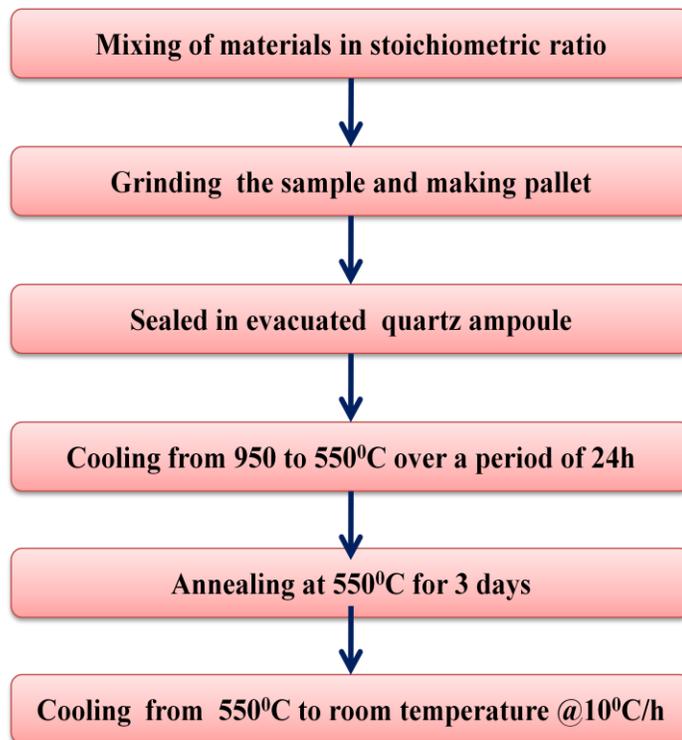


2.1 Sample synthesis

Solid state melting route has been used to prepare the materials. Single crystals of the materials were grown by modified Bridgman method. High purity powder of pure elements such as Bi (99.999%), Te (99.999%), Sb (99.999%), Cu (99.999%), Zn (99.999%) and Co (99.998%) were mixed uniformly in their stoichiometric ratios and pellets were made from these. The pellets were sealed in quartz tubes after evacuating them down to $\sim 10^{-6}$ torr. The crystal growth involves cooling from 950°C to 550°C in a period of 24 hours and then annealing at this temperature for 72 hours [33]. Silver colored single crystals were then cooled down to room temperature slowly which can be easily cleaved along basal planes. The cleaved surface was shiny, silvery and mirrorlike which is further used for the different testing.



2.2 Experimental Tools & Their Working Principle

2.2.1 X-ray diffraction pattern

When an electromagnetic radiation interacts with a periodic structure, diffraction phenomenon occurs. X-rays are electromagnetic wave having very short wavelength of the order of a few angstroms (1 Angstrom = 0.1 nm), therefore the energy of X-rays are very high. Diffraction is the phenomenon in which bending of electromagnetic wave around the corners of an obstacle takes place but the size of aperture or obstacle must be comparable to the wavelength of wave. In order to get diffraction phenomenon from the crystal, the order of the wavelength of the incident radiation should be the same as the order of repeat distance of the periodic structure. The typical 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 $2d\sin\theta = n\lambda$, then rays interfere constructively and produce a diffracted beam from a crystalline solid, here d is inter-plane distance of (i.e atoms, ions, molecules), θ is scattering angle or Bragg's angle, n is integer representing the order of the diffraction peak and λ = wavelength of the x-ray used. The X-ray pattern of a given material is obtained by measuring the intensity as a function of variation of the angle (2θ).

X-ray Diffractometer consists of basically three component, X-ray tube, sample holder and X- ray detector. For the production of X-ray, a filament of high atomic number is heated to generate electrons; these electrons are accelerated by high voltage and strike the material to be characterized, when electrons have enough energy to dislodge inner cell electrons of the target materials, characteristic X-ray is generated. Cu is the most common target material with CuK_α radiation 1.5418Å. Sample rotates at angle θ in the path of the

collimated X-ray beam whereas detector is mounted to collect the X-ray beam and rotates with angle 2θ [shown in Fig. 2.1(a)]. We have used XRD Rigaku Mini Flex II for the characterization of the samples [shown in Fig. 2.1(b)].

