Experimental techniques: synthesis and characterization

Abstract

This chapter describes the details of the synthesis of the phase pure studied materials viz; rutheno-cuprates, non-oxide perovskite MgCNi$_3$, and Fe-based chalcogenides superconductor. A series of polycrystalline bulk samples with the following stoichiometries were synthesized using the conventional solid state reaction route.

(a) Ru$_2$Sr$_2$Eu$_{1.4}$Ce$_{0.6}$Cu$_2$O$_{10-\delta}$ (EuRu-1222) with Mn and Cr substitution at Ru site
(b) Ru$_2$Sr$_2$Gd$_{1.4}$Ce$_{0.6}$Cu$_2$O$_{10-\delta}$ (GdRu-1222)
(c) Ru$_2$Sr$_2$Y$_{1.5}$Ce$_{0.5}$Cu$_2$O$_{10}$ (YRu-1222)
(d) Ru$_{0.9}$Sr$_2$YC$_{2.1}$O$_{7.9}$ (YRu-1212)
(e) MgCNi$_3$ with Boron ($^{10}$B) substitution at C site
(d) FeSe$_{0.5}$Te$_{0.5}$ with Ni and Co substitution at Fe site

Among rare earths, Eu, Gd, Sm, and Y, that from the Ru-1222 and Ru-1212 phases, Eu$^{3+}$ is non-magnetic in nature, hence does not interfere with the magnetic moment of Ru. Gd$^{3+}$ orders antiferromagnetically below 3K and exhibits paramagnetism above this temperature. Being small ionic size of Y$^{3+}$, compared to Eu, Gd and Sm, the HPHT (high pressure high temperature) treatment is required for YRu-1212 and YRu-1222 samples. Large amount of Ni in MgCNi$_3$ makes it very interesting because Ni itself exhibits the ferromagnetic nature. Similarly, Fe being ferromagnetic by nature, the same is also a good candidate to study superconductivity and magnetism in chalcogenides superconductors.
2.1 Introduction

Experimental techniques for the investigation of condensed matter physics and material science have reached a high degree of maturity. Today, many complex phenomena such as superconductivity, magnetism, structural ordering, and phase transition etc. are successfully studied using the experimental techniques. The synthesis and characterization of material is the first and foremost important thing during the experimental research in condensed matter physics and material science. The quality of samples depends to a great extent on the synthesis method used. In addition, the proper selection of synthesis parameters often helps to get desired properties of the material. Structural, magnetic, and transport (electrical and thermal) properties depend on material synthesis. There are various methods available for the synthesis of polycrystalline bulk materials like solid state reaction route by NPHT (Normal Pressure High Temperature) and HPHT (High Pressure High Temperature). Both NPHT and HPHT are used for synthesizing bulk pure and doped ruthenocuprates samples. In case of pure and doped non-oxide perovskite MgCNi3 samples, we have used the standard solid state in-situ synthesis route. Both pure and substituted FeSe0.5Te0.5 superconducting samples are synthesized by vacuum encapsulation technique. In order to characterize the polycrystalline bulk materials, experimental technique such as X-ray powder diffraction (XRD) with Rietveld refinement using FullProf program for structural analysis, DC four probe resistivity (ρ) in with and without external DC magnetic field (up to 14 Tesla) for magneto-transport, ACMS (AC Magnetrometry System) for DC/AC magnetization, TTO (Thermal, Transport Option) for thermal conductivity (κ), thermoelectric power (S) or Seebeck coefficient, and Heat Capacity Option for heat capacity (C_p) measurements in with and without magnetic field (up to 14 Tesla) are employed. All physical property measurements (transport, magnetization, thermal) were performed on standard Physical Property Measurement System (PPMS-14T) from Quantum Design, USA. The following section gives a brief explanation about the synthesis of bulk materials and various characterization techniques.
2.2 Synthesis

