Chapter 2

Characterization Details

2.1: EXPERIMENTAL TOOLS AND THEIR WORKING PRINCIPLE

2.1.1: X-ray diffraction pattern

When an electromagnetic radiation interacts with an ordered periodic structure, diffraction phenomenon occurs. X-rays are an electromagnetic wave which have very short wavelength having the order of a few angstroms (1 Angstrom = 0.1 nm) which is comparable to the distance between the consecutive planes in a crystal. Very short wavelength of X-rays demonstrates its very high energy value. Diffraction is the phenomenon in which bending of electromagnetic wave around the corners of an obstacle takes place as if the size of aperture or obstacle is comparable to wavelength of wave. In order to diffraction phenomenon takes place, the order of the wavelength of the incident radiation should be the same as the order of repeat distance of the periodic structure. An inter-atomic distance in crystalline solids is of the order of 1-10 Angstrom which makes X-rays the correct order of magnitude for diffraction from the atoms of crystalline materials. If the interference after reflection from the planes satisfies Bragg's condition then rays interfere constructively and produce a diffracted beam from a crystalline solid. The X-ray pattern of a given material is obtained by measuring the intensity as a function of variation of the angle [2θ].

William H. Bragg and W. Lawrence Bragg have given a law for the diffraction of x-ray from the crystalline planes, which is known as **Bragg's Law** [39], which elucidates a relation between the angle at which the beam diffracts from a crystalline surface and the particular wavelength used for X-rays. According to this relation

$$2d\sin\theta = n\lambda \tag{2.1}$$

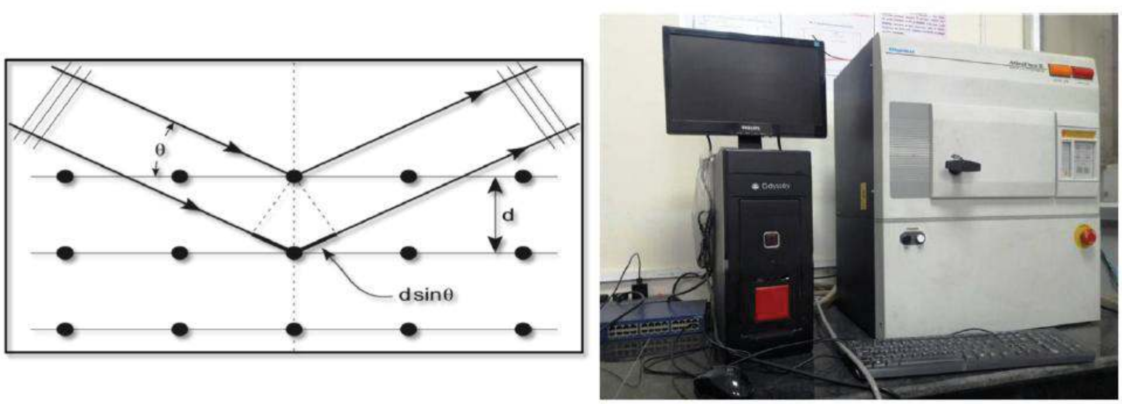
d = inter-plane distance of (i.e. atoms, ions, molecules)

θ = scattering angle or Bragg's angle, measured from the crystal surface

n = integer representing the order of the diffraction peak.

λ = wavelength of the x-ray used.

A bunch of information can be obtained from the X-ray pattern of the sample such as information about the Phase of the sample by matching the XRD pattern with reference patterns (JCPDS–ICDD file) of pure substances, quantitative information can also be accumulated on single phase and multi phase materials using pattern calculation and pattern fitting methods (so-called Rietveld refinement). In addition, one can also furnish information about the crystal structure, crystal symmetry, atom positions, lattice constant and cell volume of a unit cell, bond angle and bond length, precise values for sample composition, unit-cell dimensions, site-occupancy factors, strain and many more for pure as well as doped samples.