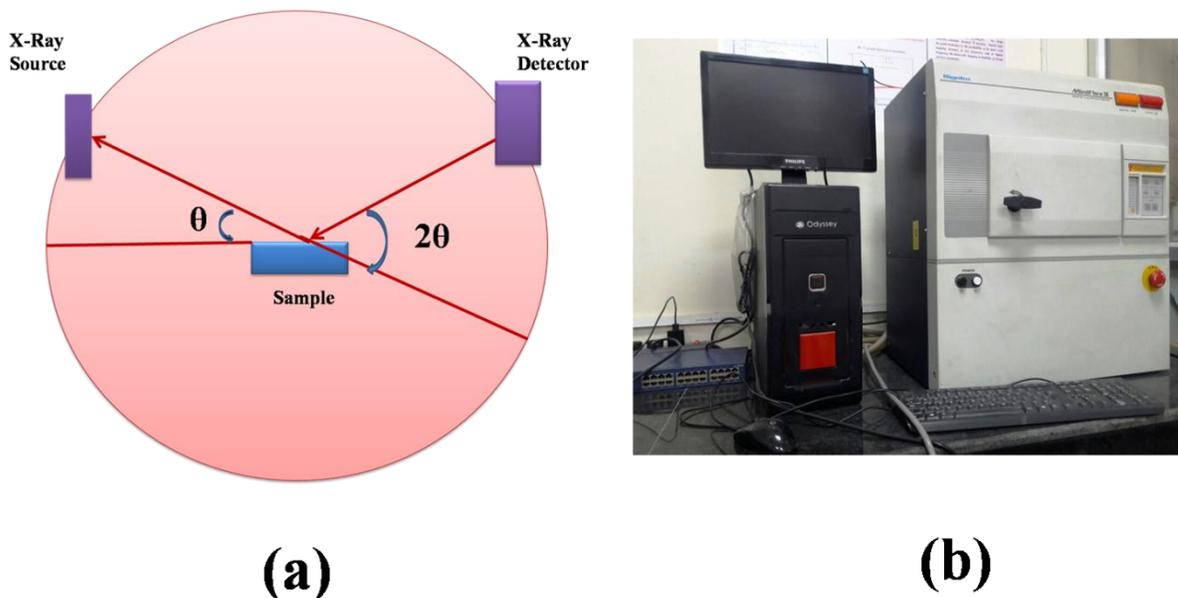


Fig.2.1 (a) Mechanism and (b) experimental set up of XRD instrument (Rigaku Mini Flex II).

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 collected on single phase and multi-phase materials using pattern calculation and pattern fitting methods (so-called Rietveld refinement). Moreover, one can also supply information about the crystal structure, crystal symmetry, atoms position, lattice constant and cell volume of a unit cell, bond angle and bond length, accurate values for sample composition, unit-cell dimension, site-occupancy factors, strain and many more for pure as well as doped samples. It has been assumed that a perfect crystal extends in all directions to infinity, but since no

crystal is perfect due to its finite size; hence the effect of this deviation from perfect crystallinity leads to the broadening of a diffraction peak.

2.2.2 Resistivity Measurement

Resistivity of the sample has been measured using physical property measurement system (PPMS) from Quantum Design using four probe resistivity mode. It is very simple to measure the value of a resistor with an ohmmeter, we easily connect the meter to the resistor, and read off the measurement from the ohmmeter. But if the resistance, we want to measure is very low (in the milli- or micro-ohm range) then the measured resistance using above mentioned two-point method is not satisfactory enough because 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. Here also, the lead resistance, due to long lead length, will affect the measurement results. Using the four-point resistance measurement method, we can eliminate 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 problematic if the connecting wires are very long, and/or the resistance of the component to be measured very low, then the measurement error introduced by wire resistance will be substantial.

An ingenious method of measuring the subject resistance in a situation like this, involves the use of both an ammeter and a voltmeter. It is obvious from the Ohm's Law that resistance (R) of the material is equal to voltage (V) divided by the current flowing (I) i.e.

