2.1 Introduction

For the study and development of any material two things that is indispensable are the synthesis technique and the range of characterization techniques by the virtue of which the properties of synthesized material is studied. Various synthesis techniques for the preparation of materials are developed and employed depending upon the material and its application that is targeted. A right synthesis technique for a particular material with a appropriate characterization techniques leads to a successful establishment of that particular material. For a fruitful research in field of material science it is important that one should be familiar with various characterizations techniques available at our exposure.

2.2 Solid state synthesis technique

The most widely used method for the preparation of polycrystalline solids is solid state reaction wherein there is a direct reaction between the mixture of solid constituents. Solids do not usually react together at room temperature over normal time scales and it is necessary to heat them to much higher temperatures often 1000 to 1500°C or even more, in order for reaction to occur at an appreciable rate. This shows that both thermodynamic and kinetic factors are important in solid state reactions; thermodynamic considerations show whether or not a particular reaction should occur by considering the changes in free energy that are involved; kinetic factors determine the rate at which reaction occurs.

To understand the process involved in the solid state reactions, for simplicity, lets us consider a reaction between the two solid starting materials A and B to form the reaction product AB. Although, thermodynamic considerations permit the reaction between A and B to form AB, in practice the reaction rate may be extremely slow at the normal temperatures. It is
only above a certain higher temperatures say for example above 900 to 1000°C that the reactions begin to occur to any significant extent and for complete reaction of a powder mixture to occur it may be necessary to heat it for several days at for example 1500°C. To understand as to why there is a need of high temperature for the solid state reactions; consider the reaction between the two powder reactants A and B which are in intimate contact across one shared surface as shown in Fig. 2.1(a). After an appropriate heat treatment, the reactants partially react to form a layer of the product AₓBₙ at the interface as shown in the Fig. 2.1 (b). The first stage of reaction is the formation of AₓBₙ nuclei. This nucleation is rather difficult because of (a) the considerable differences in the structures between reactants and product and (b) the large amount of structural reorganization that is involved in forming the product: bonds must be broken and reformed, and atoms must migrate perhaps over considerable distance (on an atomic scale). The ions of the reactants are generally being trapped on their appropriate lattice sites and it is difficult for them to hop into empty, adjacent sites. Only at very high temperatures, such ions have sufficient energy to occasionally jump out of their normal lattice sites and diffuse through the new product layer. Although the formation of nucleation centers is a difficult process, the subsequent stages, involving growth of the product layer may be even more difficult. In order for further reaction and growth to take place the reactant A has to traverse through an ever growing thicker product layer to a new reactant product interface towards reactant B and vice versa.
Hence since the diffusion rates are slow, even at high temperatures further reaction takes place only slowly and at a decreasing rates as the product layer grows thicker.

The above discussion shows that there are three important factors that influence the rate of reaction between solids.

(i) The area of contact between the reacting solids and hence their surface areas.

(ii) The rate of nucleation of the product phase and

(iii) The rates of diffusion of ions through the various phases and especially through the product phase.

Hence in order to have an efficient reaction it is necessary to consider all these three facts and try to maximize all of these in order to reduce the time taken for the solids to react together.

In the present work the MgB$_2$ samples were synthesized in the bulk form. This was achieved with the solid state reaction technique. As discussed the solid state reaction technique operates by a mechanism which includes

---

Fig. 2.1: Schematics of reactant A and B (a) in the intimate contact at one shared surface and (b) partially reacted forming a new layer with two reaction interfaces.
the solid state interdiffusion and chemical reaction where the two solid state reactants interdiffuse at the points of powder particle contact. Once the ionic reactants are in close association with each other chemical reactions can readily take place. Hence to achieve an intimate contact between the reactants Mg and B the powders were taken in agate mortar and homogenized continuously and vigorously for about not less than 3 hrs. The samples were further heat treated at about 900°C to get better phase formation. The obtained samples were characterized by various characterization techniques.

2.3 Characterization techniques

In broad sense, the characterization of materials can be classified in to several major headings like phase (compositional and structural), physical and chemical properties. The characterization of physical properties of material is mostly pertaining to electrical, magnetic, dielectric and optical properties. However, prior to any study of a solid state material, main emphasis must be paid on the phase and structural characterizations along with morphological and topographical characterizations.

