ELECTRICAL AND MAGNETIC MEASUREMENTS ON SOME HIGH Tc SUPERCONDUCTORS

V. VIDYALAL

THESIS SUBMITTED TO
THE COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE AWARD OF THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE FACULTY OF SCIENCE

DEPARTMENT OF PHYSICS
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
COCHIN - 682 022

December 1993

CERTIFICATE

Certified that the research work presented in this thesis is based on the original work done by Mr. V Vidyalal under my guidance in the Department of Physics, Cochin University of Science and Technology, and has not been included in any other thesis submitted previously for the award of any degree.

Cochin - 682 022
December 22, 1993

Prof (Dr) C P Girijavallabhan
Supervising Teacher

CONTENTS

Page

PREFACE

The discovery of high temperature superconductors in 1986 generated a great deal of excitement all over the world. These materials exhibit superconductivity above liquid nitrogen temperature. Liquid nitrogen incidentally is less expensive than liquid helium and far easier to handle and hence sparked off hectic activities in the scientific community and even those who carried out research in laboratories with moderate facilities were induced to work in the field of superconductivity. Subsequent years saw the synthesis of several new high temperature superconducting materials which became superconducting at increasingly higher and higher temperatures. In a very short period of time, the highest critical temperature increased from 23K to 35K and then to 90K, and later to a maximum of 130K. This led to a tremendous effort throughout the world to prepare, study and characterise these new materials. It should be also mentioned that the 1987 Nobel prize for Physics was awarded to two scientists *viz.* George Bednorz and K Alex Müller (I B M, Zürich) for their milestone discovery (in 1986) of superconducting ceramics. This remarkable achievement suggested an unexpected class of superconducting materials and paved the way for development of additional copper oxides based materials with even higher critical temperatures.

This thesis is the result of the author's attempt to prepare and to measure the electrical and magnetic properties of some selected high temperature superconductors (HTSC). The work was carried out in the Physics Department of Cochin University of Science and Technology in the past few years. Synthesis of various HTSC ceramics, the details of the fabrication of instruments and cryostats for characterisation and measurements, investigation of EM shielding based on HTSC materials, critical current measurements, studies on the effects of doping, degradation and aging of HTSC materials, determination of laser damage and ablation thresholds of HTSC's and the possible application of a HTSC based microwave device are included in this thesis. The basic HTSC materials synthesised for this purpose are GdBaCuO (123), BiCaSrCuO and BiPbCaSrCuO superconductors.

The whole thesis is presented in eight chapters as outlined below :

Chapter 1 starts with a brief history of high temperature superconductors and then describes the basic characteristics and the structure of these materials. Salient features of current theories to explain high temperature superconductors are also included. It concludes with a comprehensive account of the work presented in the thesis.

The second chapter discusses the details of preparation and characterisation of these materials. This includes the various synthesising routes for preparing GdBaCuO (123), BiCaSrCuO, BiPbCaSrCuO and thallium based superconductors. Various techniques like solid state reaction, co-precipitation method, freeze drying technique, preparation of single crystals, thin film preparation by laser ablation and melt textured growth are discussed. Determination of resistivity (ρ), susceptibility (χ_c), and the transition temperature (T_c) are also included in this chapter.

Chapter 3 deals with the various instruments developed for the measurement of resistivity of samples. It includes the design and realisation of a metallic cryostat, (which consumes only very little liquid nitrogen due to its unique design) for resistivity measurements, and a constant current source which forms a integral part of the measuring setup. For precise determination of resistivity these two parts play an important role along with supporting instruments (like a DC nanovoltmeter). The precision constant current source is inexpensive compared to commercially available units. It is designed essentially with easily available precision - linear IC's and constant voltage reference IC's. It has outstanding features such as low drift and low noise and is found to be ideal for measurements on high T_c materials. The effectiveness and utility of the above designs are demonstrated by making measurements on some HTSC samples. Electrical characteristics of devices which are sensitive to intrinsic power supply transients and extraneous interfering electromagnetic noise can be determined using these subsystems. The chapter concludes with the discussion on the determination of AC electrical resistivity. Such measurements can throw light on the conductivity behaviour of HTSC materials.

Chapter 4 describes the instrumentation required for the magnetic measurements of HTSC samples. This chapter contains the design of a glass cryostat with which rapid characterisation of samples is possible. The glass cryostat has added advantages like reduced consumption of liquid nitrogen and the elimination of offset voltages which appear in cryostats made of metal (where the sensing coils become unbalanced due to the proximity to a metal surface). Three methods *viz.* self inductance, mutual inductance and the frequency shift method with necessary instrumentation which can be used to determine T_c are described here. The frequency shift method has a higher resolution compared to the other two eventhough supporting electronics are required. A MOSFET based Robinson oscillator (which is highly stable and hence very low drift) is used for this purpose. The determination of T_c is accomplished by accurately measuring the frequency shift of the Robinson oscillator when the superconductor is introduced in the sensing coil.

Investigation of EM shielding based on HTSC materials and comparison with copper, aluminium and high permeability μ **metal** are also described in detail in this chapter. It concludes with a discussion with the efficacy of EM shields using HTSC materials compared to conventional shielding materials like μ metal, aluminium and copper.

As a prelude to the investigations in stepping up T_c, various dopants and substitutions were tried in Gd based 123 superconductors. Moreover chemical doping is a crucial investigative tool since it affects the structure. The objective was to assess the influence of alkali metal doping on the electrical properties of these ceramics and to evolve an understanding of the conduction mechanism in them. Details of doping studies in Gd based HTSC are described in chapter 5. Among the various dopants used, potassium was found to give positive results observed both resistively and magnetically for certain weight percentages of potassium.

Measurements of the critical currents (J_c) of HTSC samples are described in chapter 6. Various techniques used for the measurement of J_c, and enhancing J_c in oxide superconductors are discussed. The samples studied include **GdBaCuO** (123), doped GdBaCuO (123), BiCaSrCuO, BiPbCaSrCuO and Na doped BiCaSrCuO. The dependence of J_c on processing routes and the effect of Na doping are discussed.

A detailed study of degradation and aging behaviour of HTSC materials is discussed in chapter 7. The possible end products due to degradation, methods of preventing aging with a plastic solution *etc.* are discussed. The influence of synthesising routes on resistivity and degradation of Bi based HTSC materials and the possible ways of preventing degradation are discussed. A novel method of rejuvenating aged superconductors is also described.

HTSC based integrated circuits and transmission lines offer great promise basically due to its very low resistance compared to copper. The first part of chapter 8 (part A) deals with the studies of HTSC materials at microwave frequencies. Such studies have great importance in the fabrication of devices based on these new materials and hence a thorough investigation of its various electrical properties are necessary. The surface resistance of Bi based HTSC sample is determined by the cavity perturbation method and compared with reported values. A superconducting microwave device (ring resonator) has been designed and fabricated using Gd based HTSC material obtained by melt textured growth. Its various characteristics is determined using a Hewlett Packard network analyser (HP 810) and compared with a resonator made of copper.

Part B of the 8th chapter deals with the determination of laser induced damage and laser ablation thresholds of Bi based superconducting sample surfaces. Such studies are of immense importance in the context of preparation of thin films.

The last and concluding chapter summarises the overall work done by the author as detailed in the present chapter of the thesis.

Part of the work presented in this thesis has been published/communicated for publication/presented in seminars and symposia in the form of following research papers.

1] An inexpensive precision constant current source for resistivity measurements in high T_c superconductors.
V Vidyalal, and C P G Vallabhan, Int. J. Electronics (U.K), 75, 341, (1993).

2] Influence of synthesising routes on resistivity and ageing

characteristics of Bi - Cuprate superconductors.
V Vidyalal, K Rajasree, and C P G Vallabhan, Mod. Phys . Lett. B., 6, 1536, (1992).

3] Electrical and magnetic measurements in K - doped GdBaCuO high temperature superconductors.
V Vidyalal, K Rajasree, and C P G Vallabhan, Preethi Cicily Thomas, and V Unnikrishnan Nair, Int. J . Mod. Phys., 7, 18, (1993).

4] Time evolution of Nd :YAG laser induced plasma from $GdBa_2Cu_3O_7$ high T_c superconductor.
G Padmaja, A V Ravi Kumar, V Vidyalal, P Radhakrishan, V P N Nampoori and C P G Vallabhan, J. Phys : D, Appl. Phys., 22, 1558, (1989).

5] Spectral features of laser induced plasma from $YBa_2Cu_3O_7$ and $GdBa_2Cu_3O_7$ high T_c superconductors.
G Padmaja, A V Ravi Kumar, V Vidyalal, P Radhakrishan, V P N Nampoori and C P G Vallabhan, Pramana; Indian. J Phys, 32, L693, (1989).

6] Measurement of laser ablation threshold for high temperature superconductors by photothermal deflection technique.
K Rajasree, V Vidyalal, P Radhakrishan, V P N Nampoori and C P G Vallabhan, J. Appl. Phys., 74, 2004, (1993).

7] Characteristics of laser induced plasma from a high T_c superconductor.
G Padmaja, A V Ravi Kumar, V Vidyalal, P Radhakrishan, V P N Nampoori and C P G Vallabhan, Bull. Mater. Sci., 14, 545, (1991).

8] A modified MOSFET based Robinson oscillator for detection of

superconducting transitions.
V Vidyalal, K Rajasree, and C P G Vallabhan, Submitted to Supercond. Sci.Technol. (UK) (1993).

9] Use of mirage effect for the detection of phase transition in solids.
K Rajasree, V Vidyalal, P Radhakrishan, V P N Nampoori and C P G Vallabhan, Meas. Sci. Technol. (UK) 4, 435, (1993).

10] Use of mirage effect for the detection of phase transition in solids.
K Rajasree, V Vidyalal, P Radhakrishan, V P N Nampoori and C P G Vallabhan, Engineering optics (UK) 4, 241, (1993).

11] Study of electromagnetic shielding in high T_c superconductors.
V Vidyalal, K Rajasree, and C P G Vallabhan, Submitted to Mod. Phys. Lett.B, (1993).

12] A simple and inexpensive peak signal hold circuit.
V Vidyalal, K Rajasree and C P G Vallabhan, Submitted to Int. J. Electronics (U.K), (1993).

13] Microwave studies in high T_c superconducting Pb doped Bi - Sr - Ca - CuO systems.
V Vidyalal, C P G Vallabhan, K A Jose, P Mohanan, and K G Nair, Proc. of APSYM, CUSAT - 92, pg 30, (1992).

14] Superconducting circular microstrip resonator.
V Vidyalal, C P G Vallabhan, K A Jose, K K Narayanan, P Mohanan, K Vasudevan, and K G Nair, Presented at the "National symposium on Advances in Microwave", March 1 - 2, (1993), Dept. of Electronics Science, University of Delhi.

15] Application of photothermal deflection method for laser ablation threshold measurements in high temperature superconductors.
K Rajasree, V Vidyalal, P Radhakrishan, V P N Nampoori and C P G Vallabhan, " National laser symposium ", IIT Madras, Feb 17 - 19, (1993) Proc. pg 282.

16] An AC / DC constant current source for detecting superconducting transitions.
V Vidyalal, and C P G Vallabhan, "National workshop on high temperature superconductors" Feb 21 - 23, (1991), Marathwada University.

17] Detection of oxide species in laser ablated high T_c superconductor samples.
G Padmaja, A V Ravi Kumar, V Vidyalal, P Radhakrishan, V P N Nampoori and C P G Vallabhan, Presented at LASEM, Dec 1 - 3, (1989), Trivandrum.

18] Constant current source for testing high T_c superconductors.
V Vidyalal, and C P G Vallabhan, presented at the "National symposium on Physics and Chemistry of high Temperature superconductors" March 22 - 23, (1991), Department of Physics, Osmania University, Hyderabad.

19] The effect of Europium on the Bi-Sr-Ca-CuO high temperature superconductor.
Preethi Cicily Thomas, V Unnikrishnan Nair, V Vidyalal, and C P G Vallabhan, Proc. Of 5th Kerala Science Congress, Kottayam, pg 333 - 336, (1993).

20] Resistivity measurements in Gd based high T_c superconductors.
V Vidyalal, R Navil Kumar, and C P G Vallabhan, Proc.

"National Seminar on Superconductivity", Trivandrum, Kerala, Dec 1 - 3, Pg 98, (1988).

21] Effects of doping with magnetic impurity in Gadolinium based high T_c superconductors.
V Vidyalal, R Navil Kumar, and C P G Vallabhan, " Seminar on Pure and Applied Physics" Department of Physics, CUSAT, Cochin, 25th October, Proc M28, pg 53, (1988).

22] An AC/DC constant current source for detecting superconducting transitions.
V Vidyalal, and C P G Vallabhan, "Seminar on Pure and Applied Physics" Department of Physics, CUSAT, Cochin, 25th October, Proc P20, pg 32, (1988).

23] Delayed spectral emission by oxides in laser induced plasma from high T_c superconductor.
G Padmaja, A V Ravi Kumar, V Vidyalal, P Radhakrishan, V P N Nampoori and C P G Vallabhan, 2nd IPA/DST symposium on lasers and applications, BHU, Varanasi, Dec. 11-15, Proc. Pg 153 LA 17, (1989).

24] Raman spectra of Superconducting Gd 123 and Bi 2223 compounds.
Preethi Cicily Thomas , V Unnikrishnan Nair, V Vidyalal, and C P G Vallabhan, presented at the 12th Nat. Symp. on cryogenics (TNSC - 1992) 29, 30, March 1993, Jadavpur University, Calcutta.

25] Measurement of electromagnetic shielding using HTSC materials.
V Vidyalal, K Rajasree, and C P G Vallabhan, to be presented at the 13th. Nat. Symp. on cryogenics (TNSC-93), Dec. 3-5, Shivaji Univ., Kolhapur, (1993).

26] Superconducting circular microstrip resonator.
V Vidyalal, K Rajasree, and C P G Vallabhan, Submitted to Mod. Phys. Lett. B, (1993).

In addition the following papers have been published during the course of this work :-

27] Photoacoustic detection of modulated CO_2 laser beam.
K Rathnakaran, A V Ravikumar, V Vidyalal, and C P G Vallabhan, J. Acoust. Soc. India, XVIII, 48, (1990).

28] Direct measurements of internal waves using laser beam deflection technique.
Rao Tatavarthi, P N Ananth, K Rajasree, V Vidyalal, P Radhakrishan, V P N Nampoori and C P G Vallabhan, Communicated to Applied Physics Letters.

CHAPTER - I

HIGH TEMPERATURE SUPERCONDUCTORS - AN OVERVIEW

ABSTRACT

This introductory chapter begins with a brief history of superconductivity with the important landmarks in the development in this field upto the present scenario. Theoretical views put forward to explain the various aspects of superconductivity including the newly discovered high temperature superconductors are presented. The chemical composition on structural aspects of the new ceramic superconductors are briefly discussed. A comprehensive summary of the work presented in this thesis are also included.

1.1. HISTORY OF SUPERCONDUCTIVITY : A BRIEF OVERVIEW

Superconductivity is one of the most spectacular effect among the various physical phenomena.

Professor Kammerlingh Onnes, an experimental physicist at the university of Leiden discovered superconductivity in 1911. After inventing the world's first liquid helium liquefier, he investigated the resistivity of metals at low temperatures. He chose mercury (for its ease to purify by repeated distillation) and observed that the resistance dropped to zero at 4.25K. He tried metals like lead, indium and tin and found that all of them superconduct at 7.2K, 3.4K and 3.7K respectively. The critical temperature at which this phenomenon takes place is called the transition temperature (T_c) and is characteristic of the material. Prof. Onnes was then interested in producing intense magnetic fields by using these materials as wires wound as a solenoid. Two years later, to his disappointment, he found that superconductivity was destroyed or 'quenched' in the presence of moderate current densities and quite ordinary magnetic fields [1]. This was the beginning, and for his work "researches on the properties of matter at low temperature" he received the Nobel prize in Physics.

In the year 1917, F B Silsbee, a physics assistant at the U S National Bureau of Standards suggested that the quenching was due to the generation of a magnetic field at the surface of the superconductor [2]. Years later in 1933, Robert Ochsenfeld and Walter Meissner discovered that the magnetic flux was not only excluded but actually expelled from superconductors. They found that when a sphere was cooled below its transition temperature in a magnetic field, it excluded the magnetic flux. This effect was called the Meissner effect. It was then that superconductivity was recognised as a fundamental magnetic phenomenon. In 1934, Gorter and Casmir proposed a model which they called the "two fluid model". The phenomenon of superconductivity was explained on the basis of this model in which the superconducting state was considered as a result of a mixture of superconducting and normal electrons. In the same year the London brothers presented the theoretical as well as their experimental findings to the British Royal Society. They put forward the idea of the existence of an energy gap between the superconducting ground state and the lowest energy excited state. They also discovered the "anomalous skin effect" (A higher resistance of superconductors at microwave frequencies), while measuring the surface resistance of tin at 1.46GHz. In 1935 came the phenomenological theories of superconductivity proposed by F London, [3] who argued that superconductivity was a quantum mechanical phenomenon. In the early fifties, Brian Pipard introduced the concept of Coherence length ξ. It explained the non locality of electromagnetic fields in a superconductor. He showed that the current at a specific point in the superconductor was a function of the vector potential A in a region near the point and this nonlocal effect decreases exponentially away from the point with a characteristic decay length ξ. In 1950 the next theoretical advance came with the theory of Landau and Ginzburg [4] who described superconductivity in terms of an order parameter and provided a derivation for the London equations. In the same year, the isotope effect (where the transition temperature is related to the isotopic mass (T_c decreases as M increases) was predicted by H Fröhlich [5] and discovered by E Maxwell [6]. The experimental results within each series of isotopes of mass M could be fitted by a relation of the form $M^{\alpha} T_c$ = constant. This also provided the support for the electron-phonon interaction, otherwise known as the "phonon mechanism" for superconductivity. In 1950 the 'Flux quantisation' theory was put forward by F London [7]. He theoretically showed that flux ϕ_o in a superconductor is quantised to a value of h/2e. It was later confirmed by actual measurements. In 1952 Alexei Abrikosov [8] proposed that a new type of superconductor, characterised by a negative surface energy, should be recognised as a distinctly different class from the pure metallic superconductors (also called type I), which exhibit a positive surface energy. This group of alloys also called "dirty" or type II superconductors had unique magnetic properties different from type I - one of them being the ability to carry enormous current and remain superconducting in high magnetic fields. In 1955 a very sound theory to explain superconductivity called the BCS theory was put forward by John Bardeen, Leon Cooper and Robert Schriffer [9]. This theory involves the formation of bound electron pair states. According to their theory, superconductivity arises when the electrons form bound pairs through an attractive interaction with lattice vibrations or phonons (Cooper pair formation) and an energy gap that stabilises the supercondutive state. The Ginzburg - Landau and London results agree well with the BCS formalism. Later in 1972, Bardeen, Cooper and Schriffer were awarded 1972 Nobel prize in physics for their pioneering work. Until 1952, all theories considered only pure metals.

In the early 60's a newer class of superconductors with crystalline structure known as "A15" compounds also known as β - W (beta - tungsten family) were developed. The popular alloy of niobium and tin (Nb_3Sn) belonged to this class was developed by Bernd T Matthias and Ted Geballe [10, 11]. It could sustain current densities upto $10^{\sigma}A/cm^2$at fields of 88k gauss.

In 1959, Ivar Giaever [12] discovered the tunneling phenomenon in superconductors (single electron tunneling). He demonstrated the phenomenon using lead and aluminium separated by a thin layer (30Å) of aluminium oxide. The V - I characteristics changed markedly when one of the metals (lead) became superconducting. This also led to the measurement of energy gap, which was proportional to the critical voltage. When he cooled the other metal to its T_c (1.2K for aluminium) he observed negative resistance (which he had predicted) in the V - I curve. Determination of energy gap was made simpler by tunneling experiments than by the earlier infrared measurements [13].

Another important event which took place in the history of superconductivity was the Josephson effect in 1962. Brian Josephson [14] showed theoretically that cooper pairs can also tunnel. 'Pair tunneling' was carried out on very thin tunnel barriers (d <30Å) which couple the two superconducting materials to one another. Such junctions have enormous technological applications such as detection of very weak magnetic fields design of extremely sensitive magnetometers (SQUIDS), binary switching devices in microelectronics for computer, data storage etc. Later Brian Josephson and Ivar Giaever received the Nobel prize in Physics for their work on tunneling junctions.

In 1975, a different class of superconducting materials which had a perovskite structure were discovered [15]. Even though the T_c was quite low (13K), the structure was that of the perovskite family and therefore it had some similarity to the newly found high T_c materials.

Ever since the discovery of superconductivity, the main challenge was to increase the T_c and to do away with expensive coolants. Investigations of superconductivity and its practical applications remained within the reaches of a privileged few who could afford and maintain the very expensive liquid helium coolant, until the discovery of High temperature superconductors in April 1986. Till then the record for the highest T_c was 23.2K in Nb_3Ge thin films. Two scientists of the IBM Zurich laboratory - Alex Müller and Georg Bednorz while studying electrical properties of perovskites, found out that Lathanum - barium copper oxide superconducts at 30K [16]. Several groups like - Shoji Tanaka's group at Tokyo university, Bertram Batlogg group at AT & T Bell laboratories, Paul Chu and his colleagues at the university of Houston, etc confirmed the result immediately. Bednorz and Müller were awarded the 1987 nobel prize for their discovery. Late in 1986 Paul Chu and his group at the university of Houston studied the dependence of T_c of LaBaCuO with pressure [17]. They found out that with increase in pressure, T_c also increased reaching 57K at 12Kbar. This led to the investigation of chemical pressure dependence, and subsequently led to the substitution of Sr instead of Ba, increasing the T_c to 42.5K with zero at 36K [18]. M K Wu, Jim Ashburn and Chuan - Jue Torng of the University of Alabama could step up the T_c to 90K - they substituted both La and Sr with Y (Yttrium) and Ba [19]. The material had a composition $Y_{1.2}Ba_{0.8}CuO_{4-\delta}$ and it was composed of two major phases - the green phase ($Y_2Ba\ CuO_5$) and the dark superconducting phase [20].

Once the T_c was raised above liquid nitrogen temperature (77K), superconductivity became a subject of world wide interest and intensive research work were initiated in large number of institutions all over the world.

In 1988, another breakthrough followed. A new superconducting compound was discovered at the Tsukuba laboratories in Japan. Hiroshi Maeda's group reported that Bi-Ca-Sr-CuO superconducts at 110K with zero resistance at 80K. The compound was found to exhibit many superconducting phases and was not easy to separate the low T_c phases [21]. In Feb. 1988, Zhengzhi Sheng and Allen Hermann reported superconducting behaviour in a Thallium compound (Tl-Ba-Ca-CuO) [22]. It had a zero DC resistance at 106K. Even though (like Bi compound) it exhibited multiple phases, there were no low T_c phases to be separated. Both Bi based and Tl based superconductors were found to be far more stable than the YBaCuO compounds, and had higher critical current densities (J_c).

Also in 1988 a group from AT and T Bell laboratory reported superconductivity in a material $Ba_{0.3}K_{0.4}BiO_3$ [23]. Eventhough the T_c was low ($\simeq$ 30K) the material exhibited 3D superconductivity which was isotropic compared to Y, Bi or Tl based superconductors which shared anisotropic behaviour at the single crystal level. In the latter superconductivity occured in the copper - oxygen planes, while in the former there was no copper at all. Superconductivity has also been discovered in alkali metal doped La_2CuO_4, $La_{2-x}A_xCuO_4$ with A = Na or K [24] and in (Ba,K) BiO_x and (Ba,Rb) BiO_x, the first non copper containing oxide superconductors since $BaPb_{1-x}Bi_xO_3$ [15] which was discovered a decade ago. The same group later discovered a new family of superconducting compounds with the formula $(RE)Pb_2Sr_2Cu_3O_{8+\delta}$, where RE represents a wide variety of rare earths [25]. The T_c however was only $\approx$ 70K. Figure - 1.1 represents the manner of increase in T_c over the years. A quick glance at this curve is sufficient to show that a radical breakthrough happened in 1986.

1.2. A BRIEF SUMMARY OF THE THEORETICAL VIEWS

The first successful microscopic theory of superconductivity called the BCS theory was given by J Bardeen, L N Cooper and J R Schrieffer in 1957 [9]. This theory is based upon the existence of a net attractive interaction V between the electrons and the narrow energy range near the Fermi surface. This results in an excited state separated from the ground state by an energy gap. An attractive interaction produces two electron singlet bound states called Cooper pairs in momentum space. An attractive potential $V(\omega)$ between one electron and another electron produces these cooper pairs. This is the basis of BCS theory.
The expressions for the transition temperature (T_c) and energy gap (E_g) are

$$T_c = 1.134\ \Theta_D \exp[-1/\lambda] \qquad (1.1)$$

$$E_g = 4E_D \exp[-1/\lambda] \qquad (1.2)$$

Here $\lambda = V\ N(E_F)$ is the dimensionless electron - electron interaction called the electron - phonon coupling constant, Θ_D is the debye temperature and $N(E_F)$ is the density of the states at the fermi level.

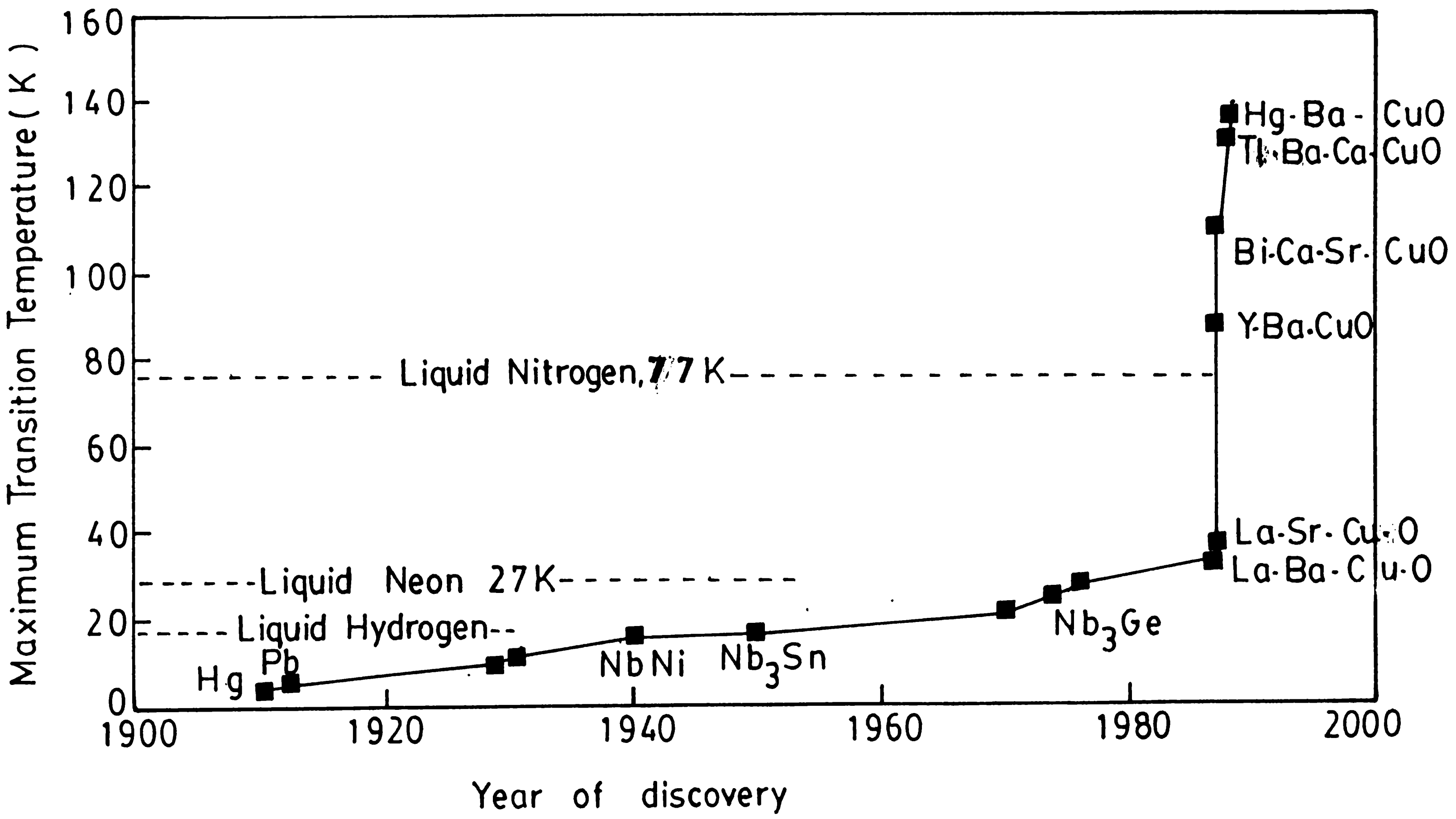


FIG-1·1 The upward change in T_c over the years.

From the above equations, the ratio $E_g/K_B T_c = 3.528$ can be deduced and it is independent of $V(\omega)$.

The coulomb interaction pseudopotential μ^* is given by

$$\mu^* = \frac{\mu}{1 + \mu \ln (E_F + E_D)}, \qquad (1.3)$$

where $\mu = \langle V_c \rangle N(E_F)$, therefore the expression for T_c can be written as

$$T_c = 1.14\, \Theta_D \exp \left[(-) \frac{1}{\lambda - \mu*} \right] \qquad (1.4)$$

The λ and μ^* for LaBaSrCuO and YBaCuO have been worked out as ~ 2, 0.2 and 5, 0.2 respectively [26]. Earlier workers support the phonon mechanisms and argue that a high T_c is achieved near a metal to insulator transition [27-34]. BCS theory could explain most of the properties of conventional superconductors. However there has been little support when it is applied to the present oxide superconductors [32, 35-38]. Anderson found that a whole lot of experimental results could not be explained based on the BCS theory and argued that superconductivity is not due to phonon induced pairing of electrons and it does not arise from cooper pair formation but from condensation of new quasiparticles of positive charge (+e) called Holons [39]. Other mechanisms have been advanced like polarons for example [40 – 42] and excitons [41, 43, 44]. The effect of polarons on producing high T_c has been discussed by various workers [40 – 42, 45, 46] and supported by photoconductivity data [47,48]. The phonon exchange (longitudinal optical phonons) between two Fröhlich polarons were shown to be attractive. The value of T_c approximately equal to 200K, with the ratio of $E_g/ KT_c \gtrsim 1.3$ may be attainable for a longitudinal optical frequency of 2×10^{14} Hz. This model predicts that as T_c increases the ratio E_g/ KT_c decreases and approaches 1.47 as $T_c \rightarrow \omega$.

Similarly the possible role of bipolarons to explain HTSC are also discussed in the literature [49]. In one approach involving an extended Hubbard model, the singlet superconducting state is unstable towards disordering if the intersite attraction is attractive and vice versa [47,48,50]. Plasmons and phonons act as attractors between electrons in the formation of cooper pairs and hence enhance T_c. Similarly others [51, 52] have considered the effects of intralayer interactions on the superconducting transitions making them doped Mott insulator [53]. The interaction of the lattice with the spin density wave (SDW) through the second harmonic involves the generation of the LF and HF modes and provides a way to enhance T_c [54, 55]. Another mechanism suggested by others includes electronic interactions (eg. electron - electron) [56-61] which lead to d - wave pairing [62].

A different magnetic mechanism known as resonant valence bond (RVB) theory was proposed by Anderson and Pauling [46, 63 - 71]. According to Anderson the ceramic superconductors have unique properties as they are strange insulators, strange metals and strange superconductors. The properties of these new ceramics are extraordinary due to the following reasons :-

The scale of T_c is large $\gtrsim$ 130K. There are indications of unstable superconductivity even at room and higher temperatures, The superconductor - normal metal tunneling is anomalous. Ultrasonic and IR absorption studies indicate that there is a strong attenuation and velocity of sound anomaly. Infrared absorption is very different from BCS materials. Similarly the values obtained for the energy gap are different from experiments such as tunneling and infrared absorption. Band structure calculations show that the charge carriers are holes contradicting the results obtained from Hall and thermopower measurements.

Anderson noted that all these newer superconductors occur near a metal to insulator transition known as the Mott transition. Wilson *et al* [72] confirmed that most copper oxides are Mott insulators. Anderson gave a Hubbard model description and provided a qualitative RVB scenario of HTSC. His basic idea was that the singlet pairs in the RVB insulator are like Cooper pairs. In the Mott insulator they are neutral owing to the absence of real charge density fluctuation in insulator [63]. The RVB state can be considered as a Bose condensate of cooper pairs of neutral solitons [69 - 70] with a gap in energy $E_g = 2\Delta$, where E_g is the energy needed to break a bond. Bonding between each atoms is through a single electron pair and the ground state is a linear coherent superposition of all the states that can be formed by such a dimerisation of the lattice [73]. Anderson argues that this state is a quantum spin liquid that interacts with short range correlations. The RVB state can be regarded as a coherent state, i e. a quantum liquid with excitations that require both local and nonlocal operators involving the entire background liquid. He argues that the low dimensionality (2D) and magnetic frustrations (the ability to achieve complete nearest neighbour antiferromagnetic pairing) favour this insulating magnetic phase.

The RVB model predicts and is compatible with several experimental results as given below.

1] The absence of an isotope effect, behaviour of low temperature specific heat, and elastic properties dominated by electronic energies.

2] Effective mass $m^* \gtrsim m_e / \delta \gtrsim 10m_e$, where δ is the doping fraction.

3] The absence of any effective energy gap

4] The insulating and / or antiferromagnetism of undoped or weakly doped copper oxide compounds.

5] Anomalous temperature dependence of the normal state resistivity and the carrier density versus Hall - Seebeck coefficient.

