Chapter-3

3. Experimental techniques

Besides chemical methods, a large variety of experimental techniques were employed to characterize the materials. Chapter -3 deals in different characterization techniques such as X-ray diffraction (XRD), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDXS), selected area electron diffraction (SAED), photoluminescence spectroscopy (PL), atomic force microscopy (AFM), magnetic force microscopy (MFM), UV-Visible optical absorption spectroscopy (OAS), Super conducting quantum interference device (SQUID) etc. The actual incorporation of TM atoms into II-VI host structure was also evidenced by the X-ray Diffraction analyses. Electron microscopy reveals formation of spherical nanostructures in ZnS based systems and nanorods in ZnO based systems. Low temperature magnetic measurements of the investigated samples were performed by utilizing SQUID within temperature limit 4K to 300K and at different magnetic fields 0.01T and 0.1T. The characterizations of our samples were carried out by utilizing modern experimental tools at different laboratories / facility centers as given below:

<table>
<thead>
<tr>
<th>Laboratories/ Facility Centers</th>
<th>Tools utilized</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (a) Tezpur University (TU)</td>
<td>EDX, SEM; XRD, UV-Vis, PL; FTIR, Pallet preparation;</td>
</tr>
<tr>
<td>(a) Dept. of Physics, TU</td>
<td></td>
</tr>
<tr>
<td>(b) Dept of Chem. TU</td>
<td></td>
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<tr>
<td>2. SAIF, NEHU, Shillong</td>
<td>TEM/HRTEM, SAED;</td>
</tr>
<tr>
<td>3. DAE UGC Consortium, Indore</td>
<td>Low temp. SQUID;</td>
</tr>
<tr>
<td>4. CMMIP, University “Politehnica” Bucharest, Romania</td>
<td>AFM, MFM.</td>
</tr>
</tbody>
</table>
3.1 X-ray Diffraction

“...every crystalline substance gives a pattern; the same substance always gives the same pattern; and in a mixture of substances each produces its pattern independently of the others.”

........ By A. W. Hull (1999)

Solid matter can be classified as amorphous and crystalline. In amorphous solid atoms are arranged in a random way similar to the disorder as observed in a liquid. Glasses are amorphous materials. On the other hand, in a crystalline solid the atoms are arranged in a regular pattern. About 95% of all solid materials can be described as crystalline. When X-rays interact with a crystalline substance (Phase), one gets a diffraction pattern. The X-ray diffraction pattern of a pure substance is, therefore, like a fingerprint of the substance. The powder diffraction method is thus ideally suited for characterization and identification of polycrystalline phases. Today, diffraction patterns have been collected and stored on magnetic or optical media as standards for about 50,000 inorganic and 25,000 organic single components, crystalline phases. By following search/match procedure the powder diffraction is used to identify components in a sample. Furthermore, the areas under the peak are related to the amount of each phase present in the sample.

An electron in an alternating electromagnetic field will oscillate with the same frequency as the field. When an X-ray beam hits an atom, the electrons around the atom start to oscillate with the same frequency as the incoming beam. In almost all directions destructive interference will be obtained, that is, the combining waves are out of phase and there is no resultant energy leaving the solid sample. However the atoms in a crystal are arranged in a regular pattern, and in a very few directions we will have constructive interference. The waves will be in phase and there will be well defined X-ray beams leaving the sample at various directions. Hence, a diffracted beam may be described as
a beam composed of a large number of scattered rays mutually reinforcing one another.

X-ray reflections are obtained for different parallel planes \((h k l)\) inside a crystal according to their orientation. When the value of any indices becomes zero, the plane is parallel to that axis. For e.g., \((2 2 0)\), the plane is parallel to c axis.

![Diagram of Bragg's Law reflection](image)

**Figure: 3.1** Bragg's Law reflection. The diffracted X-rays exhibit constructive interference when the distance between paths ABC and A'B'C' differs by an integer number of wavelengths \((\lambda)\).

The X-ray Diffraction can be easily understood with the help of Bragg’s law [199]. The constructive interference exhibited by the diffracted X-ray from two parallel planes with interplanar spacing \(d\) is shown in figure: 3.1.

