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Hyperfine interactions in dilute Se doped Fe_xSb_{1-x} bulk alloy

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Abstract Hyperfine Interaction technique like Mossbauer spectroscopy is a very sensitive tool to study the local probe interactions in Iron doped alloys and compounds. We report here the Mossbauer study of the effect of Fe concentration variations in dilute magnetic semiconducting $Se_{0.004}Fe_xSb_{1-x}$ alloys for x = 0.002, 0.004 and 0.008. The materials were characterized using X-ray diffraction technique (XRD), Fourier Transform Infra-red spectroscopy (FTIR), Neutron depolarization and Mossbauer spectroscopy. The FTIR result shows the semiconducting behavior of the alloys with band gap of 0.18 eV. From Mossbauer spectroscopy two magnetic sites (A and B) were observed. The value of hyperfine magnetic fields (HMF) of $\sim$ 308 kOe (site A) and 270 kOe (site B) was constant with increase in Fe concentration. A nonmagnetic interaction was also observed with quadrupole splitting (QS) of 1.26 mm/sec (site C) for x = 0.004 and x = 0.008. The Neutron depolarization studies indicate that the clusters of Fe or Fe based compounds having net magnetic moments with a size greater than 100 Å is absent.

This article is part of the Topical Collection on *Proceedings of the International Conference on the Applications of the Mössbauer Effect (ICAME 2015), Hamburg, Germany, 13–18 September 2015*

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1 Introduction

Dilute Magnetic Semiconducting (DMS) materials are conventional semiconductors, in which appropriate fraction of the original atoms is substituted by transition metals (TM), which are capable to add localized magnetic moment above room temperature (RT). These DMS represents challenging, promising and exciting areas of futuristic material science. They have potential semiconducting compatible magnetic components for practical spintronics applications [1–6]. Another promising application of DMS is to utilize the Zeeman Effect of the localized magnetic moments of TM in high concentration to create Faraday rotation of linearly polarized light [7–10]. The effect of magnetic ions in ternary alloys in both bulk and thin films i.e. dilute magnetic semiconducting ternary alloys (DMSA) was extensively studied by our group [11–16]. In one of our bulk study in ternary alloy Fe-Sb-Se, the Iron concentration was kept low and constant at x = 0.008. The charge carrier density was varied with an increase in Se concentration Room temperature magnetic ordering was observed in such system [13]. Mossbauer Spectroscopy (MS) and Time Differential Perturbed Angular Correlations (TDPAC) are sensitive microscopic techniques to study the dilute systems as it can probe the magnetic interaction of the nuclear spins with the surrounding electron magnetic moments through Fermi contact interaction [17, 18]. The effect of asymmetry in charge distribution and spin arrangements can be studied using these techniques.

The narrow band gap semiconductor $FeSb_2$ was studied widely since 1969 [19, 20] but it has recently retrieved as a material with promising application potential due to its different physical properties [21–28]. Some studies on Se doped $FeSb_2$ system by M. Pokharel et. al. [29] and P. Sun et. al. [30], reports the variation in thermoelectric effect. One of the study by A.M. Gismelseed et. al [31] reported hyperfine study of Tellurium doped Iron rich antimony alloy ($Fe_{0.54}Sb_{0.46}$) with two different nonmagnetic sites at RT.

In the present study, we report the room temperature magnetic ordering in dilute Se doped Fe_xSb_{1-x} bulk alloy with varying concentration of Fe The concentration of Fe was varied with x = 0.002, 0.004, 0.008 in $Se_{0.004}Fe_xSb_{1-x}$ bulk alloys. XRD and FTIR were used to see the variation in structural and electronic properties respectively. Mossbauer measurement was done to see the hyperfine fields at the local probe of Fe nucleus. The Neutron depolarization technique was used to see the Fe clusters if any in the system The authors have found no reports in this type of dilute system.

2 Experimental details

High purity (5N purity) Antimony (99.999 %, Alfa Aeser), Iron- 57 (Fe^{57}) and Selenium (99.999 %, Alfa Aeser) metals of desired quantities were taken for making $Se_{0.004}Fe_xSb_{1-x}$ alloy. Each sample of required concentration was sealed in a small quartz tube at a high vacuum of the order of $>10^{-5}$ Torr. The sealed ampules were kept at ~ 1400 °C temperature in the Oxy-butane flame and cooled. This process was repeated many times to get homogeneity of the samples. Finally the samples were quenched at RT in water. The ingots of bulk alloys were ground to fine powder. The part of alloy was used to make the Mossbauer absorbers for study at RT with a Mossbauer constant acceleration spectrometer whose line width was 0.28 mm/s. ^{57}Co in an Rh matrix was used as a source. Remaining sample was used for XRD and other characterizations.
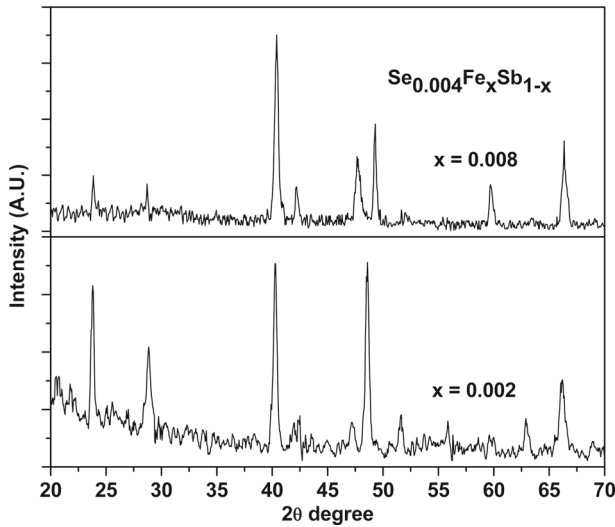
Fig. 1 Typical XRD spectra of $Se_{0.004}Fe_xSb_{1-x}$, x = 0.002, 0.008 bulk alloys

