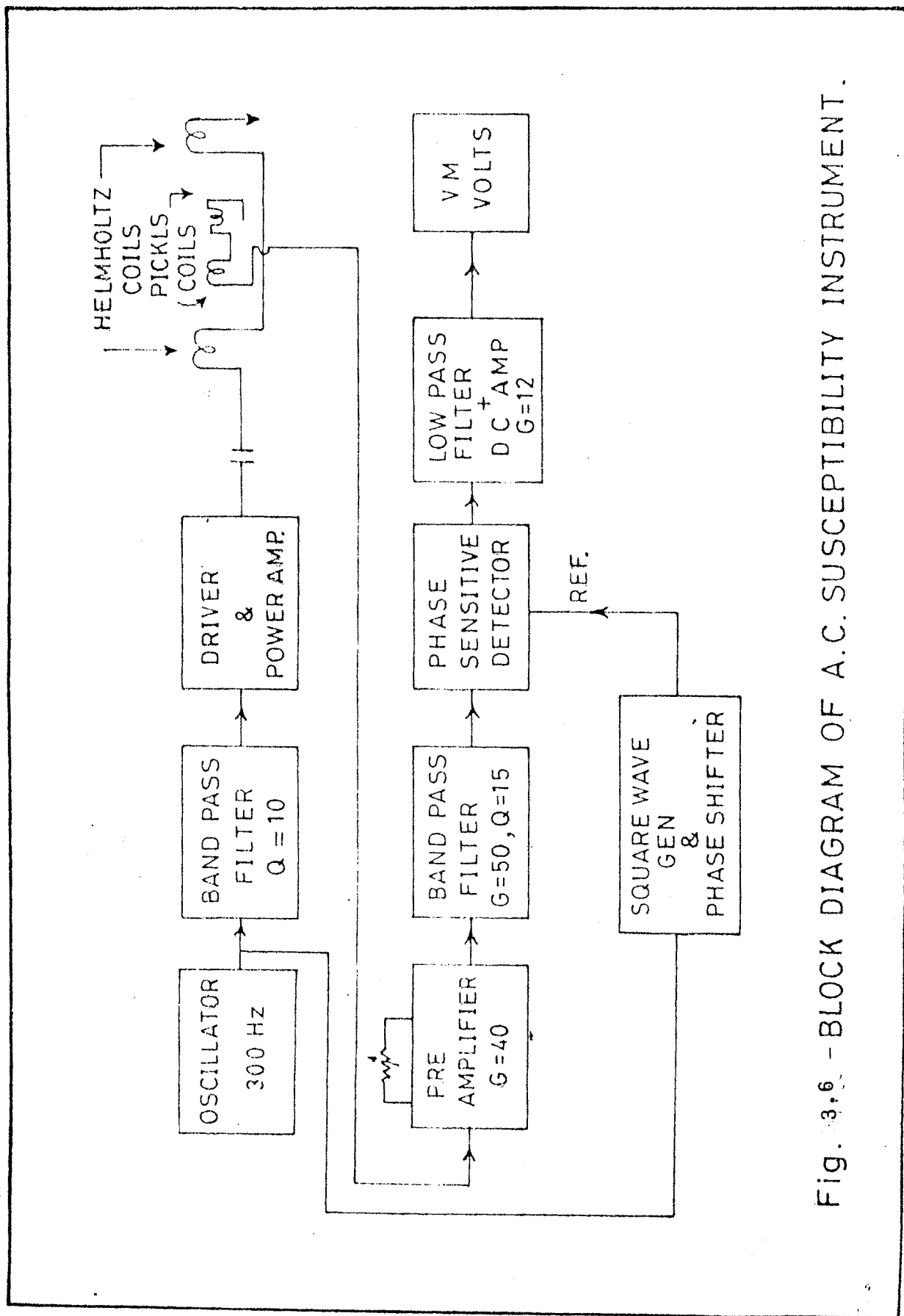


Fig. 3.6 - BLOCK DIAGRAM OF A.C. SUSCEPTIBILITY INSTRUMENT.

furnace is inserted in glass jacket which is placed in the center of pick-up coil. Height of the sample tube is maintained such as a way that the sample can stay at the center of the double coil. The current to the Helmholtz coil is supplied by an oscillator and a high quality power amplifier. The signal induced in the double coil, which is proportional to the rate of change of magnetic moment of the sample, is amplified, rectified and read out on digital voltmeter. The meter reading can be calibrated in terms of magnetic moments. The temperature of furnace is maintained by power supply. The temperature was measured by calibrated platinum-rhodium thermocouple. The sample was gradually heated and at various temperatures the signal corresponding to the magnetic moment was recorded. The heating was continued till the signal was reduced to zero. Knowing magnetic moment susceptibility is calculated and hence normalized susceptibility is calculated and hence normalized susceptibility is determined at various temperatures.