Calculations of the ratio E_g / kT_c for the RVB state indicates a small value compared to BCS prediction of 3.53. According to Pauling the mechanism of superconductivity is predominantly electronic and magnetic although weak phonon interactions may favour the RVB state. However strong doping transforms preexisting magnetic singlet pairs into charged superconducting pairs. In LaBaCuO, lines of alternating Cu - O atoms interact with layers of La and other cations to give rise to superconductivity. There is some resonance of $2Cu^{2+}$ to Cu^{-} + Cu^{3+}. Oxygen deficiency leads to the possibility of unsynchronised resonance and stabilizes the superconducting phase. Also band structure calculations of the spinel $LiTi_2O_4$ and $BaPb_{1-x}Bi_xO_3$ is consistent with the RVB theory.

1.2.a. Other models

Various other models have been proposed by other workers which are different from the RVB and BCS models. However some of the models involve multiple mechanisms which includes RVB and BCS. Many workers have cross examined the electronic properties of the Hubbard Hamiltonian and argue that the proposed ground state is not of the RVB type. The cases include strongly and weakly correlated types [74 - 80].

Some workers discuss models based on chain and one dimensional and correlation models. Okabe *et al* [81] proposed a model in which he suggests that superconductivity occurs in the copper oxide planes with T_c raised by the charge density wave (CDW) instability of the neighbouring Cu - O chains. Another linear chain model exhibits a change from a highly ionic to highly metallic behaviour as holes are added or electron states emptied [82]. These holes correlate strongly in space by occupying next nearest neighbour sites. The real space correlation length is of the order of the lattice parameter and the density of states at the Fermi surface is irrelevant to the interaction process [83]. However these chain models failed to hold ground after the discovery of Bi and Tl based superconductors which do not have chains.

In the case of elemental superconductors (such as Sn, Pb, Nb, Al, Gd etc.) most of the magnetic field interactions, fluctuations, and critical behaviour have been attributed to twin planes [84] and these have been proven theoretically. Therefore it was assumed to be responsible for the high T_c behaviour in YBaCuO and other orthorhombic copper oxide superconductors. However the discovery of Bi and Tl based superconductors in which twinning is not widespread made this theory unpopular.

1.3. STRUCTURES OF Y BASED, Bi BASED AND Tl BASED SUPERCONDUCTORS

The basic knowledge about the structure of these compounds is essential for the proper understanding of the mechanisms that make these materials superconduct. Single crystal studies have determined the dimensions of the unit cell, electronic charge distribution, locations of atoms in the cell, and the possible presence of atomic irregularities.

Various workers [90 - 106] have carried out X-ray and powder diffraction studies and has provided detailed pictures of the structure of the above mentioned compounds.

Oxide superconductors can be classified on the basis of their transition temperatures.

a) Materials with very low T_c :-

One of the well known example is the ferroelectric perovskite - $SrTiO_3$ with very low T_c (0.03 - 0.35K) [85-88], Nb doped $SrTiO_3$ has a slightly higher T_c of 0.7K . Another example is the spinel $LiTi_2O_4$ (T_c = 13.7K) [89].

b) Materials with T_c in the range 35 - 40K :-

These are also called high T_c superconductors (when T_c > 23K).

The initial high temperature superconductor LaSrCuO, belong to this class. The general formula is $La_{2-x}M_xCuO_4$ where M = Sr, Ca or Ba. The structure is shown in figure 1.2.

c) Materials with T_c in the range 90K :-

The general formula is $LnBa_2Cu_3O_7$ (123), where Ln = Y, La, Nd, Sm, Eu, Dy, Ho, Er, Tm, or Yb.

YBaCuO is the most widely studied HTSC material belonging to this group. The general formula is $Y_{1-x}Ba_{2-y}Cu_3O_{7-\delta}$. The composition with x = y = 0, $\delta \simeq 0$, i.e. $YBa_2Cu_3O_7$ has the highest $T_c \simeq 93K$.

d) Materials with T_c > 100K :-

The $Bi_2(Ca,Sr)_{n+1}Cu_nO_{2n+4}$ system, $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+4}$ and the $TlCa_{n-1}Ba_2Cu_nO_{2n+3}$ (n = 1,2,3,4) belong to this group with a recent addition of the HgBaCuO system [122-125].

1.3.a. YBaCuO and related 123 compounds

All the superconducting oxides in this family have the general formula $(Re)Ba_2Cu_3O_{7-\delta}$, (Re = Gd, Y, Nd, Sm, Eu, Dy, Ho, Er, Tm, Yb, Lu) and have an orthorhombic structure with T_c in the range 90 - 95K. However, when Re = Ce, Pr, and Tb, the compound is not superconducting and it posesses different structure. In general, (Re) ion has little effect on T_c but the T_c is markedly dependent on the oxygen stoichiometry δ. In the case of $YBa_2Cu_3O_{7-\delta}$, T_c is nearly constant ($\sim$ 90K) upto $\delta = 0.2$ but drops to a constant value of $\sim$ 55K between δ of 0.2 and 0.4; further increase in δ drastically lowers the T_c until it becomes nonsuperconducting when $\delta \sim 0.6$. The structure is orthorhombic over the entire range of 0.0 - 0.60 but becomes tetragonal when $\delta \geq 0.6$.

The structure of superconducting $YBa_2Cu_3O_7$ is shown in figure - 1.3. It is related to the perovskite structure wherein 2/3 of the copper ions from CuO_4 planar groups derived from a square pyramidal co - ordination for Cu while 1/3 of copper ions form one dimensional chains of squashed CuO_4 planar groups with no links in the a - direction [107]. The figure shows the corner linked copper oxide planar groups connected as sheets in the ab - plane and also as chains parallel to the b - axis. Of the two sets of Cu atoms, one is surrounded by four oxygen atoms at 1.929Å and 1.96Å, a fifth oxygen is located at 2.30Å giving a square pyramidal coordination for Cu forming puckerd CuO_2 sheets. In the other set the Cu atoms are surrounded by four oxygens at 1.92Å and 1.845Å and the oxygen atoms from the near rectangles connected by vertices resulting in the chains along the b-axis. The distance between O1-O4 is short (~ 2.6Å) and the O1 oxygens are associated with large amplitudes of vibration. The Cu -O chains are responsible for the orthorhombic structure of $YBa_2Cu_3O_7$. In the tetragonal non superconducting compound $YBa_2Cu_3O_6$ the chains are completely missing and the oxygen atoms occupy only 2/3 of the perovskite anions and are ordered in such a manner that 1/3 of the copper atoms is two fold coordinated while 2/3 is five fold coordinated [108-109] and the Cu - O4 bond is very short (~ 1.80Å). If the O1 sites (oxgen along the chains) are predominantly populated relative to the O5 sites (along the a- axis) the structure will be orthorhombic and the material will be superconducting. However, if both the O5 and O1 sites are equally populated then the structure will be tetragonal.

1.3.B. Bi and Tl based systems

Both these cuprates confirm to the general formula $A_2 B'_{n+1-x} B''_x Cu_n O_{2n+4}$ (A = Tl, Bi, and B', B'' = Ba, Ca, Sr). The T_c range from 80 to 130K [110-116] and has been found to depend on the number of Cu layers. Members of $Bi_2(Ca,Sr)_{n+1}Cu_nO_{2n+4}$ and $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+4}$ series have similar structures and contain two Bi, Tl - O type rock - salt layers. The Bi cuprates show modulation in the structure and a van der Waals gap of ~ 3.2 Å between the Bi- O layers. Members of the $TlCa_{n-1}Ba_2Cu_nO_{2n+3}$ have a single Tl–O type rock – salt layer. The Bi, Ca, and Sr sites in the Bi cuprates are interchangeable and the compositions (Bi:Ca:Sr ratios) are never exactly 2122 or 2223 as described by the general formula $Bi_2(Ca,Sr)_{n+1}Cu_nO_{2n+4}$. Most samples tend to be Calcium rich. Bi can be partly substituted by Pb (upto ~ 25%), and this generally favours the formation of better monophasic compositions with slightly enhanced T_c's.

BiSrCaCuO system

In the $Bi_2(Ca,Sr)_{n+1}Cu_nO_{2n+4}$ series the first three members with c parameters of ~ 25, 31 and 38 Å have been characterised, the T_c's being 60 ± 20, 85 ± 5 and 107 ± 3K respectively. The 2223 phase has a T_c ~ 110K and a c axis ~ 37Å. In this phase, the T_c increases with the number of CuO_2 layers [117-119] and it stabilises when Bi is partially substituted by Pb upto 25% . The 2212 compound namely $Bi_2(Sr,Ca)_3Cu_2O_{8+\delta}$ crystallises in the tetragonal space group I4/mmm, D_{4h}^{17} with two formula units per unit cell and has the lattice parameters a = 3.817Å , c = 30.6Å [120]. The structure is shown in figure 1.4.

The most popular, stable and easily reproducible composition is the $Bi_2(Sr,Ca)_3Cu_2O_{8+\delta}$ compound. By varying the Sr/Ca ratio it is found that the compositions close to $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_{8+\delta}$ with a slight Bi excess are ideal. Chapter 4, 6, 7, and 8 also contain the results of studies made on these compounds.

TlBaCaCuO systems

In the $Tl_2Ca_{n-1}Ba_2Cu_nO_{2n+4}$ series, the n = 1, 2, and 3 members (c parameters 23, 29, and 36 Å) shows T_c's of 80, 110, and 125K respectively. The n = 2 and 3 members of the $TlCa_{n-1}Ba_2Cu_nO_{2n+3}$ series show T_c's of 90 and 115K respectively, and these are lower than most of the corresponding members of the Tl_2 series. In the Tl cuprates, like the Bi cuprates, a progressive increase in T_c exists as well as in the c parameter with the number of Cu – O

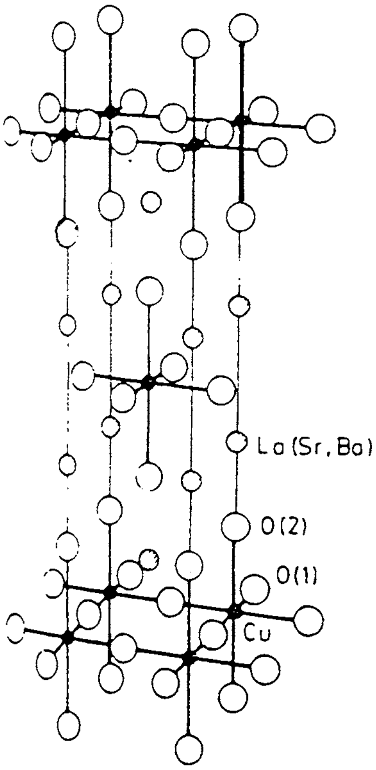


FIG - 1.2

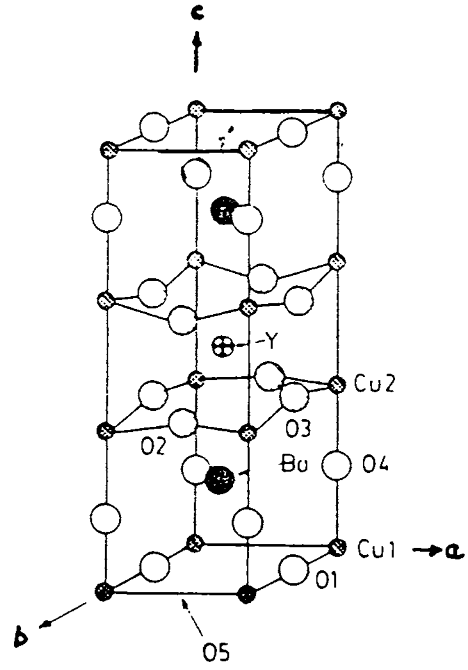


FIG - 1.3

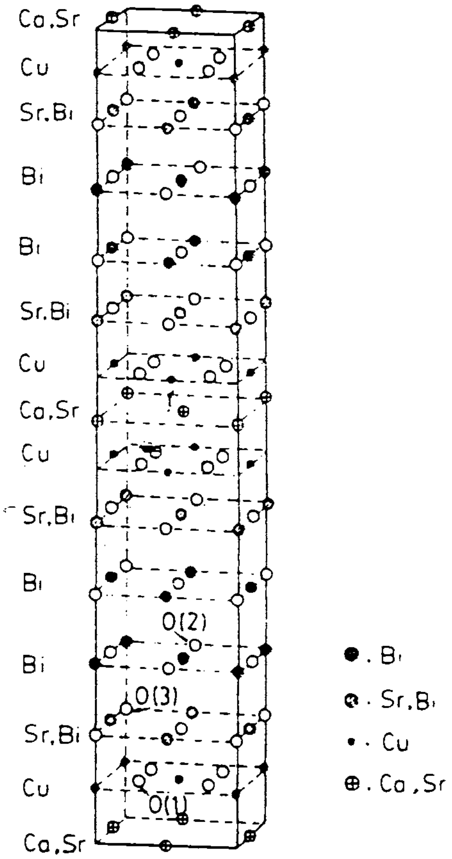


FIG - 1.4

Fig.1.2. Unit cell of $La_{2-x}Sr_x(Ba_x)CuO_4$ (Schematic).

Fig.1.3. Unit cell of $YBa_2Cu_3O_7$ (Schematic).

Fig.1.4. Unit cell of Bi_2 $(Ca,Sr)_3Cu_2O_8$ (Schematic).

sheets only upto n = 3; when n > 3 the Tl cuprates do not seem to show a further increase in T_c. The structure is similar to the Bi cuprate shown in figure 1.4.

The compound $Tl_2Ba_2CaCu_2O_8$ crystallises in the same tetragonal space group I4/mmm, D_{4h}^{17} as the bismuth compound described above, with two formula units per unit cell and the lattice parameters a = 3.8550Å, c = 29.318Å [121].

Due to the high toxicity of thallium, and the need for special hood chamber and related setups for preparation of Tl based compounds, preparation and studies based on these compounds were not attempted.

The following chapters of this thesis give detailed account of the work carried out by the author in the field of high temperature superconductivity and related areas.

A few HTSC materials were synthesised in the laboratory and the electrical and magnetic characteristics were studied. Some importance has been given to the instrumental aspects of few of these measurements. Another aspect which has come up during the course of these investigations was the stability of the characteristics of these materials and ageing process and its consequences on the material properties. In the authors view, these kinds of studies have great importance as the fabrication and use of any of the high T_c based devices will greatly depend on the stability of characteristics of these materials. Some attempt also have been made to fabricate simple devices like a microwave ring resonator using the newly synthesised material. As the method of laser deposition of thin films has gained some importance in recent years, laser ablation studies of some of these high T_c materials also have been undertaken in a preliminary manner. The thesis concludes with a listing of the overall conclusions of the above series of studies.

1.4. REFERENCES

[1] Reports on the researches made in the Leiden Cryogenic laboratory between the IInd and IIIrd international congress of refrigeration, Suppl. No. 34b, P 8-23, (1964).

[2] F B Silsbee, Note on electrical conduction in metals at low temperatures, Scientific papers, U S bureau of standards, 14, 301, (1917).

[3] F London, Superfluids, Macroscopic theory of Superconductivity, 1, 3, Wiley and sons, New York, (1950).

[4] V L Ginzburg and L D Landau, Zh. Eksp. Teor. Fiz., 20, 1064, (1950).

[5] H Frohlich, Phys. Rev., 79, 845, (1950).

[6] E Maxwell, Phys. Rev., 78, 477, (1950).

[7] F London and H London, Proc. Roy. Soc., A149, 72, (1935) and Physica, 2, 341, (1935).

[8] A A Abrikosov, Zh. Eksp. Teor. Fiz., 32, 1442, (1957) and translated in Sov. J. Phys., JETP 5, 1174, (1957).

[9] J Bardeen, L N Cooper and J R Schrieffer, Phys. Rev., 108, 1175, (1957).

[10] B T Matthias, T H Geballe, S Geller and E Corenzwit, Phys. Rev., 95, 1435, (1954).

[11] J E Kunzler, E Buehler, F S L Hsu and J H Wernick, Phys. Rev. Lett., 6, 89, (1961).

[12] I Giaever, Phys. Rev. Lett., 5, 147, (1960).

[13] R E Glover and M Tinkham Phys. Rev., 108, 243, (1957).

[14] B D Josephson, Phys. Lett., 1, 251, (1962).

[15] A W Sleight, J L Gillson and P E Bierstedt, Sol. St. Commun., 117, 27, (1975).

[16] J G Bednorz and K A Müller, Zeitschrift fur Physik - Condensed Matter., 64, 189, (1986).

[17] C W Chu, P H Hor, R L Meng, L Gao and Z J Huang, Science, 235, 567, (1987).

[18] K Fitzgerald, IEEE Spectrum, 25, 33, (1988).

[19] M K Wu, J R Ashburn, C J Torng, P H Hor, R L Meng, L Gao and Z J Huang, Phys. Rev. Lett., 58, 908, (1987).

[20] R M Hazen, "The Breakthrough - The race for the superconductors", (Summit books, New York), 145, (1988).

[21] H Maeda, Y Tanaka, M Fukutomi and T Asano, Jpn. J. Appl. Phys., 27, L209, (1988).

[22] Z Z Sheng, W Kiehl, J Bennett, A El Ali, D Marsh, G D Mooney, F Arammash, J Smith, D Viar and A M Hermann, Appl. Phys. Lett., 52, 1738, (1988).

[23] R J Cava, B Batlogg, J J Krajewski, R Farrow, L W Rupp, JR. A E White, K Short and T Kometani, Nature, 332, 814, (1988).

[24] M A Subrmamanian, I Gopalakrishnan, C Toradi, T R Askew, R B Flippen, A W Sleight, J J Lim and S J Poon, Science, 240, 495, (1988).

[25] R J Cava, B Batlogg, J J Krajewski, L W Rupp, L F Schneemeyer, T Siegrist, R B Vandover, P Marsh, W F Peck, P K Gallagher, S H Glarum, J H Marshall, R C Farrow, J V Waszczak, R Hull and P Trevor, Nature, 336, 211, (1988).

[26] J Rammer, Phys. Rev. B, 36, 5665, (1987).

[27] T Brun, M Grimsditch, K E Gray, R Bhadra, V Maroni and C K Loong, Phys. Rev. B, 35, 8837, (1987).

[28] S L Herr, K Kamaras, C D Porter, M G Doss, D B Tanner, D A Bonn, J E Greedan, C V Stager and D Timusk, Phys. Rev. B, 36, 733, (1987).

[29] D C Mattis, Phys. Rev. B, 36, 3933, (1987).

[30] W E Picket, H Krakauer, D A Papaconstantopoulos and L L Boyer, Phys. Rev. B, 35, 7252, (1987).

[31] W E Picket, H Krakauer, D A Papaconstantopoulos, L L Boyer and R E Cohen, MRS Anaheim Symp., P31, (1987).

[32] J C Phillips, Phys. Rev. B, 36, 861, (1987).

[33] W Weber, Phys. Rev. Lett., 58, 1371, (1987).

[34] J Yu, A J Freeman and J H Xu, Phys. Rev. Lett., 58, 1035, (1987).

[35] J B Boyce, F Bridges, T Claeson, T H Geballe, C W Chu and J M Tarascon, Phys. Rev. B, 35, 7203, (1987).

[36] R P Messmer and R D Murphy, ACS Symposium, 13, (1987).

[37] Z Wang, N Zou, J Pang and C Gong, Sol. St. Commun. 64, 531, (1987).

[38] X D Wu, T Venkatesan, D Dijkkamp, P Barboux and J M Tarascon, MRS Boston Symp., AA7.27, (1987).

[39] P W Anderson, Proc. of the International School of Physics, "Enrico Fermi", (1987).

[40] A S Aleksandrov, V N Grebenev and E A Mazur, Pislma Zh. Eksp. Teor. Fiz., 45, 357, (1987).

[41] W A Little, J P Collman and T J McDevitt, MRS Anaheim symposium, P37, (1987).

[42] D J Scalapino, R T Scaleter and N E Bickers, Novel SC, 475, (1987).

[43] C F Gallo, L R Whitney and P J Walsh, MRS Anaheim Symp., P165, (1987); Novel SC, 385, (1987).

[44] H Gutfreund and W A Little, Ch. 7, "Highly conducting one dimensional solids", (Eds) J T Devresse, R P Everarb, and N E Van Doren, (Plenum, New York), (1979).

[45] Y Kuramoto and T Watanabe, Sol. St. Commun., 63, 821, (1987).

[46] S Robaszkiewicz, R Micnas and J Ranninger, Phys. Rev. B, 36, 180, (1987).

[47] S Mazumdar, Phys. Rev.B, 36, 7190, (1987).

[48] S Mazumdar, Phys. Rev. Lett., 59, 2617, (1987).

[49] A S Aleksandrov, J Ranninger and S Robaskiewicz, Phys. Rev. B., 33, 4526, (1986) and J R Schrieffer, X G Wen and S C Zhang, Phys. Rev. Lett., 60, 944, (1988).

[50] J E Hirsch, Phys. Rev. Lett., 59, 228, (1987).

[51] C Chang - feng, Y Dao - Le, and H Ru - shan, Sol. St. Commun., 63, 411, (1987).

[52] Z Tesanovic, Phys. Rev. B, 36, 2364, (1987).

[53] M Cyrot, Sol. St. Commun., 63, 1015, (1987).

[54] E W Fenton and G C Aers, Sol. st. Commun. 63, 993, (1987).

[55] E W Fenton, Novel SC, 421, (1987).

[56] R L Greene, H Maletta, T S Plaskett, J G Bednorz and K A Mâller, Sol. St. Commun., 63, 379, (1987).

[57] D M Newns, Phys. Rev. B, 36, 5595, (1987).

[58] D M Newns, Novel SC, 515, (1987).

[59] H Maletta, R L Greene, T S Plaskett, J G Bednorz and K A Mâller, Jpn. J. Appl. Phys., 26, Suppl.26 - 3, (1987).

[60] T Penney, M W Shafer, B L Olson and T S Plaskett, Adv. Ceram. Mater., 2, 577, (1987).

[61] M W Shafer, T Penney, and B L Olson, Phys. Rev. B, 36, 4047, (1987).

[62] P A Lee and N Reed, Phys. Rev. Lett., 58, 2691, (1987).

[63] P W Anderson, Science, 235, 1196, (1987).

[64] P W Anderson, G Baskaran, Z Zou and T Hsu, Phys. Rev. Lett., 58, 2790, (1987).

[65] P W Anderson, Am. Phys. Soc. Meeting, New York, March, (1987).

[66] P W Anderson, Phys. Rev., 86, 694, (1952).

[67] P W Anderson, Mater Res. Bull. 8, 153, (1973).

[68] G Baskaran, Z Zou and P W Anderson, Sol. St. Commun., 63, 973, (1987).

[69] S A Kivelson, D S Rokhsar and J P Sethna, Phys. Rev. B, 35, 8865, (1987).

[70] S Kivelson, Phys. Rev. B, 36, 7237, (1987).

[71] Linus Pauling, Phys. Rev. Lett., 59, 225, (1987).

[72] J A Wilson, J. Phys. C : Sol. St. Phys., 20, L911, (1987).

[73] D J Thouless, Phys. Rev. B, 36, 7187, (1987).

[74] A Bhattcharya, P G McQueen, C S Wang and T L Einstein, MRS Boston symp., AA7.57, (1987).

[75] T Kostyoko, Phys. Stat. Sol., 143, 149, (1987).

[76] V J Emery, Phys. Rev. Lett., 58, 2794, (1987).

[77] R H Paramenter, Phys. Rev. Lett., 59, 923, (1987).

[78] A E Ruckenstein, P J Hirschfeld and J Appel, Phys. Rev. B, 36, 857, (1987).

[79] P Lederer, G Montambaux and D Poilblanc, J. Phys., 48, 1613, (1987).

[80] T M Rice, Z Phys.B, Cond. Mat., 67, 141, (1987).

[81] Y Okabe, Y Suzumura, T Sasaki and H Katayama -Yoshida, Sol. St. Commun., 64, 483, (1987).

[82] E R Gagliano, A G Rojo, C A Balseiro and B Alascio, Sol. St. Commun., 64, 910, (1987).

[83] R A Barrio, C Wang, J Taguena-Martinez, D Rios - Jara, T Akachi and R Escudero, MRS Boston Symp., 801, (1987).

[84] I N Khlyustikov and A I Buzdin, Adv. Phys., 36, 271, (1987).

[85] A Baratoff and G Binning, Physica, 188B, 1335, (1981).

[86] B Binning, A Baratoff, H E Hönig and J G Bednorz, Phys. Rev. Lett., 45, 1352, (1980).

[87] C W Chu, P H Hor, R L Meng, L Gao and Y Q Wang, Phys. Rev. Lett., 58, 405, (1987).

[88] R J Thorn, ACS Symp. P25, (1987).

[89] D C Johnston, H Prakash, W H Zachariasen and R Viswanathan, Mat. Res. Bull., 8, 777, (1973).

[90] O K Antson, P E Hiismäki, H O Pöyry, A T Tiitta, K M Ullakko, V A Trunov and V A Ul'yanöv, Sol. St. Commun., 64, 757, (1987).

[91] F Beech, S Miraglia, A Santoro and R S Roth, Phys. Rev. B, 35, 8778, (1987).

[92] J J Capponi, C Chaillout, A W Hewat, P Lejay, M Marezio, N Nguyen, B Raveau, J L Soubeyroux, J L Tholence and R Tournier, Europhys Lett., 3, 1301, (1987).

[93] D E Cox, A R Moodenbaugh, J J Hurst and R H Jhons, J. Phys. Chem. Sol., 47, 49, (1988).

[94] W I F David, W T A Harrison, R M Ibberson, M T Weller, J R Grasmeder and P R Lanchester, Nature, 328, 328, (1987).

[95] P Day, M Rosseinsky, K Prassides, W I F David, O Moze and A Soper, J. Phys. C : Sol. St. Phys., 20, L429, (1987).

[96] J E Greedan, A H O'Reilley and C V Stager, Phys. Rev. B, 35, 8770, (1987).

[97] D C Johnston, A J Jacobson, J M Newsam, T J Lewandowski, D P Goshorn, D Xie and W B Yelon, ACS Symp., P136, (1987).

[98] J D Jorgensen, M A Beno, D G Hinks, L Soderholm, K J Volin, R L Hitterman, J D Grace, I K Schuller, C U Segre, K Zhang and M S Kleefisch, Phys. Rev. B, 36, 3608, (1987).

[99] J D Jorgensen, B W Veal, W K Kwok, G W Crabtree, A Umezawa, L J Nowicki and A P Paulikas, Phys. Rev. B, 36, 5731, (1987).

[100] D Mck Paul, G Balakrishnan, N R Bernhoeft, W I F David and W T A Harrison, Phys. Rev. Lett., 58, 1976, (1987).

[101] C C Torardi, E M McCarron, P E Bierstedt, A W Sleight and D E Cox, Sol. St. Commun., 64, 497, (1987).

[102] C N R Rao, (Ed) "Chemistry of Oxide superconductors", (Blackwell, Oxford), (1988).

[103] C N R Rao, P Ganguly, R A Mohan Ram and K Sreedhar, Nature, 326, 856, (1987).

[104] D Vaknin, S K Sinha, D E Moncton, D C Johnston, J M Newsam,

C R Safinya and H E King. Jr., Phys. Rev. Lett., 58, 2802, (1987).

[105] Y Yamaguchi, H Yamauchi, M Ohashi, H Yamamoto, N Shimoda, M Kikuchi and Y Syono, Jpn. J. Appl. Phys., 26, L447, (1987).

[106] Q W Yan, P L Zhang, L Jin, Z G Shen, J K Zhao, Y Ren, Y N Wei, T D Mao, C X Liu, T S Ning, K Sun and Q S Yang, Phys. Rev. B, 36, 5599, (1987).

[107] W I F David, W T A Harrison, J M F Gunn, O More, A K Soper, P Day, J D Jorgensen, D G Harris, M A Beno, L Soderholm, D W Capone, I K Schuller, C V Segre, K Zhang and J D Grace, Nature, 327, 310, (1987).

[108] P Bordet, C Cherillout, J J Capponi, J Chenavas and M Marezio, Nature, 327, 687, (1987).

[109] J D Jorgensen, M A Beno, D G Hinks, L Soderholm, K J Volin, R L Hitterman, J D Grace, I K Schuller, C U Segre, K Zhang and M S Kleefisch, Phys. Rev. B, 36, 3608, (1987).

[110] C W Chu,P H Hor, R L Meng, L Gao, Z J Huang, J Bechtold, M K Wu and C Y Huang, MRS Anaheim Symp., P15, (1987).

[111] H Maeda, Y Tanaka, M Fukutomi and T Asano, Jpn. J. Appl. Phys. Lett., 27, L209, (1988).

[112] H W Zandberg, Y K Huang, M J V Menken, J N Li, K Kadowaki, A A Menovsky, G Van Tendeloo and S Amelincks, Nature, 332, 620, (1988).

[113] L Gao, Z J Huang, R L Meng, P H Hor, J Bechtold, Y Y Sun, C W Chu, Z Z Sheng and A M Herman, Nature, 332, 623, (1988).

[114] R M Hazen, Sci. Am., June 74, (1988).

[115] Z Z Sheng, A M Hermannm,A El Ali, C Almasan, J Estrada, T Datta and R J Matson, Phys. Rev. Lett., 60, 937, (1988).

[116] Z Z Sheng and A M Hermann, Nature, 332, 55 (1988).

[117] C N R Rao, P Ganguly, R A Mohan Ram and K Sreedhar, Nature, 326, 856, (1897).

[118] M A Subramanian, C C Toradi, J C Calabrese, J Gopalakrishnan, K J Morrissey, T R Askew, R B Flippen, U Chaudhry and A W Sleight, Science, 239, 1015, (1988).

[119] J L Tallon, R G Buckley, P W Gilberd, M R Presland, I W M Brown, M E Browden, L A Christiann and R Goguel, Nature, 333, 153, (1988).

[120] J M Tarascon, Y LePage, P Barboux, B G Bagley, L H Greene, W R McKinnon, G W Hull, M Giroud and D M Hwang, Phys. Rev. B, 37, 9382, (1988).

[121] M A Subramanian, J C Calabrese, C C Torardi, J Gopalakrishnan, T R Askew, R B Flippen, K R Morrissey, U Chowdhry and A W Sleight, Nature, 332, 420, (1988).

[122] S N Putilin, E V Antipov, O Chmaissen and M Marezio, Nature, 362, 226, (1993).

[123] I Bryntre and S N Putilin, Physica C, 212, 223, (1993).

[124] David J Singh, Physica C, 212, 228, (1993).

[125] D L Novikov and A J Freeman, Physica C, 212, 233, (1993).

CHAPTER - 2

PREPARATION AND CHARACTERISATION OF HIGH T_c SUPERCONDUCTORS

ABSTRACT

This chapter describes the different methods employed in the preparation and characterisation of HTSC materials. They include bulk samples prepared by solid state reaction methods, single crystals, and laser ablated thin films. The principles behind resistivity and susceptibility measurements are also described in this chapter.

2.1 INTRODUCTION

Preparation of high T_c superconductors meant for demonstrating levitation and zero resistance can be easily synthesised by using low purity chemicals [1] and by crude synthesising techniques. Such samples are generally multiphasic and contain fractions of superconducting phases with T_c above liquid nitrogen temperature [2]. However, copperoxide compounds are quite sensitive in their properties to the method of preparation and annealing. Therefore high quality single phase specimens require careful preparation procedures mainly because the various properties of these materials basically depend on synthesising temperature, annealing cycles, grain sizes, oxygen content of the surrounding gas and pelletising procedures.

The ratio of cations in the final sample is important, but even more critical and more difficult to control is the oxygen content (In 123 compounds sc properties are sensitive to oxygen content, but not in the case of Bi - and Tl - based materials).

The easiest to prepare are the polycrystalline materials but specialised techniques are required for the preparation of thin films and single crystals. Due to the ease of preparation, enormous amount of work has been carried out on polycrystalline materials.

2.2 METHODS OF PREPARATION

There are three main methods for preparation of copper oxide superconductors namely, solid state reaction method, coprecipitation method, and the sol - gel technique.

The most popular and widely used method is the Solid state reaction method [3] - [31] which comprises of the following steps:-

a] Weighing the appropriate amounts of the starting material (oxygen rich compounds such as oxides, nitrates or carbonates of Ba, Bi, Sr, Ca, Tl or other elements),

b] Mixing and grinding these powders to facilitate the calcination process and to get a homogeneous mixture - mixing is generally done with an agate mortar and pestle for small quantities and ball-milled for large quantities.

c] Calcining the homogeneous mixture to get the reacted material (temperatures range from 880 - 900°C, 10 - 20 hours) and grinding to get the desired particle size, (this process may be repeated a number of times with pulverising and mixing of the partially calcined material at each step, and as the reaction proceeds the colour of the charge changes).

d] Shaping the ground powder by pressing (desired form is obtained by using a suitable die and punch, the applied pressure being approximately 5 Tons / cm^2) or extrusion (the suspension of the calcined powder in a suitable organic binder is extruded through suitable extruders such as ram extruders) etc.

e] Sintering the shaped material (usually done in an oxygen atmosphere at temperatures around 920 - 950 °C for a period ranging from 4 - 24 hrs) and

f] Annealing in oxygen or air along with a slow cool (at a rate of 1-2°C per minute) to room temperature.

As an example, the synthesis of $GdBa_2Cu_3O_7$ is as follows: - Stoichiometric amounts of high purity oxides and carbonates of the constituents viz. :- Gd_2O_3, $BaCO_3$, and CuO (may be prepared separately from copper metal rod/powder by dissolution in HNO_3 and decomposition of the nitrate above 800°C in air) are taken in the appropriate stoichiometric proportions. The powdery material is then thoroughly ground and mixed in an agate mortar and pestle. The mass is then loaded in alumina crucibles and calcined at 900°C in air for 24h (with intermediate grinding). The powder is then heated again in air for 24h at 950°C. The black solid mass is then crushed, ground, sieved (300 mesh /inch) and pelletised (1cm dia, 2mm thickness) by applying a pressure of 7.5 tons. The pellets are then sintered at 930°C (tubular furnace) in flowing oxygen for 24h. Then it is cooled to room temperature within the furnace.

