Chapter II

Instrumentation & Experimental Methods

This chapter deals with the various experimental techniques employed for the synthesis, characterization and evaluation of hydrogen storage properties of the alloys/intermetallic compounds. All the samples under investigation were prepared by meting the high purity constituent elements, with stoichiometric ratio, in DC arc melting furnace, in a water cooled copper (Cu) hearth. The meting was done in argon (Ar) atmosphere and buttons were remelted several times to ensure homogeneity. The basic principle of arc melting is discussed later in this chapter. Conventional Sievert’s type volumetric hydrogen storage setup, which had been developed in our laboratory, was used for the synthesis for the corresponding hydride. The actual activation methods used during the hydride formation, the procedure to measure the pressure-composition isotherm and hydrogen absorption kinetics in the Seivert’s type setup are discussed in detail. Various characterization techniques were used for the characterization of the alloys, as well as the hydrides. They are as follows: X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX), Mössbauer Spectroscopy, Electron Probe Micro-analyzer (EPMA), Thermo Gravimetric Analyser (TGA), Differential Thermal Analyser (DTA), Differential Scanning Calorimetry (DSC) and Temperature Programmed Desorption (TPD). Brief descriptions of the general principles of these techniques are presented.
2.1 Arc Melting Setup

An arc melting furnace [118] is a furnace that transfers electrical energy to thermal energy in the form of an electric arc to melt the raw materials held by the furnace. The arc is established between an electrode and the melting bath, and is characterized by a low voltage and high current.

Fig. 2.1 shows the direct current (DC) arc melting setup used in our laboratory. The arc melting furnace used for the present work can melt a few grams of samples and the temperature can go up to 3000 °C. The melting of the raw materials is done in the chamber by means of a non-consumable tungsten electrode (cathode) on a water cooled Cu hearth (anode). Cu anode is one of the best materials due to its high melting point and very high conductivity. Before melting the raw materials, Zr metal is kept inside the chamber, and it is purged with argon (Ar) gas for at least 20 minutes. Zr metal acts as the oxygen getter, and removes the dissolved oxygen from the Cu hearth, thus greatly reduces the oxygen impurity. After the melting of the Zr metal, the raw materials are generally melted several times (2-4 times) to ensure homogeneity and during melting continuous Ar flow is maintained. The arc zone volume depends on several factors. The zone volume increases as Ar pressure decreases and increases with the increase in current. The arc zone volume also depends on the nature of the inert gas. As the ionization potential of the gas increases the zone volume increases. After melting, the sample is kept under Ar atmosphere, for proper cooling under the inert gas supply for 20 minutes, before taking out.
2.2 Sievert’s Type Setup

In the present work, the hydrides have been prepared using a standard Sievert’s type of volumetric set up developed in our laboratory. The principle of Sievert setup is based on the measurement of the change in pressure at constant volume and temperature [119].

The schematic diagram of Sievert’s type set up is given in Fig. 2.2. The apparatus consists of a high-pressure manifold connected to the pressure transducer, vacuum line, high-pressure cylinder and hydriding reactor. The setup is made of SS316 to resist high temperature and pressure. The reactor is a cylindrical one with ~24 mm inner diameter, ~37 mm outer diameter and ~210 mm height. The sample holder of 20 mm dia and 39 mm height is placed insider the reactor along with spacer rod to reduce the excess volume. The reactor is connected with the manifold with a screw connection and Viton “O” ring is placed at the connection to avoid any possible gas leakage. The Viton “O” ring is cooled externally by
passing water through the Cu coil to prevent its damage at high temperature. In the connection line between the reactor and manifold, a filter is put with 200 mesh size to prevent the entering of fine hydride particles into the system. An on-off valve ($V_5$) is put in between the reactor and manifold which is used to expose the sample in the hydrogen atmosphere. During the course of the experiment, for the high temperature activation of samples and high temperature hydrogen absorption-desorption study, the reactor is inserted into a tubular furnace. Chromel-alumel thermocouple is used for measuring the temperature of the reactor. The manifold is connected with the rotary and diffusion vacuum through the valve $V_4$. The set-up has been tested in high vacuum ($10^{-6}$ mbar) and high pressure (60 atm.). The volume of different parts of the setup has been calibrated accurately using gas law.

