Chapter 4

Fe concentration dependence study of FeSb system

4.1 Introduction:

Electric field gradients (EFG) in pure metals and semi metals have been studied extensively to investigate the origin of the EFG. The group Va of the periodic table offers very interesting elements like Arsenic, Antimony and Bismuth. These semimetals offer a suitable system for evaluation of the different contributions to EFG at different probe sites since they are isostructural. These semi metals Arsenic, Antimony and Bismuth have a structure, which is slightly distorted from simple cubic. Hence they provide us the importance of the crystal structure in determining the metallic properties (1).

Some of the earlier studies (2-5) in semimetals showed that the systematic trends of the EFG, valid generally in metals are also valid in them. It was also observed that the temperature dependence of the EFG at Fe-57 probe in antimony metal doesn't follow the $T^{3/2}$ behaviour (6). But in case of Te (7) and Se (8), the $T^{3/2}$ behaviour was found to be valid inspite of their complicated spiral structure.

All the three semimetals Arsenic, Antimony and Bismuth belong to the Va group and have the same rhombohedral crystal structure with two atoms per unit cell. The semimetallic behaviour of these elements is due to small overlap between the energy bands creating equal number of holes and electrons. The band overlap is 0.15eV for Antimony (9), 0.5eV for Arsenic(10) and 0.015 eV for Bi (11). The atomic volumes of As, Sb and Bi are 13.1, 18.4 and 21.3 W/D respectively.

In an earlier Mossbauer study of Fe in Sb, the value of the QS was quoted to be 1.29±.01 (6) at room temperature which is quite close to the value of QS of 1.28±0.001 for the $FeSb_2$ system. (12). This inspired us to find out whether compound formation is taking place even in the dilute Fe-Sb system. Hence we investigated the concentration dependence of Fe in Sb with general formula Fe_XSb_{1-X}. While preparing these samples for the study of EFG a caution has to be exercised in all these systems is to avoid the covalent bonding with probe, which leads to compound formation.

4.2 Hyperfine interaction studies at Fe-57 probe in Sb:

4.2.1 Sample Preparation:

High purity Antimony metal (99.99) and Iron was taken for making the Fe-Sb samples with general formula Fe_XSb_{1-X}. The concentration of Fe was varied from X=0.0015, 0.002, 0.005, 0.01, 0.05, 0.10 & 0.20 in Sb. Here for low Fe concentrations enriched Fe-57 foil and powder both were used and for high Fe concentrations natural Fe metal powder was used. The samples were taken in a small quartz capsule and sealed in high vacuum $>10^{-5}$ torr. All the present samples were treated in oxy-butane flame. The samples were melted and kept in melting condition for 5-10 minutes. The samples were then cooled to room temperature. The samples were again re melted. This process was repeated several times before they were finally quenched in water. Each of the samples formed into small shiny globules.

Also stoichiometric quantities of antimony and natural Iron were taken to form $FeSb_2$ and FeSb compounds. The samples were kept in furnace at temperature of 750°C for 7 days for $FeSb_2$ and 1000 °C for FeSb in small quartz tubes sealed under high vacuum. The samples were then quenched in water. The XRD of the samples was done.

4.2.2 Experimental:

The Fe-Sb samples were powdered and approximately 100mg. of each of the samples were then taken to make the Mossbauer absorbers. The samples were evenly distributed on a one mm thin sheet of paper and the diameter of the absorber is 1.2 cm. Before each run of the spectra the velocity calibration was checked and recorded. The calibration was also varied according to the need of the sample. The Mossbauer spectra were taken for the samples with constant acceleration spectrometer whose line width is 0.28 mm/sec. Co-57 in Rh matrix was used as source having activity of 50 milli Curie. All the spectra were recorded at room temperature.

4.2.3 Results and Discussion :

All the Mossbauer spectra were fitted with a computer program. The least square fitted Mossbauer parameters of the samples are given in the Table No. 4A. The experimental errors are also quoted. Mossbauer spectrum of the concentration variation of Fe in Sb and stoichiometric FeSb and $FeSb_2$ are shown in Fig. 4.1.1 to 4.1.10. The Fig. 4.1.11 show the spectrum of radioactive Co-57 diffused in Sb matrix. From the observed values of QS and IS the samples can be divided into three regimes of concentration (X) of Fe; $0.0025 < X < 0.10$, $X \geq 0.1$ and $X \leq 0.0025$. From the Table (4 A) it is seen that the values of the IS (~0.48 ±0.01mm/sec) and the Quadrupole splitting (1.28±0.01mm/sec) of the samples are constant for Fe concentration range $0.0025 < X < 0.10$. This value of Quadrupole splitting of 1.28 ±0.01 mm/sec corresponds to the Quadrupole splitting of $FeSb_2$ sample (12). This points to the fact that $FeSb_2$ compound phase formation in this concentration range is inevitable. If the concentration of the Fe in the sample is increased to $X \geq 0.10$, the Mossbauer spectra show two quadrupole doublets: the value of the first doublet is 1.28±0.01 and that of a smaller doublet having QS of 0.28±0.01mm/sec. This site is attributed to the formation of FeSb phase (13).

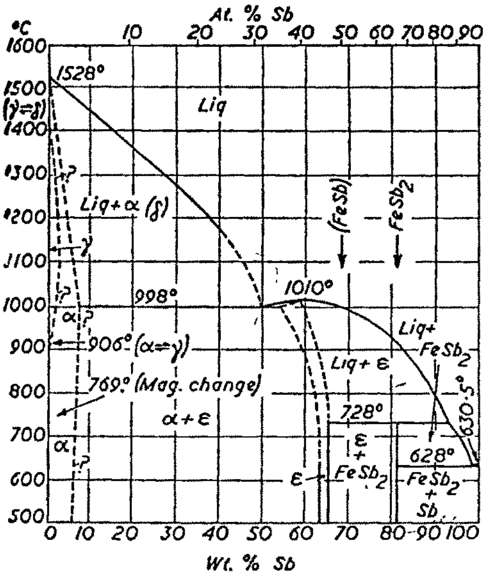
It can be seen from the area under the curve for the two doublets that the area under the smaller doublet increases with increase in Fe concentration. Hence it can be concluded that when Fe concentration X ≥0.10, a second phase is seen whose intensity increases with increase in Fe concentration. For a specific concentration range of Fe in Sb, there is a formation of $FeSb_2$ compound only and beyond that range the formation of FeSb phase also starts along with $FeSb_2$. The phase diagram of Fe-Sb is shown in Fig. 4 A (I).

When stoichiometric quantities of Fe and Sb were taken to form $FeSb_2$ compound it was found that the complete formation of $FeSb_2$ was not taking place. Along with $FeSb_2$ a second phase corresponding to FeSb was also forming. But when FeSb was made stoichiometrically, it was observed that this sample shows only one quadrupole doublet having QS of 0.28±0.01mm/sec. Thus Fe was forming a unique phase with Sb and it can be considered as the formation of FeSb phase is complete. The values of IS for the FeSb and $FeSb_2$ samples indicate the charge state of Fe is larger (~3 or more).

Table No. 4 A

General formula for the samples is Fe_XSb_{1-X}

Composition of samples	Quadrupole Splitting (mm/sec)		Isomer Shift (mm/sec)		Area under the curve (%)	
	A	B	A	B	A	B
Fe-Sb (50%)	———	0.30±0.01	———	-0.41±0.02	———	100
$FeSb_2$	1.27±.01	0.29±0.01	-0.47±0.01	-0.40±0.01	39.3	60.7
X=0.20	1.28±.01	0.28±0.01	-0.47±0.01	-0.39±0.01	54.7	45.3
X=010	1.27±0.01	0.28±0.01	-0.48±0.01	-0.40±0.01	77.7	22.3
X=0.05	1.28±0.01	———	-0.48±0.01	———	100	———
X=0.01	1.27±0.01	———	-0.47±0.01	———	100	———
X=0.005	1.28±0.01	———	-0.47±0.01	———	100	———



Phase diagram of Fe-Sb system

Fig. 4A (I)