The preparation of BiCaPbSrCuO systems (BSCCO) is as follows:- Appropriate amounts of powders of PbO (99.999%), Bi_2O_3 (99.9%), CuO, $SrCO_3$ and $CaCO_3$ (both analytical purity) are mixed and ground using an agate mortar and pestle. The mixture is the prefired in air at 870°C for 48h. The reacted black powder is then ground well and pelletised. The pellets are sintered at 850°C for 12 h (with intermediate grindings). The mass is then ground well and sieved (300 mesh/inch), and then pressed into pellets of 2mm thickness and 1cm diameter by a pressure of 7.5 tons. The pellets are then sintered at 860°C for 120 hours in air followed by furnace cooling to 250°C.

In the matrix reaction method [32,33] a matrix composing of the individual oxides (in the appropriate ratio) of $Ca_2Sr_2Cu_3O_7$ is made. The mixture is reacted at 960°C for 48h. In this reacted matrix, the required amounts of Bi_2O_3 and lead acetate are added, mixed well and pelletised. The pellets are heated at 925°C for a short period (5-10 minutes) in air. The mass is then ground well and then pressed into pellets and sintered at 860°C for 8 days with intermediate grindings. The product is again ground well, and sieved (300 mesh/inch), and pressed into pellets of 2mm thickness and 1cm diameter by a pressure of 7.5 tons. The pellets are then heated for 3-5 minutes at 910°C. It is then sintered for 50 hours at a temperature of 860°C and furnace cooled to room temperature.

A slightly different approach is described by others [34] :- Stoichiometric amounts of reagent grade Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO is dissolved in HNO_3 and then diluted with deionized water until a clear solution is obtained. The solution is slowly evaporated in a sintered alumina crucible and the reactants are then denitrated by heating with a burner. The residue is then finely ground in a porcelain mortar and reheated at 880°C in air for 16h. The black residue thus obtained is again pulverized to a fine powder.

A method for preparing superconducting single crystals of Gd-123 superconductors [35] and also followed by us is briefly as follows :- Powders of $BaCO_3$ (99.99%), Gd_2O_3 (99.99%), and CuO (99%) in the ratio of Ba:Gd:Cu = 2:1:3 are thoroughly ground, reacted in air at 930°C for 24 hrs, and then cooled to room temperature within about 10hrs. The mass is then reground and pelletised (2cm dia, 2-3 mm thickness). The whole process can be summarised as :

$1005^{\circ}C$ (2h) $\xrightarrow{2^{\circ}C/h}$ $980^{\circ}C$ (48h) $\xrightarrow{2^{\circ}C/h}$ $940^{\circ}C$ (8h) $\xrightarrow{2^{\circ}C/h}$
$900^{\circ}C$ (8h) $\xrightarrow{5^{\circ}C/h}$ $850^{\circ}C$ (8h) $\xrightarrow{5^{\circ}C/h}$ $750^{\circ}C$ (24h) $\xrightarrow{50^{\circ}C/h}$
$550^{\circ}C$ (24h) $\xrightarrow{3^{\circ}C/h}$ $400^{\circ}C$ $\xrightarrow{\text{oven cooled}}$ room temperature.

After this procedure the large sized semiconducting crystal ($2 \times 3 \times 6$ mm^3) is to be annealed in flowing oxygen for 72hrs. at 550°C to render them superconducting.

In the co-precipitation method, the starting materials for calcination are produced by precipitating them together from a solution [36]-[40] and therefore mixing of the constituents takes place in the atomic scale. Once the precipitates are formed, it is dried and then calcined as in the solid reaction mentioned above. Solution techniques permit reactions at lower temperatures, produce materials with particles size of less than 0.5μm and have a narrow size dispersion. The smaller and uniform particle sizes have the potential to yield denser compacts on sintering. Moreover the solution derived materials have a narrower transition width.

Another method to obtain the starting powder is the sol-gel technique. Here, aqueous solutions containing the proper ratios of Y, Ba, and Cu nitrates are emulsified in an organic phase and the resulting droplets are gelled by the addition of a high molecular weight primary amine which extracts the nitric acid. The process can be described in the following steps.

a) Preparation of the aqueous solution of Y, Ba and Cu salts (generally nitrates).
b) Emulsifying the solution by ultrasonic agitation with water immiscible organic compound (Heptane) and
c) Coprecipitating the metal hydroxides of the emulsion by using suitable organic amines (hydrous oxides of the cations precipitate to form an amorphous gel).
d) Drying the gel to get the homogeneously mixed powder.

A freeze drying technique for the preparation of ceramic powders has also been reported [41,42]. A nitrate solution containing salts of Y, Ba, and Cu are taken in the appropriate ratio. The solution is sprayed into a tray containing liquid nitrogen. The frozen beads of the solution are then vacuum dried. The powder is then heated to decompose the salt to obtain the starting powder. Rest of the procedure is same as the solid state reaction technique. This technique produces sintered materials homogeneous in composition and small in porosity.

Preparation of Tl based HTSC :-

Synthesis of Tl-Ca-Ba-CuO superconductors are different from the above procedures since Tl_2O_3 is highly volatile, low melting point (400^oC), high vapour pressure above 200^oC and transforms into Tl_2O at 800^oC. Moreover, it easily sublimes and inorder to avoid loss due to sublimation the reaction should be carried out at a shorter period and the matrix method should be adopted [43 - 52]. An improved form of the matrix method yielding pure phases [53] is as follows:- Stoichiometric ratios of Tl_2O_3 and a matrix composed of $CaBaCu_2O_x$ are pelletised and sintered at 920^oC for 5

- 8 minutes in flowing oxygen and quickly withdrawn from the furnace to quench the material. This avoids Tl loss and introduces controlled amount of moisture. The pellet is reintroduced into the furnace again and allowed to furnace cool in flowing oxygen. Such a procedure yields a predominant Tl-2223 (125K) phase.

The preparation procedure of Tl-2122 phase (108K) is slightly different. One starts with the matrix of $CaBa_2Cu_2O_5$ which is prepared by reacting a mixture of $BaCO_3$, $CaCO_3$ and CuO at 845°C for 24 hours, followed by heating at 925°C for 48 hours with intermediate grindings. Stoichiometric amounts of Tl_2O_3 and matrix powers are well mixed, pelletised and loaded in an alumina boat and introduced into the furnace kept at 925°C and allowed to react for 5-8 minutes in flowing oxygen. The pellet is quenched to room temperature and reintroduced into the furnace and then again furnace is cooled to room temperature.

Thallium based superconductors are extremely toxic and special care must be exercised during preparation and processing.

The presence of unreacted material can be checked by X-ray diffraction. Typical patterns for various samples ($GdBa_2Cu_3O_7$, BiCaPbSrCuO, and Na doped $Bi_2CaSr_2Cu_2O_y$, are shown in figures 2.1, 2.2, and 2.3.

2.3. PREPARATION OF HTSC THIN FILMS BY LASER ABLATION

Laser ablation technique is one of the fastest and most reproducible method of producing High T_c films [54]. Laser ablated thin films of $YBa_2Cu_3O_7$ were produced by this technique [55-57] and was found to be superior to thin films made by other methods. The technique is rather similar to the electron beam coevaporation, the main difference being that the electron sources are substituted with lasers. Therefore it is relatively easy to focus on a very small target area, and this can be an advantage when small pellets are used as the high T_c target material.

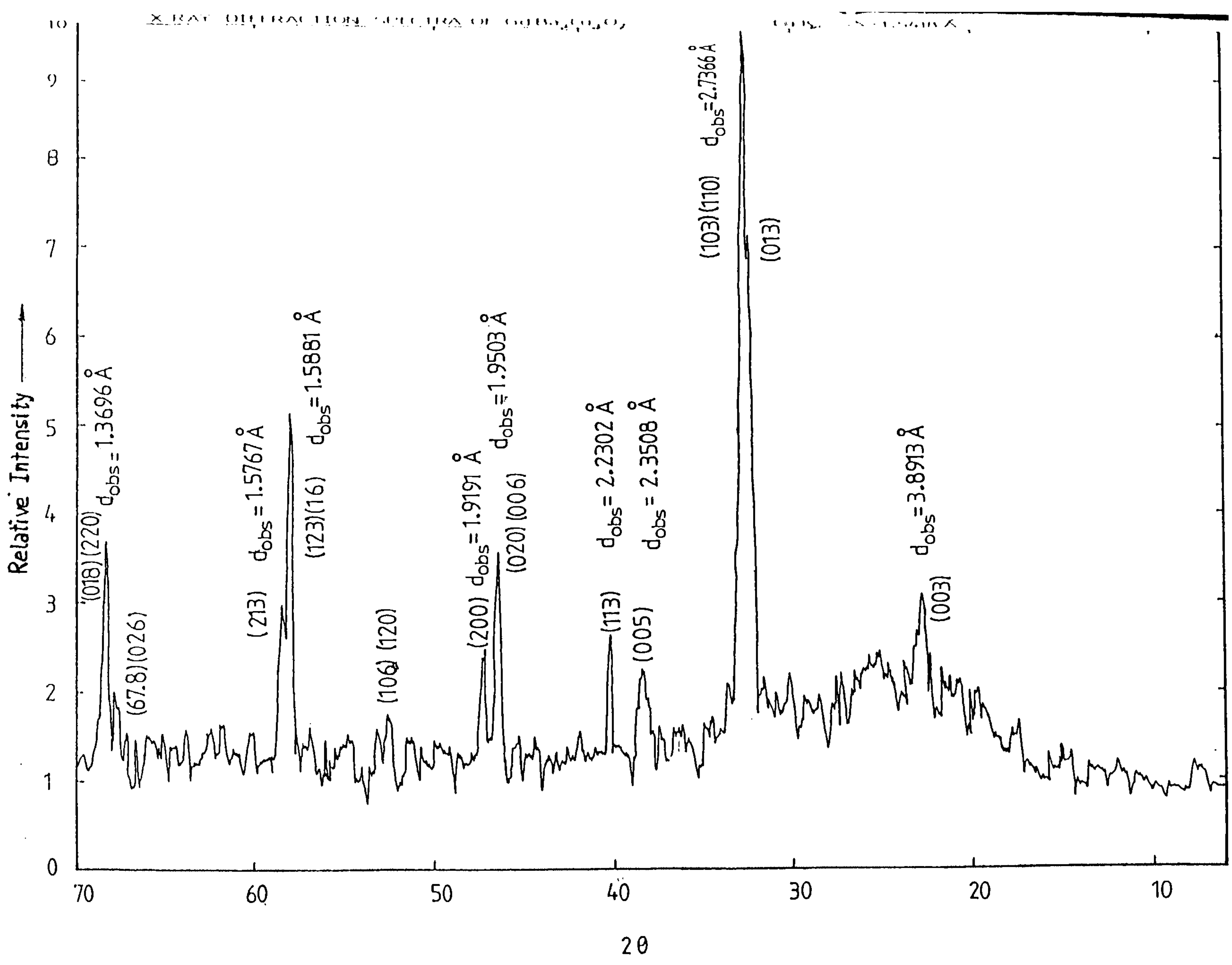


Fig.2.1. XRD pattern of $GdBa_2Cu_3O_{7-\delta}$.

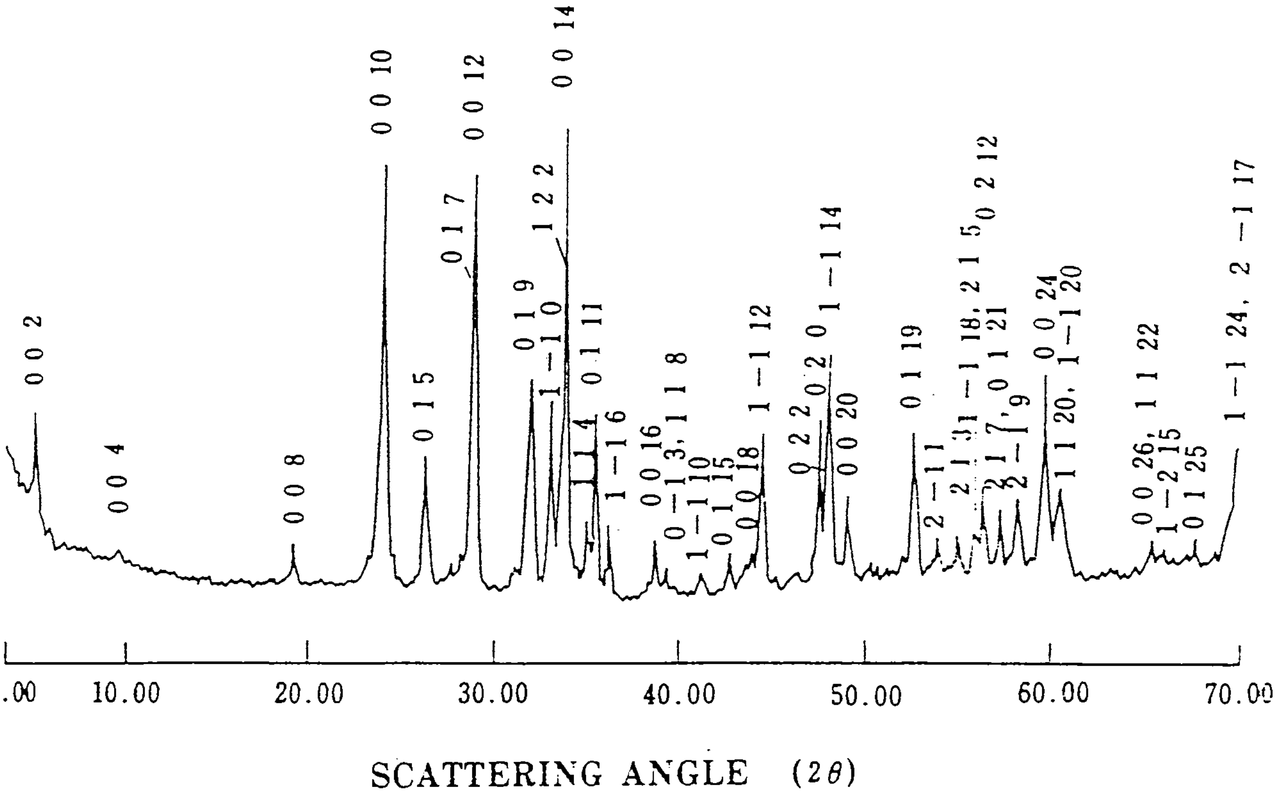


Fig.2.2. XRD pattern of Bi - 2223 (110K phase).

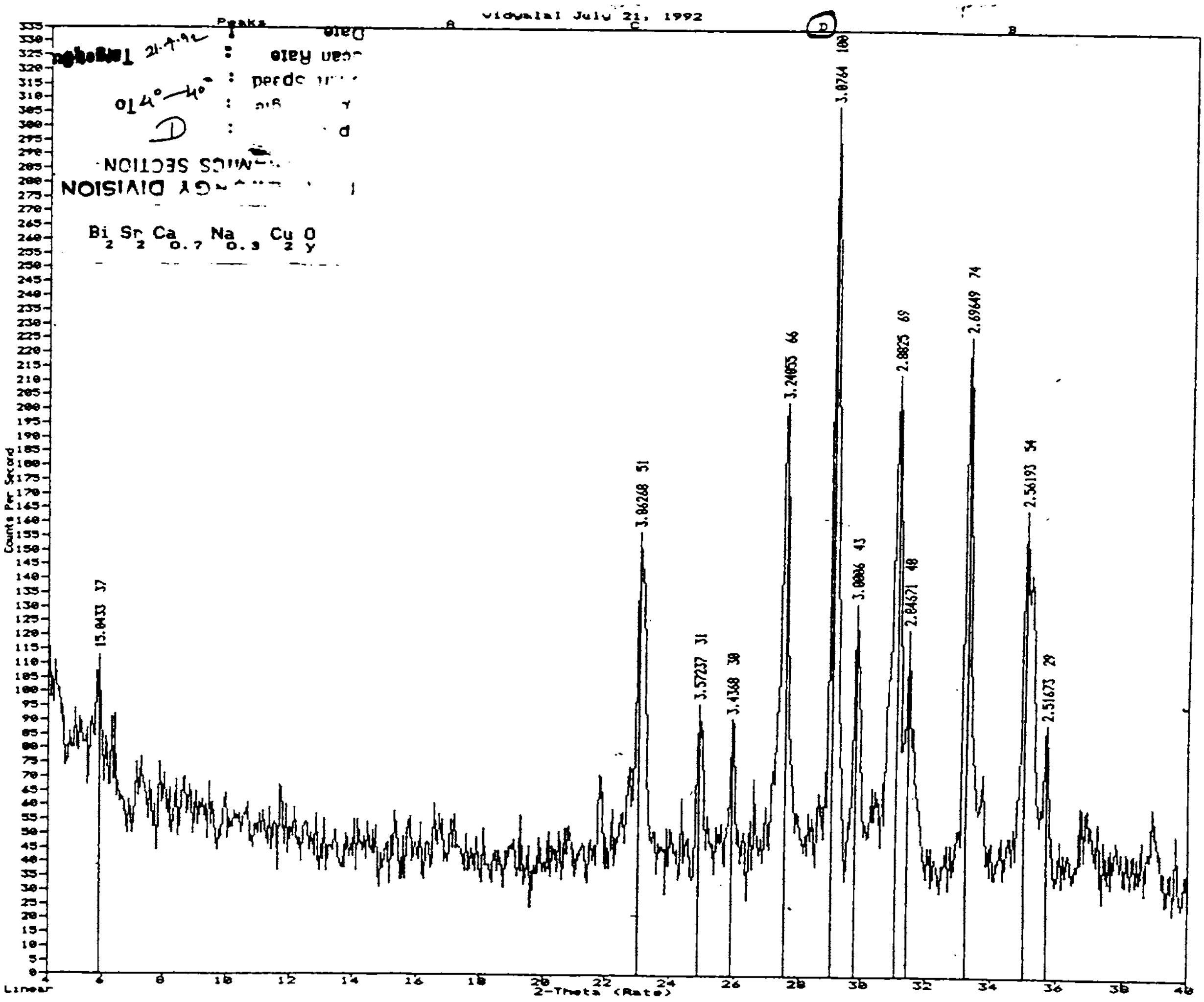


Fig.2.3. XRD pattern of Bi - 2223 doped with Na.

Other popular methods such as evaporation techniques using thermal sources, produce mainly neutral metals in the gas phase and result in the deposition of oxygen deficient films [58], whereas laser ablation has proven to give good quality, smooth high T_c film on a moderately heated substrates [59, 60] which is well suited for multilayer deposition. The reason for the application of this technique is that evaporation processes is very rapid not allowing the establishment of a thermodynamic equilibrium between the different elements as it occurs in the evaporation from the melt. If the equilibrium is allowed, then owing to the difference in the vapor pressure of the various elements the stochiometry of the deposit would differ from that of the bulk superconductor [61]. Other factors such as the difference in adherence of the different elements on the substrate may also induce a change in the stochiometry of the deposited film. The substrate on which the film is to be deposited must satisfy the following criterions :- good matching between the HTSC lattice constant and temperature coefficient, should withstand the temperature encountered in the deposition process, and must be chemically stable and inert to the HTSC material. Few substrate materials meet these criteria and best of them are Lanthanum aluminate, yttria stabilised zirconia (YSZ), sapphire, and magnesium oxide to name a few. Films made by laser coevaporation become superconducting only after annealing even though they retain their elemental content identical to that of the bulk superconductors. The post deposition annealing is necessary because the thin film thus formed usually do not retain the correct stochiometry because of oxygen deficiency [62]. Therefore, in the context of manufacturing active devices, it is desirable to form superconducting films without annealing step which may be harmful to the interconnects, protective layers and also to the substrate etc. So in-situ deposition of superconductors with sufficient oxygenation during film growth on lower substrate temperatures will avoid this problem. However thin films of Bi and Tl based materials do not require this post annealing in oxygen.

In order to prepare good quality films which are superconducting, it is necessary to control the deposition parameters like laser power, substrate temperature and pressure of the deposition chamber etc. The laser ablation of high T_c target is accompanied by the formation of the luminous plume above the solid surface. Ablation of the target is accompanied by the formation of brilliant elongated plasma located above the target surface and extending outward up to about 2 cm from the target surface [63]. Analysis of the optical emission spectrum emitted from the plasma plume has been used to identify emitting species (vaporized and ejected) from the target [63-67].

Superconducting thin films of YBaCuO can be grown using Nd:YAG laser with help of simple disc electrode geometry [68]. They are grown at 550 - 600°C (substrate temperature) in the presence of an oxygen plasma and show superconducting properties comparable to single crystal [69, 70]. However the majority of thin films deposited so far by laser ablation are using excimer lasers which are relatively costly. Cost effectiveness of laser ablation technique using excimer laser is further reduced by the fact that one has to spend money periodically on the operation and maintenance of such a laser. It is therefore desirable that the deposition of the films of 123, with comparable superconducting properties to single crystals can be achieved using a Nd - YAG laser which is much cheaper and also relatively safe.

The setup used by us for preparing thin films of high T_c material is shown in figure 2.4 [67]. Plasma is generated by laser ablation of a $GdBa_2Cu_3O_7$ target using a 1.06μm laser beam from a Q - switched Nd - YAG laser (10ns pulse width at 10Hz repetition rate). The pulsed Nd - YAG laser system used in this setup (Quanta - Ray DCR - 11) has an unstable diffraction coupled resonator. It gives uniphase, nearly diffraction limited output having a line width $<1cm^{-1}$ with 220MHz spacing between the longitudinal modes. The target material is capable of rotation

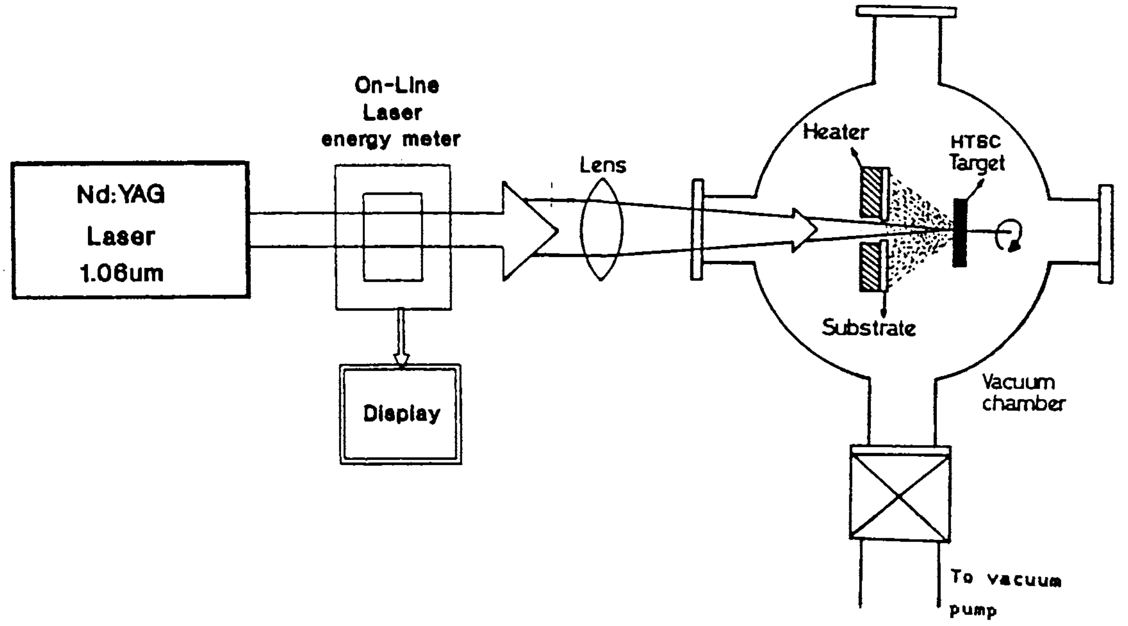


Fig.2.4. Schematic diagram of the setup for the deposition of thin superconducting films by laser ablation.

ide the chamber with the help of a small motor. The whole set is enclosed in a stainless steel vacuum chamber equipped with rtz windows so that the target can be irradiated at normal idence and the plasma ejected from the surface can be viewed right angles. The laser beam was focussed (power density – ^{9}W/cm^{2}) onto the target using a quartz lens. The substrates e mounted inclined to the incident beam close to the target erial.

The plot of resistivity versus temperature and susceptibility sus temperature of the thin film of GdBaCuO HTSC material are en in figures 2.5 and 2.6. The critical current (J_c) values ained for these films are also given in chapter 6, table 6.1.

Electrical properties of polycrystalline superconducting films ends upon the ratio of superconducting to non superconducting ins, the nature of the associated percolation network and the neling features of the junctions formed between the grains]. The transport properties especially the J_c of laser ablated CuO thin films on $SrTiO_3$ substrates (grown at 550 – 600°C in presence of oxygen plasma) show comparable values to that of gle crystals [69,70].

Laser ablation is an excellent technique for patterning high thin films and that it has number of advantages over other hniques. It is a clean dry process that does not require anic solvents. In addition to that, it is quick, extremely xible and offers the best spatial resolution without radation in the transition temperature [72].

MELT – TEXTURED GROWTH

One of the innovations made in improving the transport perties especially J_c of ceramic high T_c compounds is by a cessing technique called the melt – textured growth. In this hnique the synthesising range of temperatures vary from 1050°C

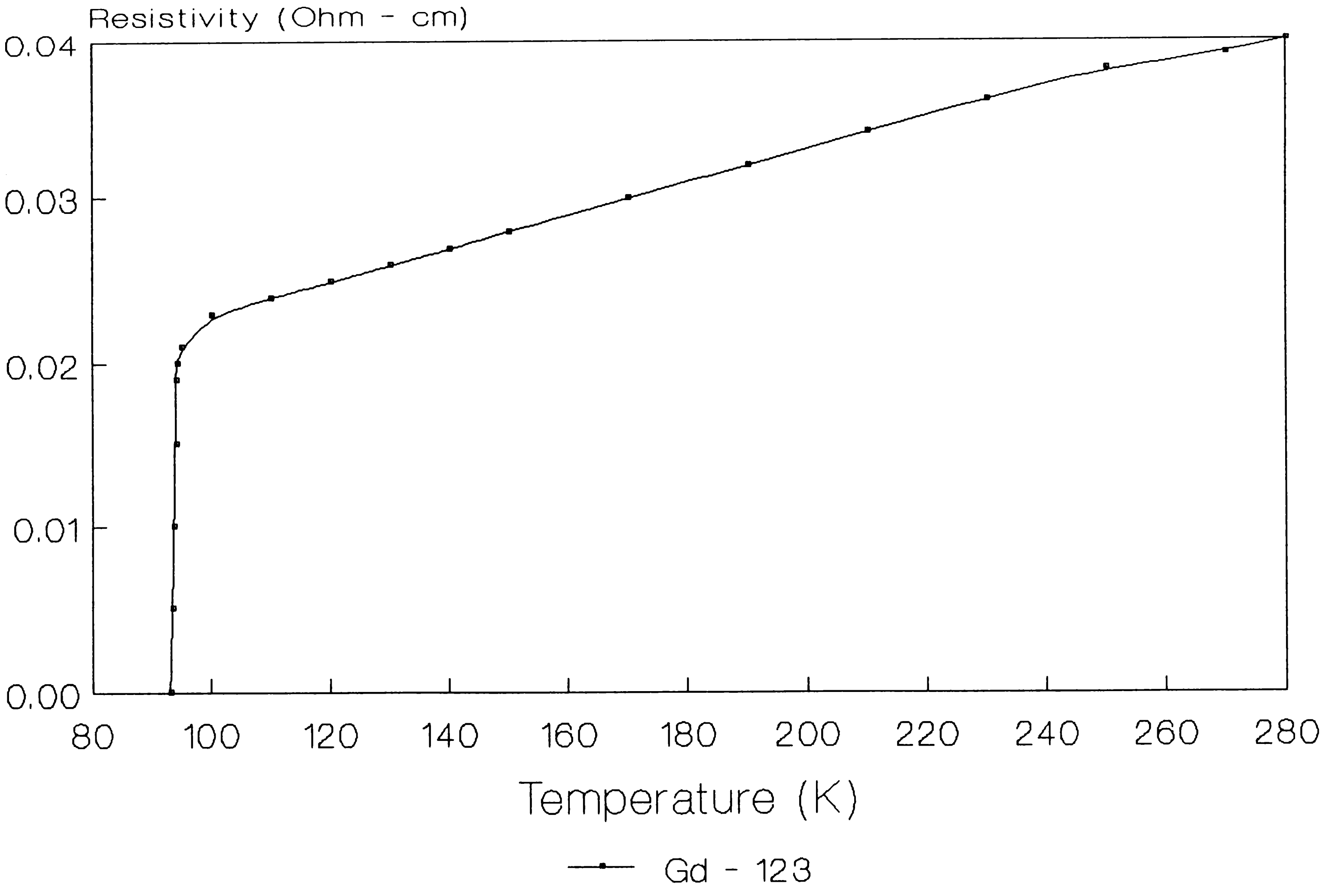


Fig. 2.5. Plot of Resistance versus temperature for the HTSC thin film of $GdBa_2Cu_9O_{7-\delta}$ prepared by laser ablation.

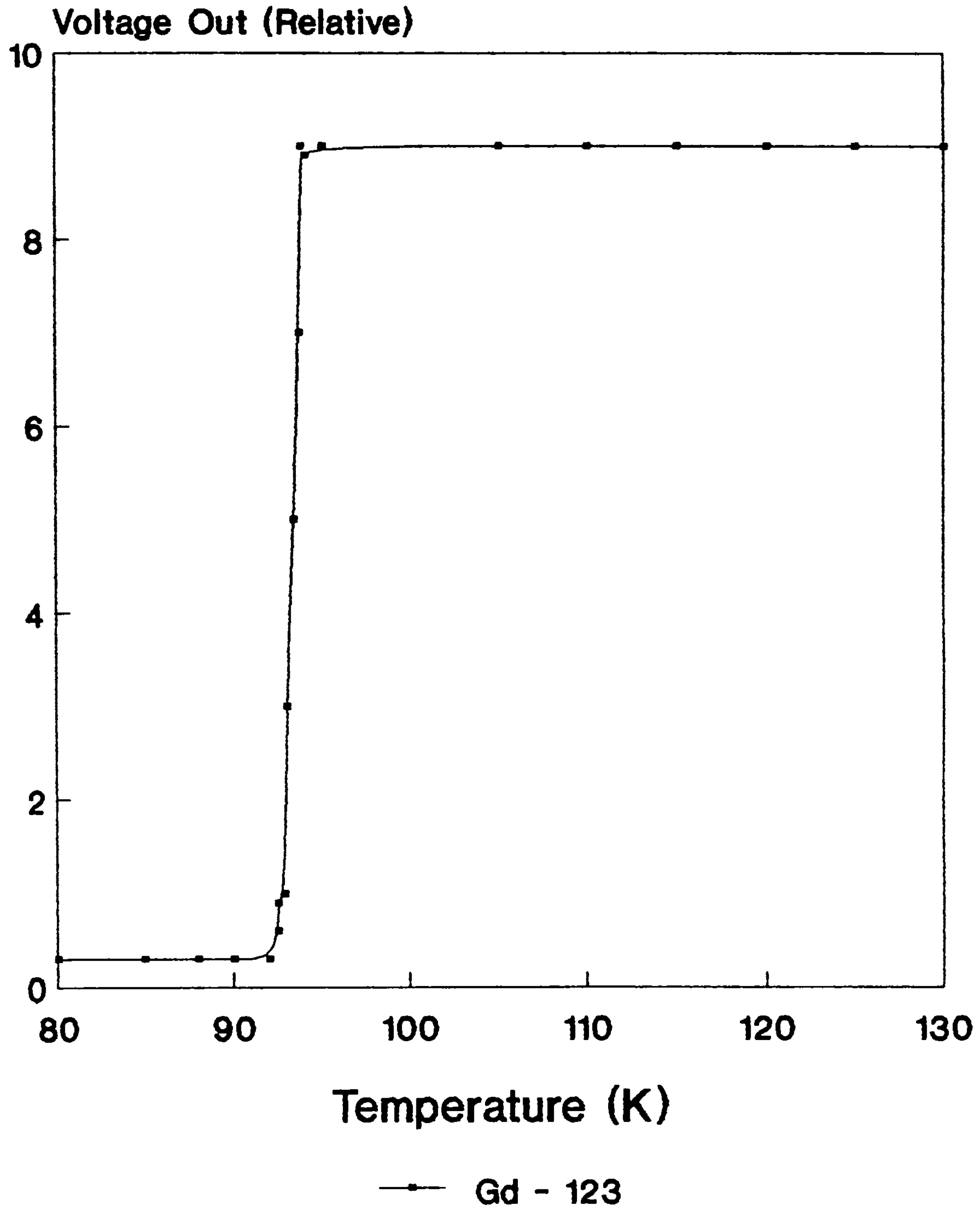


Fig. 2.6. Magnetic measurements (susceptibility) on the HTSC thin film of $GdBa_2Cu_3O_{7-\delta}$ prepared by laser ablation.

to 1200°C in the case of $YBa_2Cu_3O_x$ for production of a liquid + solid phase, and then to 1320°C for a single phase liquid [73]. This material is then held at this temperature levels for periods ranging from 30 seconds to as long as two hours, then cooled to room temperature at the rate of approximately 50°C/min. During this process, needle - like crystals are formed, compared to porous, granular structures with randomly oriented grains as formed in conventional sintering techniques.

The melt - textured structure in contrast to the former, is virtually 100% of theoretical density and exhibits locally textured structures that have the appearance of needles with radii of 2 to 5 mm and lengths upto 600mm. The value of critical current (J_c at 77K) is $\gtrsim$ 7400A/cm^2, more than an order of magnitude higher than typical sintered samples. In the presence of a magnetic field (1T), the J_c remains in the order of 1000A/cm^2, while the value for sintered materials drops to 1A/cm^2 or less.

Scanning electron microscopy (SEM) analysis of the surface of the conventional sintered $YBa_2Cu_3O_x$ exhibits a porous, granular structure with randomly oriented grains that have dimensions of the order of 5μm, with a density that is only $\sim$ 90% of the theoretical maximum.

2.5. MEASUREMENT OF RESISTIVITY AND SUSCEPTIBILITY OF SUPERCONDUCTING MATERIALS

2.5.a. Introduction

A superconductor shows vanishing resistance and pronounced diamagnetic property below a characteristic temperature called the transition temperature T_c.

