Chapter 4

Study of Germanium based Dilute Magnetic Semiconductors

4.1 Introduction

Dilute magnetic semiconductors (DMS) are those materials, which simultaneously exhibit semiconducting properties as well as the long range magnetic ordering (especially ferromagnetic). These new materials have found potential applications in spintronics [1] .On exploiting the spin of electron and its charge, these materials can be used in semiconductor memory devices (MRAM) [2], signal processing devices etc. Failure of conventional ferromagnetic metals in such applications has made these materials important to study. Such materials are Transition Metals (TM) doped in II-VI, IV-VI & III-V based DMS. Here the concentration of transition metal impurities is alloyed in a dilute limit. But the curie temperatures of many DMS systems are observed below RT [3]. Recently much effort has been put to raise the curie temperatures to RT and above. However great interest was shown in III-Mn-V based DMS [4,5,6], which exhibited RT ferromagnetic ordering in the system.

The theoretical [7] and experimental [8] evidences for the cause of ferromagnetism at RT in DMS materials are now being established. The first Zener model approach by Dietl et. al. [7] was successful in explaining the exchange interaction caused between carriers and localized spins in III-V based compound semiconductors.

In this context the group IV based ferromagnetic semiconducting materials have not been extensively studied as investigated in the compound semiconductors. However few reports on Ge based DMS materials do exist. The ferromagnetic ordering observed in Cr, Fe doped Ge [9] bulk single crystals studied by S.Choi et.al., has reported the Tc value as 126K and 233K respectively. While the dilute Mn doped Ge system studied by Park et. al. [10], reveals that there is an increase in curie temperature from 25 K to 116 K as the Mn concentration is increased to 0.04. In IV-VI based thin film GeTe compound semiconductors [11], the doping of Cr, Mn and Fe leads to the curie temperatures to 12K, 47K and 100K respectively. However in the ternary compound semiconductors like $(Cd_{0.8}Mn_{0.2})GeP_2$ [12] & $(Zn_{0.94}Mn_{0.06})GeP_2$ [13], Tc values were observed to be 320K and 312K respectively, which are quite above room temperatures. Thus, from the earlier studies it is observed that the RT magnetic ordering in bulk Ge based DMS is yet to be achieved.

In all these studies, the carrier densities are brought into the system by doping magnetic ion concentration. It is understood that on increasing the carrier densities the exchange interactions can be enhanced. But this may lead to higher magnetic ion concentration, which may cause the formation of magnetic compound phases into the host material. For e.g. MnN[14] and MnAs[14] are the phases observed in GaMnN and GaMnAs systems.

However as it was discussed recently by D. Somayajulu et. al.[15] if the dopant magnetic ion concentration is kept low and constant and the variation of charge carrier density is brought about by either doping with impurities or by varying the concentration of the anion in the semiconductor (B site in AB type), it will be still possible to keep the system in dilute limit and yet may be possible to bring about ferromagnetism at room temperature. Most of the earlier studies have kept the A and B site concentrations constant at the stoichometric proportions. Thus for the 3d metal Fe interesting evidence was produced for the ferromagnetism in a study of varying B site (Se) concentrations in such a binary system and by keeping the A site (Sb) material as the base.

In this chapter we discuss the variation of dopants (donor, acceptor and neutral impurities) in Ge based DMS materials. 3d transition metal ions Fe behave like acceptors and dilute Fe doped Ge does not show any magnetic moments. Hence we studied the effect of different kinds of simultaneous additional dopants like donors, acceptors and neutral impurities on the production of ferromagnetism in this dilute Fe doped Ge system. The transition metal impurity (Fe) was kept constant in very dilute limit (0.008) and the dopant impurities were varied from 0 to 5% concentration. Mossbauer spectroscopy (MS) was employed to study the hyperfine magnetic interactions at Fe site in Ge host lattice.

Importance of Hyperfine interaction technique:

To study the effect of magnetic interaction in such very dilute limit, one needs highly sensitive microscopic techniques like Mossbauer Spectroscopy and Time Differential Perturbed Angular Correlations (TDPAC),the details and the potential of these techniques are discussed in chapter 2. The hyperfine magnetic interaction, which is the magnetic interaction between the magnetic moments of electrons and nuclei, provides an important mechanism (D'yakonov and Perel', 1973b) [16] for ensemble spin dephasing and single-spin decoherence of localized electrons, such as those bound to donors. In addition to spin dephasing, the hyperfine interaction is relevant for spintronics as a means to couple, in a controlled way, electron and nuclear spins . The effect of interactions between localized spins and charge carriers in a dilute limit can be well studied by this microscopic technique.

4.2 Sample Preparation:

For preparation of sample series $Fe_{0.008}Ge_{0.992-x}M_x$ (M =As, Sb, Bi, S, Se, Te and In and Sn) with concentration of $0 < X < 0.05$, high purity powder materials(> 5 n pure) in the desired proportion were taken. These powder materials were imported from Aldrich Chem. Co. Material was weighed using a very sensitive micro balance [Sartorius (Germany)] make, The accuracy of the balance was about ~μ gram. The necessary quantity of the materials were taken in quartz tubes which were evacuated to 10^{-5} torr. The tubes were then sealed under

vacuum in the form of ampoules. After encapsulation, the ampoules were shaken to mix the material thoroughly and were kept vertical in a furnace for two days (48 hours). The temperature was set nearer to germanium melting point for alloying Iron, Germanium and the impurities properly. In the cooling procedure, the furnace was slowly cooled for better crystallization. After completion of cooling cycle the samples were obtained in the form of shiny globules.

One part of the globules was then cut in the form of rectangular block and polished using diamond polishing instrument. Electrical contacts were made with copper wire using tin solder on the sample surfaces. These samples were used for Hall Effect, Magnetoresistance, Resistivity and AC Susceptibility characterizations.

Remaining part of the samples was used for XRD characterization and for making Mossbauer absorbers. Iron Fe^{57} enriched isotope was used in making the sample to get better percentage absorption and statistics. For Mossbauer absorbers, approximately 100 mg of samples were taken in the form of powder and spread on the plastic film of about 1.2 cm^2 circular area. For Mossbauer measurements of samples at higher temperature, special type of aluminum sample holder was used. It was made in the ring form in which sample + Boron

nitride mixture was filled and both the sides were covered with thin aluminum foil.

In the following the details of the studies on pure Ge, Fe doped Ge, Fe doped $Ge_{0.992-x}M_x$ (M = Donors As, Sb, Bi, S, Se, Te) and Fe doped $Ge_{0.992-x}M_x$ (M= Acceptor In, Neutral Sn) are given.

4.3 Studies on Pure Ge Sample.

4.3.1 Resistivity, Magnetoresistance and Hall effect of Pure Ge Sample

Pure germanium was the host material. Fig 1 shows plot of resistance versus temperature from 4K to 300K measurement on the sample. The change in resistance was from 1Ω to 0.1Ω, without magnetic field and 1.1Ω to 0.11Ω, with magnetic field H= 8 Tesla. From the Hall Effect measurement the electron concentration was observed to be 5.27x $10^{15}/cm^3$. Fig. 2 shows the Magneto resistance versus Magnetic field at two different temperatures 4k and 300k, $\Delta\rho/\rho$ ratio changes around 4% at 300°K.

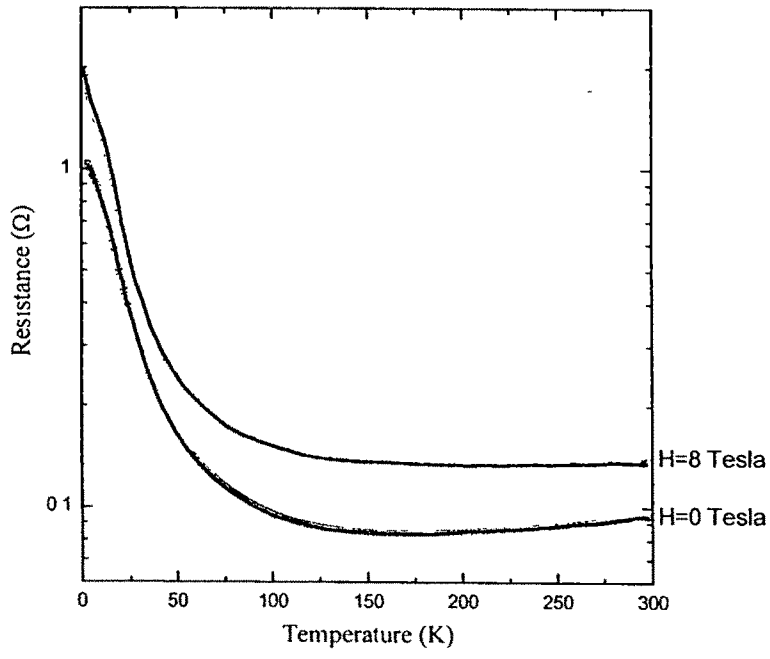

Fig 1 Resistance versus Temperature of Ge Pure

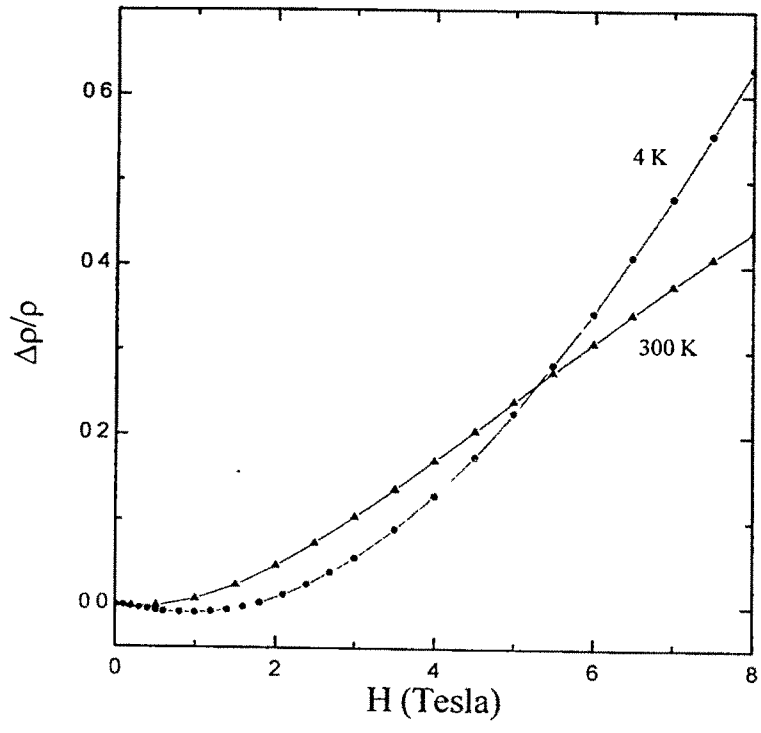

Fig 2 Magnetoresistance versus Magnetic field of Ge pure

4.4 Studies on Isotopic Iron ^{57}Fe doped Ge samples.

4.4.1 XRD measurement of of $Fe_{0.008}Ge_{0.992}$ sample

For XRD measurement, the samples were spread on glass plate with a layer of silicon grease. All the spectra were recorded at room temperature by a standard X-ray Diffractometer using Cu-Kα radiation (λ = 1.54 A°). The relative intensity I/I_0 versus 2θ of the samples were compared with standard data available in literature.

Fig 3 shows the XRD spectra of the sample $Fe_{0.008}$ $Ge_{0.992}$. Spectrum is similar to Ge base sample and no extra peak of Iron based compound phase was observed. The possible reported phase of the Fe and Ge is $FeGe_2$ and it has a tetrahedral structure. Its lattice spacing are a = 5.899 Å, c = 4.941 Å [17]. However, because of the very low concentration of Fe(0.008) in Ge, the resolution of the XRD technique restricts the observation of any such phase. But the presence of such phases in the Germanium matrix was confirmed by using Mossbauer spectroscopy.

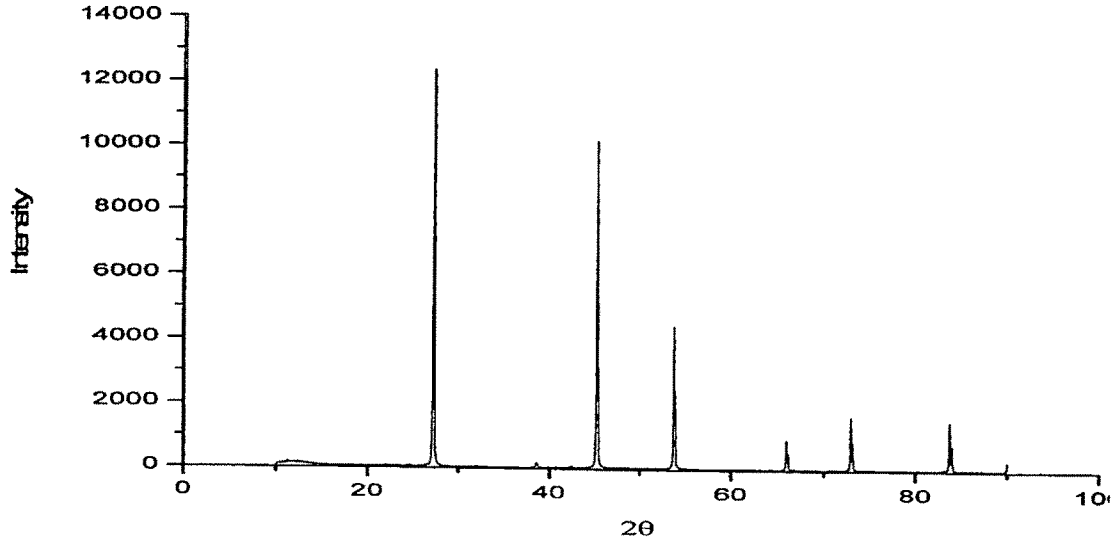

Fig 3 XRD spectra of $Fe_{0.008}Ge_{0.992}$ sample

4.4.2Mossbauer measurement of Fe_xGe_{1-x} samples

Mossbauer spectra of the samples were recorded using constant acceleration spectrometer with a line width of 0.28mm/sec. The calibration of spectrometer was done using natural Fe as detailed in chapter 2 (Fig 2.8). The source used was ^{57}Co in Rh matrix of strength 25mCi. Typical Mossbauer spectra recorded were least square fitted using Meerwal program, from which Mossbauer parameters [Qudrupole Splitting (QS), Magnetic Splitting (HMF), Isomer Shift (IS)] were evaluated. Normos Dist program was used to measure the Hyperfine Magnetic field (HMF) distribution in the spectra.

The Mossbauer spectra of the enriched Isotopic Iron Fe^{57} doped in germanium system are shown in the Fig. 4, 5 and 6. The Mossbauer parameter of the sample evaluated is given in Table 1. The maximum solubility of Iron in Germanium is around one atomic percent as reported [18]. Hence we kept the Iron concentration in dilute limit of about 0.2, 0.4 and 0.8% . In all these samples the spectra showed single line (Site C), with no indication of Magnetic or Quadrupole interaction. The Mossbauer parameters also remain constant with Fe concentration. From the spectra, it is clearly observed that as the concentration of Fe in Ge is increased, the peaks become clear even at low statistics. Hence we kept the Fe concentration at 0.008 (0.8%) in the samples to improve the statistical accuracy in our study.

Germanium is cubic in nature, substitutional or interstitial Fe in germanium are reported to be occupying tetrahedral site. Its orbitals are covalently connected with four nearest neighbors, which may result in quenching of the magnetic moment. Fig 6 shows the Mossbauer spectra of $Fe_{0.008}Ge_{0.992}$ sample, which is the starting material. The Isomer Shift value for single line was observed to be IS = 0.31 mm/sec, which corresponds to $FeGe_2$ phase [19].