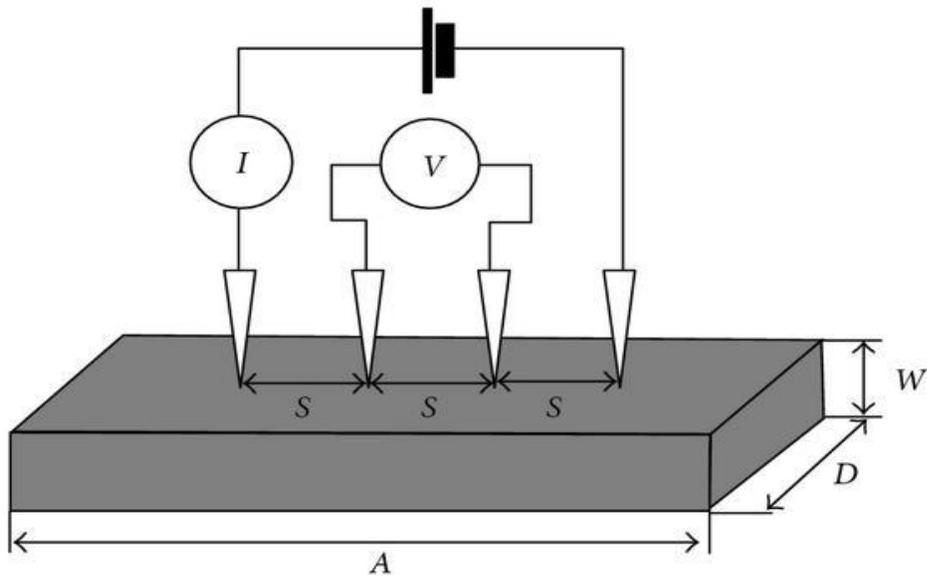


Fig.2.2 Schematic diagram of test circuit for measuring resistivity with the four-point probe method.

$(R = V/I)$. 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, because 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.

2.2.3 Hall Measurement

We have used PPMS from Quantum Design for the Hall measurement. Fig. 2.3 is showing the schematic diagram for the Hall Effect measurement. Here, in Fig.2.3, t is the thickness of the semiconducting sample, d is the width, l is the length of the sample and I is 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 sample which have direction perpendicular to the both I and B and known as a Hall voltage. 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

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

Here R_H is the Hall coefficient, n is the carrier concentration and e is the electronic charge.

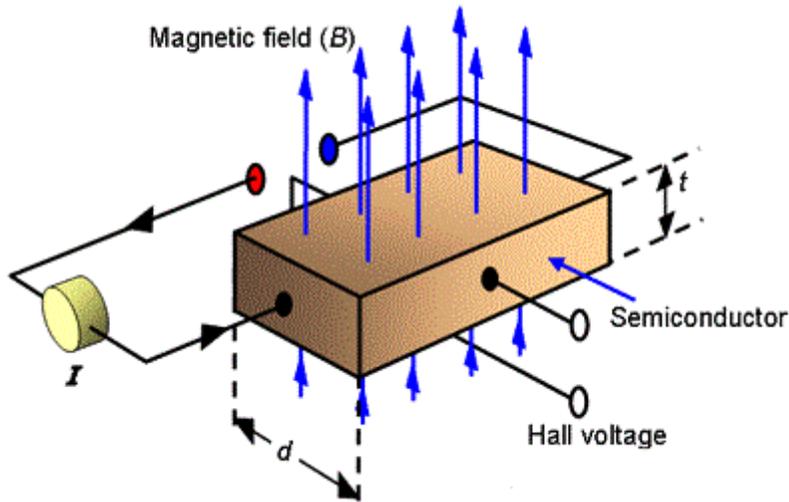


Fig.2.3 Schematic diagram for Hall measurement. Adapted from (http://tap.iop.org/fields/electromagnetism/413/img_full_46945.gif).

Moreover Hall mobility of the carriers can be also obtained using the expression

$$\sigma = ne\mu$$

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

2.2.4 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 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. 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

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

The unit of S is V/K or more commonly $\mu\text{V/K}$ is used. In Fig.2.4, ABCD is the sample, T_1 is the temperature of side AB whereas T_2 is the temperature of side CD of the sample and ΔV is the developed voltage due to temperature difference $\Delta T \sim (T_2 - T_1)$. PPMS from Quantum Design has been used for the present study of thermoelectric experiment.

