CHAPTER - III

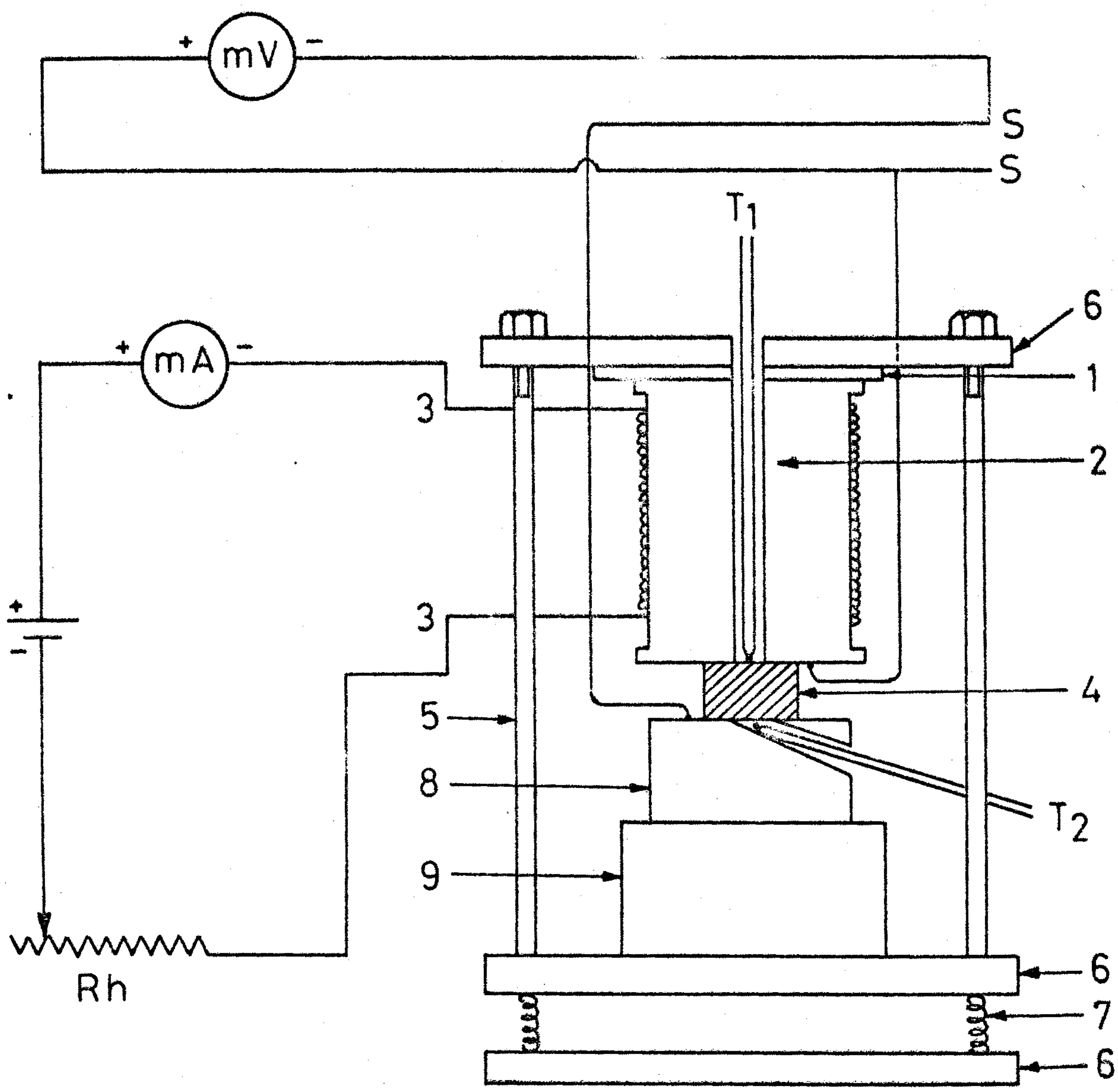
ELECTRICAL PROPERTIES

(THERMOELECTRIC POWER STUDIES)

Thermo Electric Power Studies

3.1) Introduction : The studies on d.c. electrical conductivity and thermoelectric power render comprehensive information of d.c. conduction mechanism. The temperature variation of conductivity shows breaks and changes in conduction mechanism that occur in ferrites besides the information on the magnitude of Conductivity. Studies on thermoelectric power reveal the types of carriers that govern the electrical conductivity and whether the conduction is due to thermally activated hopping. It is also possible to compute temperature variation of fermi level and explore possibilities of conduction through the impurity levels from these studies.