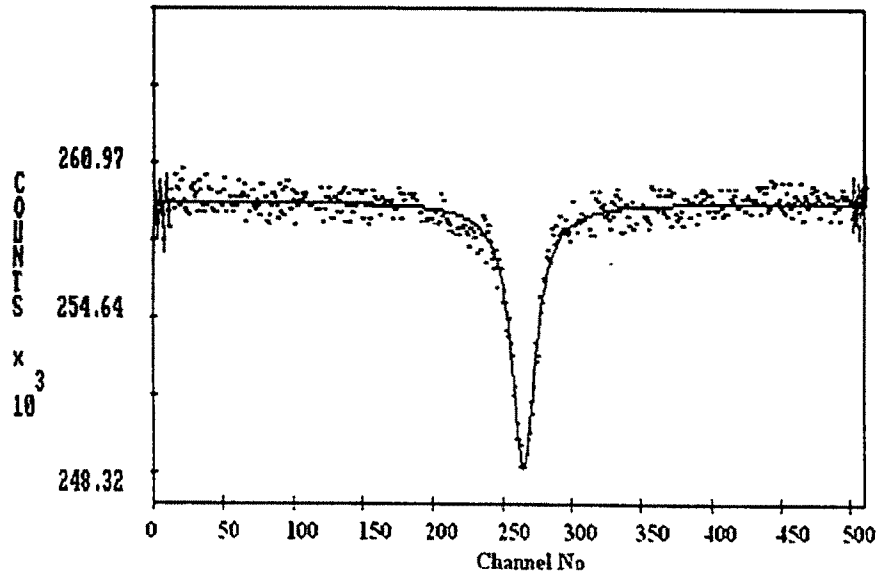

Fig 4 Mossbauer spectra of $Fe_{0.002}$ Ge $_{0.998}$ sample

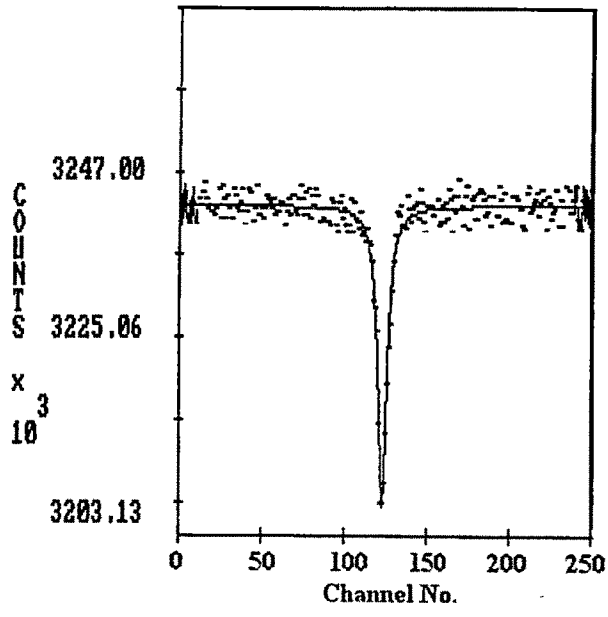

Fig 5 Mossbauer spectra of $Fe_{0.004}$ $Ge_{0.996}$ sample

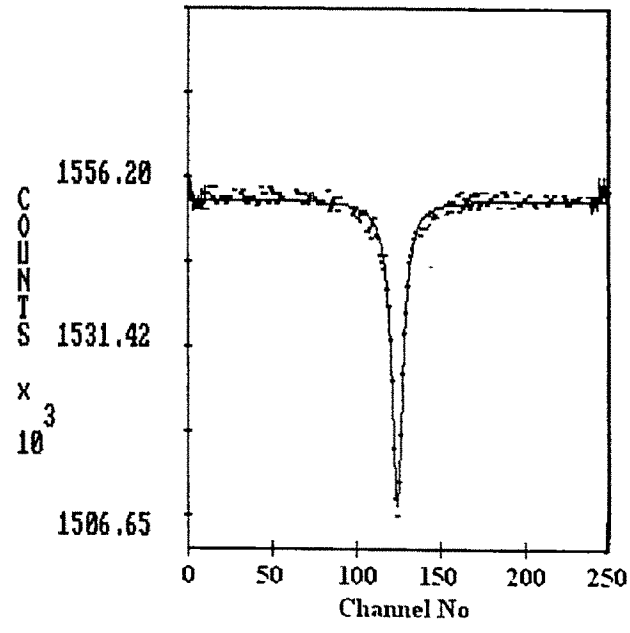

Fig 6 Mossbauer spectra of $Fe_{0.008}$ $Ge_{0.992}$ sample

Composition of Samples Fe_xGe_{1-x}	IS (mm/sec) Singlet C	Site Population (%) Singlet C
X = 0.002	0.31(2)	100(1)
X = 0.004	0.31(2)	100(1)
X = 0.008	0.31(2)	100(1)

Table 1 Mossbauer parameter of the Fe_xGe_{1-x} samples

4.4.3Resistivity, Magnetoresistance and Hall effect of $Fe_{0.008}Ge_{0.992}$ Sample

Fig 7 shows the resistance versus temperature measurement of the sample $Fe_{0.008}$ $Ge_{0.992}$ in a temperature range up to RT. The sample resistance changes from 4 Ω to 0.5Ω without field and 5Ω to 0.5Ω with 8 tesla magnetic field. From the Hall measurement, the charge carrier concentration was observed ~ $1.49x10^{15}$/ cm^3 and the sample is found to be p-type semiconductor. Fig 8 shows Magnetoresistance versus Magnetic field of the sample. The sample shows greater change in % MR at 300 K as compared to pure Ge. It is clear that Fe acts as an acceptor and creates the holes when added in to Germanium.

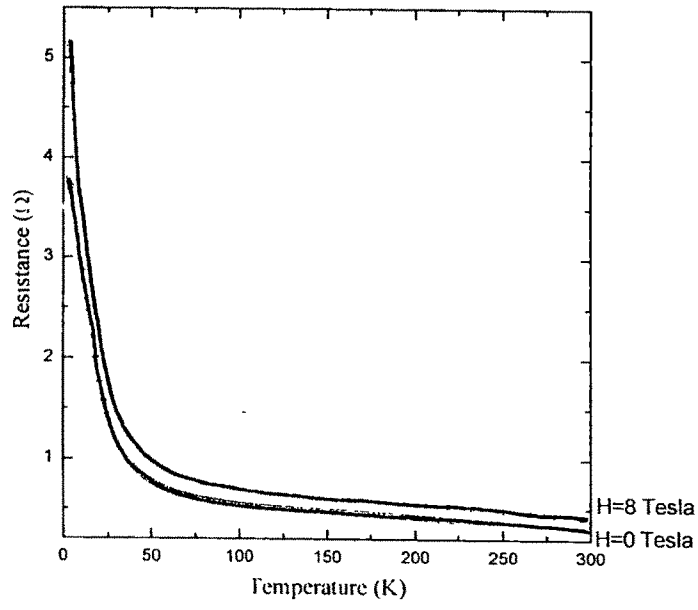

Fig 7 Resistance versus Temperature of $Fe_{0.008}Ge_{0.992}$ sample

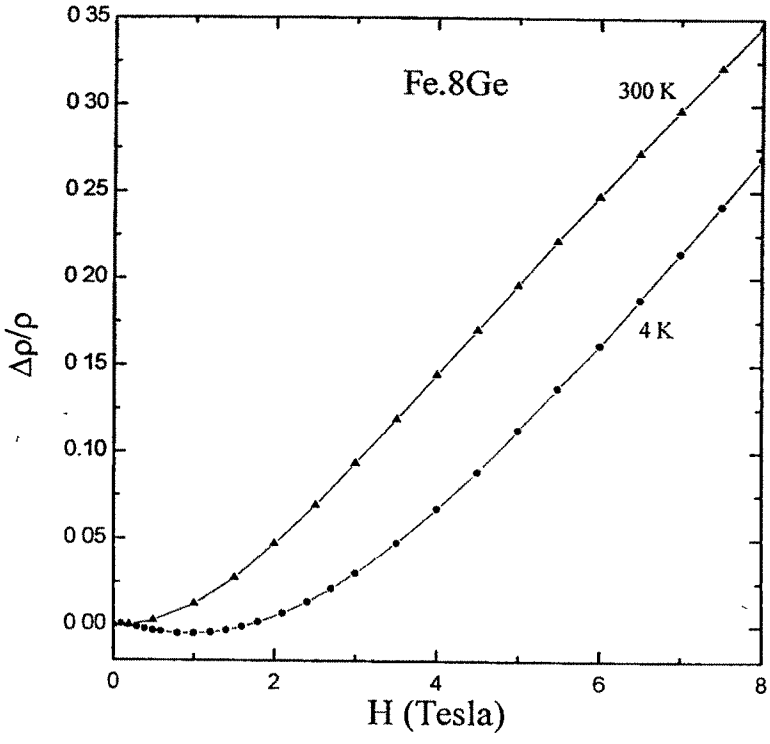

Fig 8 Magnetoresistance versus Magnetic field of $Fe_{0.008}Ge_{0.992}$ sample

Studies of Donor doped $Fe_{0.008}Ge_{0.992}$

V group (As, Sb, Bi) and VI group (S, Se, Te) donors are incorporated in to the Fe doped Ge system. The Fe Mossbauer studies, Resistivity,. Magnetoresistance, XRD and Hall coefficient measurements were done as a function of the donor concentrations in each case. The results of the study are presented in the following pages.

4.5 Studies on V Group Donor impurity As doped Samples

4.5.1 XRD Mesurement of the $Fe_{0.008}Ge_{0.942}As_{0\ 05}$ Sample.

Fig. 9 Shows the XRD spectrum of a sample $Fe_{0\ 008}Ge_{0\ 992-x}As_x$ with x=0.05. The lattice constant determined from the position of the (111) peak is 5.038Å for $Fe_{0\ 008}Ge_{0\ 942}As_{0\ 05}$, it is almost coinciding with Ge standard values. The solubility of As in Germanium is around (3 at %) and the lattice spacing of germanium remains practically unchanged on introducing As up to its maximum solubility.

The reported phases of Ge and As are $GeAs_2$ and GeAs. $GeAs_2$ has a rhombic structure with a = 3.714 kX, b = 10.10 kX and c = 14.71 kX where as GeAs phase has a monoclinic structure with a = 22.08 kX, b= 3.77 kX and c = 9.43 kX[20]. These phases can be easily identified from the spectra, if present.

The spectra shown below have no any other lines or peaks other than Ge, which indicates absence of other phases. The characterization using Mossbauer study, Magneto resistance, Resistivity, and hall effect have shown interesting results.

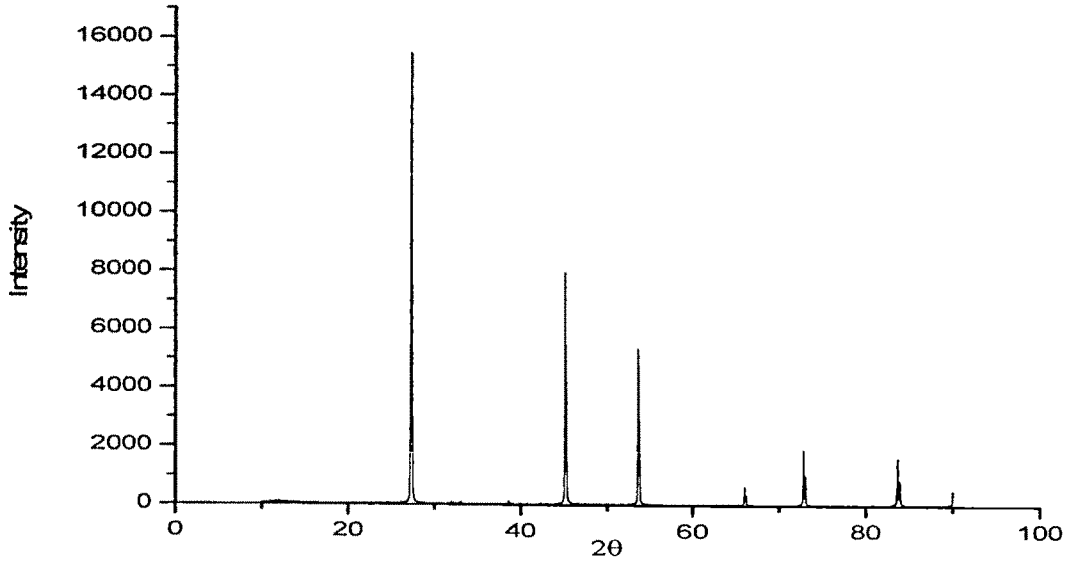

Fig 9 XRD spectra of the sample $Fe_{0.008}Ge_{0.942}As_{0.05}$.

4.5.2Mossbauer Measurements of $Fe_{0.008}Ge_{0.992-x}As_x$ Samples

Mossbauer study of the sample $Fe_{0.008}Ge_{0.992-0.01}As_{0.01}$ for As (1%) as shown in fig.10, one magnetic site (site A) and a singlet site (site C) were observed. The magnetic hyperfine field (MHF) was evaluated to be 121 kOe with IS = 0.22 mm/s. The isomer shift of the site C is IS = 0.29 mm/s. At the higher concentrations of x =0.03 and 0.05, as shown in Fig 11, 12 only a quadrupole site (site B) with QS = 1.63 mm/s and IS = 0.27mm/s was observed,all the parameters are listed in table2. The Mossbauer parameters for site B in x = 0.03, 0.05 coincide with the reported [21] values of the $FeAs_2$ compound.

The electronegativity for Fe is (1.79) and As is (2.18), hence Fe seems to have a high probability of forming the compound phase $FeAs_2$, which was seen in 3 and 5% of Arsenic. At lower concentration around 1 % Arsenic, it is possible that Fe and As enters in Ge as impurity without forming stable compound phase. The HMF observed at Fe may be due to Fe - As (sp-d) interactions without forming stable compound, Fe acting as acceptor and As as Donor in Ge.