(a) (b)

Figure. 2.1: (a) Mechanism and (b) experimental set up of XRD instrument (Rigaku Mini Flex II).

It has been presumed that a perfect crystal enlarges in all directions to infinity. Since no crystal is perfect due to its finite size, therefore the effect of this deviation from perfect crystal structure promotes to the broadening of a diffraction peak.

2.1.2: Resistivity Measurement

It is very convenient to measure the value of a resistor with an ohmmeter. We easily connect the meter to the resistor, and take the reading of the measurement from the ohmmeter. But if the resistance value under study for the measurement is very low (in the milli- or micro-ohm range) then the measured resistance using mentioned two-point method is not satisfactory enough since in this case, test contact resistance itself becomes a significant factor. Similar type of problem occurs, when making ground mat resistance tests, because long lead lengths (up to 1000 feet) are used. Due to long lead length, the lead resistance will thus affect the measurement results. Using the four-probe resistance measurement method, one can eliminates lead resistance or contact resistance.

An ohmmeter measures all of the resistance in the circuit loop, which includes even the resistance of the wires itself which connect the ohmmeter to the component being measured. Such type of scenario would be difficult if the connecting wires are very long. Also it will be difficult to measure in case when the resistance of the component to be measured very low, then the measurement error introduced by wire resistance will be considerable.

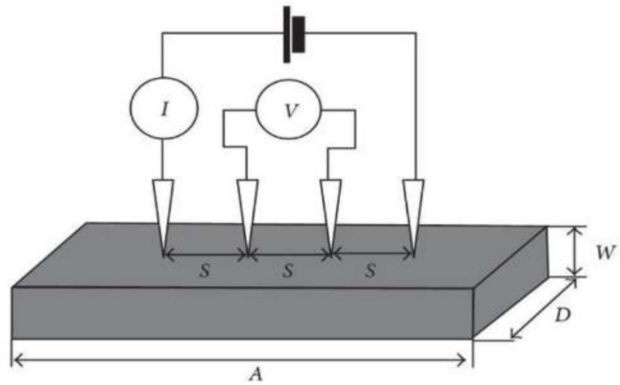


Figure 2.2: Schematic diagram of test circuit for measuring resistivity with the four-point probe method

It is an innovative procedure of measuring the subject resistance in a condition like this which involves uses of both an ammeter and a voltmeter. It is pronounced from the Ohm's Law that resistance (R) of the material is equal to voltage (V) divided by the current flowing (I) i.e. ($R = V/I$). Thus, one can be able to calculate the resistance of the subject component if the flowing current as well as voltage dropped across it is measured. Current is the same at all points in the circuit since it is a series loop. Since, we are only measuring voltage dropped across the subject resistance (and not the wire's resistances), hence the calculated resistance is indicative of the subject component's resistance alone.

2.1.3: Hall Measurement

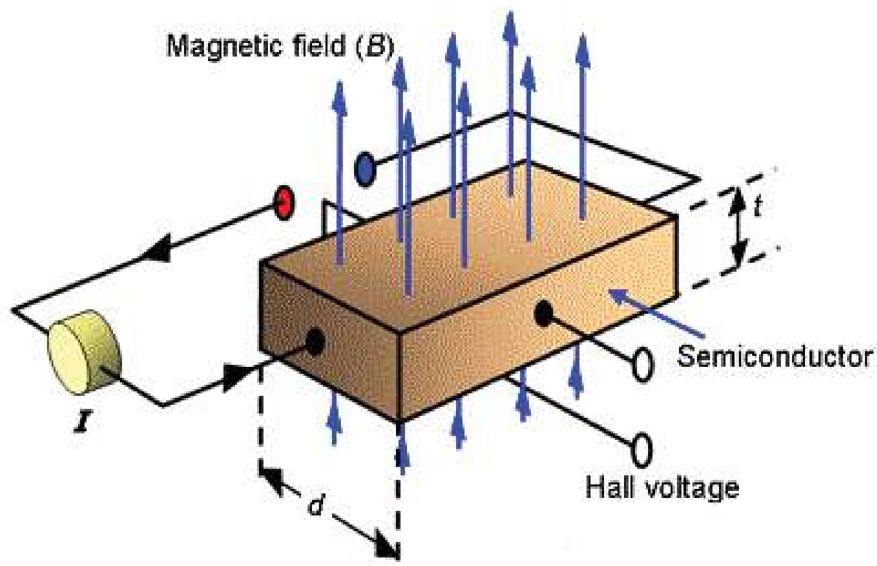
Figure 2.3 shows the schematic diagram for the Hall Effect measurement. Let t is the thickness of the semiconducting sample, d is the width and l is the length of the sample. Let I be the current flowing in the sample. If we apply a magnetic field B in the perpendicular direction of current (I) then a voltage developed in the perpendicular direction of both I and B known as Hall voltage, which we already have discussed in our introduction section. As we know

