Chapter 2

EXPERIMENTAL TECHNIQUES
To characterize the materials prepared and study their properties several techniques have been used. The microstructural studies have been carried out with different techniques such as x-ray diffraction (XRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED) and energy dispersive x-ray analysis (EDX). Defects in the nanomaterials were characterized by positron annihilation as well as optical spectroscopy. \textsuperscript{57}Fe Mössbauer spectroscopy was employed to probe the local environment around the probe atoms. A SQUID magnetometer has been used to study the magnetic properties of the samples. A brief introduction of the characterization techniques involved in this work is given below.

2.1 X-ray diffraction

X-ray diffraction method is one of the most basic and non-destructive techniques used for structural analysis of crystalline materials. In 1912, Laue first conceived the idea that x-rays can be diffracted by crystals in the same way as the visible light is diffracted by a diffraction grating. In other words, crystals can be used as a diffraction grating for x-rays. To create significant diffraction, the spacing between the scatterers and wavelength of the impinging wave should be similar in size. Since x-rays have wavelength of same order (1-100 Å) as the spacing d between planes in crystals, they are used to produce diffraction patterns.

When a beam of x-ray strikes an atom, electrons of the atom begin to oscillate with a frequency equal to that of the incident radiation. As a result of this, electrons will produce spherical waves. This is known as elastic scattering and electron is the scatterer. A regular array of spherical waves can be obtained from a regular array of scatterers. However these waves cancel one another in most directions through destructive interferences, but there will occur constructive interferences in a few directions. These constructive interferences take place when the path length difference of the reflected beam is an integer multiple of the x-ray wavelength [1]. This condition is given by the well known Bragg law that is
\[ 2d \sin \theta = n\lambda \]  

(2.1)

Here \( d \) is the spacing between diffracting planes, \( \theta \) is the incident angle, \( n \) is an integer and \( \lambda \) is wavelength of the incident beam.

![Figure 2.1: Geometry for the Bragg equation.](image)

2.1.1 Debye Scherrer equation

X-ray diffractogram of a sample with nanometer dimension shows characteristic peaks with broadened lines. After incorporating the correction due to instrumental broadening, one can estimate the average crystallite size from the broadened peaks using Debye-Scherrer equation

\[ \langle D \rangle = \frac{0.9 \lambda}{B \cos \theta} \]  

(2.1)

where, \( B \) is the full width at half maximum of the diffraction profile. This equation has been used to calculate the average crystallite size of different nanomaterials in the present work.

2.2 Transmission electron microscopy
Electron microscope is a well known scientific tool which uses a high energy beam of electrons to examine objects on a very fine scale. Electron microscopy provides several important information such as topography (the surface feature of an object), morphology (the shape and size of particles), composition (elements and compounds that the object is composed of and relative amounts of them) and crystallographic information (how the atoms are arranged in the object) [2, 3]. The electron microscope uses electrostatic and electromagnetic lenses to control the illumination and imaging of the specimen unlike an optical microscope which uses glass lenses to focus light.

The principle of a transmission electron microscope is analogous to an optical microscope. Here, the sample is irradiated with an electron beam emitted from an electron gun. The electron beam illuminates the sample after passing through a two or three-stage condenser lenses. The objective lens provides the formation of either image or diffraction pattern of the specimen. The electron intensity distribution behind the sample is magnified with a series of lenses and is viewed on a fluorescent screen. The image is recorded either by a photographic plate or by a light sensitive sensor such as a charge coupled device (CCD) camera. The accelerating voltage of the electron beam decides the velocity, wavelength and hence the resolution of the microscope. Depending on the beam sample interaction and treatment of the electron beam an electron microscope can be categorized as (i) conventional transmission electron microscope (ii) high resolution electron microscope (iii) high voltage electron microscope (iv) scanning transmission electron microscope. In the resulting TEM image, dark area reveals the area of the sample where fewer electrons were transmitted through, whereas lighter area of image represents the area where more electrons were transmitted through.

The diffraction pattern can also be obtained from the very small selected region of samples.
either with a diffraction aperture (selected area electron diffraction) or by focused electron beam of nanometer size (convergent beam electron diffraction).

Figure 2.2: Schematic diagram of optics for (a) diffraction pattern and (b) image in a TEM.