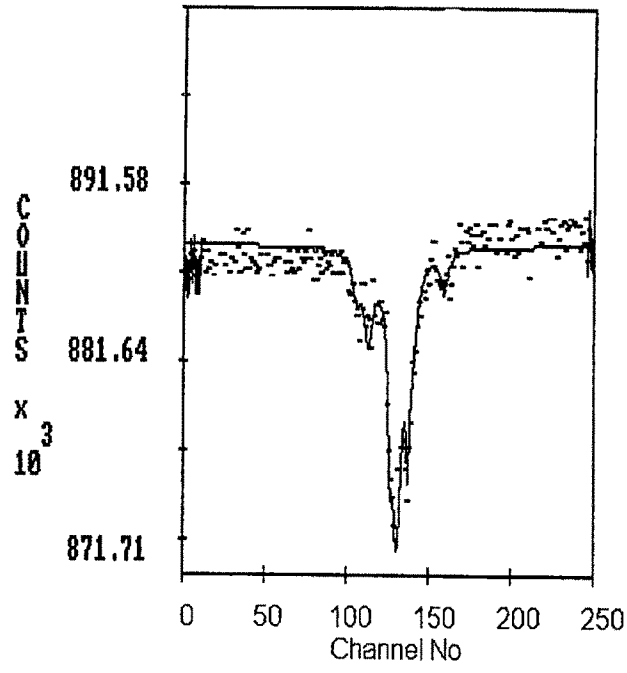

Fig. 10 Mossbauer spectra of sample $Fe_{0.008}Ge_{0.992-0.01}As_{0\ 01}$

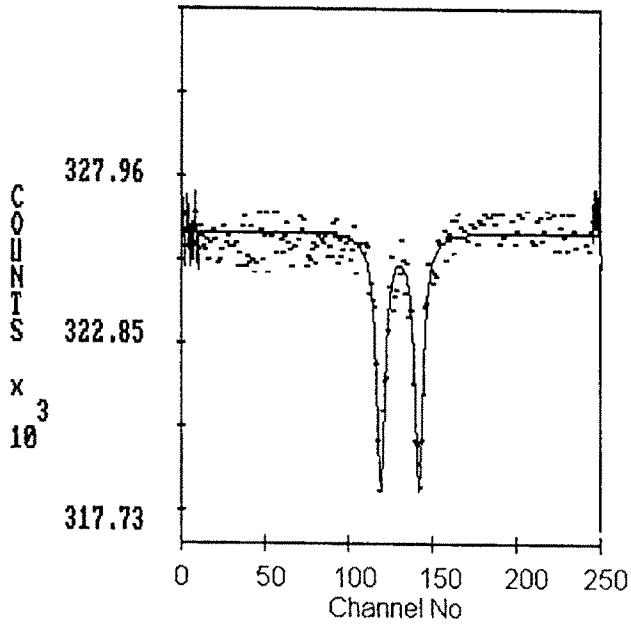

Fig. 11 Mossbauer spectra of sample $Fe_{0\ 008}Ge_{0.992-0\ 03}As_{0.03}$

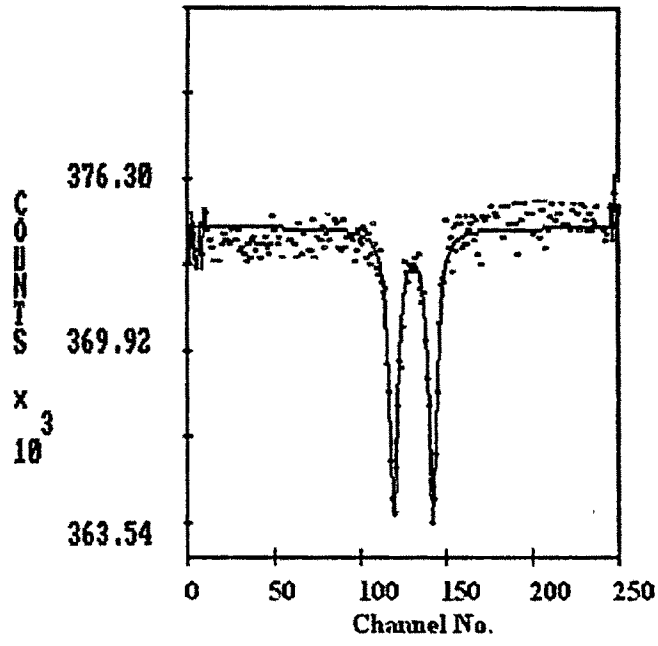

Fig. 12 Mossbauer spectra of sample $Fe_{0.008}Ge_{0.992-0\ 05}As_{0\ 05}$

Composition of Samples $Fe_{0\ 008}$ $Ge_{0\ 992-x}As_x$	HMF (kOe)	QS (mm/sec)	IS(mm/sec)			Site Population (%)		
	A	B	A	B	Singlet C	A	B	Singlet C
X =0 01	121.2 (15)	----------	0 22 (3)	-------	0.29(2)	49(2)	-------	51(1)
X =0 03	------	1 63 (2)	-------	0.27 (1)	---------	------- -	100(1)	----------
X =0.05	------	1 63 (2)	----------	0.27 (1)	-------	------- ---	100(1)	----------

Table 2 Mossbauer parameters of the samples $Fe_{0\ 008}Ge_{0.992-x}As_x$

4.5.3 Resistivity, Magnetoresistance and Hall Measurements on $Fe_{0.008}Ge_{0.992-x}As_x$

Fig 13 shows Resistivity versus temperature measurement of the sample $Fe_{0.008}Ge_{0.992-0.01}As_{0.01}$. The resistance changes from 0.022 Ω to 0.018 Ω in the zero magnetic field and 0.024 Ω to 0.019 Ω at 8 tesla field. The hall measurement of the sample has shown n-type conductivity and its electron concentration was observed to be $3.08 \times 10^{17}/cm^3$. Magnetoresistance measurement of the same sample is shown in Fig 14.

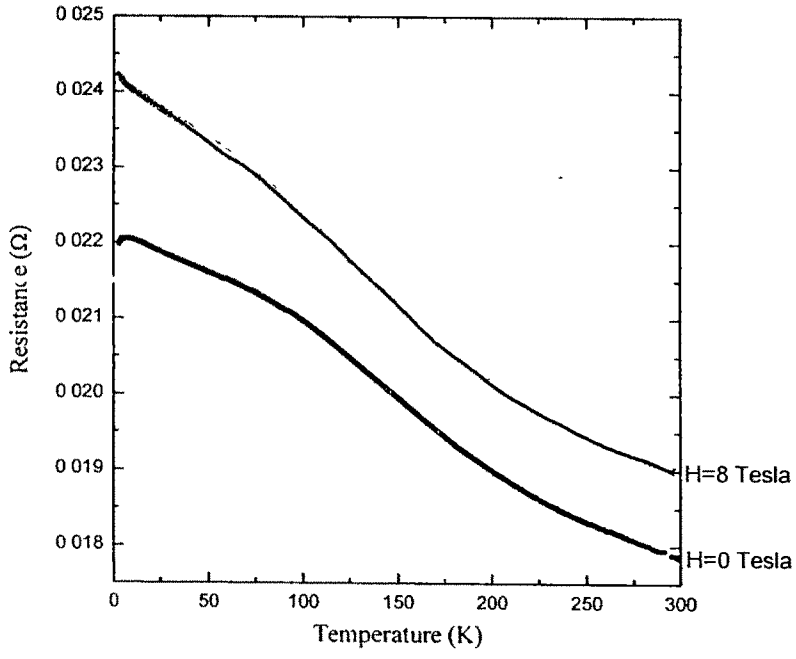

Fig.13 Resistivity versus Temperature of the sample $Fe_{0.008}Ge_{0.992-0.01}As_{0.01}$

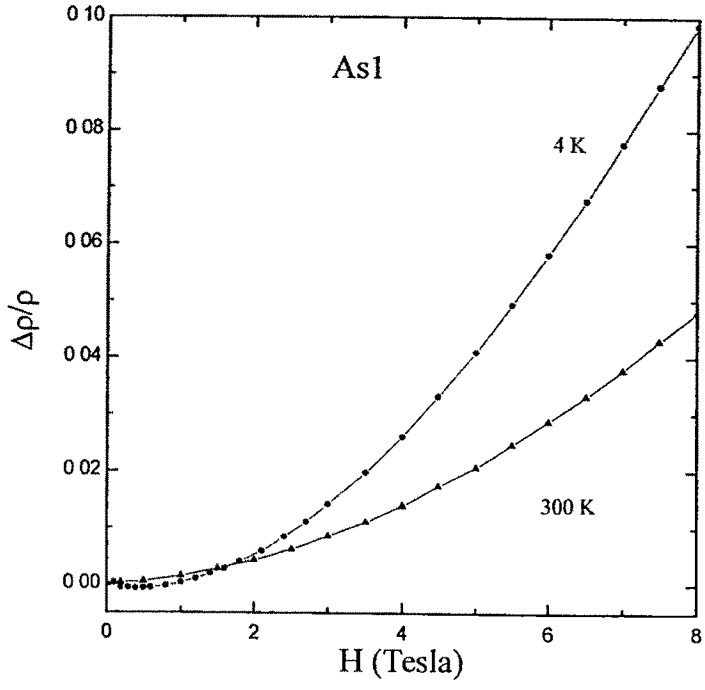

Fig 14 Magnetoresistance versus Magnetic field of the sample

$Fe_{0.008}Ge_{0\ 992\text{-}0\ 01}As_{0\ 01}$

4.6 Studies on V Group Donor impurity Sb doped samples

4.6.1 XRD Mesurement of $Fe_{0.008}Ge_{0.942}Sb_{0.05}$ Sample

Fig. 15 Shows the XRD spectrum of a sample $Fe_{0.008}Ge_{0.992-x}Sb_x$ with X = 0.05. The lattice constant determined from the position of the (111) peak is 5.058Å for $Fe_{0.008}Ge_{0.942}Sb_{0.05}$.There is no reported compound phase of Ge and Sb, but Sb enters in the Germanium lattice as a solid solution. The concentration wise change in the transport and Magnetic properties of the Ge system was observed as given in following.

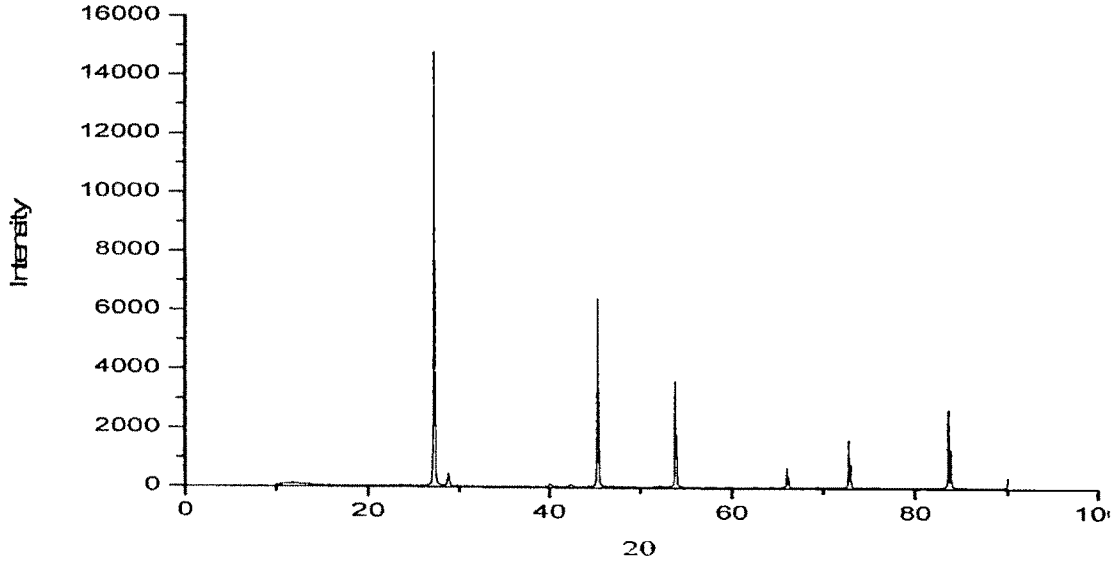

Fig 15 XRD spectra of the sample $Fe_{0.008}Ge_{0.992-0.05}Sb_{0.05}$.

4.6.2Mossbauer Mesurements of $Fe_{0.008}Ge_{0.992-x}Sb_x$ samples

Mossbauer measurement of sample $Fe_{0.008}Ge_{0.992-x}Sb_x$ was carried out for x = 0.01, 0.03 and 0.05. Fitted spectra are as shown in Fig (17, 18, 19), and the Mossbauer parameters evaluated are as shown in table 3.

The sample with Sb concentration x = 0.01 has shown three different sites. The value of HMF for the site (A) is 96.1 KOe with IS = 0.25 mm/s, a quadrupole splitting in a site (B) was QS = 1.21 mm/s and the site C represent singlet state and its isomer shift value was IS = 0.27 mm/s.

However with increase in concentration of Sb to x=0.03, the Hyperfine Magnetic Field (HMF) reduces to 81.81 KOe with IS = 0.26 and the quadrupole splitting of site B was QS = 1.46 mm/s. The Singlet site C continued and its population increases at the cost of magnetic site.

At still higher concentration of Antimony (Sb) x = 0.05, the magnetic site A vanishes completely. The quadrupole site B shows QS = 1.18 mm/s and a site C with IS = 0.31 mm/s.

As the Hyperfine Magnetic Field (HMF) was found to decrease with increase in the Sb concentration we wanted to see if there is any increase in the field value at lower concentrations than x = 0.01. Hence we studied x = 0.005,the Mossbauer

spectrum is given in fig.16. The Magnetic Hyperfine Field (A) indeed increased to HMF = 115 KOe at this lower concentration with an IS = 0.23 mm/s. A quadrupole site (B) with a QS = 1.18mm/s and the Singlet site (C) with IS = 0.27mm/s were also observed.

All the samples have shown singlet site C and it corresponds to Iron in Germanium. The Quadrupole site B corresponds to $FeSb_2$[22] , its IS values varies from [0.01 to 0.27] mm/s. The variation of IS values may be due to $FeSb_2$ phase in Ge host., population of this site varies independent of Sb concentration. The magnetic interactions observed at very low concentration of Sb doping, which completely disappears in higher concentration. At higher concentration ob Sb doping approximately 83% of Fe atom was observed to be interacting in the cubic and non magnetic surroundings. Hall measurement of the sample shows increase in the charge carrier densities with increase in Sb concentration. Thus the HMF at Fe site seems to be controlled by the donor concentration, or in other words it is controlled by charge carriers (electron) concentration.