When a crystal is bombarded with X-rays of a fixed wavelength (similar to spacing of the atomic-scale crystal lattice planes) and at certain incident angles, intense reflected X-rays are produced when the wavelengths of the scattered X-rays interfere constructively. In order for the waves to interfere constructively, the differences in the travel path must be equal to integer multiples of the wavelength. When this constructive interference occurs, a diffracted beam of X-rays will leave the crystal at an angle equal to that of the
incident beam. To illustrate this feature, let us consider a crystal with crystal lattice planar distances $d$. Where the travel path length difference between the ray paths $ABC$ and $A'B'C'$ is an integer multiple of the wavelength, constructive interference will occur for a combination of that specific wavelength, crystal lattice planar spacing and angle of incidence ($\theta$). Each rational plane of atoms in a crystal will undergo refraction at a single, unique angle (for X-rays of a fixed wavelength).

The general relationship between the wavelength of the incident X-rays, angle of incidence and spacing between the crystal lattice planes of atoms is known as Bragg’s law, it is expressed as:

$$n \lambda = 2d \sin \theta \quad .......................................\ 3.1$$

Where, the integer ‘$n$’ is the order of reflection, $\lambda$ is the wavelength of the incident X-rays, $d$ is the interplanar spacing of the crystal and ‘$\theta$’ is the angle of incidence.

In X-ray diffraction (XRD) the interplanar spacing ($d$-spacing) of a crystal is used for identification and characterization purposes. In this case, the wavelength of the incident X-ray is known and measurement is made of the incident angle ($\theta$) at which constructive interference occurs. Solving Bragg’s Equation gives the $d$-spacing between the crystal lattice planes of atoms that produce the constructive interference. A given unknown crystal is expected to have many rational planes of atoms in its structure; therefore, the collection of "reflections" of all the planes can be used to uniquely identify an unknown crystal. In general, crystals with high symmetry (e.g. isometric system) tend to have relatively few atomic planes, whereas crystals with low symmetry (in the triclinic or monoclinic systems) tend to have a large number of possible atomic planes in their structures.

In X-ray diffraction and crystallography the Scherrer equation [200] is a formula that relates the size of sub-micrometer particles or crystallites in a solid to the peak broadening in a diffraction pattern.
The equation is given by

\[ d = 2R = \frac{K\lambda}{\beta \cos \theta} \] ........................................... (3.2)

Where,

- \( d \) is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size;
- \( K \) is a dimensionless shape factor, with a value close to unity. \( K \) has a typical value of 0.89, but varies with the actual shape of the crystallite;
- \( \lambda \) is the wavelength of X-ray used;
- \( \beta \) is the line broadening at half the maximum intensity, i.e. full width half maximum (FWHM);
- \( \theta \) is the Bragg angle.

The Scherrer equation is applied to determine size under the limitations to nano-scale particles only. It cannot be applied to grains larger than about 0.1 to 0.2 \( \mu m \). It is to be noted that the Scherrer formula provides a lower bound on the particle size. The reason for this is that a variety of factors can contribute to the width of a diffraction peak besides instrumental effects and crystallite size; the most important of these are usually inhomogeneous strain and crystal lattice imperfections.

If all other contributions to the peak width were zero, then the peak width would be determined solely by the crystallite size and the Scherrer formula would apply. If the other contributions to the width are non-zero, then the crystallite size can be larger than that predicted by the Scherrer formula, with the "extra" peak width coming from the other factors.

The as-synthesized powder samples thus obtained were characterized by powder x-ray diffraction (XRD) (Philips 1730, Cu-K\( \alpha \) radiation, \( \lambda = 1.54 \) Å). The XRD experiments were carried out by utilizing the facility available at the department of physics, Tezpur University.
3.2 UV-Visible spectroscopy

For the last few years and over this period the ultraviolet and visible spectrometers have been in general use and nowadays it is the most important analytical instrument in the modern day laboratory. In many applications, UV-Visible spectrometry has been widely used for its simplicity, versatility, speed, accuracy and cost-effectiveness.

