Chapter 2
Experimental Techniques

This chapter describes the details of the experimental techniques used here to synthesize metal, metal oxide, metal-metal oxide nanostructures and graphene/graphene nanocomposites. These include (i) capping agent assisted chemical reduction technique, (ii) microemulsion technique, (iii) co-precipitation method, and (iv) mechanical attrition method. Also the working principle of various techniques used for microstructural and spectroscopic characterization and their application in characterization of nanomaterials are described in this chapter. Principles of various sophisticated tools used for the investigations of physical properties of nanostructured materials are also reported here.

2.1 Synthesis techniques

The fabrication of nanomaterials is very important to understand and determine the fundamental properties of the nanostructures. The synthesis techniques of nanostructures are broadly classified into two groups - chemical and physical methods. The chemical processes used here are i) capping agent assisted chemical reduction technique, ii) microemulsion method, iii) co-precipitation method, and high energy ball-milling method is the physical method applied for synthesis of nanostructures. The synthesis of nanostructures by mechanical attrition method can be grouped in the physical method.

2.1.1 Capping agent assisted chemical reduction method

The chemical reduction method is the most advantageous bottom-up approach of synthesis of metal nanoparticles. The precursors used in this process are solution of metal salt, reducing agent and capping agent. The commonly used reducing agents are hydrazine hydrate (N₂H₄·H₂O), sodium borohydride (NaBH₄), sodium citrate and ascorbic acid. The
capping agent (i.e. polyvinylpyrrolidone (PVP), thiols, citrates, cetyltrimethylammonium bromide (CTAB)) used in this process controls the growth of the nanoparticles, stabilizes them against agglomeration and prevents the oxidation [1-4]. The stabilization of the nanoparticles is achieved by the formation of electric double layer when the capping agent is ionic in nature. The detailed reactions are described below:

\[
\text{M}^{2+} + 2\text{NH}_4\text{OH} \rightarrow \text{M} \left(\text{NH}_3\right)_2^{2+} + 2\text{OH}^- \\
\text{M} \left(\text{NH}_3\right)_2^{2+} + \text{N}_2\text{H}_4 + \text{OH}^- \rightarrow \text{M} + \text{N}_2 + \text{NH}_4\text{OH}
\]

where, M = Cu, Ni, Au, Ag, Fe.

**Fig. 2.1. Schematic of surfactant assisted reduction process.**

The schematic of the reduction process is presented in Fig. 2.1. Depending on concentration of salt and reaction temperature, the nucleation is either homogeneous or heterogeneous. In case of homogeneous nucleation, all the nuclei are formed simultaneously and the particle size distribution is narrow. Whereas, in heterogeneous nucleation, nuclei are formed at different time and it ends up with polydispersed nanoparticles. The growth of the nanoparticles starts after the nuclei are formed and the capping agent employed in the process arrests the growth of particles at certain stage resulting in ultrafine nanoparticles. The solvent also has effect on the particle size. For example, polyols (ethylene glycol, diethylene glycol, polyethylene glycol) have a reducing effect and thus the reduction carried out in polyol medium results in smaller particle size compared to the reduction in aqueous medium [5].
We fabricated copper and nickel nanoparticles by chemical reduction method in presence of CTAB. The chloride salts of copper and nickel were used as precursors and \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \) as reduction. \( \text{NH}_4\text{OH} \) was added to the CTAB-salt solution to maintain pH 10. This is a necessary condition for the reaction to take place. To the basic salt solution was then added \( \text{N}_2\text{H}_4\cdot\text{H}_2\text{O} \) and after two hours, the colour of the solution changed indicating the end of the reaction. The reactions were carried out in different reaction medium and temperature to obtain narrow-dispersed ultrafine metal nanoparticles.

Cobalt-graphene nanocomposite was also synthesized using simultaneous reduction of graphite oxide and cobalt nitrate in aqueous medium and using \( \text{NaBH}_4 \) as the reducing agent.