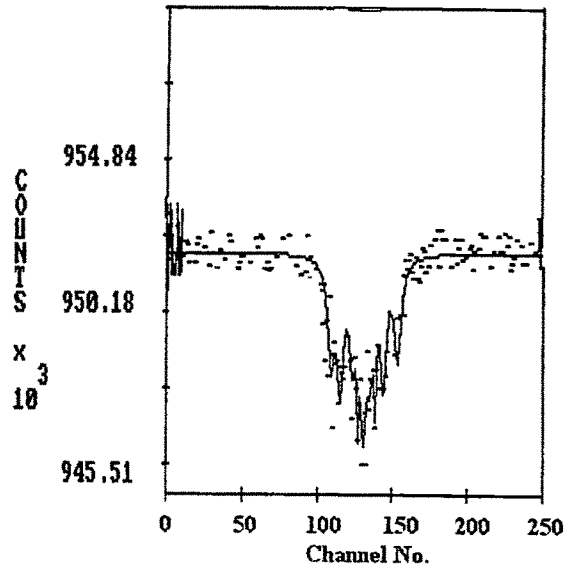

Fig 16 Mossbauer spectra of the Sample $Fe_{0.008}Ge_{0.992-0.005}Sb_{0.005}$

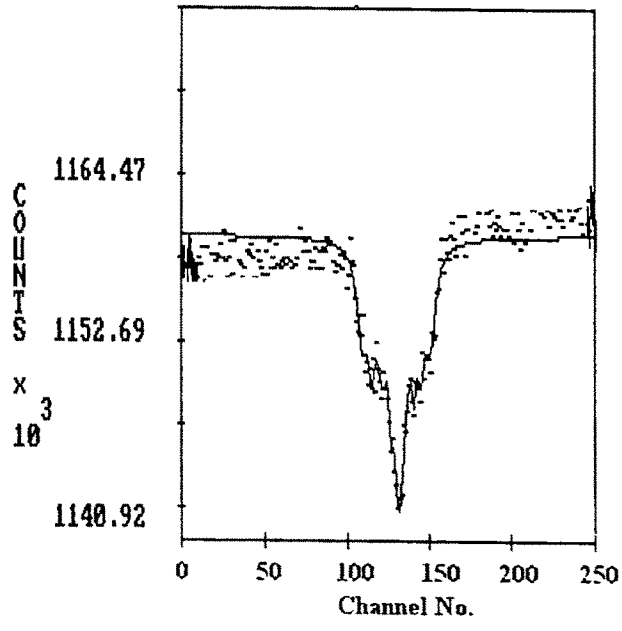

Fig 17 Mossbauer spectra of the Sample $Fe_{0.008}Ge_{0.992-0.01}Sb_{0.01}$

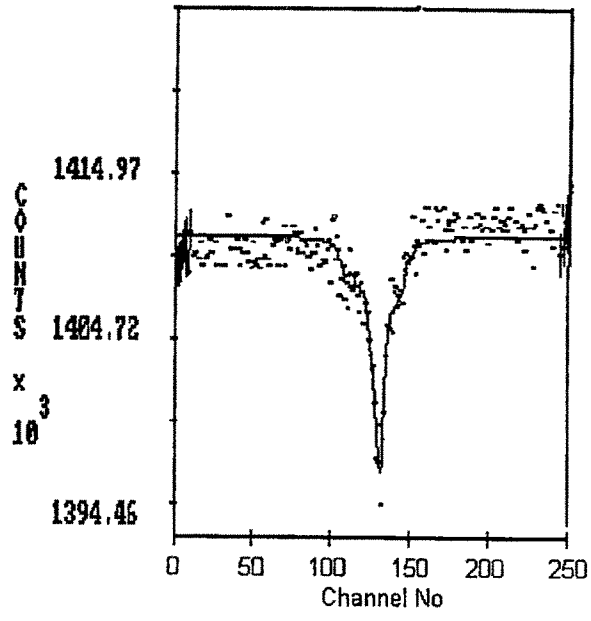

Fig 18 Mossbauer spectra of the Sample $Fe_{0.008}Ge_{0\ 992-0.03}Sb_{0.03}$

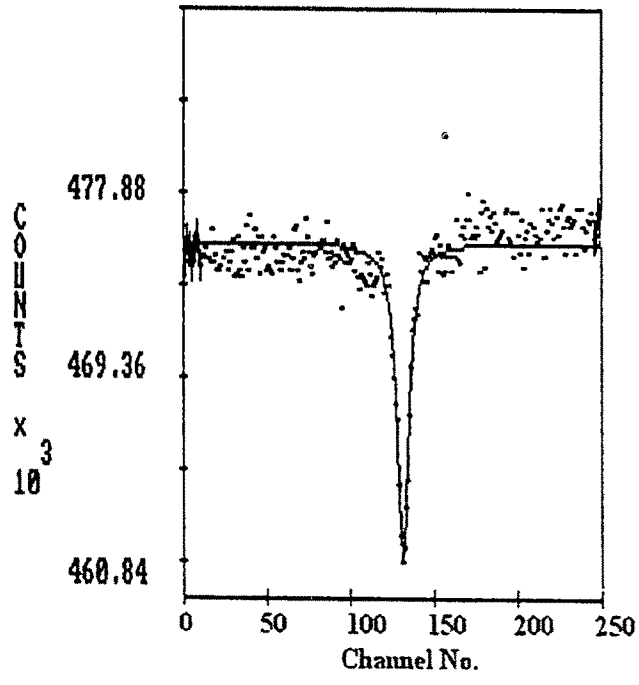

Fig 19 Mossbauer spectra of the Sample $Fe_{0\ 008}Ge_{0.992-0\ 05}Sb_{0.05}$

Compositionof Samples $Fe_{0.008}Ge_{0.992-x}Sb_x$	HMF (KOe)	QS (mm/sec)	IS(mm/sec)			Site Population (%)		
	A	B	A	B	C	A	B	C
X =0.005	115 (1.5)	1.18 (0.02)	0 23 (0.08)	0.07 (0.05)	0.27 (0.02)	70.5	9.0	20.5
X =0.01	96.1 (1.5)	1.21 (0.02)	0.25 (0.08)	0.28 (0.05)	0.32 (0.02)	62 2	13.9	23.9
X =0.03	81.81 (1 5)	1.46 (0 02)	0.26 (0.08)	0.16 (0.05)	0.29 (0.02)	37.5	2.5	60 1
X =0 05	----	1 18 (0 02)	-----	0.01 (0.05)	0 31 (0.02)	---	16.9	83.1

Table 3 Mossbauer parameters of the samples $Fe_{0.008}Ge_{0.992-x}Sb_x$

4.6.3Resistivity, Hall Effect and Magnetoresistance measurements of $Fe_{0.008}Ge_{0.992-x}Sb_x$ samples

Figs 20,21 show the Resistance versus temperature plot of $Fe_{0.008}Ge_{0.992-x}Sb_x$ sample for x = 0.005 and 0.05. For x = 0.005, the sample is semi conductor, its resistance changes from 0.10 Ω to 0.03 Ω without field and 0.115 Ω to 0.035 Ω at 8 tesla magnetic field. The sample with Sb concentration x = 0.05 is turned to semimetallic, resistance remains unaltered over a temperature range. The Hall measurement gave the electron concentration of x = 0.005 sample as $6.04x10^{16}/cm^3$ and for x =0.05 as $7.0x10^{17}/cm^3$. Figs 22, 23 show plot of Magnetoresistance versus Magnetic field, the MR ratio $\Delta\rho/\rho$ changes around 2%.

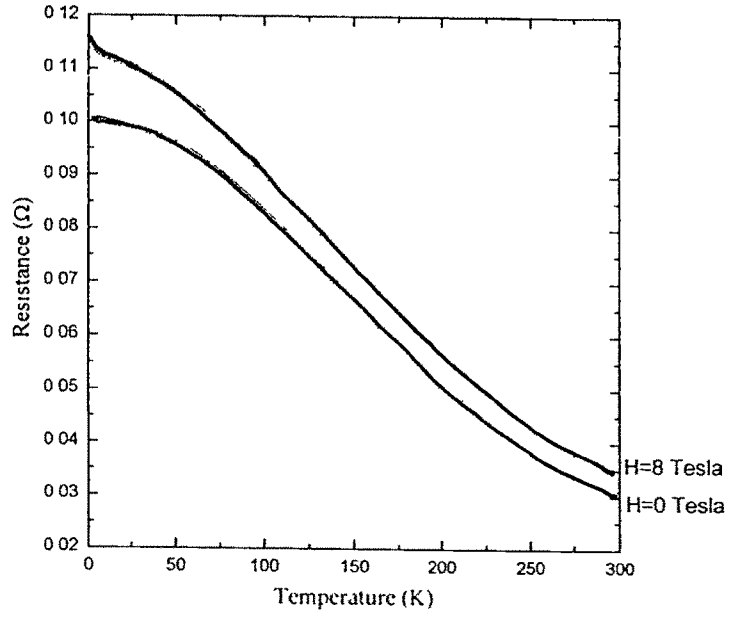

Fig 20 Resistivity versus Temperature of the sample $Fe_{0.008}Ge_{0\ 992-0.005}Sb_{0.005}$

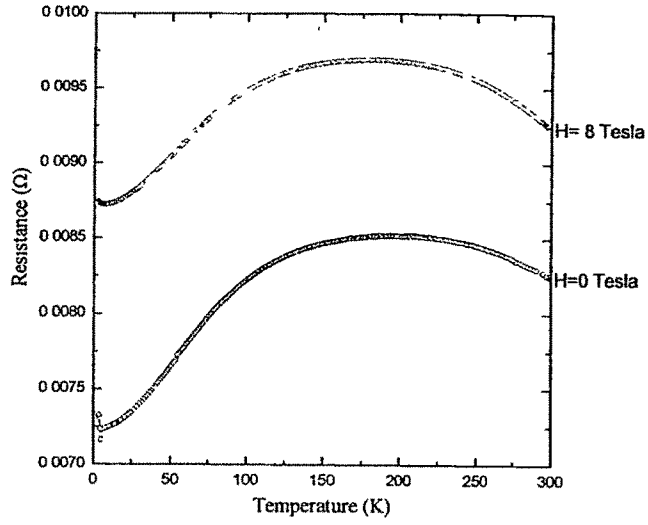

Fig 21 Resistivity versus Temperature of the sample $Fe_{0.008}Ge_{0.992-0.05}Sb_{0.05}$

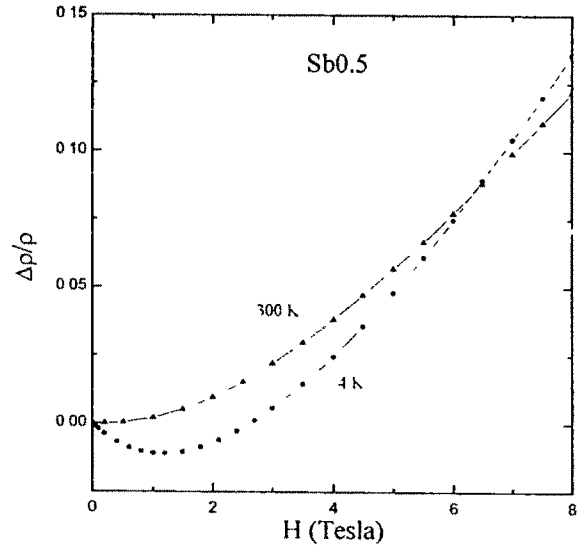

Fig 22 Magnetoresistance versus Magnetic field of the sample

$Fe_{0.008}Ge_{0.992-0.005}Sb_{0.005}$

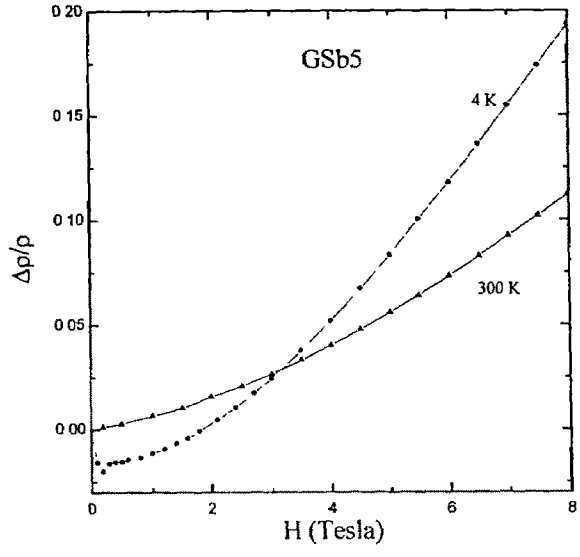

Fig 23 Magnetoresistance versus Magnetic field of the sample

$Fe_{0.008}Ge_{0.992-0.05}Sb_{0\,05}$

4.7 Studies on V Group Donor impurity Bi doped samples

4.7.1XRD Mesurement $Fe_{0.008}Ge_{0.942}Bi_5$ sample

Fig. 24 Shows the XRD spectrum of a $Fe_{0.008}Ge_{0.992-x}Bix$ sample with x = 0.05. The lattice constant determined from the position of the (111) peak is 5.059 Å and 5.039Å for $Fe_{0.008}Ge_{0.942-x}Bi_{0.05}$ and Ge, respectively. Thus a change in lattice constant with the addition of the Bi impurity in Ge was observed

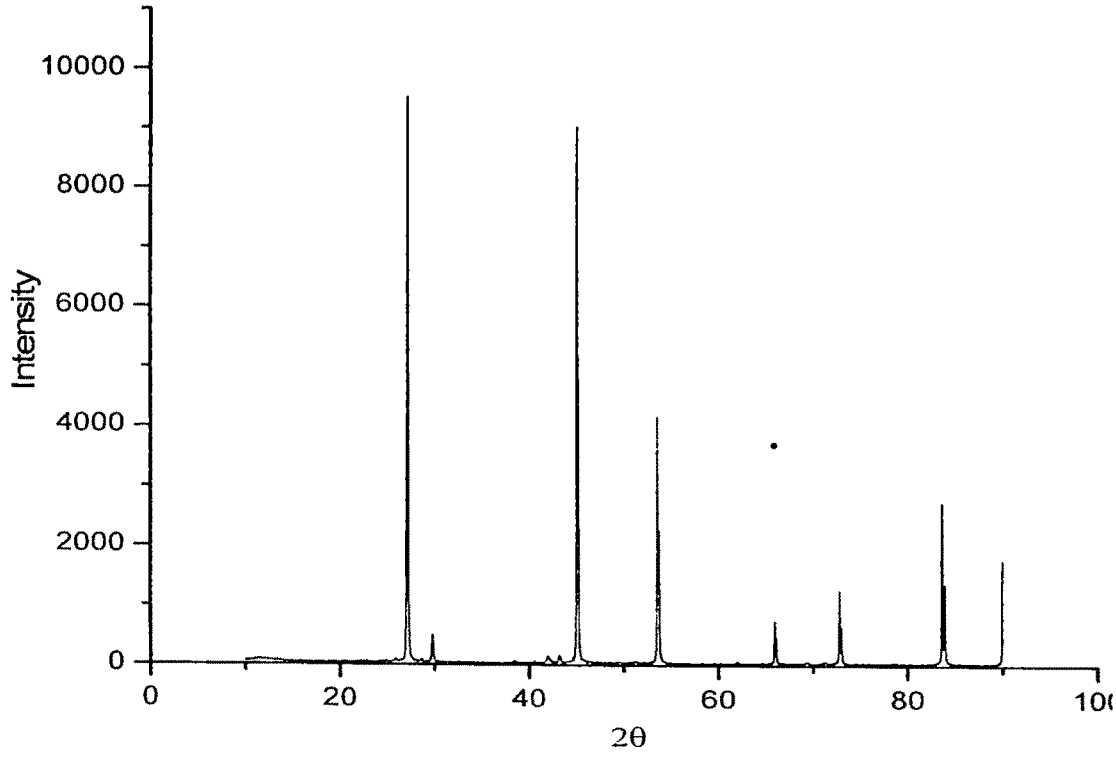

Fig 24 XRD spectrum of a $Fe_{0.008}Ge_{0.992-x}Bi_x$ sample

4.7.2Mossbauer Measurements on Bi doped $Fe_{0.008}Ge_{0.992-x}Bi_x$ samples

Figs.25-27 show Mossbauer spectra of the $Fe_{0.008}Ge_{992-x}Bi_x$ samples, for Bi concentration x = 0.01, 0.03 and 0.05. The hyperfine parameters of spectra acquired are tabulated in the Table 4. Spectra of all the samples having Bi showed a magnetic hyperfine (HMF) site A and the singlet site C. This indicates that Fe is located at two different environments in the matrix.

The singlet site C has an isomer shift of IS = 0.29±0.02 mm/s. Site A is magnetic with a hyperfine field around 130 ± 1 KOe and the IS = 0.27 ± 0.03 mm/s in all magnetic spectra. There is a gradual increase in population of site A with increasing Bi concentration as shown in table 5. It can also be seen that the population of site A increases at the cost of site C. The HMF values are not coinciding with any reported phase of Fe-Ge or Fe-Bi compounds.

Temperature Variation Study

The Mossbauer study of the sample $Fe_{0.008}Ge_{992-x}Bi_x$ for x=0.05 was also done at higher temperature 373K which showed one non magnetic sites B and site C. Fig 28 shows the Mossbauer spectra of the same and the parameters are given in Table 5. Hence the Site A vanished at this temperature. This indicates that the curie temperature of the sample is well below 373K and above RT. The quadrupole splitting observed (Site B) was evaluated to be 0.51mm/s with an isomer shift of 0.32mm/s. The singlet site C has the isomer shift value as 0.31 mm/s which is same as earlier observed.