2.3.1 X-ray diffraction technique (XRD)

X-ray diffraction technique is a very powerful and suitable technique for characterizing mainly the structure of the samples synthesized. It is a non-destructive, non-contact method that provides useful information, such as presence and composition of phases, grain size, preferred orientations in the test sample and strain generated in the structure. The basic principles of x-ray diffraction are found in reference books by Buerger [1], Klug and Alexander [2], Cullity [3], Tayler [4], Guinier [5], Barrett and Massalski [6].
The simple and schematic representation of x-ray diffractometer is as shown in Fig 2.2. This technique mainly depends on the diffraction of x-ray radiation which in general occurs only when the wavelength of the wave motion is of the same order of magnitude as the repeat distance between scattering centers. This condition of diffraction is known as Bragg’s law and is represented by equation (2.1)

\[ 2d \sin \theta = n\lambda \]  

(2.1)

where,
- \( d \) = interplaner spacing
- \( \theta \) = diffraction angle
- \( \lambda \) = wavelength of x-ray
- \( n \) = order of diffraction

Fig. 2.2: Schematic representation of x-ray diffractometer.
In crystalline solids atoms are ordered in a particular repeated pattern referred as unit cell with its interatomic spacing comparable to wavelength of x-rays (0.5 to 2.5Å). Hence crystals are the best gratings for the diffraction of x-rays. The directions of diffracted x-rays give information about the atomic arrangements and hence the crystal structure and phase formation can be confirmed by x-ray diffraction studies.

The way of satisfying Bragg’s condition is devised and this can be done by continuously varying either \( \lambda \) or \( \theta \) during the experiment. The way, in which these quantities are varied, distinguish the three main diffraction methods and tabulated in table 2.1.

<table>
<thead>
<tr>
<th>Method</th>
<th>( \lambda )</th>
<th>( \theta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laue Method</td>
<td>Variable</td>
<td>Fixed</td>
</tr>
<tr>
<td>Rotating crystal</td>
<td>Fixed</td>
<td>Variable (in part)</td>
</tr>
<tr>
<td>Method</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Powder Method</td>
<td>Fixed</td>
<td>Variable</td>
</tr>
</tbody>
</table>

In powder method the crystal to be examined is reduced to a fine powder and placed in a beam of a monochromatic x-rays. Each particle of the powder is the tiny crystal, or assemblage of smaller crystals, oriented at random with respect to incident beam. Some of the crystals will be correctly oriented so that their (100) planes, for example, can reflect the incident beam. Other crystals will be correctly oriented for (110) reflections and so on. The result is that every set of lattice planes will be capable of reflection. This is the principle of a powder diffractometer.

Ideally, according to Bragg’s law, for the particular \( d \) value, the constructive interference of x-rays should occur only at particular \( \theta \) value i.e
Bragg’s angle and for all other angles there should be destructive interference and intensity of diffracted beam will be minimum there.

**Identification of phases**

From the d-spacing, phases can be identified in a sample using the standard JCPDS powder diffraction file and the reflections can be indexed with Miller indices.

However, if the size of the diffracting tiny crystal is small, there is no more complete destructive interference at $\theta \pm d\theta$, which broadens the peak corresponding to diffracted beam in proportion to the size of the tiny crystal. This can be used to calculate the particle size. The relation for the same is given by Debye Scherrer and formulated [3] as,

$$t = \frac{0.9\lambda}{\beta \cos \theta_B}$$

where, $t =$ particle size, $\theta_B =$ diffraction angle, $\lambda =$ wavelength of x-rays and $\beta$ line broadening at Full Width at Half Maxima (FWHM).

Further, the powder diffractometer can also be used for x-ray diffraction from thin films. Epitaxial or polycrystalline (may or may not be oriented) thin films can be considered as single crystal or powder (crystals or assembly of crystals spread on substrate) respectively. Hence, a typical epitaxial or oriented film may not show all corresponding reflections and show only few reflections for example say, a c-axis oriented film will show only (hkl) for which h and k indices are zero and l is non zero. However, these hidden peaks can be detected by small angle x-ray diffraction technique.
Instrument specifications

Model: PW 3710/ PW1710 PHILIPS, Holland
Angle (2θ): 10° to 100°
Target: Cu.
Normal mode: PW3710/PW 1710 APD Controller.
Specimen: Fine Powder (quantity approximately 1 cm³)
Applications: Crystallographic studies, Quantitative analysis of organic, Inorganic minerals, metals and alloys.

