Chapter 2

r.f. INSTRUMENTATION, MEASUREMENT TECHNIQUES AND SAMPLE PREPARATION

2.1 Introduction

The high frequency measurement techniques as that of magnetic susceptibility have an advantage of being able to detect superconductivity in samples which are discontinuous. Such studies are of particular importance because electromagnetic probes are sensitive only to the electronic state while other conventional probes like specific heat, ultrasonic attenuation etc. are strongly influenced by the phonon system, which is heavily populated at the high temperatures involved in HTSCs. Several techniques have been developed at microwave frequencies to study the surface impedance \( Z_s = R_s + X_s \). Continuous wave (CW) electron paramagnetic resonance (EPR) and to a much lesser extent nuclear magnetic resonance (NMR) spectrometers are used for studying high frequency absorption. While EPR and NMR are resonant techniques the present work is on the nonresonant high frequency studies. In the cavity perturbation technique (described in the following) from the microwave power reflected by the cavity, surface resistance is determined by many groups [1-7]. To determine the microwave surface resistance in thin films microstrip resonators are developed and are effectively used by many groups [8,9].

Contrary to the vast amount of literature available on power absorption at mi-
Fig. 1 Circuit of the marginal oscillator used for the radio frequency study.
crowave frequencies there have been very few reports on similar studies at radio frequencies. Stephen Ducharme et al. [10] studied the non-resonant absorption at radio frequencies by using the modulated detection method by employing a Varian model crossed coil NMR spectrometer. Omary et al. [11] and Sridhar et al. [12] have employed a tunnel diode oscillator using which they studied field and temperature dependence of penetration depth and surface resistance. In the present work we have made use of a marginal oscillator to investigate radio frequency impedance at MHz. Magnetically modulated radio frequency absorption (MMRA) technique is developed in analogy with MMMA technique at microwave frequencies. To study the microwave response cavity perturbation technique is used. The details of these techniques are given below.

2.2 Circuit Details of the Marginal Oscillator and rf Measurement Techniques

For the present work we have built a marginal oscillator [13] whose circuit diagram is shown in the Fig. 1. The present circuit is different from that of the marginal oscillators [14-17] which are of Colpitts type and has two controls for feedback and emitter current, while the other circuits have only one or no control. The use of two controls not only gives rise to stable signal but also makes the circuit suitable for studying radio frequency absorption, penetration depth etc. of different kinds samples. Since a FET amplifier in common drain configuration has high input impedance and low output impedance [11], the output of the oscillator is fed to it in the common drain configuration to decouple the possible interdependence of power output and frequency of oscillations, and to improve stability. Because direct tapping of the signal, for
the measurement of the frequency shift, from any part of the oscillator affects the
performance of the oscillator, an additional pick up coil wound on the primary tank
coil is used to monitor the frequency shift without disturbing oscillations.

Coil selection for sensitive power and frequency measurements.

We have tested different coils with different no. of turns and gauges for frequency
and power absorption measurements and found the following. The observations are
made for coil A (35 turns, 18 SWG), coil B (20 turns, 18 SWG), coil C (35 turns, 16 SWG),
coil D (30 turns, 18 SWG). Coil A resulted in less frequency change than
that of coil B when the sample is warmed through transition. Coil A and Coil C re-
sulted in approximately same power and frequency changes through transition. Coil
B resulted in less power change and almost equal frequency change when compared
to coil D, which has more no. of turns than coil B. And hence for sensitive power and
frequency measurements different coils have to be used. To counter the problem and
for other reasons discussed below we have made a multi-purpose coil.

The sustenance of oscillations is decided by capacitor C1 and C2 in the feedback
circuit. Once C1 and C2 are tuned to marginal conditions the working of the oscillator
wholly depends on the tank coil and the sample inside it. We used samples of various
dimensions and densities. The loading and power in the coil depend on the sample
material, dimensions and density. When the loss is more than the power delivered by
the coil, oscillations seize. It is not practical to open the oscillator circuit and tune C1
and C2 for sustained oscillations for any particular sample. Therefore, we have made a variable pitch coil, shown in Fig. 2b. Such a coil facilitates one to use wide variety
Fig. 2 (a) Block diagram of the radio frequency absorption set up, (b) Varying pitch coil made to accommodate samples of various dimensions and densities.
of samples and because of its higher inductance permits sustained oscillations even when the sample is in the normal state. A sample with large dimensions and higher density can be inserted in the upper half of the coil and a sample with smaller dimensions and low density can be inserted at the bottom half of the coil. And accordingly, different positions can be tested for better frequency and power measurements.