Fig. 4.1.1

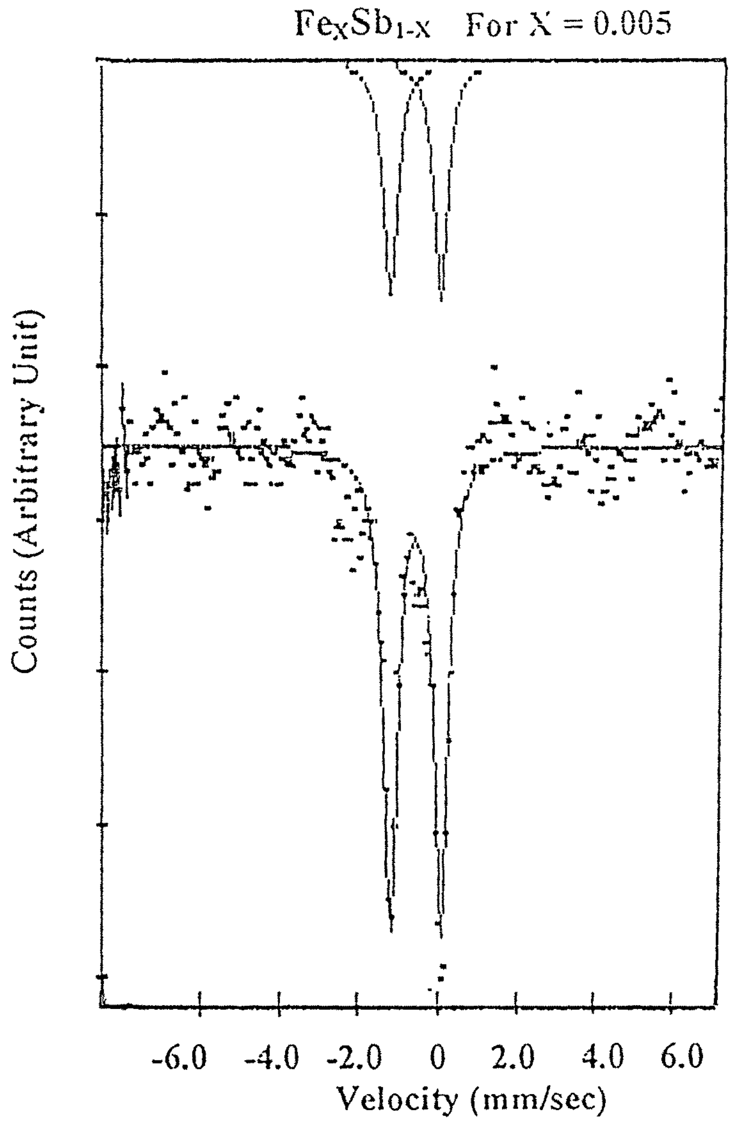

Fe_XSb_{1-X} For X = 0.005
Counts (Arbitrary Unit)
-6.0
-4.0
-2.0
0
2.0
4.0
6.0
Velocity (mm/sec)

Fig. 4.1.2

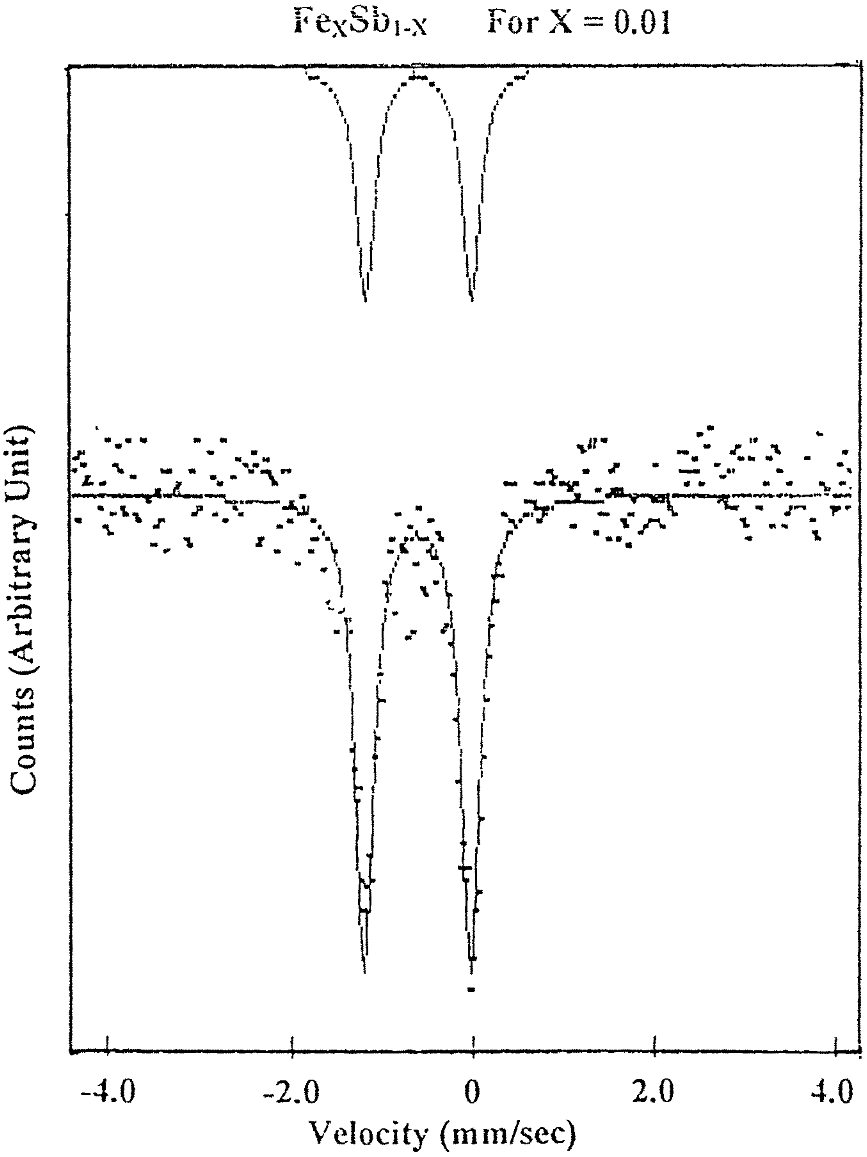

Fe_XSb_{1-X} For X = 0.01
Counts (Arbitrary Unit)
-4.0
-2.0
0
2.0
4.0
Velocity (mm/sec)

Fig. 4.1.3

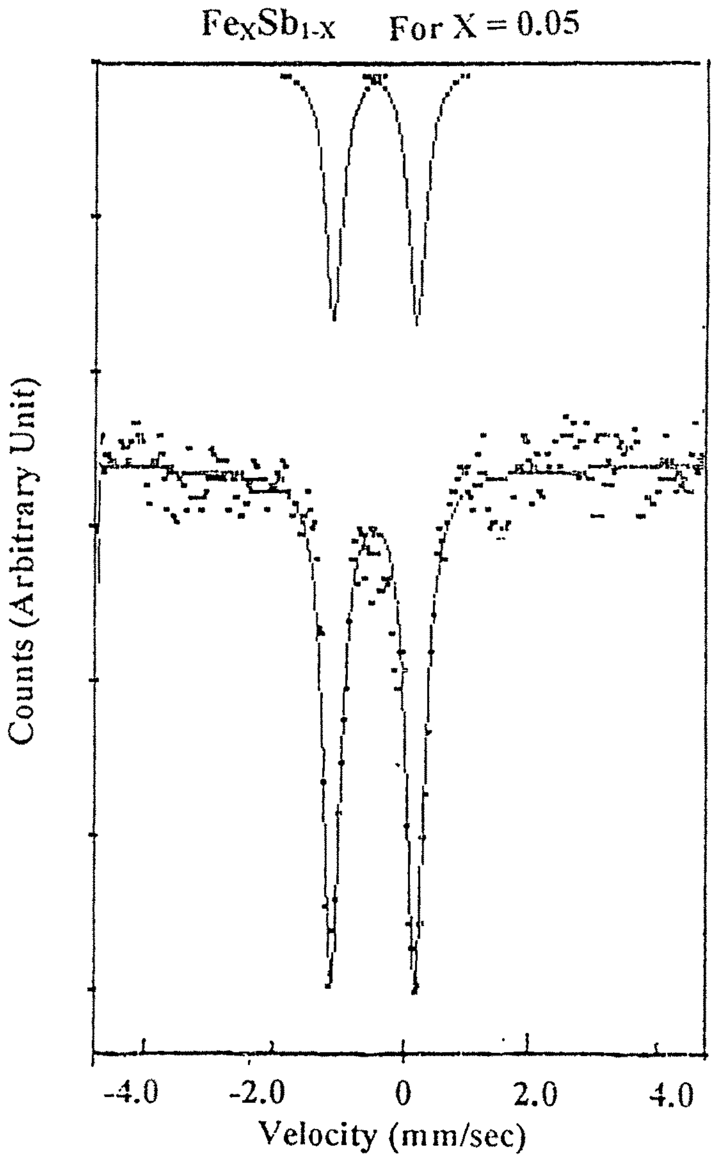

Fe_XSb_{1-X} For X = 0.05
Counts (Arbitrary Unit)
-4.0
-2.0
0
2.0
4.0
Velocity (mm/sec)

Fig. 4.1. 4.

