Chapter 3

Experimental Methodology

3.1 Introduction:

This chapter discusses the experimental technique used in the present work. The present study was done using the Fe-57 Mössbauer spectroscopic technique. One of the most important features of this technique is its good energy resolution. This is of the order of 10^{-13} for Fe-57 due to extremely small line width. This unique feature enables Mössbauer resonance to see even a slight change due to Hyperfine interaction present in samples.

3.2 Mössbauer Setup:

The basic Mössbauer setup consists of a radioactive source, a resonant absorber and a radiation detector. This experiment can be performed in two geometrys, the transmission geometry and the scattering geometry. The transmission geometry is extensively used because of its simplicity in Hyperfine interaction studies. In this geometry the source is mounted in a carriage which is moved with a velocity V with respect to the absorber and a detector detects the radiation that passes through the absorber. If the source and the absorber are made of identical atoms and the source is at rest with respect to the absorber, both the emission and the absorption line overlaps exactly and detector will get less radiation, and a minimum intensity is observed. For observing resonance

absorption the source is given a velocity so that the overlapped region becomes smaller and the transmitted intensity increases. Here a Doppler velocity

$$\Delta E = (V/C)\, E\gamma$$

Where V is the velocity given to the source of γ-ray, which is of the order of a few mm/sec. Eγ is the γ-ray energy i.e. 14.4 KeV in case of Fe-57.

There are basically two methods for measuring the transmitted γ-rays intensity at different velocities:

1. By imparting constant velocity to the source and measuring the total number of transmitted photons for a fixed time and repeating the same at other velocities. Here a step wise scanning of velocity is done.
2. The whole velocity range is scanned in the constant acceleration mode in one go and this process is repeated numerous times.

The constant velocity spectrometers now used only for special purposes. In case of a constant acceleration mode spectrometer an electromechanical drive system is used. In order to drive the system i.e. to provide the Doppler velocity, suitable waveform is applied to the coils. The waveform can be a saw tooth or a triangular waveform. The γ-ray intensity is stored in a Multi Channel Analyzer (MCA) as they pass through the absorber for every velocity given to the source.

The present study was made with a constant acceleration mode spectrometer having triangular wave to drive the transducer. The advantage to use a triangular wave is that the spectrum at the two halves is mirror image of each other. They can be folded to get double the data.

The Mössbauer system can be divided into different parts:

1. The Mössbauer source and absorber
2. The Drive Unit
3. The γ-ray detector
4. The data acquisition system

Block diagram of a typical Mossbauer setup is shown in figure (3.1A).

1. The Mössbauer source and absorber :

The Mössbauer source used in this study is Co-57. The decay scheme of the radioactive Co-57 is shown in the Figure (3.1B). Here the excited state at 136.32 KeV is populated by electron capture with 99.8% efficiency from Co-57. The 14.4 KeV γ-transition occurs between the excited state of spin 3/2 to ground state spin ½. The lifetime of the 14.4 KeV state is 99.3 ns corresponding to natural line width of 0.192mm/sec.