2.2.1 Solid state reaction: NPHT synthesis

Most widely used method for synthesizing the polycrystalline solids (powders) is the direct reaction, in the solid state, of a mixture of solids as starting materials. Solids do not usually react together at room temperature over normal time scale so it is necessary to heat them at much higher temperature for long time duration for reaction to occur at an appreciable rate. All the bulk polycrystalline rutheno-cuprates samples studied during present work were synthesized using solid state reaction method as per the steps shown in the flowchart (Fig. 2.1). There are two factors, namely thermodynamic and kinetic, which plays important role in solid state reaction, the former determines the possibilities of any chemical reaction to occur by the free energy considerations, which are involved, while the later determines the rate at which the reactions occurs [1, 2]. The atoms diffuse through the material to form a stable compound of minimum free energy. Different compounds or phases might have the lowest free energy at various temperatures or pressures or the composition of the gas atmosphere might affect the reaction. In order to prepare a single phase sample, the external conditions during any reaction are very important. During synthesis, the parameters such as temperature, pressure, gas flow rate, heating rate, cooling rate and time for the reaction are needed to be varied according to the phase requirement in the sample. The general steps involved in solid state reaction method for synthesizing rutheno-cuprates oxide ceramic superconductors are described below;

(a) The samples were synthesized from stoichiometric amounts of 99.99% pure RuO₂, SrCO₃, Eu₂O₃, Gd₂O₃, CeO₂, and CuO. First, the stoichiometric amount of each material was weighed, and then the powders were mixed together and grounded thoroughly using a mortar and pestle. Proper grinding of the powders is necessary for homogenous mixing of each constituent.

(b) The resulting powder was then transferred to a 99.9% pure alumina (Al₂O₃) boat and placed in a box furnace for heat treatment. The powder sample was first heated at 1000°C in order to remove unwanted carbonate, sulphate, etc., from the powders, and is called calcination. Further, the powder is again heated at higher temperature for the
Figure 2.1: Schematic diagram of the sample preparation using solid-state reaction route.
phase formation which is called sintering.

(e) The powder sample obtained was then sintered at number of different temperatures ranging from 1000°C to 1060°C for 24h each, followed by cooling to room temperature over a span of 12h with successive intermediate mixing and grinding to obtain the desired phase with high density. Since heat treatment was carried out at temperatures as high as 1060°C, high purity alumina boats and crucibles were used, because the Alumina has a very high melting point of 2100°C.

(d) The pellets were sintered at 1060°C. Pellets were then placed in a tube furnace and annealed at 800°C, 600°C, and 400°C in flowing oxygen for 12, 48, and 24h respectively and finally furnace is slowly cooled (control cooling) down to room temperature over a span of 24h in the presence of flowing oxygen. The tube furnace is specially designed furnace that is used when a sample is to be heat treated in presence of a flowing gas. A quartz tube is placed in the middle of the cylindrical furnace.

(e) Finally, the sample obtained is characterized using different measurement techniques. Each technique is discussed in detail in the next sections of this chapter. Details of the NPHT synthesized pure RuSr$_2$Eu$_{1.4}$Ce$_{0.6}$Cu$_2$O$_{10-\delta}$ (EuRu-1222) with Cr and Mn substitution at Ru site; pure RuSr$_2$Gd$_{1.4}$Ce$_{0.6}$Cu$_2$O$_{10-\delta}$ samples as well as experimental results are presented in chapter 3, 4 and 5 respectively.

2.2.2 Solid state reaction: HPHT synthesis

Around 60 years ago, very little was known about materials at high pressures and high temperatures. From a historical point of view, gas-compressor systems, cold-seal vessels, and autoclaves were the first devices for reactions under enhanced pressure conditions. Bridgman [3] anvil apparatus and Bundy recessed pair of anvils were steps on the way to the development of Hall belt [4], which permitted experiments up to 10GPa and simultaneously high temperatures of up to 2000°C.

The flat-belt (FB) type high pressure apparatus was designed to be utilized for high pressure and high temperature (HPHT) synthesis of diamond and related materials in the approximate pressure range 8GPa at the National Institute for Materials Science (NIMS) Tsukuba, Japan for more than 30 years. Figure 2.2
illustrates the FB apparatus and pressure-temperature control system. The upper anvil of the FB apparatus was tied to the upper press plate via an electrical insulation sheet. The sample and lower gasket assembly were set on the lower anvil, they were approached upwardly with the cylinder, and then the upper gasket assembly was inserted. The anvil displacement (0.01mm of sensitivity) versus press load (1 tone of the sensitivity) curve was checked every run to estimate sample volume change during compression. The press load was controlled using an auxiliary small plunger pump. A cooling water supply was introduced to the gap between anvil and cylinder with a water seal rubber jacket. Heating power was supplied to the graphite heater while monitoring the voltage and current in the heater. Power from the thyristor unit was supplied to keep a balance between power from the heater and the signal of the program unit. In all experimental runs, power and the electrical resistance to the heater were monitored.