Immediately after sample preparation, one generally checks its quality as a superconductor. The initial step is the four - probe resistivity check to determine whether it superconducts, and at what temperature it transforms into the superconducting state. A sharp high T_c transition is an indicator of high quality sample. Another widely used quality control method is the determination of the magnetic susceptibility of the specimen. Good quality is indicated by a sharp, high transition with both the flux exclusion and flux expulsion close to $-1/4\pi$. This is, in a sense, a more fundamental check on quality since the value of the susceptibility far below the transition temperature is a good indicator of the fraction of the sample that is superconducting. Zero dc resistivity is of course impossible to measure in an absolute sense. On the other hand the measurement of susceptibility is a better thermodynamic indicator of the superconducting state because magnetisation is a thermodynamic state variable. Moreover filamentary paths produce sharp drops in resistivity at higher temperatures than pronounced onsets of diamagnetism.

The critical temperature T_c is by convention defined for zero value of applied magnetic field. If the transition region is narrow, T_c is then the transition temperature. However, most of the copper oxide superconductors exhibit transitions of a large width, therefore one has to define onset temperatures, temperature for zero resistivity, and finally T_c itself. T_c is defined as the temperature where the resistivity has decreased to half its value at the onset temperature T_{co}. T_{co} is defined as the level where the R vs T curve just departs from the normal to superconducting behaviour (see figure 2.7). If the DC resistivity at T_{co} is ρ_o, the DC resistivity at T_c is then $\rho_o/2$. Another parameter T_{cf} is defined as the highest temperature where the material is considered to be fully superconducting (DC resistivity equals zero). Similarly the transition width (ΔT_c) is defined as the temperature range where resistivity varies between 10% and 90% of ρ_o. Therefore $\Delta T_c = T_{co} - T_{cf}$. In copper oxide superconductors ΔT_c is typically of the order of 2 - 10 K.

2.5.b. Resistivity measurement

A measure of resistance R(T) or resistivity $\rho(T)$ of a material

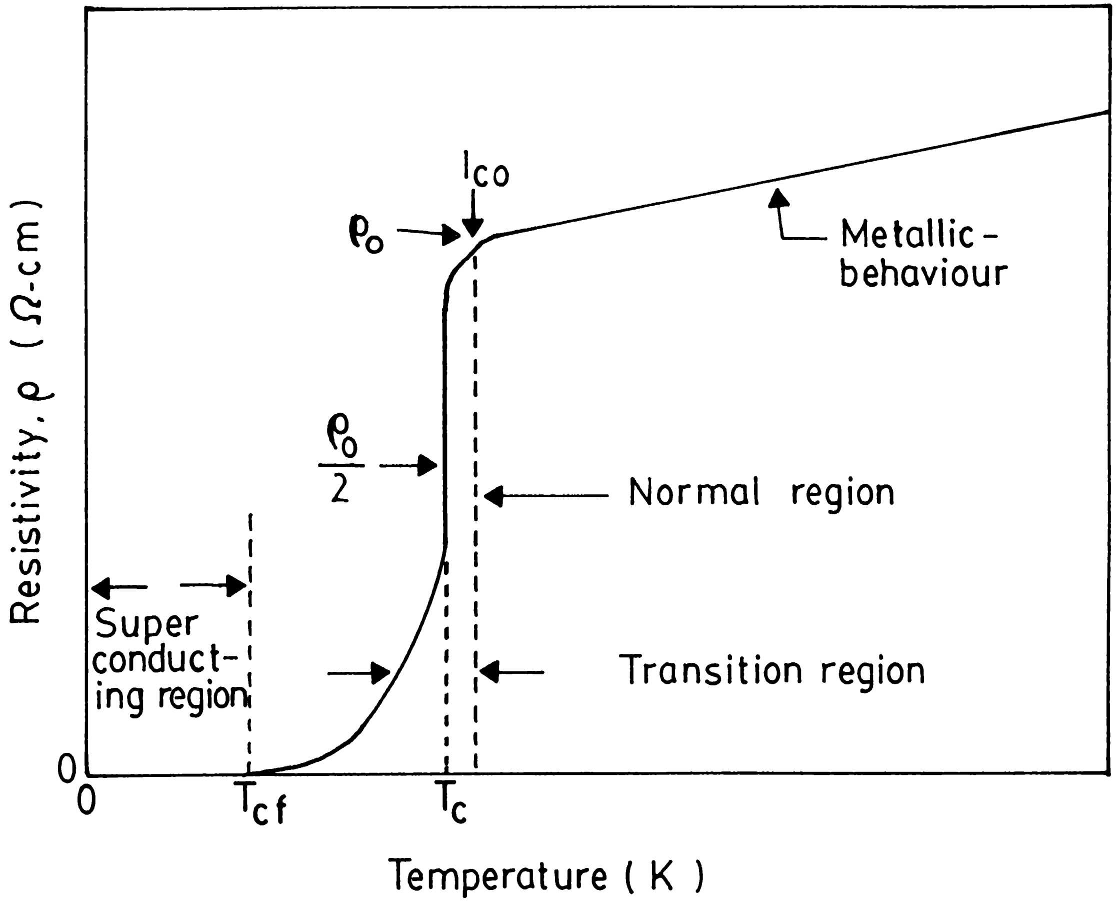


Fig. 2.7. Resistivity versus temperature curve for a typical superconductor illustrating the various regions.

as a function of the temperature is the principle technique employed to determine when a material becomes superconducting. The transition temperature manifests itself by a sharp drop in resistivity to zero. The simplest way to make this measurement is to apply a voltage across a sample and measure the current flow through it. But such a two - probe method [74] is not very satisfactory and is seldom used. Most resistivity determinations are made with the four - probe to be described below, although more sophisticated arrangements like six - probe method can also be used [75]. The fabrication of low resistance contacts by silver glazing has been reported [76]. These researchers pointed out the importance of the low - contact resistance ($\rho < \mu$ohms /cm).

The underlying principle behind the resistivity measurements is described in figure 2.8a. Four electrodes (four probe arrangement) are arranged in the form of a rectangle on top of the sample surface which has an arbitrary shape. The distance between contacts AB is a and that between BC is b. The thickness of the pellet is c and is assumed to be less than or of the order of $0.2(ab)^{1/2}$. A constant current is sent through AB and the resulting potential difference is measured across CD. The ratio between the two is noted. Now the leads are interchanged and the resulting ratio is again noted. Let us assume it to be denoted as R_1 and R_2.

The theory of calculating resistivity from R_1 and R_2 is given by Montgomery [77] and others [78]. He considered a rectangular pellet of length a′, width b′ and thickness c′. The resistivity is given by

$$\rho = HER_1. \qquad (2.1)$$

where H is a geometric parameter which is a function of (b/a), E is an effective thickness. If E is plotted against c a curve results which depend on (b/a). But for $c/(ab)^{1/2} < 0.3$, E does not depend on (b/a) significantly.

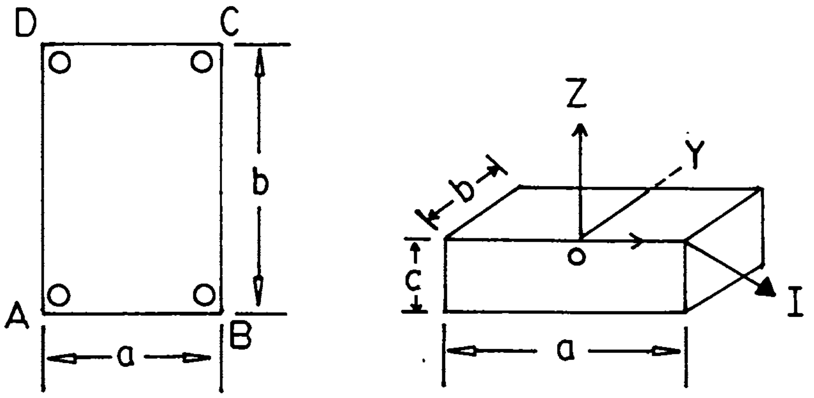


Fig. 2.8.a. Configuration of the sample for the measurement of of electrical resistivity.

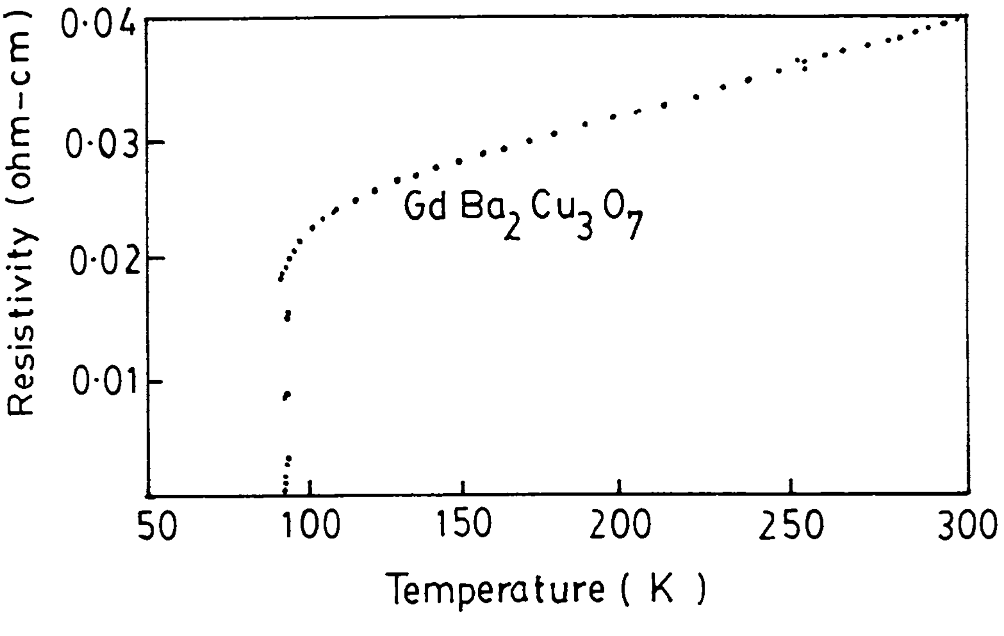


Fig. 2.8.b. A typical resistivity curve obtained for $GdBa_2Cu_3O_{7-\delta}$.

For a pellet of irregular shape but uniform thickness, an effective value for (b′/a′) can be obtained from the ratio of (R_2/R_1). Montgomery gives a graph of (R_2/R_1) as a function of (b/a). This graph is insensitive to the actual thickness of the sample. So from measurements of (R_2/R_1), the effective (b′/a′) value is obtained. Then the value of the effective thickness E and the geometric factor H are determined from this value of (b′/a′). This is used in the equation (2.1) to determine ρ. A typical curve for $GdBa_2Cu_3O_{7-\delta}$ is shown in fig. 2.8b.

2.5.c. Susceptibility measurements

There is a variety of methods for the determination of magnetic susceptibility χ. It can be broadly classified into two categories *viz.* the AC and DC measurements. The outline and principle of an AC susceptometer is illustrated in figure 2.9. The AC oscillator drives a pair of field coils, one of which encloses the superconductor and the reference input of the lock-in amplifier. The coils are wound in such a way that the induced fields are opposite and therefore the net output voltage from the sensing coil is zero. The compensation coil helps to achieve this. As the sample is cooled and superconducts, flux expulsion takes place or it exhibits diamagnetism. This will unbalance the coils and therefore a voltage appears at the input of the lock-in amplifier. A close monitoring of the phase will reveal that a difference of 90^o exists with respect to the reference. This negative phase shift denotes that the material is perfectly diamagnetic. From the amplitude of the detected signal one can determine the magnetisation taking place in the sample. The amplitude also is proportional to the volume of the sample. The susceptometer is initially calibrated with a specified volume of a known sample (eg. paramagnetic : copper sulphate).

The dc susceptibility technique is also sometimes used [79,80]. The underlying principle is the "Guoy balance method" (fig.2.10). In this approach, the superconducting material is

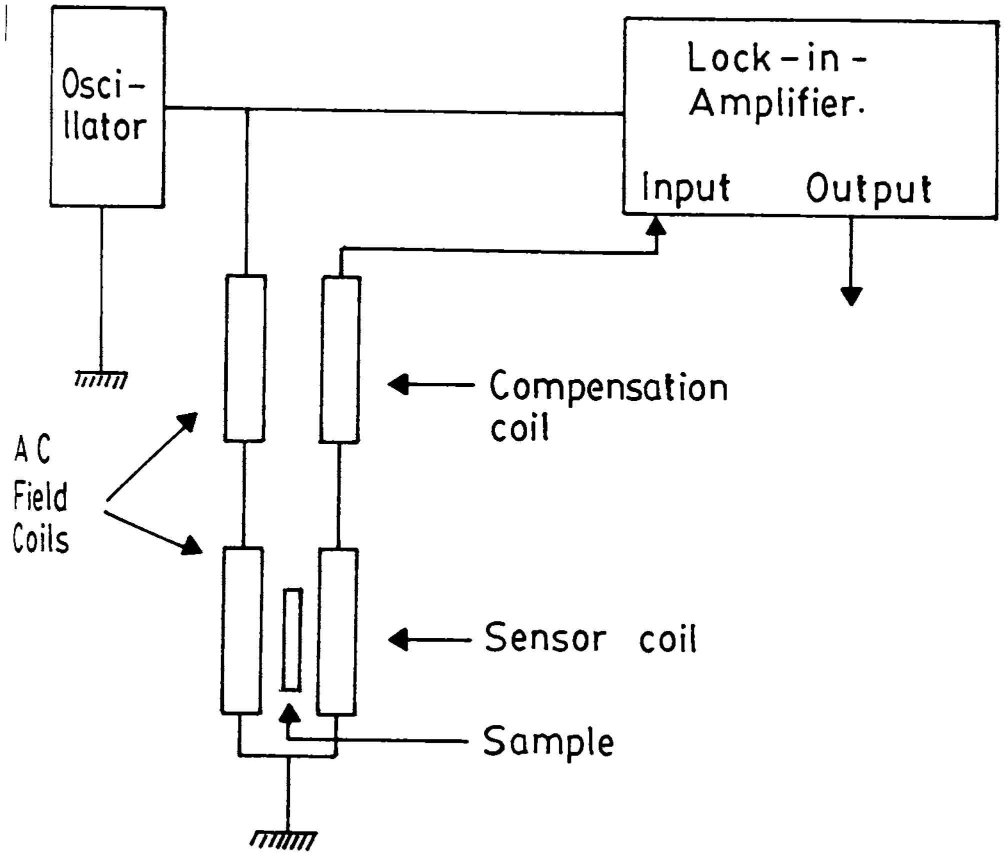


Fig. 2.9. Schematic diagram of the ac susceptometer.

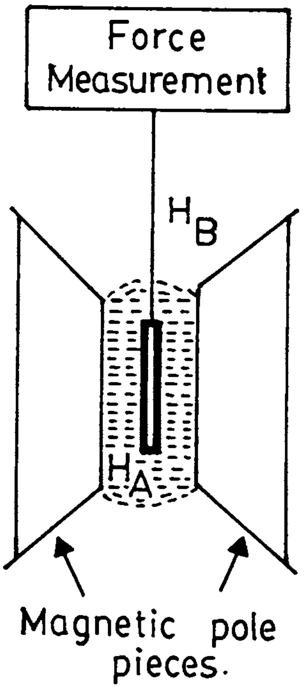


Fig. 2.10. Schematic diagram of the dc susceptometer.

suspended in a nonhomogenous magnetic field.

A relationship connecting force (F), field (H), and magnetization (M) can be written as

$$F = \frac{1}{2} \chi A \int \frac{d}{dy} (H_y^2) \, dy = \frac{1}{2} \chi A (H_a^2 - H_b^2) \qquad (2.2)$$

where χ = M/H and V is the volume and the fields at each end of the sample are H_a and H_b respectively, varying only along the Y axis of the sample having a constant cross section A.

Susceptibility may then be determined from the force produced in a field of known gradient :-

$$\chi = \frac{2F}{A (H_a^2 - H_b^2)} \qquad (2.3)$$

A sensitive vibrating sample magnetometer (VSM) capable of carrying out rapid sample measurements (100s for a complete hysteresis loop over ±10 kOe) is described in the literature [81]. The working principle of this improved VSM can be briefly described as follows: The superconducting sample is mounted on to the tip of cantilevered rod which includes a piezoelectric transducer. This transducer monitors the sample deflection. This improvement over conventional VSMs (in which a sensor coil is used and therefore affected by magnetic fields) gives the high sensitivity ($\simeq 10^{-8}$emu). The superconducting sample is magnetised by a variable dc field. It is also exposed to a smaller alternating field gradient. The alternating force on the sample (due to the alternating gradient) is proportional both to the magnetic moment of the superconducting specimen and to the magnitude of the alternating field. The alternating field is operated very near the resonant frequency of the cantilever rod (100 - 1000Hz); this increases the sensitivity considerably. Mechanical Q of the system is on the order of 25 - 250. Investigators report that the signal to noise ratio is of the order of 500, for measurements made on a 25μm diameter sphere that has a moment of 3.7×10^{-6} emu.

Fast measurements can be carried out compared to the squid magnetometer since the latter generate only point by point data.

.6. REFERENCES

1] E A Early, R L Seaman, K N Yang and M B Maple, Am. J. Phys., July, (1988).

2] J Monecke, Phys. Stat. Solidi., 143, K43, (1987).

3] J J Nuemeier, Y Dalichaouch, J M Ferreira, R R Hake, B W Lee, M B Maple, M S Torikachvilli, K N Yang and H Zhou, Appl. Phys. Lett., 51, 371, (1987).

4] C Allgeier, J S Schilling and E Amberger, Phys. Rev. B, 35, 8791, (1987).

5] M Hirabayashi, H Ihara, N Terada, K Senzaki, K Hayashi, S Waki, K Murata, M Tokumoto and Y Kimora, Jpn. J. Appl. Phys., 26, L454, (1987).

6] I K Gopalakrishnan, J V Yakhmi, M A Vaidya and R M Iyer, Appl. Phys. Lett., 51, 1367, (1987).

7] S M Fine, M Greenblatt, S Simizu and S A Friedberg, Phys. Rev. B, 36, 5716, (1987).

8] W G Gallagher, R L Sandstorm, T R Dinger, T M Shaw and D A Chance, Sol. St. Commun., 63, 147, (1987).

9] J J Rhyni, D A Neuman, J A Gotaas, F Beech, L E Toth, S Lawrence, S Wolf, M Osofsky and D U Gubser, Phys. Rev. B, 36, 2294, (1987).

10] D U Gubser, R A Hein, S H Lawrence, M S Osofsky, D J Schrodt, L E Toth and S A Wolf, Phys. Rev. B, 35, 5350, (1987).

11] T Hatano, A Matusushita, K Nakamura, K Honda, T Matsumoto and K Ogawa, Jpn. J Appl. Phys., 26, L374, (1987).

[12] R Herrmann, N Kubicki, T Schurig, H Dwelk, U Preppernau, A Krapf, H Kruger, H U Muller, L Rothkirch, W Kraak, W Braune, N Pruss, G Nachtwei, F Ludwig and E Kemnitz, Phys. Stat. Sol. B., 142K, 53, (1987).

[13] S Hikama, T Hirai and S Kagoshima, Jpn. J .Appl. Phys., 26, 314, (1987).

[14] B Jayaram, S K Agarwal, A Gupta and A V Narlikar, Sol. St. Commun., 63, 713, (1987).

[15] Y Maeno, M Kato and T Fujita, Jpn. J. Appl. Phys., 20, L329, (1987).

[16] L E Toth, M S Osofsky, S A Wolf, E F Skelton, S B Quadri, W W Fuller, D U Gubser, J Wallace, C S Pende, A K Singh, S Lawrence, W T Elam, B Bender and J R Spann, ACS Symp., P228, (1987).

[17] A R Moodenbaugh, J J Hurst, Jr., R H Jones and M Suenaga, M R S Anaheim Symposium, P101, (1987).

[18] A R Moodenbaugh, J J Hurst, T Asano, R L Sabatini and M Suenaga, Novel SC., 767, (1987).

[19] R B Poeppel, B K Flandermeyer, J T Dusek and L D Bloom, ACS Symposium, P261, (1987).

[20] E Pollert, J Hejtmanek and D Zemanova, Czech, J. Appl. Phys., 37, 655, (1987).

[21] S B Qadri, L E Toth, M Osofsky, S Lawrence, D U Gubser and S A Wolf, Phys. Rev. B, 35, 7235, (1987).

[22] J Ruzicka, T Tethal, J Pracharova, V Gregor and S Safrata,

Czech. J. Phys., 37, 653, (1987).

[23] Y Saito, T. Noji, A Endo, N Matsuzaki, M Katsumata and N Higuchi, Jpn. J. Appl. Phys., 26, L491, (1987).

[24] Y Saito, T. Noji, A Endo, N Matsuzaki, M Katsumata and N Higuchi, Jpn. J. Appl. Phys., 26, L366, (1987).

[25] H Sawada, Iwazagni, Y Saito, Y Abe, H Ikeda and R Yoshizaki, Jpn. J. Appl. Phys., 26, L1054, (1987).

[26] S I Shamoto, S Hosoya, M Onada and M Sato, Jpn. J. Appl. Phys., 26, 493, (1987).

[27] K Takita, T Ipposhi, T Uchino, T Gochou and Masuda, Jpn. J. Appl. Phys., 26, L506, (1987).

[28] P T Wu, J H Kung, A K Li, C C Kao, C M Wang, L Chang, H H Yen, S C Tsai, G F Chi, M F Tai and H C Ku, MRS Anaheim Symp., P197, (1987).

[29] C W Chu, P H Hor, R L Meng, L Gao, Z J Huang and Y Q Wang, Phys. Rev. Lett., 58, 405, (1987).

[30] M M Garland, Appl. Phys. Lett., 51, 1030, (1987).

[31] V Hajko, Jr, P Diko, K Csach and S Molokac, Czech. J. Phys. B., 37, 1205, (1987).

[32] P V P S S Sastry, J V Yakhmi and R M Iyer, Sol. St Commun., 71, 935, (1989).

[33] P V P S S Sastry, I K Gopalakrishnan, A Sequeira, H Rajagopal, K Gangadharan, G M Pathak and R M Iyer, Physica C, 156, 230, (1988).

[34] Asok K Sarkar, Binod Kumar, I Maartense and T L Peterson, J. Appl. Phys., 65, 2392, (1989).

[35] Rong - Xing Wan, Guo - Meng Zhao, Xiao - ming Tang, Wen - Zhou Li, Shi - Zhao Hu and Hon - nian Yao, J. Appl. Phys., 64, 3754, (1988).

[36] T L Aselage, B C Bunker, D H Doughty, M O Eatough, W F Hammetter, K D Keefer, R E Loehman, B Morosin, E L Venturini and J A Voigt, MRS Anaheim Symp., P157, (1987).

[37] J G Bednorz and K A Muller , Z. Phys. B, 64, 189, (1986).

[38] S I Lee, J P Golben, Y Song, X D Chen, R D McMichae and J R Gaines, ACS Symp., P272, (1987).

[39] X Z Wang, M Henry, J Livage and I Rosenman, Sol. St. Commun., 64, 881, (1987).

[40] Michael Schwartz, Michael Rappaport, Gary Hodes and David Cahen, Physica C , 153, 155, 1457, (1988).

[41] A Manthiram and J B Goodenough, Nature, 329, 701, (1987).

[42] M Strasik and N G Eror, MRS Boston Symp., Abstract AA 41, (1987).

[43] Z Z Sheng, and A M Hermann, Nature, 332, 55, (1988).

[44] Z Z Sheng, W Kiehl, J Bennett, A El Ali, D Marsh, G D Mooney, F Arammash, J Smith, D Viar and A M Hermann, Appl. Phys. Lett., 52, 1738, (1988).

[45] D S Ginley, E L Venturini, J F Kwak, R J Baughman, M J Carr, P F Hlava, J E Schirder and B Morosin, Physica C, 152, 217, (1988).

[46] S S P Parkin, V Y Lee, A I Nazzal, T C Huang, G Gorman, R Savoy and R Beyers, Phys. Rev. Lett., 60, 2539, (1988).

[47] M Kikuchi, T Kajitani, T Suzuki, S Nakajima, K Hiraga, N Kobayashi, H Iwasaki, Y Syono and Y Muto, Jap. J. Appl. Phys., 28, L382, (1989).

[48] A Sequeira, H Rajagopal, I K Gopalakrishanan, P V P S S Sastry, G M Pathak, J V Yakhmi and R M Iyer, Physica C, 156, 599, (1988).

[49] R M Hazen, L W Finger, R J angel, C T prewitt, N L Ross, C G Hadidiacos, P J Heaney, D R Veblen, Z Z Sheng, El Ali and A M Hermann, Phys. Rev. Lett., 60, 1657, (1988).

[50] D E Cox, C C Toradi, M A Subramanian, J Gopalakrishnan and A W Sleight, Phys. Rev. B, 38, 6624, (1988).

[51] S X Dou, H K Liu, A J Bourdillon, N X Tan, N Savvides, C Andrikidis, R B Roberts and C C Sorrell, Supercond. Sci. Technol., 1, 83, (1988).

[52] R M Iyer and J V Yakhmi, "Studies of high temperature superconductors", (Ed.) A V Narlikar, (Nova Science Pub. N.Y.), (1989).

[53] I K Gopalakrishnan, P V P S S Sastry, K Gangadharan, J V Yakhmi and G M Phatak and R M Iyer, Appl. Phys. Lett., 53, 414, (1988).

[54] J Frohlingsdorf , W Zander and B Stritzker, Sol. St. Commun., 67, 965, (1988).

[55] D Dikkjamp, T Venkatesan, X D Wu, S A Shaheen, N Jisrawi, Y H Min-Lee, W L McLean and M Croft, Appl. Phys. Lett., 51, 619, (1987).

[56] K Moorjani, J Bohandy, F J Adrian, B F Kim, R D Shull, C K Chiang, L J Swartzendruber and L H Bennet, Phys. Rev. B, 36, 4036, (1987).

[57] L Lynds, B R Weinberger and T W Grudkowski, Appl. Phys. Lett., 52, 320, (1988).

[58] M Naito, R H Hammond, B Oh, M R Hahn, J W P Hsu, P Rosenthal, A F Marshal, M R Beasley, T H Geballe and A Kapitulink, J. Mater. Res., 2, 713, (1987).

[59] B Roas, L Schultz and G Endres, Appl. Phys. Lett., 53, 1557, (1988).

[60] T Venkatesan, X D Wu, A Inam, Y Jeon, M Croft, E W Chase, C C Chang, J B Wachtman, R W Odom, F Radicati di Brozolo and C A Magee, Appl. Phys. Lett., 54, 581, (1989).

[61] A Hoffman, Supercond. Sci.Technol., 3, 395, (1990).

[62] E Fogarassy, C Fuchs, P Siffert, J Perriere, X Z Wang and F Rochet, Sol. St. Commun., 67, 975, (1988).

[63] Wayne a Weimer, Appl. Phys. Lett., 52, 979, (1980).

[64] H S Kwok, P Mattocks, L Shi, X W Wang, S Witanachi, Q Y Ying, J P Zheng and D T Shaw, Appl. Phys. Lett., 52, 1825, (1988).

[65] O Aucilleo , S Athavale, O E Hankins, M Sito, A F Schreiner and N Biunno, Appl. Phys. Lett., 53, 72, (1988).

[66] G Koren, A Gupta, E A Giess, A Segmuller and R B Laibowitz, Appl. Phys. Lett., 54, 1054, (1989).

[67] G Padmaja, A V Ravikumar, V Vidyalal, P Radhakrishnan, V P N Nampoori and C P G Vallabhan, J. Phys. D : Appl. Phys., 22, 1558, (1989).

[68] D S Misra and S B Palmer, J. Appl. Phys., 68, 1403, (1990).

[69] R K Singh, J Narayan, A K Singh and Krishnaswamy, Appl. Phys. Lett., 54, 2271, (1989).

[70] S Witanachchi, S Patel, D T Shaw and H S Kwok, Appl. Phys. Lett., 54, 295, (1989).

[71] G B Shinn, F Steigerwald, H Stiegler, R Saurebrey, F K Tikkel and W L Wilson jr, J. Vac. Sci. Technol., 4, 1273, (1986).

[72] J Mannhart, M Scheuermann, C C Tsuei, M M Oprysko. C C Chi, C P Umbach, R H Koch and C Miller, Appl. Phys. Lett., 52, 1271, (1988).

[73] S Jin, T H Tiefel, R C Sherwood, R B van Dover, M E Davis, G W Kammoltt and R A Fastnacht, Phys. Rev. B, 37, 7850, (1988).

[74] J Baszynski, Phys. Lett. A, 123, 31, (1987).

[75] I Kirschner, J Bankuti, M Gäl, K Torkos, K G Solymos and G Horvath, Europhys. Lett., 3, 1309, (1987).

[76] J van der Maas, V A Gasparov and D Pavuna, Nature, 328, 603, (1987).

[77] H C Montgomery, J. Appl. Phys., 42, 2971, (1971).

[78] Daniel W Koon, Rev. Sci. Instrum., 60, 271, (1989).

[79] Abrahams E and F Keffer, McGraw - Hill Encyclopedia of Science and technology, (McGraw - Hill, New York), 13, 348, (1971).

[80] C Kittel, "Introduction to Solid State Physics", 4th ed, (John Wiley and Sons, New York), (1987).

[81] P J Flanders, J. Appl. Phys, 63, 3940, (1988).

CHAPTER 3

RESISTIVITY MEASUREMENTS IN HTSC MATERIALS

ABSTRACT

The instrumentation developed for the determination of resistivity of HTSC samples is described in this chapter. The details of design and development of a precision constant current source (based on easily available linear IC's and a precision voltage regulator) and a low temperature shielded cryostat which can be used for the measurement of DC and AC electrical conductivity over the temperature range 80 - 400K are outlined.

The importance of low frequency AC resistivity measurements are also discussed. Measurements were carried out on various forms of Gd - 123 viz. laser ablated thin film, bulk materials and melt textured samples. The nature of conductivity in these materials is discussed.

3.1. A PRECISION CONSTANT CURRENT SOURCE FOR RESISTIVITY MEASUREMENTS IN HIGH T_c SUPERCONDUCTORS

3.1.a. Introduction

Resistivity measurements on high T_c superconductors are usually carried out using the four probe technique. This setup invariably requires a precision constant current source and an appropriate potential measuring instrument *viz.* a DC nanovoltmeter. The theory of the method of calculating the resistivity is described elsewhere [1-3]. A number of constant current circuits are described in the literature [4-6]. Most of the circuits are fairly complex and often employ MOSFET devices and high power transistors which are not commonly available.

In this chapter we describe the design and fabrication of a precision DC constant current source which is simple, inexpensive and very useful to material scientists who are engaged in resistance measurements of superconducting samples. This current source is also very reliable as proved by the fact that the same has been used extensively for measurements of high T_C superconductors for the past couple of years in our laboratory. Alternatively it can also be used to transfer measurands over long leads (4 wire measurements) without affecting the measurements when the resistance of the leads is part of the current loop. Electrical characteristics of devices which are sensitive to intrinsic power supply transients can be determined using this current source along with supporting instruments. Constant current sources are also required for meter drives and process control instrumentation.

A good DC constant current source should have the following features :- 1) It should possess very low unwanted ripple and minimum intrinsic noise (since voltages of interest in the measurement of transition temperature in superconducting material range from 1nV-1μV). 2) It should not introduce ground loops or extraneous signals into the system. 3) It should have very low current drift with temperature and time. 4) linear response to input voltage settings 5) Fast turn on and 6) It should be simple, inexpensive and easy to fabricate. The circuit presented in this chapter attempts to incorporate most of the above features.

3.1.b. Circuit description / Design

The circuit diagram of the constant current source is shown in fig. 3.1. It can be conveniently divided into four parts:-

1) DC voltage source:-

The main function of this source is to provide highly stable, programmable multiple output voltages. It should have low drift, good line rejection, low output impedance, low noise, fast turn on with minimum warm up time, and very low temperature coefficient. A commercially available IC AD 584 [7] closely matching the above specifications to a good extent is selected. It has 4 programmable output voltages. These outputs when selected, finally determine the output current. The fast settling time of IC1 enables one to make immediate measurements as soon as the power is switched on. Capacitor C_1 is used primarily for noise reduction.

2) Voltage to current converter:-

This stage (a combination of 3 Op-amps and a transistor) compares the input with the feedback signal from the transistor and maintains a constant current [8]. A constant voltage is fed to Op-amp IC2 (AD707) [9] configured as a buffer. It provides a high input impedance to the source and a low output impedance to Op-amp IC3 (1/2 AD708) [10]. This arrangement avoids loading of the source.