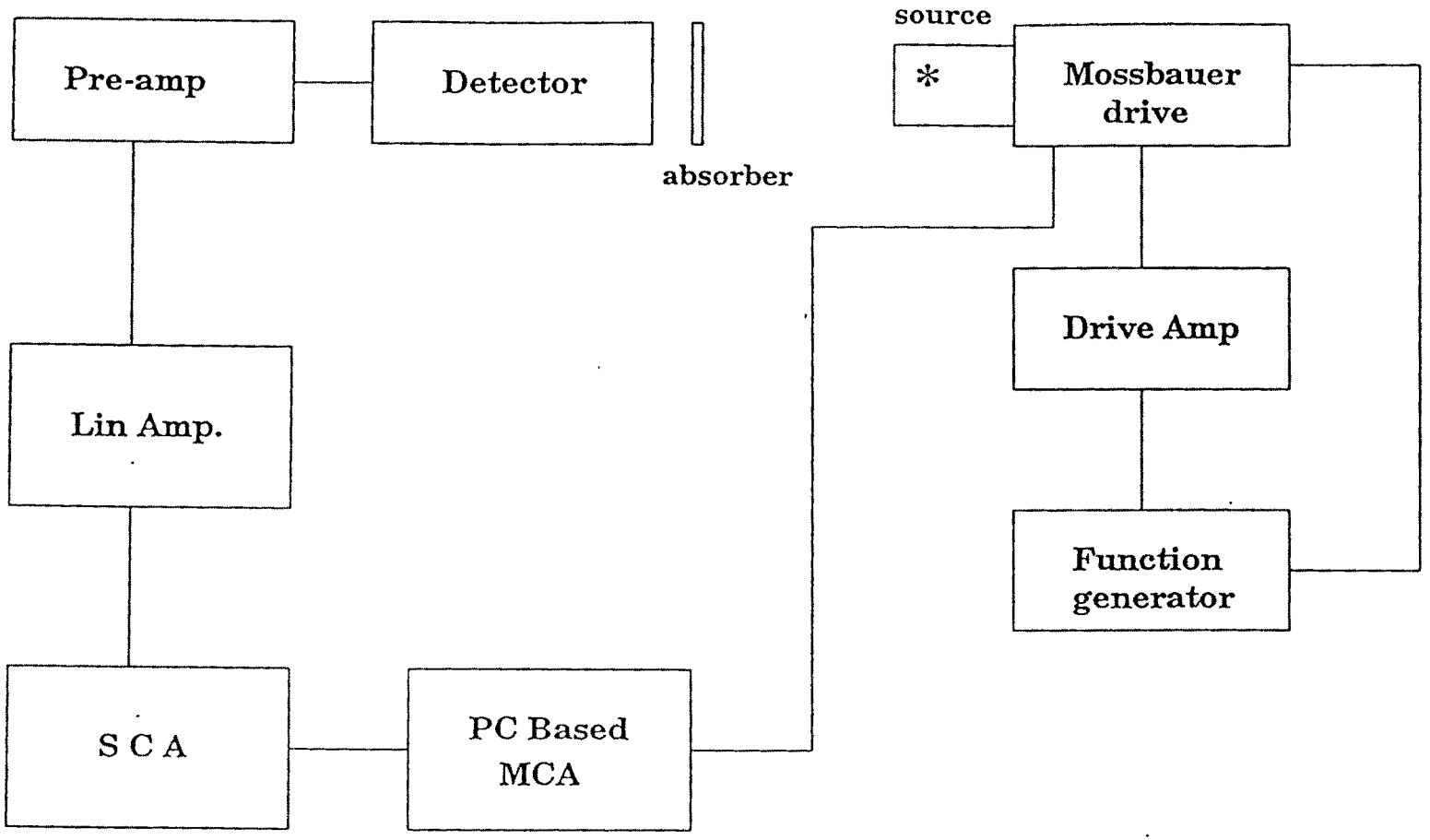
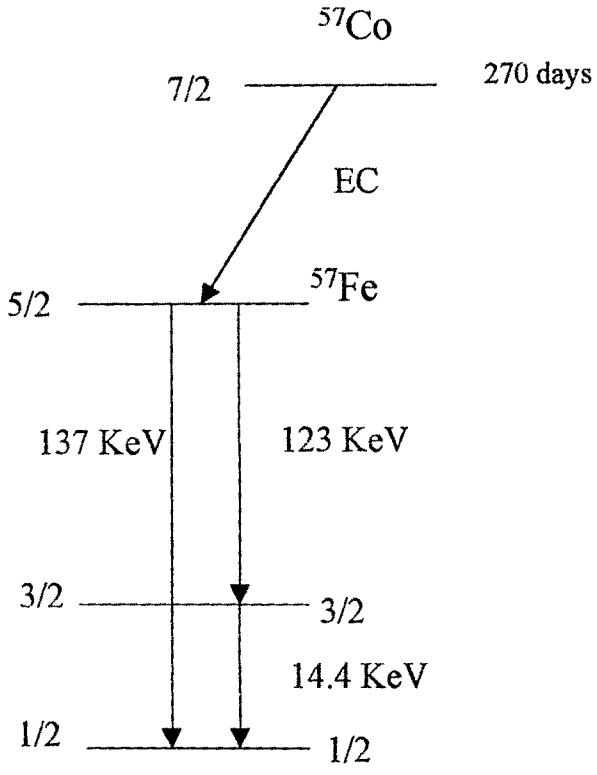