Figure 2.2: High Pressure High Temperature (HPHT) apparatus for sample synthesis

6 GPa, Belt-type HPHT apparatus at NIMS, Japan
The sample and gasket assembly is shown schematically in Fig. 2.2. We placed the current ring assembly for each end of the sample. The current ring assembly was composed of current plates (stainless steel, 26mm diameter and 0.5mm thick for the anvil side; and molybdenum plate, 26mm diameter and 0.5mm thick for the sample side), stabilized zirconia ceramic and a hard steel ring 4mm thick. The current ring assembly could supply a large heating current to the graphite heater keeping good thermal insulation to the tungsten carbide anvil. The central part of the sample cell was composed of outer NaCl plus 10wt% stabilized zirconia (hereafter called salt) compact. The salt sleeve was 26mm in diameter and 16mm in length and was used as furnace insulator and pressure medium. At the end of the outer salt sleeve, a soft steel ring 5mm thick was bounded to prevent deformation of the sleeve. The graphite heater of 12mm outer diameter and 10mm inner diameter was press fitted to the outer salt sleeve. Inside the graphite heater, a thin inner salt sleeve was used for electrical insulation between the sample and the heater. Typical size of the gold or platinum capsule is 6.0mm in diameter and 4.5mm in length, which accommodate, for example, as much as 0.3gm of amorphous SiO₂, shown in Fig. 2.2. The HPHT samples are obtained for the present work from NIMS-Japan. Details of the HPHT synthesized RuSr₂Y₁.₅Ce₀.₅Cu₂O₁₀ (YRu-1222) and Ru₀.₉Sr₂YCu₂.₁O₇.₉ (YRu-1212) samples as well as experimental results are presented in chapter 6.

2.2.3 Solid state reaction: In-situ synthesis

Polycrystalline samples of bulk MgCNi₃ were prepared by the conventional solid state reaction route using an in-situ reaction process. Briefly, high purity powders of magnesium (99.9% Riedal-de Haen), Ni (99.99% Sigma Aldrich), amorphous Carbon powder (Alfa Aesar) were used as starting materials. The initial composition was taken as Mg₁.₂C₁.₆Ni₃ to get the nominal end compound. Excess Mg and C are needed in order to get the optimal Mg and C content for stoichiometric MgCNi₃ [5, 6]. The precursor powders were weighed according to nominal atomic ratio and well mixed through grinding to get uniform and homogenous mixture, using an agate mortar and pestle. The mixed powder was pressed into rectangular pellets by applying uniaxial pressure using a hydraulic press. The pallets were placed inside an iron alloy (Fe+Mn+Cr+C, melting point around 1400-1500°C) tube for heat treatment.
Subsequently, this iron alloy tube was put in tabular furnace. The tube is heated at 600°C for 2h at the rate of 10°C/min. in continuous flow of Argon gas atmosphere of purity (99.9%), followed by heating at higher temperature 950°C for 3h and finally cooled down to room temperature in the same atmosphere. Both ends of iron alloy capsule are kept open for passage of Ar gas during the heat treatment. This iron alloy tube is used to control the evaporation of Mg and C, during heat treatment. Ar gas flow was maintained throughout the heat treatment in order to avoid the formation of oxides. After sintering and cooling the furnace to room temperature, the Fe alloys tube is opened and the sintered samples were taken out. The resultant sample is in powder form. Thus, black color bulk poly crystalline samples of MgCNi3 were synthesized. Later we also studied the effects of Boron (10B) substitution in MgCNi3 at Carbon site. A series of bulk polycrystalline samples with compositions Mg1.2C1.6-xBxNi3 (x = 0.0, 0.08, and 0.16) was synthesized by above mentioned solid state reaction in-situ procedure. Details of pure and 10B substituted MgCNi3 samples as well as experimental results are presented in chapter 7.