### 2.1.2 Microemulsion method

A microemulsion is a thermodynamically stable system comprising of three components – oil, water and a surfactant. Water-in-oil microemulsion systems containing nanodroplets of water dispersed in oil attracted a great deal of interest because of efficiency in synthesis of ultrafine nanoparticles. The nanodroplets of water in oil are stabilized by the surfactant and acts as the nanoreactors to carry out the chemical reactions to synthesize the nanostructures.

To obtain the desired nanomaterials, two microemulsions containing the appropriate reactants are mixed. After mixing of two microemulsions, the water droplets collide with each other and exchange of reactants take place. The reaction takes place inside the water droplets and thus the size of the droplets controls the size of the nanomaterials. A schematic picture of the process is presented in Fig. 2.2.

The size of the nanoparticles can be varied by varying the ratio of water and oil in the microemulsion. The concentration of reactants and the surfactant also controls the particle size. Microemulsion method has proved to be one of the versatile techniques in synthesis of different types of nanostructures including ultrafine metal colloids [6-9], core-shell nanostructures [10-12] and superlattices [13, 14].

A microemulsion system consisting of isopropyl alcohol, water and polyvinyl pyrrolidone (PVP) was employed in the synthesis of Cu-Cu\(_2\)O core-shell nanostructures. Two microemulsions one containing \( \text{Cu}^{2+} \) salt and the other containing \( \text{NaBH}_4 \) were mixed to
obtain the target material. By varying the content of water in the microemulsion, the thickness of the Cu$_2$O shell could be controlled.

![Diagram of microemulsion technique](image)

**Fig. 2.2. Schematic of microemulsion technique.**

### 2.1.3 Co-precipitation method

Co-precipitation method is a simple and rapid wet chemical method of synthesis of oxide and ferrite nanoparticles. This process is very advantageous because of the ease in the control of particle size and composition. The precursors used in this process are various salts (nitrate, sulphates, chlorides) and an alkali. The precipitation of the salt is carried out in an alkaline medium to synthesize the desired oxides or ferrites. For example, in case of synthesis of Ni-Zn ferrite salts of nickel and zinc are precipitated by addition of NaOH [15]. The resulting precipitate is further annealed so that the desired crystalline material is formed. The initial precursor concentration, pH of the solution and the rate of addition of the NaOH/NH$_4$OH solution [16] play a major role in controlling the particle size.

Synthesis of undoped and doped ZnO was carried out by precipitation technique. For synthesis of undoped ZnO, solution of zinc nitrate was precipitated using NaOH solution. In
order to synthesize different morphology, we also used the cationic surfactant CTAB. The precipitate was then washed several times with water and dried at 333 K for 3 days. To synthesize doped ZnO, a similar procedure was followed. The only change that we adopted was in the precursor – along with Zn(NO$_3$)$_2$, calculated amount of M(NO$_3$)$_2$ [M= Y$^{3+}$, Mn$^{2+}$] was added. The co-precipitation of binary salt resulted in doped ZnO. The use of CTAB resulted in interesting structures of the synthesized products.

2.1.4 High energy ball milling method

High energy ball milling is a top down method of synthesis of glass ceramics, semiconductors (sulphides, tellurides) and ferrite materials [17-20]. In this case, the particles are reduced to nanoscale by grinding with balls.

To minimize the contamination, the material of the grinding bowl and balls are taken as abrasion resistant i.e. zirconium oxide, tungsten carbide balls. The size of the grinding balls, ball to powder mass (BPMR) ratio and the choice of the milling time have crucial influence on the phase and size of the material formed. The main drawback of this process is the polydispersion of the size distribution of the synthesized product.