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

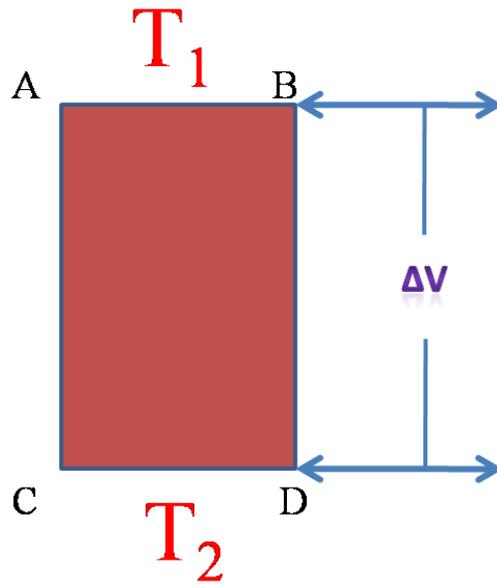


Fig. 2.4 Schematic diagram for thermoelectric measurement.

2.2.5 X-ray Photoelectron Spectroscopy

X-ray photo electron spectroscopy (XPS) is a quantitative spectroscopic technique using which we can get much valuable information about the materials such as the empirical formula, elemental composition, chemical state and electronic state of the elements [44]. X-ray photoelectron spectroscopy (XPS) is based on the explanation of the photoelectric effect phenomenon discovered in 1905 by Einstein. In XPS technique, the surface of the materials are irradiated using a beam of X-rays while simultaneously we measure the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material. Ultra-high vacuum (UHV) conditions are required in XPS; the order of vacuum may be typically $\sim 10^{-10}$ torr. Such a high order vacuum not only facilitates the transmission of the photoelectrons to the analyzer but also minimizes the re-contamination rate of a freshly cleaned sample. In order to provoke the photoelectric effect, the sample is irradiated with

