In this chapter, the principles and details of the experimental techniques used in the present work are discussed. Special emphasis is given on the methodology of measuring flux profiles. The experimental setup used for measuring the flux profiles, and its calibration, are discussed.

2.1 Optical microscope

The optical microscope is an instrument that magnifies and resolves the structure of objects and it is the most widely used instrument in metallography/ceramography. It consists of four components: A light source, condenser lens, objective lens and eyepiece. The condenser collects light rays from the light source which are focused onto the specimen. The objective lens forms a real, magnified aerial image of the object in the intermediate image plane. This real image is further magnified by the eyepiece to form the final image. The magnification of the objective is given by the ratio $/ / /$, where $/ /$ is the distance between the eyepiece and the objective and $/$ is the focal length of the objective lens.

Polarized light was used extensively to get microstructural features with clear contrast and also surface anisotropy. By introducing a polarizer into the condenser lens system the specimen is illuminated with plane polarized light, i.e, the wave vector is parallel to
a particular plane and thus giving a direct measure of the phase change at the reflecting surface. Application of polarized light microscopy includes the study of grain size and shape, preferred orientation, twinning and phase distribution which are all effectively delineated. A Lietz reflected light microscope with the facility for polarized light was used in this work.

**Sample preparation for optical observation**

In all metallographic methods emphasis is given to the need for effective sample preparation. Small pieces were cut from the bulk samples, and they were mounted in bakelite metallographic mounts. The mounted specimens were initially ground on coarse silicon carbide paper to get a flat surface. Methanol was used to wash the sample. The samples thus ground were subjected to final polishing on a diamond cloth with diamond pastes of 6 $\mu$m, 1 $\mu$m, and 0.25 $\mu$m. Polishing time with each paste was 4-6 h. The polished surface of the sample was later cleaned with fine polishing cloth. The samples thus prepared were examined using the optical microscope.

**2.2 Scanning Electron Microscope**

In a scanning electron microscope (SEM) the specimen is scanned with a finely focused electron beam of kilovolt energy. An image is formed by scanning a cathode-ray tube in synchronism with the beam and by modulating the brightness of this tube with beam-excited signals. In this way, an image is built up point-by-point which shows the variations in the generation and collection efficiency of the chosen signal at different points on the specimen.

An important feature of the SEM is that a variety of images can be obtained from the signals from the specimen, like back scattered image, related to the atomic weight of the constituent phase from the back scattered electrons. Also the X-ray and Auger
electrons available in the SEM can provide further information about the composition at the specimen surface.

In the present study a JEOL JSM 840 scanning electron microscope was used. Even though the superconducting NdBaCuO samples are electrically conducting in the normal state, silver paint was used as conducting material to avoid charge accumulation on the specimens during observation.

2.3 Quantitative analysis of microstructures

Since direct observation of a three dimensional microstructure is extremely difficult, quantitative analysis of microstructural features are usually obtained from the measurements made on two dimensional micrographs. The basic principle employed is that the volume fraction of a phase is equal to the area fraction in a random planar section and is equal to the linear fraction in a random linear line through the three dimensional microstructure. The volume fraction of a phase is also equal to the point fraction of randomly distributed points which lie within that particular phase [1].

$$V_f = \frac{V_\alpha}{V} = \frac{A_f}{A} = \frac{L_f}{L} = \frac{P_f}{P}$$

(2.3.1)

$V_f$ = Volume fraction of $\alpha$ phase

$V_\alpha$ = Volume of a phase in the specimen

$V$ = Total volume of the specimen.

$A_f$ = Area of a phase in a random planar section.

$L_f$ = Linear fraction of $\alpha$ phase in a random linear line.

$L_\alpha$ = Line fraction of a phase in a random linear line.

$L$ = Total length of random linear line.

$P_f$ = Point fraction of $\alpha$ phase.
\( P_o \) = Number of random points falling in the \( \alpha \) phase.

\( P \) = Total number of random points.

The results quoted are the average of several measurements.

**Measurement of grain size**

In metallographic research, the most widely used method for the measurement of grain size is the mean linear intercept method. In this method, a linear transverse is made on the micrograph, the transverse length \( L \) from one grain boundary to the next is measured and the number of grains \( N \) counted. The average grain size \( d \) is given by

\[
d = \frac{\Sigma L}{N}
\]  

(2.3.2)

In the present study, grain size measurements in the microstructure of melt grown samples were carried out by the linear intercept method.

