CHAPTER 2

EXPERIMENTAL TECHNIQUES
This chapter describes the experimental methodology of Mössbauer spectroscopy, Ferromagnetic resonance, and AC susceptibility measurements and the specific instruments employed to investigate the alloy systems using these techniques. Data analysis procedures for Mössbauer spectra are described in detail. The method of alloy preparation, heat treatments and characterisation are also given briefly.

2.1. MöSSBAUER SPECTROMETER

The Mössbauer spectra are recorded on a µP based Mössbauer spectrometer [1] in the standard transmission geometry in zero external magnetic field. The spectrometer operated in constant acceleration mode. A $^{57}$Co in Rh matrix source is used. The block diagram of the spectrometer is shown in Fig. 2.1. It consists of the following basic blocks:

a. Velocity Drive and Feedback System

b. Gamma Ray Detection System

c. µP based Data Acquisition System

These three blocks are described in detail as follows:

2.1.a. Velocity Drive and Feedback System

The velocity drive is an electromechanical transducer (Nuclear Electronics, Hyderabad) and is based on Kankeleit design [2]. The drive consists of a coil (energising coil) connected to a rod on which the radioactive source is mounted. An electronic
Fig. 2.1. Block diagram of Mössbauer Spectrometer,
circuit generates triangular wave form from a square wave fed to it from multi-channel scalar (MCS). This coil carries the driving signal in a magnetic field, provided by the permanent magnets fixed in the drive. The rod is held with a spring to the body of the transducer on either side. The movement of the coil does not duplicate the driving signal due to the complicated response of the transducer. A pick-up coil is also connected rigidly to the rod. When the transducer moves, there is a change in the flux and produces an induced emf. This induced emf is proportional to the velocity of the drive. In other words the voltage in the pick-up coil gives a scaled replica of the velocity. This voltage is taken to the error stage of the feedback and power amplifier and is compared with a standard velocity wave form. The feedback loop set-up adjusts in such a way that the difference between the pick-up signal and reference signal is zero. A constant acceleration mode is used in which velocity wave form is either triangular or sawtooth.

2.1.b. Gamma Ray Detection System

To detect the gamma rays which are transmitted from the sample, a gas filled proportional counter (Ranger Scientific, Inc., USA, Model PA-900) is used. This has a gas filling of 97% Xenon - 3% CO₂ at 2 atm. pressure and a Beryllium entrance window of 0.01 inch thickness. The detector bias required is in the Kilo-volt range with small current capacity (≤ 1 mA). A high voltage power supply (ECIL, India, Model HV 4286A) which operates in Kilo-volt range is used. The proportional counter has a very
high impedance (in Mega-Ohms). The input impedance of the spectroscopy amplifier (ECIL, India, Model PA572) is low and results in a drop in voltage at the input of the amplifier if the counter and amplifier are connected directly. To match the impedance, a preamplifier (EG&G ORTIC, USA, Model 142 PC) with low output impedance and high input impedance whose gain is of the order of unity is used. The spectroscopy amplifier amplifies the output of the preamplifier to a few volts. Wave shaping is also carried out at this stage. The output of the amplifier is given to single channel analyser (ECIL, India, Model SC 604). The single channel analyser is an energy discriminator i.e., it rejects all pulses which are outside the extremities of the set energy window. For Fe Mössbauer experiments we use 14.4 keV radiation of $^{57}$Fe. We have used single channel analyser window to cut the other X-rays and gamma rays so that signal-to-noise ratio can be improved. A pulse height spectrum is first recorded and the appropriate gamma energy (14.4 keV) is chosen by setting the window (setting lower level discriminator and upper level discriminator) of the single channel analyser.