Fig. 3.1 A

Block Diagram of Mossbauer Spectrometer



(Decay scheme for Co-57)

Fig. 3.1B

In Mössbauer study the source should have a line width corresponding to the natural line width. Co-57 diffused in Rh matrix is one of the Mössbauer sources, which has high recoil free fraction and narrow line width. Fe-57 is formed by electron capture in Co-57. Fe-57 formed is in the excited state and three γ-rays 14.4Kev, 123Kev and 137 KeV are emitted on decay to stable ground state. In addition to the γ-rays, X-rays of 6 KeV are emitted as a consequence of the electron vacancy created after electron capture. The present study was done with a 50 mCi source.

The Mössbauer absorbers used in the present study were Antimony based dilute alloys having different Fe concentrations. The isotopic abundance of Fe-57 bin natural Fe is only 2%. Hence the very low concentration samples were made with enriched Fe-57 obtained from Oakridge national Lab., USA enriched upto 95%. Mössbauer absorbers were prepared from finely ground powders of the samples. The thickness of the absorber was optimized to avoid the broadening of the lines. The distance between the source and absorber were kept in such a way as to compromise between counting rate and parabolic effect.

2. The Drive unit:

The velocity transducer used to impart Doppler velocity to the source of γ-rays, was controlled by a drive unit controller. The velocity transducer is a

moving coil in a constant magnetic field. There is also a second coil, which is used to get a feedback for any aberrations in velocity. This is fed to the Mössbauer drive controller for error in velocity and consequently correction is done. The maximum velocity that can be imparted to the source is ±25 mm/sec with a high degree of linearity.

A constant acceleration mode is used to drive the velocity transducer. The velocity of the driving coil is changed continuously from –V to +V in one cycle. Here a symmetric triangular wave is generated of frequency 10Hz. In this case the whole velocity range is divided into two parts, one part being the mirror image of the other. Hence spectrum can be folded to get double the data.

3. The γ-ray detector :

Sealed proportional counters are the best for the transmission Mössbauer spectroscopy, which possess speed, resolution and selectivity. Here a sealed proportional counter filled with krypton gas was used to detect 14.4KeV γ-rays. The proportional counter consists of metallic container (cathode) with a thin electrode (anode) in centre carrying positive bias voltage.

4. The Data Acquisition system:

The data acquisition was done through a Multi Channel Analyzer in multiscaling mode (MCS) coupled with the Mössbauer spectrometer controller. Each channel of the analyzer is opened and closed at a clock controlled rate. An external oscillator whose frequency is a multiple of the frequency of the driving signal scans through the channels of the analyzer. The spectra were recorded in 512 channels and folded to get in 256 channels. The Mössbauer data acquisition system separates the desired signals from those having other energies. The pulse from the detector is weak. Hence amplification of the signal has to be done. This is done in two steps: The preamplifier and the amplifier. The amplifier output is fed to the linear gate which has upper level discriminator and a lower level discriminator to allow the selection of the pulses produced by the desired γ-ray, in this case 14.4 KeV. The linear gate delivers both a linear signal and a TTL signal, which is used for counting in the MCS mode.

3.3 The Velocity Calibration:

To obtain reliable Mössbauer parameters the drive velocity should be precisely known. Different velocity per channel can be set by using the amplitude knob of the drive unit. A maximum of ±25mm/sec can be obtained with a high

degree of linearity in maximum dial settings. Atypical velocity calibration spectrum is given in Fig. 3.1 C.