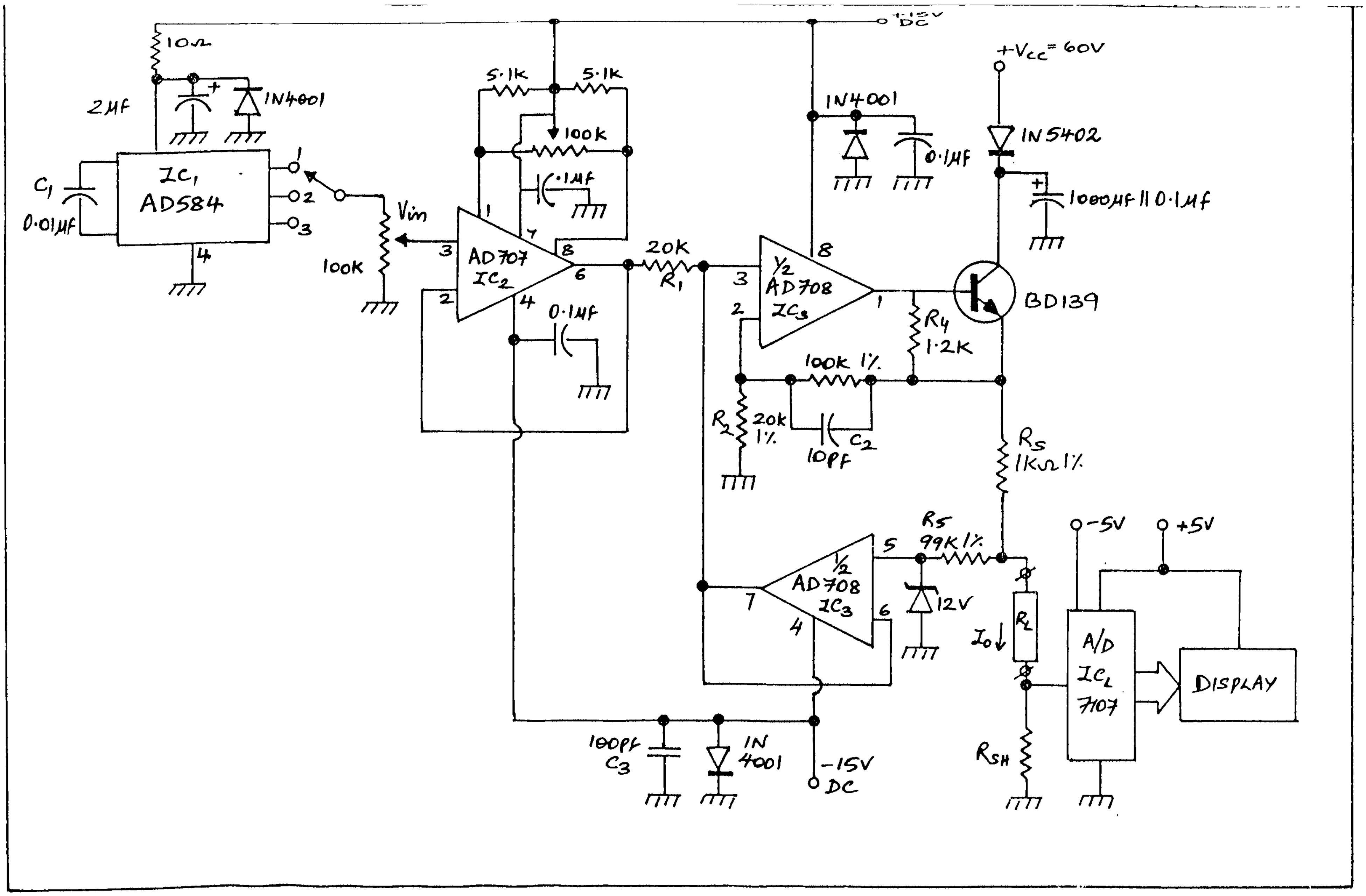


Fig. 3.1. Circuit diagram of the constant current source.

Photograph of the constant current source.

By Ohm's law the constant current I_o can be related to output voltage V_o and the current sensing resistor R_s by the relation

$$I_o = V_o / R_s \qquad (3.1)$$

Therefore a constant output voltage amplifier producing an output of V_o and a sampling resistor (R_s) is all that is required for a constant current source. Feedbacks from both sides of R_s is given back as input to Op-amp IC3 by a network comprising of R_5, Op-amp 4 (1/2 AD 708) and R_3. Any tendency for I_o to change will be counteracted by a change in V_o which results in a correction and therefore I_o is maintained a constant. Op-amp IC4 configured as a buffer provides a high input impedance and hence effects of R_5 on (R_s - R_L), and R_{sH} are minimum. The output current is given by

$$I_o = R_3 V_{in} / R_2 R_s \qquad (3.2)$$

if $R_1 = R_2$ and $R_3 = R_5 + R_s$. The maximum allowed load resistor for current to remain constant is

$$(V_{cc}/I_o) - R_s \qquad (3.3)$$

For a current of 10mA; $R_{L(max)}$ = 5K ohms. A trimming potentiometer is used along with IC2 to allow adjustments of the control circuit bias point. It removes the offset voltage of the op - amp to be produced in the output as a signal when the input is zero. It also sets the dead band point, without which an excess input voltage is required to produce significant output. Also it may be noted unlike certain commercial units the output current leads here have a rather low potential difference (<50V).

3) A to D convertor

Voltage drop across a suitable shunt resistor R_{SH} is taken and fed to a single chip A/D converter built around a single CMOS IC (ICL 7107)[11]. This IC directly drives a 3-1/2 digit LED display. It is a highly accurate, versatile and an economical circuit. Of course any A/D convertor can be used for this current indicator.

3.1.c. Operation and Performance of the Current Source

The observed performance of the circuit with respect to current drift, linearity and noise is as follows :-

Good linearity was observed on all current ranges. However, when the input is increased to more than 10V, slight deviations from the linearity was observed mainly due to the saturation of the inputs. Therefore, in our design the input voltage was limited to 10V.

For current drift measurements over a long period, a nominal level of 10mA was selected. After an initial warm up of 5 minutes both the input and the output currents were continuously recorded for a duration of 1hr. A drift of not more than ±0.06 % h^{-1} was observed. This test was repeated for various current values and loads up to 5K ohms. The above result was typical of all the tests. Noise measurements were conducted using constant loads at different current levels. At high load resistances (5K ohms) the highest ripple current of 6 μA was measured with I_o = 10mA. For superconductors, the ripple current was buried under the limits of our measurements. However, ripple currents and high frequency noise were minimized to a great extent by introducing capacitors C_1, C_2 and C_3.

To measure the resistivity, a current of 10mA from the constant current source was passed through the samples. The voltage drop of the order of 5μV depending on the resistance of the sample was measured on a nanovoltmeter (Keithley 181) after zeroing the nanovoltmeter by shorting its terminals. The current is reversed to check if the same voltage is recorded in the opposite direction. The difference was found to be not more than 10nV which may arise due to thermo-EMF's at various contacts. The current is then sent through the other two terminal and the measurements repeated.

The effectiveness and utility of the present design are demonstrated by making measurements on two types of high temperature superconductors namely $GdBa_2Cu_3O_{7-\delta}$ and $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_{y-\delta}$. The results of measurements are shown in fig 3.2. The transition to zero resistance is clearly seen in the above fig at 93K and 110K for $GdBa_2Cu_3O_{7-\delta}$ and $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_{y-\delta}$. respectively.

The flexibility of the present design makes it possible to alter or delete sections to suit different applications. For example, if one requires heavier currents for critical current measurements (J_c), the output transistor is to be replaced by a Darlington combination of suitable amperage. For isolated current measurements the mains supplies is to be replaced by appropriate battery powered voltage sources. This not only provides a very low - noise alternative but also makes the entire system portable.

3.2. METALLIC CRYOSTAT FOR ELECTRICAL MEASUREMENTS

Measurement of electrical resistivity of materials which are susceptible to moisture adsorption is to be carried out under vacuum conditions. It is observed that maintaining a dynamic vacuum in the sample cell helps to acquire reproducible data. Since the voltages of interest lie in the nanovolt region, a metallic cell provides good shielding and eliminates extraneous interfering electromagnetic noise is used.

For the above reasons it became necessary to use a specially

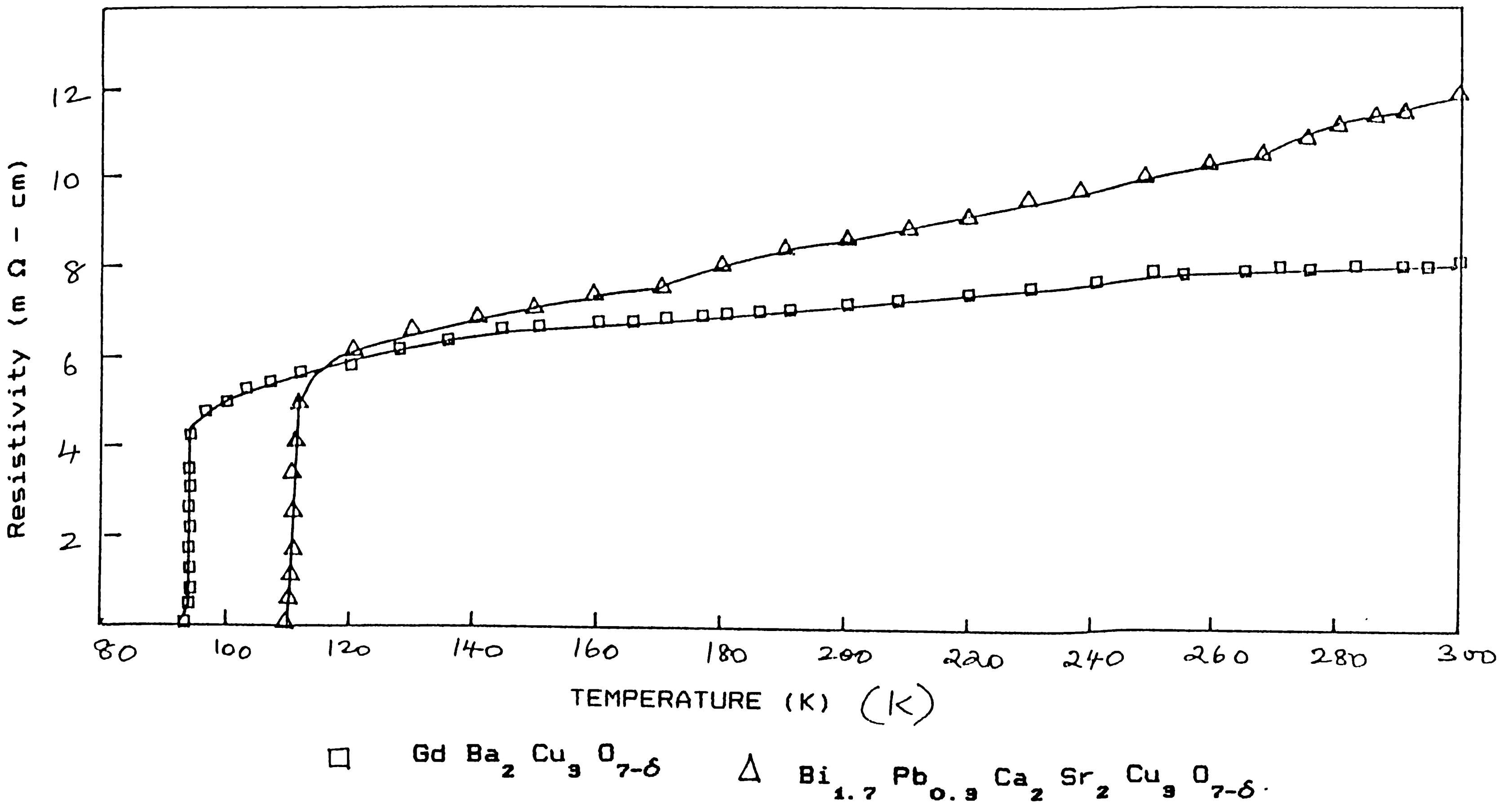


Fig. 3.2. Plot of resistivity versus temperature for $GdBa_2Cu_3O_{7-\delta}$ and $Bi_{1.7}Pb_{0.3}Ca_2Sr_2Cu_3O_{7-\delta}$ superconductors.

designed cell. The cell used here for resistivity measurements had the following features.

1) It could sustain a steady dynamic vacuum.

2) The measuring cell and leads were electromagnetically shielded with the body earthed.

3) It was capable of operating over a wide temperature range (80 - 400K) without disturbing the vacuum conditions.

4) Options for optical windows were provided to view the sample.

5) Lower consumption of liquid nitrogen (than in conventional, commercial cryostats) was made possible by virtue of the special design of the cold finger.

6) Both AC and DC electrical conductivity could be measured in the same cell with excellent sensitivity.

7) Easy sample mounting and setting up for rapid measurements were possible due to its simple design.

A schematic diagram of the variable temperature cell fabricated for the present study is shown in figure 3.3. The cell has a nickel plated MS body which acts as an EM shield. The ends of the MS cylinder are permanently fitted with MS flanges provided with grooves to accommodate neoprene O - rings for vacuum sealing. The top cover plate carries insulated electrical terminal leads for thermocouple, heater, and the four leads from the four probe. The terminals for output signal are routed through BNC connectors. The top cover carries a SS tube into which liquid nitrogen can be poured. It is filled at the bottom to a solid copper block which acts as a cold finger of dimensions 6 x 6 x 4cm. The four probes made of copper are embedded in a Teflon bush which is push fitted on to the copper block. This

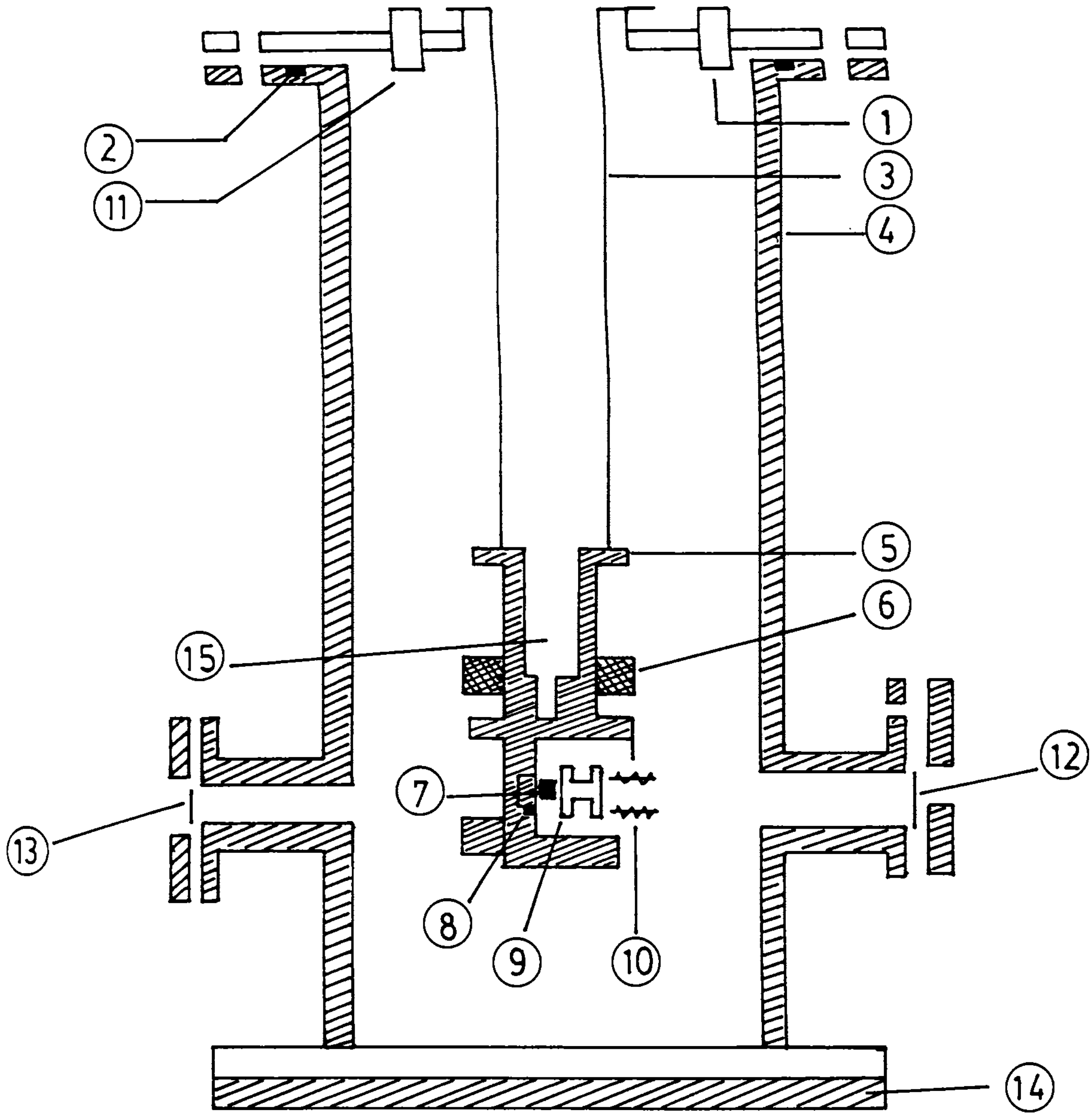
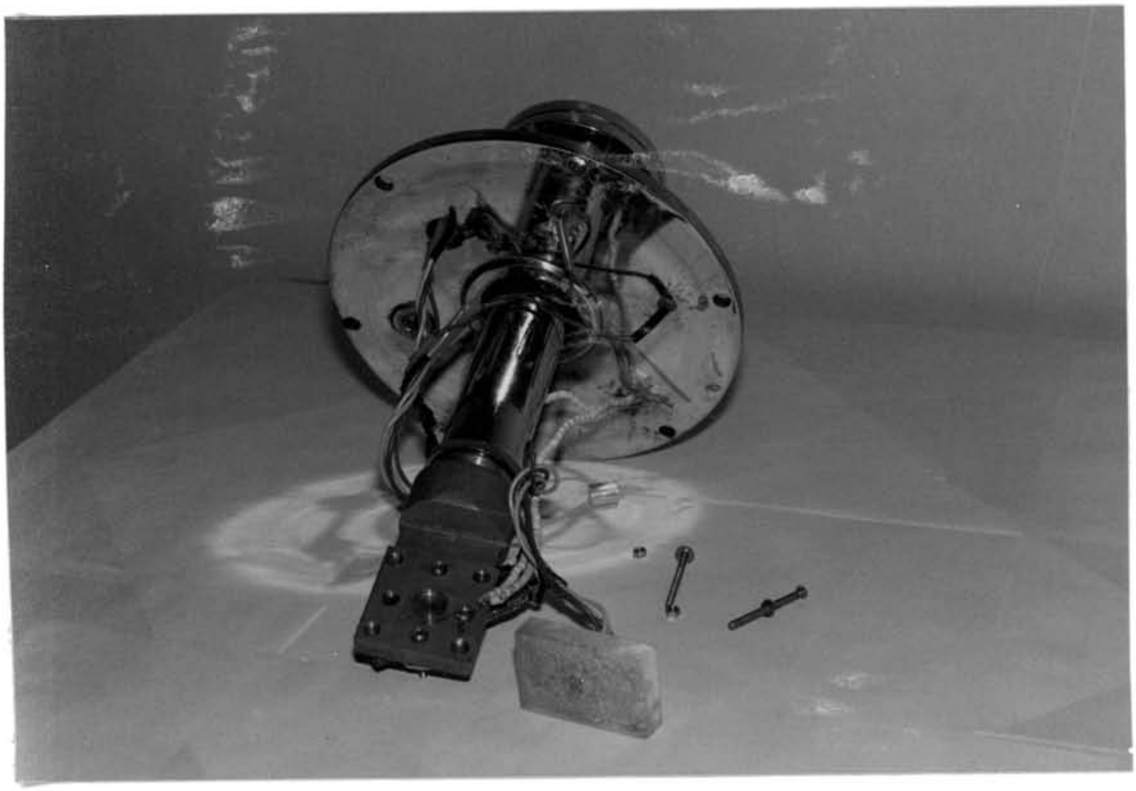


Fig. 3.3. Schematic diagram of the cryostat used for the measurement of electrical resistivity.

1) Terminal block for current and voltage leads 2) Neoprene O - ring 3) S S Tube 4) M S Body 5) Copper cold finger 6) heater block 7) Sample 8) Thermocouple 9) Electrodes 10) Spring loaded arrangement 11) Terminal block for thermocouple leads 12) View port 13) To vacuum pump 14) M S base plate.

Photograph of the experimental set - up used for the determination of electrical resistivity.



Exploded view of the low temperature cell used for resistivity measurements.

arrangement is bolted on to the cold finger and is spring loaded so that electrical contacts are always maintained irrespective of the temperature of the cold finger. A cartridge type electrical heater is attached to the cold finger. The heater is connected to a programmable power supply and a temperature controller.

3.3. AC ELECTRICAL RESISTIVITY OF COPPER OXIDE SUPERCONDUCTORS

3.3.a. Introduction

An evaluation of ac behaviour of the electrical resistivity (ρ) at low frequencies ($f < 100KHz$) is important for HTSC materials for fundamental as well for practical reasons. The dependence of frequency on the amplitude and the phase of $\rho(f)$ in both the superconducting and normal state may be used to probe various possible intrinsic effects like those associated with the effective mass of the carriers [12, 13] or with various localisation effects, including hopping conductivity [14]. This type of microscopic effects on $\rho(f)$ occur only at frequencies > 1MHz. However, measurements carried out on precursors (which do not superconduct at any of the study temperature) of copper oxide materials like La_2CuO_{4-y} or $YBa_2Cu_3O_6$ in the low frequency range suggest that they cannot be excluded from the HTSC class of materials [15 - 18]. In addition $\rho(f)$ in HTSC is also affected by various kinds of macroscopic electromagnetic effects like hysteresis or eddy current losses as in the case of conventional (low temperature superconductors) [19]. $\rho(f)$ may also be affected by certain specific factors like for eg. vortex pinning of inhomogeneous low temperature - type II superconductors which depends on the electrical current frequency [20].

Using studies of the frequency - dependent effects on the AC resistivity one can also explore the critical phenomenon occurring near the normal-superconducting transition and this can throw light on hopping like effects which may appear at low frequency in the intergrain barriers.

Studies of the dependence of $\rho(T)$ in bulk superconductors in materials like Ln $Ba_2Cu_3O_{7-\delta}$, (where Ln = Y or Ho) in zero magnetic fields and in the very low frequency range ($0 < f < 2KHz$) have revealed that the absolute resistivity is frequency dependent over the entire temperature range ($T < 300K$) for electrical current densities $J^{(eff)}_{RMS} \leq 10A / cm^2$ (where $J^{(eff)}_{RMS}$ is the effective current density) [21, 22]. Some earlier workers [23, 24] have explained this dependence as due to the poor quality of the samples. Differences between ρ_{ac} and ρ_{dc} near and below the transition temperature have been explained as spurious effects by others [25].

Measurements of complex conductivity of high T_c thin films at high frequencies (60GHz), above T_c show that the transmission loss follows the observed trend of the DC resistivity. However around the superconducting transition temperature, the AC and DC behaviours are very different [26] with the absence of a phase shift around T_c and a large negative phase shift at lower temperature.

3.3.b. Experimental

AC and DC resistivity measurements were made on different samples prepared by different procedures. They included laser ablated thin films, bulk materials (sintered pellets), and melt textured samples of Gd 123. This ensured the difference in granularity. The details of preparation of the samples are given in chapter 2. Rectangular samples of dimensions 5 x 5 x 20 mm^3 were cut out from disc - shaped samples for the bulk specimens. Coaxial shielded leads were soldered on to the probes which were spring loaded on to the samples and arranged for minimum inductive pickup. ρ was determined by the 4 probe technique. Lock in techniques were used to measure the longitudinal in - phase (x) and out of phase (y) voltage due to the transport current (Lock in amplifier :- EG & G 124A).

3.3.c. Results and discussion

Table 3.1 gives the various values of T_c's obtained from DC resistivity measurements. Sample A is a sintered compact, B is laser ablated and C is the melt textured sample.

Sample	ρ(300K) mΩ cm	dρ/dT $\mu\Omega$ cm/K	$T_{c(ons)}$ (K)	$T_{c(Zero)}$ (K)	ΔT_c	$\rho T_{c(ons)}$ mΩ cm
A	28.6	78	95.2	92	0.59	6.23
B	19.3	66	94.5	93	0.45	1.8
C	21.9	69	94.5	92.5	0.5	1.95

The variation in $T_{c(Zero)}$ and $T_{c(ons)}$ can be attributed to the difference in the granularity and to the mean - field like behaviour like normal to superconducting transition temperatures of the grains respectively [27, 28].

In the case of AC measurements, (fig. 3.4) the magnitude of AC resistivity is same as that observed from DC measurements and there is no change in the phase of the signal around T_c. Therefore we can conclude that the absence of measurable effects indicate the lack of intrinsic process in the measured plane as well as in the the intergrain links. Phase measurements confirm the absence of frequency dependent mechanism such as localisation and hopping at the frequencies investigated.

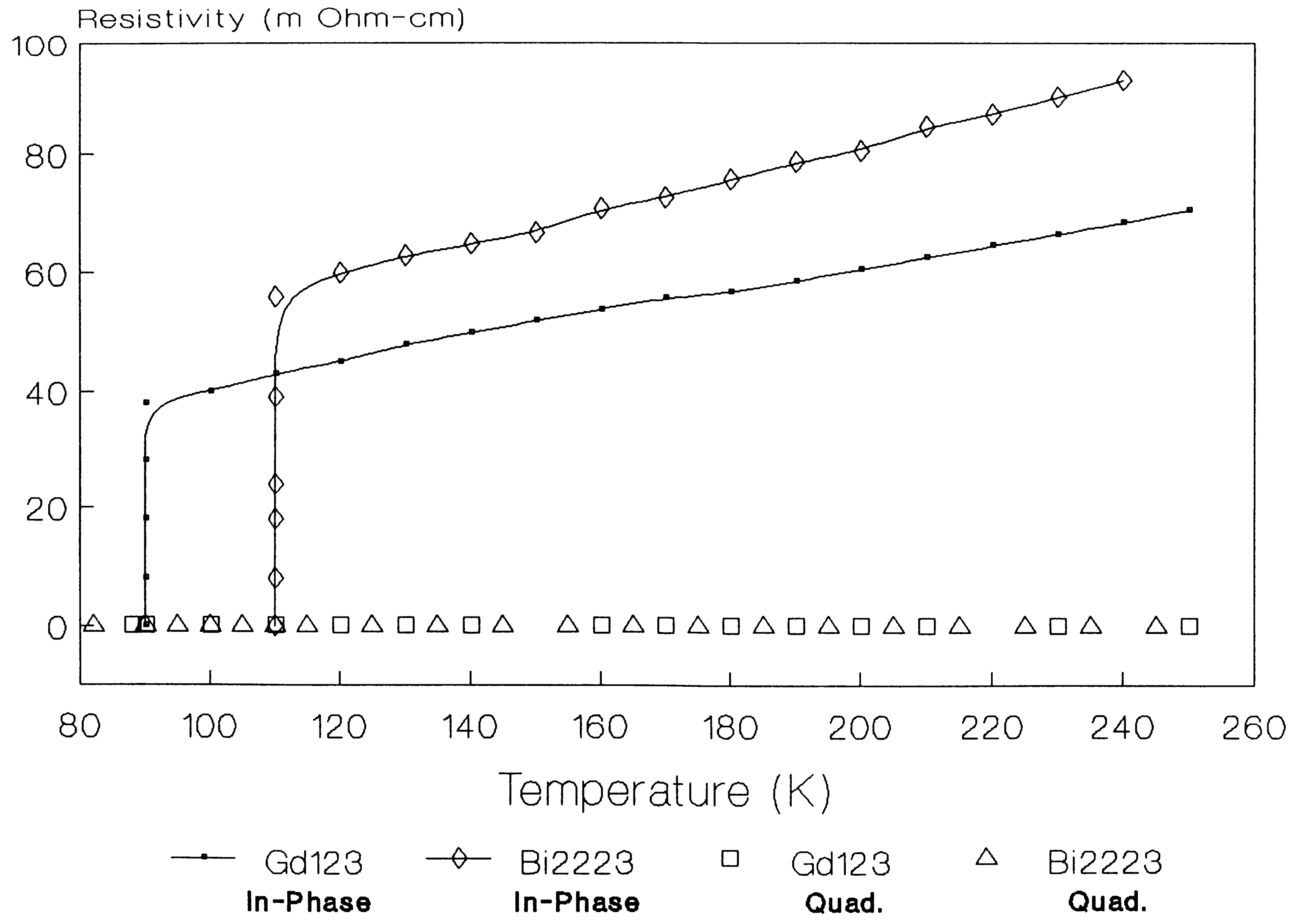


Fig. 3.4. Plot of ac resitivity versus temperature of $GdBa_2Cu_3O_{7-\delta}$ and $Bi_{1.7}Pb_{0.3}Ca_2Sr_2Cu_3O_{7-\delta}$ superconductors.

3.4. REFERENCES

[1] L J Van der Pauw, Res Rept. (Netherlands), 16, 187, (1961).

[2] H C Montgomery, J. Appl. Phys., 42, 2971, (1971).

[3] Daniel W Koon, Rev. Sci. Instrum., 60, 271, (1989).

[4] S L Bray, L F Goodrich and W P Dube, J. Sci. Instrum., 50, 261, (1989).

[5] S L Bray and L F Goodrich, Meas Sci. Technol., 1, 491, (1990).

[6] S T Ruggiero, S Schwarzbek, R E Howard and E Track, Rev. Sci. Instrum., 57, 1444, (1986).

[7] AD 584, "Analog devices - Data conversion products data book", P8-15, (1988).

[8] J G Graeme, "Designing with operational amplifiers, application alternatives", (Mc Graw - Hill, New York), P47, (1977).

[9] AD 707, "Analog devices Linear products data book", P2-103, (1988).

[10] AD 708, "Analog devices Linear products data book", P2-105, (1988).

[11] "Intersil Corp. Component Data catalog", P2-1, (1987).

[12] M Tinkham, "Introduction to Superconductivity", (Mc Graw - Hill, New York), ch.2, (1975).

[13] A C Rose-Innes and E H Rhoderic, "Introduction to Superconductivity, Int. Series in Solid state physics", (Pergamon, New York), 6, ch.1, (1978).

[14] N F Mott and E A Davis "Electronic process in Non-Crystalline Materials", (Clarendron, Oxford), (1979).

[15] M Maglione, R Böhmer, P Lunkeuheimer, M Lotze and A Loidl, Physica C, 153, 649, (1988).

[16] C Y Chen, N W Preyer, P J Picone, M A Kastner, H P Jenssen D R Gabbe, A Cassanho and R J Birgeneau, Phys. Rev. Lett., 63, 2307, (1989).

[17] J C Phillips, Phys. Rev. B, 38, 5019, (1988).

[18] G A Samara, W F Hammetter and E L Venturini, Phys. Rev., 41, 8974, (1990).

[19] D W Deis, J R Gavaler, C K Jones and A Petterson, J. Appl. Phys., 42, 21, (1971).

[20] A M Campbell and J E Evetts, Adv. in Phys., 21, 294, (1972) ch.5 and references therein.

[21] A Veira, J Maza, F Miguêlez, J Ponte, C Torrön, F Vidal, F Garcia Alvardo, E Morän, E Garcia and M A Alario, J. Phys. D, 21, 378, (1988).

[22] J A Veira, G Domarco, J Maza, F Miguêlez, J Ponte, C Torrön, F Vidal, J Amador, M T Casais, C Cascales, A Castro, M de Pedro and I Raasines, J. Less Common Met., 150, 285, (1989).

[23] Y. Schlesinger and S Havlin, Rev. Sol. St. Sci., 1, 301, (1987).

[24] Y. Schlesinger, S Havlin and I Felner, Physica C, 153 - 155, 641, (1988).

[25] A Behrooz, and A Zettl, Sol. St. Commun., 70, 1059, (1989).

[26] W Ho, P J Hood, W F Hall, P Kobrin, A B Harker and R E De Wmes, Phys. Rev. B, 38, 7029, (1988).

[27] J A Veira and F Vidal, Phys. Rev. B, 42, 8748, (1990).

[28] J A Veira and F Vidal, Physica C, 195, 468, (1989).

CHAPTER 4

DETERMINATION OF MAGNETIC SUSCEPTIBILITY OF HIGH T_c MATERIALS

ABSTRACT

The determination of magnetic susceptibility of HTSC materials is described in this chapter. The necessary theory for calculating χ , and the various techniques like self inductance, mutual inductance and frequency shift methods for the determination of T_c are discussed. A cryostat design for carrying out such measurements is also given. The efficacy of electromagnetic shielding based on HTSC materials is investigated.

4.1 INTRODUCTION

The electromagnetic response of superconductors at high frequency provides unique information regarding the nature of a superconducting material. Studies of the electromagnetic response also yield information regarding the potential of such materials for device applications.

Different kinds of method exist to characterise and study the superconducting state of the material:- electrical resistivity, microwave surface resistance, DC susceptibility and magnetisation, specific heat, electron paramagnetic resonance, the Seebeck effect, etc. But one of the most convenient, simple and commonly accepted is the inductive technique.

An obvious interest in the induction method lies in the possibility to perform post-synthesis annealings at well defined and often narrow, temperature and time intervals in order to optimise superconducting properties. It is highly desirable to perform such heat treatments in a well characterised specimen and to monitor the superconducting evolution by non - destructive methods which would allow use of the same specimen over and over again. Resistive techniques are not suitable in this respect, for two main reasons. Firstly, they need electrical contact pads (Indium solder, gold or silver paste etc) and would exclude any annealing which could pollute the specimen. By using the inductance technique rather than an electrical resistance measurement, the film can be left without pads and many hours are saved in the initial assessment of a sample. Secondly, they will not probe the magnetic state below T_{co} and important information may be neglected, such as the presence of other superconducting phases and a poor crystallisation state.

The advantages of the inductive technique are :- 1) The test can be conducted even on powder samples as there is no need for direct electrical contacts, 2) The technique allows for rapid evaluation of new processing conditions and materials without the necessity of forming solid bars, 3) Quantitative measure of the amount of superconducting phase and the critical current density is possible with this technique.

The technique has however one small disadvantage :- The highest T_c component of the specimen can shield lower T_c components, thus dominating the measurement. And more difficult is the inductive detection of a superconducting transition in thin films mainly due to the sample shape and the small overall volume.

One interesting alternative used by Xenikos et al [1] has a single flat coil, held in close proximity to the sample, which forms the inductive part of a resonant LC circuit. The transition is marked by a sharp change in the resonant frequency.

4.2. GLASS CRYOSTAT FOR MAGNETIC MEASUREMENTS

A double walled glass cryostat in which the interspace between the two glass shells could be evacuated, was used for these measurements. The schematic diagram is shown in fig. 4.1. At the end of the inner tube of 2.5 cm diameter is the copper cold finger in the form of a cylinder. This is fused to the glass tube by a glass to metal joint. This arrangement ensures very little consumption of liquid nitrogen. The coil assembly is snugly fitted on to the cold finger by the screws provided on the sides of the assembly. A thermocouple is kept in close contact with the cold finger and the leads taken through the sides of the cell. Shielded electrical leads from the coils are terminated on the outer wall through connectors. Induced currents and imbalances of the coils due to the proximity to metals were avoided by choosing glass as the material for the cell fabrication. It also ensured minimum heat leakages from the cold finger. Due to the compactness and the advantages inherent with the design, rapid characterisation of the samples are possible with this cell.