3 Results and discussion

XRD spectra were obtained with Cu-Kα radiation ($\lambda = 1.54$Å). Figure 1 shows the XRD spectra of samples for x = 0.002 and 0.008. The observed peaks in XRD pattern are due to reflection of parent Sb matrix (ASTM-JCPDS card no. 85-1324). No impurity phases of Fe-Se or Fe was observed in XRD spectra.

Fourier Transform Infra-red spectroscopy (FTIR) measurements were done for x = 0.004 in $Se_{0.004}Fe_{1-x}Sb_x$ system. The band gap was calculated from the plot of hν versus $(\alpha h\nu)^2$ shown in Fig. 2. This alloy showed semiconducting nature with a low band gap of ~ 0.18 eV.

Typical Mossbauer spectra of the samples are shown in Fig. 3. All the spectra were least square fitted using Meerwal program. The Mossbauer parameters are given in Table 1. The best fitted data revealed two Magnetic sites A & B for x = 0.002. But when Fe concentration was increased from x = 0.002 to x = 0.004 and 0.008 keeping Se concentration at 0.004 we observed two magnetic sites A, B and a nonmagnetic quadrupole doublet site C. The value of magnetic field for Site A & B was observed to be ~ 308 kOe & ~ 270 kOe respectively for concentrations of x = 0.002.

With the increase in Fe concentration to x = 0.004, a nonmagnetic quadrupole site (site C) appeared. For this site C the value of the quadrupole splitting 1.26 mm/s and isomer shift 0.44 mm/s was observed (shown in Table 1). This nonmagnetic site C is assigned to the formation of $FeSb_2$ compound phase [32]. It is also seen that the population of site C increases with increase in Fe concentration from x = 0.004 to x = 0.008.

However the value of magnetic field at both the sites does not change significantly with increase in Fe concentration. It should be noted that in our earlier study of Fe-Sb system [32]. When Fe concentration was increased to x = 0.005 and above, no magnetic interaction
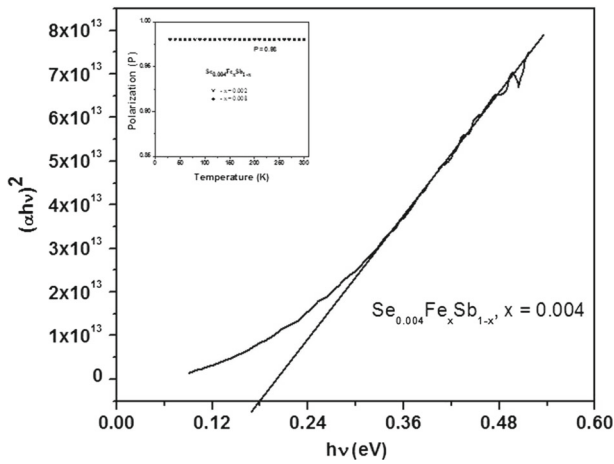
Fig. 2 $(\alpha h\nu)^2$ versus $h\nu$ spectra of $Se_{0.004}Fe_xSb_{1-x}$, x = 0.004 and typical Neutron polarization spectra of $Se_{0.004}Fe_xSb_{1-x}$, x = 0.002 and 0.008 bulk alloys shown in inset