![FRITSCH Pulverisette 7 planetary ball mill](image)

**Fig. 2.3. FRITSCH Pulverisette 7 planetary ball mill.**

We used the process of high energy ball milling to synthesize graphene. Graphite oxide powder was ball-milled for different durations with zirconium oxide balls of diameter 5mm in a FRITSCH Pulverisette 7 planetary ball mill (Fig. 2.3) in inert (Ar) atmosphere. The
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ball to mass ratio (BPMR) was kept constant at 20:1 with angular speed 800 rpm. The appropriate duration of obtaining graphene from graphite oxide was found to be 180 minutes.

2.2 Characterization techniques

This section of the chapter deals with various techniques employed to characterize the synthesized products. These involve microstructural characterization (crystal structure and morphological study) and spectroscopic characterization (study of different energy states and chemical bonds). The working principle of different techniques and their utility in characterization of nanomaterials are discussed.

2.2.1 X-Ray Diffraction (XRD) technique

2.2.1.1 Basic Concept of XRD

The materials that are dealt with throughout this research work are mainly crystalline materials. These materials comprise of periodic arrangement of atoms in parallel planes, separated by distance of the order of 0.1 nm. The crystal can thus be considered as a three dimensional grating with atoms acting as the diffraction centre. For diffraction through the crystal, the wavelength of incident radiation should be equal to the interatomic distance. X-rays are electromagnetic radiation of shorter wavelength and higher energy. Therefore X-rays are electromagnetic probe for diffraction through crystals.

When X-rays pass through the crystal, each atom scatters the incident rays in all possible directions. The scattered rays interfere constructively if the path difference between two rays is integral multiple of incident wavelength. If the condition is violated, destructive interference occurs. Let us visualize the condition:

Let us consider two rays AO and A’O’ (fig. 2.4) inclined at an angle θ (grazing angle) with the atomic planes and are scattered in the direction OC and O’C’ respectively. The path difference between these two rays is

\[ BOB' = 2d \sin \theta \]

The condition for constructive interference is

\[ 2d \sin \theta = n\lambda \]  \hspace{1cm} (2.1)

where, \( \lambda \) = wavelength of incident radiation; \( n \) = order of diffraction. This is Bragg’s law.
Fig. 2.4. Diffraction of X-rays by crystals.

From eq (2.1), we also reach at the condition that

\[ \frac{n \lambda}{2d} \leq 1 \]  

(2.2)

since maximum value of \( \sin \theta = 1 \). Thus, no diffraction occurs if \( \lambda \geq 2d \) i.e. wavelength of incident X-ray is greater than twice the interplanar spacing [21].

2.2.1.2 Setup of XRD

A simple setup of XRD is shown in Fig. 2.5. A monochromatic collimated beam of X-ray of wavelength 0.05-0.25 nm (in our case 0.154 nm), is incident on the sample. The detector detects the diffracted beam and gives a peak corresponding to an angle \( \theta \) satisfying the Bragg’s law (eq. 2.1).

Fig. 2.5. Setup of X-ray diffractometer.
By varying the angle $\theta$, Bragg’s law is satisfied for different d-spacing. The plot of $2\theta$ and the intensity of scattered beam is called a diffractogram and is a characteristic of the sample. Thus XRD technique can be considered as fingerprint of the crystal structure.

### 2.2.1.3 Utility of XRD

XRD is versatile, non-destructive and the most powerful technique for qualitative and quantitative analysis of crystalline material. The informations that can be extracted from XRD analysis are

- the presence of different phases can be identified.
- d-spacing can be calculated from the value of angle.
- atomic positions and the lattice parameters can be obtained.
- the broadness of the peaks gives an idea of the crystallite size and strains.

Bruker D8 and Rich Seifert X-ray diffractometer using CuK$\alpha$ radiation of wavelength 1.54 A was used throughout the research work. To confirm the presence of the phases, the $2\theta$ values of the diffractogram were matched with standard data of JCPDS (Joint Committee on Powder Diffraction Standards) files. The quantitative analysis using XRD was performed by Rietveld analysis of the experimental data. The software used was MAUD 2.07 which is specially designed to refine simultaneously both the structural and microstructural parameters through a least-squares method [22].