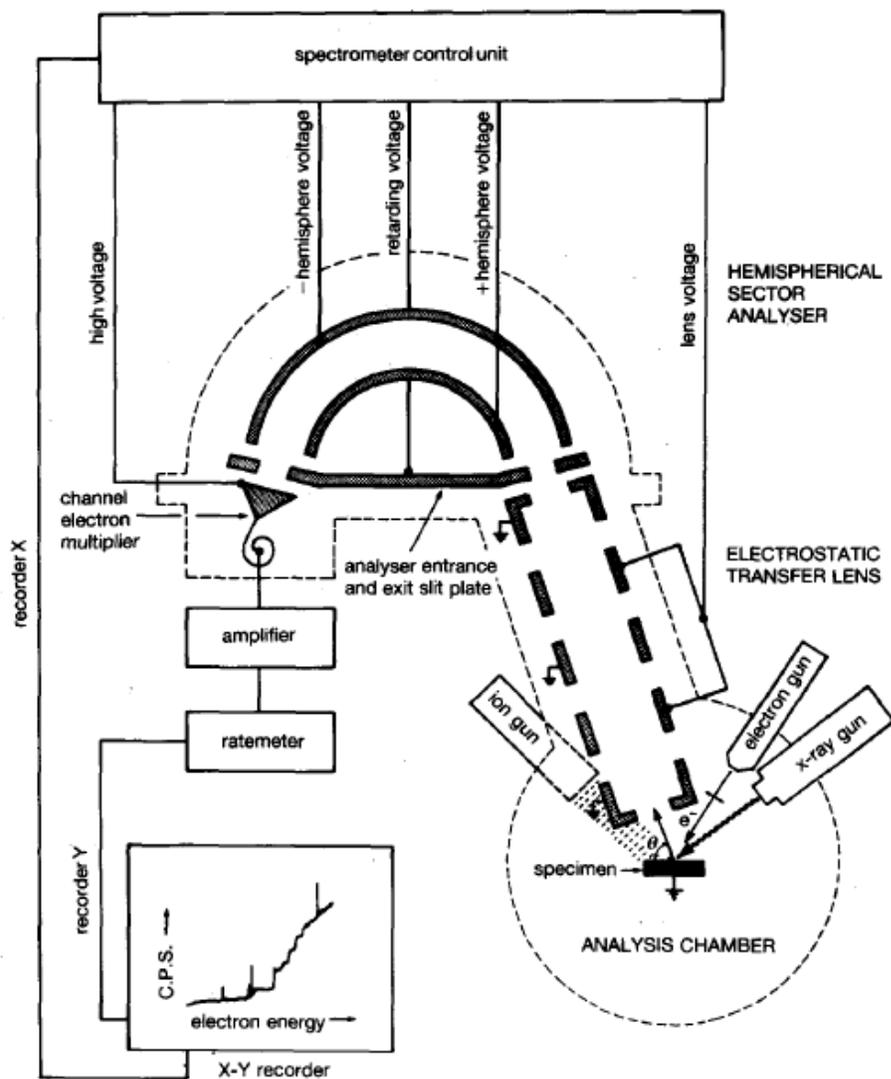


Fig.2.5 Schematic diagram of X-ray photoemission spectroscopy.

low-energy (~ 1.5 keV) X-rays. A high-resolution electron spectrometer is used to measure the energy spectrum of the emitted photoelectrons. A typical XPS spectrum is usually shown by a graph in which Y-axis represents the number of electrons detected and X-axis shows the binding energy of the photoelectrons emitted. Each emitted photoelectron produces a characteristic set of XPS peaks at characteristic binding energy values. Using this data we can directly identify each element which exists in or on the surface of the material being

analyzed. These characteristic peaks correspond to the electron configuration of the electrons within the atoms, e.g., 1s, 2s, 2p, 3s, etc. The area under the characteristic peaks is directly related with the number of detected electrons. In order to get atomic percentage values present in the material, we correct the raw XPS signal by dividing its signal intensity (number of electrons detected) by a "relative sensitivity factor" (RSF) and normalized over all of the elements detected.

Let, the binding energy (BE) of the electron is E_{Binding} , energy of the X-ray photons being used is E_{Photon} , E_{Kinetic} is the kinetic energy of the electron as measured by the instrument and ϕ is the work function of the spectrometer (not the material) then the electron binding energy of each of the emitted electrons can be determined by using an equation which is based on the work of Ernest Rutherford:

$$E_{\text{Binding}} = E_{\text{Photon}} - (E_{\text{Kinetic}} + \phi)$$

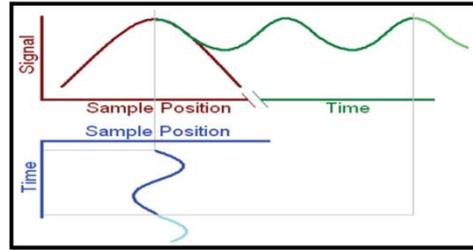
X-ray photoelectron spectroscopy (XPS) investigation were carried out using $\text{AlK}\alpha$ radiation, the samples have been sputtered with 1.5KeV argon ions.

2.2.6 Magnetic property measurement System (MPMS)

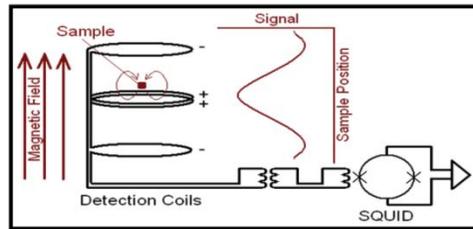
2.2.6.1 Theory of Vibrating sample magnetometer (VSM) Measurement

The vibrating sample magnetometer (VSM) is one of the most widely used instruments which are used in the measurement of the magnetization of a magnetic material placed in an 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 [45].



(a)



(b)



(c)

Fig. 2.6 (a) 2ω detection principle [45]. (b) SQUID detection schematic [45]. (c) MPMS instrument set up used for characterization.

The current in the detection coils is inductively coupled to the instrument's SQUID, which serves as an extremely sensitive 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 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

$$V(t) = AB^2 \sin^2(\omega t)$$

Because $V(Z) = Az^2$ for small vibration amplitudes, and $z(t) = B \sin(\omega t)$. Here, A is a scaling factor relating to the magnetic moment of the sample. B is the sample vibration amplitude.