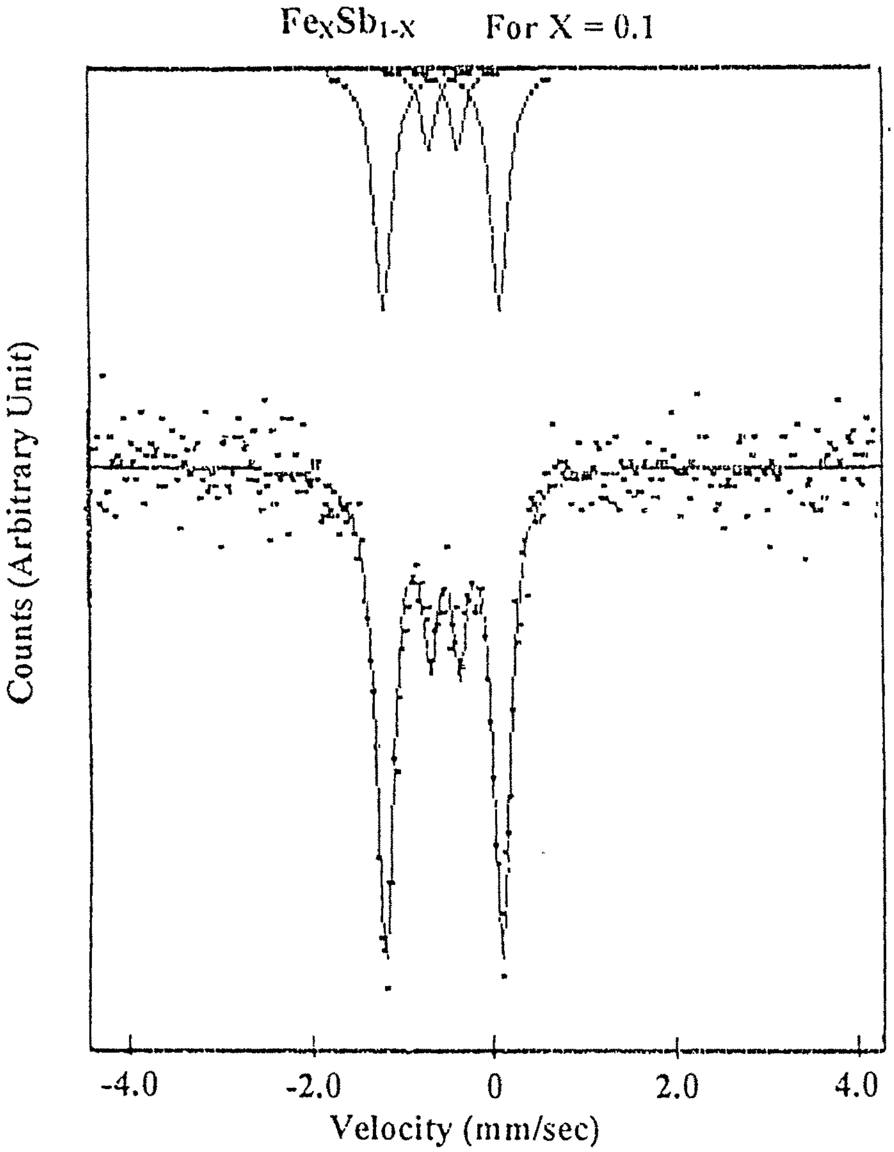

Fe_XSb_{1-X} For X = 0.1

Fig. 4.1.5

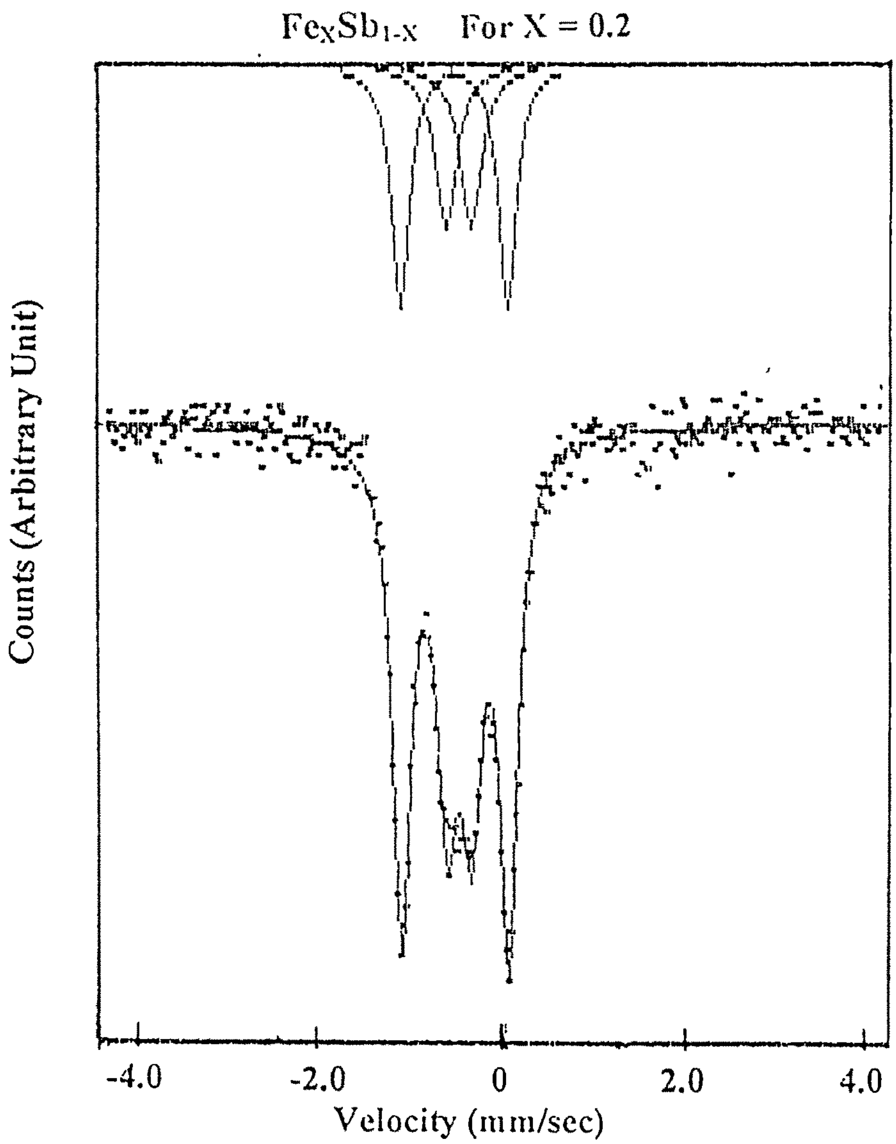

Fe_XSb_{1-X} For X = 0.2
Counts (Arbitrary Unit)
-4.0
-2.0
0
2.0
4.0
Velocity (mm/sec)