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In the case of very small diffraction angle and large radius of Ewald sphere, Bragg equation can be written as
\[ \lambda = 2d_{\text{ml}} \theta \]  

(2.3)

since, \( \sin \theta \approx 0 \) for small angle.

\[ \tan 2\theta = \frac{R}{L} \approx 2\theta = \frac{R}{L} \]  

(2.4)

From the above figure,

\[ \lambda L = R d_{\text{ml}} \]  

(2.5)

\( \lambda L \) is called camera constant. Indexing of the obtained diffraction patterns by using the above equation can give information about the material.

\section*{2.3 UV-Visible absorption spectroscopy}

Absorption of radiation by matter is still one of the most popular techniques that is used for analytical application either qualitative or quantitative. The qualitative application of absorption spectrometry depends on the fact that a given molecular species absorbs radiation only in certain region of the spectrum where the radiation has the sufficient energy to raise
the molecule to some excited state. Absorption of visible and ultraviolet radiation results an excitation of electrons in both atoms and molecules to higher energy states. All molecules suffer electronic excitation following absorption of light, but for most molecules very high energy radiation will be required. The absorption rate in a medium depends on the number of photon collisions with absorbing atoms or molecules per unit time. Absorption of radiation is proportional to the path length of the radiation and the concentration of absorbing species. It can be described by Beer equation given below [4].

\[
\text{Absorbance, } A = \log \frac{I_0}{I} = \varepsilon b c
\] (2.6)

Where \( I_0 \) is the intensity of incident radiation, \( A \) is the absorbance, \( b \) is the path length in centimetre, \( c \) is the solution concentration in moles/litre, and \( \varepsilon \) is the molar absorptivity or molar extinction coefficient in litre/mole/cm. It can be seen that \( \varepsilon \) is a function of wavelength; it can be used to quantify the amount of chemical present in the medium. UV-1601PC UV-Visible spectrophotometer (Shimadzu, Japan) has been used for the absorption measurements in this work. The deuterium and halogen lamps are used as light source for UV and visible region respectively.

### 2.4 Photoluminescence spectroscopy

Photoluminescence (PL) spectroscopy is a powerful and non-destructive technique widely used for characterization of semiconductors. Photoluminescence spectroscopy provides detailed information about the electronic structure and more importantly the defects in the specimen. Essentially in a PL measurement, the sample is optically excited by the excitation sources which are having the photon energy more than the band gap of the material. Electron – hole pairs are created in the sample with the absorption of light. When excited electrons return to their equilibrium state then release energy that may be associated with emission of
light (radiative process) or may not give light emission (non radiative process). The energy of the emitted light corresponds to the energy difference involved in transition from the excited state to the equilibrium state. The energy of the emitted photon is characteristic of radiative recombination process. A typical PL spectrum consists of a plot between intensity and energy. Fluorescence measurements in the present work were done using a Perkin Elmer Luminescence Spectrometer (Model No. LS-55). A 20 kW discharge xenon lamp of 8μs duration and pulse width at half height < 10μs was used as the source for excitation of the samples. All measurements were carried out using a quartz cuvette of 1x1 cm² dimension supplied by Perkin Elmer. The fluorescence signals were collected at right angle to the incident light.

2.5 Fourier transformed infrared spectroscopy

Infrared (IR) spectroscopy is an important and an efficient analytical technique to characterize samples. Infrared spectroscopy examines twisting, bending and vibrational motion of atoms in a molecule. When infrared radiation is directed on a molecule, it will absorb the radiation at a particular wavelength. The resulting spectrum represents the fingerprint of the molecule with absorption peaks which correspond to frequencies of vibrations between the atoms making up the molecule. Since each molecule is a unique combination of atoms thus it has its own distinct quantized vibrational energy levels. Therefore infrared spectrum can provide qualitative analysis of any kind of material [4, 5].

The original infrared instruments were of the dispersive type and slow scanning was main drawback of this method. To overcome the encountered problems in dispersive instrument, Fourier Transform Infrared (FTIR) spectrometry was developed. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal that has all of the infrared frequencies
"encoded" into it. The signal can be measured very quickly, usually on the order of one second or so. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes. Most interferometers employ a beamsplitter which takes the incoming infrared beam and divides it into two optical beams. One beam reflects off of a flat mirror which is fixed in place.