2.2.4 Vacuum encapsulation technique

Bulk polycrystalline sample of FeSe0.5Te0.5 was synthesized by vacuum encapsulation technique. The stoichiometric ratio of highly pure element (> 3N) Fe, Se, and Te are ground, pelletized and then encapsulated in an evacuated (10⁻³ Torr.) quartz tube. The encapsulated quartz tube is put in tabular furnace and then heated slowly with the rate of typical 1°C/min. at 700°C for 12h after which reground, pelletized, encapsulated and reheated with the same heating rate (1°C/min.) at 750°C for 24h and then slowly cooled down to room temperature over a span of 12h. All grindings were performed in high purity argon (3N) filled glove-box (shown in Fig. 2.3, LABstar, MBRAUN made by Germany) with controlled oxygen and humidity (less than 1 ppm). The sintered sample is hard and stable in air but kept in evacuated desiccators to protect it from moisture. Recently, one of the important issues raised is the presence of interstitial Fe (Fint) in the FeSe0.5Te0.5 unit cell. We also studied the quenching effect on FeSe0.5Te0.5. For this sealed quartz tube was quenched from 300°C, 500°C and 700°C to room temperature. Being the magnetic nature of Fe atom, it would be interesting to substitute other transition metals at Fe site in FeSe0.5Te0.5.
Consequently, two main series, viz., Fe$_{1-x}$Co$_x$Se$_{0.5}$Te$_{0.5}$ ($x = 0.0, 0.01, 0.02, 0.05$ & $0.10$) and Fe$_{1-x}$Ni$_x$Se$_{0.5}$Te$_{0.5}$ ($x = 0.0, 0.01, 0.02, 0.05$ & $0.10$) were synthesized by the method described above. Details of the pure, quenched and substituted FeSe$_{0.5}$Te$_{0.5}$ samples as well as experimental results are presented in chapter 8.

### 2.3 Diffraction techniques

For the structural characterization 3-D polycrystalline bulk and 2-D thin films, usually X-ray diffraction (XRD) technique is used to identify the phase purity, types of phases and crystallographic structure of the samples. For detailed structural studies like bond length bond angle variations, magnetic structure refinement, determination of different types of magnetic ordering etc., neutron power diffraction (NPD) is a most powerful tool. Generally, three sources of radiation are important in material science: X-rays, synchrotron radiation and neutrons. The law of diffractions, i.e., the interference of diffracted beams holds equally well for all kind of radiations.
2.3.1 X-ray powder diffraction

Diffraction occurs when waves interact with a regular structure, whose repeat distance is about the same as the wavelength of X-ray waves. X-rays have wavelengths of the order of a few angstroms, the same as typical interatomic distances in crystalline solids so they can interact with atoms and can obtain the information at atomic level. Crystalline materials can be described by their unit cell which is the smallest unit describing the material. In the bulk material, the unit cell is then repeated over and over in all directions. This will results in planes of atoms at certain intervals. Figure 2.4 shows the schematic representation of X-ray diffractometer.

![Figure 2.4: Schematic representation of X-ray diffractometer.](image)

X-ray powder diffraction is a powerful non-destructive testing method to determine the phase formation, crystal structure, lattice parameters, and phase purity of the prepared samples. It is widely used in all fields of science and technology. X-ray diffraction results from the interaction between X-ray and electrons of atoms. Depending on the atomic arrangement, interferences between the scattered rays are constructive, when the path difference between two diffracted rays differs by an integral number of used wavelengths. This condition is described by Bragg’s equation, also called “Bragg’s law”;

\[ 2d_{hkl} \sin \theta = n\lambda \]

\[ \sim 62 \sim \]
where $d_{hkl}$ is the interplaner distance ($d$-spacing), $\theta$ is angle between the incident beam and the atomic plane, $n$ is an integral number, and $\lambda$ is the used wavelength. If an X-ray beam, having a wavelength $\lambda$ similar to the order of the interatomic distance $d$ is incident on a crystalline material making an angle $\theta$ between the incident beam and the atomic plane, the incident X-ray beam interacts with the periodic atomic structure, causing elastic scattering of the X-ray beam. The scattered X-ray beams are reflected from the atomic planes and constructively interfere to produce a diffraction pattern on the detector (Fig 2.4).

Figure 2.5: Schematic representation of diffraction of X-rays by crystallographic plane (Bragg’s law).

In this work, X-ray diffraction patterns of all samples were collected with a Rigaku MiniFlex-II (shown in Fig. 2.6) X-ray diffractrometer using monochromatic Cu-$K_\alpha$ radiation, having wavelengths $\lambda_{K\alpha 1} = 1.5405$ Å and $\lambda_{K\alpha 2} = 1.5443$ Å. To perform an X-ray diffraction measurement, a pellet of desired sample was broken and a piece of the pellet was finely ground using a mortar and pestle. The powder was then fixed onto a sample holder as a flat thin layer using the glass slide. The sample holder was placed in the measuring chamber of the X-ray diffractometer. The X-ray source was remaining fixed and the sample holder rotate about its own axis and detector also moved with sample holder. X-ray diffraction patterns of all the samples were scanned between $20^\circ \leq 2\theta \leq 80^\circ$ with scanning rate $2^\circ$/min. and step size of $0.02^\circ$. The collected data was analyzed (lattice parameters and other structural
Figure 2.6: Photograph of Rigaku MiniFlex-II Desktop X-ray diffractrometer at NPL.

information) using FullProf and/or Winploter based Rietveld refinement suites as described below [7].

