Chapter 1

Introduction
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1.1. AC techniques

Accurate measurements are essential to understand underlying physical properties of a system. The crucial part of any measurement is the ability of the techniques adopted to reduce any potential sources of errors. The significant error which has dire consequences in measurement is the \textit{dc offset error} which may arise because of the impedance mismatch of the internal circuitry of the instrument as well as mismatch between the measuring instruments and the loads. These errors also include therm-electric EMFs, contact potentials and the offsets produced by rectification of RFI (Radio Frequency Interference). Thermo-electric EMFs generally arise when dissimilar metals are joined together and such junctions experience different temperatures. These EMFs cause maximum error in low voltage measurements. The offsets due to the rectification of RFI are produced by the non-ohmic contacts in a circuit. These \textit{dc offset errors} can be minimized using \textbf{ac techniques} which have been extensively used over the years for studying microscopic as well as macroscopic phenomena in materials. The basic idea is to send a time-varying signal into a system to analyze it in terms of its time-varying response. This technique allows one to use very low exciting signals due to extremely high noise rejection. It also makes it possible to study the precise phase relationship between the exciting signal and the response which can yield very important information regarding relaxation times and internal dissipative phenomena. The study of non-linearity of a system is also possible through the analysis of higher harmonics in these experiments. \textit{AC resistivity} and \textit{AC susceptibility} form two of the most common measurements falling within the broad class of AC techniques.

AC resistivity measurements can be made either by simply making contacts with the sample or by the contactless technique. The contactless resistivity measurement technique is based on \textit{eddy current} which arises in a conductor when it is placed in a varying magnetic field. A review of many contactless techniques has been made by Delaney and Pippard (1972). Two of these techniques have been used frequently because of their apparent simplicity: (i) \textit{The eddy current decay method} [1] and (ii) \textit{contactless ac resistivity method}. The contactless technique is
very useful for resistivity measurement in such samples which exhibit end-to-end non-conductivity in general but may contain some conducting clusters surrounded by non-conducting layers. This probe is very effective for powdered samples or for pure specimens, to minimize the effects of chemical diffusion of impurities into the specimen and to minimize the effects of physical damage from mechanical strain. The eddy current decay method is not so accurate for the specimens of high resistance. The ac resistivity [2] is calculated from the imaginary part of the ac susceptibility of sample in an alternating field of constant frequency.

1.2. A brief review of magnetic susceptibility measurement techniques

The magnetic susceptibility ($\chi$) is related to the degree to which a material can be magnetized by an external magnetic field. It is defined as the ratio of the induced magnetization ($M$) to the inducing magnetic field ($H$). When a material is placed in a magnetic field $H$, a magnetization (magnetic moment per unit volume) $M$ is induced in the material which is related to $H$ by $M = \chi H$, where $\chi$ is called the volume susceptibility. Since $H$ and $M$ have the same dimensions, $\chi$ is dimensionless.

1.2.1. Different techniques for measuring magnetic susceptibility

Several methods have been used for magnetic susceptibility measurement which includes the old methods like Faraday’s scale method, Gouy’s method, Quincke’s method and new methods like inductive method with SQUID magnetometer, Magnetic resonance method, ac susceptometry method. In this section some of the methods have been discussed briefly.

1.2.1.1. The method of extraction

The basic principle on which this method (fig 1.2.1) is based is the voltage induced due to flux change in the search coil when a magnetic specimen is removed (or extracted) from the coil, or when the specimen and the search coil together are extracted from the magnetic field [3]. The total flux through the search coil, when the solenoid is producing a field is

$$\Phi_1 = \mu_0(H + M)A = \mu_0(H_a - H_d + M)A$$  \hfill (1.2.1)
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Figure 1.2.1.: Block diagram of the experimental arrangement of the method of extraction

where $\mu_0$ is the permeability of vacuum, $H_a$ is the applied field, $H_d$ is the demagnetizing field, $M$ is the magnetization (Magnetic moment per unit volume) and $A$ is the area of the specimen and search coil (both are assumed equal). If the specimen is suddenly removed (extracted) from the search coil the flux through the coil becomes

$$\Phi_2 = \mu_0 H_a A$$  \hspace{1cm} (1.2.2)

The difference of the fluxes, which can be calculated by integrating the induced emf with respect to time, directly measures the value of $M$ at a particular field strength. A modification of this method uses two identical coils in series opposition. When the specimen is moved out of one coil and into the other, the measured signal is twice that obtained with a single coil, which increases the sensitivity.