Fig. 3 Typical Mossbauer spectra of $Se_{0.004}Fe_xSb_{1-x}$, x = 0.002, 0.004 and 0.008 bulk alloys
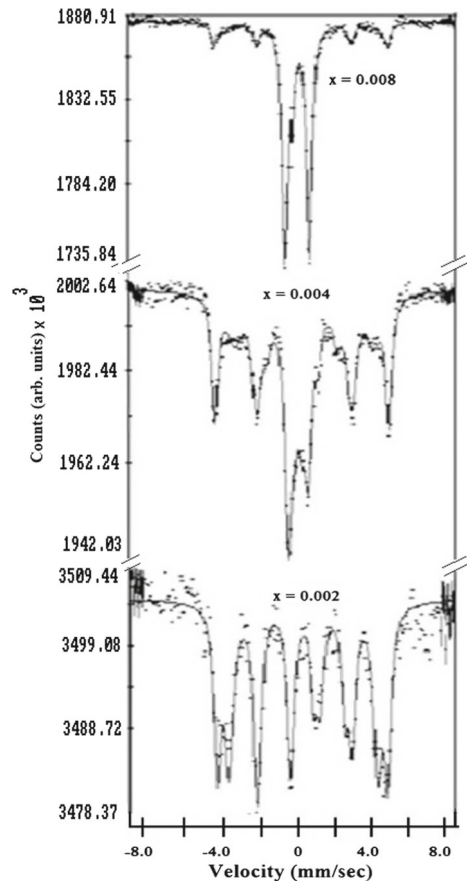
Table 1 Mossbauer parameters of $Se_{0.004}Fe_xSb_{1-x}$

Composition of the samples	Hyperfine Magnetic Field (kOe)			Quadrupole splitting (QS) mm/s	Isomer shift (IS±0.02) mm/s			Fractional Area (%)		
$Se_{0.004}Fe_xSb_{1-x}$	A	B	C	A	B	C	A	B	C
x = 0.002	308.2	270.2	—	0.78	0.70	—	0.462	0.538	—
	(3.4)	(3.4)		(0.02)	(0.02)				
x = 0.004	308.2	267.6	1.26	0.69	0.69	0.44	0.452	0.362	0.186
	(3.4)	(3.4)	(0.02)	(0.02)	(0.02)	(0.02)			
x = 0.008	308.7	272.5	1.26	0.66	0.53	0.44	0.110	0.156	0.734
	(3.4)	(3.4)	(0.02)	(0.02)	(0.02)	(0.02)			

was observed. Only quadrupole interaction of $FeSb_2$ compound was seen. Also for low concentration of Fe x = 0.0025 only a sextet with hyperfine magnetic field of $\sim$ 310 kOe along with a doublet was observed. On comparing the present study with the previous study of Fe-Sb system [32]. It is seen that with the inclusion of Se in the system a second magnetic site B appears. The inclusion of Se in the system is inhibiting the $FeSb_2$ compound phase formation at higher concentration of Fe. It is also responsible for bringing in magnetic interaction in the system at higher Fe concentrations of x = 0.004 and x = 0.008 Although the value of magnetic field is constant $\sim$ 308 kOe for all Fe concentrations the Isomer Shift (IS) is found to decrease with increase in Fe content. This decrease in IS may be due to changes in the neighborhood of Fe due to compound phase formation. The observed magnetic interaction of site (A) $\sim$ 308 kOe was thought to be due to the formation of Fe clusters in the Sb-Se alloy. Hence the samples were prepared for a second time. This time the process of sample preparation was prolonged. The powder was divided into four parts and Mossbauer spectra were taken again for these portions of the powder. This time too, the obtained spectra were same as previous one.

To make sure that clusters are not giving the magnetic signals the Neutron Depolarization study was done to find the presence of Fe clusters in these systems. Neutron depolarization is an excellent tool to probe the inhomogeneity length up to 100 Å in the samples. The powder samples were palletized and kept in front of neutron beam in such a way that its plane surface remains perpendicular to the propagation direction of the polarized beam. This experiment was carried out using the neutron polarization analysis spectrometer at Dhruva reactor, Trombay, Mumbai, India. The study showed that the value of polarization over the entire temperature ranges from 15 K to 297 K is found to be the same as neutron beam polarization (polarization is **0**.98) *i.e.* no depolarization was observed. The temperature vs polarization spectra is shown in inset of Fig. 2. It seems that the clusters of Fe or Fe based compounds having net magnetic moments with a size greater than 100 Å is absent. This type of interaction may be due to the formation of local moment of Fe in Sb-Se matrix at low concentration of Fe or cluster of Fe less than 100 Å.

Since the introduction of Se brings in magnetic field (site B) in the system, there is a possibility of magnetic interaction due to magnetic compound phase of Fe-Se which is Fe_7Se_8. But the value of the magnetic field of Fe_7Se_8 is $\sim$ 211 kOe [13]. The observed value of site B corresponding to any magnetic phase of Fe-Se can be ruled out. The Site B

seems to be due to the formation of a ternary alloy of Fe-Sb-Se. The magnetic interaction observed could be due to the long range Fe–Fe interaction via conduction electron densities, which are brought into the system through doping of Se ions as Se acts as donor impurity in Sb. This type of interaction was reported in our earlier study in FeSbSe system [13].

4 Conclusion

The Mossbauer study of the effect of Fe concentration variations in $Se_{0.004}Fe_xSb_{1-x}$ alloys for x = 0.002, 0.004 and 0.008 is studied. The system is found to be narrow band gap semiconductor. The magnetic interactions found seemed to be due to carriers induced p-d exchange interaction and local moment formation. No depolarization effect was observed by neutron depolarization studies which indicate the absence of clusters greater than 100 Å.

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