Fig. 4.1.6

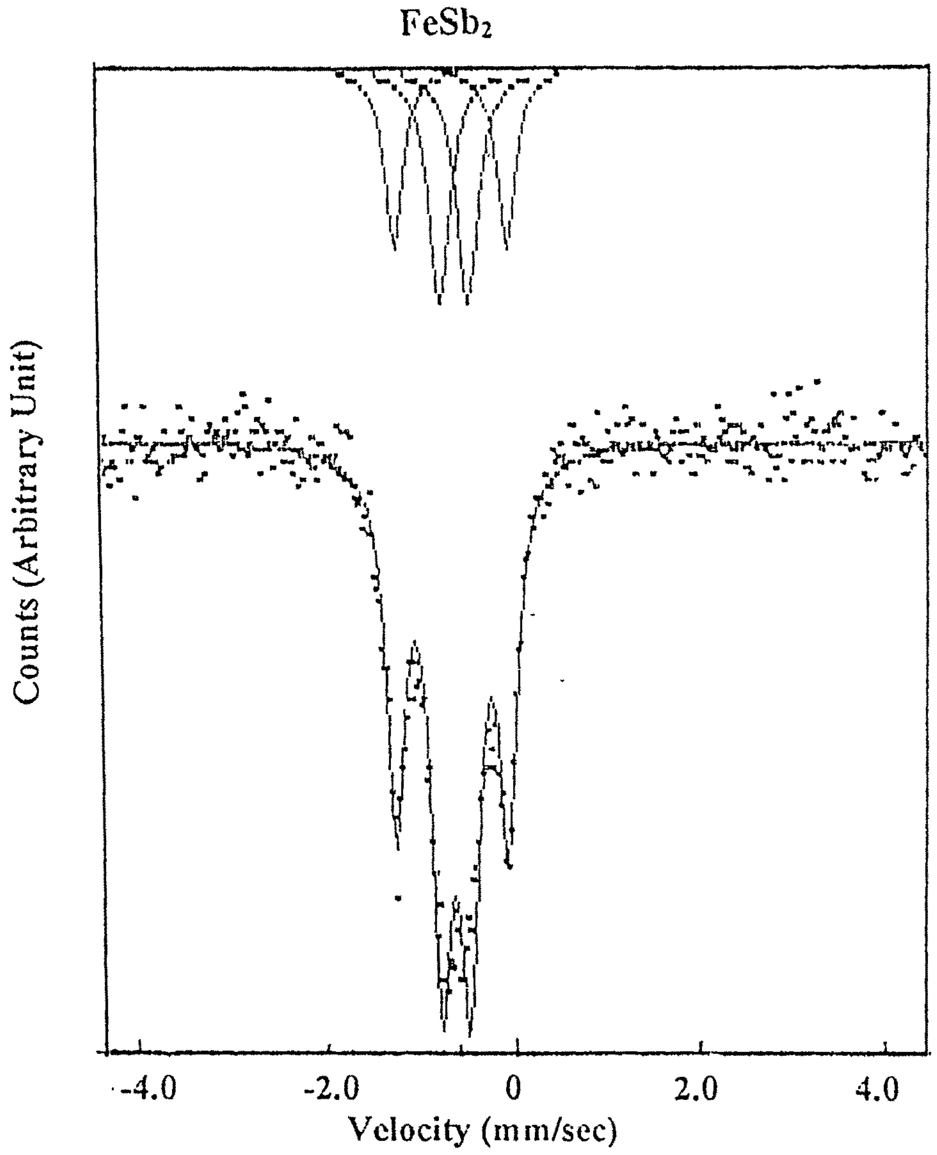
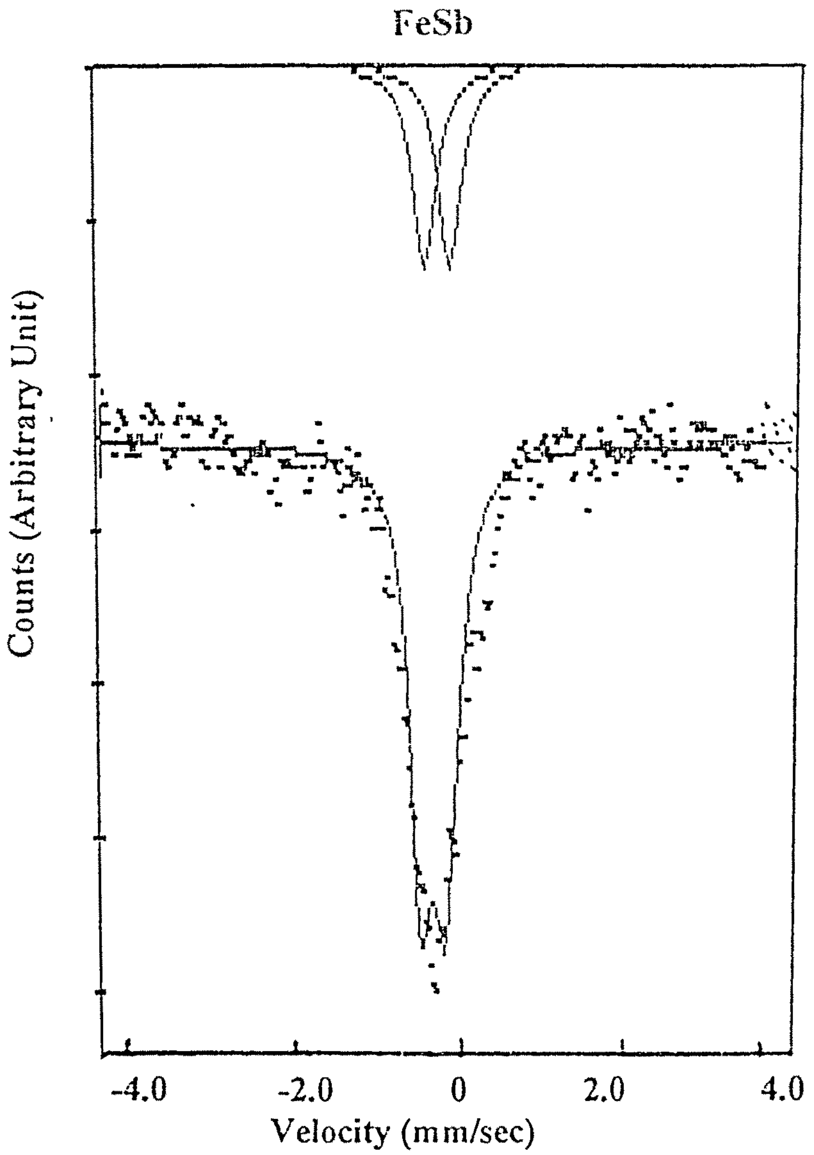


Fig. 4.1.7



This result is quite interesting because it points to the fact that there is an optimum concentration for Fe beyond which it is unable to make $FeSb_2$ compound fully. The data on the Fe-Sb phases i.e. area under the curves given in the Table 4A shows the variation of intensity of the two doublets.

The XRD of the samples of Fe concentration X = 0.05, 0.10 , $FeSb_2$ and FeSb are given in fig. (4.1A and 4.1B). It can be seen from the XRD pattern that for X = 0.05 of Fe concentration in Sb the FeSb phase is not detectable. But on increasing the Fe concentration to X=0.10, the FeSb compound phase starts to appear and at stoichiometric proportion of FeSb the first quadrupole doublet of $FeSb_2$ phase disappears.

To find out the lowest concentration of Fe at which $FeSb_2$ formation starts a sample of X=0.0025 in Sb was made. The spectrum of this sample gave us a magnetic sixtet and a Quadrupole doublet.

As the concentration of Fe is still decreased to see the effect of Fe concentration for X = 0.002, a sixtet indicating the presence of a magnetic interaction was seen. It was also observed that in this case Fe was going to an almost unique site resulting in unique value of the field. When the concentration of Fe was further reduced to X=0.0015 also a sixtet was observed. These results