![Diagram of Sievert's type hydriding setup]

**Fig. 2.2 Sievert’s type hydriding setup**

Before staring the experiment the whole setup is evacuated under diffusion vacuum. In our study most of the activation procedure involved heating the sample under diffusion vacuum ($10^{-6}$ mbar) for 2 hours at 673 K. Some of the samples studied in this thesis absorb hydrogen without prior heat treatment, which will be discussed in the respective chapters.
After activation the sample is cooled to the working temperature under vacuum. Before starting the hydrogen absorption experiment, the manifold is purged with little amount of hydrogen repeatedly and after that evacuated completely. For the pressure-composition isotherm measurements, at the experimental temperature, certain pressure of hydrogen is put in manifold opening the valve $V_1$, keeping the reactor isolated by putting off the $V_5$ valve. After that the valve $V_5$ is opened to equilibrate hydrogen gas between reactor and manifold. As the volume of the reactor, manifold and the total volume is calibrated, so from the final pressure (equilibrium pressure) of the system, the amount of the absorbed hydrogen gas in the sample can be calculated. During hydrogen absorption, initially the sample forms solid solution with the hydrogen ($\alpha$-phase) and the equilibrium pressure increases steadily with introduction of hydrogen. After a certain pressure, the hydride formation ($\beta$-phase) takes place and the equilibrium pressure remains almost constant. This is plateau region where the $\alpha$- and $\beta$-phase coexist together and the alloy can absorb and desorbs hydrogen reversibly. After that again the equilibrium pressure increases as it can’t take more hydrogen. During the desorption study the reverse procedure is followed. Small amount of hydrogen is taken out from the manifold using rotary pump opening the valve $V_4$, and keeping the valve $V_5$ closed. After that opening the valve $V_5$ the sample reactor is allowed to equilibrate. From the increase in the equilibrium pressure the amount of the desorbed hydrogen can be calculated. When the equilibrium pressure is plotted against the amount of hydrogen absorbed/desorbed then we get the pressure-composition isotherm. For most of the cases the pressure-composition isotherms were studied in the temperature range 298-473 K and up to hydrogen pressure of 25 atm., using freshly crushed samples. For the kinetic study the alloy is kept at a certain pressure and temperature, and the amount of hydrogen absorbed with respect to time is monitored. The surface poisoning of the hydride samples were done by air exposure at liquid nitrogen temperature.
The limitations of the instrument are as follows. In this instrument the transducer can
not measure pressure below 0.02 atm. Again the instrument has not been tested above 60 atm.

2.3 Hydrogen Estimation Setup

After preparing the hydride, it is very essential to estimate the hydrogen content of the
hydride independently. The most common method for analyzing the hydrogen content in
hydrides is the vacuum fusion technique, in which the material is heated in vacuum and the
amount of hydrogen gas released is measured.

The experimental set-up used in the present study, for the estimation of hydrogen
content of metal hydride systems, was assembled in our laboratory. The principle is based on
the measurement of pressure change, when a known amount of the hydrogenated sample is
heated in a standard volume. The schematic diagram of apparatus is given in Fig. 2.3.

The apparatus mainly consist of glass manifold with a mercury manometer for
pressure measurement. One end of manifold connected to a vacuum system and the other end
to a quartz tube, which serve as sample holder. There is a provision for heating the sample up
to 1473 K using an induction heater.

Any apparatus of this type needs to be calibrated for its volume. In present case, we
have calibrated our set-up by decomposition of calcium carbonate (CaCO$_3$) inside the set-up.
Known amount of calcium carbonate is heated at high temperature, which evolves known
amount of CO$_2$ gas. Now by observing the pressure change in the mercury level, the volume
of the cell and manifold can be calibrated. A known amount of the hydride sample normally
in the range of 20-30 mg is introduced into the sample holder and heated to 1473 K using an
induction heater. This temperature is found to be sufficient to decompose completely all the
hydride studied in this work. From the fall in mercury level the volume of H$_2$ released could be calculated.