1.2.1.2. Vibrating Sample Magnetometer (VSM)

The Vibrating Sample Magnetometer (VSM) was invented more than 50 years ago and was a breakthrough in magnetic measurement methods [4]. A VSM is based on Faraday’s law which states that an electromagnetic force is generated in a coil when there is a change in flux linking the coil [5]. In the measurement setup, a magnetic sample is moving in the proximity of two pickup coils as indicated in figure 1.2.2. The oscillator provides a sinusoidal signal that is translated by the transducer assembly into a vertical vibration. The sample which is fixed to the sample rod vibrates with a given frequency and amplitude. It is centered between the two pole pieces of an electromagnet that generates a magnetic field ($\vec{H}_0$) of high homogeneity. Stationary pickup coils are mounted on the poles of the electromagnet. Their center of symmetry coincides with the magnetic center of the sample. Hence, the change in magnetic flux originating from the vertical movement of the magnetized sample induces a voltage ($V_{ind}$) in the coils. $\vec{H}_0$,
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being constant, has no effect on the voltage but is necessary only for magnetizing the sample. The voltage in a single turn of the pickup coil can be written as

\[ V_{\text{ind}} = -\frac{\partial \Phi}{\partial t} \]  

(1.2.3)

where \( \Phi \) is the magnetic flux. For the pickup coils with a flat surface \( A \) and \( n_w \) turns, Eq. 1.2.3 gives

\[ V_{\text{ind}} = -n_w A \frac{\partial \vec{B}}{\partial t} \]  

(1.2.4)

When the sample is brought into the homogeneous field \( \vec{H}_0 \), it will be magnetized with a magnetization \( \vec{M} \). The magnetic flux density \( \vec{B} \) near the sample is now

\[ \vec{B} = \mu_0(\vec{H}_0 + \vec{M}) \]  

(1.2.5)

where \( \vec{M} \) is defined as

\[ \vec{M} = \frac{d\vec{m}}{dV} \]  

(1.2.6)

with \( \vec{m} \) the magnetic moment.

In the constant magnetic field \( \vec{H}_0 \)

\[ \frac{\partial \vec{B}}{\partial t} = \frac{\partial \vec{M}}{\partial t} \]  

(1.2.7)

So, combining equation (1.2.4) and equation (1.2.7) we get

\[ V_{\text{ind}} = -n_w A \frac{\partial \vec{M}}{\partial t} \]
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This means the output voltage of the coil is proportional to the change of magnetization. Furthermore, \( V_{\text{ind}} \) can be increased by increasing the number of windings \( n_w \) and the number of pickup coils \( n_c \). Also, the geometry of the sample influences the induction.

The advantages of a VSM [6] are:

∗ High sensitivity – up to \( 10^{-6} \) emu.

∗ Fully automated.

∗ Broad temperature range possible.

∗ Sufficient high fields possible – especially if a superconducting magnet is used.

The disadvantages are:

∗ Magnetically open system – needs correction for demagnetizing field.

∗ In the case of a superconducting magnet liquid He is generally necessary. However, nowadays some companies offers already cryogen free magnets.

∗ Slow and limited \( dH/dt \).

1.2.1.3. Alternating (Field) Gradient Magnetometer (AFGM / AFM)

The alternating (field) gradient magnetometer (AFGM / AFM) [7] is a modification of the well-known Faraday balance that determines the magnetic moment of a sample by measuring the force exerted on a magnetic dipole by a magnetic field gradient. The sketch diagram of the instrument is shown in fig 1.2.3.

The force is measured by mounting the sample on a piezoelectric bi-morph, which creates a voltage proportional to the elastic deformation and, hence, to the force acting on the sample. By driving an alternating current through the gradient coils, with lock-in detection of the piezo electric voltage, and by tuning the frequency of the field to the mechanical resonance of the sample mounted on the piezoelectric element by a glass capillary, a very high sensitivity can be achieved. The main advantage of the AGM is its relative immunity to magnetic external noise and the high signal-to-noise ratio and short measuring time. A major disadvantage is the difficulty in obtaining an absolute calibration of the magnetic moment because the signal is not only proportional to the sample magnetic moment but also the \( Q \)-factor of the sample-capillary-piezo system, which varies with mass and temperature. This problem can be minimized by inserting
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Figure 1.2.3.: Schematic diagram of a AFGM / AGM

a small calibration coil close to the sample. Also, difficulty in obtaining the exact angular orientation of the sample relative to the magnetic filed is a drawback of this instrument.