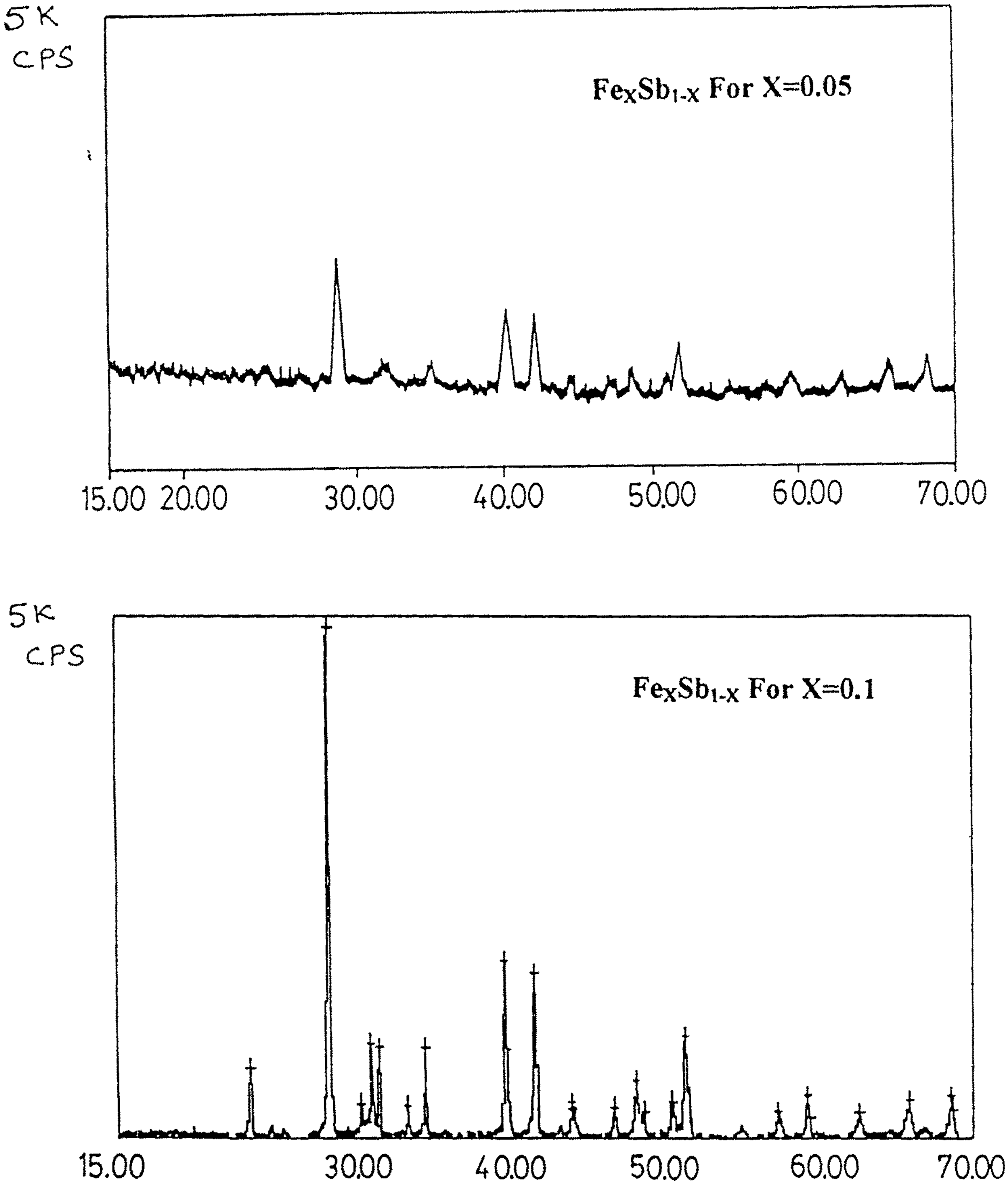
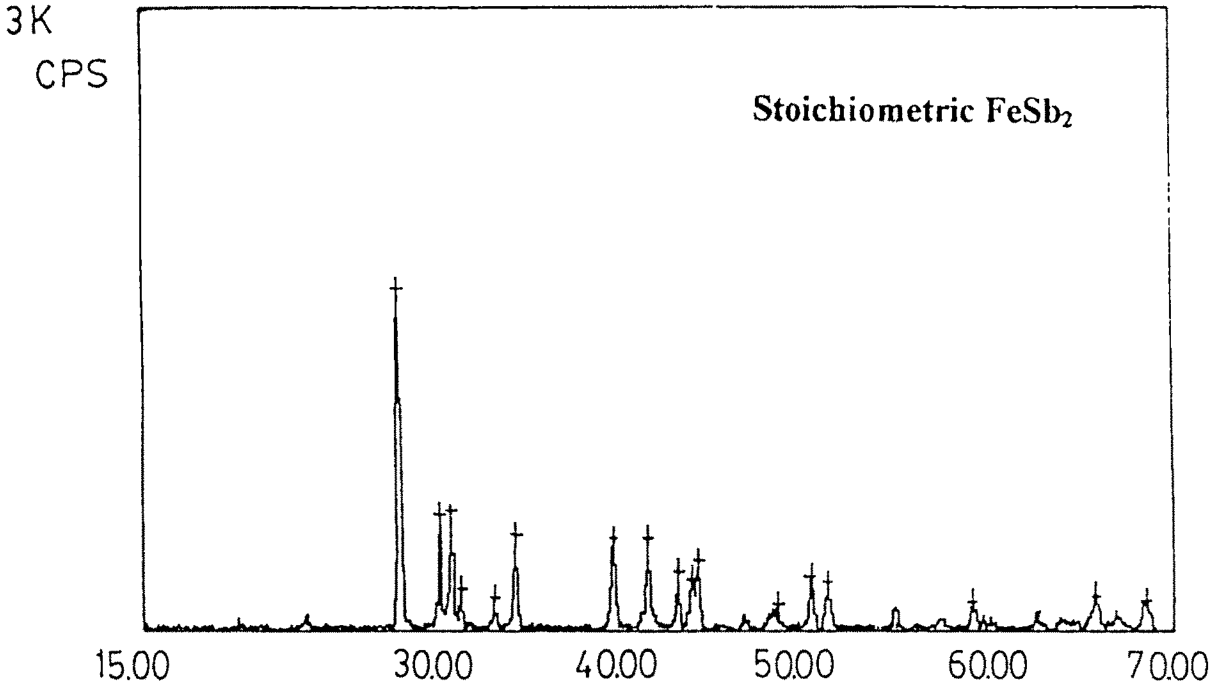

5K
CPS
Fe$_X$Sb$_{1-X}$ For X=0.05
15.00
20.00
30.00
40.00
50.00
60.00
70.00
5K
CPS
Fe$_X$Sb$_{1-X}$ For X=0.1
15.00
30.00
40.00
50.00
60.00
70.00

Fig. 4.1 A


3K
CPS
Stoichiometric FeSb$_2$
15.00
30.00
40.00
50.00
60.00
70.00

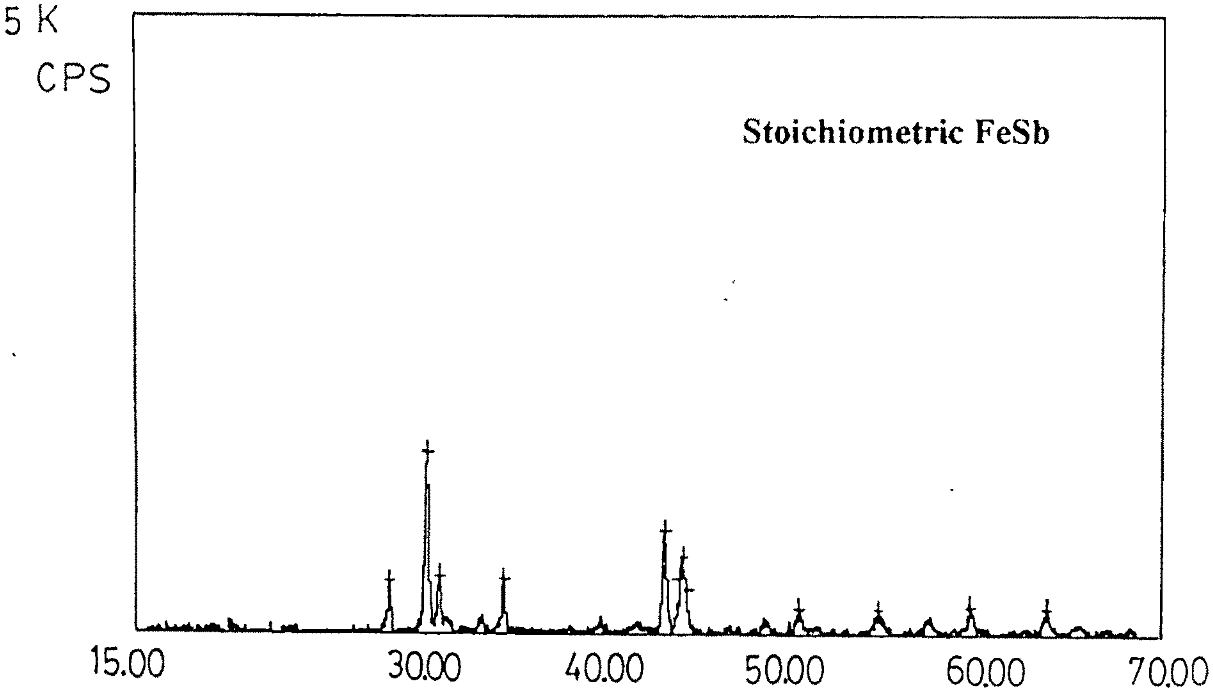

5 K
CPS
Stoichiometric FeSb
15.00
30.00
40.00
50.00
60.00
70.00

Fig. 4.1 B

were unusual as Fe was expected not to show a magnetic interaction in Sb host at such concentrations of Fe-57 in Sb. The various parameters of this interaction are given in the Table No. 4 B.