### 2.2.2 Transmission Electron Microscopy (TEM)

#### 2.2.2.1 Basic concept of TEM

In similar manner to XRD, energized beam of electrons can also be used to characterize materials. The wavelength ($\lambda$) associated with high energy electron beam, accelerating through a very high potential (100-1000 kV), is

$$\lambda = \frac{h}{\sqrt{2mE}} \approx 3 \text{Å}$$  \hspace{0.5cm} (2.3)

where, $h$ = Planck’s constant $= 6.634 \times 10^{-34}$ Js; $m$ = mass of electrons $= 9.11 \times 10^{-31}$ kg [23].

Thus, the high energy accelerated electron beam has much lower wavelength compared to visible light (400-800 nm). In case of electron microscopes, the use of magnetic focusing
lenses reduces the angle between the incident ray and the deflected ray \((\alpha)\) to 0.5°. These two factors governs the resolution \((R)\) of microscope and \(R\) for transmission electron microscope

\[
\frac{0.61\lambda}{\sin \alpha} \approx 1\text{ Å}.
\]

Also, the magnification of electron microscope is as high as \(2 \times 10^6\) times where as that of optical microscope is \(\sim 10^3\) times. The electron microscope can thus be utilized in imaging of material in nanometer dimension and even upto atomic level.

### 2.2.2.2 Setup of TEM

The schematic of TEM is illustrated in fig. 2.6. The high energy electron beam after being ejected from the electron gun, passes through magnetic lenses and interacts with the specimen. The transmitted electron beam forms an impression of the sample on a fluorescent screen and photographic plate. In the micrographs, the portion of the sample having higher electron density appears dark and that having lower density appears brighter.

![Fig. 2.6. Setup of transmission electron microscope.](image)

The microstructures of the samples synthesized in the present work were investigated by a JEOL Model JEM 2010 transmission electron microscope (Tokyo, Japan)
operated at 200 kV. The sample for TEM was prepared by dispersing a small amount of the sample in a volatile solvent (acetone/ethanol). By using ultrasonication, well-dispersed solution was formed and a drop of the solvent was cast on a carbon coated copper grid having 300 mesh size. The solvent evaporates very quickly due to its volatile nature and the sample stucked to the grid.

### 2.2.2.3 Utility of TEM

TEM is very powerful tool for morphological study of nanomaterials.

- The micrographs help in determination of the size distribution of the synthesized particles.
- The high resolution transmission electron micrographs (HRTEM) help in determining the spacing between lattice planes.
- The selected area electron diffraction (SAED) recorded by diffraction mode is useful in determining the type of crystallinity present in the sample (single crystallinity/polycrystallinity).
- The interplanar spacing can also be calculated from SAED pattern.

### 2.2.3 Energy Dispersive X-Ray spectrometry (EDX)

#### 2.2.3.1 Basic concept of EDX

The energy dispersive X-ray spectrometry is an analytical technique for chemical analysis of materials, used in conjunction with TEM. When the sample is bombarded with high energy electron beam, the core electrons are excited to higher energy states. The excited electrons then cascades to lower energy states to attain a minimum energy states. During transition to lower energy state, X-rays are emitted and recorded by the detector. As the emitted X-ray is a characteristic of the sample, the spectrum is a simple yet powerful tool for qualitative and quantitative analysis of elemental composition of samples.

#### 2.2.3.2 Applications of EDX analysis

- Identification of lines in the X-ray spectrum helps in identification of elements in the sample.
Determination of the elemental composition (in percentage) of the sample from the ratio of the intensity of peaks corresponding to individual elements in the sample.

The elemental composition of the samples was analysed by the EDX analyzer attached to JEM 2010 TEM. The samples for EDX analysis were prepared in a similar manner as that of TEM.