Many molecules absorb ultraviolet or visible light. The absorbance of a solution increases as attenuation of the beam increases. Absorbance \( A \) is directly proportional to the path length, \( b \), and the concentration, \( c \), of the absorbing species. Beer’s Law [201] states that,

\[
A = ebc,
\]

Where \( e \) is a constant of proportionality, called the absorptivity. The figure: 3.2 shows a beam of monochromatic radiation of radiant power \( P_0 \), directed at a sample solution (S). Absorption takes place and the beam of radiation leaving the sample has radiant power \( P \).

The amount of radiation absorbed may be measured as:

Transmittance, \( T = P/P_0 \)

\%Transmittance, \( %T = 100T \)

Absorbance, \( A = \log_{10}(P/P_0) = 2 - \log_{10}(\%T) \) .......................... (3.3)

Equation: 3.3 allows one to calculate absorbance from the transmittance data.

![Figure 3.2: Change of radiant power due to absorption by sample solution.](image)

Different molecules absorb radiation of different wavelengths. An absorption spectrum will show a number of absorption bands corresponding to structural groups within the molecule. When white light falls upon a sample,
the light may be totally reflected, in which case the substance appears white or
the light may be totally absorbed, in which case the substance will appear
black. If, however, only a portion of the light is absorbed and the balance is
reflected, the colour of the sample is determined by the reflected light. Thus, if
violet is absorbed, the sample appears yellow-green and if yellow is absorbed,
the sample appears blue. The colours are described as complementary.
However, many substances which appear colourless do have absorption
spectra. In this instance, the absorption will take place in the infra-red or
ultraviolet and not in the visible region. Table: 2 in the appendix illustrates the
relationship between light absorption and colour.

A close relationship exists between the colour of a substance and its
electronic structure. A molecule or ion will exhibit absorption in the visible or
ultraviolet region when radiation causes an electronic transition within its
structure. Thus, the absorption of light by a sample in the ultraviolet or visible
region is accompanied by a change in the electronic state of the molecules in
the sample. The energy supplied by the light will promote electrons from their
ground state orbitals to higher energy, excited state orbitals or antibonding
orbitals. In semiconductor material this corresponds to a transition from the
valence band to conduction band edge. This characteristic absorption peak is
used to study semiconductor materials in the bulk form or in the nano resigm.
In semiconductor nanostructures, the band gap enhancement is observed with
decreasing cluster size due to quantum confinement effect. For this effect, a
blue shift in the absorption edge is observed with decreasing crystalline/cluster
size. The band gap energy of nanostructures can be estimated from UV-Visible
study by using Bruss equation [202]

The energy of the nanocrystallite \( (E_{gn}) \) can be calculated from the UV-Vis
absorption spectra using the relation \( \frac{hc}{\lambda_c} \), where \( \lambda_c \) represent the
corresponding absorption edge.
3.3 Photoluminescence spectroscopy

Beside UV-Visible spectroscopy, photoluminescence (PL) experiments are most widely used spectroscopic tool among the researchers to investigate optical transition in nanostructures especially in semiconductor nanostructures. The emission characteristics of most of the nanostructures consist of a single-broad emission band, which is symmetric and comes from states that fall in the nanostructure’s band gap. These states are not detectable in absorption spectra. According to L. Brus [202], the luminescence characteristics depend upon the nature of the semiconductors, the physical dimension as well as the chemical environment and the luminescence property can be manipulated in useful ways. Luminescence is the general term used to describe the emission of radiation from a solid when it is excited with some form of energy. When excitation arises from the absorption of photons, the phenomenon is known as photoluminescence. Whatever be the form of energy input, the final stage in the process is an electronic transition between two energy states \( E_1 \) and \( E_2 \) \((E_2 > E_1)\), with the emission of radiation of wavelength \( \lambda \).

\[
hc / \lambda = E_2 - E_1 \quad \ldots \quad 3.4
\]

\( h \) and \( c \) being the Planck’s constant and velocity of light respectively.

According to Stoke’s law, the fundamental law of luminescence, the wavelength of emitted light is generally equal to or longer than that of the exciting light (i.e., of equal or less energy). This difference in wavelength is caused by a transformation of the exciting light, to a greater or lesser extent, to non-radiating vibration energy of atoms or ions. In rare instances e.g. when intense irradiation of laser beam is used or when sufficient thermal energy contributes to the electron excitation process—the emitted light can be of shorter wavelength than the exciting light (anti-Stokes radiation).