But as we know $\sin^2(\omega t) = \frac{1}{2} - \frac{1}{2} \cos(2\omega t)$, the techniques of a lock-in amplifier can be applied to isolate and quantify the signal occurring at frequency 2ω [45].

2.2.6.2 Theory of Superconducting Quantum Interference Device

Superconducting quantum interference device (SQUID) is a mechanism which is used for the measurement of the extremely small changes in magnetic field. These changes can be used to measure a physical quantity related to the flux such as magnetic flux, voltage, current and magnetic susceptibility etc. It consists 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.

The principle of SQUIDs is based on the combination of the two physical properties of superconductors, flux quantization and Josephson tunneling effects. It employs Meissner effect as well as the Lenz's law to a superconductor simultaneously so that there is no resistance in the current circulating in the superconducting loop and a precession occurs to perfectly cancel any change in the external magnetic field. The basic principle of the mechanism used in SQUID has been shown in the Fig. 2.7.

The inner diameter of the superconducting loop in SQUID is $\sim 100 \mu\text{m}$. It contains 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 after that 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 matter of fact it affects the overall current which causes a phase difference between the electrons passing through the junction, because, now the net current through each junction is no longer the same. As a result, we can get a potential difference across the loop which can be measured to determine the magnetic field. For the present study Quantum Design SQUID magnetometer has been used.

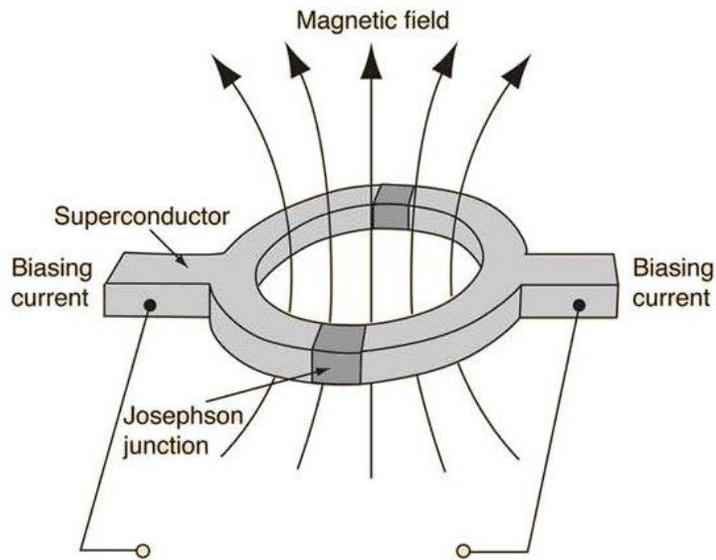


Fig. 2.7 Schematic diagram of SQUID magnet.

2.2.7: Scanning electron microscopy (SEM)

Secondary and backscattered electrons results when the scattering of electrons from the atom takes place. We can get information about the microstructure of the sample in the form of image using these scattered electrons. The Scanning Electron Microscope (SEM) is the characterization technique which uses the secondary and backscattered electrons emitted from the sample surface due to excitation by the primary electron beam and thereby produces images of the sample. In this technique, the surface of the sample is scanned

by the electron beam in a raster pattern, with detectors building up an image by mapping the detected signals with beam position.

Schematic diagram of the scanning electron microscope (SEM) has been shown in Fig. 2.8.