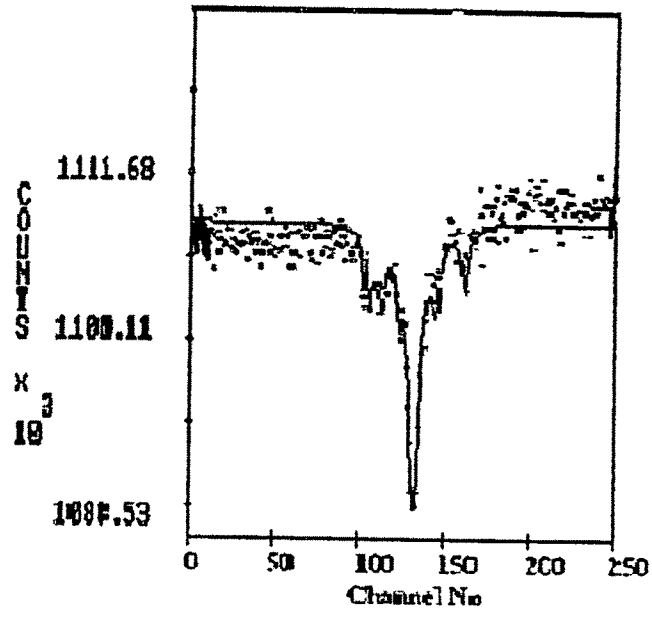

Fig 25 Mossbauer spectrum of the Sample $Fe_{0.008}Ge_{0.992-0.01}Bi_{01}$

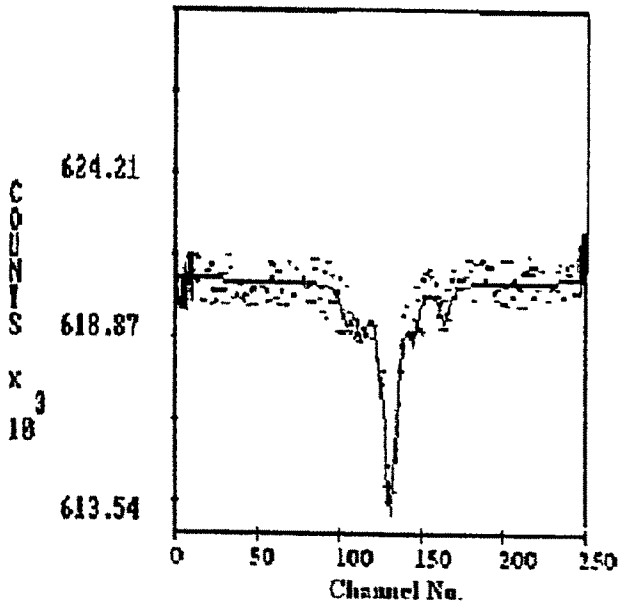

Fig 26 Mossbauer spectrum of the Sample $Fe_{0\ 008}Ge_{0\ 992\text{-}0\ 03}Bi_{.03}$

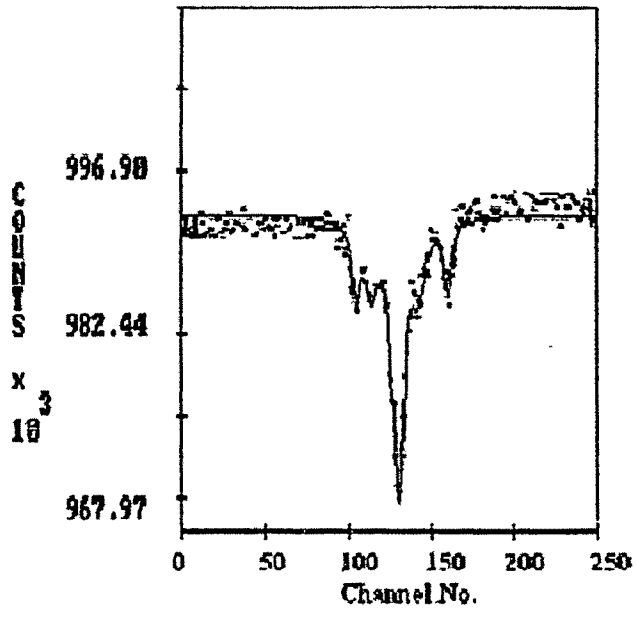

Fig 27 Mossbauer spectra of the Sample $Fe_{0.008}Ge_{0.992-0.05}Bi_{.05}$

Composition of Samples $Fe_{0.008}$ $Ge_{0.992-x}Bi_x$	HMF (kOe) A	QS (mm/sec) B	IS (mm/sec) A	B	Singlet C	Site Population (%) A	B	Singlet C
X =0 01	129 6(1.2)	------	0.21(8)	----	0 29(8)	46(2)	------	54(1)
X =0.03	131 4(2.0)	------	0.27(1)	----	0.27(7)	51(2)	------	48(1)
X =0.05	129 (1.0)	---------	0.22(4)	-------	0 29(1)	67(2)	-----	33(1)

Table 4 Mossbauer parameters of the samples $Fe_{0.008}Ge_{0.992-x}Bi_x$

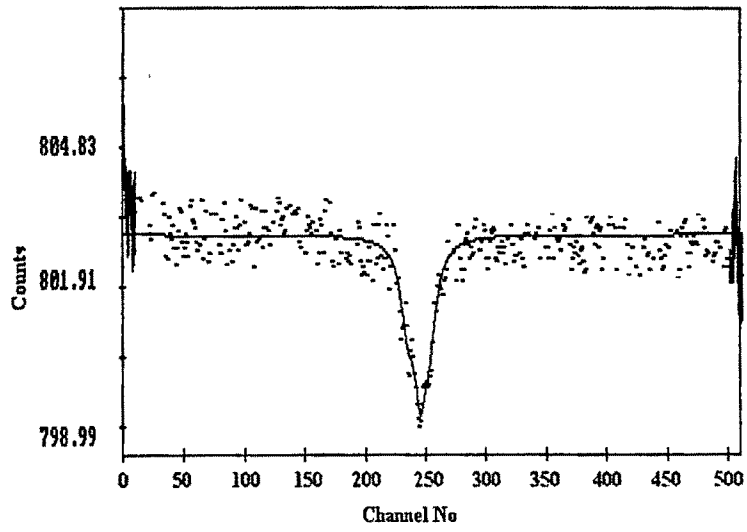

Fig 28 Mossbauer spectra of the Sample $Fe_{0.008}Ge_{0.992-0.05}Bi_{05}$ as a function of temperature

Temperature	HMF (kOe) A	QS (mm/sec) B	IS (mm/sec) A	B	Singlet C	Site Population (%) A	B	Singlet C
300K	129 (1.0)	--------	0.22(4)	-------	0.29(1)	67(2)	-----	33(1)
373K	------	0 51	------	0 32	0.31	------	54	46

Table 5 Mossbauer parameters of the samples $Fe_{0.008}Ge_{0.992-0.05}Bi_{05}$ as a function of temperature

4.7.3 Resistivity, Hall measurement and Magnetoresistance of Bi doped $Fe_{0.008}Ge_{0.992-x}Bi_x$ samples

Figs 29, 30 show the Resistance versus temperature plot of $Fe_{0.008}Ge_{0.992-x}Bi_x$ sample for x = 0.01 and 0.05. It shows semi conducting behavior for x = 0.01, the resistance changes ~ 10Ω . The X =0.05 sample is metallic, its resistance increases from 0.0075Ω to 0.03Ω in the temperature range 4K to 300K. Both the samples are showing n type conductivity in Hall measurements. The electron concentration of x = 0.01 sample is $1.15x10^{17}/cm^3$ and for x =0.05 it is $6.8x10^{17}/cm^3$. Fig 31, 32 show % change in magneto resistance values with magnetic field. For both the samples it is equal in magnitude.

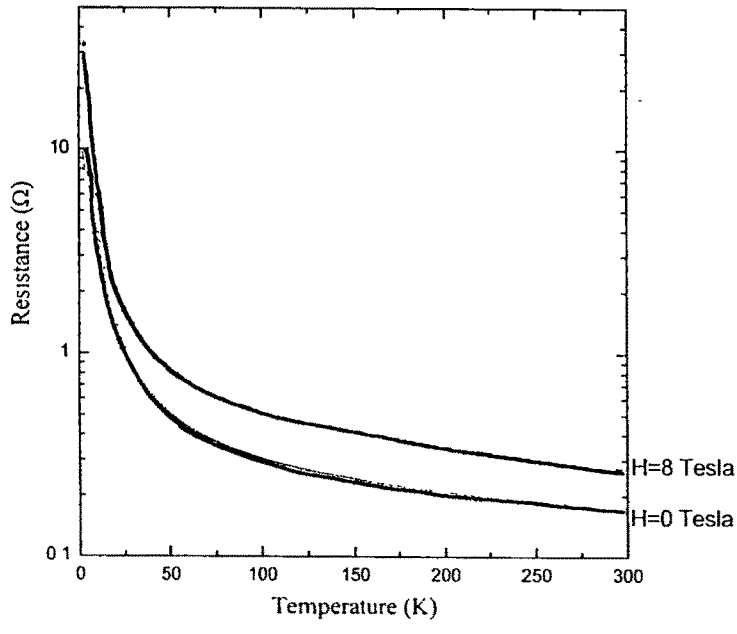

Fig 29 Resistivity versus Temperature of the sample $Fe_{0.008}Ge_{0.992-0.01}Bi_{0.01}$

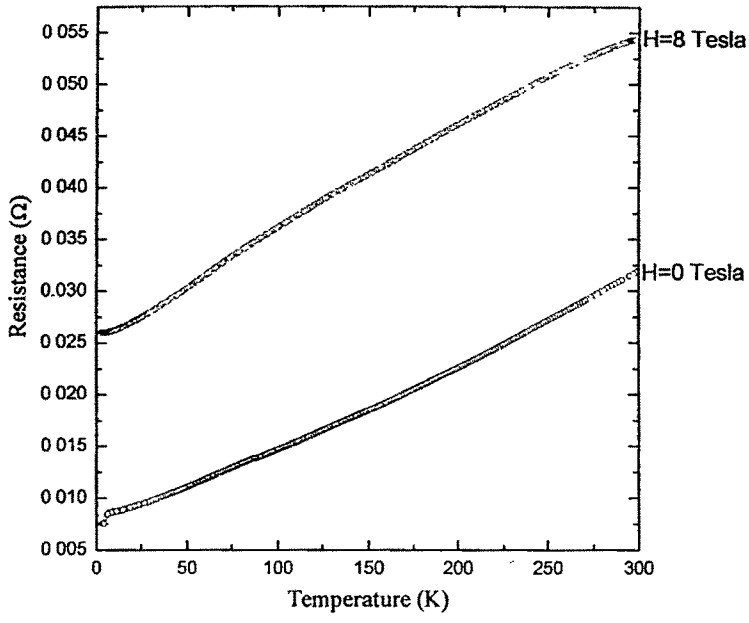

Fig 30 Resistivity versus Temperature of the sample $Fe_{0.008}Ge_{0.992-0-05}Bi_{0.05}$

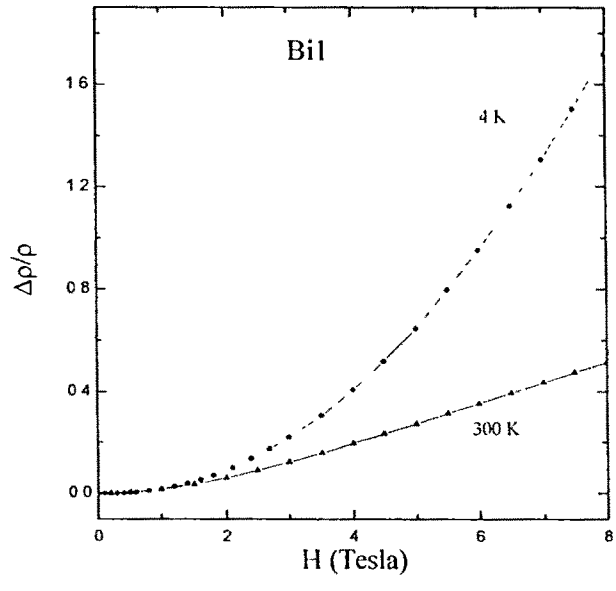

Fig 31 Magnetoresistance versus Magnetic field of the sample

$Fe_{0.008}Ge_{0.992-0.01}Bi_{0.01}$

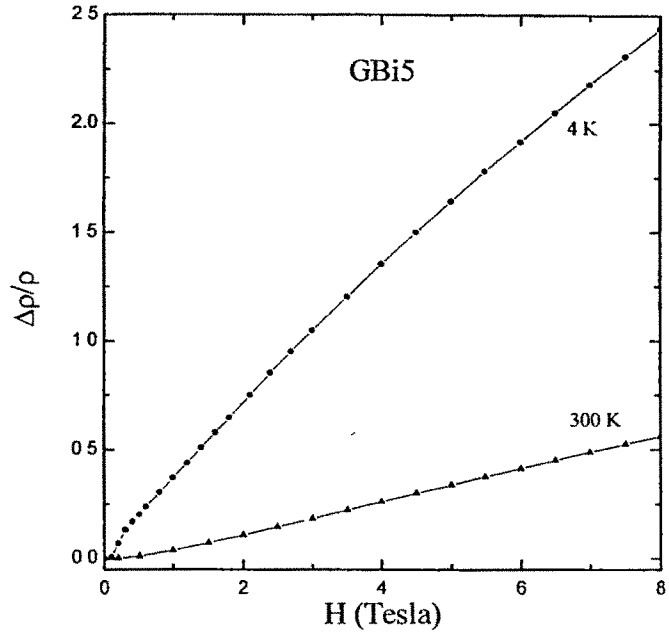

Fig 32 Magnetoresistance versus Magnetic field of the sample

$Fe_{0.008}Ge_{0.992-0.05}Bi_{0.05}$

4.7.4 AC Susceptibility Measurements of Bi doped $Fe_{0.008}Ge_{0.942}Bi_5$ sample

AC susceptibility versus temperature of $Fe_{0.008}Ge_{0.992-0.05}Bi_{0.05}$ sample was recorded at 131.11Hz frequency. The sample show magnetic ordering at 5 % (Bi) in our study. On plotting X^{-1} real vs T, intercept of linear extrapolation have a positive intercept on temperature axis as shown in Figure 33. The transition observed at 233 K here could be due to ferromagnetism observed in Fe doped Ge system by S Choi et.al.[23].