Ghani et al[1] have studied the effect of annealing on the conduction mechanism in Cu ferrite. The annealing temperature changes the sign of conduction from P-type to n-type. Effect of firing temperature and atmosphere on iron Cobalt and Iron Zinc ferrites is studied by Gilliot et al.[2] The Iron-excess ferrites obtained at low preparation temperature or firing in vacuum above 600^{o}C showed n-type and higher conductivity while iron deficient obtained by oxidation at 300^{o}C or by firing in air with development of vacancies on octahedral sites showed p-type conduction. Iron-deficient Nickel[3] and Cobalt[4] ferrites have shown high resistivity and positive Seebeck coefficient when slow cooled while



[1-Mion sheet; 2,8-Hard metal electrods; 3-Sub heater leads; 4-Sample pellet; 5-Metal rod; 6-Metal plates; 7-Spring; 9-Metal block; T_1 T_2 - Thermocuples; S- Silver wires welded at Ag electrods.]

Fig. 3·1 – Experimental set-up for the measurement of thermoelectric power.

these ferrites have shown low resistivity and negative Seebeck coefficient on quenching which is attributed to ferrous ions.[5] $CuFe_2O_4$ has exhibited low resistivity and positive seebeck coefficient when quenched from elevated temperature[6] and other interesting semiconducting properties.[7,8]

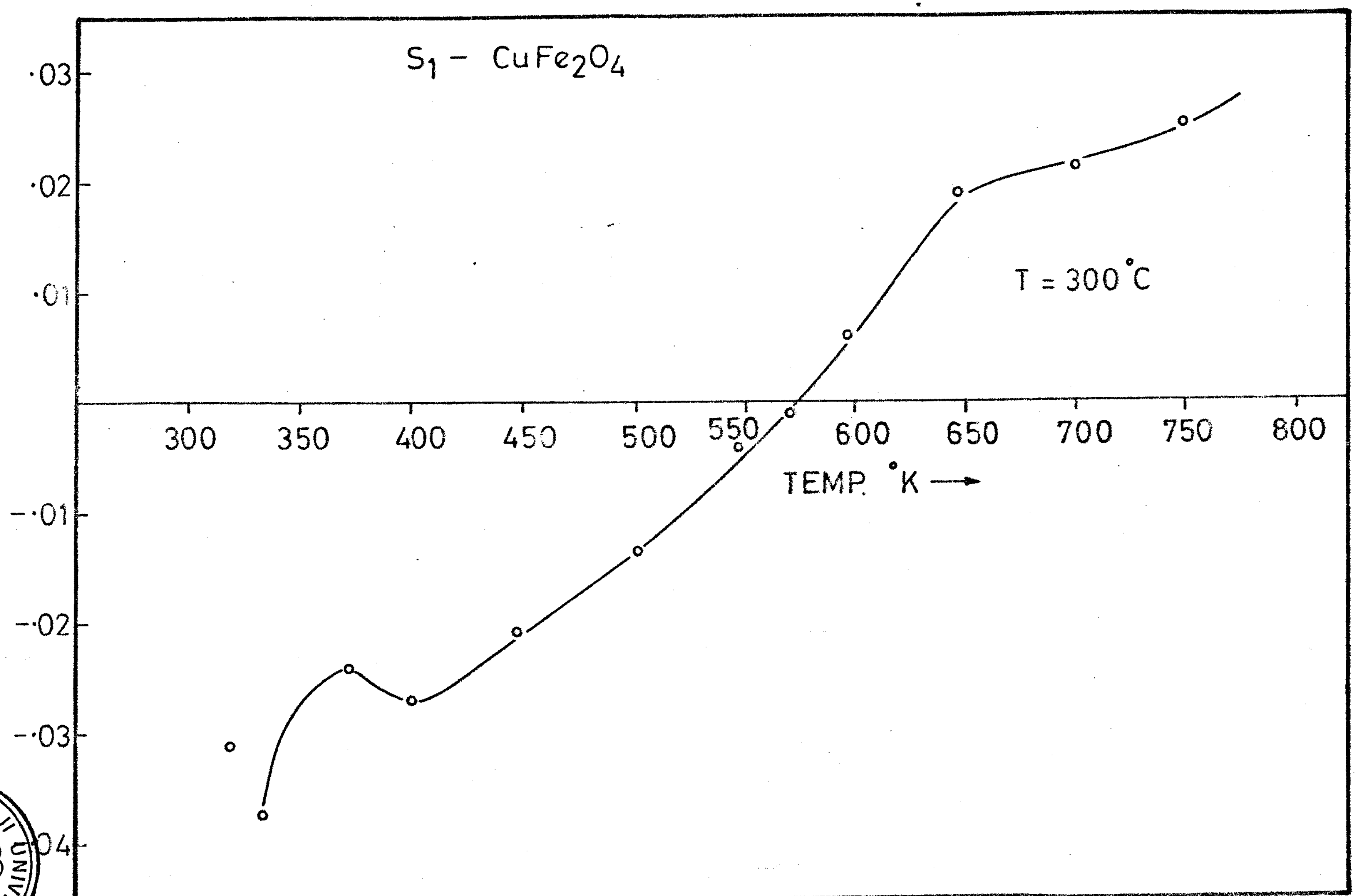
In this chapter we have carried out studies on temperature variation of Seebeck coefficient on the system $Cu_xZn_{1-x}Fe_2O_4$ with a view to studying the effect of addition of $ZnFe_2O_4$ in $CuFe_2O_4$. The results are explained giving appropriate theory.