![Diagram of experimental setup](image)

**Fig. 2.3** *The schematic diagram of the estimation set up used during the study*

### 2.4 X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is the most extensively used technique to identify the crystalline phases and to determine the crystal structures. In our present study we have used the technique to identify the phase structure of the entire alloys and their corresponding hydrides. X-rays are electromagnetic radiation with typical photon energies in the range of 100 eV - 100 keV. For the diffraction applications, only short wavelength X-rays (hard X-rays) in the range of a few angstroms to 0.1 angstrom (1 keV - 120 keV) are used. As the wavelength of X-rays is comparable to the size of atoms, they are ideally suited for probing the structural arrangement of atoms and molecules in a wide range of materials. The energetic X-rays can penetrate deep into the materials and provide information about the bulk structures.
The principle of XRD technique is based on scattering of X-rays by a crystal consisting of well-defined array of atoms, ions and molecules. Since the crystal lattice consists of parallel arrays of atoms equivalent to the parallel lines of the diffraction grating, the inter-planar spacing could be successfully determined, from the separations of bright fringes of the diffraction pattern. Interaction of X-rays reflected by a set of parallel planes satisfying Bragg’s condition lead to constructive interference only at a particular angle. The peaks positions in a X-ray diffraction pattern are directly related to the atomic distances. The Bragg condition for the occurrence of such diffraction can be written as:

$$n\lambda = 2d \sin \theta$$

Where, $\lambda$ is wavelength of X-rays, $\theta$ is the glancing angle (called as Bragg’s angle), $d$ is inter-planar separations, and $n$ is the order of diffraction.

A typical classical powder X-ray diffractometer consists of a source of X-rays and a detector for the detection of diffracted X-rays. Common diffractometer geometries are based on the Bragg-Brentano geometry. A block diagram of the typical powder diffractometer is shown in the Fig. 2.4.

![A simplified diagram of the X-Ray diffractometer](image)

Fig. 2.4 A simplified diagram of the X-Ray diffractometer
There are several kinds of sources for X-rays are available, but the most common laboratory diffractometer uses a sealed tube X-ray source. Bombarding high-speed electrons on a metal target produces the X-rays. A part of the electron energy is used in producing X-ray beam, which is a combination of a continuous radiation with wavelength ranging from a particular shortest value ($\lambda_{cut}$) onwards and several intense spikes, which are characteristic of the target elements (called characteristic radiation). The typical X-ray spectrum of elemental cu is given in Fig. 2.5.

The intense continuous radiations or the monochromatic wavelength radiations are to be used for the diffraction experiments. The latter is used in the most common diffraction instruments (angle dispersive) [120, 121]. Though the X-rays are produced in all the directions, it is allowed to escape from a particular direction (commonly using a beryllium window) for experiments. The background and $\beta$-radiations are filtered using $\beta$-filters. The beam of X-rays is passed through the divergence slits and then allowed to fall on the sample.

![Characteristic X-ray of metallic Cu](image)

**Fig. 2.5** Characteristic X-ray of metallic Cu

In case of powder diffraction, the fine grains of sample are generally spread uniformly over a rectangular area of a glass slide, so that all the orientations get exposure. The sample is
usually adhered to a glass slide either using binders like collodion or grease or wax. The amounts of the sample exposed generally depend on the scattering power of the elements, absorption coefficient, X-ray source intensity and of course on availability of the sample. The crystalline sample usually shows good scattering and sharp diffraction lines. The X-rays diffracted from the powder samples are collected either by a film or movable counters. In the diffractometer, the diffracted beams are passed through the soller slits and divergence and receiving slits. Then it is usually allowed to fall on a monochromator before detection.