Usually, luminescence can be classified in two types: fluorescence and phosphorescence. One can distinguish them depending on the duration of the emission. The fluorescence is an instantaneous process whereas in
phosphorescence, the presence of vacant lattice sites or other impurities, lattice defects, and/or irregularities in the host lattice, provide unoccupied states (traps) and delay the luminescence by detaining (trapping) the charge carriers (electrons/holes) before their radiative recombination with the luminescent centres.

Depending on the nature of the ground and the excited states, the photoluminescence can be divided into two types. Singlet and triplet are the two different kinds of excited states. In a singlet state, the electron in the higher-energy orbital has the opposite spin orientation as the second electron in the lower orbital. These two electrons are said to be paired. On the other hand, in a triplet state these electrons are unpaired, i.e. their spins have the same orientation. An excited singlet state does not require an electron to change its spin orientation during the return to ground state. Contrary to this, a change of spin orientation is required for a triplet state to return to the ground state.

**Figure 3.3:** Radiative and non radiative emission and trap states.

In photoluminescence spectroscopy, photons with energy greater than the band gap of the semiconductor material studied are directed onto the surface of the material. The incident monochromatic photon beam is partially
reflected, absorbed, and transmitted by the material being probed. The
absorbed photons create electron-hole pairs in the semiconductor. The
electrons are excited to the conduction band, or to the energy states within the
gap. Moreover, electrons can lose part of their energy and transfer from the
conduction band to energy levels within the gap. Photons produced as a result
of the various recombinations of electrons and holes are emitted from the
sample surface and it is the resulting photon emission spectrum (PL spectrum).
The photon energies reflect the variety of energy states that are present in the
semiconductor. In PL spectra, a direct conduction band-to-valence band
recombination is rarely observed. Even if direct band-to-band recombinations
occur, the crystal will strongly reabsorb the photons emitted. Therefore, in PL
spectra, recombination processes are observed with emission energies less
than $E_g$. These processes include excitonic recombinations and indirect
transitions, which involve the trapping of electrons (or holes) by impurities. The
nature of the quantum dot surface is critical for photoluminescence
experiments. The influence of the surface on photoluminescence can be
understood in terms of the trap states described in figure: 3.3\[203\]. The
created electron–hole pair may recombine immediately to produce light
(radiative recombination).

These trap states are created due to defects, such as vacancies, local
lattice mismatches, dangling bonds, or adsorbents at the surface. The excited
electron or hole can be trapped by these local energy minima states and
become less available for the radiative recombination of luminescence.
Radiative recombination of the trapped charge carriers then produces
luminescence that is substantially redshifted from the absorbed light. Surface
passivation is a well-known phenomenon that decreases the possibility of
charge carriers residing in traps.

To have a better understanding regarding the PL experiments with
semiconductors we can have a look through the simple description presented
by Hannewald, K., et al. [204].
A typical luminescence experiment in semiconductors can be realized in three stages, as presented in figure: 3.4; first, the sample is excited out of the ground state which is described by a completely filled valence band and an empty conduction band (figure: 3.4a).

![Figure 3.4: Three stages of a typical Luminescence experiment](image)

Here, optical band-to-band excitation was considered by using a femtosecond (fs) laser pulse with mean photon energy of $\hbar \omega_{\text{pump}}$. The laser pulse creates electron-hole pairs due to a transfer of electrons from the valence into the conduction band. Second, the nonequilibrium electron and hole distributions tend to relax back into the ground state. The initial intraband relaxation is caused by energy transfer to the crystal lattice, i.e., a step-by-step excitation of lattice vibrations (figure: 3.4b), which are at low temperatures primarily longitudinal optical (LO) phonons in polar semiconductors such as Gallium Arsenide (GaAs). Finally, the electron-hole pairs recombine under emission of light which is the photoluminescence process (figure: 3.4c). Due to the attractive Coulomb interaction between the charge carriers, the emission spectrum does not only contain contributions from states at or above the fundamental energy gap $E_{\text{gap}}$ but also sharp discrete lines just below $E_{\text{gap}}$ which originate from bound excitonic states.
3.4 Transmission Electron Microscope (TEM)

![Transmission Electron microscopy at SAIF, Nehu, Shillong.](image)

Nowadays, Transmission electron microscopy (TEM) is the most important tool for the researchers, particularly in the field of nanotechnology, since, by utilizing high resolution TEM (HRTEM) it is possible to detect the positions of atoms within a material.