### 2.2.4 UV-Visible absorbance spectroscopy (UV-Vis)

#### 2.2.4.1 Basic concepts

When a material is irradiated with electromagnetic radiation, three processes can occur – reflection, transmission and absorption. The basic principle behind the UV-Visible absorbance spectroscopy is the absorption characteristic by the material when photon having wavelength in UV-Visible range (200-800 nm) is directed on it. The energy of photon with wavelength in this range is sufficient enough to induce electronic transitions. If the incident photon energy is greater than the band gap energy (in case of semiconductors), the electron absorbs the energy and transits to the conduction band. In case of metallic samples, the absorption occurs due to the phenomenon called “surface plasmon resonance (SPR)”. The interaction of the metal particles with the oscillating electric field of the incident electromagnetic radiation causes coherent oscillation of the conduction electrons. This collective oscillation of conduction electrons is called surface plasmon resonance. The detector of the optical spectrometer records the wavelength of photon and the corresponding absorbance.

![Varian Cary 5000 UV-Vis-NIR spectrophotometer](image)

*Fig. 2.7. Varian Cary 5000 UV-Vis-NIR spectrophotometer.*
The UV-Vis absorbance spectra of the samples were recorded using Varian Cary 5000 UV-Vis-NIR spectrophotometer (fig. 2.7) within the wavelength range (200-800 nm). For spectroscopic characterization, the powder samples were dispersed in ethanol. To obtain a stable dispersion, the samples were sonicated for a suitable time interval.

### 2.2.4.2 Applications of UV-Vis spectroscopy

- The absorption spectrum is useful in determining the band gap of semiconducting material. The relation obeyed is

  \[
  \left( \frac{a \nu}{\alpha} \right)^n = \left( \nu - E_g \right) \tag{2.4}
  \]

  where, \( \nu \) = energy of incident radiation, \( \alpha \) = absorption co-efficient, \( E_g \) = band gap of the semiconductor, and \( n \) = \( \frac{1}{2} \) (allowed direct transition); 2 (allowed indirect transition); 3/2 (forbidden direct transition); 3 (forbidden indirect transition).

- Particle size can be calculated from the absorption spectrum using the relation

  \[
  E^* - E_g = \frac{\hbar^2}{8 \varepsilon_0} \left( \frac{1}{m_e} + \frac{1}{m_h^*} \right) - \frac{1.8e^2}{4 \pi \varepsilon_0 \hbar^2} - \frac{4 \times 0.124 \epsilon_0^4}{\hbar^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \tag{2.5}
  \]

  where, \( E^* \) is the observed band gap, \( E_g \) is the band of bulk material, \( h \) is Planck’s constant, \( e \) is electronic charge, \( r \) is the particle radius, \( m_e^* \) is effective mass of electrons, \( m_h^* \) is holes effective mass, \( \varepsilon_0 \) is the permittivity of free space, \( \varepsilon \) is the relative permittivity of the material, \( m_0 \) is rest mass of electrons.

- The absorption spectrum gives an idea of the particle size distribution of the material and shape of the particles.

### 2.2.5 Fourier Transform Infra-Red (FTIR) spectroscopy

#### 2.2.5.1 Basic Principle of FTIR spectroscopy

The total energy of a molecule is the sum of electronic, vibrational and rotational energy terms. The radiation of infrared region (lower energy) is incapable of inducing electronic transitions in a material but can excite vibrational and rotational transitions in a
molecule. The infrared spectroscopy is an absorption method where the incident electromagnetic radiations of higher wavelengths (1-100 μm) interact with the material. The molecule absorbs that frequency whose corresponding energy coincides with the vibrational energy of the molecule.

2.2.5.2 Setup of FTIR Spectrometer

The FTIR spectrometer uses a beam splitter which splits the incident ray into two halves – one is reflected to a fixed mirror and the other is transmitted to a moving mirror (Fig. 2.8).

![Schematic of interferometer.](image)

Fig. 2.8. Schematic of interferometer.