2.1.c. µP based Data Acquisition System

The input to the data acquisition system is in the form of standard pulses which are generated at the output of the single channel analyser. The number of these pulses are a function of drive velocity and these can be stored in a conventional multi-channel analyser (MCA), which works in the time mode or multi-channel scaling (MCS) mode. The MCS is a mode in which the counts
are stored at different times in different memory locations. Here, times means the times at which the drive remains between two velocities v and v+dv. The velocity of the drive is divided into small intervals of times (memory locations or channels) in which the counts are stored. Usually the number of channels are 256, 512 or 1024. We have chosen a 1024 channel spectrum (512+512) to record Mössbauer data using a home built data acquisition system based on a 8085 Intel microprocessor [1]. The important feature of this system is its low dead time (0.15 μsec per channel). Dead time is the time required by the processor to get data from the buffer counter, to transfer it to the memory and then clear the buffer counter for fresh counts. A low dead time has been achieved by implementing the flow chart of Fig. 2.2 using the 8085 microprocessor. In this algorithm the 8253 counter of the microprocessor is loaded with a number. It is down counted at every input pulse from the detector. The difference in counts between the beginning and end of dwell time is the number of counts accumulated in that time. The counter is read at the beginning and end of dwell time very quickly (in half a clock pulse of the microprocessor) without resetting it by using "on the fly" instruction. The down counting goes on during the next dwell time but meanwhile the difference in counts accumulated in the previous dwell time is put in the appropriate memory location. Thus a very low dead time is achieved. Data is transferred to the PC through RS 232 in the asynchronous mode. The data received at the PC is stored in an ASCII file after converting the hexadecimal values to decimal. The program to run the spectrometer, to collect and transfer data has been loaded on the EPROM.
Fig. 2.2. Flow chart to implement low dead time in data acquisition.
Everytime, whenever we run the spectrometer we copy this program on the RAM and run it.

2.1.1 Low Temperature Measurements

The Mössbauer spectra in the temperature range 35 K – 300 K are recorded using a closed cycle variable temperature Mössbauer cryostat (Cryo Industries of America, Inc., USA, Model No. REF-399-D22). Fig. 2.3. shows the diagram of the cryostat. Vibration free bellows are provided to make the sample free from vibrations which are coming from the movement of the displacer. The flange just above the vibration free bellows is fitted to a rigid stand. This stand is fixed to a heavy table and table is isolated from any vibration on the floor by mounting on vibration free mountings. The whole cryostat is rigidly clamped on a concrete pillar. The sample is fixed to a hole in copper plate which is attached to one end of the stainless steel tube. This stainless steel tube is mounted in the cryostat such that the mylar windows and sample are in a line as shown in Fig. 2.3. The r-rays pass through the mylar windows and sample and are detected by the detector on the other side. The sample temperature is controlled with a temperature controller (Lake Shore Cryotronics, Inc., Model DRC 80C) using a silicon-diode sensor. The sample is heated with a heater which is wound just above the copper plate. Helium gas is used as exchange gas to make contact between the sample and cold head. The temperature stability is ± 0.5 K. Some of Mössbauer spectra at low temperatures (10 K – 300 K) are recorded at Low Temperature Physics Group Laboratory, TIFR, Bombay, using a continuous flow
Fig. 2.3. Set-up for Variable temperature Mössbauer experiments using closed cycle refrigerator (Model REF-399-D22, Cryo Industries). 1: Source mounted on the drive, 2: Detector, 3: Copper plate with sample, 4: Silicon diode sensor, 5: Heater, 6: Exchange gas inlet, 7: Bellows, 8: Flange, 9: Rigid stand, 10: Electrical feed-thru, 11: Heavy steel plate, 12: Cold head, 13: Heavy table, 14: Helium tubes, 15: Foundation, 16: Compressor.
cryostat (Lake Shore Cryotronics, Inc., Model 310).

2.2. MOSSBAUER DATA ANALYSIS

For calibration runs and simple well resolved spectra a commercial Fast Fourier Transform (FFT) program (supplied by Ranger Corporation) is used to determine line positions, widths and intensities of the absorption peaks in the Mössbauer spectrum. When the spectrum consists of two or three sets of distinct hyperfine field split six line patterns at different field values, the FFT program can not be used due to the presence of several lines. For such complex spectra a stripping method is evolved which consists of the following steps for a spectrum arising from two hyperfine fields.

(i) In the first step, the approximate value of the outer field is estimated by a visual inspection of the experimental spectrum. The spectrum corresponding to outer field is subtracted from the overall experimental spectrum to get a single stripped spectrum corresponding to a lower field. This is fitted to a six line pattern using FFT program to get the line positions, widths, and intensities of the spectrum.

(ii) In the second step, the spectrum generated for the inner field using the parameters obtained in the first step is subtracted from the experimental spectrum to get the stripped spectrum for the outer field alone. This was again least square fitted using FFT program to get the fitted parameters for this
outer field.

