Chapter 2

EXPERIMENTAL TECHNIQUES

In this chapter, various experimental techniques employed in the course of this study have been described. These include X-ray diffraction (XRD), AC susceptibility, DC four probe resistivity and thermoelectric power (TEP).

2.1 X-ray Diffraction studies

The diffraction data which depends on the lattice parameters is unique for a particular material and can be employed in the identification of a material, just as fingerprints are used to identify a human being. X-ray is that part of the electromagnetic spectrum which covers the wavelength range 0.1-200 Å. Only a relatively small part of the total X-ray region is covered by the conventional X-ray spectrometer. The X-rays used for the material characterization is CuK₂, whose wavelength is 1.5418 Å. The basic principle involved in the X-ray studies is the Bragg’s law i.e., \( n\lambda = 2d\sin\theta \), where \( \theta \) is the glancing angle at which the X-ray strikes the surface of the crystal, \( \lambda \) is the wavelength of the X-ray used, \( n \) (an integer) is the order of diffraction and \( d_{hkl} \) is the distance between the parallel planes having miller indices \( h,k,l \). The lattice parameters \( a, b, c \) can be calculated by indexing the sharp peaks (assigning \( h,k,l \) values) and using the equation

\[
\left( \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \right) d^2_{hkl} = \%
\]

(2.1.1)

In polycrystalline samples or powder of a crystalline material, the crystals are randomly oriented. If such a sample is struck by an X-ray beam, there may be many planes which
are oriented in such a way that Bragg’s law is satisfied and we obtain a resultant diffraction pattern with peaks corresponding to all such planes. In order that more number of planes are exposed, the sample is rotated by an angle $\theta$ on its own axis during exposure. The diffracted beams are collected by scintillating counter, which acts as a detector, at an angle $2\theta$. This output is fed to a recorder which records the output (which is proportional to the intensity of the diffracted beam) versus $2\theta$. From the positions, relative intensities of the peaks and from the area under its profile, the position of the atoms in a unit cell can be determined. The orientation of the crystallites can also be determined from the relative intensities. The shape of the peak provides information regarding the crystallite size and lattice imperfections including strains.

The XRD studies at room temperature were carried out using a SIEFERT X-RAY diffractometer, the schematic diagram of which is given in Fig.2.1. The fine powder of the material under study was mounted on a perspex plate using vacuum grease as a binder. CuK$_\alpha$ radiation ($A = 1.5418 \, \text{Å}$) was used. The machine was operated with a beam current of 30 ma and power of 40 kV. For phase identification, the patterns were compared against standard patterns reported in the literature. The cell parameters were calculated by using the least square refinements with an accuracy of 2 decimal places. The error in estimation of cell parameters could be due to small error in reading the $2\theta$ values which is $\pm 0.1^\circ$.

2.2 AC susceptibility

The ac susceptibility measurements were carried out using a mutual inductance method. Schematic diagram of the set-up is shown in Fig.2.2. It consists of a primary coil and two co-axially wound secondary coils. Current was driven through the primary coil using an oscillator. In the absence of any sample, the mutual inductance of the combined coils
Fig. 2.1 Schematic diagram of an X-ray Diffractometer
Fig. 2.2 Schematic diagram of AC susceptibility set-up
should be zero. When the sample is kept at the center of one of the secondary coils, voltage is induced across the secondaries depending on the magnetization and hence upon susceptibility of the sample. In practice, it is difficult to make the two secondary coils exactly identical in all respects. Hence, even when there is no sample, a small voltage is observed across the secondaries. This is nullified by subtracting the background voltage (voltage appearing when sample is not present) from the voltage obtained with sample present.

The primary coil was wound on a bakelite former of length 11.0 cm and inner diameter 3.0 cm. The primary coil assembly is fixed on the outside of the $Be-Cu$ extension tube as shown in Fig.2.2. The primary coil resistance is 35 Ω and it could produce a field of 0.036 Tesla for the applied current of 1 Amp. Additional number of turns were wound at both the edges of the primary coil for field uniformity throughout its length. Both the secondaries are kept inside the cryostat and length of each secondary is 2.54 cm. Each secondary coil has 3250 turns of 38 gauge standard insulated copper wire. The sample to be measured was kept at the center of the upper secondary coil. Temperature of the sample was measured using a calibrated Si-diode sensor which is placed close to the sample.

The primary coil was energized by sending an ac current at a frequency of 33 Hz and an amplitude of 1.999 V using the internal oscillator of the dual phase EG & G PAR-5210 lock-in amplifier whose output impedance is 600 Ω. The induced voltage at the secondaries was measured using the same lock in amplifier in differential mode to get better signal to noise ratio. The field generated by the primary is calculated by measuring the current flowing through it. This current is estimated by measuring the voltage drop across a standard 1 K Ω resistor connected in series with the primary coil.
The temperature of the sample was measured using a Si-diode sensor and was controlled using a **temperature** controller (Scientific Instruments **Inc**, series 5500). The accuracy of the temperature measurement was better than 0.5 K. The **in-phase** (inductive) component ($x'$) and out of phase (resistive) component ($x''$) of the complex susceptibility were measured simultaneously as a function of temperature.