Both the rays are reflected back from the two mirrors, to the beam splitter. The beam splitter thus receives two rays and each ray is again splitted into two parts – one goes back to the source and the other to the detector. The two rays reaching the detector interferes either constructively or destructively, depending upon the path difference between the two rays generated due to the mirror in motion. The resulting signal at the detector (frequency vs
intensity) is called interferograms. This type of interferometers measures simultaneously all the infrared frequencies resulting in faster scanning process. The mathematical technique “Fourier Transform” is then performed to decode the individual frequency of the interferograms and obtain the spectrum (plot of wavenumber vs transmittance).

The spectrometer FTIR 8400S supplied by Shimadzu was used for recording FTIR spectrum of the samples. The wavenumber range used in the spectrometer is 4000-400 cm\(^{-1}\). A small amount of the powder sample was pelletized with KBr for FTIR spectroscopic characterization.

### 2.2.5.3 Advantages of FTIR spectroscopy

The FTIR spectrum is the molecular fingerprint of a material. The main advantages of this spectroscopy is

- It is a powerful, non-destructive and very fast scanning process.
- Helps in identification of different chemical bonds present in the material.
- Determination of the amount of the components in the sample.

### 2.2.6 X-Ray Photoelectron Spectroscopy (XPS)

#### 2.2.6.1 Basic Principle of XPS

The basic principle of X-ray Photoelectron Spectroscopy is photoelectric effect. When a sample surface is irradiated with X-ray beam, the energy of the X-ray photon is completely absorbed by the core electrons of the sample. If the energy of the photon (\(h\nu\)) is sufficient enough for the core electrons to overcome the binding energy (\(E_B\)), the electrons are emitted with kinetic energy (\(E_K\)) depending on incident energy and binding energy (fig. 2.9). The relationship between binding energy of core electrons, kinetic energy of photoelectron and energy of incident X-ray is

\[
   hv = E_B + E_K + \varphi ,
\]

where \(\varphi\) = work function of the material. If \(\varphi\) is eliminated by artificial means, then

\[
   hv = E_B + E_K \Rightarrow E_B = h\nu - E_K
\]  

(2.6)
The XPS instrument measures the kinetic energy of the collected electrons and subsequently the binding energy is calculated. The spectrometer used in our work is supplied by Specs (Germany).

![Conduction Band and Valence Band](image)

**Fig. 2.9. Schematic illustration of emission of electrons from valence band.**

### 2.2.6.2 Applications of XPS

XPS is a powerful technique for surface analysis of materials. The electrons are extracted from a depth ~10 nm from the surface of the sample, so the information is obtained within this depth. The applications are

- Identification of elements present on the surface of the material.
- Determine the chemical states of the constituents elements.
- Measurement of thickness of overlayers on the sample.

### 2.2.7 Raman spectroscopy

Raman spectroscopy is a powerful tool for determining chemical species. It is based on inelastic scattering of monochromatic light, usually from a laser source. Inelastic scattering means that the frequency of photons in monochromatic light changes upon interaction with a sample. Photons of the laser light are absorbed by the sample and then reemitted. Frequency of the reemitted photons is shifted up or down in comparison with the original monochromatic frequency, which is called the Raman shift. This shift provides information about vibrational, rotational and other low frequency transitions in molecules. In
resonance Raman spectroscopy the excitation wavelength is chosen to overlap with (or be very close to) an electronic transition. In such cases the scattering intensities increase by factors of $10^2$-$10^6$.

Raman scattering study was performed with 514.5 nm excitation of continuous He/Cd laser and dispersion with 2400 gr/mm grating in the backscattering configuration using Raman spectrometer (inVia Renishaw). A thermoelectric cooled ‘back-thinned’ charged coupled detector was used for the detection of scattered intensity.

### 2.3 Physical Property Measurements

#### 2.3.1 Optical Property

**2.3.1.1 Photoluminescence property (PL)**

Photoluminescence spectroscopy is a powerful, non-destructive technique of probing the electronic states, defect states as well as surface properties. The photoluminescence experiment is generally divided into three parts. Firstly, the electrons are excited from valence band to conduction band under excitation by light source. Second, the electrons in conduction band and holes in valence band relax by transferring energy to the crystal lattice. Finally, the electron-hole pairs recombine by emission of light [23]. The emitted light is detected by the detector and the peaks in the spectra represent a direct measure of the energy levels in the material. The typical setup of the PL experiment is shown in fig. 2.10.