For the detection of X-ray, the gas filled tube or scintillation counters are commonly used. These tubes can either be the proportional counter or Geiger-Muller counter. This particular tube is usually filled with a gas, which gets ionized by the impact of the radiation. Applying a potential difference between the two electrodes, the ions are collected. The typical current obtained is proportional to the number of photons reaching to the detector. The diffracted rays are scanned by sweeping the detector from one angle to another. The angle where the Bragg’s law is satisfied for a particular plane, a constructive interference among the diffracted X-rays from that plane takes place, giving a sharp rise in the intensity (peak). Thus, the counts or count rates of the X-ray photon are measured at different angles. The output is obtained as plot of the intensity of diffracted X-rays (Y-axis) vs angle (X-axis).

The peaks (also called as reflections) in the plot correspond to a set of parallel planes with inter-planar spacing $d_{hkl}$. The d-values are calculated from the position of the peaks. Thus, for a particular sample a set of d-values giving constructive interference is observed. The peak positions (d values) are related with the unit cell parameters of the lattice. Hence they can be used for identification of the materials and they generally act as the fingerprint for the crystalline materials. The intensity distribution of the reflections is governed by the nature and kind of distribution of atoms in the unit cell.
In the present work, a Philips 1710 diffractometer was mostly used for the characterization process. Philips-1710 diffractometer is based on the Bragg-Brentano reflection geometry. The Cu Kα emissions from sealed tube are used as the incident beam. The Philips (PW-1710) diffractometer has a proportional counter (Argon filled) for the detection of X-rays. The X-ray tube rating was maintained at 30 kV and 20 mA in the Philips unit.

The data collection protocols often depend on the specific purpose of the data collections. In general a short time scan in the two-theta (2θ) range of 10 to 80° is sufficient for the identification of a well crystalline inorganic material. However, low symmetry samples and samples with not good X-ray scattering power may need a slow scan. The scan time was optimized for getting good intensity peaks. Prior to data collections, the goniometer needs to be properly aligned for correct zero position. After the proper alignment, the instrument has to be calibrated with standard known materials for the accurate peak position. Usually silicon is used for calibration. The silicon peak positions are adjusted by the correct angle and set angle command or by applying the zero settings to the diffractometer. After the data collection, the observed d-values were fitted to standard patterns and the unit cell parameters were refined with respect to the standard values. By comparing the observed diffraction pattern with JCPDS (Joint Committee on Powder Diffraction Standards, 1974) files available for reported crystalline samples, fingerprinting of sample materials is normally done. The refinements are usually done by a least square method. The computer software used for this purpose was “Powder-X” [122]. The unit cell parameters are made free to adjust in the best way to fit the observed experimental data. The use and interpretation of the powder diffraction patterns are explained in several books [120-122].

The approximate crystalline size and the stain can be estimated from broadening of the X-ray peak by the Scherrer’s formula. The line broadening is measured as
\[ \beta^2 = \beta_M^2 - \beta_s^2 \]

where, \( \beta_M \) is the measured peak width in radians at half peak height and \( \beta_s \) is the measured peak width of a peak of a standard material, mixed in the sample, having a diffraction peak near to the relevant peak of the sample [123]. Line broadening \( \beta \) can be written as

\[ \beta = \varepsilon \tan \theta + \frac{0.9 \lambda}{B \cos \theta} \]

Where \( \varepsilon \) is the parameter defining approximate strain, \( \lambda \) the X-ray wavelength measured in angstrom (Å) or nanometer (nm) units and \( \theta \) the Bragg angle and \( B \) is the parameter defining approximate crystallite size. Now, the equation can be rearranged as

\[ \beta \cos \theta = \varepsilon \sin \theta + \frac{0.9 \lambda}{B} \]

So if we plot \( \cos \theta \) vs \( \sin \theta \), then from the slope we can calculate the strain and from the intercept we can calculate the approximate crystalline size. The actual sizes in a number of crystalline samples and their hydrides were actually investigated by means of SEM, as explained in another section.

### 2.5 Scanning Electron Microscope (SEM) and Energy Dispersive X-ray (EDX)

The scanning electron microscope technique is used to study the microstructure evolution (grain size, porosity, etc.) of the samples and their hydrides. The instrument used were a SEM SERON INC, South Korea made, Model number ATS 2100. EDX instrument is made by Oxford Instrumentation, UK, Model Number INCAE350.