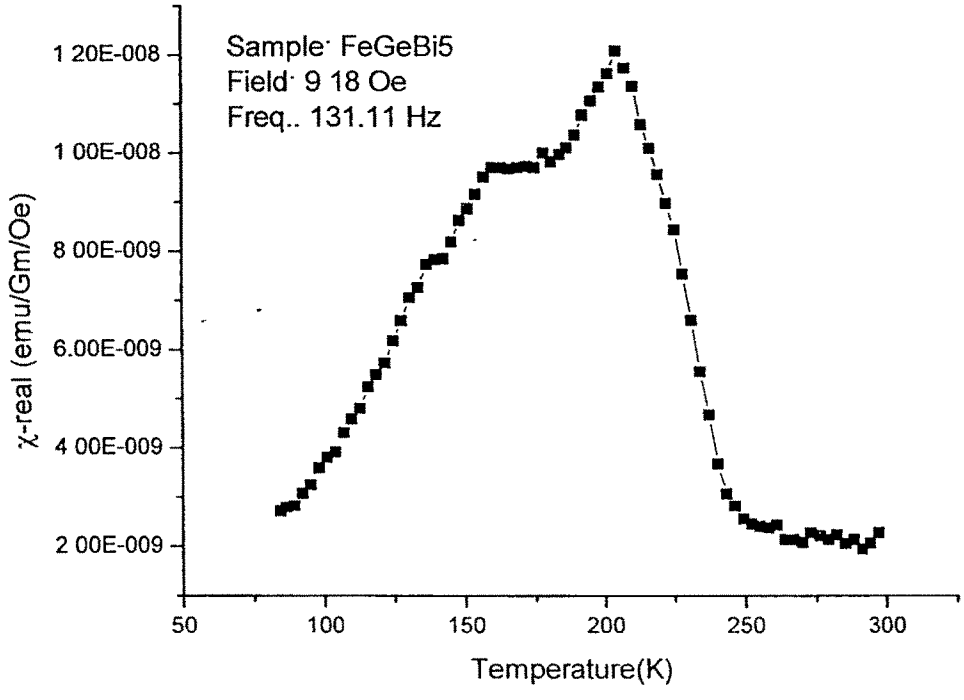

Fig 33 shows AC Susceptibility versus temperature of the sample

$Fe_{0.008}Ge_{0.942}Bi_{0.05}$

4.8 Studies on VI Group Donor impurity S doped Samples

4.8.1Mossbauer Studies of $Fe_{0.008}Ge_{0.992-x}S_x$ Samples

In a $Fe_{0.008}Ge_{0.992-x}S_x$ samples concentration was varied from x = 0.01 and x = 0.03.Mossbauer spectra recorded are given in Fig [34, 35], and the Mossbauer parameters evaluated are given in a table 6. For both the x values Mossbauer spectra shows site A with HMF = 302 KOe, a Qudrupole site (B) with QS= 2.9mm/s and a Singlet Site C with IS = 0.29 mm/s. The HMF parameters for site A are coinciding with reported values of FeS compoundphase [24]. Sulphur doped Germanium samples were difficult to bring in the form of ingot. Due to large difference in melting point and high vapour pressure of S, most of the time there is segregation of S from the sample.

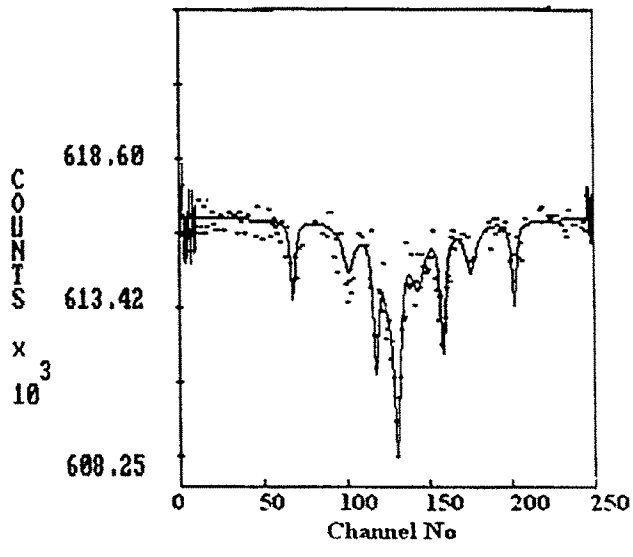

Fig 34 Shows Mossbauer Spectrum of the sample $Fe_{0.008}Ge_{0.982}S_{0.01}$

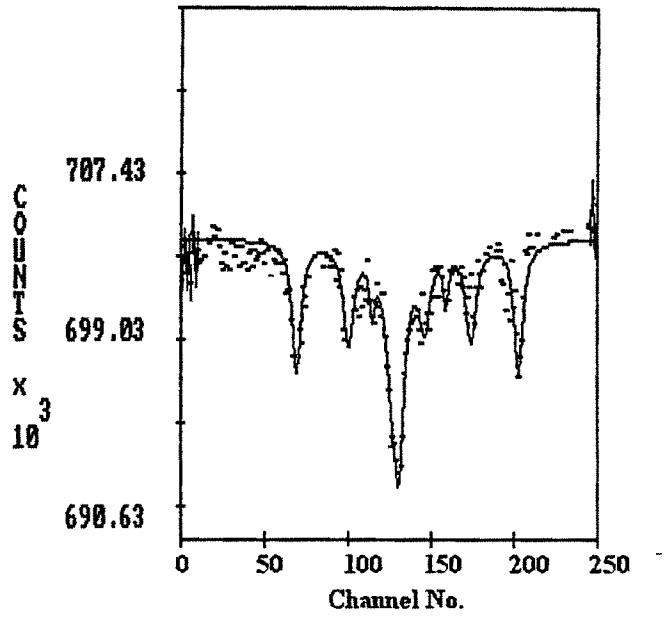

Fig 35 Shows Mossbauer Spectrum of the sample $Fe_{0.008}Ge_{0.962}S_{0.03}$

Composition of Samples $Fe_{0.008}Ge_{0.992-x}S_x$	HMF (kOe) A	QS (mm/sec) B	IS(mm/sec) A	B	Singlet C	Site Population (%) Singlet A	B	C
X =0.01	302.51(1.5)	2.9 (2)	0.67(3)	0.8(2)	0.29(2)	55.9	22.4	21.7
X =0 03	303.2(1.5)	2.9 (2)	0 7(3)	0.8(1)	0 27(2)	67	6.5	25 9

Table 6 Mossbauer parameters of the samples $Fe_{0.008}Ge_{0.992-x}S_x$

4.9 Studies on VI Group Donor impurity Se doped Samples.

4.9.1Mossbauer Studies of $Fe_{0.008}Ge_{0.992-x}S_{ex}$ Samples

Mossbauer study of Se concentration variation in $Fe_{0.008}Ge_{0.992-x}Se_x$ system was carried out for X =0.01, 0.03, 0.05, spectra are as shown in Fig [36,37,38]. For X = 0.01 a singlet site C was observed with IS = 0.30 mm/s. For X = 0.03 concentration two different sites, site A with HMF = 133.31 KOe, and site C with IS = 0.29 mm/s were observed. At X = 0.05, two magnetic sites (A_1 and A_2) viz. HMF = 221KOe, 198KOe and a site C with IS = 0.30mm/s were observed. The least square fitted parameters are given in table 7.

The site C is present in all the spectra and it corresponds to Fe in germanium ($FeGe_2$ phase). The HMF at site A for X =0.05 is coinciding with reported values of HMF field of the Fe7Se8 phases[25]. But the magnetic interaction in x =0.03 sample does not match with HMF values of any of the phases of Fe-Se, it may be due to some ternary phase of Fe-Ge-Se or carrier induced triggering of the magnetic field.

The Se doped samples were difficult to bring in ingot form,because of high vapour pressure of Se.

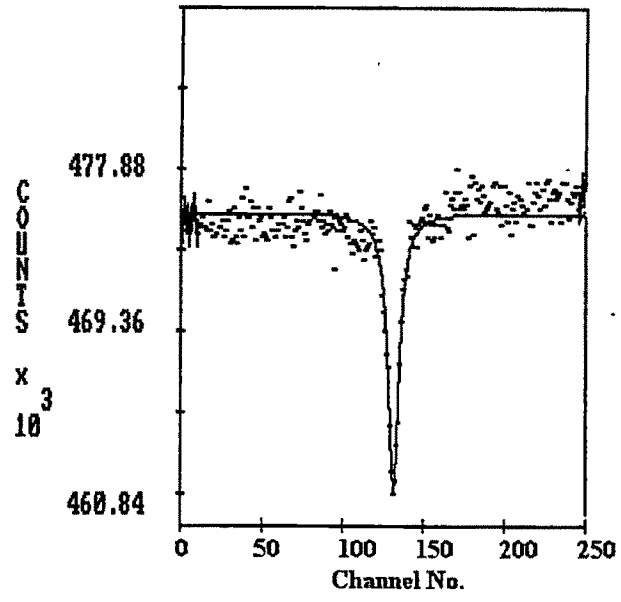

Fig 36 Mossbauer Spectrum of the sample $Fe_{0.008}Ge_{0.982}Se_{0.01}$

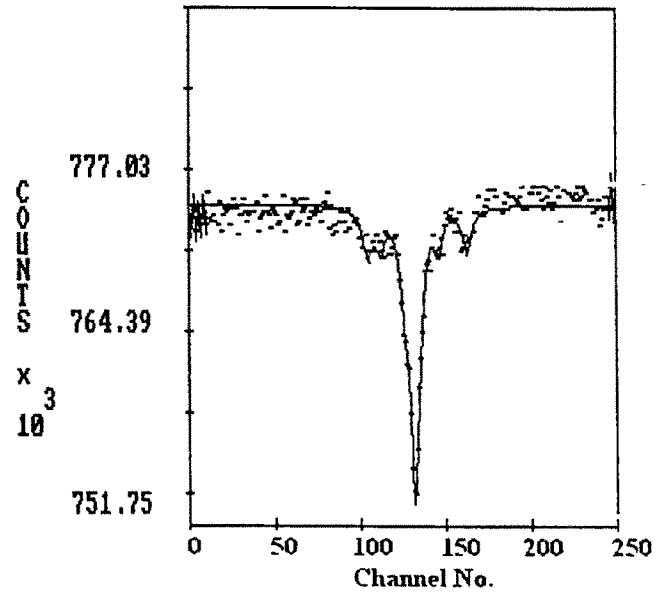

Fig 37 Mossbauer Spectrum of the sample $Fe_{0.008}Ge_{0.962}Se_{0.03}$

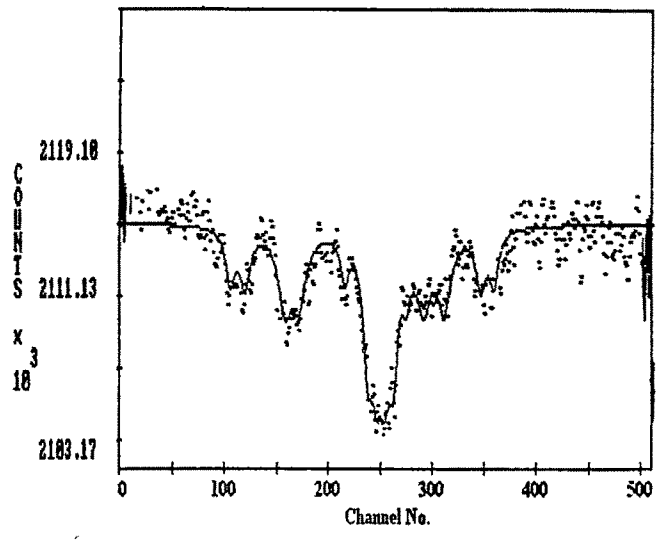

Fig 38 Mossbauer Spectrum of the sample $Fe_{0.008}Ge_{0.942}Se_{0\,05}$

Composition of Samples $Fe_{0\,008}Ge_{0\,992-x}Se_x$	HMF (kOe)		IS(mm/sec)		Singlet	Site Population (%)		Singlet
	A_1	A_2	A_1	A_2	C	A_1	A_2	C
X =0 01	------		------	------	0 30(2)	----	------	100(1)
X =0 03	133 31 (1.6)		0 29(2)	------	0 29(2)	63		37
X =0.05	221	198	0 66	0.63	0 3	32.5	44.1	0 231

Table 7 Mossbauer parameters of the samples $Fe_{0\,008}Ge_{0\,992-x}Se_x$

4.10 Studies on VI Group Donor impurity Te doped Samples

4.10.1XRD Measurements of $Fe_{0.008}Ge_{0.942}Te_{0.05}$ Sample

Fig. 39 Shows the XRD spectrum of a sample with x=0.05 and reveals shifts in the peak positions with respect to Ge standard 2θ values. The lattice constant determined from the position of the (111) peak is 5.069 Å for $Fe_{0.008}Ge_{0.942}Te_{0.05}$. The change in lattice constant with the addition of the Te impurity in Ge indicates that the Te ions are incorporated in substitutional sites of the Ge host lattice.

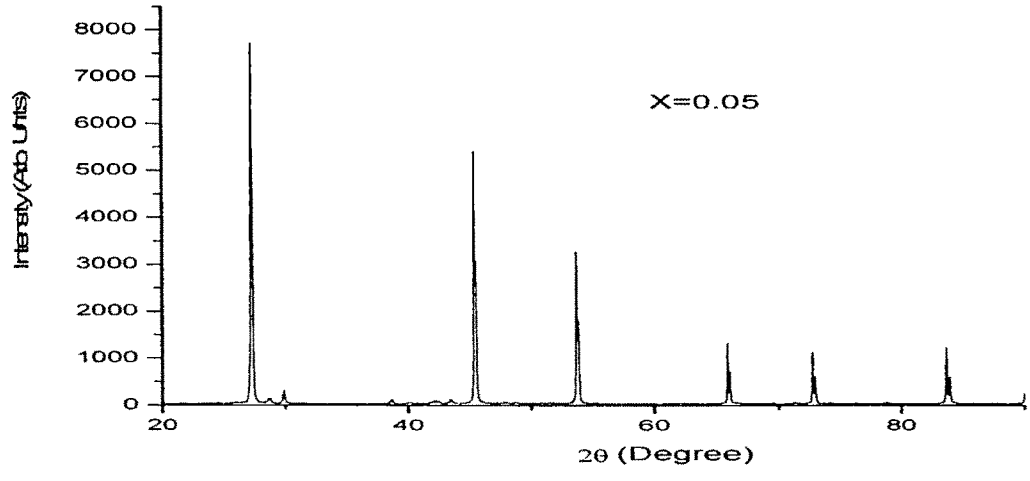

Fig 39 XRD spectrum of the sample $Fe_{0.008}Ge_{0.942}Te_{0.05}$

4.10.2Mossbauer Studies of $Fe_{0.008}Ge_{0.992-x}Te_x$ Sample

Figs.40 to 44 show Mossbauer spectra of all the $Fe_{0.008}Ge_{992-x}Te_x$ samples. Different concentrations of Te were introduced in to the $Fe_{0.008}Ge_{992-x}Te_x$, where x = 0,004, 0.008, 0.016, 0.03, 0.05. The least-square fitted parameters of Mossbauer spectra acquired are listed in the Table 8. In all the samples except Te concentration x = 0.004, we observed a magnetic hyperfine (HMF) site A, a quadrupole (QS) site B and a singlet site C. For x = 0.004 the sample show only a singlet state (Site C). This indicates that Fe is located at three different environments in the matrix. The calculated values of hyperfine interaction parameters for sites A, B and C remain constant for Te concentrations [0.008 to 0.05], even though the site population keeps varying with increase in Te concentration.

The singlet site C has an isomer shift of IS = 0.29±0.02 mm/s. For x = 0.004 of Te doping only site C was observed and has a site population 100%. However it decreases with increasing concentration of Te and at the end when x = 0.05, the singlet site C almost disappears.

Site B parameters are QS = 0.51±0.02 mm/s and IS = 0.30±0.02 mm/s, which matches with the earlier reported values for $FeTe_2$ [26] at RT. The quadrupole splitting remains constant for all Te concentrations, but the population of site B decreases with increasing concentration of Te.

The site A is magnetic with a hyperfine field of 136 ± 1 KOe in all magnetic spectra. The Isomer Shift values for Magnetic site are around 0.37mm/s. There is a gradual increase in population of site A with increasing Te concentration as shown in Figs. X. The HMF value is not coinciding with any reported phase of Fe-Ge or Fe-Te.

Fig.45 shows the plot of Site population versus Tellurium concentration in a Mossbauer studies. One can see that with increase in Te concentration, site B and Site C falls with almost equal slope. The Magnetic site A is forming at the cost of site B and site C. The systematic change in site population with increase in Tellurium concentration indicates role of charge carrier induced interactions.