![Schematic of FTIR spectrometer](image)

*Figure 2.4: A schematic presentation of the working principle of an FTIR spectrometer.*

The other beam reflects off of a flat mirror which is on a mechanism which allows this mirror to move a very short distance (typically a few millimeters) away from the beamsplitter. The two beams reflect off of their respective mirrors and are recombined when they meet back at the beamsplitter. Because the path that one beam travels is a fixed length and the other is constantly changing as its mirror moves, the signal which exits the interferometer is the result of these two beams "interfering" with each other. The resulting signal is called an interferogram which has the unique property that every data point (a function of the moving mirror position) which makes up the signal has information about every infrared frequency which comes from the source (Figure 2.4). This means that as the interferogram is measured, all frequencies are being measured simultaneously. Thus, the use of the interferometer results in extremely fast measurements. Because the analyst requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make identification, the measured
interferogram signal cannot be interpreted directly. A means of “decoding” the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the Fourier transformation. A Perkin Elmer spectrometer (spectra GX) with a resolution of 2 cm\(^{-1}\) and scan range of 370 - 4000 cm\(^{-1}\) was used in this work.

2.6 Raman spectroscopy

Raman spectroscopy is another effective technique that can be used for sample identification and quantitation depending on molecular vibration. For quite a long time this technique was devoted to fundamental research but instrumental progress like laser miniaturization, CCD detectors, notch filters, data processing softwares etc. have rendered it a general characterization method. Not only it can be used for phase identification but also can be used to assess nanoscale structural changes and to probe micromechanical behaviour [7-9]. This technique involves shining a monochromatic light source on a sample and detecting the scattered light. Specifically, Raman spectroscopy technique is based on inelastic scattering of light usually from a laser source upon interaction with a material. The majority of the scattered light is of the same frequency as the incident light; this is known as Rayleigh or elastic scattering. A very small amount of scattered light is shifted in energy from the incident light frequency due to interaction between the incident electromagnetic waves and vibrational energy levels of molecules in the sample. Plotting the intensity of this shifted light against frequency results in a Raman spectrum of the samples. Typically, Raman spectra are plotted with respect to incident light frequency such that Rayleigh band lies at 0 cm\(^{-1}\). On this scale the band position will lie at frequencies that correspond to the energy level of different functional groups. Recently, Raman spectroscopy has also become one of the important tools for nanostructures characterization. The peak broadening in Raman intensity peak also indicates lower dimension of the material similar to XRD peak where we also see similar effect in diffraction peaks with reduced particle size [10 - 13]. Once the Raman spectra are
known, phase transition can be characterized through mode variations. In addition to this, observation of any theoretically forbidden mode gives very important information about lattice distortion in samples [14].

2.7 Positron annihilation spectroscopy

In 1928, Dirac predicted about the existence of an antiparticle that was experimentally observed later by Anderson in 1932 [15, 16]. The positron \((e^+)\) as the antiparticle of electron was the first antiparticle discovered. The annihilation of positrons with electrons in matter was first studied in 1940. It was also found that the energy and momentum conservation during the annihilation process could be used to study the properties of solids. In addition to annihilation, electron and positron can also form a bound state, called positronium [17]. Initially, experiments with positrons were done for determining electronic structure like Fermi surface in metals and alloys [18, 19]. Based on the fact that annihilation parameters are sensitive to lattice imperfections, positron annihilation studies have been employed mainly for studying crystal defects.

![Diagram of positron annihilation experiments](image)

*Figure 2.5: Schematic diagram of different positron annihilation experiments.*
Positron lifetime spectroscopy also became an important technique for obtaining qualitative and quantitative information on defects in semiconductors in late 1980s. Positron annihilation measurements can be categorized into two main groups (i) positron lifetime measurement that uses sensitivity of positrons to the electron density and (ii) measurement of electron momentum distribution in the sample (Doppler broadening spectroscopy and angular correlation of annihilation radiation). Different possible positron experiments have been shown schematically in Figure 2.5. Positron annihilation lifetime spectroscopy (PALS) and Doppler broadening of annihilation radiation (DBAR) technique that are used in this work have been discussed below.