2.3.2 Scanning electron microscopy (SEM)

Interaction of electrons with elements is well understood and has been extensively used for characterizing the materials. As the electrons can be focused to micron or sub-micron size, it is well suited for analyzing sub-micron sized areas or features. When an electron strikes the atom, variety of interaction products are evolved. Fig. 2.3(a) illustrates these various products and their use to obtain the various kinds of information about the sample. Scattering of electron from the electrons of the atom results into production of backscattered electrons and secondary electrons. Electron may get transmitted through the sample if it is thin. Primary electrons with sufficient energy may knock out the electron from the inner shells of atom and the excited atom may relax with the liberation of Auger electrons or x-ray photons. All these interactions carry information about the sample. Scanning electron microscope is an instrument that uses electron beams to observe the morphology of a sample at higher magnification, higher resolution and depth of focus. Of these, backscattered electrons, secondary electrons and transmitted electrons give information about the microstructure of the sample. Auger electron, ejected electrons and x-rays are energies specific to
the element from which they are evolved. These characteristic signals give information about the chemical identification and composition of the sample.

**Fig. 2.3(a):** Different interaction products evolved due to interaction of electron beam and sample.

**Principle of scanning electron microscope**

A well-focused mono-energetic (~25KeV) beam is incident on a solid surface giving various signals as mentioned above. Backscattered electrons and secondary electrons are particularly pertinent for SEM application, their intensity being dependent on the atomic number of the host atoms. Each may
be collected, amplified and utilized to control the brightness of the spot on a cathode ray tube. To obtain signals from an area, the electron beam is scanned over the specimen surface by two pairs of electro-magnetic deflection coils and so is the C.R.T. beam in synchronization with this. The signals are transferred from point to point and signal map of the scanned area is displayed on a long persistent phosphor C.R.T. screen. Change in brightness represents change of a particular property within the scanned area of the specimen [7]. The ray diagram of scanning electron microscope is shown in Fig. 2.3(b). Interaction of energetic electron beam with solid surface leads to several signals like elastically scattered electrons (i.e. change of direction without change of energy) from the Coulomb field of the nucleus whereas some others includes inelastically scattered electrons (with change of energy) from the electrons of the host atoms giving rise secondary electrons, Auger electrons and x-rays characteristics to host lattice. The secondary electrons (signal from approximately top 100 Å) are used to get contrast from surface morphology.

The scattering cross section for back-scattered electrons is given as [8],

$$Q = 16.2 \times 10^{-30} \left( \frac{Z}{E} \right)^2 \cot \left( \frac{\phi}{2} \right) \quad \text{..........................(2.3)}$$

where, $Z$ is atomic number and $E$ is electric field.

Here the cross-section is proportional to $Z^2$. Hence, the back-scattered electrons are used for the $Z$ contrast or for compositional mapping.
2.3.3 Energy dispersive x-ray analysis (EDAX)

The interactions of electron with solid as mentioned above leads to different signals like secondary electrons, backscattered electrons and x-rays which are characteristic to atoms of host lattice. These x-rays can be used for
element detection and its quantification for compositional analysis. Two techniques are used for analyzing x-ray spectrum.

1. Wavelength dispersive x-ray analysis (WDAX) or (WDS)
2. Energy dispersive x-ray analysis (EDAX) or EDS

These techniques deals with diffraction of x-rays under analysis and can be termed as wavelength (or energy) dispersive spectroscopy also.

(a) *Wavelength dispersive x-ray Analysis (WDAX) or (WDS)*

The characteristics x-ray are identified by their wavelengths by diffracting them on a crystal monochromator of known ‘d’ spacing and following Bragg’s law \( n\lambda = 2d \sin\theta \). In fully focusing spectrometer sample, crystal and detector all lies on the same circle called as Rowland circle such that Brag’s law satisfied in all cases. The crystal moves on a linear path in order to maintain constant take off angle. The centre of Rowland circle moves on arc with x-ray source as centre.

(b) *Energy dispersive x-ray analysis (EDAX) or (EDS)*

Here, the characteristics x-rays are identified by their energy using solid state detectors. It consists of semiconductor Si(Li) counter and FET preamplifier, both cooled by liquid nitrogen and multichannel analyzer (MCA). The utility of this kind of spectrometer is based on two properties

1. The excellent energy resolution of Si(Li) counter.
2. The ability of MCA to perform rapid pulse height analysis.

Semiconductor counter produces pulses proportional to the absorbed energy with better energy resolution than any other counter. The silicon and germanium are the best detector for x-rays and \( \gamma \)-rays respectively. The pure silicon in intrinsic semiconductor has very high electrical resistivity especially at low temperatures [9]. Hence, only few electrons are thermally
excited across the energy gap into conduction band. However, incident x-ray can cause excitation and thereby create a free electron in the conduction band and free hole in the valance band. If high voltage is maintained across opposite faces of the silicon crystal, the electrons and holes will be swept to these faces, creating small pulse in the external circuit. The schematic diagram of EDS detector is shown in Fig. 2.4.