3.2) Thermoelectric Power measurement :

The measurement of thermoelectric power for the pellet was done by holding the sample between two cylindrical metal electrodes. By passing D.C. current through the axillary heating coil, the temperature difference across the pellet was maintained constant at about $20^{\circ}C$. The whole arrangement was placed in the furnace. The measurements were carried out at different temperatures by keeping the cell in a furnace. The details of thermoelectric cell construction are shown in the Fig. 3.1.

3.3) Result and Discussion :

Figs. 3.2 to 3.6 show temperature variation of α - the seebeck coefficient for the system $Cu_xZn_{1-x}Fe_2O_4$. The following observations have been made from these plots :



S1 - CuFe2O4
T = 300°C
α (mV / °K)
TEMP. °K
·03
·02
·01
-·01
-·02
-·03
·04
300
350
400
450
500
550
600
650
700
750
800

Fig. 3·2

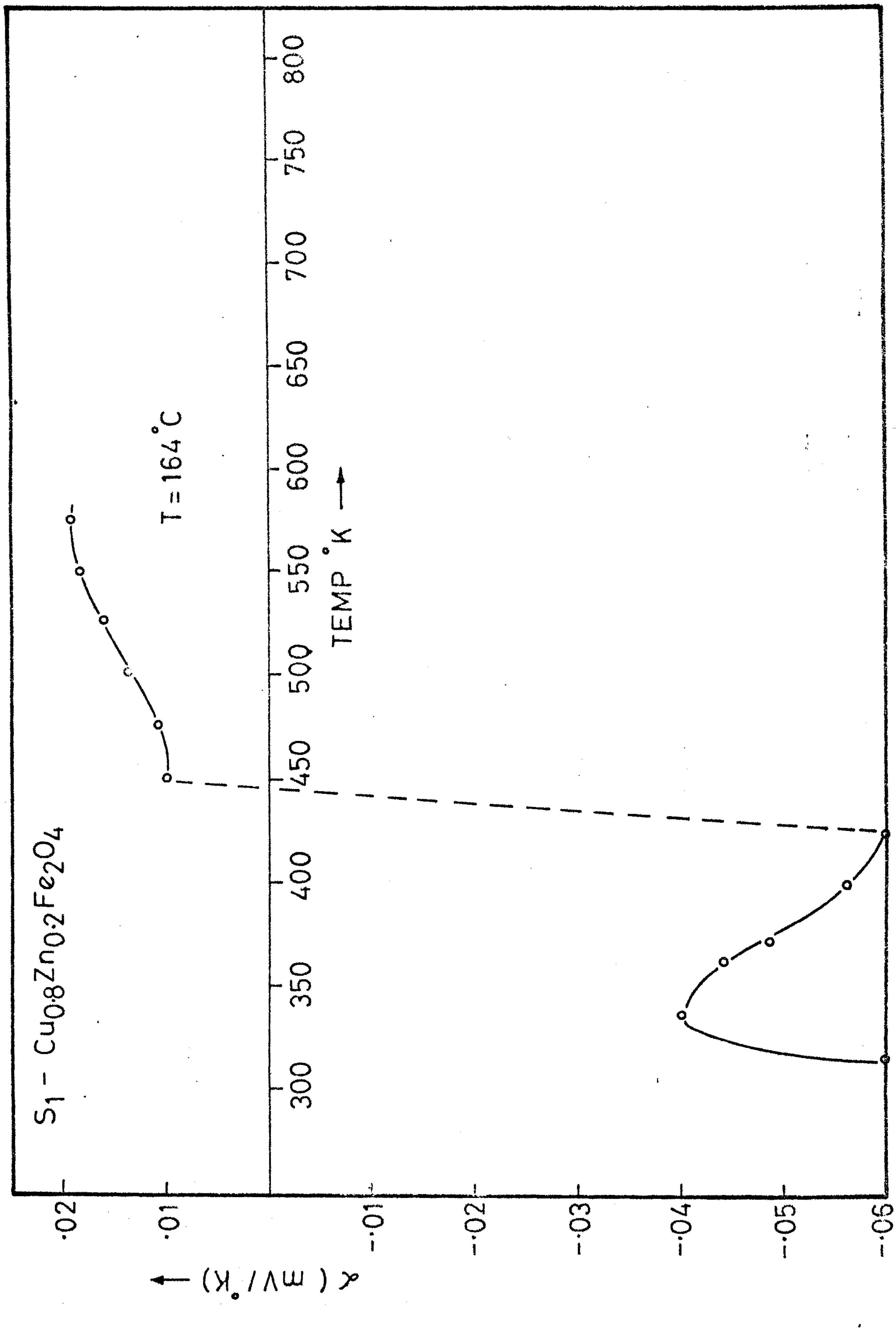

S1 - Cu0·8Zn0·2Fe2O4
T = 164°C
TEMP °K
300
350
400
450
500
550
600
650
700
750
800
·02
·01
-·01
-·02
-·03
-·04
-·05
-·06
α (mV/°K)