2.7.1 Positron source

$^{22}\text{Na}$ is a well known positron source for positron annihilation spectroscopic studies. Positron can be obtained from $\beta^+$-decay of radioactive isotopes as shown below.

$$^{22}\text{Na} \rightarrow ^{22}\text{Ne} + \beta^+ + \nu_e + \gamma$$

Figure 2.6 (a) shows decay scheme of $^{22}\text{Na}$, which decays by emission of a positron and an electron neutrino to the excited state of $^{22}\text{Ne}$. Finally it comes to the ground state with emission of 1.27 Mev $\gamma$ quanta. $^{22}\text{Na}$ isotope gives a relatively high positron yield of 90.4%. The rather longer half life (2.6 year) and reasonable price make it the most suitable positron source. The positron source used in the present positron experiment was prepared by evaporating carrier-free $^{22}\text{NaCl}$ on an Al foil of thickness 2.4 mg cm$^{-2}$. It was then covered with an identical Al foil and sealed with a gum. The source sample sandwich arrangement that was used in positron annihilation measurement has been shown in Figure 2.6 (b).

2.7.2 Positron lifetime spectroscopy
Chapter 2

A $\gamma$ quantum of energy 1.27 MeV (start - $\gamma$) is emitted almost simultaneously with the positron emitted from the $^{22}$Na source. Positron after entering into the sample loses its kinetic energy within a few picoseconds after suffering several non-elastic collisions with the electrons. This is called thermalization process. After that, positron diffuses into the solid before getting trapped in a lattice defect. When a positron annihilates with surrounding electron, it will emit a $\gamma$-quanta of energy 511 keV. The time difference between the birth $\gamma$ quantum (1.27 MeV) and annihilation $\gamma$ quantum (511 keV) is the measure of positron lifetime in the sample.

The positron lifetime $\tau$ is a function of electron density at the annihilation site. The positron annihilation rate $\lambda$ is proportional to the electron density at the site of positron annihilation:

$$\lambda = \frac{1}{\tau} = \frac{m_0^2 c}{r_0} \int d\mathbf{r} |\psi_+(\mathbf{r})|^2 n(\mathbf{r}) \gamma[n],$$

(2.7)

Where $r_0$ is the classical radius of the electron, $c$ is the velocity of light, $n(\mathbf{r})$ the electron density, $\gamma[n]$ the enhancement factor of electron density at the annihilation site [20, 21].

In a material with vacancy or void, the average electron density is found low at the defect site than that of the defect-free material. This will give slow rate of annihilation of positron at the defect site in comparison to defect-free site. Therefore increased positron lifetime values are
obtained when it is trapped in vacancies or their agglomerates in comparison to a defect-free sample.

2.7.3 Instrumentation

Positron lifetime measurements in the present case were performed by using two BaF$_2$ scintillators and photomultipliers tubes with a short pulse rise time to obtain high time resolution. The detectors and source sample sandwich were arranged in a linear geometry. Scintillator–photomultiplier detector assembly converts the detected $\gamma$ – rays into an analog electrical pulse. The timing signals from the detectors were fed to constant fraction differential discriminators (CFDD, Ortec 583). The discriminators suppress noise and generate standard timing pulses by the constant fraction discriminator principle. It also ensures the selection of 1.27 MeV and 0.51 MeV $\gamma$ – rays in appropriate channels.

The appropriate timing pulses from the output of CFDDs were fed to inputs of time to amplitude converter (TAC, Ortec 567) and energy pulses were sent to inputs of the