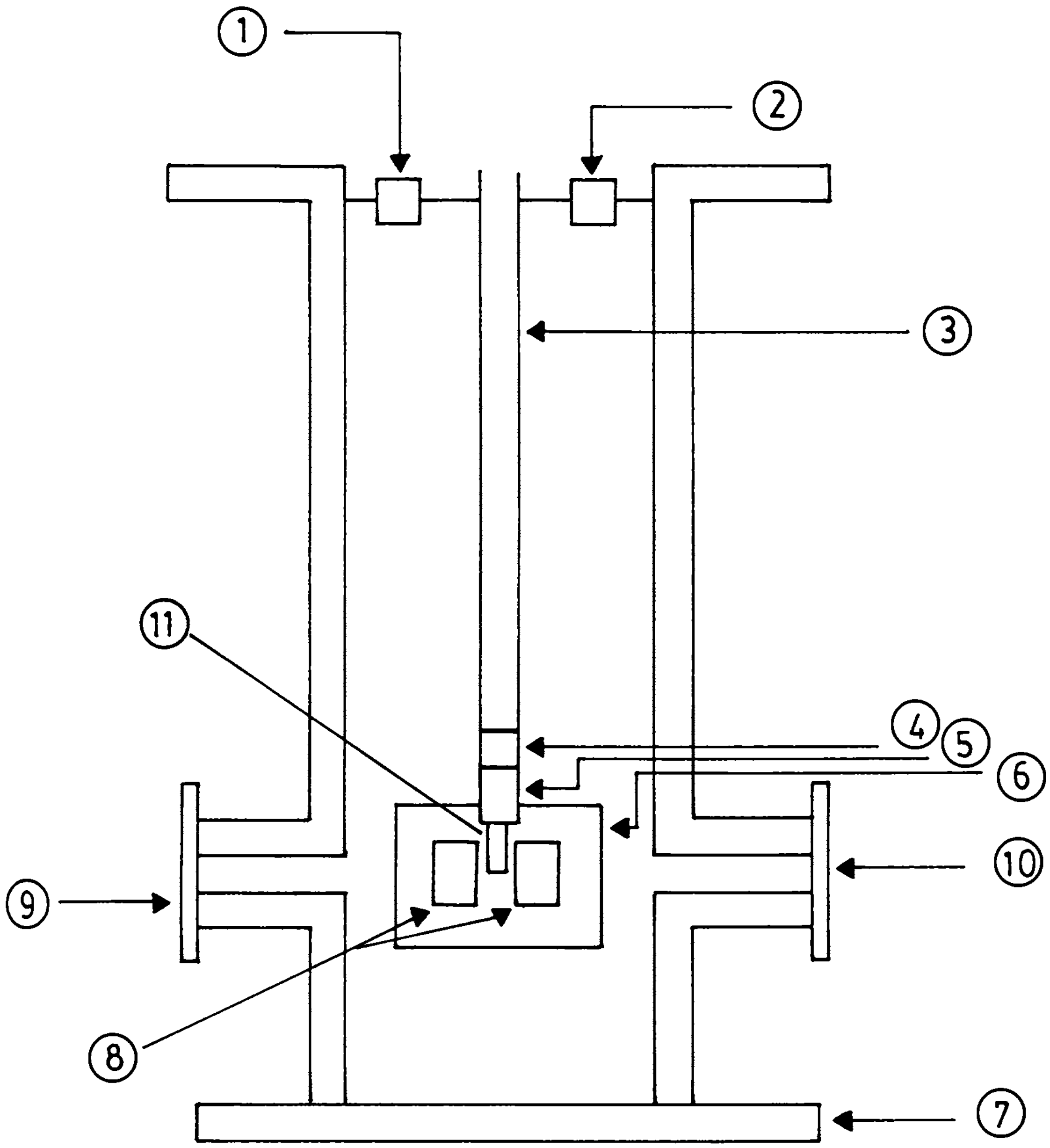
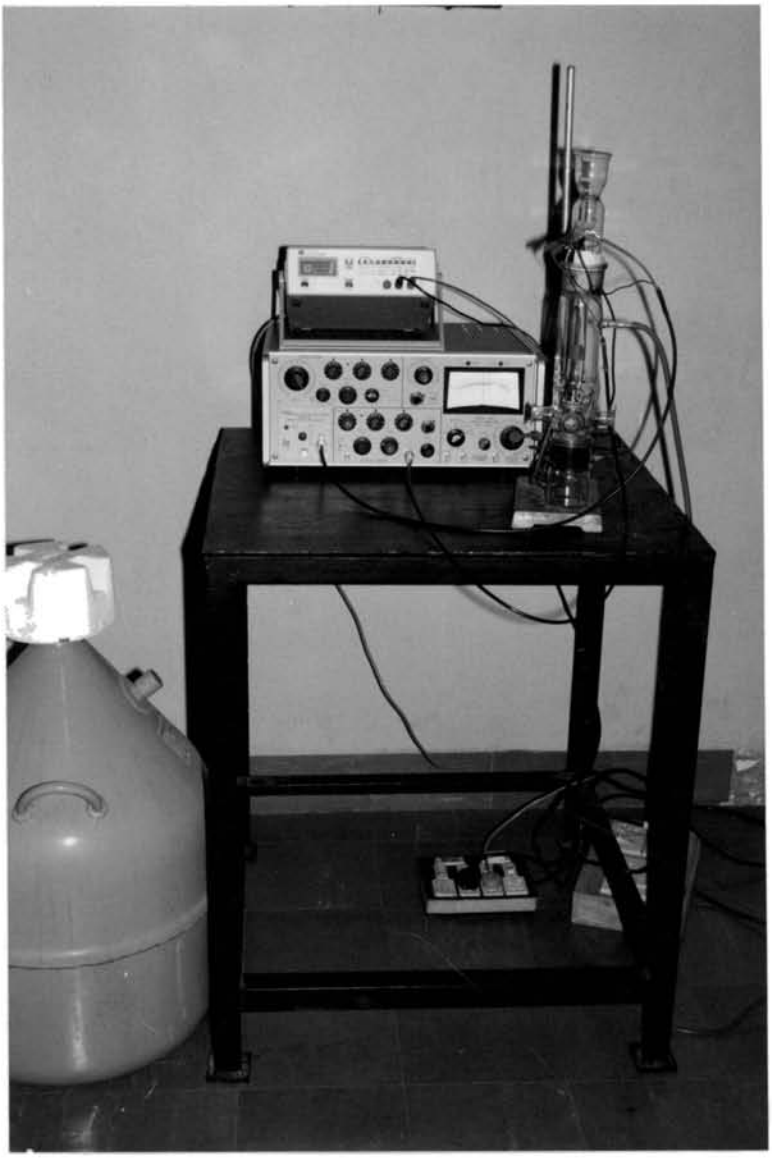
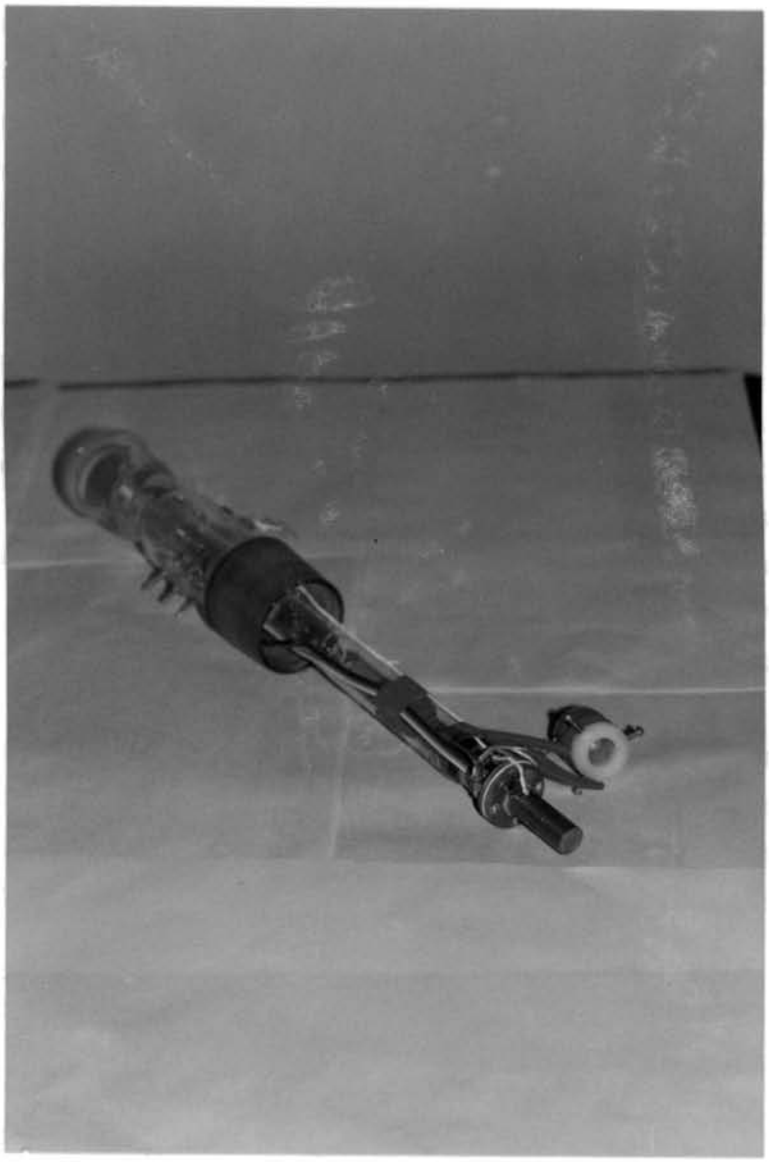


Fig. 4.1. Schematic diagram of the glass cryostat used for the measurement of magnetic properties.

1) Terminal block for electrical leads 2) Terminal block for thermocouple leads 3) glass tube 4) glass to metal joint 5) Copper cold finger 6) Mu - metal shielding 7) base plate 8) coils 9) View port 10) To vacuum pump 11) Sample.



Photograph of the experimental setup used for the determination of magnetic properties



Exploded view of the low temperature cell used for magnetic measurements.

4.3. CHARACTERISATION OF HTSC MATERIALS

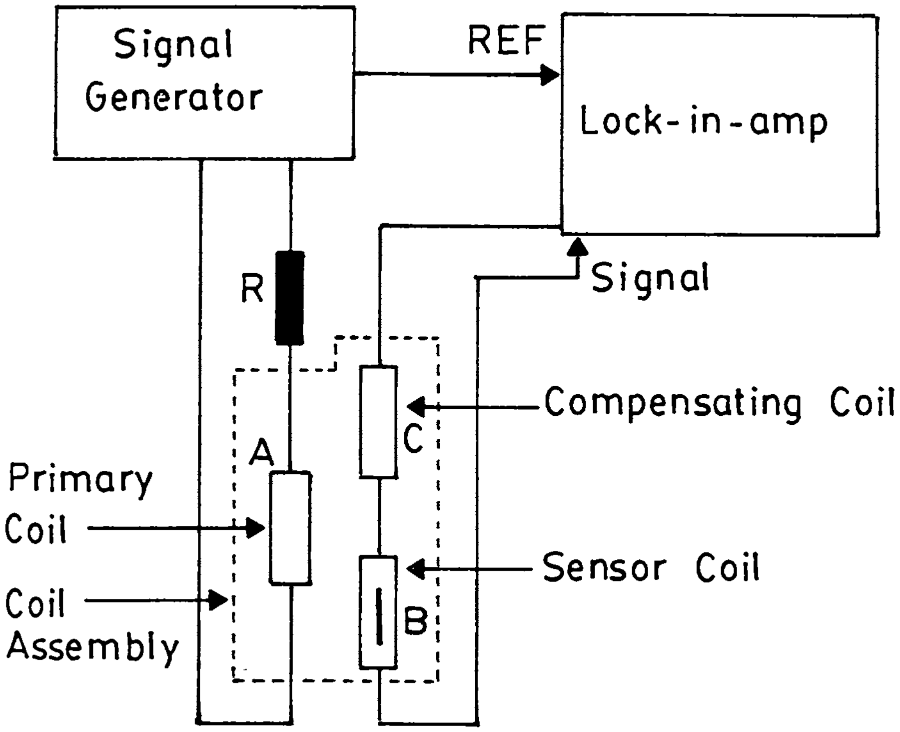
Characterisation of HTSC materials using low frequency magnetic measurements has been stressed by many workers [2-7]. The sample is placed in an ac magnetic field and the response of the sample to field variations is detected by a pickup coil that surrounds the sample. The picked up signal gives the information about the magnetic field inside the samples such as ac susceptibility, penetrated and trapped magnetic flux, and magnetization. Depending on the method used for processing the pickup coil signal, different instrumentation is used. The most common way to measure the ac susceptibility is to use a phase sensitive detector [8,9]. Determination of the real and imaginary parts of the ac susceptibility by the induction method has been discussed by many workers [10-13]. This method is briefly discussed below :- The schematic diagram is as shown in fig. 4.2.

An ac signal generator is used to feed the coil (a) to generate the ac magnetic field. Two pick up coils (b,c) are placed inside the primary coil (a). One of them (b) contains the sample and is wound opposite to the second coil (c). The voltage in pickup coil b, $u_b(t)$, is added to the voltage in the pickup coil c, $u_c(t)$, to give the total voltage

$$u(t) = u_b(t) + u_c(t) \qquad (4.1)$$

If no sample is inside the pickup coil b, $u_b(t) = (-)u_c(t)$, so that $u(t) = 0$. The measured induced voltage in the presence of a sample is proportional to the susceptibility [13].

Let the external field B_{ext} be $= B_o \cos \omega t$, (where B_o is the peak field and $\omega = 2\pi / T_o$ the angular frequency). When the sample is in the normal state the signal $u_b(t)$ is equal but opposite to the signal $u_c(t)$. This is the case if there is no



4.2. Setup for the determination of magnetic susceptibility.

sample in pickup coil b. The total voltage u(t) is then zero.

The theoretical analysis is similar to the one described by P Fabbricatore et al [11]. When the sample is in the superconducting state the voltage u(t) is then not equal to zero. The general form of u(t) can then be written as

$$u(t) = -k\,[\,\dot{\phi}_i(t) - \dot{\phi}_o(t)\,] \qquad (4.2)$$

where $\phi_i(t)$ is the magnetic flux in the region occupied by the sample as detected by the pickup coil b. $\phi_o(t)$ is the magnetic flux in a region of the same dimensions of the sample and of the pickup coils; for the sample used in this case k = 0.8. In the superconducting state the magnetic flux is expelled by the sample so that $\dot{\phi}_i(t) < \dot{\phi}_o(t)$. When the sample is in a full superconducting state (Meissner state) the magnetic flux is completely expelled. In that case $\phi_i(t) = 0$, and the voltage u(t) can be written as

$$u(t) = k\,\dot{\phi}_o(t) = k\omega\, B_o S_s N_s \sin \omega t = C \sin \omega t \qquad (4.3)$$

where S_s is the cross - sectional area of the sample and N_s the number of turns of the pickup coils; $C = k\omega\, B_o S_s N_s$. The ac susceptibility is defined as

$$\chi = \chi' - j\chi'' = \frac{dB_i}{dB_{ext}} - 1. \qquad (4.4)$$

B_i is the average internal field and is related to the magnetic flux by $\phi_i(t) = B_i(t)\ S_s$. For a parallelopiped of dimensions $2x_o$ (thickness) $y_o x\ Z_o$,

$$B_i = 1/x_o \int_o^{x_o} B(x)\,dx \qquad (4.5)$$

where the field is in the Z direction. The internal field B (x) is assumed to be constant along the Y and Z direction; this assumption is true if $y_o >> 2x_o$. The real and imaginary parts of the susceptibility can be written as

$$\chi' = 1 - \frac{2}{C}\,\frac{1}{T_o} \int_o^{T_o} u(t)\mathrm{Sin}\,(\omega t)\,dt, \qquad (4.6)$$

$$\chi'' = \frac{2}{C}\,\frac{1}{T_o} \int_o^{T_o} u(t)\mathrm{Cos}\,(\omega t)\,dt, \qquad (4.7)$$

The penetrated depth and trapped magnetic flux [8] can be written as

$$s' = 1 - \frac{\pi}{2C}\,\frac{1}{T_o} \int_o^{T_o} u(t)\,g(t)dt, \qquad (4.8)$$

$$s'' = \frac{\pi}{2C}\,\frac{1}{T_o} \int_o^{T_o} u(t)\,g(t + \frac{T_o}{4})\,dt, \qquad (4.9)$$

where g(t) is the unit square wave g(t) = 1 at $0 < t < \frac{T_o}{2}$, $g(t) = -1$ at $\frac{T_o}{2} < t < T_o$. The magnetisation during a cycle of the external magnetic field is

$$M(t) = B_i\,(t) - B_{ext}\,(t) \qquad (4.10)$$

it can also be expressed as

$$M(t) = \frac{1}{kS_sN_s}\int_0^t u(t)dt. \tag{4.11}$$

If u(t) is expanded in a fourier series, then we obtain

$$u(t) = kS_s\left[\dot{B}_i(t) - \dot{B}_{ext}(t)\right] \tag{4.12}$$

$$= \sum_n \left[A_n \text{Cos } n\omega t + B_n \sin n\omega t\right] \tag{4.13}$$

The coefficents A_n, 90^o out of phase with external field, and the in phase coefficents B_n are obtained through

$$A_n = \frac{2}{T_o}\int_0^{T_o} u(t)\text{Cos } n\omega t \; dt, \tag{4.14}$$

and $$B_n = \frac{2}{T_o}\int_0^{T_o} u(t)\text{Sin } n\omega t \; dt, \tag{4.15}$$

limiting the analysis to the fundamental harmonics, the real and imaginary parts of the ac susceptibility are obtained :

$$\chi' = 1 - B_1/C \tag{4.16}$$

and

$$\chi'' = A_1/ C. \tag{4.17}$$

4.4. DETERMINATION OF TRANSITION TEMPERATURES

4.4.a. Self Inductance Method

A technique to measure the T_c of HTSC materials by the principle of self inductance is described by various workers [14-16] and the feasibility of the above mentioned technique based on theory has been studied by Ekin et al [17]. The technique briefly is as follows :- When a material transforms into the superconducting state there is a large decrease in magnetic permeability of the material. Therefore if one uses a superconductor as a core material in an inductor, it would decrease inductance from some finite value to a negative value at T_c. If non superconducting phases are present, then the change in inductance at T_c would correspond to the fraction of the superconducting phase in the sample [16].

The self inductance of the coil can be calculated from the coil dimensions knowing the permeability of the core material. Since the inductance can be calculated from the geometry, the presence of superconducting phase can be viewed as excluding flux and therefore removing solenoid core volume [18]. Thus the reduction in inductance can be calculated if the amount of superconducting phase is known. On the other hand the amount of superconducting phase can be determined if the change in inductance is measured.

The inductance L can be defined as

$$L = \frac{\mu n^2 A}{[4R^2 + l^2]^{1/2}} \qquad (4.18)$$

where n, R, l, and A are the no. of turns, radius, length and area of cross section of the coil respectively, (area of the cross section $A = \pi \times R^2$). For the coil used in our setup, n = 150, radius = 6mm, l = 2.5 cm, $\mu = 4\pi \times 10^{-7}$. The calculated value of L was found out to be = 66μH and measured value using an impedance analyser (HP 4192) was 68.7μH.

If the cross section of the area of the cavity is A_{cr} and the volume filling fraction F_r, then the effective area of the sample crossing the magnetic flux is $A_{cr}F_r$.

Therefore the drop in inductance ΔL is =

$$A_{cr} \times F_r \times \frac{\mu\, n^2}{[4R^2 + l^2]^{1/2}} \qquad (4.19)$$

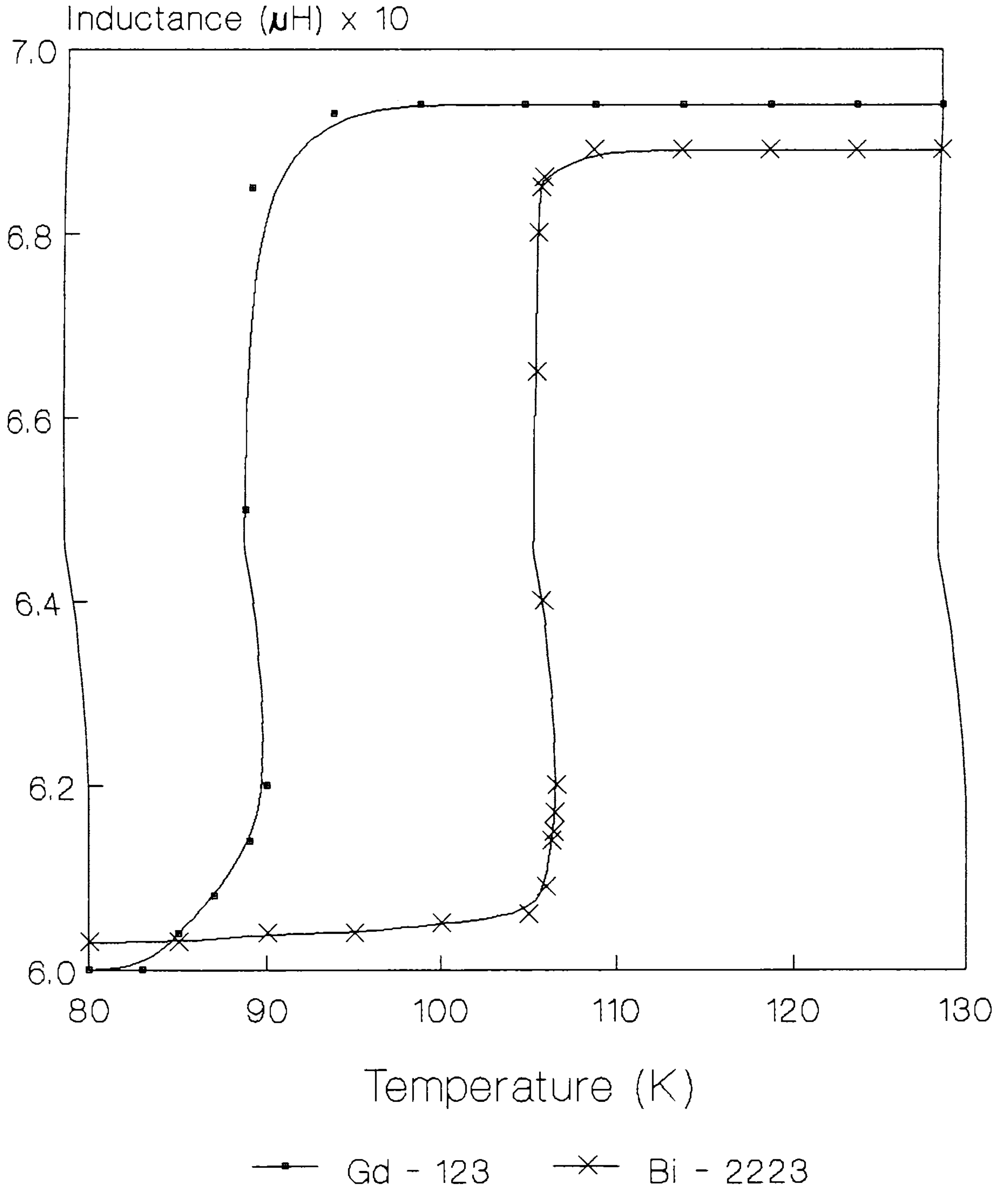
or $\Delta L = [A_{cr} \times F_r]/A \times$ measured L (without sample).

A typical plot obtained for Bi-2223 is shown in figure 4.3.

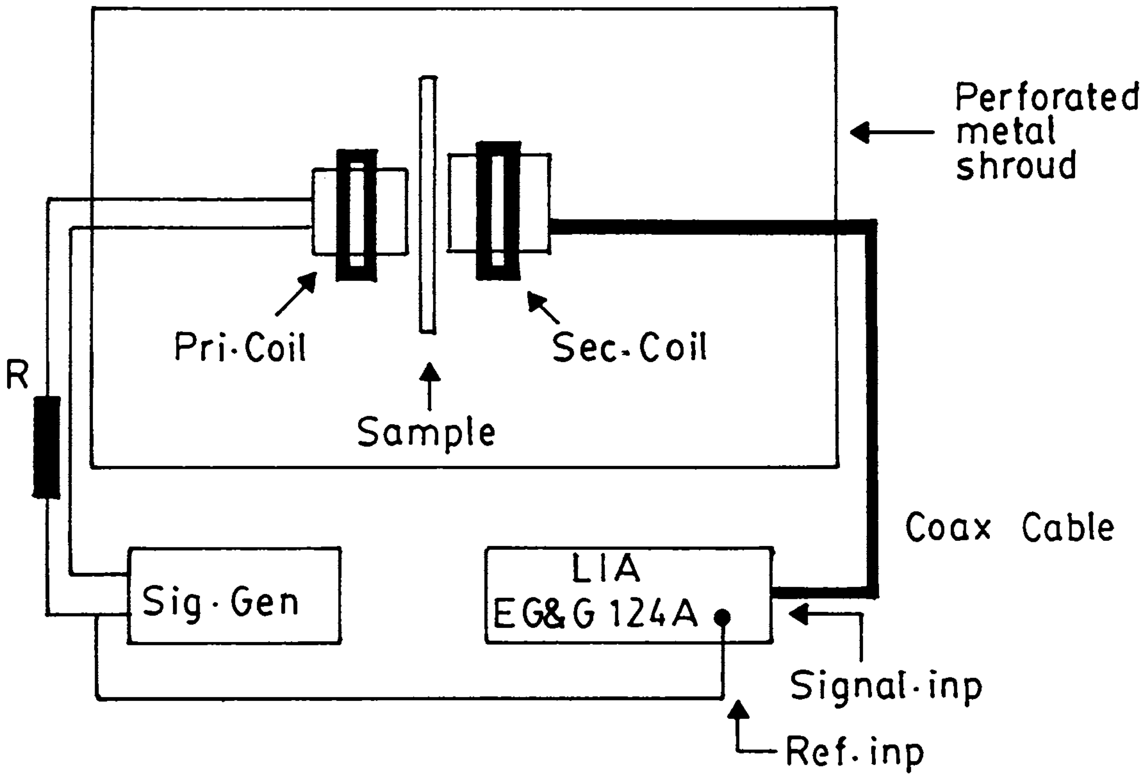
4.4.b. Mutual Inductance method

Crowley et al and Ishida et al describe a method in which coupled inductor bridges and lock in amplifier are used to detect eddy - current quadrature signals induced in the sample [19,20]. *Shalow and Devlin [21] describe a solenoid that encloses a rod* shaped sample for T_c measurements at 100K. Eddy current technique was exploited in determining the T_c and ΔT_c for copper oxide superconductors in the frequency range 100Hz-100KHz.

The setup used for the present work for the measurements is described in fig 4.4. The sample is placed in contact with a copper cold finger and placed in vacuum. The coils remain at room temperature. Slow cooling at the rate of 4K/min ensured uniform sample temperature. A mutual inductance bridge operating at the above frequencies was constructed and a signal generator was used to drive an alternating current (i_{AC}) to excite the primary coil and to produce an AC field perpendicular to the sample surface.



4.3. Plot of the inductance versus temperature for $GdBa_2Cu_3O_{7-\delta}$ and $Bi_{1.7}Pb_{0.3}Ca_2Sr_2Cu_3O_{7-\delta}$ superconductors.



ig. 4.4. Mutual inductance setup used for the detection of T_c.

The induced voltage in the secondary was then analysed by a lock - in detector. Both the in phase χ' and out - of - phase χ'' signals were recorded during cooling. Results are given in fig. 4.5 and 4.6.

It is important to distinguish between the voltage picked up in phase and in quadrature (ie at 90° phase difference) relative to the drive voltage. If we consider the two coils without a sample between them, and with no conducting material in the vicinity, the induced voltage will naturally be in antiphase with respect to the drive voltage. In other words, the in phase signal will be large (and negative) while the quadrature signal will be ideally zero. When we insert the sample, the currents induced in the sample will of course change the pick - up signal. The mutual inductance setup described has more than adequate sensitivity for small samples, giving a clear indication for the onset of transition temperature with an uncertainty of around 0.5K.

4.4.c. Frequency shift method

In this technique, the sample is introduced into an inductor which forms an integral part of an oscillator. A MOSFET based Robinson oscillator [22, 23] was used for this purpose. The circuit is given in fig. 4.7. This fully compact, solid state, battery operated oscillator has outstanding features compared to R F bridges and vacuum tube operated oscillators which are prone to drift, microphonics and noise inherent in the circuit and from the power supplies feeding them. The use of MOSFETS in the input stages ensures a high input impedance and therefore the Q of the tank circuit remains unaffected.

An oscillation frequency (depending on L and C) of 6MHz was chosen even though it is not very critical. Feedback from Q_2 drain to gate of Q_1 sustains the oscillation. The circuit uses commonly available inexpensive components. Typical sample induced frequency shifts are 40-600KHz. Results are shown in Fig. 4.8.

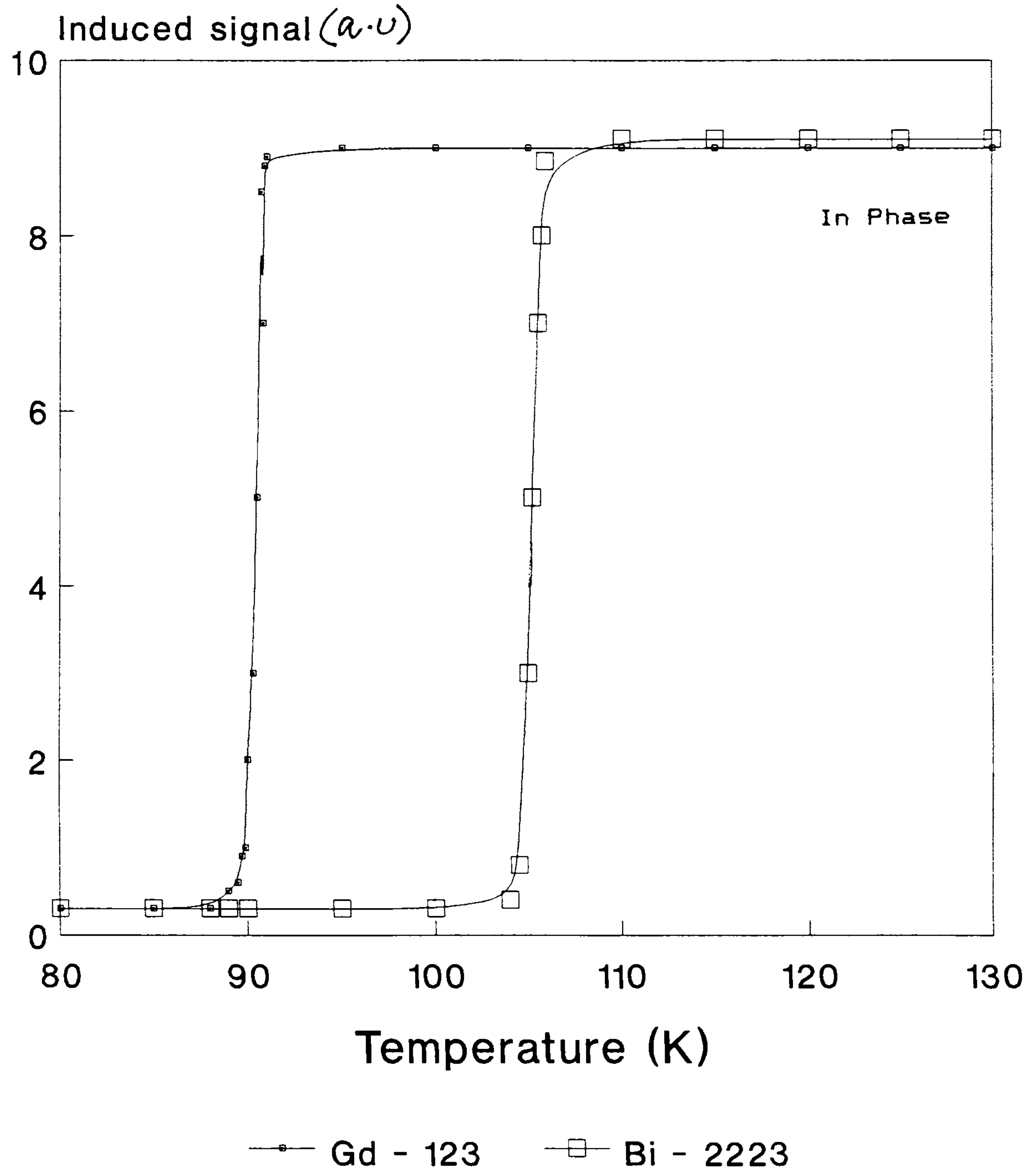


Fig. 4.5. Plot of the in - phase signal in the mutual inductance measurement against temperature for Gd-123 and Bi-2223 superconductors.

