Chapter 4

TEMPERATURE VARIATION OF EFG IN Sb_2Se_3

Contents

TEMPERATURE VARIATION OF EFG IN Sb_2Se_3

4.1 Introduction

In the just concluded chapter (chapter 3) of Mossbauer study of Fe-Sb-Se system, we reported a quadrupole splitting of 0.51 mm/sec. XRD of this sample showed peaks corresponding to Sb2Se3 compound and hence assigned this quarupole splitting to the compound Sb_2Se_3.In the literature we have not found any reference of Fe in Sb_2Se_3. In order to confirm the Mossbauer parameter of Sb_2Se_3 a complete quadrupole interaction study and its temperature variation study was undertaken. Electric Field Gradient (EFG) in metals at probe nuclei is well established and is now paramatized into the lattice contribution and conduction electron contribution [1-2]. It is well known that in metal a major contribution to EFG comes from conduction electrons. In metals generally the temperature dependence of EFG follows $T^{3/2}$ law [3]. Measurement of EFG in semiconductors offers the possibility to change the electron densities either by adding impurities or by varying the temperature, whereas in metals the electron density is temperature independent. First such experiment in the semiconductors Sb_2Te_3, In_2Se_3 and Bi_2Te_3 carried out using TDPAC technique indicated an increase in EFG with increase in temperature [4]. It was known that in low band gap semiconductors EFG increases with temperature and conduction electron density varies drastically. In high band gap semiconductors EFG is insensitive to temperature variation. This behaviour is observed in compounds like ZnO [5].

Some of the earlier studies in Sb based semiconductors have shown interesting behavior [6]. Here in this chapter we discuss the effect of temperature on dilute Fe doped in Sb_2Se_3 compound using Mossbauer Spectroscopic Technique. Sb_2Se_3 is a V-VI group semiconducting compound with orthorhombic structure. Sb_2Se_3 is reported to have a bandgap of 1.18 eV [7]. The EFG and the effect of temperature on EFG in this compound semiconductor is still not reported previously to the best of our knowledge.

4.2 Experimental Details

Stoichometric quantities of high purity Antimony (99.99%), Selenium (99.99%) and Iron (99.95%) were taken to make the compound $Fe_{0.002}(Sb_2Se_3)$. As the concentration of Fe being very low, enriched Fe-57 powder was used for a Mossbauer absorber. However for characterization of XRD and Hall Effect we made the samples using natural iron. All the samples were sealed in small quartz tubes at a high vacuum of the order of 10^{-5} torr. They were then melted in furnace at a temperature of 630°C which is slightly above the formation temperature of Sb_2Se_3 phase. The samples were kept in melted condition for about one week and then slowly cooled to room temperature. The samples were formed in the shape of globule. One of the globules made with enriched Fe^{57} was powdered by grinding it properly. Sample in powdered form was mixed thoroughly with Boron Nitride and spreaded uniformly over 1.2cm diameter of O-ring to make Mossbauer absorber. Mossbauer spectra at temperatures 300K,

373K, 473 K and 573K were recorded using constant acceleration Mossbauer spectrometer whose characterization were given in Chap 2. The absorber was kept in a small programmable furnace typically made for Mossbauer studies. The furnace was evacuated through vacuum system to around 10^{-3} torr so that sample does not get oxidized at high temperatures. The accuracy of furnace to maintain the particular temperature was ± 1°C.

The sample was analyzed by XRD for their composition. Fig. 4.1 shows the XRD spectra of typical composition, it has excellent agreement with Sb_2Se_3 phase which is confirmed by standard ASTM data. It also shows some additional peaks that are attributed to be residual Se peaks. As the composition of Fe being very low, the possible phases like FeSe, $FeSe_2$, $FeSb_2$, FeSb were not seen in the system. This is later confirmed by Mossbauer spectra which show only one doublet. The Hall measurements determine the charge carrier concentration (η) to be equal to 3.5 x 10^{15} atoms/cm^3 and conductivity (σ) as 75.3 cm^2/sec. These parameters exactly match with the earlier reported values of Sb_2Se_3 [5].