![Figure 2.7: Scheme of positron lifetime experiment in fast-fast coincidence.](image-url)
coincidence unit (Canberra 2020). This will generate an output pulse only if both the inputs receives signal within the set resolving time. This output is sent to strobe the TAC. The amplitude of the output pulse is proportional to the time difference between the start and stop signals and therefore it measures the positron lifetime. This annihilation event is stored after analog to digital conversion of the TAC output in the memory of a multi channel analyzer. A schematic diagram of the positron annihilation set up has been presented in Figure 2.7 that is called a fast-fast coincidence set up. In this configuration, time measurement as well as energy selection is performed in the CFDD units. To obtain the complete lifetime spectra, generally $10^6$ annihilation events are recorded. The calibration (equivalent time corresponding to each channel) is needed to be done before making analysis of the recorded spectra. It was done by recording the time spectra for a fixed number of counts by using a $^{60}$Co source with making variation in the delay connected to the stop channel. The slope of the graph between the delay values and the shift of centroid channel number gives calibration that is obtained as 58 ps/channel in the present set up. The time resolution of a spectrometer depends mainly on scintillator-multiplier part. The instrumental resolution is determined from full width at half maximum of the recorded lifetime spectrum using a $^{60}$Co source with $^{22}$Na gate (CFDD gates are set at 1.27 and 0.511 MeV).

2.7.3.1 Data treatment

The time dependent positron decay spectrum $D(t)$ of the sample is given by

$$D(t) = \sum_{i=1}^{k} I_i \exp \left( -\frac{t}{\tau_i} \right)$$

(2.8)

where $k$ is different type of defects which are having individual lifetime $\tau_i$ and intensities $I_i$. If there is no defect in the sample, the above equation will reduce to $D(t) = \exp \left( -t/\tau_b \right)$, where $\tau_b$
is the positron lifetime in the defect-free bulk sample. The positron lifetime spectrum is defined by the time derivative of positron decay spectrum $D(t)$.

$$N(t) = \sum_{i=1}^{k+1} I_i \exp \left( \frac{-(t-t_0)}{\tau_i} \right) + B(t)$$

(2.9)

Where $B(t)$ is the background function and $t_0$ is centroid channel of the shifted spectrum due to insertion of delay cable. Figure 2.8 shows positron lifetime spectra of a defect-free and irradiated Si samples. Experimentally obtained spectra differ from analytical expression given in equation (2.9) by the convolution with the time resolution function which in most cases represented by a single Gaussian function centred at $t_0$:

$$G(t) = \frac{1}{\sigma \sqrt{\pi}} \exp \left[ -\left( \frac{t-t_0}{\sigma} \right)^2 \right]$$

(3.0)

The time resolution is characterized by full width at half maximum (FWHM) given by

$$FWHM = 2\sigma \sqrt{\ln 2}$$

(3.1)

Where $\sigma$ is the standard deviation. Standard computer program PATFIT 88 has been used to fit the experimentally obtained spectrum [22].

Due to finite time resolution, annihilation in the source materials and random background only 2-3 lifetime components can be used to analyze the spectra. Even then separation between two lifetimes can be obtained only if $\lambda_1/\lambda_2 > 1.5$ [23].

The average lifetime ($\tau_{av}$) is a good and statistically accurate parameter because it is the centre of mass of lifetime spectrum. The average or mean lifetime parameter is more reliable though decomposition may be ambiguous. From positron lifetime studies, the average lifetime is defined as
If average lifetime value is larger than the free positron lifetime in bulk, it would indicate positron trapping in vacancy type defects. Its statistical accuracy is about $1/\sqrt{N} \sim 10^{-3}$, $N$ being the number of counts, i.e., well below 1 ps when at least $10^6$ counts are accumulated under the total spectrum [23].

2.7.3.2 Source correction

A small fraction of positron annihilation event occurs in the source itself that amounts to 2-15% depending on the foil thickness and atomic number of the sample. For the analysis of positron lifetime spectra this contribution must be determined and subtracted. This is called source correction which is an essential task for lifetime spectra evaluation. This correction should be determined using defect-free reference samples with well-known spectra. An empirical formula for foil intensity is given here.
Chapter 2

\[ I_{\text{fwhm}}(\%) = 0.324Z^{0.93}S^{3.45}/Z^{3.44} \]  

(3.3)

Where \( Z \) is the sample atomic number and \( S \) is the sample thickness in mg.cm\(^{-2}\) [24].

2.7.4 Doppler broadening of annihilation radiation

The momentum distribution of electron-positron pair is conserved in the annihilation radiation. The momentum component in the \( \gamma \)-ray propagation direction leads to a small Doppler shift to the annihilation energy. It is given by

\[ \Delta E \approx \frac{p_z c}{2} \]  

(3.4)

Where, \( p_z \) is the momentum component in the direction of annihilation \( \gamma \) emission. Numerous annihilation events are measured for Doppler broadening spectra, this result a line broadening in annihilation radiation due to individual Doppler shift in both directions, \( \pm z \). The Doppler broadening experiment is done using a Ge gamma detector (HPGe, Ortec 70230) with high resolution because broadening shows only small changes due to defects [25].