The Scanning Electron Microscope is discussed briefly in the paragraph below. When a finely focused electron beam interacts with the matter (specimen) there are three major
phenomena occur: (i) emission of secondary electrons (SE) (ii) back-scattering electrons (BSE) and (iii) transmission of electrons. These three phenomena and some other important phenomena are depicted in Fig. 2.6.

In Scanning Electron Microscopy, the signals generated from the surface by secondary and back-scattered electrons are detected and are fed to a synchronously scanned CRT as an intensity-modulating signal and thus displays a specimen image on the CRT screen [124]. The CRT raster width divided by the electron probe scanning width determines the image magnification. Scanning microscope is composed of (i) electron optical system, (ii) specimen stage, (iii) display and recording system and (iv) vacuum system.

In SEM technique [124], the electrons from a finely focused beam and get restored across the surface of the sample. Electrons are reflected by the surface of the sample and emitted secondary electrons are detected to give a map of the surface topography of the sample. It is useful for looking at particle size, crystal morphology, magnetic domains, surface defects, etc. A wide range of magnification can be used, the best achievable
resolution being about 2 nm. An electron beam incident on a metal gives rise to the emission of characteristic X-rays from the metal. In electron microscopy, the elements present in the sample also emit characteristic X-rays. These are separated by a silicon-lithium detector, and each signal collected, amplified and corrected for absorption and other effects, to give both qualitative and quantitative analysis of the elements present (for elements of atomic number greater than 11) in the irradiated particle, a technique known as energy dispersive analysis of X-rays (EDAX or EDX). In the present study we have used SEM as a tool to determine the particle size and to see the surface morphology. Again from the EDX analysis the qualitative and quantitative analysis of the elements present in the sample was done to confirm their composition.

### 2.6 Electron Probe Micro Analyser (EPMA)

The principle electron probe forming and emerging components of the EPMA are similar to SEM. They include an electron optical column to produce a finely focused electron beam, a scanning system, one or more electron detectors and a cathode ray tube (CRT) display system. Differences arise from the fact that in the EPMA emphasis is placed on micro chemical analysis while the main use of SEM is microscopic imaging [125]. Micro chemical analysis in EPMA is based on the measurement of X-rays generated by the focused electron beam. The ability to perform chemical analysis in an EPMA is a result of existence of a relationship between the wavelength $\lambda$ of the characteristic X-ray emitted from an element and its atomic number $Z$ (for K radiation) which can be given as

$$Z \propto \lambda^{-1/2}$$

When an electron incident on the sample having sufficient energy to exceed the excitation potential $E_c$ (the bonding energy of the core electron), then core electron is ejected from atom leaving a vacancy, which is then filled by the electron from higher energy state by
the electronic relaxation by simultaneous release of a discrete energy corresponding to the difference between the orbital energy levels. This energy may be either in the form of X-rays or Auger electron. The probability of the ejection of core electron of an atom by the incident electron is one out of ten thousand.

These X-rays are detected and characterized either by means of an energy-dispersive spectrometer (EDS) or a crystal diffraction spectrometer (CDS, also known as wavelength-dispersive spectrometer WDS). The basic operating principles of the instrument are illustrated in Fig.2.7.

![Electron Probe Micro-Analyzer](image)

**Fig. 2.7 Operating principle of EPMA**

An electron optical column containing an electron gun, magnetic lens, a specimen chamber and various detectors are maintained at vacuum of at least $10^{-5}$ mm Hg. A directly heated filament provides a source of electron for the electron gun. The filament is held at a
negative potential, 5 to 30 kV relative to the gun anode, which is grounded. A grid placed between the filament and the anode is biased at a potential slightly less than that of the filament. Thus electrons are attracted from the filament to the anode focused by the field of the grid cap. The electron gun acts as a lens, forming an image of the filament which is then demagnified by two or more magnetic lenses to form the final probe. The probe size is in the range of 0.1 to 1 μm with corresponding probe currents in the range of about 10-1000 nA. When the focused electron beam strike the sample a variety of signals are generated, including backscattered electrons, secondary electrons and X-rays. Although the backscattered electron signal varies with atomic number but mainly it is the X-rays that provides a unique way of performing both quantitative and qualitative analysis which can be detected by either WDS or EDS systems. By using wavelength dispersive spectra better resolution in the composition analysis can be found in EPMA than the energy dispersive SEM analysis. In this thesis we have used WDS-EPMA to confirm any phase segregation and also to find the composition of the different existing phases.