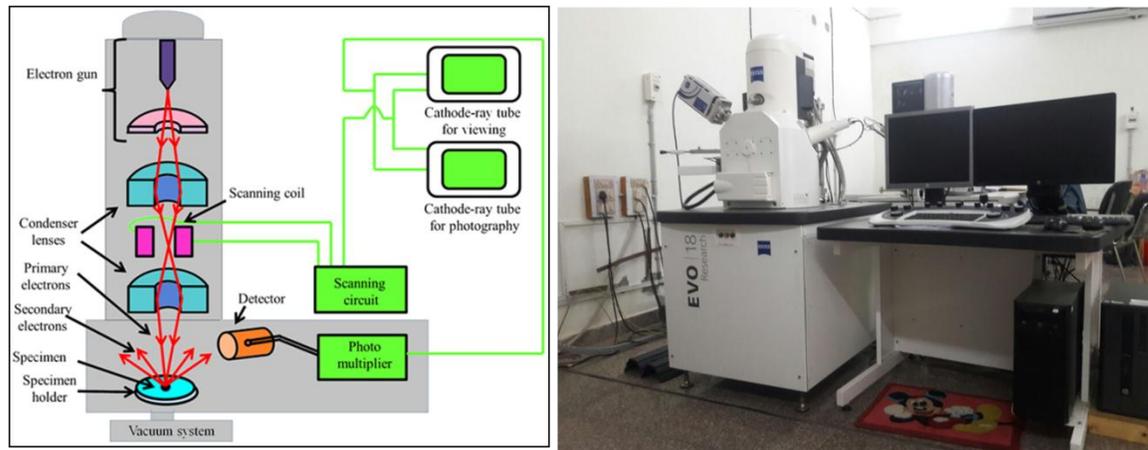
Based on the nature of the scattered electrons, we can classify the as obtained images from SEM in to two parts,

1. Secondary electron image

2. Backscattered electron image

1. Secondary electron image

These images are the most common imaging mode which monitors low energy (<50 eV) secondary electrons. Since the energy of these electrons is very low hence they originate within a few nanometers from the surface. Scintillator- photomultiplier device is used as an electron detector in SEM which renders the detected signal into a two-dimensional intensity distribution. These as obtained signals can be viewed and saved as a digital image. This process relies on a raster-scanning of the primary beam. The brightness of the signal depends on the intensity of electron i.e. number of secondary electrons reaching the detector. Let us consider for the condition when the incident direction of beam and the surface of sample is perpendicular to each other then the activated region is uniform about the axis of the beam and certain number of electrons “escape” from within the material. If we increase the angle of incidence, the ‘escape’ distance of one side of the beam will decrease; as a result more secondary electrons will be emitted from the sample. Thus steep surfaces and edges will be brighter than the flat surfaces, which results in images with a well-defined, three-dimensional appearance. By this technique, even 1 nm resolutions is possible.



(a)

(b)

Fig.2.8 (a) A simplified schematic diagram of a Scanning Electron Microscope, Adapted from (<http://nptel.ac.in/courses/102103044/18>). (b) Instrumental set up for the SEM instrument using for the characterization.

2. Backscattered Electron imaging

In contrast to the Secondary electron the energy of the backscattered electrons (BSE) are very high. When the electron beam is reflected or back-scattered out of the specimen interaction volume, backscattered electrons originates. Backscattered electrons are very useful in detecting contrast between areas with different chemical compositions. If the average atomic number of various regions is different, the backscattered electrons are very useful, as the brightness of the backscattered electrons image increases with the atomic number as a result backscattered electrons give rise to different contrast in the image. Backscattered electrons are also used in the formation of electron backscatter diffraction (EBSD) image. Such type of image is often used to determine the crystallographic structure of a material. The number of backscattered electrons leaving the sample surface upward might be significantly lower than those that follow trajectories toward the sides and hence the number of backscattered electrons emitted from a sample is less than the secondary electrons.

Moreover, we cannot significantly improve the collection efficiency of backscattered electrons by the use of a positive bias on the detectors. Due to the small acceptance angles, the detector positioned on one side of the sample has low collection efficiency for backscattered electrons. Using a “doughnut” type of arrangement for the sample and detector assembly, we can increase the solid angle for the collection of the backscattered electrons. In the “doughnut” type arrangement, the detector lie in a doughnut shape and the electron beam passes through the hole of the doughnut and hence it detects more number of backscattered electrons.

Energy-dispersive X- ray spectroscopy (EDX) and scanning Electron Microscopy (SEM) measurements have been done using ZEISS –EVO/18 Oxford instrument.

2.2.8 Atomic force microscopy

The Atomic force microscopy is one of the techniques which are used now days for measuring, imaging and manipulating matter at the nano scale order. In AFM, a sharp tip of a probe is used for the raster scanning of the surface which can generate an image of the surface topography with extremely high magnifications, comparable or even better than electronic microscopes.

