Chapter 3

Chapter 3 Bulk Characterisation techniques

3.1 X-Ray Diffraction

X ray interaction with material shows variety of phenomenon like Photoelectric effect, fluorescence, production of auger electrons, Compton Effect and scattering. A perfect elastic collision between photon and electron leads to coherent scattering, superposition of scattered wave gives X-ray diffraction [1].

Diffraction pattern generated by scattering of X – ray from different planes of the crystalline materials can help in determining the structural arrangement of atoms in that material. The relation between wave length λ, lattice spacing d, and the diffraction angle θ are given by Braggs diffraction condition

$$n\lambda = 2d\sin\theta$$

Constructive interference can only occur if all waves scattered at a set of parallel planes, and the path length of wave between two plane is integer multiple of wave length i.e. nλ. In practice not all the order of diffraction are considered but the first order for virtual set of planes (*nh nk nl*), so the above equation becomes

$$\lambda = 2d_{hkl}\sin\theta$$

In a conventional XRD measurement, the angle of incidence relative to the sample surface is varied and the angle of detection is kept equal to it, hence 2θ versus intensity are recorded.

3.2.1 Hall effect

The Hall Effect describes the behavior of free carriers in a semiconductor when an electric field is applied in presence of magnetic field. A particle with charge Q, moving with velocity v in a magnetic field B will experience the force given by the Lorentz force equation $F = Q\ (v \times B)$. The direction of force is mutually perpendicular to direction of the velocity and magnetic field. When a conductor carrying a current I is placed in a magnetic field, the moving charge will experience a net force mutually perpendicular to direction of current flow and the applied magnetic field. Under these circumstances there is deposition of charges on one edge of the test specimen; hence there will be voltage difference V between two surfaces. Redistribution of electric charges creates an electric field E, the force due to electric field is given by $F = QE$. The relation between voltage, current and strength of magnetic field is given by

$$V_H = \frac{IB}{ned}$$

where V_H = Hall voltage,

I = Hall Current,

d = Thickness of the sample,

B = applied magnetic field perpendicular to sample surface,

n = Carrier concentration.

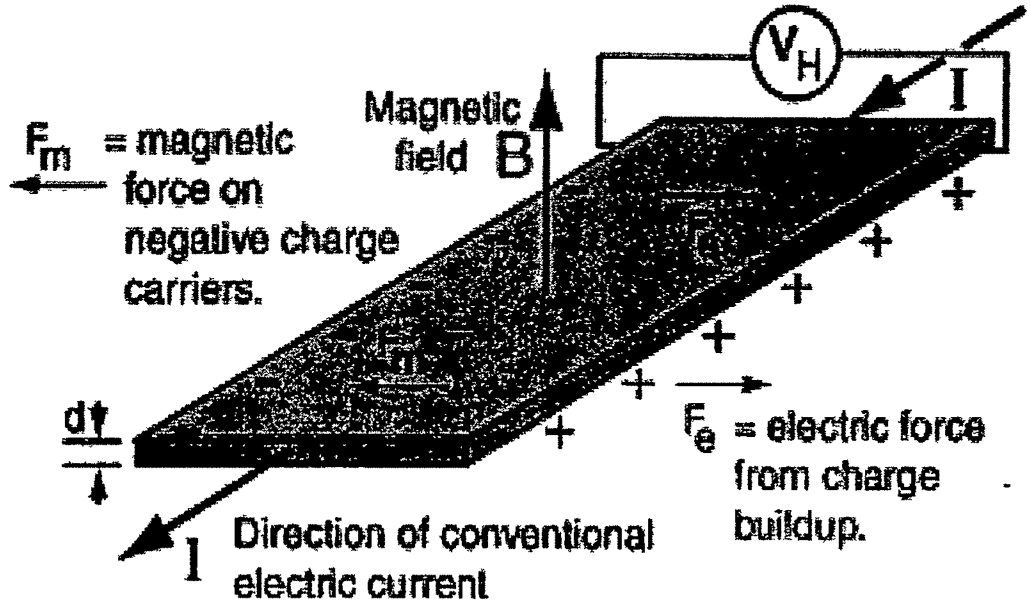

Fig : 3.1 : Arrangement for Hall voltage measurement

3.2.2 Importance of Hall effect :

1. From the sign of the Hall Coefficient, one knows whether the conduction is through holes or electrons.
2. Resistivity and Mobility of charge carriers can be calculated as

$$R = \frac{\rho L}{A}$$

$$\rho = \frac{RWd}{L} = \frac{V/I}{L/Wd}$$

The conductivity $\sigma = \frac{1}{\rho}$ is equal to q μ_p p , the mobility μ_p is ratio of the Hall coefficient and the Resistivity.