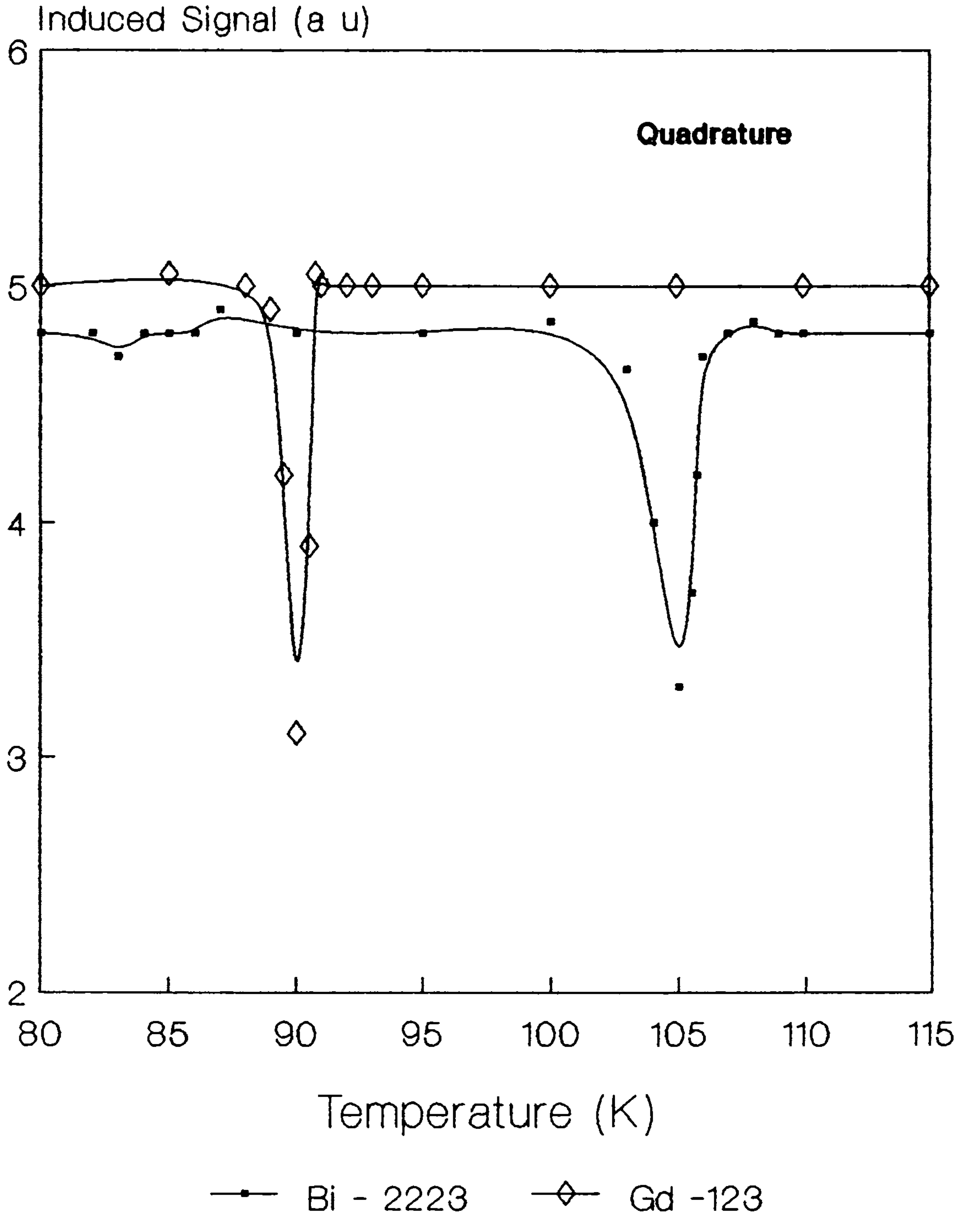


Fig. 4.6. Plot of the quadrature signal versus temperature for Gd-123 and Bi-2223 superconductors in the mutual inductance measurements.

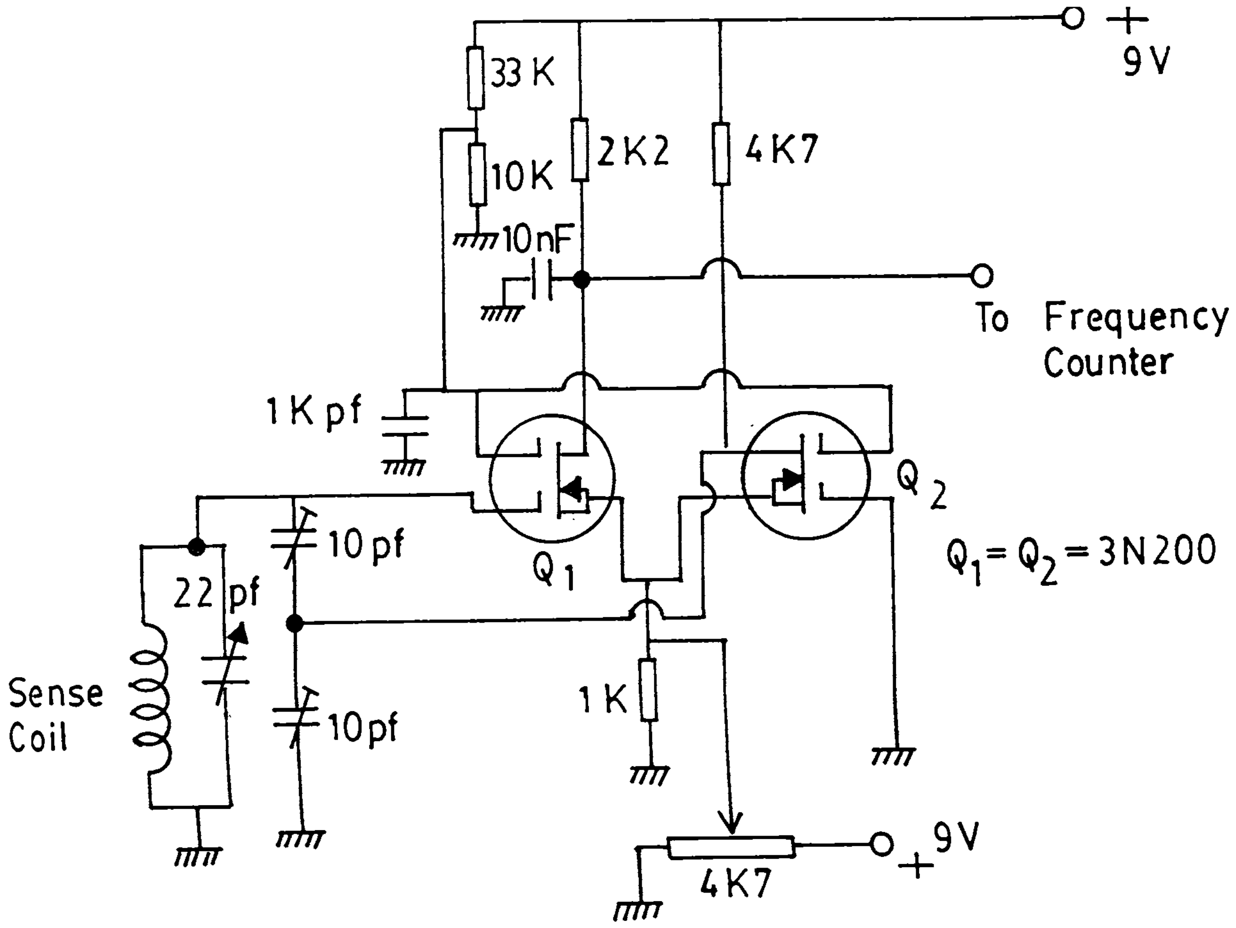


Fig. 4.7. The MOSFET based Robinson oscillator circuit used for the determination of T_c.

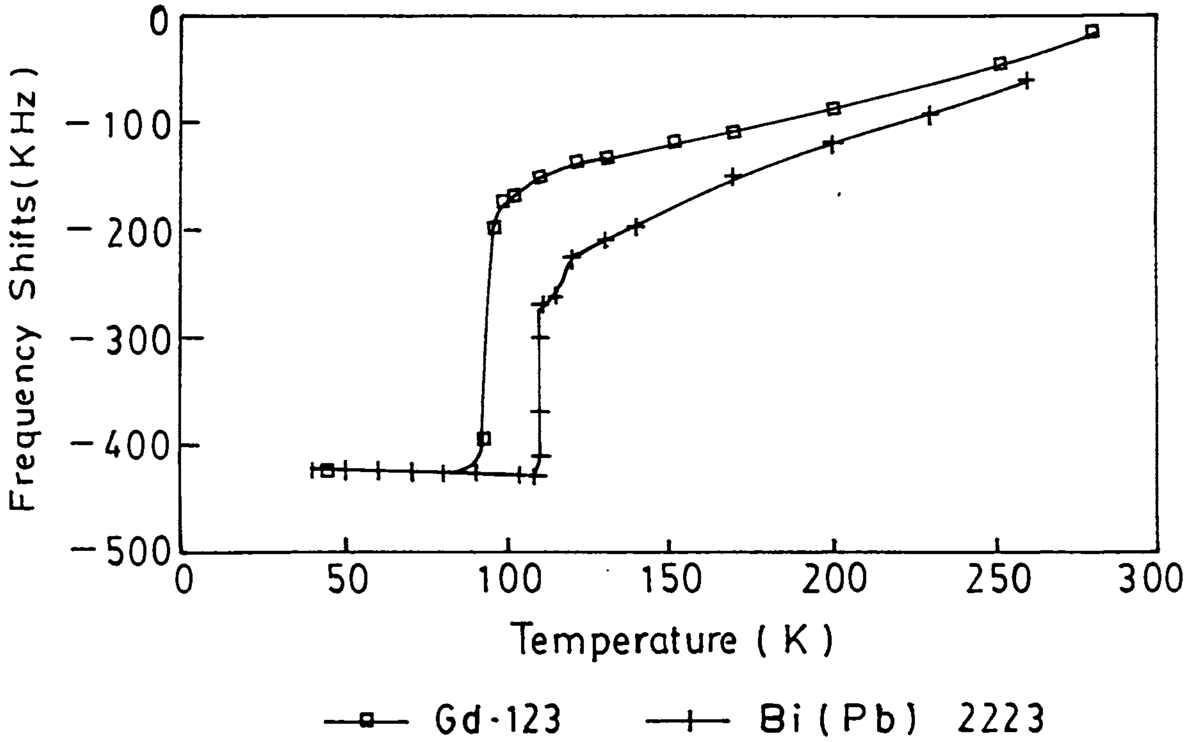


Fig. 4.8. Frequency shifts versus temperature for Gd-123 and Bi-2223 superconductors.

The selection of a suitable standard is not necessarily straightforward and there is no overall consensus in the scientific literature as to what to use. Paramagnetic salts which obey Curie's law are often used to test the temperature dependence of a magnetic system, although they may not be the best choice to serve as absolute standards. Common examples of material used are chromium potassium alum etc.

4.5. SHIELDING MEASUREMENTS

The small volumes of films and crystals together with the unfavourable demagnetising factors for longitudinal directions, affect the accuracy and reliability of the above mentioned methods, and more sensitive and difficult techniques (such as SQUID magnetometry) are needed. A more suitable method is to detect a shielding effect which takes the advantage of the large surface of films, slabs or crystals placed between the primary coil (which produces the AC field) and the secondary pickup coils. When the sample is introduced, the currents induced will change the pick - up signal.

If a superconductor is exposed to an external magnetic field it generates a current near its surface to screen out the magnetic field. The characteristic depth to which the shielding currents flow is the magnetic penetration depth λ. It depends on various parameters such as the sample temperature, thickness and the nature of the crystal structure (single crystal or polycrystalline). The relevant parameter is the sample's admittance Y, in general, a complex quantity with units Ω^{-1}. The real part of the admittance (the conductance - G) determines the size of currents induced in phase with the voltage at the film, while the imaginary part (the susceptance - B) determines currents leading or lagging by 90°. The admittance is simply related to the complex conductivity σ^{*} (units of Ω^{-1} m^{-1}): $Y = d\sigma^{*}$ for a sufficiently thin film of thickness d.

The voltage induced in the sample is again in antiphase with the drive voltage. The currents proportional to conductance G therefore induce maximum voltage in the pick - up coil when the sample voltage, and hence the drive voltage is changing most rapidly. So it is the quadrature signal which measures the real part of the admittance (or conductivity), while the in - phase signal measures the imaginary part of the admittance (or conductivity). The quadrature signal is often referred to as the loss signal.

In the magnetic approach, it is the real part of the susceptibility which affects the in - phase signal, while the imaginary part affects the quadrature signal. Screening currents induced at the surface of the sample will create a magnetic field opposed to the applied one. The induced current will be detected through the in - phase χ' (diamagnetic transition) and the out of phase χ'' (power losses) components. Especially important is the loss factor which depends on the crystallisation state, on the intergranular coupling strength and on the number of barriers (weak links) between the superconducting grains. Grain percolation or flux motion will give rise to a peak in the dissipation component χ'' as supercurrents develop at the outer surface of the sample. Intergranular coupling may occur at very different temperature values even if different samples exhibit the same resistive critical superconducting temperature.

4.5.1. Investigations of HTSC EM shields

A) Introduction

One of the promising applications of HTSC materials is in the fabrication of magnetic shields. Moreover shielding measurements can also detect flaws such as cracks that cannot be easily detected by resistivity or from Meissner effect measurements. Investigations of the shielding effects of $YBa_2Cu_3O_{7-x}$ have shown that YBaCuO shields are more effective (at low frequencies) than aluminium or high permeability ferrous materials like Mu metal etc. [24,25]. Workers investigating on thin films have found out that oriented monocrystalline films of thickness 1μm can shield power densities of upto 10^6 W/cm^2 from DC to ultraviolet [26]. 100% flux shielding was observed in $YBa_2Cu_3O_{7-x}$ at 4.2K by Larbalestier et al [27]. One added advantage of high T_c materials over conventional materials like aluminium is the effectiveness at low frequency and the reduction in thickness (several mm of thickness is needed for Al at low frequencies).

B) Experimental

Our studies on HTSC materials in the form of laser ablated thin films, powders and sintered pellets are described below. The high T_c materials were synthesised according to the procedures mentioned in chap. 2. The HTSCs used were thin film of laser ablated Gd 123, bulk and powder samples of Gd123, Gd 123 + K, BiCaSrCuO + Pb and BiCaSrCuO + Na. For comparison similar measurements were carried out on metals like aluminium, copper and μ metal. The shielding properties is then evaluated at different frequencies at both room and at liquid nitrogen temperatures.

The schematic diagram of the setup is given in fig. 4.4. The primary coil consists of 25 turns and the secondary coil had 35 turns of 0.3mm insulated copper wire and the diameter of the coils were less than the sample diameter. This would minimise the flux leakage to the secondary winding. The coils were wound on teflon formers. The primary winding was excited using a bias current between 5 - 50mA (kept constant). A lock in amplifier was used to detect the voltage induced in the secondary. The samples were introduced between the coils. Powdered samples were sandwiched between two thin glass slides. Measurements were carried out at 77K by immersion in liquid nitrogen. Noise free data was obtained by using the lock in technique (EG & G 124 A).

C) Results and discussion

The shielding factor (S_F) was determined by performing the measurements both at room as well as at liquid nitrogen temperatures. The shielding factor is the ratio of voltage at room temperature to the voltage at liquid nitrogen temperature.

$$\text{ie} \quad S_F = \frac{U_{RT}}{U_{LN2}} . \tag{4.20}$$

From fig. 4.9, it is clear that at a given frequency, as the sample is cooled to liquid nitrogen temperature, the output voltage of the secondary coil decreases to a value mainly depending on the sample used. Fig. 4.10 gives the S_F values for certain HTSC materials. Poor S_F was obtained for powders and doped HTSC materials. This is probably due to the poor interconnectivity between the grains and flux lines being concentrated between the grains. Therefore good bonding between the particles is essential for effective shielding. This is observed in melt textured samples which have better S_F. Therefore it can be concluded that powders and to some extent ceramics synthesised by conventional preparation methods are ineffective for shielding purposes. This has been observed by other workers also who measured the critical shielding current density for YBCuO superconducting ceramic plates [28]. Their results show that the value is proportional to the thickness of the sample as expected from the Beans critical model [29].

The values obtained for copper, HTSC material (laser ablated Gd - 123), μ metal and aluminium are shown in figure 4.11. There was no appreciable change in the value of S_F, at different frequencies both at room temperature and at liquid nitrogen temperature for the metals compared to the ceramic.

The exceptional shielding properties of these new materials at

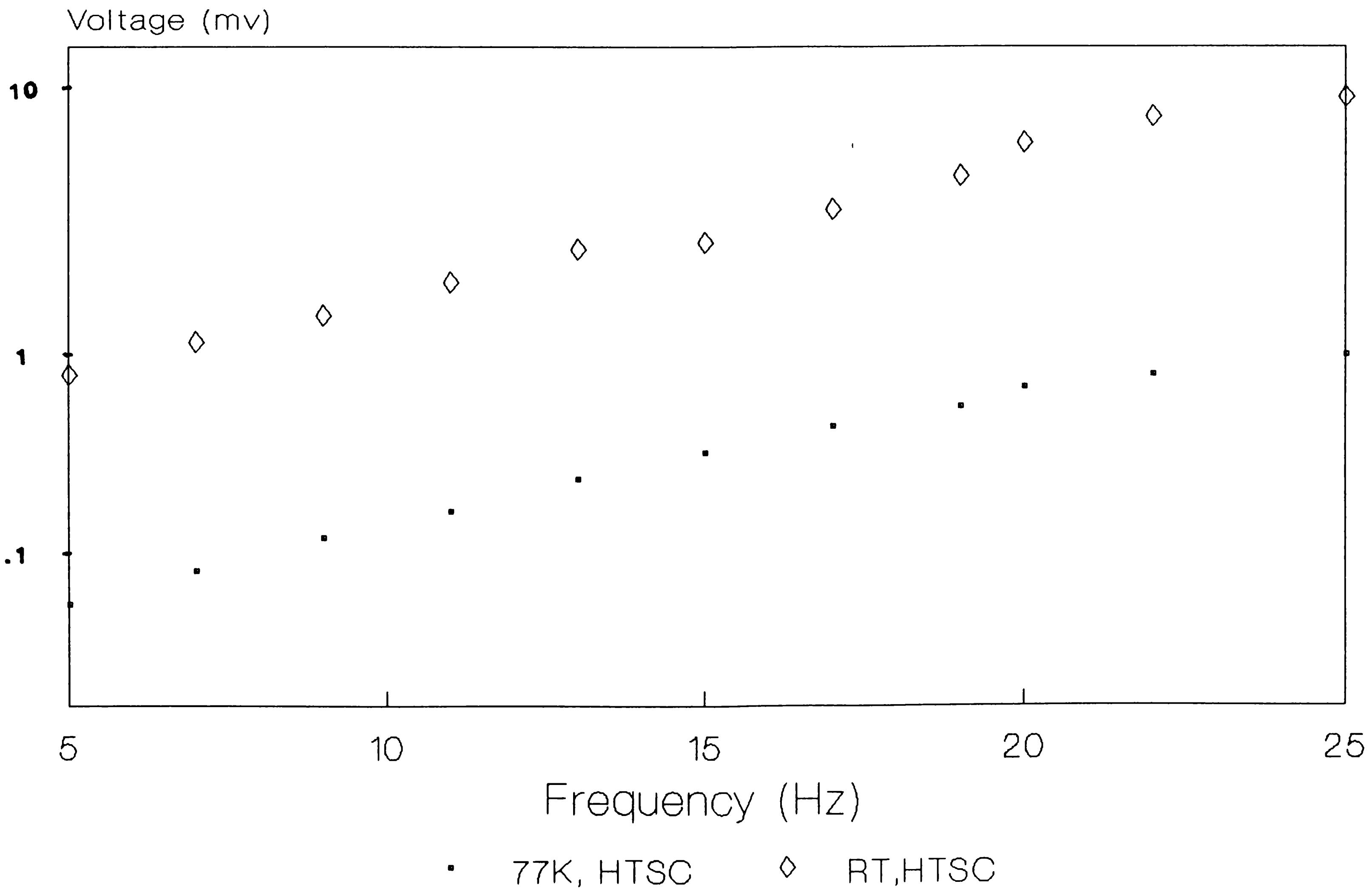


Fig. 4.9. Sheilding measurements : Plot of the output voltage of the pickup coil versus frequency for a HTSC (Gd - 123) sample used for shielding.

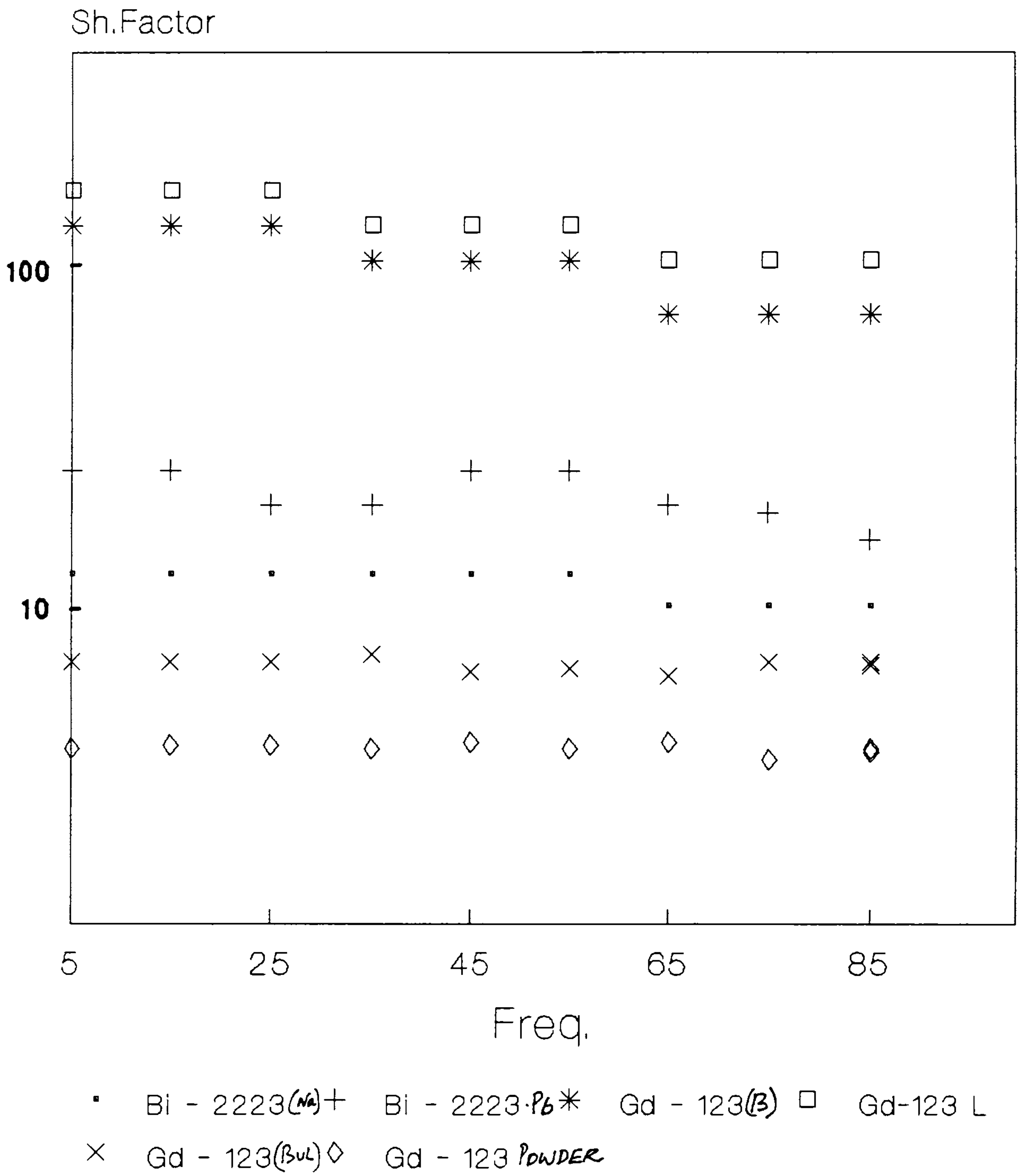


Fig. 4.10. Plot of the shielding factor versus frequency for HTSC materials such as Bi-2223 + Na (Bulk), Bi-2223 Pb (Bulk), Gd-123 (Bulk), Gd-123 laser ablated thin film, Gd-123+K (Bulk), and Gd-123 powder.

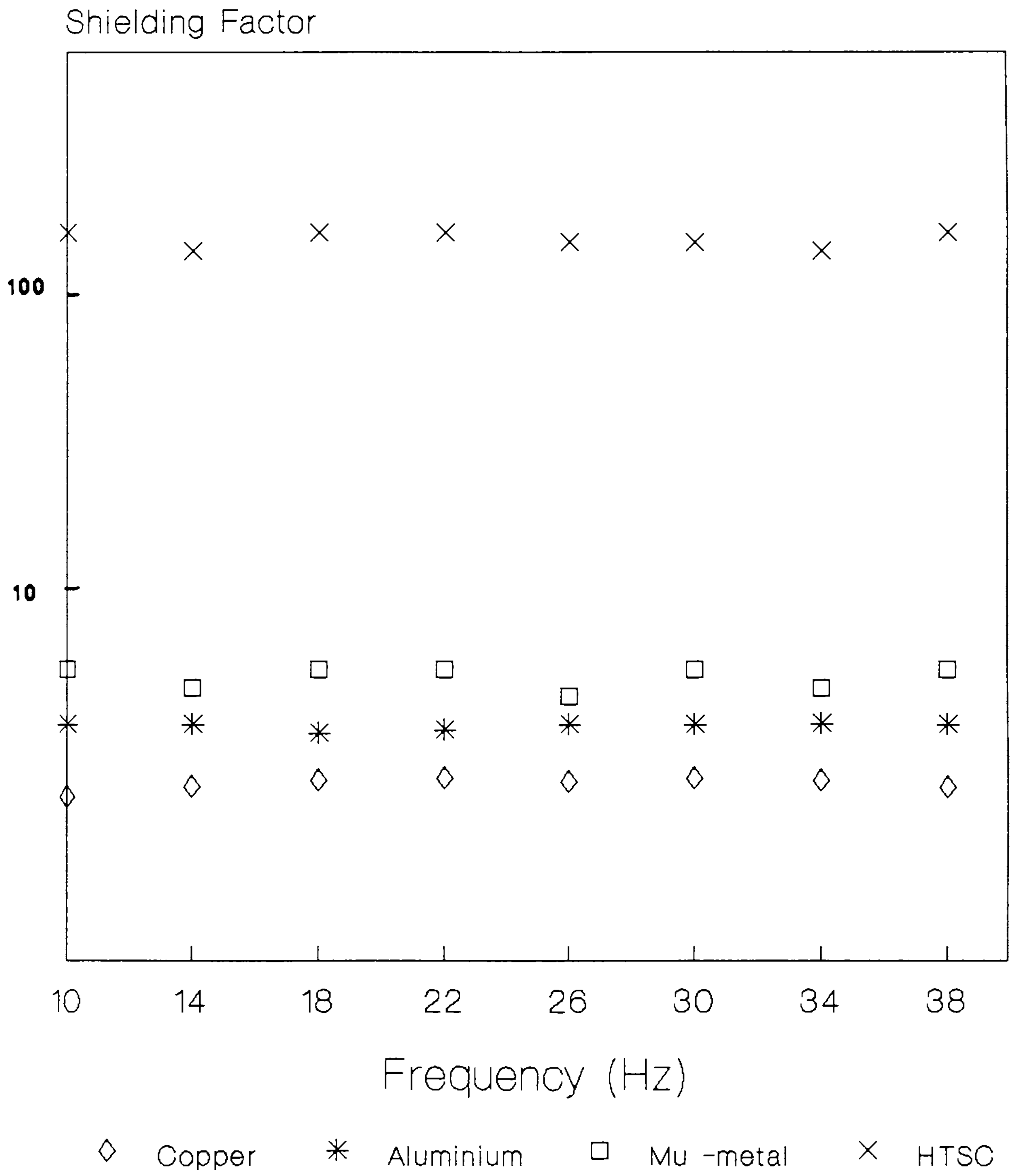


Fig. 4.11. Plot of the shielding factor versus frequency for copper, aluminium, μ metal and a HTSC (Gd - 123) sample.

low frequencies and low power densities makes them superior to conventional methods of low frequency shielding using materials like aluminium, μ metal and copper. The main parameters that control the shielding is the critical current density and thickness of the sample.

4.6. REFERENCES

[1] D G Xenikos and T R Lemberger, Rev. Sci. Instrum., 60, 831, (1990).

[2] R B Goldfarb, Cryogenics, 26, 621, (1986).

[3] D X Chen, A Sanchez, T Puig, L M Martinez and J S Munöz, Physica C, 168, 652, (1990).

[4] A Mehdaoui, B Loegel and D Bolmont, J Appl. Phys., 66, 1497, (1989).

[5] H Kûpfer, I Apfelstedt, F Flûkiger, C Keller, R Meier - Hirmer, A Turowki, U Wiech and T Wolf, Cryogenics, 28, 650, (1988).

[6] F Gömöry and P Labotka, Sol. St. Commun., 66, 645, (1988).

[7] P Labotka and F Gömöry, Phys. Stat. Solidi. A, 109, 205, (1988).

[8] A Campbell, J. Phys. C2, 1492, (1969).

[9] K H Mûller, J C McFarlane and R Driven, Physica C, 158, 366, (1989).

[10] T Soumura, K Tsutsui, T Azuma, S Saito and T Maeda, Rev. Sci. Instrum., 63, 4006, (1992).

[11] P Fabbricatore, U Gambardella, F Gomory, R Musenich, M Occhetto, R Parodi and P Pompa, Rev. Sci. Instrum., 62, 1796, (1991).

[12] Octavio Pena, Meas. Sci. Instrum., 2, 470, (1991).

[13] R B Goldfarb and J V Minervini, Rev. Sci. Instrum., 55, 761, (1984).

[14] R Gotszalk and M Lisowski, Rev. Sci. Instrum., 58, 1771, (1987).

[15] R G Humphreys, J S Satchell, N G Chew, J A Edwards, S W Goodyear, S E Blenkinsop, O D Dosser and A G Cullis, Supercond. Sci. Technol., 3, 38, (1990).

[16] T K Vethanayagam, W A Schulze, J A T Taylor and R L Snyder Int. J. Mod. Phys. B, 3, 763, (1989).

[17] J W Ekin, "Materials at low temperatures", ed R P Reed and A F Clark, American Soc. for metals, P663, (1983).

[18] See for eg., A C Rose - Innes and E H Rhoderick, "Introduction to Superconductivity", P22, 2nd Ed (Pergamon press), (1978).

[19] J D Crowley and T A Rabson, Rev. Sci. Instrum., 47, 6, (1976).

[20] T Ishida and K Monden, Rev. Sci. Instrum., 57, 12, (1986).

[21] A L Shawlow and G E Devlin, Phys. Rev., 113, 120, (1959).

[22] K J Wilson and C P G Vallabhan, Meas. Sci. Technol., 1, 458, (1990).

[23] F N H Robinson, J. Sci. Instrum., 42, 653, (1959).

[24] J C MacFarlane, R Driver, R B Roberts and E C Horrigan, Cryogenics, 28, 303, (1988).

[25] J C MacFarlane, R Driver, R B Roberts, E C Horrigan and C Andrikidis, Physica C, 153, 1423, (1988).

[26] K K Likharev, Supercond. Sci. Technol., 3 , 325, (1990).

[27] D C Larbalestier, M Daeumling, X Cai, J Seuntjens, E E Hellstorm and R Joynt, J. Appl. Phys., 62, 3308, (1987).

[28] A Yahara and H Matsuba, IEEE Trans. Magn. MAG. 25, 2498, (1988).

[29] C P Bean, Rev. Mod Phys., 36, 31, (1964).

CHAPTER 5

SUBSTITUTION AND DOPING STUDIES IN Gd BASED HIGH T_c SUPERCONDUCTORS

ABSTRACT

Doping studies on HTSC materials especially the incorporation of potassium in $GdBa_2Cu_3O_{7-\delta}$ were carried out. Stable and reproducible transitions between 92K and 100K were observed both resistively and magnetically in these materials. Subtle changes in T_c occur for certain weight percentage of potassium. The effect of changing composition on T_c is also discussed.

5.1 INTRODUCTION

Chemical doping is a crucial investigative tool for the study of HTSC because the substituents affect the structure including bond lengths and also produce band filling in the parent compound. The determination of crystallographic structure, and measurement of magnetic, and transport properties of doped cuprate materials provides important information regarding the correlation between superconductivity and other physical properties. Also the sensitivity of superconducting and normal state properties to the electronic structure of the dopants will be very much useful for the confirmation of the theories of superconductivity.

Ever since the discovery of HTSC's, numerous early investigators have carried out substitutions of each element of the copper oxide superconductors primarily aimed to enhance T_c and also to improve its electrical and magnetic properties.

In the $La_{2-x}M_xCu_{4-\delta}$ compound (M = Sr, Ca or Ba), several investigators substituted various rare earth elements for La and also made double substitution for La with Ba_xSr_{y-x} [1-13].

Similarly rare earth substitutions in the YBaCuO were also studied intensively [14-33]. The subject has been thoroughly reviewed by many authors [34 - 44]. The effect of such substitutions on T_c are summarised in Table 5.1.

TABLE - 5.1.

Effect on T_c due to substitution of various atoms at RE and M sites of (RE) $M_2Cu_3O_7$.

(RE)	M	T_c(K)	(RE)	M	T_c(K)	(REF)
Y	Ba	93.3	Ce	Ba	NSC	A
La	Ba	59.2	Pr	Ba	NSC	A
Nd	Ba	78.3	Tb	Ba	NSC	A
Sm	Ba	88.6	Pm	Ba	NSC	A
Gd	Ba	90.9	Eu	Ba	91.1	A
Lu	Ba	72.6	Tm	Ba	90.5	A
Yb	Ba	89.3	Er	Ba	90.7	A
Ho	Ba	91.1	Dy	Ba	91.8	A
La	Ba	60	$Pr_{0.1}Eu_{0.9}$	Ba	82	[23]
$Y_{0.75}Sc_{0.25}$	Ba	91	$Y_{0.5}La_{0.5}$	Ba	87	[23]
$Y_{0.25}Eu_{0.75}$	Ba	95	$Y_{0.1}Eu_{0.9}$	Ba	94.5	[23]
Eu	Ba	95	$Eu_{0.75}Sc_{0.25}$	Ba	93	[23]

A = [16, 17, 22, 30, 31, 45 - 49] and NSC = Non superconducting.