2.3.2 Rietveld analysis

Rietveld refinement is a technique developed by H. Rietveld for characterization of crystalline solid materials [8]. The Rietveld method is an extremely powerful tool for the structural analysis of virtually all types of crystalline materials. This method uses a least squares approach to refine a theoretical line profile until it matches the measured profile. This technique was a significant step in the diffraction analysis of powder samples. There are six factors affecting the relative intensities of the diffraction lines on a powder pattern, namely, (i) polarization factor, (ii) structure factor, (iii) multiplicity factor, (iv) Lorentz factor, (v) absorption factor, and (vi) temperature factor. The method makes use of the fact that the peak shapes (variations
of their width $FWHM$) of Bragg reflections can be described analytically with the scattering angle $2\theta$.

The parameters refined in the Rietveld method fall mainly in three classes: peak-shape function, profile parameters and structural/atomic parameters. The peak shapes observed are function of both the sample (e.g., domain size, stress/strain, defects) and the instrument (e.g., radiation source, geometry, slit size) and they vary as a function of $2\theta$. The profile parameters include the lattice parameters and those describing the shape and width of Bragg peaks (changes in $FWHM$ and peak asymmetry as a function of $2\theta, 2\theta$ correction, unit cell parameters). In particular, the peak widths are smooth function of the scattering angle $2\theta$. It uses only five parameters (usually called $U, V, W, X$, and $Y$) to describe the shape of all peaks in powder patterns. The structural parameters describe the underlying atomic model include the positions, types and occupancies of the atoms in the structural model and isotropic/anisotropic thermal parameters. The changes in the positional parameters cause changes in structure factor magnitudes and therefore in relative peak intensities, whereas atomic displacements (thermal) parameters have the effect of emphasizing the high angle region (smaller thermal parameters) or de-emphasizing it (larger thermal parameters). The scale, the occupancy parameters and the thermal parameters are highly correlated with one another and are more sensitive to the background correction than are the positional parameters. Occupancy parameters are correspondingly difficult to refine and chemical constraint should be applied wherever possible [9].

Once the structure is known and a suitable starting model is found, The Rietveld method allows the least-squares refinement [chi-square ($\chi^2$) minimization] of an atomic model (crystal structure parameters) combined with an appropriate peak shape function, i.e., a simulated powder pattern, directly against the measured powder pattern without extracting structure factor or integrated intensities. With a complete structural model and good starting values of background contribution, the unit cell parameters and the profile parameters, the Rietveld refinement of structural parameters can begin. A refinement of structure of medium complexity can require hundred cycles, while structure of high complexity may easily require several hundreds. The progress of refinement can be seen from the resultant profile fit and the
values of the reliability factors or R-values. The structure should be refined to convergence. All parameters (profile and structural) should be refined simultaneously to obtain correct estimated standard deviations can be given numerically in terms of reliability factors or R-values [10].

The weighted-profile R value, \( R_{wp} \) is defined as;

\[
R_{wp} = 100 \left[ \frac{\sum_{i=1,n} w_i |y_i - y_{\text{c},i}|^2}{\sum_{i=1,n} w_i y_i^2} \right]^{1/2}
\]

Ideally, the final \( R_{wp} \), should approach the statistically expected \( R \) value, \( R_{\text{exp}} \),

\[
R_{\text{exp}} = 100 \left[ \frac{n - p}{\sum_{i=1,n} w_i y_i^2} \right]^{1/2}
\]

where \( n = \text{NPTS} - \text{NEXE} \) = total number of points in the pattern minus total number of excluded points and \( p \) is the number of refined parameters. \( N = n - p \) is called the number of degrees of freedom. Thus, the ratio between the two (goodness of fit),

\[
\chi^2 = \left[ \frac{R_{wp}}{R_{\text{exp}}} \right]^2 = s^2
\]