3. The charge carrier concentration can be determined from Hall coefficient

   i.e. $R_H = \frac{1}{ne}$

   where, n is the carrier concentration and R_H = Hall coefficient.

3.3.1 Resistivity

The electrical resistivity of solid can be estimated by passing current i through the sample of cross section area (a) and measuring the resultant voltage drop (V) over a distance (l). The electrical resistivity can be given by equation:

$$\rho = \frac{Va}{il} = \frac{Ra}{l}$$

Where R is resistance of specimen between the electrical contacts. The lattice vibrations (Phonons) cause a deviation of the periodic potential. An electron traveling thorough the perturbed lattice gets scattered. This is the cause of resistance in a substance. Thus The resistivity will be a function of electrons and lattice parameters.

From the simple treatment, it may be shown that

$$\frac{1}{\rho} = \frac{ne^2\tau}{m}$$

Where n = number of electrons / unit volume,

τ = Relaxation time,

m, e = mass and charge of electron

Using Fermi - Dirac statistics in to account the energy dependence of τ, gives

$$\frac{1}{\rho} = \frac{ne^2\tau_F}{m}$$

Here n = Number of free electrons / unit volume.

τ_F = Relaxation time at Fermi energy,

Introducing the mean free path Λ_F of the electrons

$$\Lambda_F = \upsilon_F \tau_F$$

Where υ_F is velocity of electron at Fermi energy.

Bloch treatment for resistivty of metal gives

$$\frac{1}{\rho} = \frac{2.83x10^{-32} nM\theta^2}{C^2T}$$

Where M = atomic weight

C = coupling between lattice and electrons, is roughly equal to Fermi energy

θ = Debye Temperature

3.3.2 Importance of Resistivity measurement

From Resistivity measurement following parameters can be calculated

(1) Mean Free Path [Λ_F].

(2) electron - phonon coupling constant or Fermi energy.

(3) Debye Temperature.

3.3.3 Resistivity Setup

Resistivty can be measured by two probe or Four probe method. The two probe method has its own demerits only sample of well define geometry can be measured. Conventionally Four probe methods are employed; it has no geometrical factor in calculation. Hence resistivity of any irregular shape can be measured with better accuracy.

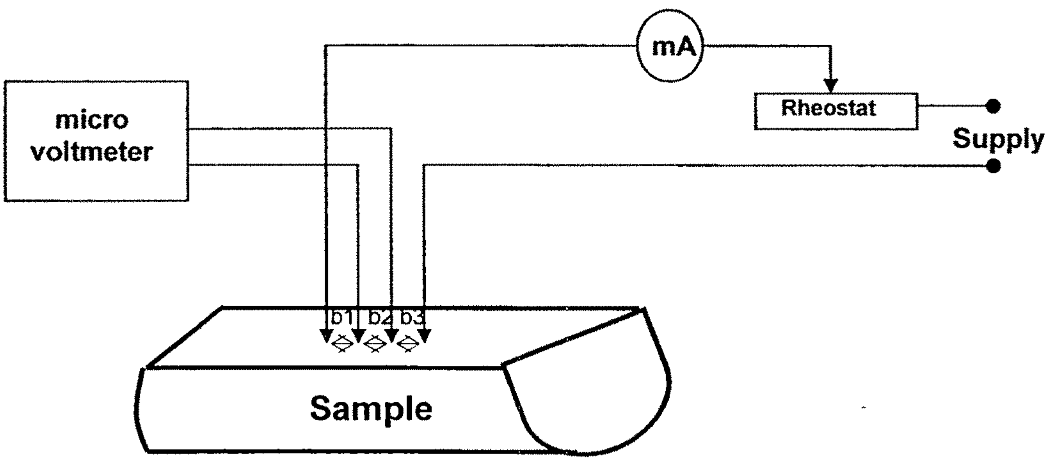

Fig :3.2 the arrangement of Resistivity set up

As shown in the figure voltage V_x is applied at first and last probes, and the current I_x are measured at the central probes. The resistivity ρ is given by