The inductance (L) of the coil with varying pitch can be written as

\[ L = L_1 + L_2 + \ldots + L_n + \sum_{i=1}^{n} M \]

where \( L_1, L_2, \ldots L_n \) are inductances of each turn and \( M \) is the mutual coupling between the turns. As the temperature or field is varied change in the penetration depth in the sample causes a change in the inductance in some part of the coil depending on where the sample is kept. This change in inductance is reflected in the total inductance change.

Sample coil assembly

Sample coil forms the tank coil of the oscillator and is connected to the oscillator through a long coaxial transmission line which goes into a dewar or the sample chamber of the closed cycle refrigerator, Fig. 2a. The coil is fixed in a highly thermally conducting and electrically insulating potting compound mould to arrest the vibrations of the turns and to achieve uniform temperature along the length of the coil. Both the sample and temperature sensor are kept in thin walled glass tube which is kept inside the coil. A heater wire is wound astatically on the potting compound to facilitate temperature variation.
Principle

The basic difference of high frequency absorption at microwave and radio frequencies is that at microwave frequencies absorption is detected maintaining the cavity at resonance by continuously controlling either cavity dimension or klystron reflector voltage so that frequency is always kept constant. Whereas, in the present marginal oscillator the feed back circuit maintains a constant current through parallel resonance circuit. The inherent feed back ensures that the oscillator is at resonance even while the frequency of oscillation changes continuously due to the variation in the inductive impedance of the load. The oscillation level is sensitive only to the resistive losses but not to the inductive losses and hence pure absorption signal is detected.

The absorption in the sample surrounded by a coil forming part of the tuned circuit affects the quality factor $Q$ of the resonance circuit and is given by the absorption of energy of the coil field $h$. Power dissipated in the coil is given by $P = (R_s/2) \int h^2 dA$. Time averaged energy stored in the coil is $W = (1/2)\mu \int h^2 dV$. Therefore, $Q$ factor

$$\frac{1}{Q_0} = \frac{P}{\omega W} = \frac{R_s \int h^2 dA}{2 \frac{\omega W}{\omega W}}$$

$$\rightarrow R_s = \tau / Q_0$$

where the field integral is cast in the geometry factor $r$. Thus the change in the surface resistance of the sample would reflect as a change in the quality factor and cause change in the power output. From Eq. 1 normalized power absorption $P/P_n = R_s/R_n$, where $P_n$ and $R_n$ are normal state power absorption and surface
resistance, respectively. Hence, studying absorption would directly give information on surface resistance.

At temperatures much less than $T_c$ and at low applied frequencies (so that $\hbar \omega \ll kT$), the effects due to proximity of induced transition across gap is negligible. In these conditions, the high frequency screening of normal electrons (skin depth) can be assumed to be negligible. The penetration of rf field is then solely determined by the screening of superelectrons and the penetration depth can be termed as screen depth $\lambda_s$. The absolute value of $\lambda_s$ at a particular temperature is difficult to measure, but its temperature variation can be studied by monitoring the change of inductance of the sample [19]. The inductance of the coil is proportional to the cross sectional area of the space occupied by the flux, that is the space between the coil and the sample plus whatever distance the flux penetrates into the surface of the sample. As the temperature or field is changed, penetration depth changes, and inductance changes with it. Then [19]

$$\frac{\text{change in inductance}}{\text{total inductance}} = \frac{\text{change in } \lambda \times \text{circumference of the sample}}{\text{total cross section occupied by flux}}$$

When inductance $L$ alters, oscillator frequency shifts as

$$\frac{\delta f}{f} = -\frac{1}{2L} \delta L$$

so that

$$\delta \lambda = -\left[\frac{A}{\pi r} \frac{\delta f}{f}\right]$$
where \( r \) is the radius of the sample and \( A \) is the cross sectional area between the sample and the coil. The changes in the surface reactance are obtained from

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

In the materials which obey the skin-depth limit in the normal state, one can use the criterion that \( R_n = X_n \) above \( T_c \) to determine \( X_0 \), the value of \( X \) at \( T=0K \).