2.7 Mössbauer Spectroscopy

The phenomenon of recoilless emission and resonance absorption of γ-rays by identical nuclei bound in solid is known as Mössbauer effect [126, 127]. Rudolph Mössbauer first observed “Mössbauer Effect” [Fig. 2.8] in 1957 in $^{191}$Ir and received the Nobel Prize in Physics in 1961 for his work. He discovered that, when the atoms are within a solid matrix, the effective mass of the nucleus is very much high. The recoiling mass is effectively the mass of the whole system, so if the gamma-ray energy is small enough, the recoil of the nucleus is too low to be transmitted as a phonon (vibration in the crystal lattice) making the recoil energy practically zero (recoil-free event). The relative number of recoil-free events (and hence the strength of the signal) is strongly dependent upon the gamma-ray energy and
so the Mössbauer effect is only detected in isotopes with very low lying excited states. Similarly the resolution is dependent upon the lifetime of the excited state. These two factors limit the number of isotopes that can be used successfully for Mössbauer spectroscopy. $^{57}$Fe is the most commonly used isotope for Mössbauer spectroscopy, which has both a very low energy gamma-ray and long-lived excited state, matching both requirements well.

![Simple Mössbauer spectrum from identical source and absorber.](image)

Fig. 2.8 *Simple Mössbauer spectrum from identical source and absorber.*

In the present thesis, $^{57}$Co source embedded in the Rh matrix is used as a monochromatic source of $\gamma$-ray. Room temperature $^{57}$Fe Mössbauer spectra were recorded using the 14.4 keV gamma ray energy, emitted from $^{57}$Fe (produced from $^{57}$Co by electron capture process), which is modulated by Doppler motion provided by constant acceleration mode. The spectrometer was calibrated with $\alpha$-Fe and the isomer shift values given in this work are with respect to $\alpha$-Fe. The experimental data were fitted by least square curve-fitting program.

### 2.7.1 Isomer shift

Basically, the isomer shift arises due to the difference in chemical environments of the emitting and absorbing nuclei. The isomer shift arises because of the non-zero volume of the nucleus, and the electron charge density of the s-electrons within it. This leads to a monopole (Coulomb) interaction, altering the nuclear energy levels. Thus any difference in the s-
electron environment between the source and absorber produces a shift in the resonance energy of the transition. The shift of the whole spectrum becomes positive or negative depending upon the s-electron density, and sets the centroid of the spectrum. As the shift cannot be measured directly it is quoted relative to a known absorber. For example, $^{57}$Fe Mössbauer spectra will often be quoted relative to $\alpha$-iron at room temperature. The isomer shift value is defined by the following equation:

$$IS = \delta = \frac{4\pi}{5} Ze^2 R^2 \frac{\Delta R}{R} \left[ \left| \Psi(0) \right|_{\text{abs}}^2 - \left| \Psi(0) \right|_{\text{g}}^2 \right]$$

Here $Ze$ is the positive charge of the nucleus, the term $\Delta R/R$ is the fractional change in the nuclear charge radius on the excitation and $\Delta R$ is the difference in the radii of the nuclear exited and ground states.

The isomer shift is useful for determining valence states, ligand bonding states, electron shielding and the electron drawing power of electronegative groups. For example, the electron configurations for Fe$^{2+}$ and Fe$^{3+}$ are (3d)$^6$ and (3d)$^5$ respectively. The ferrous ions have less s-electron at the nucleus due to the greater screening of the d-electrons. Thus ferrous ions have larger positive isomer shifts than ferric ions. Intermetallic compounds, on hydriding, show an increased isomer shift. Even equivalent sites with different number of hydrogen neighbors and geometrical arrangements could be distinguished by their different IS values.