It was initially thought that the sixtet might be due to cluster formation of Fe in Sb matrix i.e. Fe may not be dispersing properly. Hence another sample was prepared again to see if the same result persists. Thus a fresh sample was prepared by weighing the desired proportion of Fe-57 and Sb. This time the melting process was prolonged and quenched many times in air for proper mixing. Also the sample preparation time was increased. This sample also showed the Mossbauer spectrum with a sixtet. These samples were prepared by taking a small thin piece from Fe-57 foil. We thought that Fe might not be dispersing properly as it is a piece of foil and hence giving rise to this type of spectrum.

However, if this was the case then for higher concentration of Fe-57 in Sb one should also get a magnetic spectrum, as then also the Fe may not be dispersing properly and the quantity of Fe in the sample was also much higher. But that was not the case and for higher concentrations of Fe-57 (X =0.005 and 0.01) in Sb no magnetic spectrum was seen. Only a Quadrupole doublet was seen.

Table No. 4 B

Composition of samples	Magnetic Field (KOe)	QS (mm/sec)	Isomer Shift (mm/sec)		Area under the curve (%)	
	A	B	A	B	A	B
Fe_XSb_{1-X} (X=0.0025)	310.5±2.4	1.26±0.02	-0.76±0.03	-0.47±0.01	70.1	29.9
Fe_XSb_{1-X} (0.002)	311.5±2.1	____	-0.76±0.03	____	100	___
Fe_XSb_{1-X} (X=0.0015)	312.0±2.4	____	-0.76±0.03	____	100	___

Fig. 4.1.8

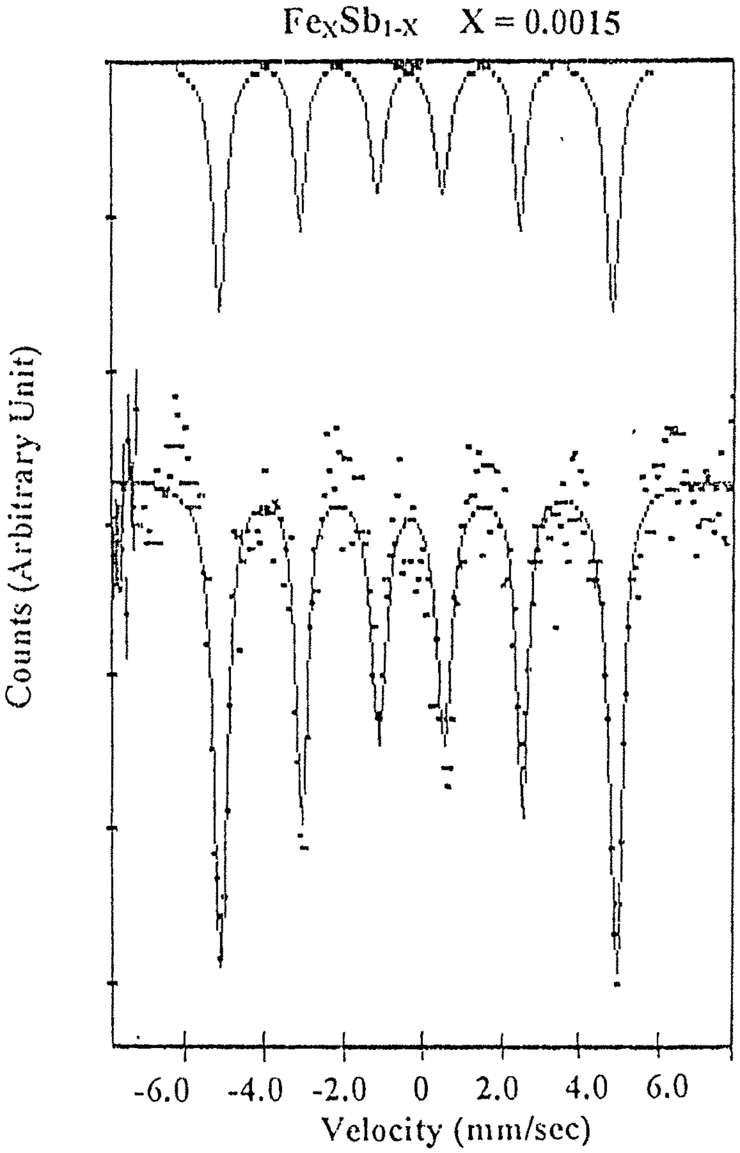
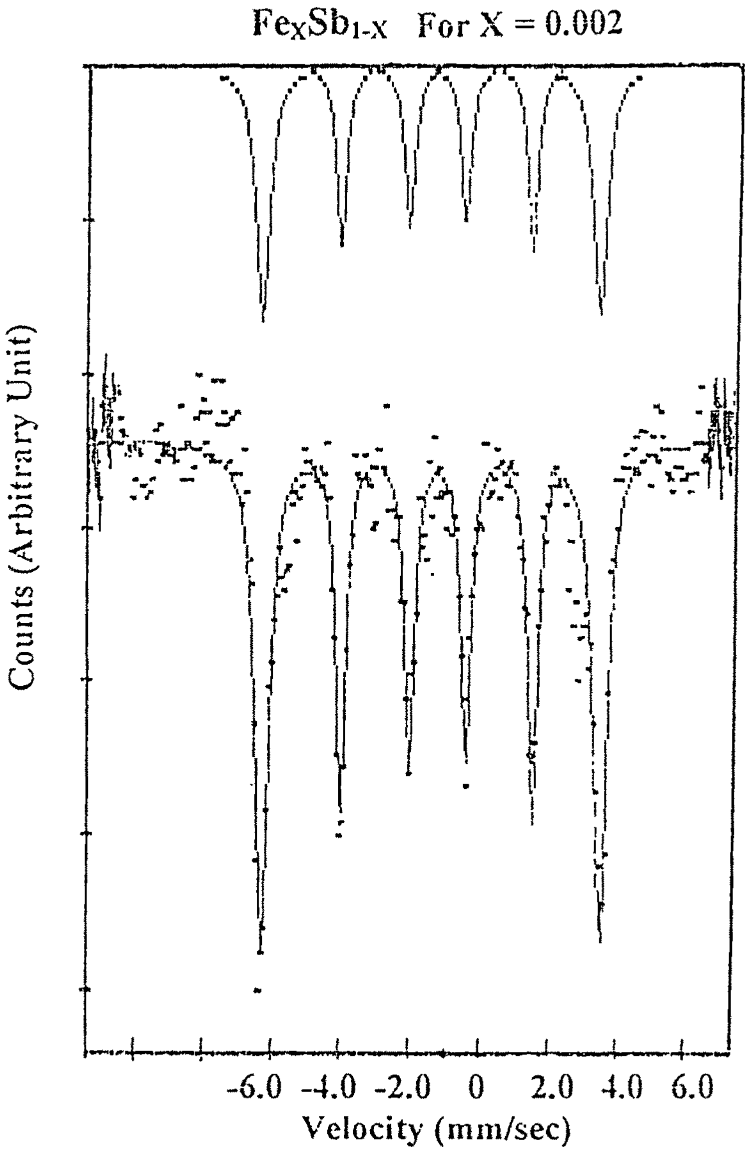
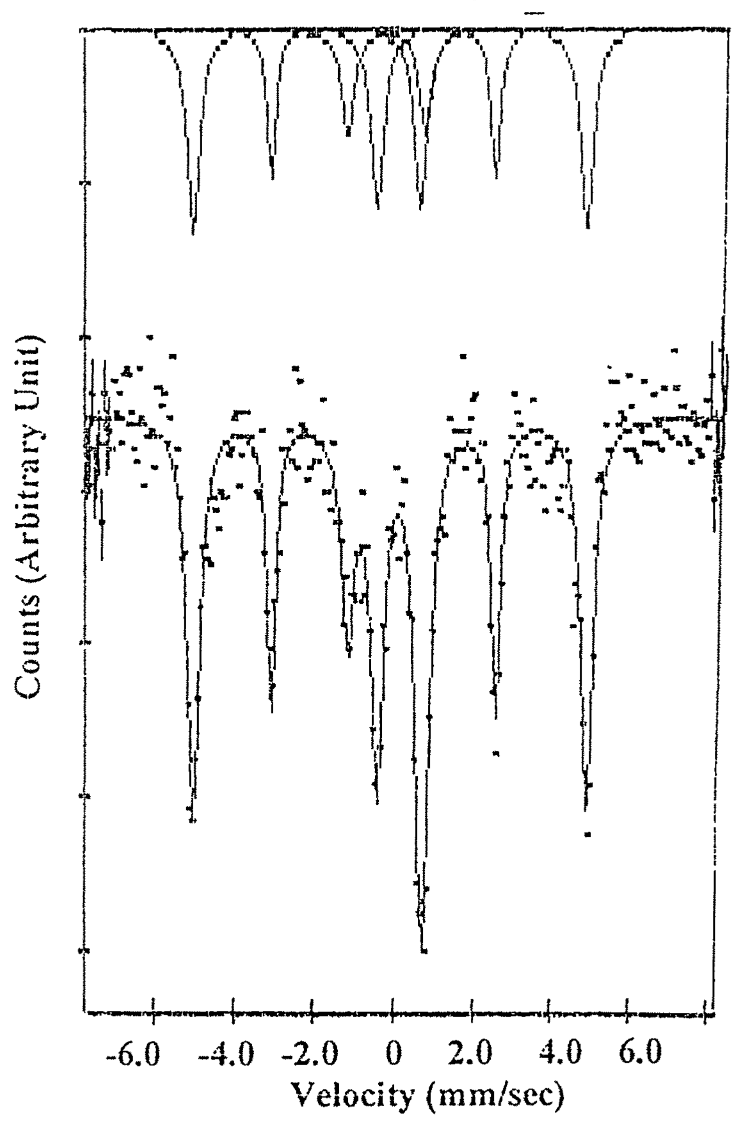