**2.4 X-ray diffractometer**

A knowledge of the crystal structure of materials is essential in understanding their properties and in identifying them, in predicting their behavior under various conditions, and for the characterization of the material at all stages of its preparation. The reproduction of materials with tightly controlled properties often requires X-ray analysis. Although single crystals are preferred for determining crystal structures of new materials, some materials are available only as small polycrystals. Many structures are already known, and the available information is used with the powder method in many types of studies.

The principal uses of the X-ray powder method are

(a) identification of crystalline phases, including qualitative and quantitative analysis of mixtures of phases.

(b) distinguishing between mixtures, various types of solid solutions.
(c) precision measurement of lattice parameters and crystalline states.
(d) determination of the degree of preferred orientation and crystalline texture

Principle

When a beam of parallel monochromatic X rays of approximately 0.1 nm wavelength strikes a crystal, the crystal acts as a three-dimensional diffraction grating and produces an X-ray diffraction pattern. This diffraction consists of a three dimensional array of reflections which satisfy the conditions of Bragg’s law:

\[ nX = 2d \sin \theta \]

where \( n \) is a small integer giving the order of diffraction, \( A \) is the wavelength of the incident X rays, \( d \) is the distance between a set of parallel lattice planes, and \( \theta \) is the angle between the incident X-ray beam and the atomic lattice plane in the crystal.

The reflection angle for a particular set of lattice planes \((hkl)\) is

\[ 2\theta = 2\sin^{-1}\left(\frac{\lambda}{2d_{(hkl)}}\right) \]

where \((hkl)\) are the Miller indices defining the orientation of the plane with respect to the crystallographic axes.

The powder pattern is a set of reflections in which the lattice spacings and the relative intensities are unique from each crystalline substance. It is this property that makes it possible to identify a substance by comparing its pattern with that of a known substance.

Similar crystal structures give similar x-ray patterns in which the peak positions will be shifted if the materials have different lattice parameters. The lattice spacing \(d\) is related to the lattice parameters \(a_0\) in cubic crystals by

\[ d_{(hkl)} = \frac{a_0}{(h^2 + k^2 + l^2)^{1/2}} \]
The lower symmetry crystal systems require additional terms.

In the present study we have used a Siemens X-ray diffractometer with Cu Kα radiation, whose characteristic wavelength is 1.5418 Å. Diffraction lines corresponding to various \((hkl)\) values are recorded in the 20 range from 20° to 60° and the lattice parameters \(a\), \(b\), and \(c\) are calculated from them using a powder diffraction computer package.

2.5 dc electrical resistivity

The electrical resistivity measurements are performed using a home-made apparatus which employs the dc four probe technique. This technique avoids contact resistance. The contacts are made using silver paint with the two outer leads as the current leads and the two inner leads as the voltage leads. The heater wire is wound astatically around the sample holder to heat the sample above the liquid nitrogen temperature. A copper-constantan thermocouple is used to measure the sample temperature. Sample temperatures could be varied up to room temperature from 77 K.

Block diagram of the experimental set up for precise dc electrical resistivity measurements is shown in Fig. 2.1. Constant dc electrical current (I) was supplied to the sample using a Keithley 224 constant current source. A Keithley 181 nanovoltmeter was used to measure the voltage drop across the inner leads. To avoid the thermo e.m.f due to thermal gradient across the sample, the voltage drop across the inner leads was measured for both the forward \((V1)\) and reverse \((V2)\) directions of the current \((I)\) and the resistance was calculated as \(R = (V1 - V2)/(2I)\). The resistivity is given by \(RA/l\), where \(A\) is the area of cross section of the sample normal to the direction of the current, and \(l\) is the distance between the voltage leads. The error in the measured resistivity is ±1 \(\mu\Omega\cdot\text{cm}\).
Fig. 2.1 Block diagram of dc electrical resistivity measurement setup.
2.6 ac susceptibility

Principle

The ac susceptibility measurement is based on a mutual inductance coil assembly where a primary coil and two secondary coils with equal number of turns mounted co-axially, form the basic unit of the measuring circuitry. In the absence of a sample, the voltage across the secondary coils is zero. In the presence of a sample the induced magnetization due to the ac field in primary coil, will result in off-balance signal of the secondary coils detection system.