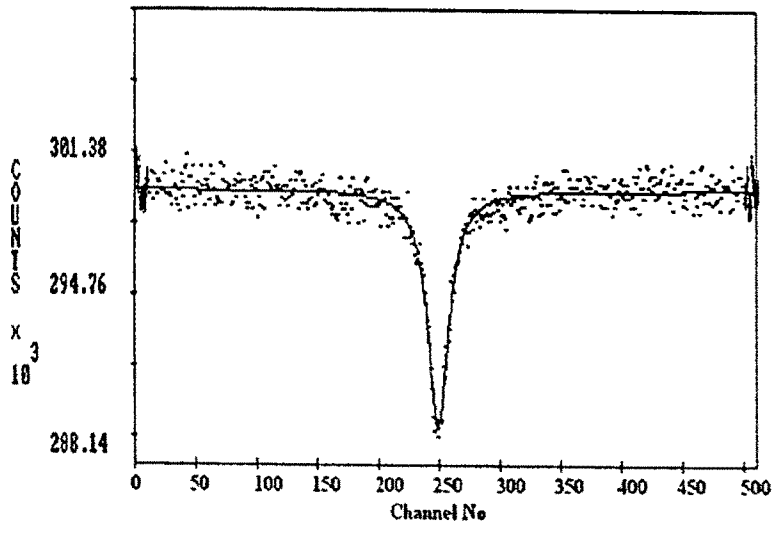

Fig 40 Mossbauer Spectrum of the sample $Fe_{0.008}Ge_{0.988}Te_{0.004}$

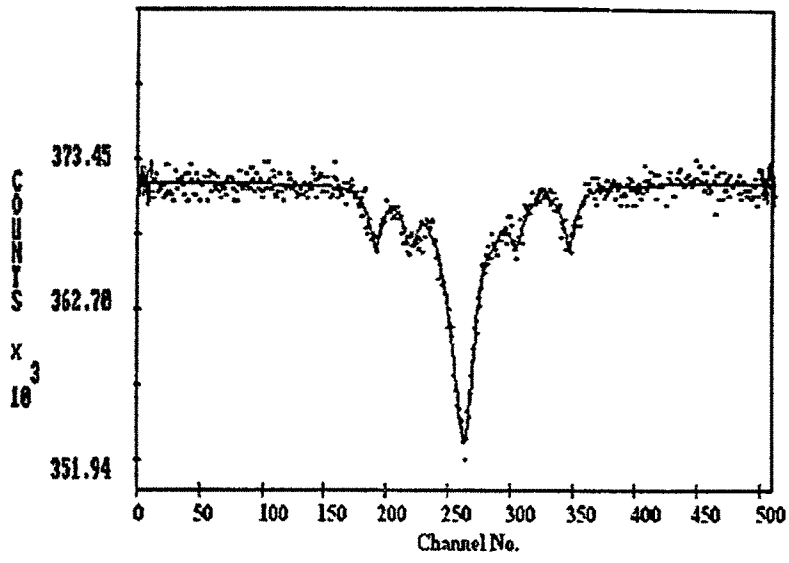

Fig 41 Mossbauer Spectrum of the sample $Fe_{0.008}Ge_{0.992-0.008}Te_{0.008}$

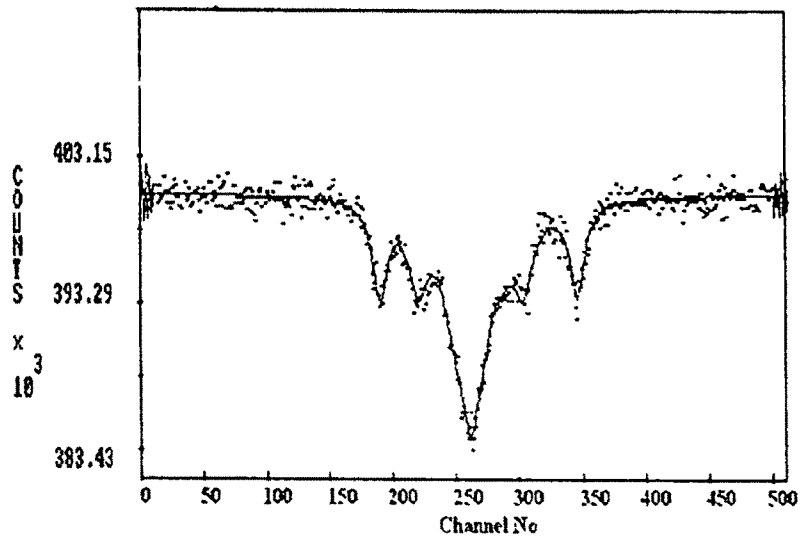

Fig 42 Mossbauer Spectrum of the sample $Fe_{0.008}Ge_{0.992-0.016}Te_{0.016}$

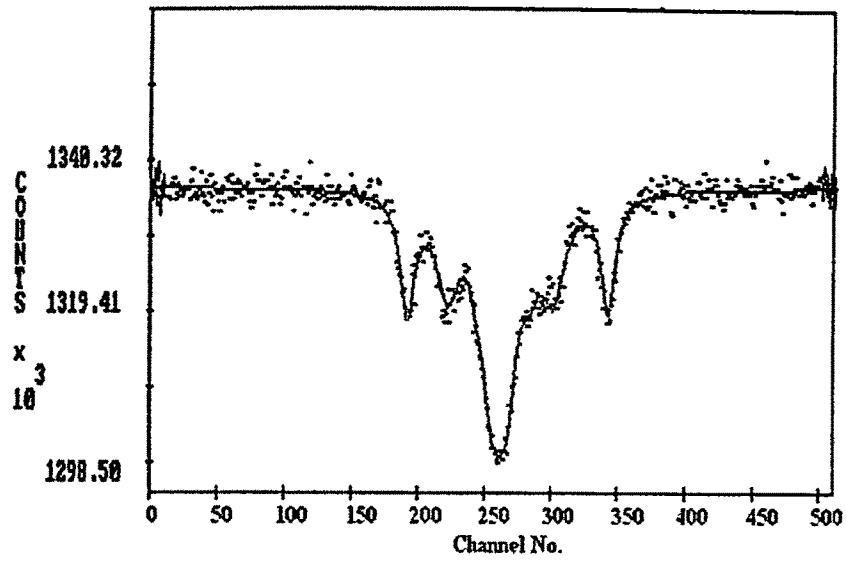

Fig 43 Mossbauer Spectrum of the sample $Fe_{0.008}Ge_{0.992-0.03}Te_{0.03}$

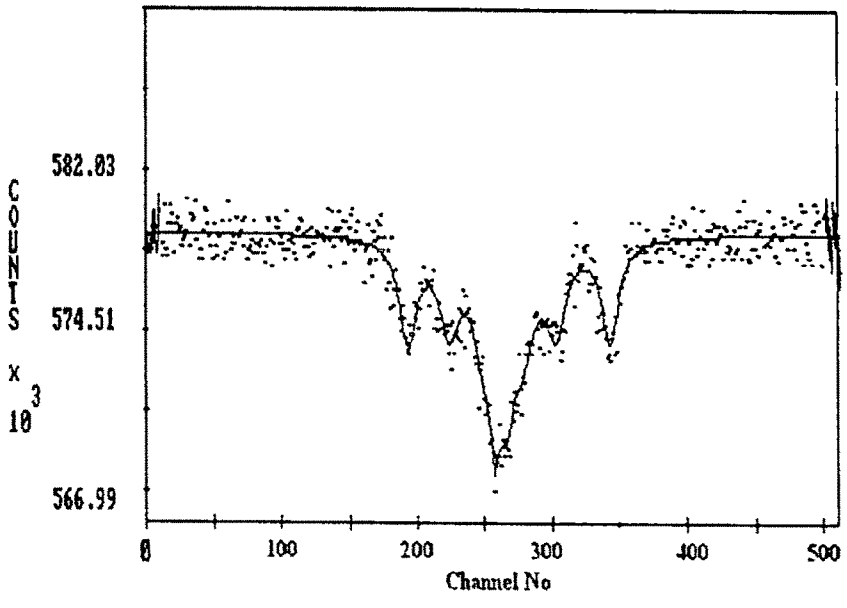

Fig 44 Mossbauer Spectrum of the sample $Fe_{0.008}Ge_{0.992-0.05}Te_{0.05}$

Composition of Samples $Fe_{0.008}Ge_{992-x}Te_x$	HMF (KOe) A	QS (mm/sec) B	IS(mm/sec) A	B	Singlet C	Site Population (%) A	B	Singlet C
X =0.004	--	---	---	---	0.30 ± 0.02	--	--	100
X =0.008	136 ± 1.47	0.51 ± 0.02	0.37 ± 0.02	0.26 ± 0.02	0.29 ± 0.02	43.1	43.2	13.7
X =0.016	136 ± 1.47	0.49 ± 0.02	0.35 ± 0.02	0.26 ± 0.02	0.25 ± 0.02	53.8	31.9	14.3
X =0.03	135 ± 1.47	0.51 ± 0.02	0.35 ± 0.02	0.27 ± 0.02	0.27 ± 0.02	63.7	29.4	6.9
X =0.05	136 ± 1.47	0.50 ± 0 02	0.37 ± 0.02	0.30 ± 0.02	0.25 ± 0.02	78.4	21.2	0.04

Table 8 Mossbauer parameters of the samples $Fe_{0\,008}Ge_{0.992-x}Te_x$

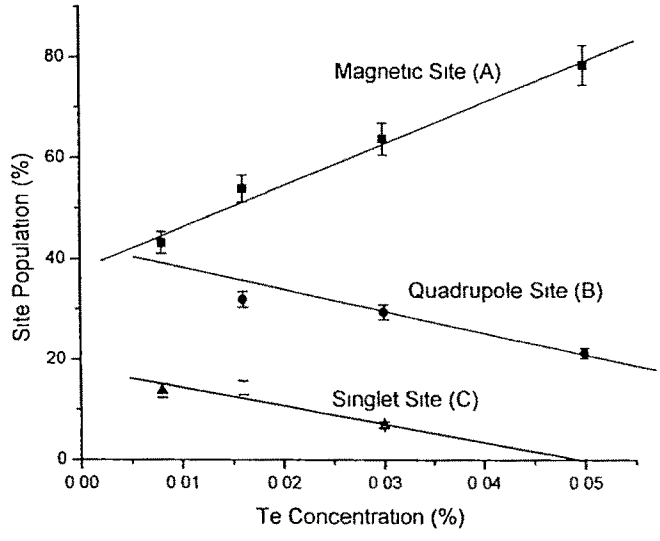

Fig 45 Site Population versus Te concentration in a $Fe_{0.008}Ge_{0\,992-x}Te_x$ system

4.10.3Resistivity, Magnetoresistance and Hall effect of $Fe_{0.008}Ge_{0.992-x}Te_x$ Sample

The Resistance versus temperature plot of $Fe_{0.008}Ge_{0.992-x}Te_x$ sample for x = 0.008 and 0.05 are given in a Figs 46, 47. For x = 0.008 sample resistance changes from 6Ω to 0.5Ω without field and 7Ω to 1Ω at 8 tesla field. The x = 0.05 sample shows increase in resistance in a temperature range of 70-300 K, resistance of the sample decreases in the temperature interval 20 - 60 K which is further observed to increase in 4 - 20 K range. The occurrence of resistance minima is connected with some phase transition or scattering of conduction electrons at Fe local moment above spin fluctuation Temperature. Hall Effect measurement of the sample shows n type conductivity. The electron concentration for $Fe_{0.008}Ge_{0.992-0.008}Te_{0.008}$ is approximately ~ 9.8 x $10^{16}/cm^3$, it reaches to ~ 1.86 x $10^{17}/cm^3$ for $Fe_{0.008}Ge_{0.992-0.05}e_{0.05}$. The electron concentration keeps increasing with increase in Te. Fig 48, 49 shows Magnetoresistance versus Magnetic field of above samples

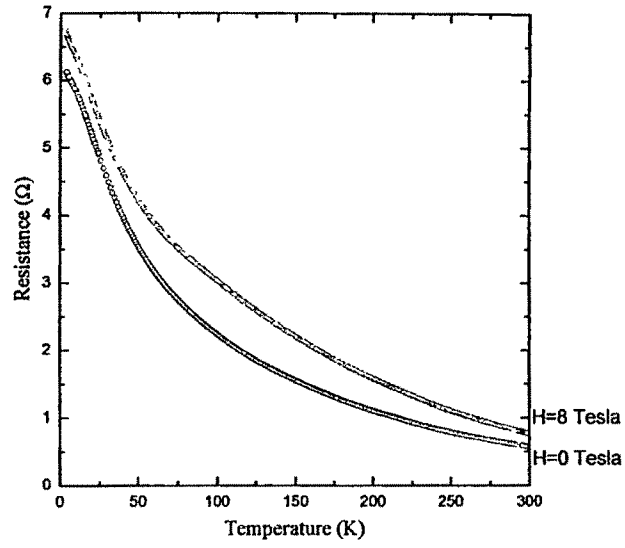

Fig 46 Resistance versus Temperature of the sample $Fe_{0.008}Ge_{0.992-0-008}Te_{0.008}$

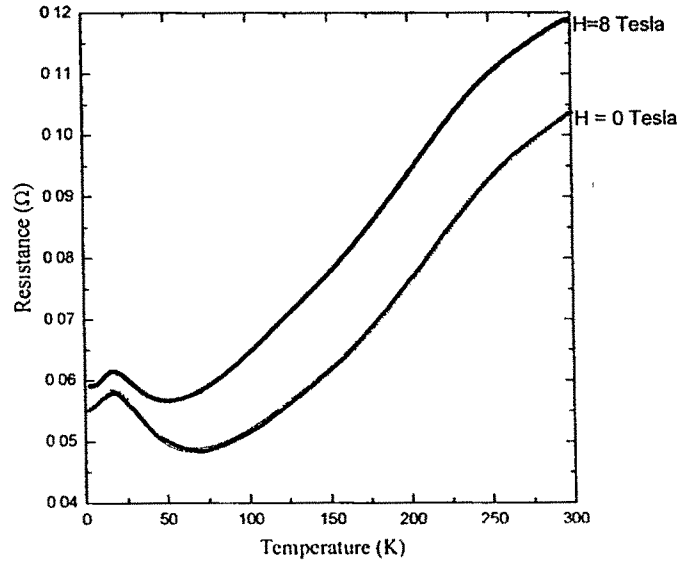

Fig 47 Resistance versus Temperature of the sample $Fe_{0.008}Ge_{0.992-0-05}Te_{0.05}$

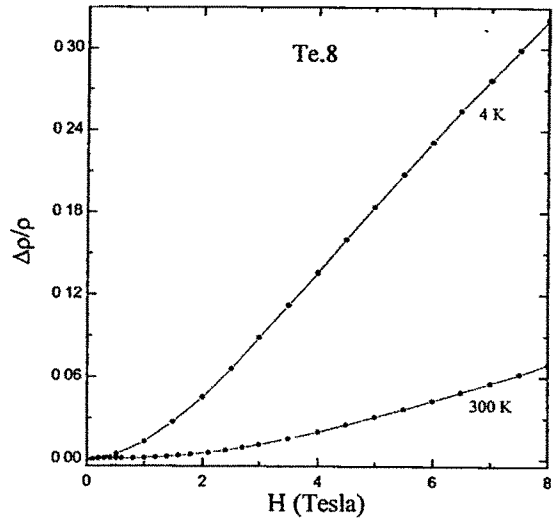

Fig 48 Magnetoresistance versus Magnetic field of the sample

$Fe_{0.008}Ge_{0.992-0.008}Te_{0.008}$

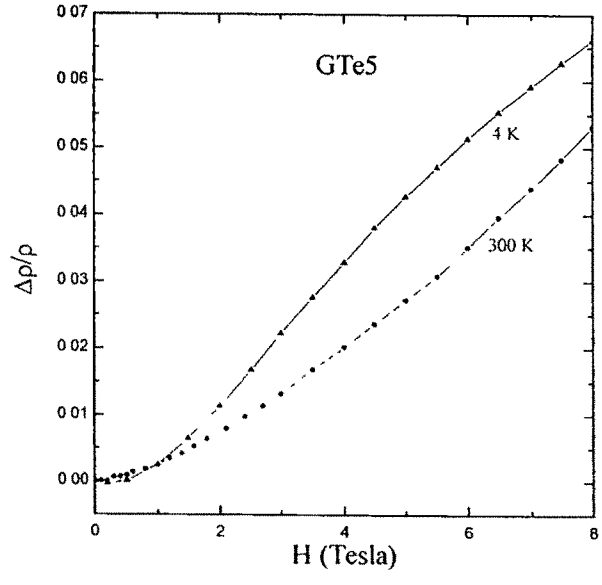

Fig 49 Magnetoresistance versus Magnetic field of the sample

$Fe_{0.008}Ge_{0.992-0.05}Te_{0.05}$

4.11Studies on Acceptor (In) and Neutral (Sn) impurity doped $Fe_{0.008}Ge_{0.992}$ Samples.