$$R=\frac{\rho l}{A} \tag{2.2}$$

Where R is the resistance of the sample, ρ is the resistivity, l is the length and A is area under perpendicular cross section. It is clear from the Figure 2.3,

$$R = \frac{\rho l}{lt} \tag{2.4}$$

Hence Hall resistivity of the sample may be given as



$$\rho = R \times t \tag{2.5}$$

Figure 2.3: Schematic diagram for Hall Effect measurement
(**Source:** http://tap.iop.org/fields/electro-magnetism/413/img_full_46945.gif)

The unit of Hall resistivity is ohm-m in MKS system. We can also determine the carrier concentration (n) by the use of Hall measurement using the formula

$$R_H = \frac{1}{ne} \tag{2.6}$$

Here R_H is the Hall coefficient, n is the carrier concentration and e is the electronic charge. Moreover Hall mobility of the carriers can be also obtained using the expression

$$\sigma = ne\mu \tag{2.7}$$

Here σ and μ are the conductivity and mobility of the carriers.

2.1.4: Thermoelectric Measurement

If we create a temperature difference on each side of a specimen then there is development of a voltage across it, such type of effect in the materials is called thermoelectric effect. Hence we can say that thermoelectric devices creates a voltage if different temperature is applied on each side of the specimen and in the similar manner it creates a temperature difference if voltage is applied across the specimen. Actually, temperature difference on the either side of the specimen causes a temperature gradient due to which there is diffusion of the carriers from hot side to the cold side which induces a thermal current across the specimen. Actually, temperature difference on the either side of the specimen causes a temperature gradient due to which there is diffusion of the carriers from hot side to the cold side which induces a thermal current.

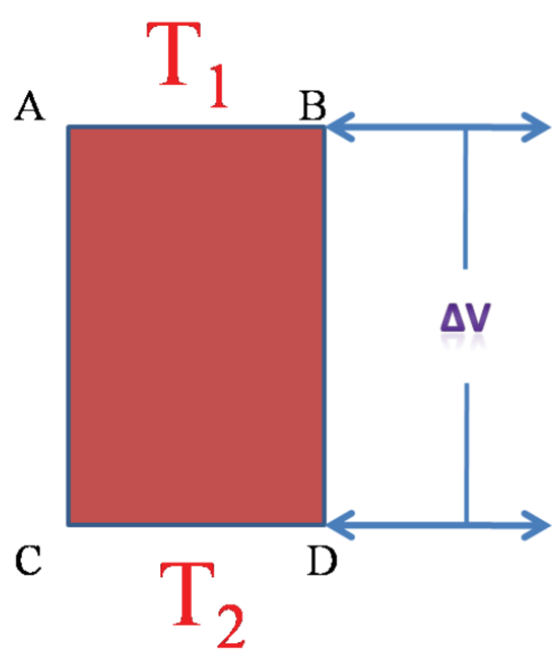


Figure. 2.4: Schematic diagram for thermoelectric measurement.