Fig. 4.2-4.5 shows typical Mossbauer spectra of the sample. All the spectra were least square fitted with standard Meerwal program available. The Mossbauer parameters of the samples evaluated are tabulated in Table 1 The best fit resulted into quadrupole splitting of 0.51±0.02 mm/sec at room temperature. The Isomer Shift (IS) was found to be 0.18± 0.01 mm/sec at RT. These values do not coincide with the reported values of Quadrupole splitting and Isomer Shift of any of the

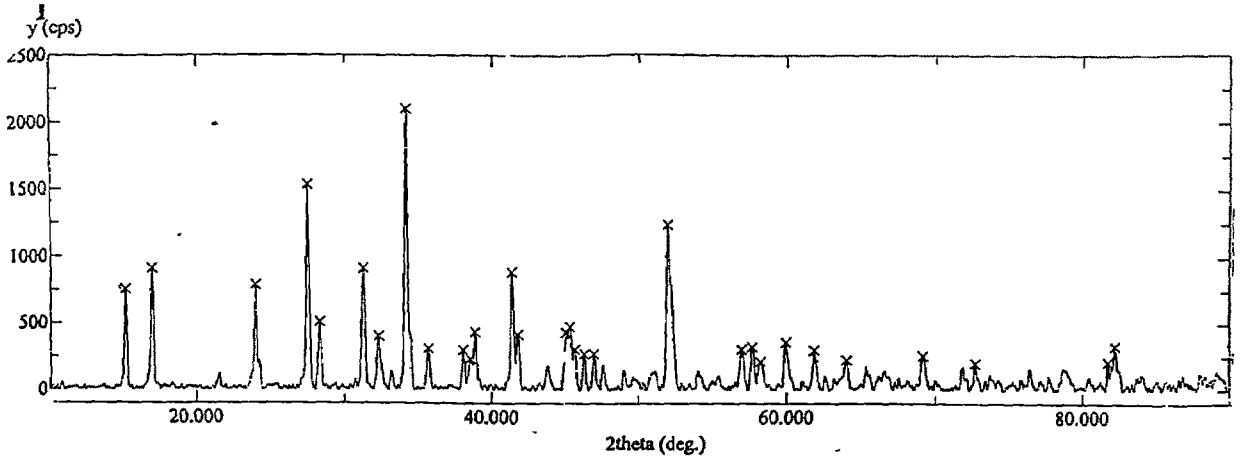

Fig 4.1 XRD Spectra of a Sample $Fe_{0.002}(Sb_2Se_3)$

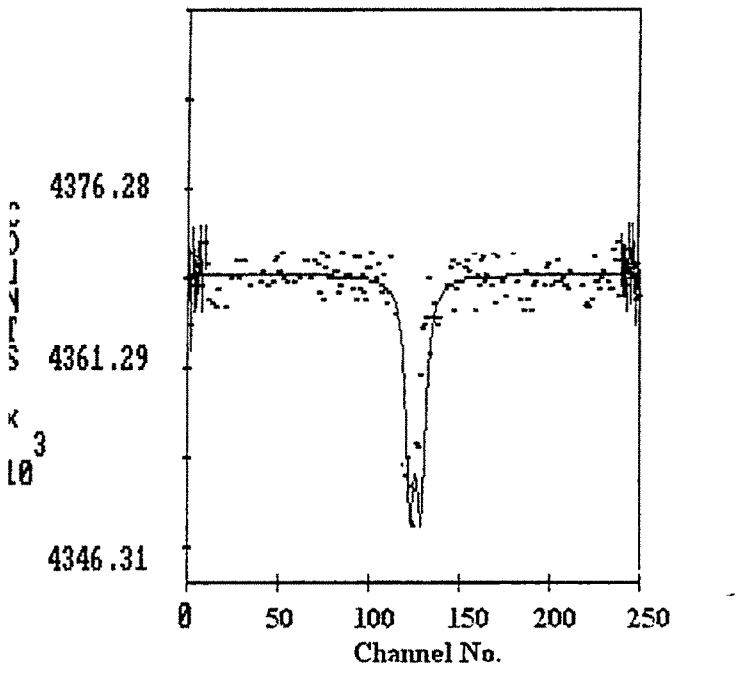

Fig 4.2 Mossbauer spectra of $Fe_{0.002}(Sb_2Se_3)$ at 300°K

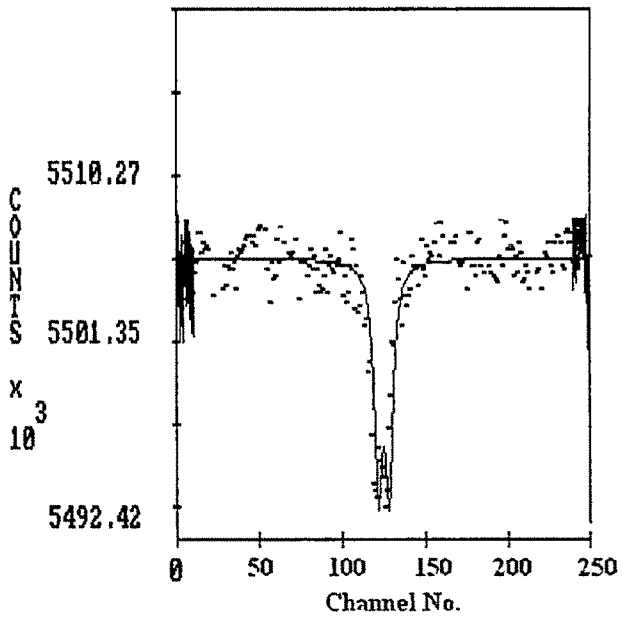

Fig 4.3 Mossbauer spectra of $Fe_{0.002}(Sb_2Se_3)$ at 373°K

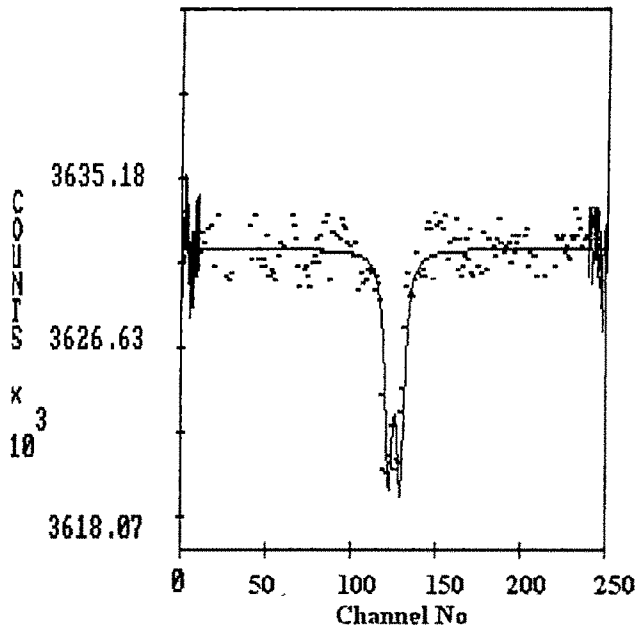

Fig 4.4 Mossbauer spectra of $Fe_{0.002}(Sb_2Se_3)$ at 473°K

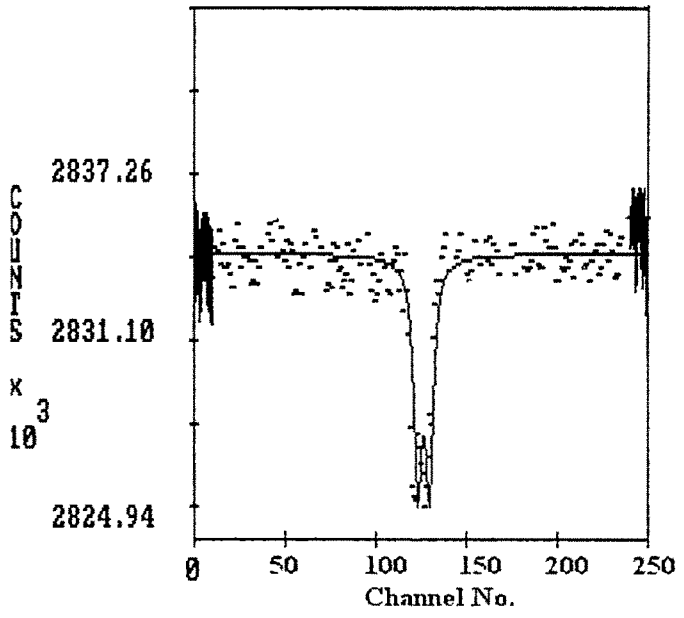

Fig 4.5 Mossbauer spectra of $Fe_{0.002}(Sb_2Se_3)$ at 573°K

other compound of Fe & Sb or Fe & Se, hence presence of any of those phases like FeSe, $FeSe_2$, $FeSb_2$, FeSb in present sample is ruled out.

The QS was found to be constant within experimental errors where as Isomer shift was found to be gradually decreasing over the temperature range studied from 300 to 573°K.The IS values indicate the Fe in 3+ charge state, hence Fe may be expected to be substituting Sb site in Sb_2Se_3. EFG in non-cubic systems have been parameterized in to conduction electron contribution and lattice contribution. Probability of transition of charge carriers from valence to conduction band with change in temperature is comparatively low in high Eg materials. Thus the electronic enhancement factor, i.e. V_{zz} (exp)/ V_{zz} (latt) seems to have a very slow response over the range of temperature studied. Thereby showing the EFG constant within experimental errors.