1.2.1.4. The SQUID Magnetometer

The SQUID (Superconducting QUantum Interference Device) magnetometer [7] uses superconducting pick-up coils with a superconducting quantum interference device as flux detector. The DC SQUID consists of two superconductors separated by thin insulating layers to form two parallel Josephson junctions [8-11]. The radio frequency or RF SQUID uses a superconducting ring with one Josephson junction. The magnetometer can detect very small magnetic fields. It is sensitive enough to measure the magnetic fields in living organisms. The great sensitivity of the SQUID devices is associated with being able to measure changes in magnetic field associated with a fraction of a flux quantum. In one form of SQUID-based magnetometer, the schematic of which is given in figure 1.2.4, the sample executes a periodic linear motion with a vibration frequency of $0.1 - 5 \text{ Hz}$. This causes a change of magnetic flux in the pick-up coils, which are part of the totally superconducting circuit. The SQUID itself is operated in a constant-flux mode and serves as an extremely sensitive zero detector in a feedback loop. The output signal of the magnetometer is proportional to the current in the feedback coil required to compensate for the flux change sensed by the pick-up coils.

The advantages of a SQUID magnetometer are:

- Highest sensitivity (10-8 emu) → this allows measurement in thin films or single grains.
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(a) Cutaway view of a MPMS SQUID

(b) Principle of SQUID

Figure 1.2.4.: Diagram of a SQUID

The disadvantages are:

* Magnetically open system.

* Complex handling.

* Difficulty in handling large samples.

1.2.1.5. The Pulsed Field Magnetometer (PFM)

Pulsed field magnetometers [12] allow very fast tracing of the hysteresis loops of hard magnetic materials in sufficiently high external fields. figure 1.2.5 shows the block diagram of a PFM. It has a condenser bank as energy source, a charger, a high field magnet and a measuring device. The condenser bank is charged up to a voltage between 1 kV and several kV (the stored energy is equal to \( \frac{CV^2}{2} \)) and then discharged through the magnet. The capacitance \( C \) and the inductance \( L \) determine the pulse time, which lies typically between 1 to 100 ms.

The advantages of a PFM for characterizing permanent magnets are:

* High external fields.

* Can be operated at room temperature.
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- Large sample volume is possible.
- Fast measurements.

The disadvantages of a PFM for characterizing permanent magnets are

- It is a magnetically open system.
- Limited sensitivity.

The magnetometers discussed above can only measure the DC magnetization, the SQUID can be operated in RF (Radio Frequency) signal range.

1.2.1.6. Susceptibility

There are mainly two categories of methods used to measure the susceptibility of materials: AC and DC. In the DC method, the measured parameter is magnetization, $M$, which may be converted to the susceptibility $\chi$ using the relation $\chi_{dc} = \frac{M}{H}$, where $H$ is the applied magnetic field. In contrast, the AC method gives the susceptibility directly as $\chi_{ac} = \frac{dM}{dH}$, when an alternating (AC) magnetic field is applied. The DC-magnetometer and the AC susceptometer are two entirely different tools that provide different approaches to the study of magnetic properties. Both these techniques rely on sensing coils used to measure the variation in the magnetic flux due to a magnetic sample.

In a DC magnetization measurement a value for the magnetization $M$ is obtained for some applied DC field $H$. Usually the moment is measured, as a function of field, and the material’s magnetization curve ($M$ versus $H$) is determined. A detection coil is used, so a change in magnetic flux is necessary. However, since the applied magnetic field is constant, there will be no signal associated with $H$ and the magnetization will also not change with time. So, the flux coupled with the detection coil is made to vary by moving/vibrating the sample. Though the principle behind both the DC magnetometer and AC susceptometer is detection of change of magnetic flux, the main difference lies in how the flux variation is achieved. In an AC susceptometer the sample is magnetized by an AC magnetic field. The change in flux produced by the varying magnetization of the sample is sensed by the detection coil. The detection coil is often balanced with, a second identical but oppositely wound coil, to cancel out the contribution.
due to the air-core mutual inductance. As a result, any experimentally detected change in flux is due only to the changing magnetic moment of the sample \((dm)\) as it responds to the AC field (no sample movement is required to produce an output signal) and not to the moment itself as in the DC technique. The ac susceptibility is:
\[
\chi_{ac} = \frac{dm}{VH_{ac}} \rightarrow \frac{dM}{dH}.
\]
Thus, it appears that ac susceptibility is the slope \((dM/dH)\) of the magnetization curve \((M \text{ versus } H\) curve). But this slope is the local slope of the magnetization and the integration of this will not give the untrue dc susceptibility \((M/H)\).