Fig. 3·3

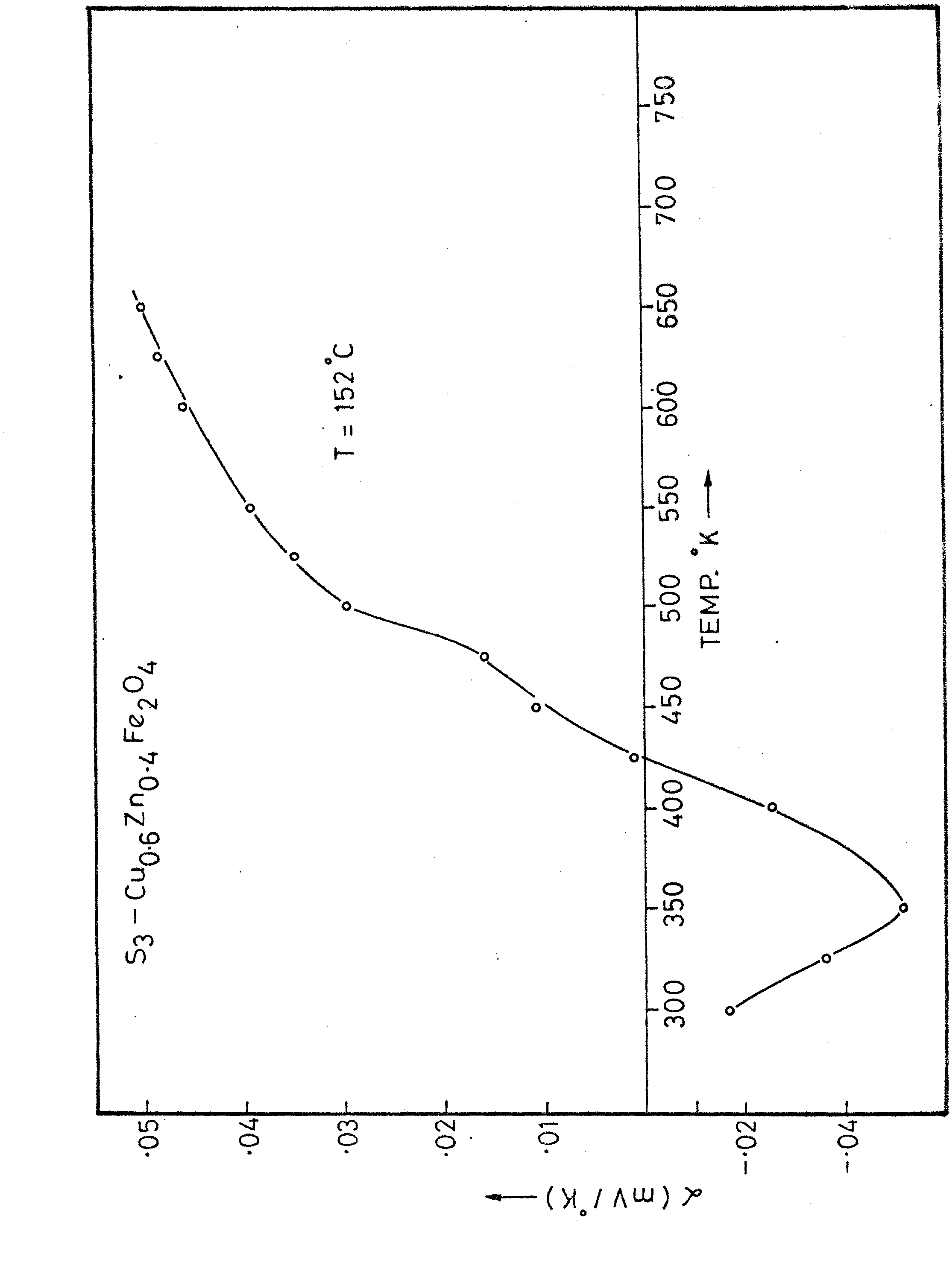