![Experimental arrangement of Doppler broadening spectroscopy.

Figure 2.9: Experimental arrangement of Doppler broadening spectroscopy.]
The output of the detector is fed to input of the pre-amplifier and then it enters to amplifier (Ortec 672). The output of the amplifier is fed to ADC to be digitized. This signal passes to MCA and that sends data to computer system.

2.8 Mössbauer spectroscopy

The discovery of recoilless gamma ray emission and absorption is known as Mössbauer Effect. It was named after the discoverer of this event Rudolf Mossbauer, who received Nobel prize in 1961 for his work. Nuclei in atoms undergo different type of transitions between the energy levels associated with the emission or absorption of gamma ray. These energy levels are influenced by their surrounding environment. The changes in energy level can provide information about the atom’s local environment via resonance-fluorescence. However, recoil of the nucleus was main obstacle to get resonance.

Mössbauer discovered that when atoms are embedded in a solid matrix, the mass of the recoiling nucleus, M, becomes effectively that of the entire crystal which can be of the order of 10$^{15}$ times greater than the mass of a single nucleus. Provided the gamma ray energy is small enough, the recoil of the nucleus is very less and so the whole system recoils, making the recoil energy practically zero: a recoil free phenomenon [26].

The natural linewidth of excited nuclear state is a limiting factor for the resolution of gamma ray energy. For the most common Mössbauer isotope, $^{57}$Fe, the linewidth is 5x10$^{-9}$ eV. Compared to Mössbauer gamma-ray energy of 14.4 keV this gives a resolution of 1 in 10$^{12}$. This exceptional resolution is of the order necessary to detect the hyperfine interactions in the nucleus.

Mössbauer spectra of a sample can give important information regarding the atomic and molecular structure because the energy levels of the nucleus are dependent on a number
of external factors. Depending on the nature of interaction, there may be a resultant change in Mössbauer parameters like isomer shift, electric quadrupole and magnetic hyperfine splitting.

2.8.1 Isomer shift

The isomer shift arises due to non-zero volume of the nucleus and the electron charge density owing to s-electron density within it. This leads to electro static interaction (Coulomb), altering the nuclear energy levels. Any difference in s-electron environment between the source and absorber produces a shift in the resonance energy of the transition. The whole spectrum is shifted either in positive or negative direction depending on s-electron charge density. Generally the isomer shift is not affected with temperature, though small changes are ascribed to second order Doppler shift. Isomer shift or chemical shift can be expressed as

\[
\text{Isomer shift} = K (R_e^2 - R_g^2) \left\{ [\Psi^2_s(0)]_s - [\Psi^2_s(0)]_b \right\}
\]

(3.5)

Where K is a nuclear constant, the difference between \( R_e^2 \) and \( R_g^2 \) implies the difference of effective nuclear charge radius between excited state and the ground state and difference between \([\Psi^2_s(0)]_s\) and \([\Psi^2_s(0)]_b\) is the electron density difference on nucleus of source and absorber [26]. As the shift cannot be expressed directly it is referenced relative to a known absorber. For example Fe\(^{57}\) Mössbauer spectra are often estimated relative to alpha iron at room temperature. Isomer shift gives information regarding the oxidation state, types of ligand coordinated to iron.

2.8.2 Quadrupole splitting

Quadrupole splitting is like a mirror image of interaction between the nuclear energy levels and surrounding electric field gradient [27]. Nuclei are having non-spherical charge distribution i.e. all those with angular momentum (I) greater than \( \frac{1}{2} \), have a nuclear
quadrupole moment. The quadrupole moment interacts with the electric field gradient that splits the nuclear energy levels. For example, in case of Fe\textsuperscript{57} the excited state with I = 3/2 is split into two substates m\textsubscript{I} = ± 3/2 and m\textsubscript{I} = ± 1/2. The two specific peaks observed in spectrum referred to as doublet (Figure 2.10). Quadrupole splitting is measured as the separation between these two peaks and reflects the charge symmetry around the nucleus.