![Schematic diagram of EDS detector in EDAX.](image)

**Fig.2.4:** Schematic of working of Si(Li) detector in EDAX.

It is very difficult to get pure silicon. Hence a p-type Si, lightly doped with boron, were used and to make it intrinsic this is again doped with Li. Typically the resolution of Si(Li) detector is given as 147 eV for manganese Ka radiation of 5.9 KeV energy. The energy dispersive system can analyze whole x-ray spectrum simultaneously. Due to low ionization potential of Si(Li) the count rate is very high (>10,000 c/s/nA) and hence very low current is required. It is used in conjunction with SEM, TEM where current used is very low (of the order of pA)

### 2.3.4 Thermal analysis

Thermal analysis includes a group of techniques in which a physical and chemical property of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature
program in different gas environments. Modern thermal analysis instrument measures phase transitions temperature, weight losses in materials, energies of transitions, dimensional changes, modulus and viscoelastic properties. Current applications include environmental measurements, product reliability, compositional analysis, stability, chemical reactions and dynamic properties.

**Differential thermal analysis (DTA)**

In DTA, the temperature of a sample and a thermally inert reference material are measured as a function of temperature (usually sample temperature). Any phase transition which the sample undergoes will result in liberation or absorption of energy by the sample with a corresponding deviation of its temperature from that of the reference. This differential temperature ($\Delta T$) versus the programmed temperature ($T$) at which the whole system is being changed yield the temperature of transitions and the nature of the transition such as exothermic or endothermic.

**Thermogravimetric analysis (TGA):**

It provides a quantitative measurement of any weight change associated with a transition. Thermogravimetry can directly record the loss or gain in weight with time or temperature due to oxide phase formation, dehydration or decomposition. Thermogravimetric curves are characteristic for a given compound or systems because of the unique sequence of physiochemical reactions, which occur over definite temperature ranges and at rates that are function of the molecular structures. Changes in weight are due to rupture or formation of various physical and chemical bonds at elevated temperatures that lead to the evolution of volatile products or the formation of heavier reaction products. From such curves data are obtained concerning the thermodynamics and kinetics of the various chemical
reactions, reaction mechanism and the intermediate and final reaction products. The usual temperature range is from ambient to 1200°C with inert or reactive atmospheres. All weight-change processes adsorb or release energy and are thus measurable by DTA or DSC, but not all energy-change processes are accompanied by changes in weight. This difference in the two techniques enables a clear distinction to be made between physical and chemical changes when the samples are subjected to both DTA and TGA tests. In general, each substance will give a DSC or DTA curve whose shape, number and position of the various endothermic and exothermic features serve as a means of qualitative and quantitative identification of the substance. When an endothermic change occurs the sample temperature lags behind the reference temperature because of the heat in the sample. The initiation point for a phase change or chemical reaction is the point at which the curve first deviates from the base line. When the transition is complete thermal diffusion brings the sample back to equilibrium quickly. The peak (or minimum) temperature indicates the temperature at which the reaction is completed. Endotherms generally represent physical rather than chemical changes. Sharp endotherms are indicative of crystalline rearrangements, fusion, or solid-state transition for relatively pure materials. Broader endotherms cover behavior ranging from dehydration, temperature-dependent phase behaviors to melting of polymers. Exothermic behavior (without decomposition) is associated with the decrease in enthalpy of a phase or chemical system. Narrow exotherms usually indicate crystallization (ordering) of a metastable system, whether it is supercooled organic, inorganic, amorphous polymer or liquid, or annealing of stored energy resulting from mechanical stress. Broad exotherms denote chemical reactions, polymerization or curing of thermosetting resins. Exotherms with decomposition can be either narrow or broad depending on kinetics of the behaviour. The area of exotherms or
endotherms can be used to calculate the heat of the reaction or the heat of a phase formation.

**Specifications:** It is SDT-2960 from TA Instruments, USA. It is capable of performing both differential Scanning Calorimeter (DSC) and Thermo Gravimetric Analysis (TGA) at the same time. Differential Thermal Analysis (DTA) can also be carried out using SDT 2960. It measures the heat flow and weight changes associated with transitions and reactions in material over the temperature range from RT to 1500°C. These experiments can be carried out in either of the optional environment like N₂, O₂, Ar or air at pre decided flow-rate (ml/min) and heating rate (°C/min). The gas switching accessory is used to turn on and off or to switch between two different purge gases during SDT experiment. Heat-flow accuracy is equal to 1% where as DTA sensitivity is 0.001°C and that of weight is 0.1μgm. This SDT- 2960 controller is connected to PC and the special software makes the thermal analysis. It stores the data as well as runs the analysis programs [10].