1.2.1.7. The ac susceptometer: A brief review

The measurement of ac susceptibility is an important experimental tool for measuring the magnetic and electronic properties of materials. This technique can be used for studying magnetic transitions [13-46], spin-glass transitions [47-75], superconducting transitions [76-94], re-entrant spin glass [95-99] behaviour and dissipative processes. The information regarding the dissipative nature can be calculated from the complex part of the magnetic susceptibility \((\chi = \chi' + i\chi'')\). Study of the frequency and field dependence of real and imaginary parts of ac susceptibility has become an established tool for investigating magnetic and superconducting materials. Through a measurement of higher harmonics [100-104], this technique has become even more versatile as it provides a quicker and easier way to acquire a wealth of information that is contained in the nonlinear part of the ac susceptibility. The AC susceptibility measurement technique became particularly popular following the discovery of High-Tc Superconductors (HTS) in 1986 and research laboratories now almost invariably possess either commercial or home-built AC susceptometer systems.

In the past, the Hartshorn (1925) mutual inductance bridge has been widely used for measuring the complex ac magnetic susceptibility of a variety of materials. In low temperature work, it has been used for measurements on paramagnetic substances and it was also used for observing superconducting transitions. The original Hartshorn bridge circuit makes use of a calibrated variable mutual inductor that is very expensive. An electronic modification of the Hartshorn circuit, in which the variable mutual inductor is replaced by a fixed mutual inductance in combination with a resistive potential divider and isolating triode, has been described by Pillinger, Jastram, and Daunt (1958) [105]. This modification circumvents the need for a variable mutual inductor, but at the expense of some additional complication in circuitry. In 1965, E. Maxwell [106] modified the instrument by replacing the decade mutual inductor by a decade auto-transformer in combination with a small fixed inductor. Slight variations of the same technique have been reported by Daybell 1967 [107], Parks and Swenson 1967 [108],
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Other designs have been presented (Dundon and Kretschmar 1978 [112], Brodbeck et al 1978 [113], Ryan et al 1978 [114], Gentile et al 1981 [115]) for mutual inductance bridges using operational amplifiers. Although these designs were successful in providing economical and versatile alternatives to the conventional ratio transformer design, their sensitivity was limited by the finite gain and inherent noise of the operational amplifiers.

In 1982, Corson [116] designed and constructed a high-precision, low-noise mutual inductance bridge by employing operational amplifiers and a Kelvin-Varley divider for operation in the frequency range 10-300 Hz. This bridge was used for susceptibility measurements in the $^3\text{He} - ^4\text{He}$ dilution refrigerator. Later, by using the same principle of measurement S. Ramakrishnan et al (1985) [117] constructed an ac susceptometer of much higher sensitivity.

A Banerjee et al. (1988) [118] have modified the ac inductance bridge by using only operation amplifiers. They have replaced the Kelvin-Varley divider by a set of active Butterworth filters.

Hardware and software details of an automated ac susceptometer have been reported by A. Chakravarti et al [119] in 1991. The automation of the sample rod movement, bridge control and offset nulling have been implemented with the help of an inexpensive Z-80A microprocessor via a home-made IEEE-488 interface.

In 1994, Hibbs et al [120] developed a high-resolution ac susceptometer that uses an RF superconducting quantum interference device (SQUID) to directly measure the flux coupled into a superconducting detection coil from a sample’s changing magnetic moment in an applied ac field. The instrument is based on an existing dc magnetometer system and uses that system’s temperature control and dc superconducting magnet to allow operation over a temperature range from 2 to 400K. This susceptometer is fully automatic and controlled by a personal computer.