Photoluminescence studies of the materials under investigation were performed using F-2500 FL spectrometer at room temperature. The excitation wavelength was set according to the band gap of the material.

![Fig. 2.10. Setup of PL experiment](image)
2.3.2 Electrical Properties

To investigate the electrical transport properties of the materials under study, variation of resistivity of the samples with temperature and their I-V characteristics were studied.

For electrical property measurements, the powder samples were pelletized at room temperature under a pressure of 5 tons/cm$^2$. Electroding on the two surface of the pellet was done with Silver paint (supplied by Acheson Colloiden B.V. Holland). Two copper leads were connected to the two electrodes by silver paint. The pellets with two copper leads were mounted on the sample holder for further measurements.

2.3.2.1 Resistivity measurements

The variation of resistivity with temperature within the temperature range 150-473 K was measured. Two different measurements setup were employed for the measurement in this temperature range. For resistivity measurement in the high temperature range (300-473 K), the sample holder was inserted in a metal chamber which is placed within a vertical furnace. For low temperature measurements, the sample holder was inserted in a glass chamber placed within a dewar. To attain the low temperature, liquid nitrogen was poured into the dewar and after attaining the lowest possible temperature, the heating coil wound around the sample holder is set on to heat the chamber upto room temperature. The chamber was evacuated by a vacuum pump up to a pressure level $10^{-3}$ torr before measurements. The dc electrical resistances of the samples were measured using Keithley electrometer.

2.3.3 Magnetic Properties

For magnetic property measurement of the sample, Magnetic Properties Measurement System (MPMS) Superconducting Quantum Interference Device (SQUID) magnetometer (supplied by Quantum Design, USA), was employed. The representative image is presented in Fig. 2.1.1. It is a very sensitive instrument and is based on quantum effects in superconducting loop.

The powder sample was wrapped in parafilm and inserted within the diamagnetic straw which was attached to the sample rod of the MPMS apparatus. We mainly performed two sets of measurement – measurement of magnetic moment as a function of temperature and magnetic field. The variation of magnetic moment with temperature was performed
under both zero-field-cooled (ZFC) and field-cooled (FC) conditions. In case of ZFC, the sample was cooled to 2K in absence of magnetic field where as in FC, a specific magnetic field was applied during the cooling of sample. In both the cases, the variation of magnetic moment with temperature was recorded during ascend of temperature from 2 to 300 K. The variation of magnetic moment with applied field (hysteresis loops) was also measured for the temperature range 2-300 K and for magnetic field upto 5 T.

Fig. 2.11. SQUID magnetometer supplied by Quantum Design, USA.

2.3.4 Thermal Properties

2.3.4.1 ThermoGravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

Thermogravimetric analysis is an analytical technique to study the thermal stability of the material and determine the amount of volatile phase in the material. The weight of the sample under investigation is recorded as a function of temperature. The measurements can be performed in air as well as inert atmospheres.

Differential thermal analysis refers to measurement of temperature difference between a reference pan and pan with sample. In practice, Al₂O₃ serves as the reference pan owing to its greater thermal stability.
The thermal properties of the samples were measured using TA Instruments SDT Q600 DTA-TGA (Fig. 2.12). This instrument also serves as thermal magnetic analyzer (TMA) to measure the Curie temperature of magnetic material. In TMA, the thermogravimetric curve of the sample under investigation is measured in presence of inhomogeneous magnetic field, generally from a permanent magnet, placed on the top of the furnace directly over the test specimen. At Curie temperature (transition from ferromagnetic to paramagnetic phase), the sample is no longer attracted by the magnet and the weight of the sample increases sharply.
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References