**Applications:** Melting point, crystallization behaviour, glass transition temperature, thermal stability, dehydration, oxidation, phase-transition, specific heat, reaction kinetics etc can be determined.

### 2.3.5 Microwave analysis

The interaction between microwave and superconductors has not only led to understanding of many fundamental properties of superconductors but also helped in formulating both passive and active microwave devices. The fabrication of high performance RF and microwave devices with superconductors has forecasted the possibility of economical and viable devices especially in power, communication, biomedical and pharmaceutical applications (MRI and NMR) in 21st century. The MgB₂ superconductor with
two energy gaps (Δ~2 meV due to \( \pi \) bonding electrons and ~ 6 meV due to \( \sigma \) bonding electrons) has important application in microwave electronic devices such as mixers with quasiparticle SIS Josephson junctions for heterodyne microwave detection. Maximum theoretical operation frequency for the mixer is \( f_{\text{max}} = 2\Delta/\hbar \). For Nb based superconductor the \( \Delta \sim 1.5 \) meV offers the possible \( f_{\text{max}} \sim 700 \) GHz. However, the MgB\(_2\) superconductor even with its smaller (amongst the two) energy gap (~2meV) can yield \( f_{\text{max}} \sim 1.4 \) THz, which is not achievable with GaAs based gunn diode or Nb based superconductor. However the microwave measurements can also be used to characterize the samples at its different stages of the growth.

2.3.5.1 Theoretical background

The insight of interaction between high frequency fields and superconductor is given by the surface impedance. The surface impedance is defined as, the characteristic impedance seen by a plane wave incident perpendicularly upon a flat surface of the conductor.

\[
Z_s = \frac{E}{H} = R_s + j X_s \quad \quad \text{............... (2.4)}
\]

Where,
- \( R_s \) \( \Rightarrow \) The surface resistance.
- \( X_s \) \( \Rightarrow \) The surface reactance.
- \( E \) \( \Rightarrow \) The electric field tangent to the conductor surface.
- \( H \) \( \Rightarrow \) The magnetic field tangent to the conductor surface.

Surface impedance being a complex quantity, the real part i.e. the surface resistance \( R_s \) characterizes the dissipated microwave power per unit surface area,

\[
\frac{\partial P}{\partial A} = \frac{1}{2} R_s H_s^2 \quad \quad \text{...............(2.5)}
\]
with \( H_s \) the microwave magnetic surface field.

The surface impedance studies yield the information on transport mechanism of superconductors. Surface resistance determines the quality of the superconductor used for the fabrication of microwave devices and circuits. The imaginary part of \( Z_s \) i.e.

\[
X_s = \omega \mu_0 \lambda
\]

describes the non-dissipative energy exchange between the microwave field and the superconductor sample within the penetration depth \( \lambda \). Surface reactance is directly related to microwave penetration depth and its behavior with temperature has importance in exploring the nature of superconducting states in superconductor.

The surface impedance of normal conductors such as Silver, Copper, Gold with a conductivity of \( \sigma \), can be derived from Maxwell’s equations as,

\[
Z_s = R_s + j X_s = \sqrt{\frac{j \omega \mu_0}{\sigma}} = (1 + j) \sqrt{\frac{\omega \mu_0}{2\sigma}} \]

where, \( \omega = 2\pi f \) is the angular frequency.

For the normal conductor, the conductivity \( \sigma \) is a real number and accordingly the surface resistance and surface reactance are equal.

\[
R_s = X_s = \left[ \frac{\omega \mu_0}{\sigma} \right]^{1/2}
\]

However, in case of superconductor, the general query arises is about the conductivity \( \sigma \). In superconductors, conductivity \( \sigma \) can be obtained by considering the contributions of both the superconducting carriers and the normal carriers.

\[
\sigma = \sigma_r - \varphi \sigma_i
\]
Where, $\sigma_r$ is the real component of conductivity and represents the loss from normal carriers and $\sigma_i$ is the imaginary component of conductivity and represents the kinetic energy of superconducting carriers.

The real part of complex conductivity $\sigma_r(T)$ is due to normal electrons resulting from the excitation from the ground state, as such it is affected by the scattering rate and density of normal electrons. The imaginary part of conductivity depends on the number of supercarrier density $n_s(T)$, which is clear from equation (2.10) below.

$$\sigma_i = \frac{1}{\omega \mu_0 \lambda^2} \quad \text{and} \quad \lambda = \sqrt{\left[ m_s / (\mu_0 q_s n_s) \right]} \quad \text{.................(2.10)}$$

Where $m_s$ is the mass and $q_s$ is the charge of supercarrier.