(iii) The **spectrum** generated for the outer field using the fitted parameters in the step (ii) is once again subtracted from the experimental spectrum to get the spectrum for the inner field. This is least square **fitted** to get improved estimates of parameters for the inner spectrum. These improved parameters are used to get the stripped spectrum for the outer field.

(iv) This procedure is continued till the best fit parameters are obtained. Finally, the two stripped spectra are **combined** and the complete spectrum for the inner and outer fields is **generated**.

Spectra which consist of strongly overlapping and widely distributed fields are **analysed** using model independent field distribution analysis [3-6]. In Window's method the field distribution is expanded in a Fourier series

$$P(H) = \sum_{n=1}^{N} a_n \left[ \cos(n\pi H/H_{\text{max}}) - \cos n\pi \right] \quad (2.1)$$

The Mössbauer spectrum generated at velocity $v$ due to this distribution is given by

$$S(v) = \int_{0}^{H_{\text{max}}} P(H) L_6(v, H) dH \quad (2.2)$$
where \( L_6(v, H) = \sum_{i=1}^{6} \frac{\Gamma_i/2}{(\Gamma_i/2)^2 + (v - \alpha_i H)^2} \)

is the normalised shape function of the lines of a component spectrum for field \( H \), \( \Gamma_i \) are the linewidths of the six lines of the component spectrum and \( \alpha_i H \) are their positions. If the experimental spectrum is denoted by \( \tilde{W}(v) \), the coefficients \( a_n \) of the field distribution are found by minimising the function

\[
\phi = \sum_v [S(v) - \tilde{W}(v)]^2
\]

with respect to the parameters \( a_n \).

In the method proposed by Hesse and Rubertsch [5] and its modification by Le Cäer and Dubois [6] the range of hyperfine field is divided into \( N \) equal intervals \( AH \) with \( H_n = n\Delta H \) and the calculated spectrum is written as

\[
S(v) = \sum_{n=0}^{N} P(H_n) L_6(H_n, v) \quad (2.5)
\]

The probability for each field \( H_n \) is then obtained by minimisation of difference in calculated and experimental spectrum based on the procedure of Phillips [7] and Twomey [8]. The improvements in this procedure made by Le Cäer and Dubois avoid problems of non-physical negative value of probability density which can sometimes arise if the background is not well defined.

It has been suggested [9] that one can assume the true dis-
tributions of hyperfine fields to be represented simply by a sum of \( m \) Gaussians

\[
P(H) = \sum_{i=1}^{m} A_i \exp \left( -\frac{(H - H_i)^2}{2\sigma_i^2} \right)
\]  

(2.6)

with different positions \((H_i)\), widths \((\sigma_i)\) and weighting factors \((A_i)\). This seems to work well because hyperfine field distributions obtained from model independent analysis are Gaussian shapes to a good approximation. The advantage is that less number of variables can be used in carrying out the fits, since usually two or three Gaussians suffice to fit the data. The optimised parameters of the Gaussians viz. position, intensity and width are obtained by minimising chisquare. A grid search method works efficiently once initial guesses of the parameters are obtained from some model independent field distribution analysis as outlined earlier.

2.3. FERROMAGNETIC RESONANCE SPECTROMETER

A commercial ESR spectrometer [JEOL FE-3X, Japan] operating in the X-band with a fixed microwave frequency of \( \approx 8.23 \) GHz is used for FMR measurements. The block diagram of the ESR spectrometer is shown in Fig. 2.4. A klystron tube is used to generate the microwave radiation which passes as a linearly polarised beam through a wave guide. After traversing a ferrite isolator, which prevents the back reflections, and a variable attenuator, the beam is divided into arms 2 and 3 at a magnetic tee or hybrid tee
Fig. 2.4. Block diagram of FMR Spectrometer used in the present work (JEOL, FE-3X).
so that there is no net transmission into arm 4 of the microwave 
bridge. The sample is placed in a cavity resonator that is posi-
tioned between the pole pieces of an electromagnet. The electro-
magnet produces a steady uniform magnetic field which can be 
swept at a constant rate. The sample is then exposed to a trans-
verse microwave field of constant frequency. When the resonance 
condition is fulfilled, sample absorbs a part of the microwave 
energy and the \textbf{Q-value} of cavity resonator changes. The imbalance 
of the bridge occurs so that transmission into arm 4 takes \textbf{place}. 
The signal is detected by crystal detector, then amplified and 
displayed on an oscilloscope or graphic recorder. In the off-
resonance condition, the reference wave is so \textbf{adjusted} to give a 
reflection equal in amplitude and opposite in phase to the re-
fection from the \textbf{sample} and cavity, sending zero power to arm 4. 
The magnetic field can be \textbf{modulated} with a low frequency 
(100 kHz) modulation which gives a first derivative representa-
tion of the microwave power with respect to the \textbf{field} (dP/dH).