An R value is observed and calculated structure factors, \( F_{\text{hkl}} \), can also be calculated by distributing the intensities of the overlapping reflections according to the structural model,

\[
R_F = 100 \frac{\sum_h |F_{\text{obs},h} - F_{\text{calc},h}|}{\sum_h |F_{\text{obs},h}|}
\]

Similarly, the Bragg-intensity R value can be given as,

\[
R_B = 100 \frac{\sum_h |I_{\text{obs},h} - I_{\text{calc},h}|}{\sum_h |I_{\text{obs},h}|}
\]

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R values are useful indicators for the evaluation of refinement, especially in the case of small improvements to the model, but they should not be over interpreted. The most important criteria for judging the quality of Rietveld refinement are (i) the fit of the calculated pattern to the observed data, and (ii) the chemical sense of structural model.

2.4 Magnetic property measurements

In this thesis, the main emphasis is on the understanding of the magnetic behavior of rutheno-cuprates, non-oxide perovskite MgCNi$_3$, and Fe-based chalcogenides FeSe$_{0.5}$Te$_{0.5}$ superconductors. Detailed magnetic measurements have been performed in the temperature range of 1.9-300K. The magnetic response of the samples in the presence of DC fields of 100e to 120kOe was measured using an AC/DC Magnetometry System (ACMS) coil on Physical Property Measurement System (PPMS) made by Quantum Design (shown in Fig. 2.7). Similarly, Magnetic measurements with AC drive amplitude (AC fields) of 0.02Oe to 17Oe and frequency varying from 10Hz to 10kHz, and higher degree harmonics (first-, second-, third-, and so on) of AC magnetization with the same drive amplitude and frequency range were also obtained on the same ACMS coil using PPMS-14T. This ACMS coil assembly has been used to measure the magnetic behavior of samples in DC and AC fields due to the difference in the method of extracting the magnetic moment of the sample in DC and AC field. More details about DC and AC magnetic measurements are provided in the following two sections.

2.4.1 DC magnetic measurements

In DC magnetic measurements, a magnetic field is applied to the sample and magnetization of the sample is measured as a function of applied field, producing DC magnetization curves $M$-$T$ and $M$-$H$. Since a DC field is applied, the equilibrium value of the magnetization in the sample is obtained. The magnetic moment is measured by utilizing DC measurements technique called extraction magnetometry. Moving a magnetized sample through the detection coil induces a voltage in the detection coil set. The amplitude of this signal is proportional to the magnetic moment and speed of the sample during extraction. The DC servo motor employed in the
Figure 2.7: Photograph of Physical Property Measurement System (PPMS-14Tesla), at National Physical Laboratory (NPL), made by Quantum Design USA.

ACMS can extract the sample at a speed of approximately 100cm/sec., thus significantly increasing the signal strength over conventional extraction systems. The greater extraction speed also reduces errors that may result from non-equilibrium time-dependent effects.

2.4.2 AC magnetic measurements

AC magnetic measurements on the RERu-1222 (RE = Eu, Gd and Y), pure and doped MgCNi₃, and FeSe₀.₅Te₀.₅ samples were carried out on Quantum Design’s Physical Property Measurement System (PPMS). PPMS is a multi-purpose measurements device that is designed to perform both DC and AC magnetic measurements as well as electrical/thermal transport measurements. PPMS incorporate an AC/DC magnetometry system (ACMS) that can perform AC susceptibility and DC magnetization measurements at ultra-low fields. To perform an
AC magnetic measurement, a signal is applied to the drive coil and the sample is centered in one of the two detection coils. The Digital Signal Processor (DSP) then records the voltage across the detection coils for a predetermined amount of time. Multiple AC waveforms are averaged point-by-point to reduce noise with a single averaged waveform as the final output. The calibration coil array is used to precisely determine the instrument phase lag and also the amplitude of the applied AC magnetic field for improved M-H measurements. The detection system phase shift can then be removed from the sample signal. These two capabilities combine to give the ACMS an effective method for separating sample signal from instrumentation effects. The photograph of ACMS insert and coil set is shown in Fig. 2.8.