Electron Microscopes are scientific instruments that use a beam of highly energetic electrons to examine objects on a very fine scale. This examination can yield information regarding:

- The topography (surface features of an object),
- Morphology (shape and size of the particles making up the object),
- Composition (the elements and compounds that the object is composed of and the relative amounts of them) and
- Crystallographic information (how the atoms are arranged in the object).

Electron Microscopes were developed due to the limitations of Light Microscopes which are limited by the physics of light to 500x or 1000x magnification and a resolution of 0.2 micrometers [205]. In the early 1930’s this theoretical limit had been reached and there was a scientific desire to see the
fine details of the interior structures of organic cells (nucleus, mitochondria...etc.). This required 10,000x plus magnification which was just not possible using Light Microscopes.

The Transmission Electron Microscope (TEM) was the first type of Electron Microscope to be developed and is patterned exactly on the Light Transmission Microscope except that a focused beam of electrons is used instead of light to "see through" the specimen. It was developed by Max Knoll and Ernst Ruska in Germany in 1931. The first Scanning Electron Microscope (SEM) debuted in 1942 with the first commercial instruments around 1965. Its late development was due to the electronics involved in "scanning" the beam of electrons across the sample. Electron Microscopes (EMs) function exactly as their optical counterparts except that they use a focused beam of electrons instead of light to "image" the specimen and gain information as to its structure and composition.

The basic steps involved in all Electron Microscopes are:

- A stream of electrons is formed in high vacuum (by electron guns).
- This stream is accelerated towards the specimen (with a positive electrical potential) while is confined and focused using metal apertures and magnetic lenses into a thin, focused, monochromatic beam.
- The sample is irradiated by the beam and interactions occur inside the irradiated sample, affecting the electron beam.
- These interactions and effects are detected and transformed into an image.

The above steps are carried out in all EMs regardless of type.

Transmission Electron Microscopy (TEM) is a technique where an electron beam interacts and passes through a specimen. The electrons are emitted by a source and are focused and magnified by a system of magnetic lenses. The electron beam is confined by the two condenser lenses which also control the brightness of the beam, passes the condenser aperture and “hits”
the sample surface. The electrons that are elastically scattered consist the transmitted beams, which pass through the objective lens. The objective lens forms the image display and the following apertures, the objective and selected area aperture are used to choose of the elastically scattered electrons that will form the image of the microscope. Finally, the beam goes to the magnifying system that is consisted of three lenses, the first and second intermediate lenses which control the magnification of the image and the projector lens. The formed image is obtained either on a fluorescent screen or in monitor or both and is printed on a photographic film. To detect the image, a high resolution phosphor may be coupled by means of a CCD (charge–couple device) camera. The image, thus detected by the CCD camera can be interfaced to a PC for data actuation and image display [206].

We have performed TEM investigations of our samples at SAIF, Nehu, Shillong by utilizing a JEOL model 1200 EX transmission electron microscope (figure: 3.5). The detailed specification is given in the appendix in table: 5.

### 3.5 Scanning Probe Microscope (SPM)

The basic principle of this microscope [207] is to measure forces or to measure interactions between a sharp probing tip and sample surface led to the creation of a variety of other scanning probe microscopes (SPM), such as:

- The magnetic force microscope (MFM),
- The dipping force microscope (DFM),
- The friction force microscope (FFM), and
- The electrostatic force microscope (EFM).

By these new developments the field became further subdivided. Concurrently, there is also an unifying tendency to combine different methods such as STM/AFM, AFM/MFM, AFM/FFM. This provides the unique opportunity to characterize a single nm-sized spot by a combination of methods and therefore gain more information than by the separate application of a single method.
Figure 3.6: Basic principle of AFM/AMF. A sharp tip is mounted on a cantilever-type spring. The force between the tip and the sample causes cantilever deflections which are monitored by using a deflection sensor.