The sample is mounted in \textbf{sandwiched} mode as shown in 
Fig. 2.5. The sample is first cleaned with ethanol and mounted in 
the groove of the flat surface of half-cut portion of the quartz 
rod at one end (Fig. 2.5a). The sample is sandwiched with a small 
flat quartz piece by placing on the sample. The \textbf{copper-constantan} 
thermocouple is attached to the quartz rod in such a way that the 
thermocouple bead could touch the sample (Fig. 2.5b). The whole 
assembly is slowly inserted in a quartz tube (Fig. 2.5c), which 
is then inserted into the cavity. The cavity is provided with a 
goniometer arrangement which enables the rotation and orientation
Fig. 2.5  a. Quartz rod with a half cut at one end and a groove to place the sample.
b. Sample is sandwiched between the half cut end of the quartz rod and quartz piece. Copper-constantan thermocouple is attached to the quartz rod.
c. The quartz rod with sample and thermocouple is pushed into a quartz tube.
of the sample plane at specific angles with respect to the external field. FMR measurements are carried out in two sample geometries (Fig. 2.6) - (i) horizontal-parallel ($\|^h$), in which the external field $H$ lies in the sample plane and directed along the length of the sample, (ii) vertical-parallel ($\|^v$), in which $H$ lies in the sample plane and is directed along the breadth of the sample. FMR spectra consist of recording the power absorption derivative (dP/dH) curves as a function of external static magnetic field $H$ as shown in Fig. 1.10.

The low temperature (100 K - 300 K) FMR measurements are carried out with a variable temperature accessory. The sample is cooled with cold nitrogen gas, obtained by boiling liquid nitrogen, circulated through the cavity. The temperature outside the microwave cavity is measured with a pre-calibrated copper-constantan thermocouple at every set temperature by regulating the cold nitrogen gas flow. A proper gas flow regulation is achieved by controlling the power input to a heater, immersed in the liquid nitrogen container, with the help of PID controller. The accurate temperature of the sample is monitored with a pre-calibrated copper-constantan thermocouple in physical contact with the sample. The temperatures above room temperature (300 K - 500 K) are achieved by sending hot air through the cavity with the help of a compressor. The spectra at 77 K are recorded by immersing the sample in liquid nitrogen, contained in a tailed dewar, which had been inserted into the cavity.
Fig. 2.6 a. Horizontal-parallel (∥) sample geometry in which the static magnetic field $H$ lies in the sample plane and is directed along the length of the sample.

b. Vertical-parallel (\(\perp\)) sample geometry in which the static magnetic field $H$ lies in the sample plane and is directed along the breadth of the sample.
2.4. AC SUSCEPTIBILITY

AC susceptibility (ACS) measurements in the temperature range 10 K - 400 K are carried on the same samples which are used for FMR measurements. The mutual inductance technique at a fixed frequency of 33 Hz is used. AC magnetic field, \( H = 0.5 \text{ Oe} \) without superimposed dc magnetic field is applied in the primary excitation coil. The resistance of the primary coil is 35 \( \Omega \). The secondary consists of two closely matched and oppositely wound coaxial coils. In the absence of the sample, the voltages induced at the two secondary coils cancel each other. The sample is placed in one of the coils and the difference between the voltages induced in the coils is measured using dual phase lock-in-amplifier (Model 5210 from PARC) in the A - B mode. The reference signal is derived from a 1 k\( \Omega \) resistor in series with the primary coil. The in-phase and quadrature phase signals give the loss (\( \chi'' \)) and inductive (\( \chi' \)) components of the complex ac susceptibility \( x = X' - ix'' \). The sample is cooled to 10 K with a closed cycle refrigerator (APD Cryogenics Inc., USA, Model HC-2). The cold head tip temperature is controlled using a small heater present on it and silicon diode sensor near to it. The sample temperature is controlled with a silicon diode sensor present near the sample. The cold head and sample temperature are controlled with a microprocessor based temperature controller (5500 series from Scientific Instruments Corporation). The temperature stability is \( \pm \) 30 mK. To obtain the accurate value of the sample signal, background (without sample) signal is measured throughout the temperature range and subtracted from the actual signal.
2.5. SAMPLE PREPARATION