Generally, AC measurements are performed by applying a small AC drive magnetic field to the sample resulting AC moment can be measured. Compared to the DC measurement, where the measured magnetization is time invariant, in AC magnetic measurements, the time dependent response of the magnetic moments is induced. At low applied AC field and low frequencies the induced AC moment is the same as that measured by the DC experiment, and the AC moment is given by

\[ M = \frac{dM}{dt} H_{ac} \sin(\omega t) \]  

(4.1)

where \( H_{ac} \) is the amplitude of the driving field and \( \omega \) is the driving frequency, \( \chi = \frac{dM}{dt} \) is the slope of the M-H curve, called AC susceptibility.

In the case where the measurements are performed at AC fields with high frequencies, the AC moment no longer follows the DC magnetization curve. AC susceptibility of the sample in this case lags behind the applied AC field and results in an in-plane component \( \chi' \) and out-of-phase component \( \chi'' \). In a sinusoidally modulated magnetic excitation field \( H(t) \), magnetization will also be time-dependent [13]. So, if

\[ H(t) = H_{ac} \text{Im}(e^{i\omega t}) = H_{ac} \sin(\omega t) \]  

(4.2)

The time dependent magnetization \( M(t) \) can be expanded as a Fourier series of the non-linear complex AC susceptibility [13]

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Figure 2.8: Photograph of (Right) ACMS insert, and (Left) ACMS coil set used in PPMS system.

\[ \chi = \chi' + i \chi'' \] (4.3)

giving,

\[ M(t) = H_{ac} \sum_{n=1}^{\infty} \text{Im}(\chi e^{i\omega t}) = H_{ac} \sum_{n=1}^{\infty} [\chi' \sin(n\omega t) + \chi'' \cos(n\omega t)] \] (4.4)

Here \( n = 1 \) denotes the fundamental susceptibility, while \( n = 2, 3, 4, \ldots \) etc. are the higher order harmonics associated with non-linear terms of the AC susceptibility. The real and imaginary components of the susceptibility, are derived directly from \( M(t) \) through the relationship [13]

\[ \chi' = \frac{1}{\pi H_{ac}} \int_{0}^{2\pi} M(t)\sin(n\omega t) d(\omega t) \] (4.5)

\[ \chi'' = \frac{1}{\pi H_{ac}} \int_{0}^{2\pi} M(t)\cos(n\omega t) d(\omega t) \] (4.6)
$\chi'$ is the fundamental real component associated with the dispersive magnetic response and $\chi''$ is the fundamental imaginary component, which comes from energy dissipation within the sample. AC susceptibility is one of the finest tools for the study of complex phenomena such as spin-glass, cluster ferromagnetism, superconducting transitions, vortex dynamics, and critical current densities. This is because the measurements can be performed at low applied fields, and hence any critical change in the magnetic susceptibility due to the sample phase transition can be recorded, which otherwise could have been masked by high DC magnetic field measurement.

2.5 Transport property measurements

2.5.1 Electrical transport measurements

Resistivity measurement is quite easy and straightforward to provide much useful information about the electrical properties of the sample. The measurement of electrical resistivity as a function of temperature gives information about the various temperature dependent phase transitions. Resistivity as a function of temperature was measured without field and at different applied DC magnetic fields from 0Oe to 140 kOe in the temperature range of 2 to 300K using the four probe resistivity technique [14] set up of the PPMS. A low contact resistance is required due to the small resistance of the samples. The four probe technique is named so because it makes use of four wires to measure the resistivity. Two wires are connected on to the opposite ends of the sample to pass the current $I$ through the sample, and the other two wires are collinearly connected between the current probes to measure the corresponding voltage $V$ across the sample (shown in Fig. 2.9) Resistance $R$ of the sample is thus measured using Ohms law, $V = IR$. Separate current and voltage probes are used in such a way that voltage probe ideally does draw any current. To measure the resistivity using this technique, the sample was cut in a rectangular bar shape of dimensions $6\times2\times0.9\text{mm}^3$ and polished using sandpaper to remove any contamination. The sample was then fixed to the resistivity sample holder of the PPMS, which provides three channels and all the channels, could be used at a time to measure the resistivity of three different samples. Fine copper wire were used for soldering on each channel’s current and voltage connection points, and the other end of the copper
wires were fixed to the sample with the help of silver paste. In order to reduce the contact resistance, the contact points were heated to completely dry off the silver paste. The contact points were then checked using a standard multimeter to find out whether proper connection between sample and probes has been established. The sample puck holder was then mounted to the sample chamber of the PPMS with the help of puck extractor. To measure the resistance of the sample, a current of 1mA order was passed through the sample and the corresponding voltage drops across both voltage probes observed. The resistivity of sample was calculated using the formula:

$$\rho = \frac{R A}{L}$$  \hspace{1cm} (4.7)

where $R$ is the measured resistance, $A$ is the area of cross-section of sample, and $L$ is the distance between the two voltage probes.