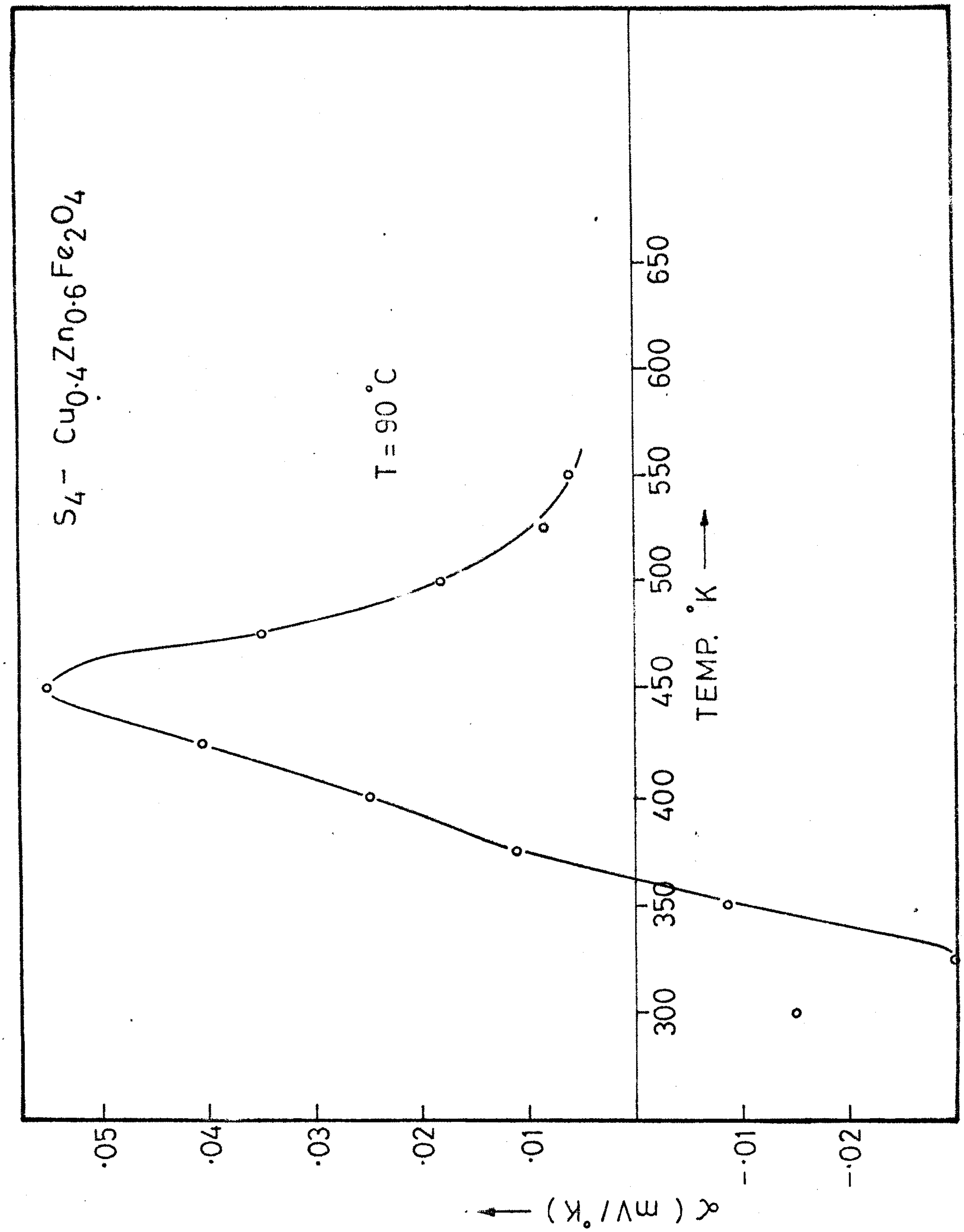