Construction and Working in AFM

We generally measure the force between the sample and the probe which has a sharp tip composed of silicon or silicon nitride having nanometer size radius. Generally, the probe is attached to the free end of a cantilever and we brought the tip very close to a surface of specimen. For the image resolution in AFM, we normally measure the vertical and lateral deflections of the cantilever. There is attractive or repulsive Vander Waals force between the

tip and the sample surface hence bending of the cantilever phenomenon takes place, as a result hence there is deflection in the cantilever. Hooke's law is applicable for this bending in cantilever which spring constant is known. Basic concept of AFM has been shown in Fig. 2.9 (a). We generally measure the deflection using the laser spot detection from the top of the Cantilever in to an array of photodiodes. Moreover, the probe of atomic force microscopy is piezoresistive hence it may also used to determine the cantilever deflection. We normally plot a graph between the deflection of the cantilever versus its position on the sample and using this we obtain a topographic image of the specimen. The force between the specimen and tip depends on the properties of specimen and the distance between tip and specimen, which gives rise to the image contrast in AFM images.

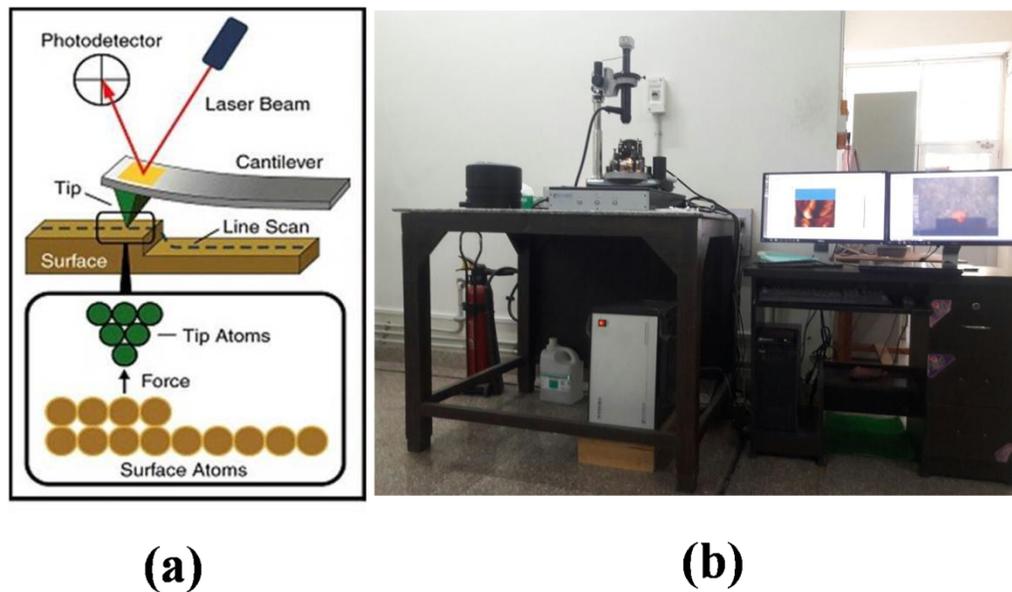


Fig. 2.9 (a) Principle of Atomic Force Microscopy (AFM) (b) instrumental set up of AFM used for characterization.

The interaction force between the tip and the sample is the important property of the atomic force microscope imaging which depends on the distance between tip to specimen. When tip and specimen are very nearer to each other the force will be repulsive, in contrast to

this if the separation between these two is large then the force will be attractive. Using this phenomenon we can use AFM in different mode of operation such as tapping mode, contact mode and non contact mode. The method which we want to use, among three of them, depends on the characteristics of the sample because each mode has their own different advantages. The beauty of Atomic force microscopy is that it can be applied to various environments (air, liquid, vacuum) and also for different types of materials such as soft biological samples, conductive and non-conductive materials, metals and semiconductors etc. Using AFM technique we can measure the size or even the manipulations of nano-objects may be performed. Microscope (AFM) experiment has been carried out in semi contact mode using NT-MDT (NTEGRA PRIMA) instrument.