Assuming that the conductor current is much larger than any displacement current measured at frequency $\omega$, the surface impedance is given by,

$$Z_s = \sqrt{\frac{j \omega \mu_0}{\sigma_i}} - \sigma_i \quad \text{...............(2.11)}$$

In the limit, when $\sigma_r << \sigma_i$ typically at low temperatures compared to $T_c$ and $\hbar \omega << k_B T_c$ with the surface impedance will become

$$Z_s = \left[ \frac{\omega \mu_0}{\sigma_i} \right] \left[ \frac{\sigma_r}{2 \sigma_i} + j \right] \quad \text{...............(2.12)}$$

which can be split into real and imaginary parts giving $R_s$ and $X_s$ as,

$$R_s = \left( \frac{\sigma_r}{2 \sigma_i} \right) \left[ \frac{\omega \mu_0}{\sigma_i} \right] \quad \text{...............(2.13)}$$

$$X_s = \left[ \frac{\omega \mu_0}{\sigma_i} \right] \quad \text{...............(2.14)}$$

Considering $\sigma_r << \sigma_i$ for superconductors and $\sigma_r >> \omega \mu_0$ which is valid in all practical cases the values of $R_s$ and $X_s$ can be expressed as

$$R_s = \frac{1}{2} \omega^2 \mu_0^2 \lambda^3 \sigma_r \quad \text{and} \quad X_s = \omega \mu_0 \lambda \quad \text{...............(2.15)}$$
2.3.5.2 Surface resistance measurements

The resonant techniques are the most widely used techniques for the surface resistance measurements. The technique employs the use of some form of resonating structure of which sample is either part and contributes to conduction loss or placed inside the resonating structure perturbing the electromagnetic field and thus producing additional losses. At resonance, the impedance of a resonator is real and resistive. The $R_s$ of the sample can be extracted from the measured quality factor (often called unloaded Q value) of the resonator. The quality factor of a resonating structure is defined as the ratio of the time average stored energy inside the resonator to the energy loss per second.[11]

$$Q_o = \frac{\text{time average stored energy}}{\text{energy loss per second}} = \frac{\omega_o}{\Delta \omega} \quad \text{.........(2.16)}$$

where $\omega_o$ is the resonant frequency and $\Delta \omega$ is the resonator half power bandwidth as illustrated in the Fig. 2.5

![Diagram of Resonator 3dB power bandwidth and Q](image)

**Fig.2.5:** Resonator 3dB power bandwidth and Q

The unloaded quality factor $Q_o$ depends on the loss which sidelines other losses. All types of losses such as dielectric loss, radiation loss and conductive loss contribute to the power dissipation in the cavity. We are
concerned with the determination of surface resistance of sample from measured $Q_0$. So for efficient and sensitive measurement, the design of resonator should be such that the conductive loss due to the sample dominates all other losses in the resonator. This can be nearly achieved by properly designing the resonating structure.

The surface resistance of the conducting material provides a very precise test of their quality. The surface resistance measurement provides results, which is averaged over entire surface of sample. It is affected by any impurities and defect inclusions that may get introduced in the sample surface at the time of processing.

### 2.3.5.3 The $Q$-measurement

In a resonator, coupled to an external circuit, additional power losses out of the coupling ports occur. A quality factor attributed to this is termed as external quality factor $Q_e$. The combination of external $Q$, $Q_e$ and the unloaded $Q$, $Q_0$ gives rise to the loaded quality factor $Q_l$.

\[
\frac{1}{Q_l} = \frac{1}{Q_e} + \frac{1}{Q_0} \quad \text{..........................}(2.17)
\]

At resonance $Q_l$ measured by simply taking the ratio of resonant frequency $f_0$ to the 3-dB bandwidth $\Delta f$ as shown in Fig. 2.6.
\[ Q = \frac{f_0}{\Delta f} \quad \ldots \ldots \ldots \ldots \ldots (2.18) \]

For symmetrically coupled resonator

\[ Q_e = \frac{Q_l}{10^{-(IL/20)}} \quad \ldots \ldots \ldots \ldots \ldots (2.19) \]

Where \( 10^{-(IL/20)} \) is the \( S_{21} \) parameter, \( IL \) is the measured insertion loss in dB.

Combining equation (2.17) and (2.19) will give the unloaded \( Q \) values \( Q_0 \) of the resonator as [12]

\[ Q_0 = Q_l [1-10^{-(IL/20)}]^{-1} \quad \ldots \ldots \ldots \ldots \ldots (2.20) \]

Thus the unloaded quality factor \( Q_0 \) can be determined from the measured insertion loss and loaded \( Q \)-value.