$S_3 - Cu_{0.6}Zn_{0.4}Fe_2O_4$
T = 152°C
TEMP. °K ⟶
300
350
400
450
500
550
600
650
700
750
·05
·04
·03
·02
·01
-·02
-·04
α (mV / °K) ⟶

Fig.3·4



$S_4 - Cu_{0.4}Zn_{0.6}Fe_2O_4$
T = 90 °C
TEMP. °K →
α (mV / °K) →
·05
·04
·03
·02
·01
-·01
-·02
300
350
400
450
500
550
600
650

Fig. 3.5

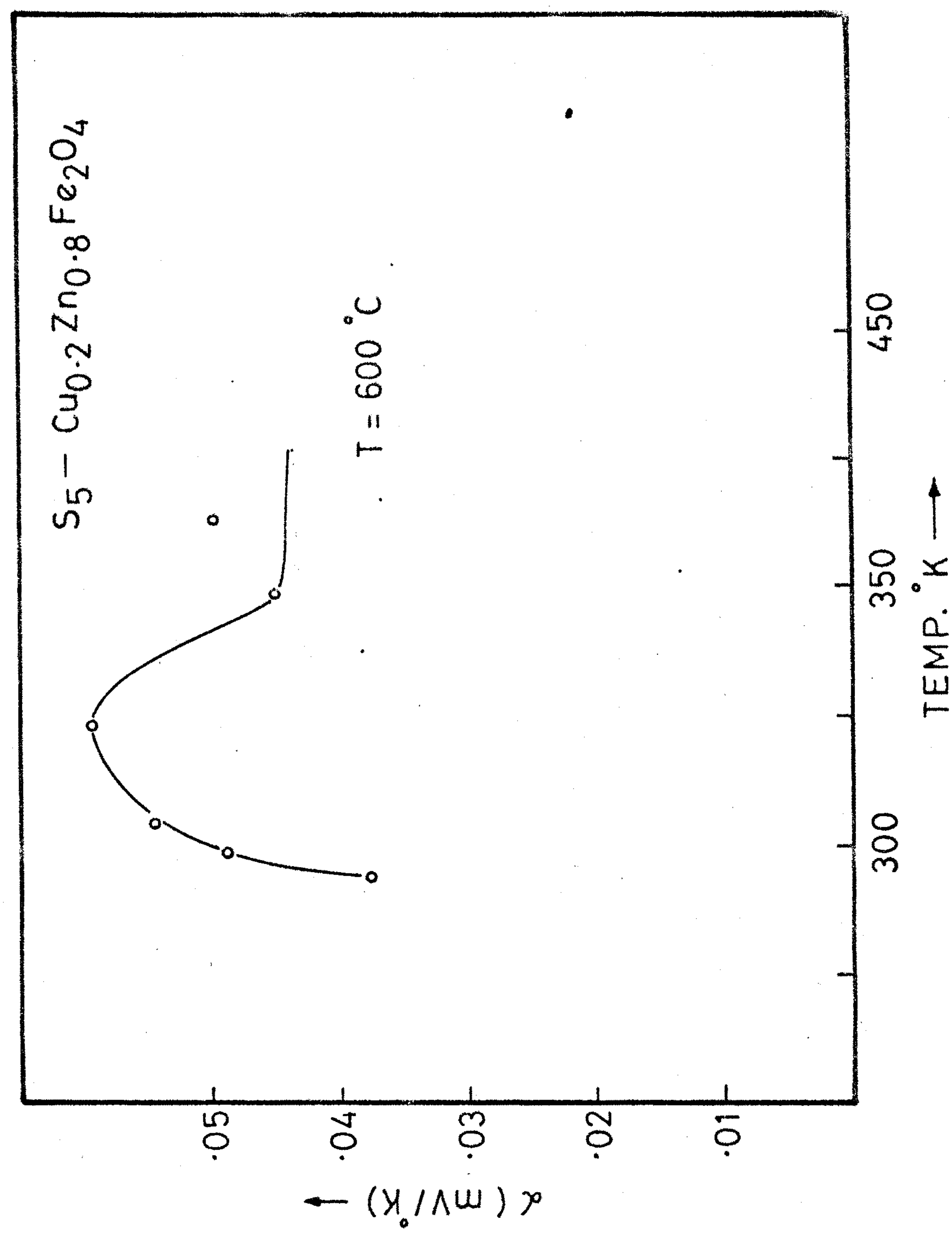


Fig.3·6

1) For $CuFe_2O_4$ the Seebeck coefficient is negative upto 300^oC indicating that the majority carriers are electrons i.e. the material is n-type. Similar behaviour is exhibited by the samples for which x = .8, .6, .4. The following table (3.1) gives the temperature at which the Seebeck coefficient, changes its sign i.e. transition-temperature.

Table 3.1

Transition and Peak temperatures

Sample	Transition temperature	Peak temperature
$CuFe_2O_4$	300^oC	127^oC
$Cu_{.8}Zn_{.2}Fe_2O_4$	164^oC	-
$Cu_{.6}Zn_{.4}Fe_2O_4$	152^oC	77^oC
$Cu_{.4}Zn_{.6}Fe_2O_4$	90^oC	177^oC
$Cu_{.2}Zn_{.8}Fe_2O_4$	-	52^oC

Thus it is seen that with the addition of Zn in the system the transition temperature decrease which bears one to one correspondence with compositional variation of T_c.

Above the transition temperature the samples exhibit p-type of behaviour except for the ferrite $Cu_{.2}Zn_{.8}Fe_2O_4$

which has only positive value of α.

2) Visible peaks are observed during the n-type conduction. These peaking temperatures are given in table 3.1. It is seen that as Zn content increases the values of the peak temperature changes and the peaks also become pronounced. An interesting behaviour is exhibited by the ferrite $Cu_{.8}Zn_{.2}Fe_2O_4$ for which there is no peak and the change of conduction from n-type to p-type is abrupt.