3B.3 Results and Discussion

The measurement of low field a.c. susceptibility with temperature for samples of the ferrite system



where ($x = 0, 0.2, 0.4, 0.6, 0.8$ and 1) are carried out. The variation of normalized susceptibility (χ_T/χ_{RT}) with temperature (T) is shown in Fig. 3.7. The following observations are made from these curves -

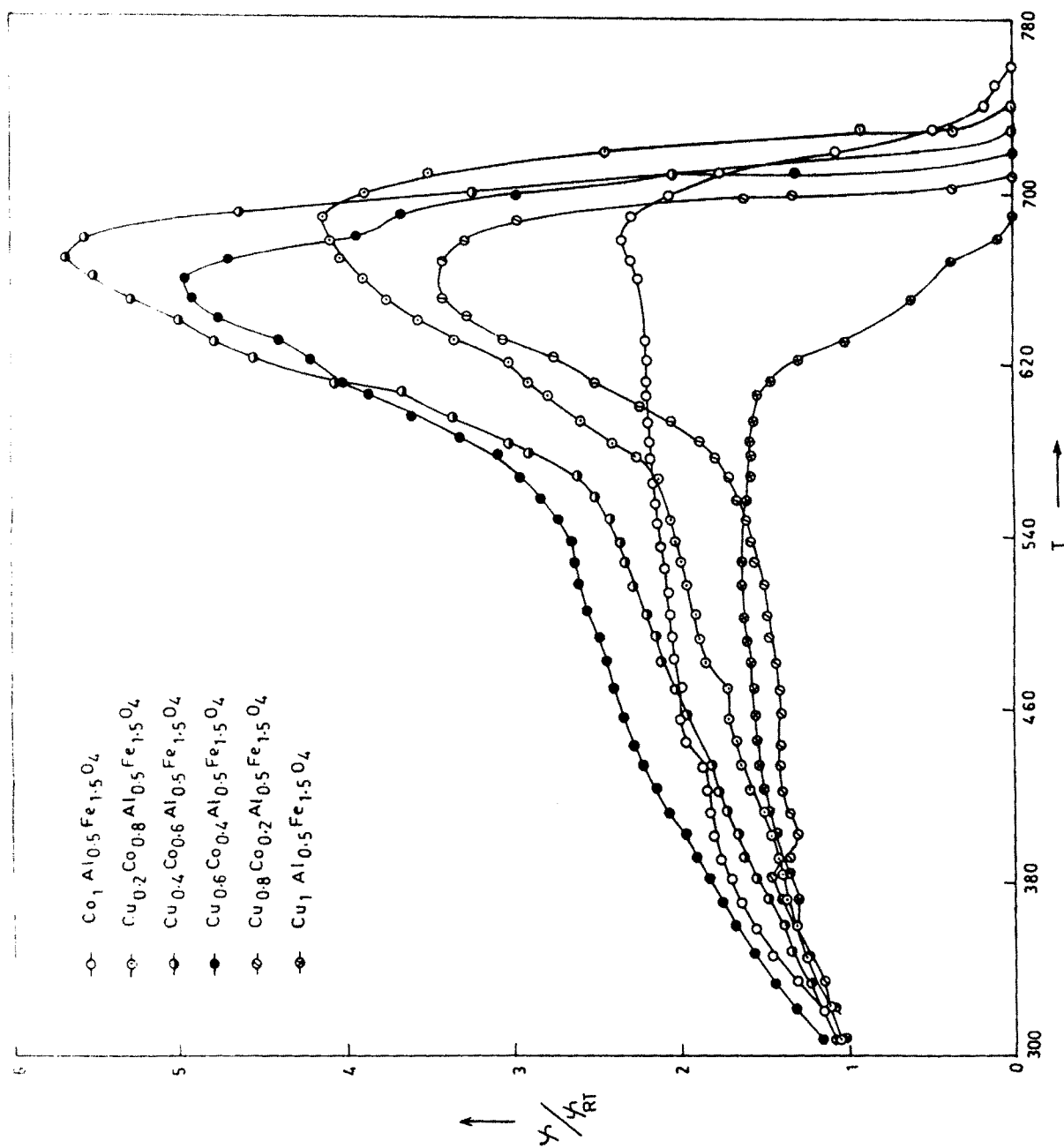


Fig.3.7 : Variation of A.C.Susceptibility with temperature

1. All the curves drops sharply.
2. From the curves Curie temperature can be determined. For the present series the Curie temperature (T_c) decreases with increase in copper content.
3. For the samples with $x = 0, 0.2, 0.4, 0.6$ and 0.8 the susceptibility increases rapidly with temperature reaches a maximum and then drops very sharply near Curie temperature and a tailing effect is observed.
4. For the samples $x = 0$, the susceptibility is constant and it increases slightly at peak with temperature and for $x = 1$, the susceptibility is constant and falls sharply at Curie temperature and a tailing effect is observed.
5. The curves obtained in the present study indicates the ferrimagnetic behaviour and sharp fall for each sample indicates the single phase formation of the ferrite which has been already confirmed by XRD studies.

Peaking behaviour was first observed by Hopkinson [28] and the corresponding peak is called as Hopkins peak. Srivastav et al. [29] have carried out the susceptibility behaviour on typical ferrimagnetic material. It has been suggested that the shapes of the curves give the idea of domain state in the material [30].

Domain structure in ferrite has been studied by number of workers [31, 32]. A polycrystalline material may contain three types of particles namely

- 1) Multi domain (MD)
- 2) Single domain (SP)

3) Super paramagnetic (SP) particles.

For SD particles coercive force H_c is large, where it tends to zero for SP particles [33] and is small for MD particles. Thus susceptibility which is inversely proportional to H_c , is large for SP particles of the same materials and hence there is peak in (χ_T/χ_{RT}) at T_b . The samples with predominantly MD particles show almost constant susceptibility with increasing temperature till T_c [29].