Temperature (K)	QS Mm/sec	Isomer Shift (mm/sec)
Room Temp	0.51 (0.02)	0.18 (0.01)
373	0.48 (0.02)	0.12 (0.01)
473	0.51 (0.02)	0.07 (0.01)
573	0.49 (0.02)	0.01 (0.01)

Table 4 Mossbauer parameters of the sample $Fe_{0.002}(Sb_2Se_3)$

Fig 4.6. Shows the plot of the Isomer Shift variation with increase in temperature. The isomer shift is found to decrease with increase in temperature in the studied temperature range.

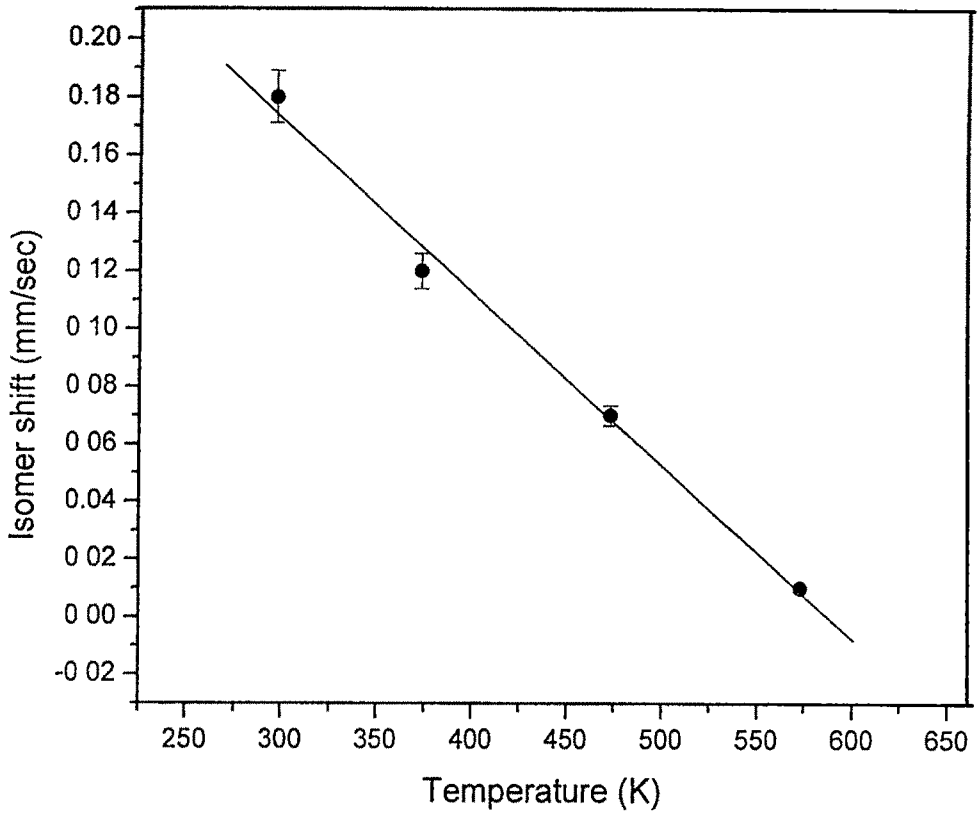

Fig 4.6 Plot of Isomer Shift vs Temperature

If the observed variation is due to the Second Order Doppler Shift (SOD), a least square fit to the experimental data in the high temperature region $T \geq \theta_D$ should give a slope of $-3k/2mc = -7.3 \times 10^{-4}$ mm/sec/K for ^{57}Fe[8]. The experimental data for the isomer shift of ^{57}Fe in Sb_2Se_3 system yields a slope of -5.6×10^{-4} mm/sec/K, which is different from the above expected value for SOD. Thermal expansion of the lattice can only decrease the s-electron density at the nucleus. Hence the observed temperature dependence of the isomer shift in this system can only be understood in terms of change in the character of occupied valance states as a function of temperature.

References:

1. Kaufmann, E.N and R.J.Vianden; Review of Modern Physics. 51 (1979)161

2. W. Witthuhn; Hyperfine Interactions. 24-26(1985)547-564.

3. J Christiansen et.al Z.Phys. B24 (1976) 177

4. H. Barfuss , G Bohnlein, H. Hohenstien and A Reiner, Z. Phys B 45 (1982)193

5. H. wolf and D.Forkel, Private Communications

6. A Svane, Physical Review B, 68 (2003) 64422

7. CRC Hand book of Physical Quntities, I.S.Grigoriev, E.Z.Meilikhow.

8. K. Venugopalan, Thesis, M.L.S.University, Udaipur, India . 1984