3) In sample of $Cu_{.4}Zn_{.6}Fe_2O_4$ and $Cu_{.2}Zn_{.8}Fe_2O_4$ the peaks are observed at the temperature 117°C and 52°C respectively in the p-region of conduction.

The observed maxima in α in all cases imply the conduction through impurity levels. This means that mixed conduction takes place in each case and the samples are partly compensated due to simultaneous presence of acceptor and donor centres with relative predominance. Formation of both types of the centres results from loss of oxygen during sintering process. Ghani et al[1] have studied thermoelectric power as a function of temperature in the case of $CuFe_2O_4$ before and after annealing. They concluded that, simply presence of Cu^{1+} ions does not explain the p-type conduction, since they act as donors[9]. Thus the interstitial cations act as accepter centres and p-carriers may be identified as holes on oxygen ions ($\bar{O}$). Such type of p-carriers was proposed by Gardner et al.[10]

From the figures 3.2 to 3.5 in the n-region and from the figures 3.5 and 3.6 in the p-region, it is seen that the number of carriers around the R.T. is not constant because α would be constant with respect to temperature.[11,12]

The fact that α varies with temperature and show peaking indicate that the variation in charge carrier concentration plays an important role in the conductivity temperature variation. Below the peak temperature it can be assumed that the conduction is of two types i.e.

$$\sigma = \sigma_n + \sigma_i \qquad \ldots 3.1$$

where σ_n - is the free electron conductivity σ_i - is the impurity conductivity.