### 2.3 Resistivity measurements

The resistivity measurements were carried out using the standard four probe method. The measurements were performed from 8 K to room temperature using a closed cycle refrigerator (APD make). The temperature of **the** specimen was monitored and controlled by using Lakeshore 330 auto tuning temperature controller. The electrical contacts were made on the sample by the application of silver paint (Elteks). The sample was mounted directly on the cold head of the closed cycle system using General Electric adhesive and the leads were taken out through a 10 pin connector. Temperature of the specimen is monitored and controlled by using a calibrated Si-diode (DT-470-SD-12) sensor mounted on the cold head. The accuracy of temperature measurement was better than ±0.1 K. A heater wire of 100Ω was wound on the cold head. The diode sensor and the heater are connected to the Lakeshore temperature controller, which supplies controlled amount of power to the heater.

Schematic diagram of the resistivity measurement setup is given in Fig.2.3. A constant current (I) was passed through the sample using a constant current source (Keithley model 224) and the voltage drop (V) across the sample was measured with a resolution of 10 nV by using Keithley model 181 nanovoltmeter. Care was taken to eliminate the **thermo-e.m.f.** developed across the voltage leads.
Fig. 2.3 Schematic diagram of Resistivity setup.

- **Keithley 181 Nanovoltmeter**
- **Lakeshore 330 Temperature Controller**
- **Keithley 224 Constant Current Source**
- **Current Leads**
- **Si- Diode Sensor**
- **Cold Head of Closed Cycle**
- **Sample**
- **Voltage Leads**
The resistivity at a given temperature is calculated by using the relationship

$$\rho(T) = R(T)A/l$$  \hspace{1cm} (2.3.1)$$

where $R(T) = V/I$, is the resistance at temperature $T$, $A$ is the area of cross section of the sample and $l$ is the distance between the voltage leads. The accuracy of the absolute value of resistivity is $\pm 10 \mu\Omega$ cm.

### 2.4 Thermoelectric Power

Seebeck coefficient is the e.m.f., $\Delta V$, developed when two conductors $A$ and $B$ are joined together with their two junctions at different temperatures $T_1$ and $T_2$ under the condition that no current flows in the circuit. It is the thermal e.m.f. which is measured in an ordinary thermocouple arrangement. The TEP is the e.m.f. produced per unit temperature difference between the two junctions i.e. $AV/dT$.

A thermal gradient $\Delta T$ is created between the two junctions ($\Delta T = T_2 - T_1$), where $T_1$ and $T_2$ are the temperatures of the two ends. The voltage developed between the two junctions is $AV$, then TEP is defined as

$$S = \frac{\Delta V}{\Delta T} \hspace{0.5cm} \text{for} \hspace{0.5cm} \Delta T \rightarrow 0$$  \hspace{1cm} (2.4.1)$$

i.e., $S$ is the voltage produced per unit temperature difference between the two junctions.

There are two methods of measuring TEP of a sample. One is the integral method and another the differential method. In the integral method, one end of the sample is kept at a fixed temperature (in liquid nitrogen or liquid helium) and the temperature of the other end is changed continuously. This method can be used for long specimens like wires. In the second method a small temperature gradient $\Delta T$ is maintained across the
sample and the seeback voltage (AV) developed across the sample is measured. Owing to the size of our samples, the differential method was adopted to obtain the TEP data.

The schematic diagram of the experimental set-up is shown in Fig.2.4. TEP measurements were carried out on well characterized samples using dc differential technique in a closed cycle refrigerator system (APD make) in vacuum in the temperature range 40-300 K. The sample is held between the two copper electrodes. The sample and electrode assembly is mounted on the cold head of the closed cycle refrigerator. The temperature of the assembly is controlled and measured by the Si-diode sensor (DT-470) which is mounted on the cold head. One of the electrodes is mounted on the cold head itself, the second copper electrode is placed at the other end of the sample. The heater mounted on the second electrode is used to create a small temperature gradient of 1-3 K across the sample. The temperature gradient is measured by using calibrated copper-constantan thermocouple. The junctions of the thermocouples were fused on thin copper foils which were attached to the electrodes by using GE Varnish and Cigarette paper in between, which ensured good thermal contact as well as electrical isolation. Thin copper wires were attached to copper foils, which in turn were attached to the sample faces with silver paint. The voltage developed across the sample due to the temperature gradient is fed to a Nanovoltmeter (Keithley 181 model) through these copper leads. The entire sample assembly was covered by mylar foils to minimize the radiation losses.

The TEP measurements were carried out in the temperature range 40-300 K because of the poor sensitivity of the differential thermocouple below 40 K. At a fixed sample mean temperature, the voltage ($\Delta V$) across the sample was measured for different values of AT between 1-3 K. TEP was calculated from the slope of AV vs AT curve. The measured TEP is the difference between the TEP of copper and the sample. So, the
Fig. 2.4 Schematic diagram of Thermoelectric power set-up
absolute TEP of the sample was obtained by correcting it for the thermoelectric power of the copper leads.