Conversion of temperature difference directly in to electricity is called the Seebeck Effect. Thermo power or Seebeck coefficient (S) of a specimen measures the magnitude of an induced thermoelectric voltage with respect to the temperature difference across the material. Let ΔT be the temperature difference across the ends of the materials and the induced voltage is ΔV then the thermo power of the materials can be given as

$$S = \frac{\Delta V}{\Delta T} \tag{2.8}$$

The unit of S is V/K or more usual μV/K is used. In Figure 2.4, ABCD is the sample, T_1 and T_2 be the temperature of side AB and CD of the sample and ΔV is the developed voltage due to temperature difference $\Delta T = (T_2 - T_1)$.

Thermoelectric materials are considered as a promising means of energy saving and power generation. The properties of thermoelectric materials such as eco-friendly, easy to maintain, free of noise and vibration less makes the TE coolers more reliable compared to existing refrigeration systems.

2.1.5: Magnetic Property Measurement System (MPMS)

2.1.5.1: Theory of Vibrating Sample Magnetometer (VSM) measurement

The vibrating sample magnetometer (VSM) is one of the most frequently used instruments in the measurement of the magnetization of a magnetic material placed in an applied external magnetizing field. It measures the magnetization by converting the induced dipole moment of the sample into an equivalent ac electrical signal.

The theory of VSM based on a 2ω detection principle, detection coils only generate a current in response to local magnetic field disturbances. The current in the detection coils is inductively coupled to the instrument's SQUID, which acts as an extremely delicate current-to-voltage converter. The voltage of SQUID is digitized and amplified by the use of the instrument electronics. The SQUID VSM measurement technique vibrates the sample with the frequency ω about the very center of the detection coils, where the signal peaks as a function of z which is the position of sample. The expression for generated SQUID signal (V) as a function of time t can be given as

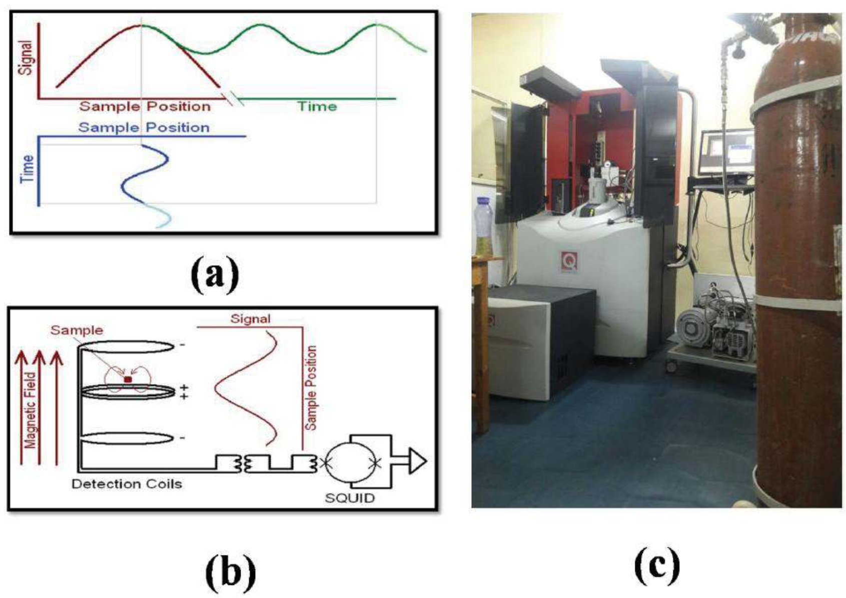


Fig. 2.6: (a) 2ω detection principle [4]. (b) SQUID detection schematic [4]. (c) MPMS instrument set up used for characterization.

$$V(t) = AB^2Sin^2(\omega t) \quad (2.9)$$

Because $V(Z) = Az^2$ for small vibration amplitudes, and z(t) = Bsin(ωt). Here, A is a scaling factor relating to the magnetic moment of the sample and B is the sample vibration amplitude. As one may know $Sin^2(\omega t) = \frac{1}{2} - \frac{1}{2}Cos(2\omega t)Sin^2(\omega t)$ the techniques of a lock-in amplifier can be applied to isolate and quantify the signal occurring at frequency 2ω.