In probing force microscopy the probing tip is attached to a cantilever-type spring. In response to the force between tip and sample the cantilever is deflected. Images are obtained by scanning the sample relative to the probing tip and digitizing the deflection of the lever or the z-movement of the piezo as a function of the lateral position x, y. Typical spring constants are between 0.001 to 100 N/m and motions from microns to ~0.1 Å are measured by the deflection sensor (figure: 3.6). Typical forces between probing tip and sample range from $10^{-11}$ to $10^{-6}$ N. One can realize this, from the comparison of the interaction between two covalently bonded atoms, that is of the order of $10^{-9}$N at separations of ~ Å. Thus, non-destructive imaging is possible with these small forces. Force regimes can be classified as: (a) Contact mode and (b) Non-contact mode. When the microscope is operated in non-contact mode at tip-sample separations of 10 to 100 nm, forces, such as Vander-Waals, electrostatic, magnetic or capillary forces, can be sensed and get information regarding surface topography, distributions of charges, magnetic domain wall structure or liquid film distribution. At smaller separations of the order of Å the probing tip is in contact with the sample. In this mode, ionic repulsion forces allow the surface topography to be traced with high resolution. Under best
conditions atomic resolution is achieved. In addition, frictional forces and elastic or plastic deformations can be detected under appropriate conditions.

In our investigations we have utilized the unique combination probing force microscopy (AFM/MFM) to obtain surface morphology and magnetic behaviour of the Cr:ZnS and Mn:ZnS systems. For MFM measurements, the tip used in AFM measurements has been changed with a magnetic tip.

### 3.6 Electron Dispersive X-ray spectrometry (EDX)

An EDX instrument can be attached to Scanning electron microscope (SEM) to provide supplementary information. By utilizing EDX investigations, one can get information about composition of individual crystals or features. EDS makes use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized chemical analysis. **Qualitative analysis** involves the identification of the lines in the spectrum and is fairly straightforward owing to the simplicity of X-ray spectra. **Quantitative analysis** (determination of the concentrations of the elements present) entails measuring line intensities for each element in the sample and for the same elements in calibration Standards of known composition. As the SEM electron beam strikes the sample surface, X-rays are produced. An X-ray photon impinging on the surface of the EDX detector produces electron hole pairs which are detected as a single pulse by the liquid nitrogen cooled pre amplifier. The pulse energy is determined by the X-ray energy which in turn is determined by the element being determined. The EDX analyser produces a spectrum of the elements present in targeted areas of the samples allowing detectable elements to be quantified or mapped.

### 3.7 Fourier Transform infrared spectroscopy (FTIR)

FT-IR Spectroscopy is the abbreviation of "Fourier Transform Infrared Spectroscopy". This is the analytical technique developed in 1970s to qualify and quantify compounds utilizing infrared absorption of molecules.
In organic chemistry, Infrared spectroscopy is an important technique. It offers easy way to identify the presence of certain functional groups in a molecule. Moreover, one can use the unique collection of absorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities. Infrared (IR) lights are electromagnetic radiation with their wavelength longer than those of visible lights, measuring from the nominal edge of visible red light at 0.74 micrometers, and extending conventionally to 300 micrometers. Absorption occurs when the energy of the beam of light (photons) are transferred to the molecule. The molecules get excited and move to a higher energy state. The energy transfer takes place in the form of electron ring shifts, molecular bond vibrations, rotations and translations. FTIR is mostly concerned with vibrations and stretching.

An FTIR (Fourier Transform Infra Red) is a method of obtaining infrared spectra by first collecting an interferogram of a sample signal using an interferometer, and then performing a Fourier Transform (FT) on the interferogram to obtain the spectrum. An FTIR Spectrometer collects and digitizes the interferogram, performs the FT function, and displays the spectrum.

An FT-IR is typically based on The Michelson Interferometer. The interferometer consists of a Beam-splitter, a fixed mirror, and a mirror that translates back and forth, very precisely. The beam splitter is made of a special material that transmits half of the radiation striking it and reflects the other half. Radiation from the source strikes the beam splitter and separates into two beams. One beam is transmitted through the beam splitter to the fixed mirror and the second is reflected off the beam splitter to the moving mirror. The fixed and moving mirrors reflect the radiation back to the beam-splitter. Again, half of this reflected radiation is transmitted and half is reflected at the beam splitter, resulting in one beam passing to the detector and the second back to the source.
3.8 Superconducting quantum interference device (SQUID)

Figure 3.7: SQUID facility at DAE consortium, Indore.