Coil assembly and the bridge design

Secondary coils are first wound in 3 cm with an equal number of turns (1250). A 6cm long homogeneous primary coil is wound over the secondaries. Secondary coils are connected in series opposition to give a null output in the absence of a sample. A voltage from a Wavetek 178 waveform synthesizer is applied to the primary coil and off-balance signal from the pair of secondary coils, when the sample is introduced in center of one of the secondaries, is detected using an EG&G PAR 5210 dual phase lock-in amplifier (LIA). A synchronous signal from the Wavetek is fed to the reference channel of the lock-in amplifier. Voltage drop across a standard 10 ohm resistor connected in series with the primary coil is measured using a Kiethley 196 multimeter to calculate the field generated by the primary coil. The temperature of the sample is measured using the copper-constantan thermocouple. All the instruments are controlled through IEEE 488 interface and the data were acquired using a personal computer.

The field produced by a current at any point in a solenoid, is given by

\[ H_{\text{rms}} = \frac{4\pi N_p I_{\text{rms}}}{10 L_p} \]  

(2.6.1)
where \( N_p \) is number of turns in the primary coil, \( L_p \) is the length of the primary coil in cm and \( I_{rms} \) is rms value of the current through the primary coil. The field amplitude \( H_{ac} \) in Oe is \( \sqrt{2} H_{rms} \).

When the induced voltage in the secondaries is sensed at the input of the dual phase LI A, it gives out a signal in the form of dc voltages \( \varepsilon_R, \varepsilon_I \) proportional to the real and imaginary parts of \( M \) that are in phase and out of phase, respectively, with respect to the applied ac field. In practice, the net output from secondaries is often non-zero even in the absence of any sample and this is eliminated by subtracting the measured background signal from the signal measured after inserting the sample under the same conditions. Additionally, there is a need to correct for the extraneous phase shifts arising from various sources in the setup. This is done by shifting the phase of the references so as to obtain \( \chi'' - 0 \) well above \( T_c \) as well as well below \( T_c \).

The measured voltages \( \varepsilon_R, \varepsilon_I \), are related to \( \chi_R, \chi_I \) as \[ \begin{align*}
\chi_R &= \frac{\varepsilon_R}{\alpha \omega AN \mu_0 H_m (1 - D)} \\
\chi_I &= \frac{\varepsilon_I}{\alpha \omega AN \mu_0 H_m (1 - D)}
\end{align*} \] (2.6.2) (2.6.3)

Here, \( N \) is the number of turns of the secondary across the sample, \( H_m \) is the amplitude of the applied ac field, \( A \) is the area of cross section of the sample, \( D \) is the demagnetization factor and \( \alpha \) is the filling factor [3]. The absolute values of susceptibility for non-zero demagnetization \( (D) \) values are calculated using the expressions given by Murphy [2]

\[ \begin{align*}
\chi'_1 &= \frac{\chi_R - D(\chi_R^2 + \chi_I^2)}{(1 - \chi_R D)^2 + D^2 \chi_I^2} \\
\chi''_1 &= \frac{\chi_I}{(1 - \chi_R D)^2 + D^2 \chi_I^2}
\end{align*} \] (2.6.4) (2.6.5)

Following this procedure, the temperature variation of \( \chi'_1 \) and \( \chi''_1 \) are obtained from the measured temperature dependence of \( \varepsilon_R, \varepsilon_I \).
2.7 Magnetic flux profile measurements

The magnetic flux profiles are measured using an ac inductive method suggested by Campbell [4].