### 2.5.2 Thermal transport measurements

The Quantum Design Thermal Transport Option ($TTO$) of Physical Property Measurement System (PPSM) enables measurements of thermal properties, including thermopower (also called Seebeck coefficient) and thermal conductivity for a sample over the entire temperature and magnetic field range of the PPMS. The $TTO$ measures the thermoelectric power and thermal conductivity both of the sample.
2.5.2.1 Thermoelectric power measurements

The thermopower ($S$) or thermoelectric power (also called the Seebeck coefficient) of a material is a measure of the magnitude of an induced thermoelectric voltage in response to a temperature difference across that material. The thermopower has unit of volts per Kelvin ($V/K$) [15], although it is more often given in microvolts per Kelvin ($\mu V/K$). The thermopower of a material, represented by $S$, depends on the material’s temperature and crystal structure. The thermoelectric power of a superconductor is zero below its transition temperature. So, the superconducting transition ($T_c$) obtained from resistivity measurements and magnetization measurements can also be verified from the thermopower measurement. However, the main importance of this technique lies in the facts that sign of thermopower (Seebeck coefficient) tells about the charge carriers in the sample. The thermopower is positive and negative according to the charge carriers are holes and electrons respectively.

![Diagram of two probe lead configuration](image)

**Figure 2.10:** (Left) Two probe lead configuration using bar shaped oxygen free Copper leads, (Right) Mounted sample on TTO puck.

The two probe lead configuration method is the most convenient because it involves attaching only two leads, but this method scarifies accuracy because heater/$I^+$ and $T_{hot}/V^+$ share one lead while coldfoot/$I^-$ and $T_{cold}/V^-$ share the other lead (shown in Fig. 2.10). Thus, the thermal and electrical contact resistances between the leads and sample contribute to the measured quantities. The two probe lead configuration method can be used only when the thermal and electrical resistances of the sample are
far greater than those of the leads. The oxygen free copper (OFC) strips are used as a lead for making the two probe contact. The thermal conductance of the epoxies decreases very rapidly below 100K, so the thermal contact resistance may be significant at low temperature even if it is not at room temperature. Sample mounted in this fashion is shown in Fig. 2.10.

2.5.2.2 Thermal conductivity measurements

Thermal conductivity ($\kappa$) is the property of a material’s ability to conduct heat. Thermal conductivity is the heat energy transferred per unit time and per unit surface area, then divided by the temperature difference. It is measured in watts per degree Kelvin. Heat transfer across materials of high thermal conductivity occurs at a higher rate than across materials of low thermal conductivity. Thermal conductivity is measured by applying heat from the heater shoe in order to create a user-specified temperature differential between the two thermometer shoes. The $TTO$ system dynamically models the thermal response of the sample to the low frequency, square-wave heat pulse, applied heater power, resulting $\Delta T$, and sample geometry. The sample geometry and arrangement to measure the thermal conductivity is shown in Fig. 2.10. The thermoelectric power and thermal conductivity both measurements were performed simultaneously on a common Thermal Transport Option ($TTO$) puck.

2.5.2.3 Specific heat measurements

The specific heat is the amount of heat per unit mass required to raise the temperature by one degree Celsius. The measurement of the specific heat of solids can provide considerable information about lattice, electronic, and even magnetic properties of materials. Specific heat measurements, particularly when taken at temperatures that are well below the Debye temperature, directly probe the electronic and magnetic energy levels of a material. From a practical point of view, materials used in the construction of thermal devices, such as refrigerators, cryostats, and so on, must be characterized thermally. In the heat capacity option, the basic puck configuration accommodates small, but not microscopic, samples weighing approximately 1 to 100 mg. A single specific heat measurement can require nearly 10 time constants for the settling the time that occurs between measurements. Here we
used relaxation technique to measure the specific heat of the sample that combines the best measurement accuracy with robust analysis technique. After each measurement cycle, which is a heating period followed by a cooling period. The specific heat option fits the entire temperature response of the sample platform to a model that accounts for both the thermal relaxation of the sample platform to the bath temperature and the relaxation between the sample platform and the sample itself. The exploded view of heat capacity puck is shown in Fig. 2.11.
2.6 References