The variation of a.c. susceptibility with temperature shows that the samples with $x = 0.2, 0.4, 0.6$ and 0.8 can be assigned single domain + multi domain (MD+SD) to super paramagnetic (SP) particles transition. The samples with $x = 0$ and $x = 1$ do not show or exhibit peak implies that these samples contain MD particles [34].

Based on above nature of variation of normalized $\chi_{ac}-T$ curves, it can be noted that the transition from ferri to para region is not sharp in each case but gives tailing effect due to spin clusters i.e. short range and spin ordering. The spin clustering formation is observed in aluminium containing ferrite [35]. The continuous decrease of $\chi_{ac}-T$ curves also gives the idea about canting behaviour or cluster formation.

In Table 3.1 Curie temperatures for our samples determined from a.c. susceptibility measurement and from D.C. conductivity technique have been given. The results obtained by a.c. susceptibility measurement D.C. conductivity measurement are in good agreement with each

other. The results obtained at end, ferrites are in good agreement with the previously reported results [36, 37, 38]. But there is a difference in Curie temperature compared to earlier reported results. This is due to the substitutions of magnetic ions by non magnetic ions. Obviously reduces the number of linkages per formula unit, thereby decreasing the Curie temperature.

Table 3.1

II. Curie temperature in °K obtained by two methods for
Cu_x Co_{1-x} Al_{0.5} Fe_{1.5} O₄ samples

Composition	d.c. Conductivity	a.c. Susceptibility
CoAl _{0.5} Fe _{1.5} O ₄	743	758
Cu _{0.2} Co _{0.8} Al _{0.5} Fe _{1.5} O ₄	730	740
Cu _{0.4} Co _{0.6} Al _{0.5} Fe _{1.5} O ₄	723	730
Cu _{0.6} Co _{0.4} Al _{0.5} Fe _{1.5} O ₄	715	720
Cu _{0.8} Co _{0.2} Al _{0.5} Fe _{1.5} O ₄	703	710
CuAl _{0.5} Fe _{1.5} O ₄	693	690

**a.c. susceptibility of Copper and Cobalt ferrite without
Aluminium.**

CoFe ₂ O ₄	775	36(Ref.)
CuFe ₂ O ₄	757	36(Ref.)
"	748	37(Ref.)
"	736	38(Ref.)

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