$$\rho = \frac{V_x}{I_x}\left[\frac{2}{\frac{1}{b_1}+\frac{1}{b_3}+\frac{1}{b_1+b_2}+\frac{1}{b_2+b_3}}\right]$$

b_1, b_2, b_3 distance between probes for $b_1 = b_2 = b_3 = b$, above equation reduces to

$$\rho = \frac{V_x}{I_x} 2b$$

For resistivity measurement Oxford set up (At IUC -Indore) was used. Sample was kept in a liq He cryostat, it has a Lakshore temperature controller and interfaced with computer to record the resistivity versus temperature from 5K to 300K. For Magnetoresistance measurement same setup was used, this set up has a inbuilt arrangement of magnetic field up to 10 Tesla with the help of superconducting magnet.

3.4 Magneto Resistance

The study of magnetic field effect on the transport properties of metal and semiconductors has become a well established and invaluable tool for the investigation of mobile carriers in crystals. Magnetoresistivity measurements determine the resistivity of materials in the presence of magnetic fields. In metals with closed Fermi surface the magnetoresistivty saturates for each crystal orientation, similar type of behavior observed for n-type and p-type semiconductor. Semimetals with equal number of electrons and holes Bi, Sb, the magnetoresistivity does not saturate for any crystal orientation and keeps on increasing as magnetic field increases. Magnetoresistance is measured in Hole measurement geometry. In an isotropic media the application of a small electric field drives a current density parallel and perpendicular to it. It is represented as

$$J = \sigma E$$

Where σ is conductivity and it is scaler.

When a magnetic field is applied carrier are deflected, the current density is no more parallel to the electric field. The conductivity becomes a tensor even for an isotropic material.

The conductivity tensor and current density is related as

$$J_i = \sum_j \sigma_{ij}(H) E_j$$

Where $\sigma_{ij}(H)$ (i, j = x, y, z)are component of magnetoconductive tensors and the magneto resistivity tensor is just inverse of it. The standard geometry in which a magnetic field H is applied orthogonally to a long current carrying conductor and the current flows along x direction. The x and y direction are represented as longitudinal and transverse direction respectively.

In a standered geometry in which transport is in xy plane and furthermore $J_y = 0$, The current density J and the electric field E are related by

$$\begin{bmatrix} E_x \\ E_y \end{bmatrix} = \begin{bmatrix} \rho_{xx}(H) \rho_{xy}(H) \\ \rho_{yx}(H) \rho_{yy}(H) \end{bmatrix} \begin{bmatrix} J_x \\ J_y \end{bmatrix}$$

The above matrix equation can be written in the form

$$E_x = \rho_{xx}(H)\, J_x$$

$$E_y = \rho_{yy}(H) J_x$$

The diagonal element $\rho_{xy}(H)$ of the magnetoresistivity tensor is measured by the ratio between the longitudinal electric field E_x and current density J_x in the x direction. The off diagonal component $\rho_{yx}(H)$ is measured by the ratio between transverse electric field E_y and current density J_x. It can be shown that

$$\rho_{xy}(H) = - \rho_{yx}(H)$$

The transverse electric field E_y also called Hall field is produced by the space charges accumulated at the borders of the conductors.

The Hall resistivity coefficient is defined as

$$R(H) = \frac{1}{H}\frac{E_y}{J_x}$$

3.5.1 AC Susceptibility

Different properties of magnetic materials can be probed by AC Susceptibility or Vibrating Sample Magneto meter. From this measurements one can characterize paramagnetic, Ferromagnetic, ferrimagnetic and antiferromagnetic materials. In addition to that one knows Spin Glass state, Blocking Temperature and Magnetic moment of the clusters. AC Susceptibility has an advantage of dynamic and a static response to an external applied magnetic field. Fig shows block diagram of AC susceptometer.