As can be seen with all the V and VI group donor impurities, one magnetic site always appears. In order to check whether these interactions are donor impurities specific we studied the doping of acceptor and neutral impurities in the system. Samples $Fe_{0.008}Ge_{0.942-x}In_x$ and $Fe_{0.008}Ge_{0.942-x}Sn_x$ were made by doping Indium (In) and Tin (Sn) concentration x = 5%. The Mossbauer measurement of both the samples have shown single line (Site C) spectrum ((Fig. 50 & Fig. 51) with no Magnetic or electric Quadrupole interaction. There is no reported phase of In or Sn with Iron which is magnetic at room temperature. The least square fitted parameters are given in table 9, its isomer shift value IS = 0.31 coincides with Fe doped Ge samples. From the spectra it can be concluded that structure of the Germanium remains unaltered when these impurities substituted.

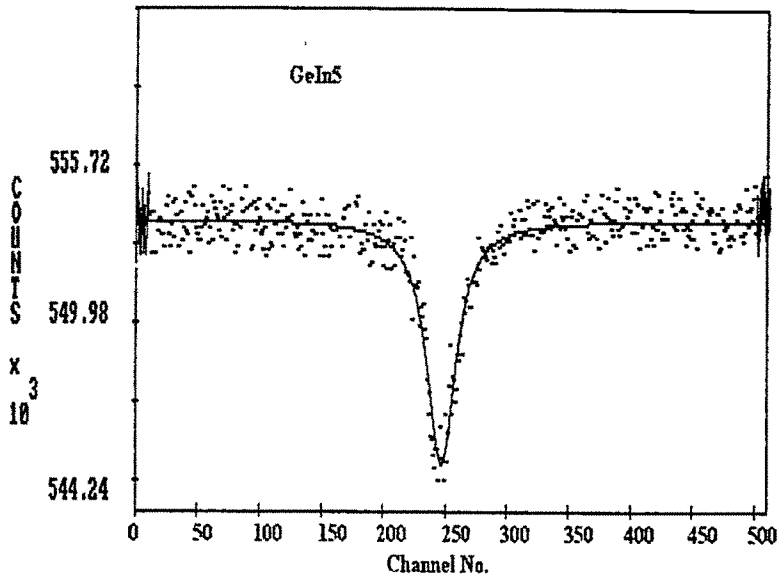

Fig 50 Mossbauer sample of $Fe_{0.008}Ge_{0.992-0-0.05}In_{0.05}$

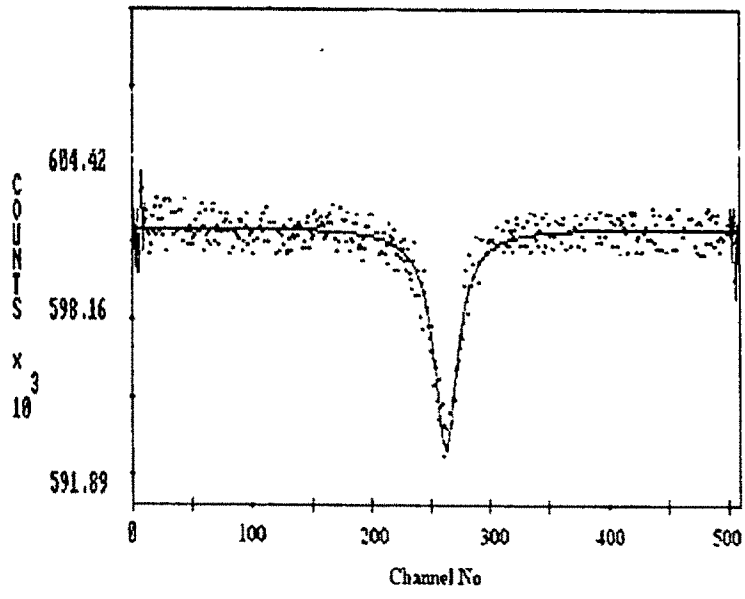

Fig. 51 Mossbauer sample of $Fe_{0.008}Ge_{0.992-0.05}Sn_{0.05}$

Composition of Samples	IS (mm/sec) Singlet C	Site Population (%) Singlet C
$Fe_{0.008}Ge_{0.992-0.05}In_{0.05}$	0.31(1)	100(1)
$Fe_{0.008}Ge_{0.992-0.05}Sn_{0.05}$	0.31(1)	100(1)

Table 9 Mossbauer parameters of the samples $Fe_{0.008}Ge_{0.992-x}In_x$ and $Fe_{0.008}Ge_{0.992-x}Sn_x$ with x=0.05

4.12 Discussion

In this chapter we have presented the experimental results of a system $Fe_{0.008}Ge_{0.992-x}M_x$, Investigated with donors M = As, Sb, Bi, S, Se, Te, Acceptor (In) and Neutral (Sn) impurities at different concentrations of M [0 to 0.05]. The magnetic interaction was found in electron donor doped samples.

From the XRD measurements it is clear that all the samples are in single phase, their crystal structures are similar. With impurity doping like Sb, Bi, and Te, the sample shows small change in peak positions. From the spectra there is no indication of phase formation of any other compound in any of the samples.

In a magnetoresistance study the Lorentz force is so effective in preventing electrons from acquiring energy from the electric field that the uniform drift velocity perpendicular to the electric field gives the dominant contribution to the current. The limiting of electrical current by the electric field in a magnetic field depends on whether all occupied and un-occupied electronic levels lie on electronic orbits that are closed, or not closed but extended (open) in the momentum space. Magnetoresistance tends to saturate if electron/hole orbits are closed, in a compensated material it does not saturate for any value of magnetic field. The occupancy of electronic states at different temperatures is different, hence Magnetoresistance measurement at different temperatures reflects their contribution to conduction. For a TM doped system the electrical

resistance as a function of temperature gives evidence of interaction between conduction electrons and TM moments.

Magneto resistance measurement of all samples has shown positive slope. The $\Delta\rho/\rho$ values do not saturate at any value of magnetic field in any sample. This shows that our samples are consisting of both the type of charge carriers and the electron orbits are open at the Fermi surface [23].

For pure germanium sample, electrical resistivity shows semiconducting behavior. The number of states for which electron orbitals are open at Fermi surface are less at 300K, in other words the relaxation time τ is greater than cyclotron resonance frequency ω at that temperature. Hence the $\Delta\rho/\rho$ ratio changes slowly on application of magnetic field, that is why the two plots coincides around 5 Tesla magnetic field.

Iron doped Germanium sample is p type semiconductor. The cross over in magnetoresistance disappears when Iron is doped into the system. It only happens when relaxation time is too large that MR ratio at both the temperatures change effectively on application of magnetic field. The time interval between two successive collisions (relaxation time) increases, when the electron concentration reduces. The MR and Resistivity is the evidence of d level hole contribution to the conduction band (sp) of the Fe Ge system.

After the introduction of 1% As also, the sample $Fe_{0.008}Ge_{0.982}As_{0.01}$ continue to show the semiconductor nature. The $Fe_{0.008}Ge_{0.987}Sb_{0.005}$ system is semiconducting, with increase in Sb concentration the sample $Fe_{0.008}Ge_{0.942}Sb_{0.05}$ turns to semimetal. At low concentration of (Bi) the $Fe_{0.008}Ge_{0.982}Bi_{0.01}$ sample is a semiconductor which completely changes to metallic nature with increase in Bi concentration. There is no indication of any phase transition, in the Resistivity versus temperature plots of above samples, for any given concentration.

The Resistivity versus temperature graph of the $Fe_{0.008}Ge_{0.984}Te_{0.008}$ has shown semiconducting nature, which turns to metallic as Te concentration goes to x = 0.05($Fe_{0.008}Ge_{0.942}Te_{0.05}$) sample. This sample has shown Resistance minima at around 50-60 k. The minimum in resistance is due to scattering of conduction electrons at the local moments formed at Fe above the spin fluctuation temperature $T > T_{sf}$, which is known as *Kondo temperature.*

For majority of the donor doped $Fe_{0.008}Ge_{0.992}$ samples, the plots between two temperatures in MR versus Magnetic field crosses each other, notably the change in $\Delta\rho/\rho$ ratio at 300K is slower compared to 4K temperature. Since, all these systems are donor doped and at room temperature it is possible that the majority of donors release its electrons. The larger value of the conduction electron density can reduce the relaxation time, which may be the reason for smaller change in resistance or weaker response to magnetic field at higher

temperature. It was also observed that the cross over shifts to lower magnetic fields at higher concentrations.

The semiconductor can conduct in impurity band by electrons hopping from donor to donor. The process of impurity band conduction occurs at lower concentrations of donor if there are Acceptors also present. The Sample doped with acceptor Fe and the donor [As, Sb, Bi, Te] together, it is possible that some of the Donors are always ionized to form Donor -Acceptor Pairs (DAP). This DAP can remain in a virtually bound state and compensate the hole and electron charges, and can alter the relaxation time τ .

The electro-negativity of Fe, Ge, As, Sb and Bi are 1.83, 2.01, 2.18, 2.05 and 2.02, respectively.

The electro negativity difference between As and Fe is large compared to others, thus As has a strong affinity towards Fe to form compounds. Indeed, for higher concentrations of As, $FeAs_2$-compound formation was observed (site B) in Mossbauer measurement. At the lower As-concentration (x = 0.01), Iron is not completely converted in to stable compound. The magnetic interaction observed may be due to spin moment exchange at Fe site due to As donor.

The Sb doped sample has shown a HMF field varying as a function of Sb concentration. With heavy doping of Sb the magnetic field completely vanishes and a Qudrupole doublet corresponding to $FeSb_2$ is seen. Thus, as in the case of

As, here also the $FeSb_2$ compound formation must be inhibiting the magnetic interaction. There is no reported compound phase of either binary or ternary Fe-Ge-Sb which is magnetic at room temperature.

For all concentrations of Bi a HMF magnetic site was observed. The population of this site gradually increased as Bi concentration is increased with a corresponding decrease in the $FeGe_2$ component. There is no reported phase of Fe-Bi Magnetic compounds in the literature. From the Hall measurement, the electron concentration was found to be increasing in the system as Bi concentration increases.

AC susceptibility of Bi doped sample shows ferromagnetic to paramagnetic transition at 233K which belongs to FeGe system. The magnetic order seen by the Mossbauer measurements seems to be of a short range nature.

However in all other donor doped samples the AC Susceptibility measurements gave a very weak signal (except in the case of the higher concentration of Bi doped samples). Hence it appears that it is possible to get reasonably good strength of the AC signal if the donor concentrations are higher (than studied presently) in the system, which can give better evidence for the carrier mediated magnetism.

The VI group donors S, Se and Te are doped in to Fe- Ge system, where electronegativity of S =2.58, Se = 2.55 and Te =2.1.

Sulphur has much attraction toward Fe and hence it reacts with Iron to form a FeS compound, which is reported to be ferrimagnetic in nature with HMF =302 KOe. In a sulphur doped $Fe_{0.008}Ge_{0.992-x}S_x$ sample at both the concentrations of S the Magnetic interaction is due to this compound phase.

In the case of Se doping the HMF(221KOe,198KOe)in Se doped $Fe_{0.008}Ge_{0.992-x}Se_x$ with x= 0.5 sample is due to Fe_7Se_8 phase, which is also ferrimagnetic.

HMF(133 KOe) seen in Se doped sample at intermediate concentration of 0.3 was completely different from Se compound phase, which vanishes when the Se concentration was reduced to 0.1%.

For Te doped $Fe_{0.008}Ge_{0.992-x}Te_x$ sample, HMF was observed to be remaining constant for x = 0 008 to x = 0.05. The decrease in the population of the quadrupole site B with simultaneous increase in the population of A site was observed as the Te concentration increases. The sample $Fe_{0.008}Ge_{0.992-x}Te_x$ for x = 0.004 has shown single line, which corresponds to Fe in Germanium($FeGe_2$). This indicates that the strength of the Mossbauer signal for detecting the HMF in these samples is reasonably good from the Te concentration of around x = 0.008. Hence the interactions are not due to any stable phase formation but are due to electron mediated interactions.

In all these samples where there is no stable compound phase formation, are considered to forming the Donor and Acceptor pairs, which electrostatically interact to form Hydrogen like atomic state. The virtual binding can rearrange electronic arrangement depending on the strength of interaction. The spin interactions within the hydrogen molecule will help in understanding this interaction. For two hydrogen atoms with spin ($\pm$ 1/2) interacting with each other, there are four possibilities of spin states. The singlet state has the spin antiparallel, so that S = 0 and m_s = 0, and the triplet state has spin parallel with S =1 and m_s= 1, 0, -1. In the absence of electron - electron interactions these four states will be degenerate. The ground state is the shell for n =1, as this shell can have only two levels (l =0). The electrons must have their spins opposite (to satisfy exclusion principle), thus the magnetic interaction that arises may be antiferromagnetic ordering. The next state is however n > 1 will have more levels, one has to see the effect of electron - electron interaction which will cause the singlet or triplet state to have the lowest energy. The Coulomb energy will be same for both the states, but there is an additional contribution to the energy from the exchange interactions which splits the energies of the two states.

The interaction of the d electrons of Iron with the sp band of the host is called sp-d exchange interaction which possibly can split the non degenerate levels of Fe, and can create a local moment. The magnetism of interacting Donors was reported in the work of Efros and Shklovski [27]. In a germanium system for the

DAP, the radius of the first Bohr orbit is reported to be $\varepsilon m/m_e$ = 10A°[28]. This is relatively large in comparison to inter atomic distance, so that the donor orbitals overlap even at large distances at relatively low donor concentrations. With the change in concentration of the donors the orbital overlap can be varied, which can result in antiferomegnetic or ferromagnetic interactions[28]. Thus It is investigated that a Donor Acceptor pair (DAP) formation may be the cause for the formation of magnetic moment.

The above hypothesis of DAP formation was confirmed by doping In (acceptor) and Sn (neutral) impurities. $Fe_{.008}Ge_{.942}In_{.05}$ and $Fe_{.008}Ge_{.942}Sn_{.05}$ systems did not show any magnetic interactions, Only singlet sites (C) were observed thereby strengthening the view that in the case of donor impurities, a virtual bound state of Donor-Acceptor pair formation may be taking place and sp-d interaction may be creating magnetic moment on Fe ions in the Ge matrix. Increasing number of donor impurities brought more carrier (electron) densities in to the system and the magnetic interactions were found to be changing with concentration, thus showing the dependence of magnetic interaction on the charge carrier densities.

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