According to Bosman and Crevecoeur[11] and Dutt et al,[12] the following expression exists for thermo-electric power

$$\alpha = -\frac{K}{e}\left[\frac{\sigma_n}{\sigma}\left(\frac{E_F}{KT} + A\right) + \frac{\sigma_i}{\sigma}\left(\frac{E_D - E_F}{KT}\right)\right] \qquad \ldots 3.2$$

where E_F is the Fermi level, A-term connected with Kinetic energy K.E. of free electrons, E_D - energy of donor w.r.t. transport level. From the theory of partly compensated semiconductor it is known that at low temperatures the mixed conduction occurs where electrons are majority carriers.

$$E_F = E_D + KT \ln\left(\frac{N_D - N_A}{N_A}\right) \qquad \ldots 3.3$$

where $N_D > N_A > 0$.

N_A and N_D are concentration of acceptor and donars respectively at $T = 0$ $E_F = E_D$; as the temperature increases $E_F > E_D$ i.e. $E_F - E_D$ becomes positive. The first term in the equation(3.2) dominates as long as $\sigma_i / \sigma \ll 1$. When the temperature is increased the thermoelectric power first increases with increasing temperature. However, as soon as σ_i becomes comparable with σ_n the first term in the equation (3.2) decreases while the second term increases positively. This explains the peak in α-T variation in negative region.

For the samples which show peaks after the transition from n- to p- region the following explanation holds good. Below the peak temperature the conduction due to impurity conduction (σ_i) and free hole conduction (σ_p).

$$\sigma = \sigma_p + \sigma_i \qquad \ldots 3.4$$

The expression for α-T variation will be

$$\alpha = \frac{K}{e} \left[\frac{\sigma_p}{\sigma} \left(\frac{E_F}{KT} + A \right) + \frac{\sigma_i}{\sigma} \left(\frac{E_F - E_A}{KT} \right) \right] \qquad \ldots 3.5$$

The Fermi level is given by[13,14]

$$E_F = E_A - KT \ln \left(\frac{N_A - N_D}{N_D} \right) \qquad \ldots 3.6$$

At $T = 0$, $E_F = E_A$ with increasing temperature $E_F - E_A$ becomes negative. Thus as long as $\frac{\sigma_i}{\sigma} \ll 1$. The first term in equation (3.6) govern α-T variation i.e. α increases initially with decreasing T.

When σ_1 becomes comparable to σ_p the first term in equation (3.5) decreases while the second term increases lowering the value of α. This explains peak in α-T variation in the positive region.

In the region where conduction is by one type of carriers say by holes then α and E_F are related by

$$E_F = e\alpha T - AKT \qquad \ldots 3.7$$

These samples of $Cu_xZn_{1-x}Fe_2O_4$ (x = 1, .8, .6, .4) which show negative value of α upto transition temperature have more donar centres in comparison with the acceptor centres. Also this variation goes on becoming weaker with the addition of Zn^{+2} which suggests that acceptor centres become predominant over donar centres, after this temperature leading to change in sign of α. It is known as transition temperature when $\alpha = 0$. Basically α is created due to difference in the mobility of carriers or their densities. The fact that α becomes zero suggests that at temperature of transition whatever difference exists either in the mobilities or the density of carriers reduces to zero.

From the study of thermoelectric power; temperature variation of E_F can be plotted and the extrapolation E_F axis gives value of $E_F(0)$. The relation of resistivity and temperature in case of ferrites is given by

$$\sigma = \sigma_o \text{ Exp } \left(\frac{\Delta E}{KT} \right) \qquad \ldots 3.8$$

In case $\Delta E > E_F(0)$ then it can be said that the activation energy of conductivity contains an additional part due to thermal activation of electrons between Fe^{+2} and Fe^{+3} in B-sites. Thus it can be assumed that

$$\Delta E = \Delta E_1 + \Delta E_2 \qquad \ldots 3.9$$

ΔE_1 - activation energy contributed to the concentration of charge carriers. ΔE_2 - activation energy of mobility (hopping activation energy). The activation energy of hopping is ΔE_2 = 0.2eV in case of ferrites.[15,16]

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