2.7.2 Quadrupole splitting

Nuclei in states with an angular momentum quantum number I>1/2 have a nonspherical charge distribution. This produces a nuclear quadrupole moment. In the presence of an asymmetrical electric field (produced by an asymmetric electronic charge distribution or
ligand arrangement) the nuclear energy levels split. The charge distribution is characterised by a single quantity called the Electric Field Gradient (EFG).

In the case of an isotope with \( I = 3/2 \) excited state, such as \(^{57}\text{Fe}\) or \(^{119}\text{Sn}\), the excited state is split into two substates \( m_I = \pm 1/2 \) and \( m_I = \pm 3/2 \). This is shown in Fig. 2.9, giving a two lines spectrum or 'doublet'. The extent of the splitting depends on the electron charge asymmetry. For \(^{57}\text{Fe}\) the magnitude of the quadrupole splitting is given by

\[
QS = \frac{1}{2} \left( e^2 q_{ZZ} Q \right) \left( 1 + \eta^2 / 3 \right)^{1/2}
\]

where \( q_{ZZ} \) is the principal component of the electric field gradient, \( \eta \) is asymmetry parameter \( = (q_{ZZ} - q_{YY})/q_{ZZ} \). QS is highly sensitive function of charge state (high spin and low spin) as well as the nearest neighbor environment of the probe atom.

**Fig. 2.9** Quadrupole splitting for a 3/2 to 1/2 transition.
2.7.3 Magnetic hyperfine interaction

In the presence of a magnetic field the nuclear spin moment experiences a dipolar interaction with the magnetic field which is called as Zeeman splitting. There are many sources of magnetic fields that can be experienced by the nucleus. The total effective magnetic field at the nucleus, $H_{\text{eff}}$ is given by:

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

The first three terms are due to the atom’s own partially filled electron shells. $H_{\text{contact}}$ is due to the spin on those electrons polarising the spin density at the nucleus, $H_{\text{orbital}}$ is due to the orbital moment on those electrons, and $H_{\text{dipolar}}$ is the dipolar field due to the spin of those electrons.

This magnetic field removes the nuclear degeneracy and splits nuclear levels with a spin of $I$ into $(2I+1)$ substates, so that the $m_I$ levels have energies given by

$$E_{m_I} = -g_n \beta_n m_I H_{\text{eff}}$$

Where $g_n$ is the electronic g factor or gyromagnetic ratio, $\beta_n$ is the nuclear Bohr magneton and $m_I$ is the component of nuclear spin $I$. Transitions between the excited state and ground state can only occur where $m_I$ changes by 0 or 1. This gives six possible transitions for a $3/2$ to $1/2$ transition, giving a sextet as illustrated in Fig. 2.10, with the line spacing being proportional to $H_{\text{eff}}$. 
Fig. 2.10 Magnetic splitting of the nuclear energy levels

The line positions are related to the splitting of the energy levels, but the line intensities are related to the angle between the Mössbauer gamma-ray and the nuclear spin moment. Thus a purely polycrystalline Fe-metal gives a symmetric six line spectrum (sextet), with intensities in the ratio 3:2:1:1:2:3 and the line separation gives a measure of hyperfine field at the nucleus.

These interactions, Isomer Shift, Quadrupole Splitting and Magnetic Splitting, alone or in combination are the primary characteristics of many Mössbauer spectra.

2.8 Thermo Gravimetric Analyser (TGA)

In thermo gravimetric analysis the sample is heated at a constant heating rate and the sample weight is measured as function of temperature [128]. In this technique the heating can be done under air (oxidative) or nitrogen/argon (inert) atmosphere. This technique is quite
effective in hydrogen storage study as the desorption of hydrogen leads to the mass change which can be monitored during the temperature ramp, and from the temperature of the mass loss, the hydrogen desorption temperature can be estimated. In a properly calibrated instrument, the hydrogen storage capacity also can be estimated roughly by the amount of mass loss. Fig. 2.11 shows a simplified diagram of the thermogravimetric analyzer.