2.1.5.2: Theory of Superconducting Quantum Interference Device

Superconducting quantum interference device (SQUID) is a phenomenon which is used for the measurement of the exceptionally small changes in magnetic field [45]. These changes can be utilized to measure a quantity related to the flux such as magnetic flux, voltage, current and magnetic susceptibility etc. It comprised of two superconductors which are separated by thin insulating layers to form two parallel Josephson junctions. The device may be configured as a magnetometer to detect incredibly small magnetic fields; it can measure even the magnetic fields present inside the living organisms. SQUIDs have versatile application in various fields such as medicine, geophysics and research etc.

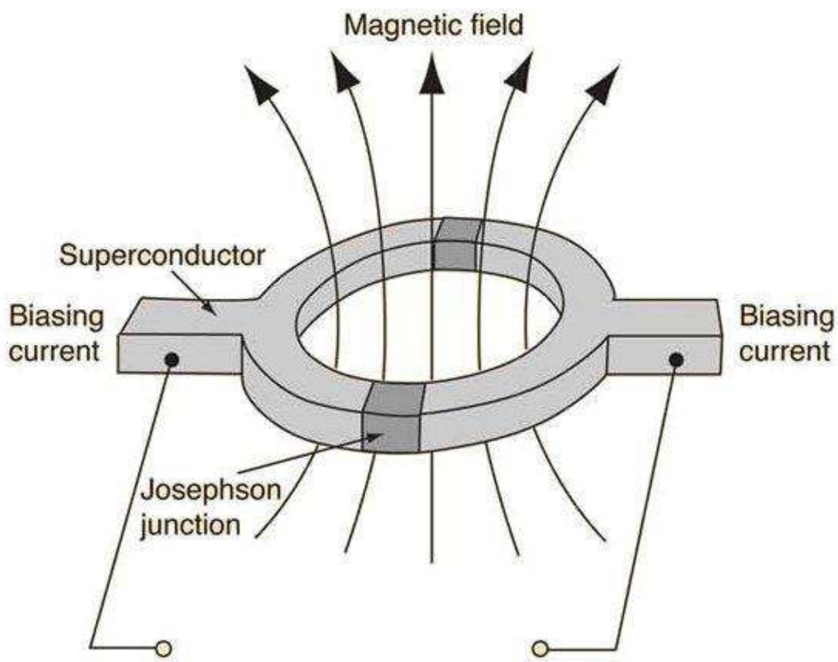


Figure 2.7: Schematic diagram of SQUID magnet

SQUID is based on principle of the combination of the two physical properties of superconductors, flux quantization (Duzer, T. V.; 1999) and Josephson tunneling (Barone, A; 1982) effects. It employs Meissner effect as well as the Lenz's law to a superconductor simultaneously such that there is no resistance in the current circulating in the superconducting loop and a precession occurs to perfectly nullify any change in the external magnetic field. The fundamental principle of the mechanism used in SQUID has been shown in the Figure 2.7.

The inner diameter of the super conducting loop in SQUID is ~100 μm. It comprises two Josephson junctions which support the certain maximum (critical) current in the superconducting state. The flow of current is made around the loop through both Josephson junctions. The electrons tunnel through the junction and thereafter interference takes place. Now, let us consider that a magnetic field or flux passes through the loop; hence it will induce a current around the loop as a consequence. It affects the overall current, which causes a phase difference between the electrons passing through the junction, as now the net current through each junction is no longer be the same. As a result, one can get a potential difference across the loop, which can be measured to determine the magnetic field. One can find the more details about SQUID, which can be found from the literature (Duzer, T. V.; 1999, Barone, A; 1982). For the present study, Quantum Design SQUID magnetometer has been used.