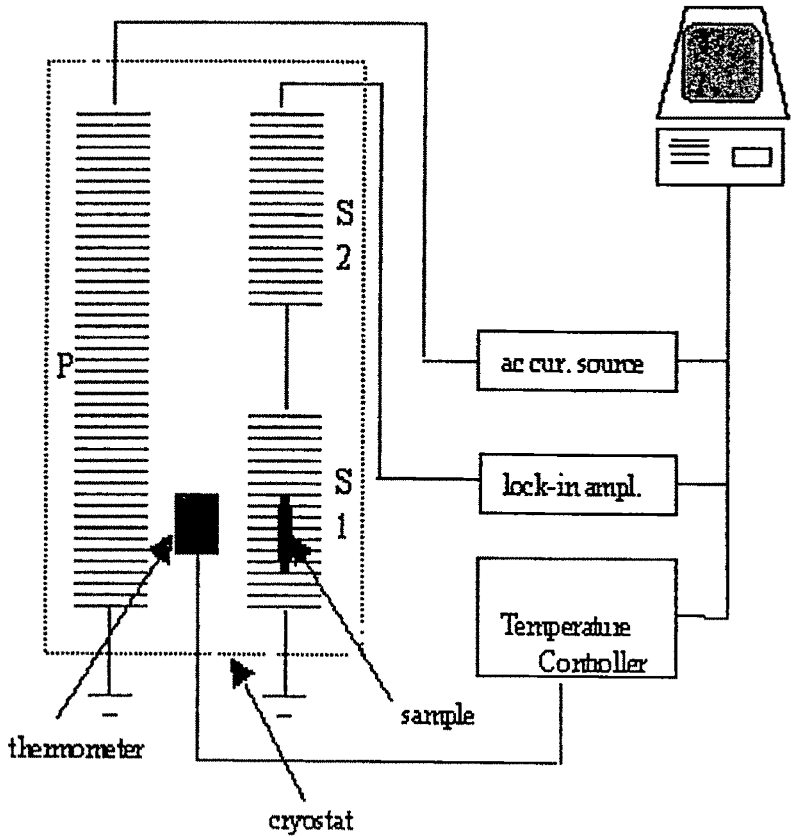

Fig :3.3 the block diagram of AC Susceptometer

3.5.2 Basic Principles

In this Technique, AC field is applied to sample and resulting AC moment is measured as a function of temperature. As the AC field is varying with time, measurements gives different dynamics which are not obtained in DC measurements.

AC Susceptometer mainly consists of a primary coil and two secondary coils. An AC current passing through the coil produces a varying field over a sample kept between primary and secondary coils. The secondary coils are wounded in opposite direction, hence the difference in flux created by the sample can be observed. The resultant signal is measured by phase sensitive detector which produces out put voltage proportional to AC susceptibility of the substance. The component of induction which is in phase is real (χ^1) and out of phase i.e. imaginary (χ^2) are measured separately.

AC susceptibility of the sample over the temperature range gives the idea about multi domain, single domain or super paramagnetic limit of magnetic materials. This measurement is proved to be valuable tool for characterization of ferromagnetic particle in different size range [2]. In these phenomena, the particle exhibit single domain ferromagnetic behavior below the blocking temperature T_B, and are super paramagnetic above T_B. In the super paramagnetic state, the moment of each particle freely rotates according to magnetic induction, so the magnetic particles collectively act like a paramagnetic substance in the magnetic field. The spontaneous fluctuation of magnetic domain yields zero coercivity , as a result the peak is observed in low field AC Susceptibility versus temperature [3]. The characteristic cusp nearer to freezing temperature in the low field AC Susceptibility versus temperature shows spin glass behavior [4].

References

1. R.L Snyder, X ray diffraction. In: X-Ray characterization of materials, (E D s. E. Lifshin and Weinheim), Wiley -VCH New York, 1999.

2. L. Néel, C. R. Hebd. Seances Acad. Sci. 228, 664 (1949); Ann. Géophys. 5, 99 (1949). 5 W. F. Brown, Phys. Rev. 130, 1667 (1963).

3. Radhakrisnamurthy C, Likhite S.D., Deutch E.R. and Murthy G.S. Phys. Earth and planertary interiors, 26,37 (1981).

4. Murani A. P. J. Magn. Magn. Mater.5, 95 (1977).