The alloys studied in this thesis work are prepared by melting in an arc melting furnace (Materials Research Corporation, USA, Model AF-82C). To prepare the alloys of required composition, grade I purity iron powder (JMC Puratronic), m3N7 purity manganese chips, m3N5 aluminium shots, m3N nickel powder, m3N5 silicon powder and m3' 5 chromium powder (Alfa Division) are used. The elements in the powder form are mixed thoroughly in a mortar and pestle and compressed into a pellet applying a pressure of $8 - 10 \text{ tons/cm}^2$ using a hydraulic press. The pellet and chips and/or shots are kept together in a groove in the copper hearth of the furnace. The entire lower surface of copper hearth is cooled with a water flow of 2 gpm. The chamber is first evacuated to a pressure of 30 inches of Hg and flushed three times with argon gas to remove the residual gases. Finally, chamber is filled with argon at a pressure of 20 to 25 inches of Hg. Then the arc is generated from the tip of a water cooled movable tungsten electrode and is directed on to the materials kept in the groove end melting is done. The melt is reversed and melted again to ensure the homogeneity. The weight loss in melting process is calculated. The typical weight loss is approximately 2 – 5%.

The alloy ingots are sealed in quartz tubes under a pressure of 10 torr after flushing three times with argon gas and homogenised at required temperature for sufficient time. To prepare Mössbauer absorbers, a part of homogenised alloy ingot is filed
into coarse powder and subsequently ground into finer powder using mortar and pestle. The powders are sealed in quartz tubes under a pressure of $10^{-2}$ torr after flushing three times with argon gas and annealed for sufficient time at required temperature to relieve strains. Mössbauer absorbers are prepared from annealed powders after mixing with boron nitride powder and pressing into pellets. For FMR and AC susceptibility measurements, 3 samples of typical dimension $2 \times 1 \times 1$ mm are cut from the homogenised alloy ingots.

To prepare the disordered alloys of $\text{Fe}_{3-x} \text{Mn}_x \text{Al}_x$ alloys, the alloy ingots are homogenised and quenched from $1000^\circ$ C in liquid nitrogen. Some of the homogenised ingots of $\text{Ni}_{3-x} \text{Fe}_x \text{Si}_x$ alloys are splat quenched in an Edmund Bühler ultra quenching apparatus. Powder is prepared from the quenched ingot of $\text{Fe}_{1-x} \text{Mn}_x \text{Al}_x$ alloy and annealed at $300^\circ$ C for different periods of time to study the kinetics of disorder-order transformations.

2.6. CHARACTERISATION OF SAMPLES

The samples are characterised by powder diffraction on a Siefert Isodetyleflex Model 2002 X-ray diffractometer using CuK radiation. Some of the samples are also characterised using CoK and MoKα radiations. 2θ values are measured from the diffraction patterns. Then the d values, hkl values and lattice parameter(a) are calculated. In the case of $\text{Fe}_{1-x} \text{Ni}_x \text{Si}_x$ alloys, a previously available computer program [10] is used to calculate the lattice parameters and other parameters. In the case of $\text{Ni}_{3-x} \text{Fe}_x \text{Si}_x$ and $\text{Ni}_{3-x} \text{Mn}_x \text{Al}_x$ alloys, a previously available computer program [10] is used to calculate the lattice parameters and other parameters.
alloys, lattice parameter (a) values are calculated using Br?dley and Jay plots [11]. The value of `a` is calculated for each line in the x-ray diffraction pattern with indexed hkl values and are plotted against cos θ. By the extrapolation of a vs. cos θ plot to θ = 90°, the intercept on the ordinate gave the exact value of a.
REFERENCES