3.4 DATA ANALYSIS:

The samples studied in the present work showed both quadrupole as well as the magnetic hyperfine interactions. A lorentzian curve fitting program developed by Meerwal was used to fit the data. The fitting procedure used in this program was selected to yield a maximum region of convergence in the presence of strongly overlapping lines. The minimum in χ^2 is tested by specifying a number of random parameter displacements, after each of which a new fitting cycle is initiated, retaining the optimum parameters.

The mathematical function used to fit the data has the form

$$F(x,P) = P_{L+1} + \sum_{j=3m-2}^{L} P\ (P_j,\ P_{j+1},\ P_{j+2},\ x)$$

Where P_{L+1} represents a background and P_j, P_{j+1}, P_{j+2} are the centroid, full height and FWHM respectively of the m^{th} line. The function F has the lorentzian form

$$F(P_j,\ P_{j+1},\ P_{j+2},\ x) = P_{j+1}\left\{\frac{4(x-p_j)^2}{P_{j+2}}+1\right\}^{-1}$$

Calibration Mossbauer Spectrum of Natural Fe

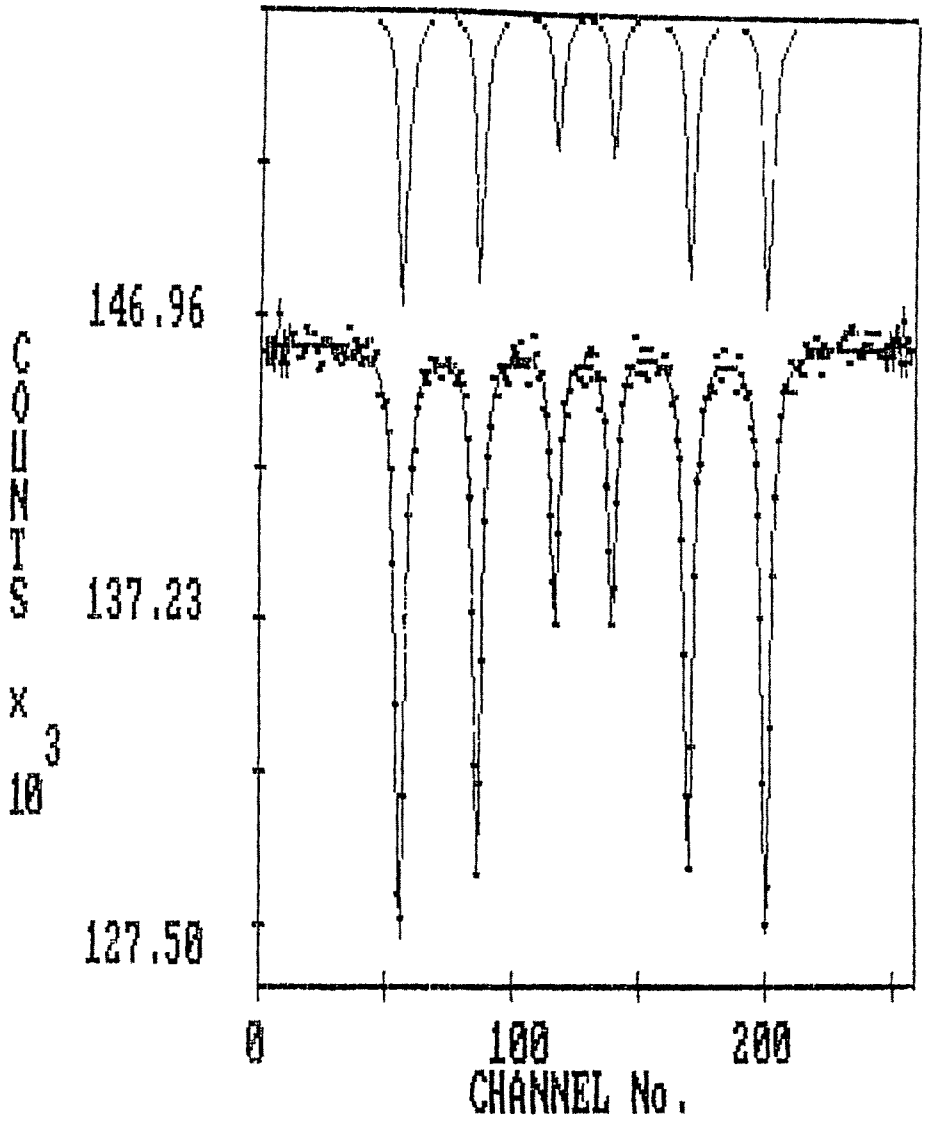


Fig. 3.1 C

The computer analysis of the Mössbauer data yielded peak position, intensity, line width, and the total area of the spectrum. From these parameters the value of the Isomer shift, Quadrupole splitting, line width and Magnetic Interaction strength were evaluated using the velocity spectrum.