![Diagram showing isomer shift and quadrupole splitting of nuclear energy levels](image)

\textbf{Figure 2.10: Isomer shift and quadrupole splitting of nuclear energy levels and corresponding Mössbauer spectra.}

\textbf{2.8.3 Magnetic splitting}

Magnetic splitting appears as a result of interaction between the nuclear magnetic moment and surrounding magnetic field. There are several sources of magnetic field that can be
experienced by the nucleus. The total effective magnetic field at the nucleus can be expressed as

$$B_{\text{eff}} = (B_{\text{contact}} + B_{\text{orbital}} + B_{\text{dipolar}}) + B_{\text{applied}}$$

where the first three terms come from the atom’s own partially filled electron shells. $B_{\text{contact}}$ is due to the spin on those electrons polarising the spin density at nucleus, $B_{\text{orbital}}$ is due to the orbital moment of those electrons, and $B_{\text{dipolar}}$ is due to the spin of those electrons. In presence of this magnetic field, a nucleus with spin $I$, splits into $2I+1$ sub-energy levels. For Fe$^{57}$, the ground state ($I = \frac{1}{2}$) splits into two levels while the excited state ($I = \frac{3}{2}$) splits into four levels. The transition between excited and ground state only occurs with the selection rule $m_I = 0, \pm 1$. Therefore it produces six possible transitions between the excited state and ground state which are having spacing proportional to $B_{\text{eff}}$. It is shown in Figure 2.11 below.

![Figure 2.11: Magnetic splitting of nuclear energy levels and corresponding Mössbauer spectrum.](image)

### 2.8.4 Instrumentation

Primarily, Mössbauer spectrometer needs a radioactive source, sample, detector, and a drive unit to move the source. The essential components involved in Mössbauer spectroscopy has
been shown in Figure 2.12. The required source is attached to the drive unit to provide the velocity. The velocity can be selected up to ± 50 mm/sec. The gamma rays after passing through the sample are detected in a proportional counter. Signal from the counter is fed to a preamplifier and a linear amplifier before arriving at a single channel analyzer (SCA). The digital output from the SCA is fed into the computer. The obtained data is deconvoluted by using a least squares fitting program. This is based on chi-square minimization method. LGFIT2 program was used for discrete Lorentzian line shape [28].

![Block diagram of Mössbauer spectroscopy instrumentation.]

2.9 Magnetic measurements

Magnetic measurements are essential to characterize different types of magnetic materials. It also provides information about some specific characteristic of magnetic materials like spin-glass and superparamagnetic behaviour. AC magnetic measurements where a small AC field is applied to the sample, give idea about the magnetization dynamics because induced sample moment is time dependent. DC magnetic measurements determine the equilibrium values of magnetization in the sample. The temperature dependent magnetization measurements have been performed in two conditions. In zero field-cooled condition the samples are cooled down to lowest possible temperature in absence of field. After that, a constant field is applied during the warm up scan. In field-cooled measurements, the sample is cooled from room temperature to lowest possible temperature in presence of the same magnetic field and data is
recorded during the warm up. These measurements can determine spin state, Curie or Neel temperature of materials. Another important characterization is magnetization with varied magnetic field at constant temperature, that gives insight information on nature of the sample, is called hysteresis measurements. Magnetic behaviour of the samples was studied mostly by a super conducting interference device magnetometer (SQUID, MPMS XL7).

At present, SQUID magnetometry is one of the most beautiful measurement techniques to study the magnetic property of extremely sensitive magnetic materials. Generally, it contains a SQUID sensor, magnetic flux transformer including pick up coils, magnet coils, heat switches, magnetic shielding, and He bath at 4.2 K. The measurement in SQUID-MPMS is carried out by moving the sample through the detection coils. As a result of this, sample having magnetic moment will result an electric current in the detection coil. Any change in magnetic flux in the detection coils induce a change of current in detection circuit; this is proportional to change in magnetic flux. As SQUID performs like a linear current to voltage convertor, any change in current in detection coils gives corresponding variation in SQUID output voltage that is directly proportional to magnetic moment of the sample [29].
References