The linear and non-linear ac susceptibilities of $Ce(Fe_{0.9}Al_{0.1})_2$ have been experimentally investigated in 1996 by S. Mukherjee et al [121] using a modified mutual inductance bridge where the higher harmonics were measured from the residual signal with a LIA ‘after’ the large linear signal was zeroed out by main bridge. In 1997 A. Bajpai and his co-workers have modified the ac susceptometer to study non-linear characteristics of some ferromagnetic materials. This modification minimizes the errors originating from the non-linearity of the electronic components in the offset nulling circuit.

The ac susceptibility measurement technique faces limitations when it is used to study the ferromagnetic domain structure. In such cases the contribution to
the change in the magnetization in response to a change in the applied magnetic field comes from two sources. The first one is the change in the alignment of the individual spins within the domains. This is small in the case of a normal ferromagnet well within the ferromagnetic phase, because the spins are already aligned to a very large extent. However, in the presence of conflicting interactions and near critical temperatures, this contribution may be significant. The second contribution comes from the change in the proportion of domains aligned with the applied field because of domain wall movement and domain rotation. Measurement of this effect is considerably complicated by domain wall pinning at impurities and defects. The enhancement ac susceptibility technique has been used to overcome the above limitation. With this technique, contributions from the domain wall movement and domain wall rotation may be studied. In 1976, Wilson et al [122,123] first studied the effect of enhancement using pulsed and sinusoidal enhancing fields. The modified ac enhancement technique has also been used by S. Mukherjee [124] and his co-workers in 1997. They have measured the ac susceptibility of gadolinium (Gd) as a function of temperature in the presence and in the absence of an ac biasing enhancing field. They have also reported that by using the modified technique the exact domain nucleation point can be determined which in turn gives the exact Curie-Wiess temperature of ferromagnets. In 2001, they [125] have also observed enhancement of ac susceptibility for typical reentrant spin glasses like ($Fe_{1.5}Mn_{1.5}Si$) and canted spin systems ($Ce(Fe_{0.96}Al_{0.04})_2$). They have interpreted the experimental data with the help of a simulation model based on dry friction-like [126] pinning of domain walls for systems having ferromagnetic domain structures. They reported that a strong pinning mechanism appeared in the reentrant spin-glass-like and canted spin systems at low temperatures in addition to the intrinsic one in the ferromagnetic phase.

Recently, the effects of disorder on domain wall propagation along magnetic nanostrips induced by fields have been estimated numerically considering the dry-friction [127,128] effects of the domain wall. The Micromagnetic study of magnetic materials is the recent trend in research for theoreticians and as well as experimentalists.

1.3. Aim of the work

The work aims to develop some necessary instruments in-house for the study of response (transport and susceptibility) of different materials (like ferromagnetic materials, composites, etc.) by using AC probes. The probes which were developed are useful for AC susceptometry and AC resistivity. These are particularly
suitable for the study of bulk materials because of the multiple parameters (temperature, amplitude, frequency, etc.) that may be varied during experimentation.

The work has been divided into two major categories, development of instrumentation and the actual measurements for the study of properties of materials.

1.3.1. Instrumentation

We have fabricated the necessary sub-systems and developed a simple, low-cost ac susceptometer working in high temperature. The subsystems are:

- Lock-in-amplifier
  - Analog lock-in-amplifier.
  - PHOENIX kit-based digital lock-in-amplifier.
  - A simple lock-in-amplifier for magnetic enhancement studies.

- A 16-channel voltmeter interfaced through microprocessor.

- Temperature controller.

- Sample movement systems.

- Coil system

- Bridge circuit for detecting null.

- Automation, data acquisition and control of the total setup with the help of computers and microprocessors.

One of the main thrusts of the work was to avoid purchase of complicated and expensive equipment to the extent possible by the in-house development of sub-systems. It may be noted that one of the major advantages of the in-house development is the ease of maintenance, and customized configuration in accordance with the particular requirements of an experiment, apart from the huge saving in costs. This type of developmental work may be very effective for low budget laboratories.

1.3.2. Measurements

We have calibrated the susceptometer with pure nickel (Ni) sample at room temperature (306K). We have measured the ac susceptibilities of Nickel ferrites $Ti^{4+}$ doped samples. We have verified the ac susceptibilities and transition temperatures of Double pervoskite ($BFMO$ and $SFMO$) samples. We have also studied the magnetic enhancement susceptibility of the samples.
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