![Simplified diagram of a TG apparatus](image)

**Fig. 2.11 The simplified diagram of a TG apparatus**

The heart of the instrument is the micro-balance. During the measurement, the change in sample mass affects the equilibrium of the balance. This imbalance is fed back to a force coil, which generates additional electromagnetic force to recover equilibrium. The amount of additional electromagnetic force is proportional to the mass change. During the heating process the temperature may go as high as 1500 °C inside the furnace depending upon the configuration of the instrument.

### 2.9 Differential Thermal Analyser (DTA)

Differential Thermal Analysis measures the temperature difference between a sample and a reference material as a function of temperature, when they are heated or cooled at a constant heating rate [129]. Reaction or transition temperatures are then measured as a
function of the temperature difference between the sample and the reference. Any transition occurring in sample, which are associated with heat change can be monitored by this analysis. It provides vital information of the materials regarding their endothermic and exothermic behavior at high temperatures. As most of the hydrogen storage materials the hydrogen desorption reactions are highly endothermic in nature, so the desorption temperature can be determined from the DTA peak. The technique finds most of its applications in analyzing and characterising clay materials, ceramic, ores, etc.

2.10 Differential Scanning Calorimeter (DSC)

Differential scanning calorimetric technique is quite similar to DTA, except that, it is an isothermal measurement. It means that, during the measurement the sample and reference material are simultaneously heated or cooled at a constant rate just like DTA [129]. But here the amount of heat absorbed or released by a sample, to keep both the sample and reference at the same temperature is measured. In case of any exothermic/endothermic transition, the amount of heat flow from the system varies in order to keep both the sample and the reference at same temperature. The difference in temperature between them is proportional to the difference in heat flow (from the heating source i.e. furnace), between the two materials. This technique is applied to most of the polymers in evaluating the curing process of the thermoset materials as well as in determining the heat of melting and melting point of thermoplastic polymers, glass transition temperature (T_g), endothermic & exothermic behaviour. As desorption of hydrogen occurs with absorption of heat, so it can detected for the endothermic peak of DSC. The instrumentation of DSC [Fig. 2.12] is exactly similar to that of DTA, except for the difference in obtaining the result.
2.11 Temperature Programmed Desorption (TPD)

When the hydride is heated at a constant heating rate, and the amount of hydrogen desorbed measured with respect to temperature, then it can be found that, the hydrogen desorption takes place at definite well defined temperature, depending on the site in which the hydrogen atoms are trapped. This particular method is known as Temperature Programmed Desorption (TPD) and is widely used for determining the H site occupancy [130]

The instrument used for TPD/TPR/TPO studies was TPDRO – 1100 of Thermoquest (Italy) make. Fig. 2.13 depicts a typical block diagram of the instrument used. This instrument is based on the in-flow method where analysis is carried at atmospheric pressure using continuous flow of inert or reactive gases. In a typical TPD experiment the sample is placed in a quartz reactor system that constitutes of two concentric tubes as shown in Fig. 2.13.
Before start of actual analysis, the hydride sample is first preconditioned under argon flow, at room temperature for 40 minutes. The desorption profile is thereafter recorded by heating the sample at a fixed rate under the controlled flow of Argon. A thermal conductivity detector is employed to monitor the change in hydrogen concentration with time. Initially, as temperature is low for desorption to occur, a steady baseline is obtained. As the desorption process starts, the hydrogen concentration in effluent stream increases and this change is recorded by TCD. Any water vapor present in the system is removed from the flowing gas with the help of a soda lime trap placed just before the detector. Hence the signal obtained is primarily due to change in thermal conductivity of the hydrogen produced in the desorption process. As the desorption rate increases with increasing temperature the signal intensity also increases. Later on with the decrease in concentration of hydrogen the rate of desorption...
decreases and so does the signal intensity. After completion of desorption of hydrogen from a particular site of the hydride the signal comes back to baseline despite of the high sample temperature. The sample is cooled after completion of the analysis. This dehydrided sample can be analysed by subsequent XRD analysis, in order to identify product. From this we can also ensure that after the hydrogen removal the alloy comes back to its original structure.