The quality factor \( Q_0 \) and \( \Delta f \) the 3dB frequency difference is related to surface resistance by the following relations.

\[ R_s = G \left( \frac{1}{Q_0} \right) \quad \text{and} \quad X_s = -2G \left( \frac{\Delta f}{f_0} \right) \quad \ldots \ldots \ldots \ldots \ldots (2.21) \]

Where \( Q_0 \) is the quality factor, \( f_0 \) is the frequency of the resonant mode, \( \Delta f \) is the resonator 3 dB-power bandwidth and \( G \) is a quantity, which depends on the mode and the geometry of the resonator.
2.3.5.4 Scattering parameter (S-parameter)

The S-parameter describes the relative strengths of reflected and transmitted signals at each port. Or it is a measure of microwave loss or absorbance.

For a device under test (DUT) as shown in Fig.2.7, the different $S_{ij}$ parameters are defined as follows,

Where, i and j stands for measured amplitude and incident amplitudes of signals at a point.

- $S_{11} = \text{Forward Reflection coefficient (Input Match)}$
- $S_{22} = \text{Reverse Reflection coefficient (Output Match)}$
- $S_{21} = \text{Forward Transmission coefficient (Gain or loss)}$
- $S_{12} = \text{Reverse Transmission coefficient (Isolation)}$

![Fig.2.7: Device under test (DUT) used for measurement of S parameter.](image)

2.3.6 Resistivity measurement technique

The most widely used method for measuring electrical resistivity in $10^{-3}$ to $10^3$ ohm-cm range is a colliner four probe method with equal separation between the probes. If I is the current passing between the outer probes and V is the potential drop between the inner probes with a probes spacing 's', then resistivity ($\rho$) for the specimen of infinite volume is given by [13]

$$\rho = 2\pi s \frac{V}{I} \tag{2.22}$$

If specimen dimensions are comparable to the probe spacing, then the resistivity for various geometries and different types of boundaries is given by,
\[ \rho = 2\pi \frac{V}{I} f\left(\frac{V}{s}\right) \] ..........................(2.23)

A useful simplification of collinear four-probe relation obtained for a thin specimen (t<<s/2)

\[ \rho = 4.53 \frac{V}{I} \times t \] ..........................(2.24)

which is clear and convenient relation to use. Furthermore,

\[ \frac{\rho}{t} = 4.53 \frac{V}{I} \] ..........................(2.25)

gives the resistivity of the sample. The contacts between probe and samples can be made by air-drying silver paste. A commonly used probe spacing is s = 0.159 cm which makes the \(2\pi s\) factor unity in equation (2.23). The temperature dependence of resistivity measurement of the sample was performed using a conventional four-probe method. A photograph of the low temperature resistivity measurement setup and block diagram of close cycle cryogenic system is shown in Fig. 2.8 and 2.9 respectively.

Fig. 2.8: Photograph of the low temperature resistivity measurement setup.
Fig. 2.9: Block diagram of close cycle cryogenic refrigerator.

Fig. 2.10: Schematic diagram of the four probe collinear contacts drawn on MgB$_2$ sample.

The sample was fixed on a PCB and four collinear contacts were made by air drying silver paste and mounted on a cold head of close cycle cryogenic...
refrigerator (CCR). The schematic of sample fixed on PCB and contacts drawn is as shown in Fig. 2.10.

**Experimental set up for resistivity measurement**

Experimental set up for resistivity measurement consists of

(a) Constant current source  
(b) High precession multi-meter/nanovoltmeter  
(c) Temperature sensor and controller unit  
(d) Compressor  
(e) Gas lines and  
(f) Expander

**(a) Constant current source**

Keithly 224 programmable current source (0.001 mA to 200 mA) was used as constant current source interfaced with the computer through the GPIB cables and IEEE interface in connection with the Keithly -2001 multimeter.

**(b) High precession multi-meter**

Keithly-2001 multi-meter was used to measure the voltage drop between two contacts. This was also interfaced to the computer through the GPIB cables and IEEE interface in connection with constant current source.

**(c) Temperature sensor and controller unit**

The series 9600-1 microprocessor based digital Temperature Indicator/Controller have been used to measure and control the process temperature via a calibrated silicon diode temperature sensor. Silicon diode scientific instruments, Inc. Model Si-400 capable of sensing the temperature in the range of 1.5 to 450 K is used as a temperature sensor with resolution
0.1 K. Electrical resistivity measurements were carried out using automatic data recording with software developed in visual basic.