Fe_xSb_{1-x} X = 0.0015
Counts (Arbitrary Unit)
-6.0
-4.0
-2.0
0
2.0
4.0
6.0
Velocity (mm/sec)

Fig. 4.1.9



Fe_XSb_{1-X} For X = 0.002

Fig. 4.1.10


Fe_XSb_{1-X} For X = 0.0025
Counts (Arbitrary Unit)
-6.0
-4.0
-2.0
0
2.0
4.0
6.0
Velocity (mm/sec)

In order to make sure that the metal piece of Fe-57 is not confusing the studies, the samples were prepared with Fe-57 powder. This time also there was no change in the result. If Fe-57 were not dispersing properly and remaining as clusters the same spectrum may not be seen in different parts of the sample. Hence the Mossbauer spectra were taken for four different parts of the sample. The Mossbauer spectra of all the four parts of the sample were identical.

After taking the Mossbauer spectra these same samples were extracted and again the samples were melted to rule out clusters of Fe. The samples were subjected to one more round of melting and quenching process and the Mossbauer spectra were taken and the same result was observed.

It has been reported by Anila et. al. (6) that the QS value for X= 0.002 in Sb as 1.29 ±0.01 mm/sec at room temperature. They had also reported that they had done the X-ray for the dilute sample and found no evidence of $FeSb_2$ formation. They also made some samples with higher concentration of Fe in Sb but the formation of $FeSb_2$ was not seen by XRD. This could be due to the amount of $FeSb_2$ formed which may be so low that it may not be seen by XRD.

The samples were made by Anila et. al. (6) was in an Argon Arc furnace. The temperature in Argon Arc furnace is of the order of 3000 ^{o}K. At this high temperature a Semi metal like Sb whose melting point is 610 ^{0}C and boiling point

1380 ^{0}C will start to evaporate making the exact proportion of Fe-Sb sample to change.

Further repeated melting at such a high temperature may have added to the loss of Sb. Hence the concentration of Fe-57 in Sb must have been much higher than the estimated concentration of Fe present in the sample. This can be seen from the values of QS for $0.0025 < X < 0.10$ samples.

Concentration lower than X=0.0025 namely X=0.002, 0.0015 yielded only a magnetic spectrum with no signs of a doublet. The value of magnetic field is about 311±2.5 KOe.

Neutron depolarisation study is an excellent tool to probe the existence of magnetic clusters and the magnetic inhomogeneity of samples. The neutron depolarisation study is a mesoscopic probe. It can measure spatial magnetic inhomogeniety on a length scale from 100 Å to several microns.

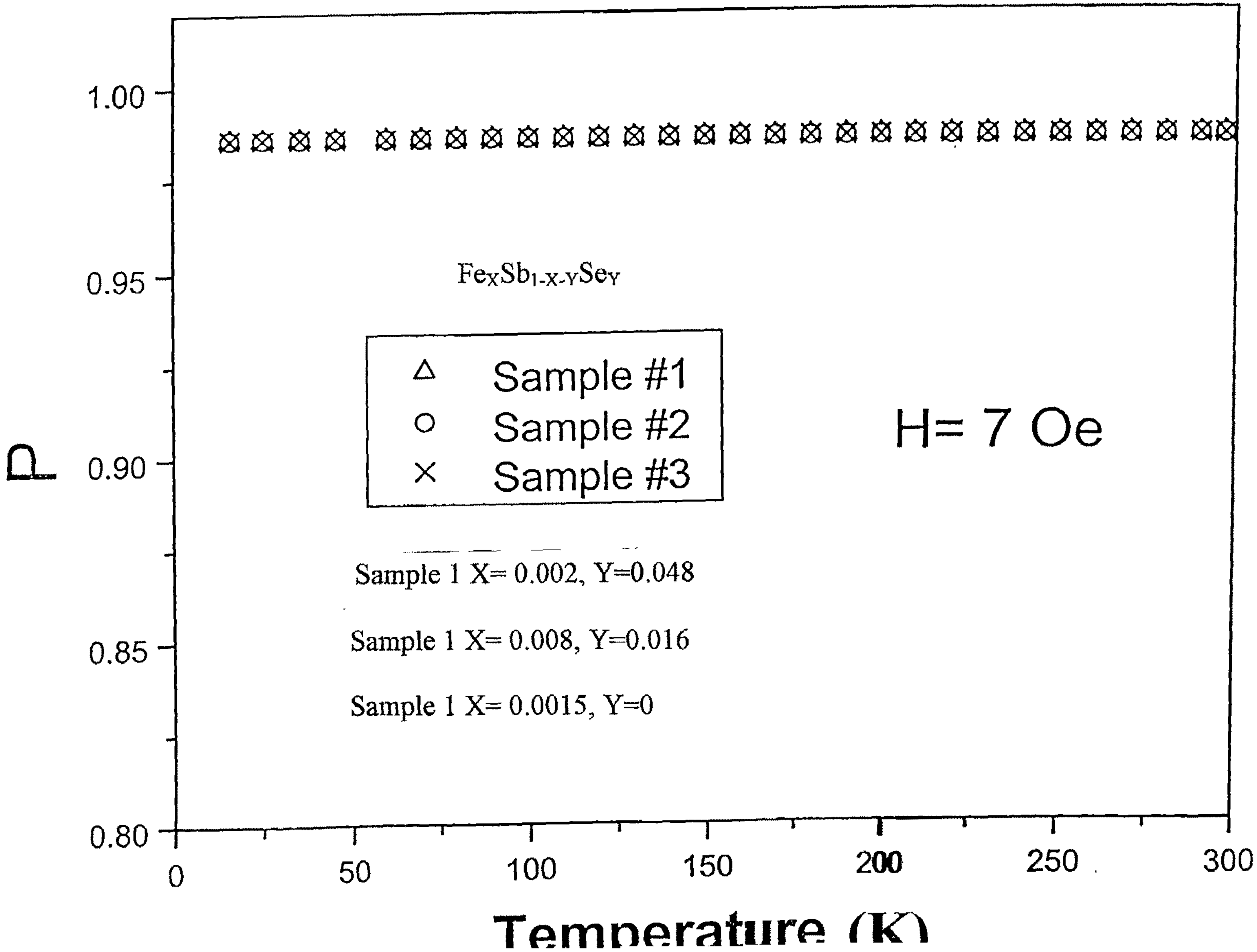
In an unsaturated ferromagnet or ferrimagnetic, the magnetic domains exert a dipolar field on the neutron polarisation and depolarise the neutrons owing to Larmor precession of the neutron spins in the magnetic field of the domains

One would expect depolarisation for the case of clusters of spins (atleast of mesoscopic length scale) with net moments. The advantages of neutron depolarisation technique are the domain size information can be obtained (as an average over the entire sample), and there are essentially no resolution restrictions on the size of the domains, which can be measured.

The temperature in the present study was varied from 15K to 300K. The sample was cooled in zero field and then a 7 Oe external field was applied to study the depolarisation effect on the neutrons by the samples. The powder sample was used in the form of a pellet of cylindrical dimension. The sample was kept in the neutron beam in such a way that its plane surface remains perpendicular to the propagation direction of the polarised neutron beam. Also the beam size was restricted with a cadmium slit, which is within the size of the samples. This experiment was carried out using the neutron polarisation analysis spectrometer (PAS) at Dhruva reactor, Trombay.