Coil assembly

Coil assembly to measure the flux profiles is similar to the one which is used for ac susceptibility measurements. Two secondary coils (S1 and S2) with equal number of turns (1115) are first wound on two ends of the perspex cylinder within 12 mm length of each one. A 3.76 cm long homogeneous primary coil (P) to generate ac field is wound over the secondaries. Secondary coils are connected in series opposition to give a null output in the absence of a sample. The size of the coil assembly is chosen so as to fix it in between the poles of a dc electromagnet (Bruker-make). The maximum dc magnetic field that could be applied in this measurement was 1 T at 7 cm pole gap. The experimental setup used for the study is given in Fig. 2.2. The coil assembly is very rigidly fixed between the commercial dc electromagnet poles in order to avoid any relative displacement. A temperature sensor (TS) is placed near the sample. A waveform synthesizer (wavetek 178) is used to generate sinusoidal ac field in primary coil. The voltage across the standard 10 ft resistor is measured using Keithley 196 digital multimeter (DMM) and this provides a measure of the alternating field applied to the specimen. A maximum ac field of 100 Oe can be obtained with this setup. The TTL output of the wavetek is a square wave with the same frequency and phase as of the voltage applied to the coil generating the ac magnetic field and it is used as the reference signal to the lock-in amplifier (Princeton applied research EG&G model 5210). It is operated in wide-band mode, where it measures all the harmonics of the signal without filtering. All these equipment are controlled by a computer through general purpose interfacing bus (GPIB) card.
Fig. 2.2 Block diagram of ac magnetic susceptibility/flux profile measurement setup.
ac (33 Hz) and dc fields were applied along the sample length. When the sample is placed in one of the secondary coils the resultant output of secondaries is proportional to the rate of change of magnetization \((dM/dt)\). Campbell [4] and other workers [5-7] have reported a sensitive method in which a lock-in analyzer operated in the flat-band mode is used for performing the integration of \(dM/dt\). The lock-in output is proportional to

\[
\int_{\theta}^{\theta+\pi} \frac{dM}{dt} = C \{M(\theta + \pi) - M(\theta)\}
\]

where \(M\) is the magnetization of the specimen and \(C\) is a constant of the apparatus. The in-phase signal, which can be measured by the lock-in amplifier, refers to any signal produced by the flux motion in phase with the oscillating field. Thus it gives the magnetization of the specimen at the peaks of the ac field.

In general, ac field amplitudes are sufficiently small so that \(J_c\) is independent of field over the amplitude of the ac signal. If the amplitude \(H_{ac}\) is increased by \(\delta H_{ac}\) the extra flux introduced at the peak is

\[
\delta \phi = \delta H_{ac}(\pi r^2 - \pi r^2),
\]

where \(r\) is the radius to which the field has penetrated and \(R\) is the radius of the specimen. Hence, if \(S\) is the in-phase signal,

\[
\frac{dS}{dH_{ac}} = 2C \frac{dM}{dH_{ac}} = \frac{2C \pi}{\pi R^2 (R^2 - r^2 - R^2)} = -K \frac{r^2}{R^2}
\]

The constant \(K\) is determined as the signal per Gauss, when the sample is in perfect Meissner state. The above equation can be rewritten to get the penetration depth, \(p\) as

\[
p = R - r = R(1 - \sqrt{-\frac{1}{K} \frac{dS}{dH_{ac}}})
\]
The in-phase signal is measured as a function of the amplitude of the ac field at 77K for all the samples. This is repeated at various fixed dc fields. Flux profiles are obtained by plotting $p/R$ as a function of ac field amplitude.

Calibration of the penetration depth

When the sample is in one of the secondary coils, the output of pair of the secondaries is given by [5-7],

$$
\mu_0 \alpha N V \omega (1 - D) \frac{dM(\theta)}{d\theta}
$$

where $N$ is the number of turns per unit length of the secondary coil, $V$ is the volume of the sample, $\omega$ is the angular frequency of the applied ac field, $D$ is the demagnetization factor of the sample, $a$ is the filling factor [3], and $M(\theta)$ is the magnetization at a phase angle $\theta$. The in-phase signal measured by the lock-in amplifier in the flat band mode is given by

$$
S = 4\mu_0 \alpha N V f(1 - D)M(\theta = 0)
$$

$$
S = KM
$$

Where $K = 4\mu_0 \alpha N V f(1 - D)$ is the calibration factor.

2.8 SQUID magnetometer

Principle

A superconducting quantum interference device (SQUID) is used to determine the magnetic moment of a material, in a SQUID magnetometer. The squid response signal is a periodic function of the magnetic flux. The period of this function equals the flux quantum. The magnetic moment due to the specimen is measured by monitoring the change in flux through the pickup coil as the specimen is moved through another coil
in the feedback loop to offset the change in field at SQUID and the voltage output is directly proportional to the feedback current. Therefore the change in field at the main pick-up coil is read as an output voltage from the squid controlling electronics, i.e. \( \Delta V_{\text{SQUID}} \alpha \Delta \Phi \), where \( \Phi \) is the magnetic flux through the pick-up coil. The magnetic moment of the specimen is then obtained from the SQUID response curve with the help of various algorithms. The SQUID magnetometer used in the present work is a fully automated, computer controlled one from Quantum design.

References