The frequency change could also be affected by the loss in circuit. When the resonator is lossy and \( Q \) of the resonance circuit is low there can a reasonable shift in the frequency apart from that produced by the sample. To see this effect, consider a familiar equation of motion for a damped harmonic oscillator which is sinusoidally driven [20],

\[
md^2x/dt^2 + \beta dx/dt + kx = F \cos(\omega t) \text{ or } \]

\[
d^2x/dt^2 + \frac{\beta}{m} dx/dt + \omega_0^2 x = A \cos(\omega t)
\]

where \( \omega_0 = k/m \) is the undamped oscillation frequency and the damping parameter is \( \beta/m \). If the damping is light enough \( (\beta/m < \omega_0) \), the system will undergo damped oscillations with an oscillation frequency reduced from its undamped value, \( \omega_{res} = \omega_0 - (\beta/m)^2 \). With \( Q = \omega_{res}/(\beta/m) \) the oscillation frequency in the presence of damping is

\[
\omega_{res}^2 = \omega_0^2 [1 + (1/2Q^2)]^{-1}
\]
or \( \omega_{res} - \omega_0 \sim -(1/4Q^2) \). Thus the fractional change in the oscillation frequency due to losses is

\[
\frac{\omega_{res} - \omega_0}{\omega_0} \sim -\frac{1}{4Q^2}
\]

For the present \( Q \approx 400 \) value such a shift \( \approx 15 \) in the resonance frequency is negligible compared to the large frequency change \( \sim \text{a few thousand Hzs} \) due to the inductance change. Hence any effect of finite losses on the resonant frequency can be neglected.

Because we are able to measure both the real and imaginary parts of the impedance \( Z_s \), it is possible to obtain the complex conductivity \( \sigma_s = \sigma_1 - i\sigma_2 \) from the present measurements, using the relation \( Z_s = R_n \sqrt{2i/(\sigma_s/\sigma_n)} \) where \( R_n \) and \( \sigma_n \) are the normal state surface resistance and conductivity, respectively [21]. \( \sigma_2 \) is particularly important as it gives a measure of the superfluid density \( n_s \) which is proportional to \( \sigma_2 \). It is also related to the penetration depth via \( \sigma_2 = 1/\mu_0\lambda^2 \). The radio frequency resistivity \( \rho_n^r(T) \) in the normal state can be obtained from the surface resistance using \( R_n = \sqrt{\pi \mu_0 f \rho_n^r} \). Therefore, from the measurements of power at output and frequency changes of the oscillator, surface resistance, surface reactance and penetration depth of the superconductors can be obtained.

2.3 Magnetically Modulated Radio Frequency Absorption (MMRA)

Because the superconducting phase transition is a function of both field and temperature, there are many ways (corresponding to different paths in the H-T plane of
the superconducting phase diagram) in which the superconducting phase transition can be detected. All these ways are well discussed in literature [22,23]. In the present modulation technique constant dc field is applied to the sample which is modulated by much lower ac field, and the temperature is scanned through transition. As the temperature is varied through the transition the power change is detected using a lock-in analyzer at the modulation frequency. Such a field modulation is then equivalent to temperature modulation in the region of phase transition [22]. The present method is similar to the NMR technique in that the quantity directly measured is the derivative of the power with respect to the magnetic field. The difference between the MMRA and NMR methods is that in the latter technique, the field is varied as the temperature is kept constant while in the former technique the converse procedure is followed. The particular importance of field modulation is that any signal is recorded only if the rf response is magnetic field dependent, such as superconducting transition. Thus any other non field dependent phenomena like metal insulator-transitions are not detected. As described briefly in the last chapter, such a modulation technique, though more sensitive than direct power absorption, suffers from a few disadvantages and can be effectively used to determine superconducting phase transitions.

To carry out the MMRA experiments two pairs of Helmholtz coils are used for generating dc and ac fields. The applied dc field is \( \sim 100 \, \text{Oe} \) and the ac modulation field is about 2-5 Oe. MMRA studies are carried out on various HTSCs. The results obtained are published elsewhere, they do not form part of the thesis. However, a typical MMRA signal recorded on BSCCO is shown in Fig. 3.
Fig. 3 A typical MMRA signal of BSCCO 11 OK phase powder.
2.4 Cavity Perturbation Technique

Cavity perturbation methods have been widely used in the measurement of dielectric parameters of a variety of samples. The perturbation theory of resonant cavities was first proposed by Bethe and Schwinger [24]. The assumptions were further redefined by Spencer [25] and Waldron [26]. In this technique the stationary microwave electric field of the resonant structure is perturbed by the small superconducting material. So there is a resultant change in resonant frequency and quality factor of the resonator. In the present Bruker ESR spectrometer automatic frequency controller is used to arrest the frequency change and the microwave current is monitored by a crystal detector.