The parabolic effect was nullified by folding the two halves of the data, which are the mirror images of each other.

3.5 Neutron Depolarisation Setup:

Neutron depolarisation study is an excellent tool to probe the magnetic inhomogeneity of samples (2-9). 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. As the neutron depolarisation technique probes the magnetic inhomogeniety on a mesoscopic length scale, a magnetic inhomogeniety on an atomic scale-as in true spin glass state- has no effect on the neutron polarisation. In a true spin glass phase, the spins are

randomly frozen in space on a mesoscopic length scale and, as a result the magnetic induction averages out to zero on a mesoscopic length scale. Hence no depolarisation is found in true spin glass systems.

Similarly no depolarisation is expected in a paramagnetic state because the temporal spin fluctuations is too fast ($_{10}^{-12}$s or faster) for the neutron polarisation to follow the variation in the magnetic fields B acting on the moving thermal neutron. However, 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.

From the observed depolarisation an estimate of the average size of domains/clusters can be made by using the expression (1)

$$P_f = P_i \exp\left(-\alpha\left(\frac{d}{\delta}\right)\langle\Phi_\delta\rangle^2\right)$$

where P_i and P_f are initial and final neutron beam polarisation, α is a dimensionless quantity $\approx$ 1/3, d is the effective thickness of the sample, δ is the average domain length scale and the precession angle $\Phi\delta = 4.63 \times 10^{10}\ \delta\lambda\beta$ (G-1 Å-2). The internal mean induction B(G) = $4\pi M\rho$ within a domain at low temperature can be determined from the bulk magnetisation measurements. Here

M is the spontaneous magnetisation in emu/g and ρ is the density of the material in g/cm^3. The equation is valid with the assumption that the Larmor precession angle of the neutron spin due to the internal magnetic fields of the sample is small fraction of 2π over a typical domain/cluster length. The value of $\Phi\delta$ for a 1.205 Å neutron in a 10μm Fe domain (B ~ 20 KG) is ~1.1 rad. However, a better quantitative estimate of the domain size can be obtained by measuring the wavelength dependence of the transmitted neutron beam polarisation P(λ) (2)).

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.

References :

1. E.V. Meerwal, Comp. Phys. Commun., 9, 117, 1975.
2. G. Halperin and T. Holstein, Phys. Rev., Vol. 59, (1941), p-960.
3. S. Mitsuda and Y. Endoh, J. Phys. Soc. Jpn., Vol. 54, (1985), p-1570.
4. I. Mirebeau, S. Itoh, S. Mitsuda, T. Watanable, Y. Endoh, M. Hennion and P. Calmettes, Phys. Rev., Vol. B44, (1991), 5120.
5. Yusuf S.M., L. Madhav Rao, P.L. Paulose and V. Nagarajan, J. Magn. Magn. Mater, Vol. 166, (1997), p-349.
6. Yusuf, S.M. and L. Madhav Rao, J. Phys. Condens. Matter, Vol. 7, (1995), p-5891.
7. Yusuf, S.M. and L. Madhav Rao, Pramana J. Phys., Vol. 47, (1996), p-171.
8. Yusuf, S.M. L. Madhav Rao, R. Mukhopadhyay, S. Giri, K. Ghoshray and A. Ghoshray, Solid State. Commun. Vol. 101, (1997), p-145.
9. Rao, Madhav L, S.M. Yusuf and R.S. Kothare, Indian J. Pure and Appl. Phys., Vol 30, (1992), p-276.