(d) Compressor

The HC-2D compressor is a single stage cooled rotary compressor designed to deliver high-pressure oil free helium gas to cryogenic refrigerator. Self-sealing coupling allow easy connections and disconnections from rest of closed cycle.

(e) Gas line

Each cryogenic system includes interconnecting gas lines to carry helium gas refrigerant to and from the components. The gas line carries high pressure helium gas from the compressor to the expander and another gas line returns low pressure gas to the compressor.

(f) Expander

The expander is two-stage refrigerator operating on Gifford McMohan refrigeration cycle. The high-pressure gas drives the reciprocating displacer assembly with the cylinder and gas expands in two stages. At the second stage, cold head is provided from which connections for four probe resistivity were taken out.

2.3.7 DC magnetization by superconducting quantum interference device (SQUID)

DC magnetization measurement was performed using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design Inc. Model MPMS). A schematic diagram of the magnetometer is shown in Fig. 2.11. The system consists of a superconducting magnet, a sample holder along with sample transport mechanism, pick-up loop arrangement and rf SQUID sensor. The magnetic field is provided by a superconducting solenoid. The pick up coils are made of
superconducting wire wound in a second derivative configuration in which the two turn of center coil are wound in opposite direction to the upper and the lower single turns. In this configuration, as the sample is moved, the second derivative of the field produced by the magnetic moment (of the sample) is coupled to rf SQUID sensor, reducing interference from nearby magnetic sources. The sample is mounted on a fiber using low temperature varnish and lowered into the magnetometer using the sample insert. The measurement technique can be described as follows. Initially the sample is placed far below or above the detection coil (but within the range of uniform field from magnet). For the magnetization measurement the sample is moved through the pickup coil. The movement of the sample in the pick-up-coil results in a change in the magnetic flux linked to the pickup coil arrangement. The consequent signal is exactly compensated and the resulting “null” status is confirmed using flux locked loop mode with the help of the SQUID sensor, which is placed (in nearly zero field region) away from the superconducting solenoid. For a typical measurement the sample is moved a small distance at a time (typically 1.25mm) and an overall traversal of ~ 4/6 cm through the pickup coil, and the SQUID output at each step is acquired by a PC (personal computer). This data is used to determine the magnetization of the sample by a least square fit.

This technique is used for the measurement of transition temperature, the magnetization of a superconducting sample, the superconducting volume fraction and critical current density. In case of a superconducting sample, the difference between the magnetization values measured when the sample is cooled in zero field (zero field cooled: ZFC) and applied field (field cooled: FC) gives an idea about the vortex state. The critical current density can be calculated from the difference of magnetization during increasing field and decreasing field of the hysteresis loop [14].
2.3.8 Vibrating sample magnetometer (VSM)

This technique was first developed by Foner in late 1950's. It is a basic research tool for determining the magnetic properties in a variety of studies of the structure of paramagnetic, ferromagnetic, antiferromagnetic, and diamagnetic materials. It is ideal for superconductivity measurements (Meissner effect, diamagnetic shielding and critical field determination) and for the study of magnetic properties of thin film or single crystals. Basically it is an induction technique. In this technique sample is mounted on the end of a rigid rod attached to a mechanical resonator which oscillates the sample (usually in a vertical direction) at a fixed frequency. Surrounding the sample is a set of sensing coils. As the sample moves, its magnetization, M, alters the magnetic flux through the coils. In other words if any material is placed in a uniform magnetic field, a dipole moment will be induced in the sample proportional to the product of the sample susceptibility and the applied field.
If the sample is made to undergo sinusoidal motion, the resulting magnetic flux changes near the sample and will induce an electrical signal (I) in suitably placed stationary coils. This signal will be proportional to the moment, amplitude and frequency of vibration. This produces an AC voltage directly proportional to \( M \), which can be amplified and detected using a lock-in-amplifier. The external magnetizing field is usually provided by a horizontal electromagnet. The design of VSM ensures that the vibration of the sample produces no vibration of the sensing coils relative to the magnet; otherwise it will cause large spurious signals. This problem is reduced if the magnet’s field is very homogeneous and for this reason only, large

**Fig. 2.12:** Block diagram of vibrating sample magnetometer
electromagnet with large pole pieces are used. VSM can measure permanent moments and hysteresis curves of ferromagnetic materials and strongly paramagnetic salts. However, their moment sensitivity (typically $10^{-4}$ emu of moment with a 1 second time constant) is not really adequate for weakly magnetic systems or very small samples.
References