This study was carried out on the sample of Fe_XSb_{1-X} for X=0.0015. The temperature dependence of the transmitted neutron beam polarisation P with a field of 7 Oe. is depicted in the fig. 4.1c. This value of P over the entire range (15 to 297k) is found to be the same as the incident neutron beam polarisation (=986±0.003). The study showed that there is no depolarisation over the entire range of temperature (Fig. 4 B). Hence the absence of clusters of spins of Fe or Fe

Fig. 4.1 C


P
1.00
0.95
0.90
0.85
0.80
0
50
100
150
200
250
300
Temperature (K)
$Fe_XSb_{1-X-Y}Se_Y$
△ Sample #1
○ Sample #2
× Sample #3
H= 7 Oe
Sample 1 X= 0.002, Y=0.048
Sample 1 X= 0.008, Y=0.016
Sample 1 X= 0.0015, Y=0

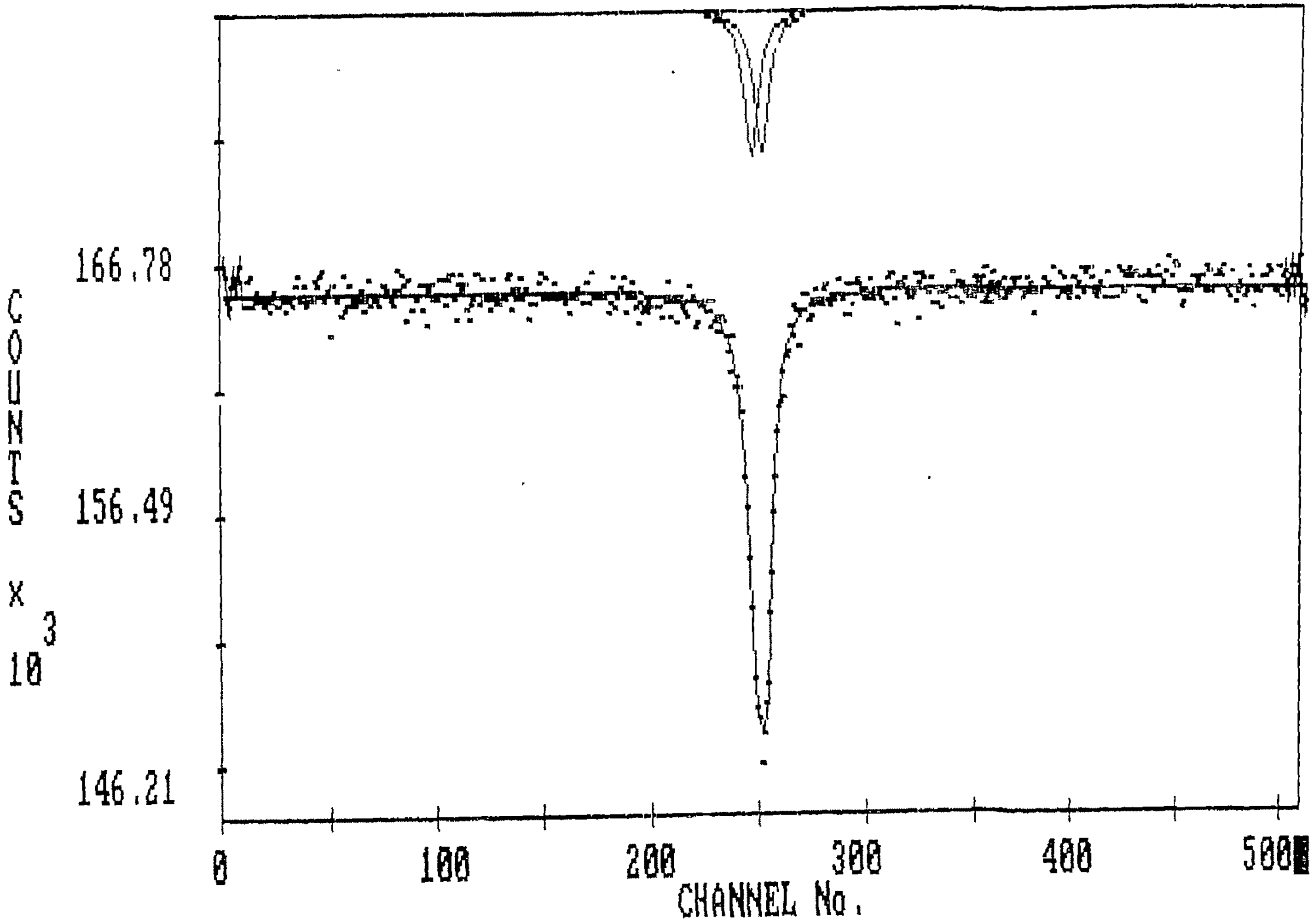
based compounds having net moments with a size about >100 Å is confirmed by this neutron depolarisation study. However clusters of the size <100 Å can not still be ruled out entirely.

In order to check the field in Sb a sample was made by diffusing radioactive Co-57 in Sb. This sample was made to avoid the $FeSb_2$ and FeSb compound formation, which was taking place in the FeSb system. The spectrum of this sample showed a single line with a line width of 0.5 mm/sec, which shows that if there is a quadrupole doublet the splitting will be less than 0.5 mm/sec.

If we assume that the clusters of Fe are not present then one of the possible explanations of the present result may be the formation of the local moments. The formation of local magnetic moment of transition metal atoms in host metal has been of considerable interest and studied experimentally as well as theoretically in detail (14, 15,19,20). The main problem in finding the local 3d magnetism has been the strong 3d-conduction electron hybridization, so that the 3d conduction electrons are often regarded as partially delocalised. Now if this interaction of the 3d mixing can be made small compared to the atomic configurational interactions then we will be able to see localised 3d shell behaviour in an isolated 3d atom in a metal host.

Fig 4.1.11

Mossbauer Spectrum of Co-57 diffused in Sb matrix



Many experiments were carried out to see the local moment formations (14, 15,19,20) and their interpretation was made on the basis of Friedel-Anderson model (16), kondo type models (17) and ionic model (18). Self consistent cluster calculations with 3d, 4d, and some sp impurities in copper were done by Braspenning et. al. (14). Riegel et. al (19) have studied 3d- shell behaviour of Fe ions in alkali metal hosts like K, Rb, and Cs. They produced these types of non alloying systems by heavy ion reactions and implantation technique and measurements were done by Time Differential perturbed angular distribution method (TDPAD). The concentration of Fe in the host in all these studies was in the ppm levels.

In the present study at the low concentration Fe-Sb dilute system seems to be forming which does not hybridize that leads to the compound formation. The idea of studying 3d-ions in alkali metal hosts systems by Riegel et, al. was stimulated by a sharp contrast in the atomic volume, electronegativity, electronic structure and density of states. They found that because of the sharp contrasts such systems do not alloy. Also it was argued that the orbital local moment could survive if the impurity maintains an ionic configuration.

In the present case the value of the IS of –0.76mm/sec indicates that Fe is in a high charge state (> +4). This could be only possible if Sb acts as an acceptor. Sb is known to make a charge state of –3. Fe can donate 3 electrons to Sb making its charge state to –3. The ionic radius for Sb in –3 charge state is 2.45Å. From this value if the volume of Sb is calculated it comes to 61 W/D. Also the volume of Fe in comparison to Sb is extremely small (0.9W/D). This vast difference in volume can make Fe to behave like an isolated ion surrounded by large Sb ions. Also the value of field is very high of ≈ 311±2.4 KOe. As the Fe atom has the probability of transferring several electrons, (≅4 to 5) to Sb atoms, only few (≅ 2 to 3) 3d electrons can remain with the Fe ions. These few electrons may not be pairing up and hence showing the magnetic field.

Further, since the observed magnetic field is very high and the contribution of few electron spins (2 to 3) may only give rise to $2.8\mu_B$ to $3.8\ \mu_B$ it will not be enough to produce the observed field (311KOe) and hence one can expect a non zero orbital contribution in this system. This non-zero contribution of orbital motion of the electrons along with the unpaired spins gives rise to such a large field. In this case the orbital local moment can be understood to be surviving due to the high ionicity of Fe atoms. The same type of result was observed for Fe in Ca (20).

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