2.5 Samples used for the present study

Sintered and press sintered \(Bi_{1.2}Pb_{0.3}Sr_{1.5}Ca_2Cu_3O_y\)(BSCCO).

Sintered \(GdBa_2Cu_3O_7\)(GdBCO).

Melt textured GdBCO with different percentages of \(Gd_2BaCuO_6\)(211), namely,

GdBCO + 0 mol % 211
GdBCO + 10 mol % 211
GdBCO + 20 mol % 211 and
GdBCO + 30 mol % 211.

Sintered \(DyBa_2Cu_3O_7\)(DyBCO).
2.6 Preparation of the samples

Sintered BSCCO

The 110K phase of Bi - Sr - Ca - Cu - O system is unstable and attempts by several groups to stabilize this phase often resulted in multiphases including a small percentage of 85K phase. Substitution of Pb for Bi in small amounts is found [27] to stabilize the 110K phase with repeated cycles of cold pressing and sintering. It has been found in our laboratory that this phase can be prepared in a stable and single phase form from a starting composition \( \text{Bi}_{1.2}\text{Pb}_{0.3}\text{Sr}_{1.5}\text{Ca}_2\text{Cu}_2\text{O}_y \) without intermediate cold pressing [28]. The precursor powders required to make the BSCCO sample are prepared using a chemical route. Stoichiometric quantities of \( \text{Bi}_2\text{O}_3 \), \( \text{SrO}_3 \), \( \text{CaCO}_3 \) and Cu are dissolved in concentrated nitric acid while \( \text{Pb(NO}_3\text{)}_2 \) is dissolved in distilled water and mixed with the above solution. Then 1 gm mol. of nitric acid is added to 1 gm mol each of trivalent metal nitrates and correspondingly \( 2/3 \) gm mols of citric acid is taken for the divalent metal nitrates. The light blue color solution thus obtained is mixed with ethylene glycol. A small amount of ammonia is added to maintain the pH value around 4.5 so that the formation of precipitates can be avoided. The solution is then heated to form a jelly which eventually decomposes by an explosive reaction and yields a homogeneous black powder. The black powder was then ground well and sintered twice at 800° C with intermediate grinding. The sintered powders are pressed into pellets and annealed at 860° C for 15 days and quenched in air.

Press Sintered BSCCO
Tanaka et al. [29] reported that repeated cold pressing and sintering improves the critical current density of the sintered BSCCO. Press sintering results in texture in the material and higher density. The BSCCO pellets were annealed at 860°C for 5 days and quenched to room temperature in air. The air quenched pellets were subjected to uniaxial pressing under 4 tons of pressure. The pellets were then partially melted at 880°C for 50 mts, followed by annealing at 860°C for 5 days before quenching to room temperature.

**Sintered ReBCO**

Stoichiometric amounts of $Re_2O_3$, $BaCoO_3$ and $CuO$ are mixed thoroughly and calcined at 800°C with intermediate mixing for 24 Hrs. The mixture is then made into pellets and and sintered at $T_s$ ($T_s = 930^0C, 935^0C, 940^0C$ for Re= Y, Gd, Dy respectively) for 24 hrs. The pellets are then oxygenated at 450°C for 72 Hrs.

**Melt textured GdBCO**

The four, Gd-0, Gd-10, Gd-20 and Gd-30, melt textured samples are obtained from the Defence Metallurgical Research Laboratory [30]. The process used essentially consists of melting GdBCO into the pro-peritectic $Gd_2BaCuO_5$ and liquid phase at high temperature. The mixture is cooled slowly through the peritectic formation temperature ($\approx 1000^0C$) to 900°C and then furnace cooled. The samples are then oxygenated at $450^0C$ for 7 days.
References


[24] H.A.Bethe and J.Schinger, NDRC Rre, D 1, 117 (1943)