Superconducting interference device (SQUID) is a very useful tool that can measure extremely low magnetic field. It is potentially more sensitive than a normal vibration magnetometer. It is sensitive enough to measure magnetic fields as low as $5 \times 10^{-18}$ T [208], for which researchers usually prefer SQUID measurements for characterization of magnetic samples. SQUID offers many advantages like high sensitivity, low noise, less error etc., for which it plays a vital role among the research groups particularly in the field of magnetic semiconductor nanostructures. SQUID is basically based on the superconducting loops containing Josephson junctions. The phenomenon of supercurrent (current flows indefinitely long without any voltage applied across a device) is known as a Josephson junction (JJ), that consists of two superconductors coupled by a weak link. It is named after the British physicist Brian David Josephson, who predicted in 1962 the mathematical relationships for the current and voltage across the weak link [209,210].
A superconducting quantum interference device (SQUID) is a mechanism used to measure extremely weak signals, such as subtle changes in the human body’s electromagnetic energy field. Using Josephson junction, a SQUID can detect a change of energy as much as 100 billion times weaker than the electromagnetic energy that moves a compass needle. A Josephson junction is made up of two superconductors, separated by an insulating layer so thin that electrons can pass through. A SQUID consists of tiny loops of superconductors employing Josephson junctions to achieve superposition: each electron moves simultaneously in both directions. Because the current is moving in two opposite directions, the electrons have the ability to perform as qubits (that theoretically could be used to enable quantum computing). SQUIDs have been used for a variety of testing purposes that demand extreme sensitivity, including engineering, medical, and geological equipment. Because they measure changes in a magnetic field with such sensitivity, they do not have to come in contact with a system that they are testing. SQUIDs are usually made of either a lead alloy (with 10% gold or indium) and/or niobium, often consisting of the tunnel barrier sandwiched between a base electrode of niobium and the top electrode of lead alloy. A radio frequency (RF) SQUID is made up of one Josephson junction, which is mounted on a superconducting ring. An oscillating current is applied to an external circuit, whose voltage changes as an effect of the interaction between it and the ring. The magnetic flux is then measured. A direct current (DC) SQUID, which is much more sensitive, consists of two Josephson junctions employed in parallel so that electrons tunnelling through the junctions demonstrate quantum interference, dependent upon the strength of the magnetic field within a loop. DC SQUIDs demonstrate resistance in response to even tiny variations in a magnetic field, which is the capacity that enables detection of such minute changes.

We have utilized SQUID facility at UGC DAE Consortium, Indore to investigate magnetic properties of our samples within temperature range 10K to 300K. The magnetometer is shown in figure: 3.7.
3.9 Significant observations

By utilizing different characterization techniques the structural, optical and magnetic properties of TM doped ZnO (TM=Mn, Co and Ni) and Mn, Cr doped ZnS was investigated systematically.

- **Structural** study of as-synthesised TM doped ZnO, ZnS samples was carried out by utilizing XRD, FTIR, HRTEM, and EDX. The HRTEM study confirmed the formation of elongated nanostructures for bare and TM doped ZnO, while most of the nanostructures were found to be spherical in nature for TM doped ZnS samples. In case of Cr:ZnS development of fractal pattern were detected at low resolution TEM study. XRD patterns exhibited the wurtzite nature of all TM doped and bare ZnO samples, while cubic crystalline structure for TM:ZnS system. Surface morphology and existence of magnetic domains of TM:ZnS system were depicted from AFM and MFM experiments.

- **Optical** properties of the samples were explored from PL and UV-Visible study. PL intensities for doped and bare ZnO and ZnS samples were found to exhibit typical nature of DMS. Band gap study of the sample was studied through UV-Vis measurements.

- **Magnetic** properties of the samples were explored with SQUID within temperature range 4K to 300K. M~T response were studied for both ZFC and FC. M~H responses were measured at both low temperature (10K) as well as room temperature (300K). Existence of room temperature ferromagnetism was confirmed through SQUID measurements for Co, Mn and Ni doped ZnO samples.