Replacement of yttrium by other rare earth ions does not change T_c of the compound (with exceptions such as Ce, Pr, Tb, and Pm), substitution at the barium site and particularly at the Cu-site by either an ion of the same valency (Sr, Ca or Zn, Ni) or aliovalent ions (Fe^{3+}, Al^{3+}) drastically change the T_c of pure $YBa_2Cu_3O_7$ and at sufficiently high concentrations, destroys the superconducting property completely. Effect of partial substitution of yttrium by bismuth and barium by lead in $YBa_2Cu_3O_7$ [50] has shown that the T_c remained unchanged while the normal state resistivity decreases by an order of magnitude. Both Bi and Pb oxides act as fluxes in the sintering process during the synthesis and changes in the morphology of the sintered grains took place. However, there exists the possibility of the formation of impurity phases of the type $BaBiO_3$ and $BaPbO_3$, along with the substituted $YBa_2Cu_3O_7$.

In the $(La_{1-x}M_x)_2 CuO_{4-\delta}$ systems, substitution of Sr^{2-} for La^{3-} [the Sr^{2-} ion which has a size (1.1Å) nearly equal to that of La^{3-} (1.14 Å)] produces higher T_C and three times diamagnetic χ than the larger Ba^{2-}(1.34Å) ion [51]. However when Sr is substituted for Ba in the system $Y(Ba_{1-x}Sr_x)_2 Cu_3O_{7-\delta}$ T_c drops from 90K to 78K in the range x = 0 to 0.75 [52, 53]. Meissner flux exclusion is about 45% from x = 0 to x = 0.5 with a maximum at x = 0 and drops thereafter [54].

Substitution of paramagnetic ions for Cu in the $YBa_2(Cu_{0.9}M_{0.1})_3O_{7-\delta}$ (where M is a transition element) system, have revealed that the T_c is supressed and the normal state properties are altered. It has been established that dopants at the Cu(2) plane reduce T_c more drastically than those at the Cu (1) chain site. [5, 42, 55 - 58]. The depression of T_c correlate with the magnetic moment of the ion. The substitution of Ni^{2+} and diamagnetic Zn also have been carried out by many workers [47, 59 - 64]. The effect of Zn on T_c is more remarkable than that of Ni. It is similar to that in YBaCuO [65]. When copper is replaced by Ni or Zn upto a certain composition, the compound becomes nonsuperconducting even though the structure remains orthorhombic [63]. It was also noted that the substitution of Ni in the YBaCuO system is less harmful to T_c than Ni in LaSrCuO [47, 72].

The change in electronic structure of high T_C superconductors with 3d metal - ion doping at different sites has been studied extensively by different experimental techniques. However, few studies have been carried out on these systems with the addition rather than substitution of these metal ions. The addition of 3d metal ions to the high T_C superconducting oxides seems to change the electronic structure in a way entirely different from that of substitution at different sites [66, 67].

Addition of Sn upto a certain concentration, as an impurity in the YBCO system, yielded an increase in the critical temperature while substitution at the Cu site leads to a decrease in T_c [66, 67]. Same is the case in the 2212 BiSCCO system. This reveals that the whole electronic structure of the system or a part of it, at the Cu-O planes may be changing with the partial replacement of Cu with Sn. In conclusion, addition of Sn in this system increases the T_c unlike the substitution which is reported to decrease it. Studies on $(BiPb)_2Sr_2Ca_1Cu_2Sn_xO_y$ (x = 0.1, 0.2, 0.3) suggest that Sn^{4+} ions go to the Cu site rather than Sr or Ca. As observed in the YBCuO system, near T_c phonon softening may be occurring for the Bi system also and this phonon-softening temperature should be dependent on Sn concentration. This indicates that phonons and Cu - O bonds may also play an important role in these systems of superconductors.

Similarly nonmagnetic substitutions for Cu with elements such as Zn and Ga which has almost identical ionic radii that of Cu also degrades T_c. When 15% of Cu is replaced with Zn superconductivity is destroyed. In the case of Ga, 20% replacement reduces T_c by 30% [68]. Substitution of Ag (which is ordinarily monovalent) for Cu in $(La_{0.9}Sr_{0.1})Cu_{1-x}Ag_xO_{4-\delta}$ decreased T_c by 50% at x = 0.15 level [69] to a lesser extent than that of Ni and Zn substitution.

Addition of silver oxide (Ag_2O) or Ag increases the steepness of the superconducting transition (and hence decrease of ΔT_c), improved contact resistance, resistance to water and an increase in J_c [58, 70-72]. Partial replacement of Cu by monovalent Ag in YBaCuO depressed T_c [73] and in one report total replacement lowered the onset of T_c to 50K and widened the transition width to 30K [74]. This replacement increased the Cu^{3+}/Cu^{2+} ratio for charge balance, although an increase in oxygen vacancies may also occur. Ag replacement was found to enhance the J_c by a factor of

15 [75]. The replacement of a part of the oxygen by sulphur forms the compound $YBa_2Cu_3O_\delta S$ which has a sharper transition than $YBa_2Cu_3O_7$ [76] and full meissner effect with the T_c remaining unchanged [57]. However the crystal is transformed to a tetragonal form [77]. Similarly the substitution of oxygen with fluorine gave encouraging results with an increase in T_c to 155K in $YBa_2Cu_3O_\delta F_2$ [78, 79].

In the following section we present the results on the measurements carried out in $GdBa_2Cu_3O_7$ in which an alkali metal has been added as an impurity.

5.2 ELECTRICAL AND MAGNETIC MEASUREMENTS IN K DOPED $GdBa_2Cu_3O_{7-\delta}$

5.2.1. Introduction

Studies pertaining to the effect of alkali metal impurities in rare earth based 123 systems have attracted considerable attention as these investigations can shed some light on the nature of the mechanism involved in the phenomenon of high T_c superconductivity and its relation to the electronic structure of the constituent elements. Investigations on the effect of K doping in Tl and Bi based systems have revealed some interesting features. Studies made by incorporation of K in Tl-Ba-Ca-CuO systems were carried out and it has been found that up to 70% of Tl can be replaced without much reduction in T_c(zero) [80,81].

Similarly in BSCCO system incorporation of an other alkali metal - Li increased the T_c to 98K from 93K and also lowered the formation temperature of the 2212 phase [82]. It also increased the percentage of the superconducting phase [83]. The effect of nonmagnetic impurities on T_c and $[dH_{c2}/dT]_{T_c}$ is well known from the dirty limit WHH (Werthamer, Helfand and Hohenberg) formulas [11]. Substitution of K in 123 system like $YBa_{2-y}K_yCu_3O_x$ and $EuBa_{2-y}K_yCu_3O_x$ has shown opposite effects on T_c. In the former case T_c remained unchanged whereas in the latter system, T_c was observed to decrease with increasing K concentration [84], clearly indicating the effect of K on the rare earth ions. Moreover the superconducting transitions became sharper than those in the undoped samples. Replacement of Ba^{++} with K^{+} in $YBa_{2-x}Cu_{3}K_{x}O_{7-\delta}$ upto x = 0.5 did not destroy superconductivity with T_c = 92 to 90K, even though the charge of the cation is reduced. A small decrease in T_c (T_c = 88K) was observed for x = 1. However when x > 1, it forms a multiphase system. Since the ionic radii of Ba^{++} and K^{+} are similar, no measurable lattice parameter changes were observed. In the $EuBa_{2-y}K_{y}Cu_{3}O_{x}$ system, small amounts of K^{+} shifted the symmetry from orthorhombic to tetragonal [85]. Small additions of Ti [86], Ag [87], and Pd [88] do not decrease in any substantial manner the T_c for $YBa_2(Cu_{1-x}M_x)_3O_{7-y}$ where M = Li, Ti, Ag, and Pd. It has been pointed out that the introduction of K^{+}decreases the mean cation charge which is one of the criterion for fulfillment of the optimal conditions for superconductivity [89]. Potassium dissolves in the 1-2-3 structure at low concentrations and superconductivity is observed in samples with $x \leqq 0.3$, $T_{c(onset)}$ = 135K and $T_{c(mid)}$ = 116K [90].

This chapter discusses the preparation of pure and K doped GdBaCuO superconductors, measurement of their electrical resistivity and ac susceptibility made with an objective to understand basically the features of K doped $GdBa_2Cu_3O_{7-\delta}$ system.

5.2.2. Experimental

Details of the sample preparation are described in chapter 2. X-ray studies showed that the samples were single - phase materials. The reflections corresponding to the starting constituents were absent in the final product. Electrical resistivity was measured by the usual four probe technique in the temperature range 300-77K in a temperature controlled cryostat in vacuum (to avoid any effect of moisture). Electrical contacts were made using air drying silver paste. The voltage drop across the sample when biased at 10mA (maximum 50mA) by a constant current source was measured with a Keithley nanovoltmeter (model 181). The temperature was measured with an accuracy of ± 0.5K by a chromel - alumel thermocouple placed near to the sample.

Magnetic measurements were carried out by the coupled differential transformer method described in chapter 4 [91, 92]. Accurate and noise free magnetic data was obtained with the help of a lock-in-amplifier which was used for these measurements.

5.2.3. Results and discussions

X-ray diffraction pattern of $GdKBa_2Cu_3O_{7-\delta}$ compounds showed that essentially single phase specimens were obtained for K concentration upto 1.7 wt%. Resistivity and susceptibility measurements indicate an irregular variation in T_c with wt% of K (fig 5.1 and 5.2). However, for a certain wt% there is a marked increase in T_c (a sharp drop of R and c at 108K with a zero resistance at 100K). Fig. 5.3 shows the variation of T_c with composition. The values of T_c for various wt % are given in table 5.2. The value of T_c and in general R Vs T characteristics did not change with I even if the current was increased from 10mA to 50mA. The T_c of the sample did not degrade with increase of I and this indicates that the sample can endure current density variations.

The room temperature resistivity is much higher than that of pure 1-2-3 compounds. Magnetic measurements have confirmed that these sharp drops of resistance originate from the onset of superconductivity. The measurements were carried out for the samples from different batches ensuring the reproducibility of the transitions. Unlike in sulphur substituted YBaCuO compound [76] (T_c as high as 108K) these samples exhibited stable characteristics and repeated thermal cycling did not degrade the superconductivity. The sample processing here is easy to follow

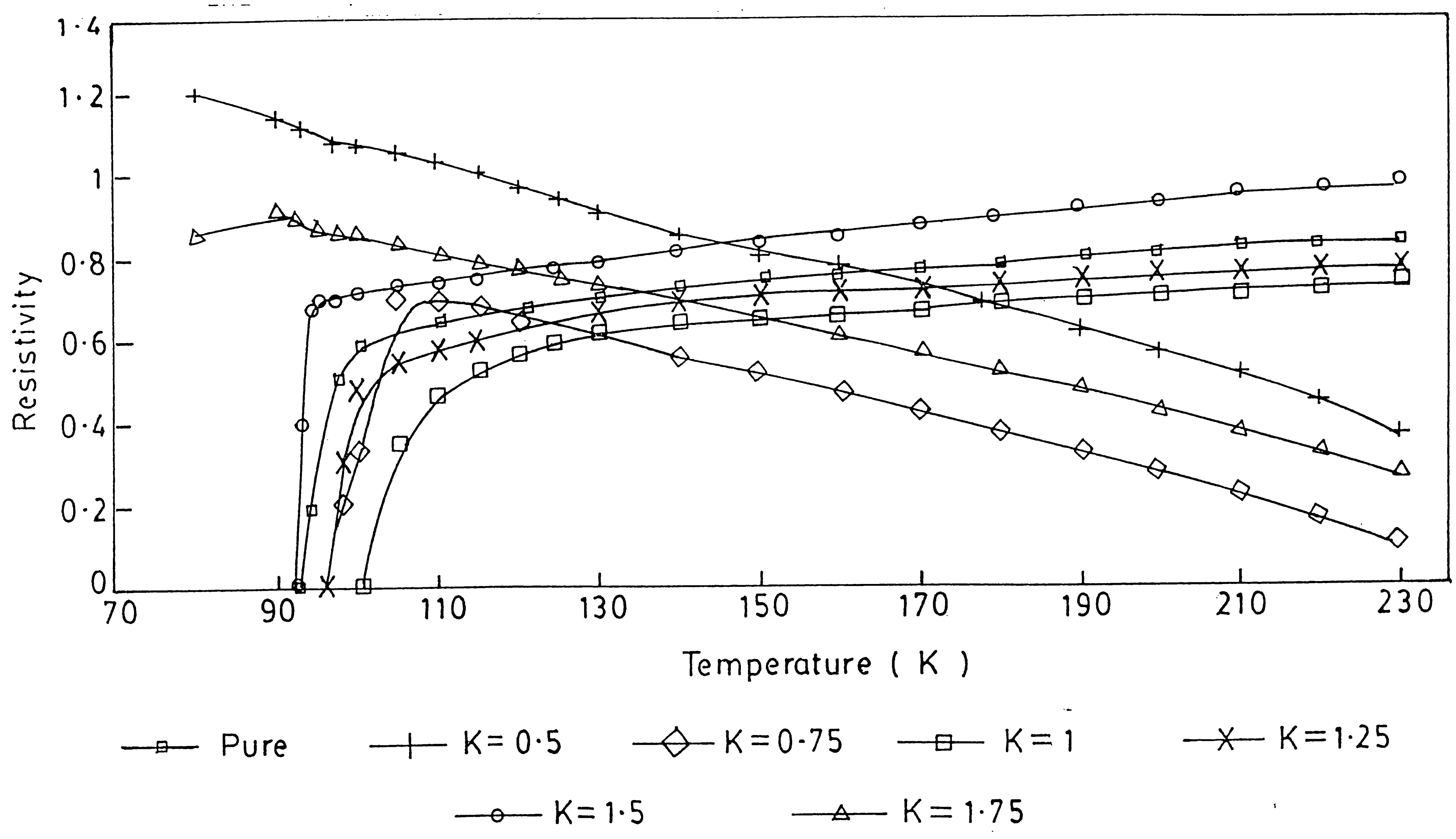


Fig. 5.1. Plot of electrical resistivity versus temperature for various wt. % of K in Gd Ba_2 Cu_3 $O_{7-\delta}$ samples.

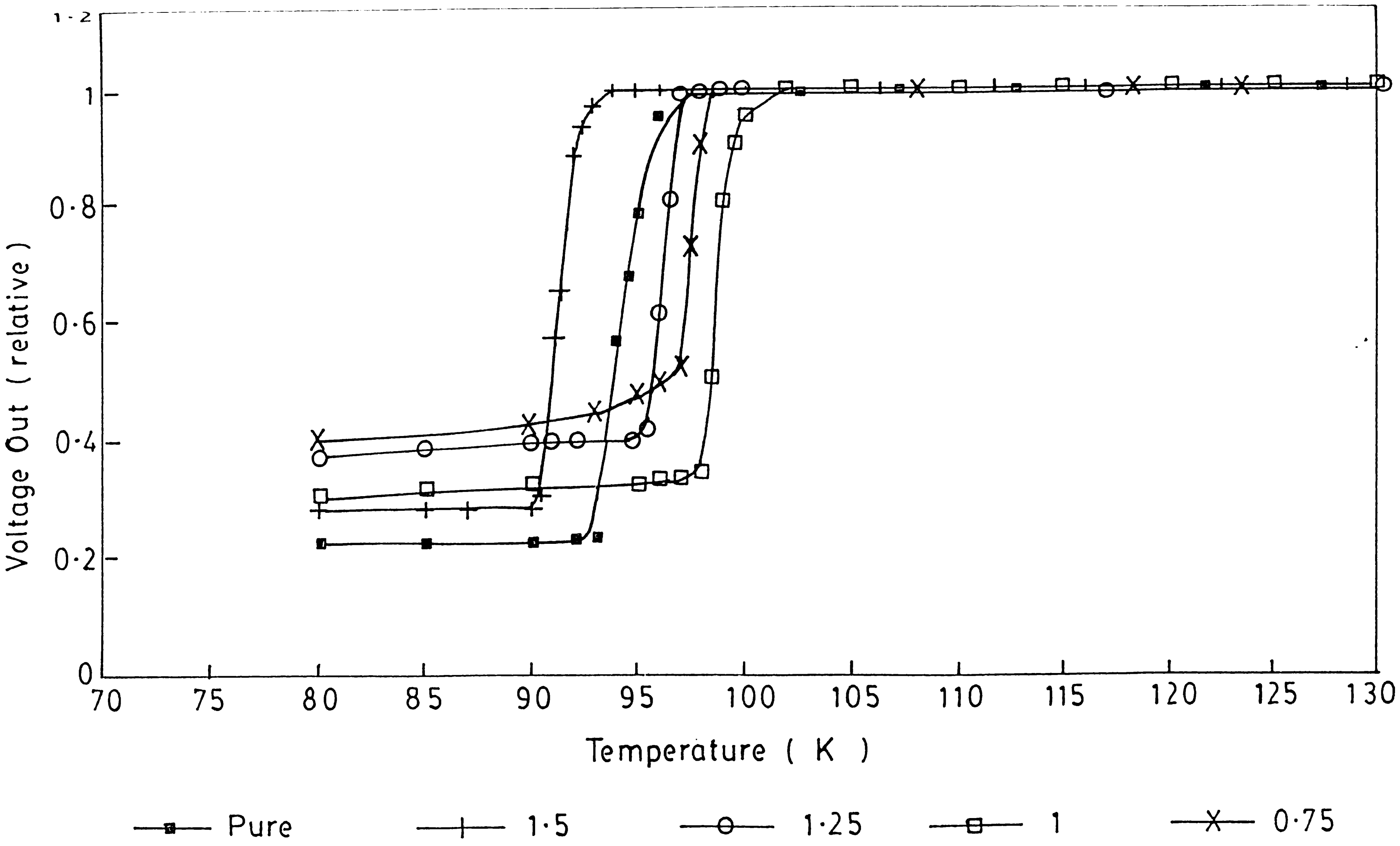


Fig. 5.2. Plot of magnetic susceptibility versus temperature for various wt. % of K in Gd Ba_2 Cu_3 $O_{7-\delta}$ based samples.

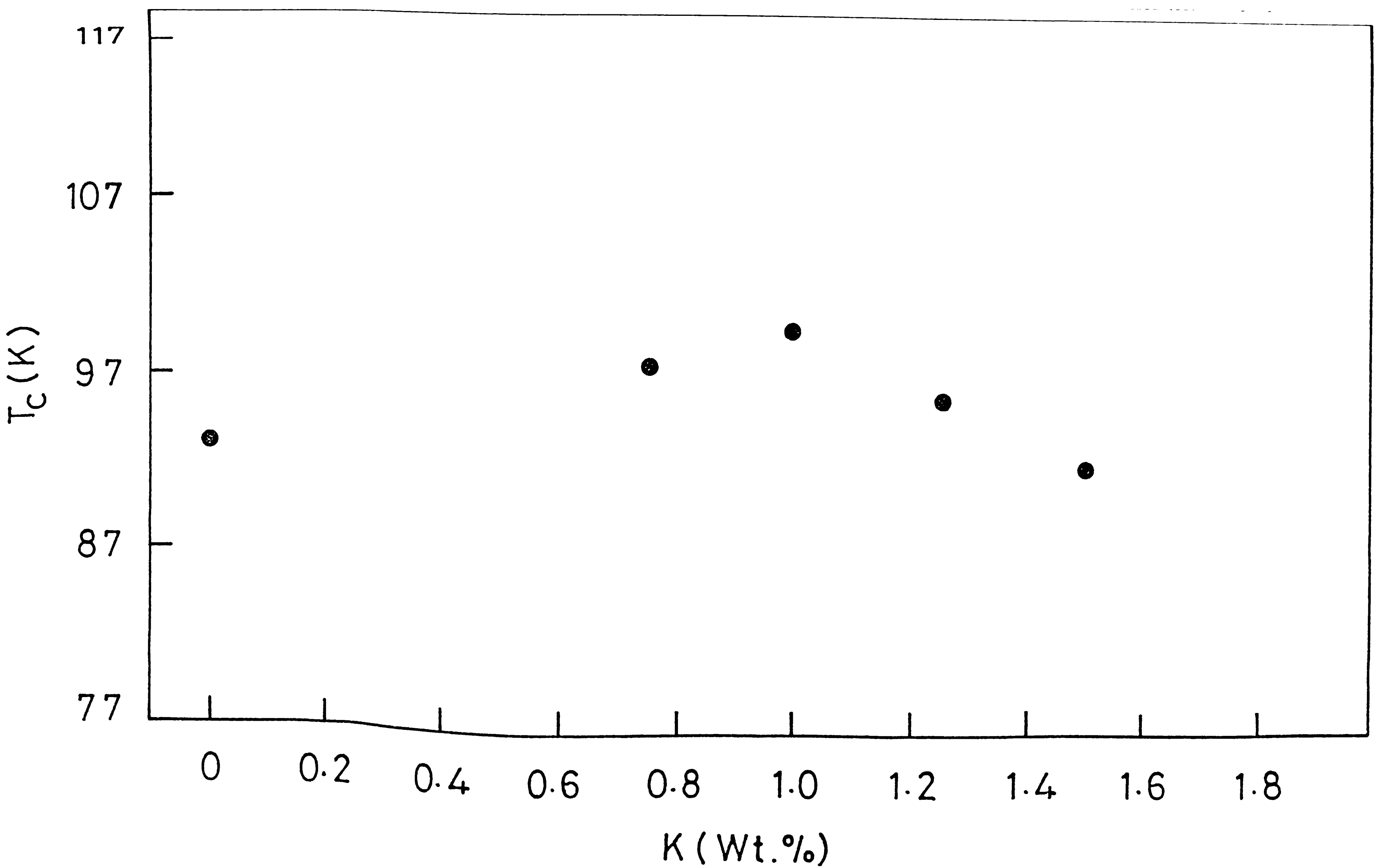


Fig. 5.3. Variation of T_c for different wt. % of K in Gd $Ba_2Cu_3O_{7-\delta}$ based samples.

and they showed stable properties in air for at least two months. It may be noted that the final material was sintered in oxygen for an extra longer duration of time. It has been reported that oxygen pressure during sintering is a controlling factor [93]. In comparison with doping of other impurities like elements of transition metals, calcined pellets of K doped GdBaCuO samples were softer and as a result they could be comminuted easily. However sintered pellets were difficult to grind as easily as the pure samples.

Changes in T_c can be attributed to various reasons like the modification of the local density of states due to K substitution or insertion in the Cu-O planes. From band structure calculations of $ReBa_2Cu_3O_{7-d}$ crystal, it has been revealed that the dominant contribution to superconductivity is the CuO layer and / or CuO chains. A large number of experiments have revealed that high T_c would not exist without the Cu-O layer or CuO chain. Superconductivity in GdBaCuO is thought to be due to holes in the hybridised Cu (3d)-O (2p) band. Any change in carrier concentration should be reflected in the electronic structure of the Cu-O network and thus influence the superconducting properties of the compound.

For pure GdBaCuO, the f- electrons of Gd are localised around Gd and the ion exists in the 3^+oxidation state. However, at low temperature the f-electrons order antiferromagnetically with $T_n \sim$ 2.22K possibly without the destruction of superconductivity. When one closely examines the Gd^{3+} in the lattice, it has a F Configuration S- state ion in the crystal field of the compound. Having zero orbital angular momentum , the Gd^{3+} ion does not interact to first order within the crystalline electric field and it regains the degeneracy of its half integral spin S = 7/2. Band structure calculations revealed that the conduction bands form only in the Cu-O octahedral layers due to the strong hybridization of Cu 3d and O 2p orbitals and the fermi energy E_f lies near a Van Hove singularity for incipient Peierls instabilities. The high T_c was then attributed to the high electron density of the states N (E_f) and soft modes associated with the Van Hove singularity. The high vibrational frequency of the oxygen band - stretching modes are also found to be important [94]. K may play two crucial roles in the superconducting compound - stabilising a structure conducive for the formation of bilayer/trilayer Cu perovskite like slabs and also promoting Cu^{2+} and Cu^{3+} through a redox reaction with Cu. Changes in T_c could likely be caused by the oxygen concentration differences.

A carrier concentration C^* is one of the dominant factions to control the T_c. C^* is expressed as $N / \exp(\pm eQ / k-A)$, where N, Q, k, e and A are the density of the states, Seebeck coefficient, Boltzman constant, electronic charge and a constant respectively [95,96]. A can be assumed to be zero because of the small band gap compared to semiconductors [97]. The exponential term is ~ 1. Therefore C^* is dominated by the density of states (N). It is related to the electrical resistivity R_e by the relation $N = A' / (R_e)^{1/2}$ where A′ is a constant dominated by electron mass, charge, Planck constant and mean free path [98]. If the addition of K does not largely change the mean free path, N depends mainly on R_e. Figure 3 shows the changes in R_e at 150K with K concentration. The lower the R_e values larger become the N and C^* values resulting in a higher T_c. The significant improvement observed with the additions of K (as small as 1%) as an impurity rather than as a substitution suggests a catalytic role of K in the nucleation of the 123 high T_c phase. Addition of similar amounts of Na decreased the formation temperature to 800°C but failed to enhance the T_c [99].

K is monovalent (K^+) with ionic radius $r_i = 1.51Å$, and its introduction decreases the mean cation charge fulfilling the optimal condition for superconductivity. The K minority exerts an influence on the Cu^{3+}/Cu^{2+} valence ratio as well as the charge compensation by oxygen vacancies. Local distortions arise around the impurity site which also affect the Cu - O bonding and the resulting band structure. It can also alter the number of oxygen vacancies occurring in the two dimensional Cu-O network which control the metallic and the superconducting properties of the system. This number of vacancies affect both the Fermi level by changing the charge balance of the formula unit and the band structure by altering the Cu-O overlap. One cannot rule out the formation of inter granular weak link structures which are insulating or normal state materials. Doping improves the bulk properties by reducing or converting this weak link structure by decreasing the grains which are smaller than the penetration depth effective at a given temperature thereby raising the onset of T_c of the weak links considerably. This occurs in spite of the higher void fraction present after annealing and result in preferential growth in the platelet planes which has the effect of increasing the 3-D extent of the sample. A high T_c sample can be modeled as a composite material consisting of superconducting particles embedded in a non superconducting matrix. The effective resistivity of such a medium depends on the packing fraction of the spheres [100]. Such systems may undergo a transition into a coherent state when the intergrain coupling energy overcomes the thermal fluctuations [101]. This state manifests itself by zero resistance at some temperature T_{cs} which is less than T_s and depends sensitively on the applied field effects. Enhancement of $T_c(0)$ may also be possibly due to the improvements in the structural disorder such as incommensuration or some additional electronic reasons associated with the introduction of K.

TABLE - 5.2.:- Variation of T_c with wt % of K.

Weight %	Transition temperature (T_c) K
pure	93
0.5	NSC*
0.75	98
1	100
1.25	96
1.5	92
1.75	NSC*

* Non Superconducting at LN_2.

5.3. REFERENCES

[1] J M Tarascon, L H Greene, W R McKinnon and G W Hull, Sol. St. Commun., 63, 499, (1987).

[2] G M Phatak, A M Umarji, J V Yakhmi, L C Gupta, K Gangadharan, R M Iyer and R Vijayaraghavan, Sol. St. Commun., 63, 905, (1987).

[3] N Ogita, K Ohbayashi, M Udagava, Y Aoki, Y Maeno and T Fujita, Jpn. J. Appl. Phys., 26, L415, (1987).

[4] K Kishio, K Kitazawa, T Hasegawa, M Aoki, K Fueki, S I Uchida and S Tanaka, Jpn. J. Appl. Phys., 26, L391, (1987).

[5] T Hasegawa, K Kishio, M Aoki, N Ooba, K Kitazawa, K Fueki, S I Uchida and S Tanaka, Jpn. J. Appl. Phys., 26, 337, (1987).

[6] S Hosoya, S Shamoto, M Onoda and M Sato, Jpn. J. Appl. Phys., 26, L456, (1987).

[7] A K Grover, S K Dhar, P L Paulose, V Nagarajan, E V Sampathkumaran and R Nagarajan, Sol. St. Commun., 63, 1003, (1987).

[8] K Fukei, K Kitazawa, K Kishio, T Hasegawa, S I Uchida, H Takagi and S Tanaka, ACS Symp., P38, (1987).

[9] W K Kwok, G W Crabtree, A Umezawa, E E Alp, L Morss and L Soderholm, Jpn. J. Appl. Phys., 26, Suppl. 3, (1987).

[10] P Diko, M Reiffers, I Batko, K Csach, O Hudak, V Kavecansky, J Miskuf, M Timko and A Zentko, Czech. J. Phys., 37, 1085, (1987).

[11] G W Crabtree, W K Kwok, A Umezawa, L Soderholm, L Morss and

E E Alp, Phys. Rev. B, 36, 5258, (1987).

[12] J V Yakhmi, L C Gupta, I K Gopalakrishnan, A M Umarji, R M Iyer and R Vijayaraghavan, Jpn. J Appl. Phys., Suppl 26, 1085, (1987).

[13] S Hosoya, S I Shamoto, M Onoda and M Sato, Jpn. J. Appl. Phys., 26, L325, (1987).

[14] C W Chu, P H Hor, R L Meng, L Gao, Z J Huang, J Bechtold, M K Wu and C Y Huang, MRS Anaheim symposium, P15, (1987).

[15] Z Fisk, J D Thompson, E Zirngiebl, J L Smith and S W Cheong, Sol. St. Commu., 62, 743, (1987).

[16] P H Hor, R L Meng, Y O Wang, L Gao, Z J Hung, J Bechtold, K Forster and C W Chu, Phys. Rev. lett., 58, 1891, (1987).

[17] S Kurihara, S Tsurumi, M Hikita, T Iwata, K Semba and J Noda, MRS Anaheim symposium, P145, (1987).

[18] H C Ku, H D Yang, R W Mc Callum, M A Noack, P Klavins, R N Shelton and A R Moodenbaugh, MRS Anaheim symposium, P177, (1987).

[19] Y Le Page, T Siegrist, S A Sunshine, L F Schneemeyer, D W Murphy, S M Zahurak, J V Waszezak, W R Mc Kinnon, J M Tarascon, G W Hull and L H Greene, Phys. Rev.B, 36, 3617, (1987).

[20] M B Maple, K N Yang, M S Torikacvili, J M Ferreira, J J Neumeier, H Zhou, Y Dalichaouch and B W Lee, Sol. St Commun., 63, 635, (1987).

[21] J Marcos, C Escribe - Filippini, C Schlenker and P L Reydet, Sol. St. Commun., 63, 129, (1987).

[22] W R McKinnon, J M Tarascon, L H Greene and G W Hull, MRS Anaheim symposium, P185, (1987).

[23] D W Murphy, S A Sunshine,R B Van Dover, R J Cava, B Batalog, S M Zahurak and L F Schneemeyer, Phys. Rev. Lett., 58, 1888, (1987).

[24] S B Nam, MRS Anaheim symposium, P115, (1987).

[25] S B Nam, S W Nam and J O Nam, Novel SC , 993, (1987).

[26] S Tanaka, S I Uchida, H Takagi, K Kitazawa, K Kishio, S Tajima and K Fueki, MRS Anaheim symposium, P5, (1987).

[27] J M Tarason, W R Mc Kinnon, L H Greene, G W Hull and E M Vogel, Phys. Rev. B, 36, 226, (1987).

[28] J B Torrance, E M Engler, V Y Lee, A I Nazzal, Y Takura, M L Ramirez, J E Vazquez, R D Jacowitz and P M Grant, ACS Symposium, P85, (1987).

[29] G Xiao, F H Streitz, A Gavrin and C L Chien, Sol. St.Commun., 63, 817, (1987).

[30] T Yamanda, K Kinoshita, A Matsuda, T Watanabe and Y Asano, M R S Anaheim symposium, P119, (1987).

[31] K N Yang, Y Dalichaouch, J M Ferreira, B W Lee, J J Neumeier, M S Torikacvili, H Zhou and M B Maple, Sol. St. Commun., 63, 515, (1987).

[32] K N Yang, Y Dalichaouch, J M Ferreira, R R Hake, B W Lee, M B Maple, J J Neumeier, M S Torikacvili and H Zhou, MRS Anaheim symposium, P77, (1987).

[33] K N Yang, Y Dalichaouch, J M Ferreira, R R Hake, B W Lee, J

J Neumeier, M S Torikacvili, H Zhou and M B Maple, Jpn. J. Appl. Phys., 26, Suppl. 26, 3, (1987).

[34] R Escudero, T Akachi, R Barrio, L E Rendon-Diazmiron, C Vazquez, L Banos, G Gonzalez and F Estrada, Sol. St. Commun., 64, 235, (1987).

[35] Z Qi-rui, Q Yi-tai, C Zu-yao, G Wei-yan, Z Yong, X Jian-sheng, C Lie-zhao, P Guo-qang, Z Han, Y Dao-Qi, H Zheng-hui, Z Ming-Jian, S Shi-fang, F Min-hu and Z Tao, Sol. St. Commun., 63, 415, (1987).

[36] A Poddar, P Mandal, P Choudahary, A N Das and B Ghosh, J.Phys. C : Sol. St. Phys., 20, L669, (1987).

[37] J R Thompson, S T Sekula, D K Cristen, B C Sales, L A Boatner and Y C Kim, Phys. Rev. B, 36, 718, (1987).

[38] F Zuo, B R Patton, D L Cox, S I Lee, Y Song, J P Golben, X D Chen, S Y Lee, Y Cao, Y Lu, , J R Gaines, J C Garland and A J Epstein, Phys. Rev. B., 36, 3603, (1987).

[39] B D Dunlap, M Slaski, D G Hinks, L Soderholm, M A Beno, K Zhang, C U Segre, C W Crabtree, W K Kwok, S K Malik, I K Schuller, J D Jorgensen and Z Sungaila , J.Magn. and Magn. Mater., 68, L139, (1987).

[40] G V Subbarao, U V Vardaraju, R Vijayasree, K Padmanabhan, R Balakrishnan, T A Mary, N P Raju, R Srinivasan, U De, J Janaki and T S Radhakrishnan, Physica B, 114, 148, 237, (1987).

[41] U V Vardaraju, S Natarajan, T S Sampathkumar, M Paranthaman, G V Subbarao, N P Raju and R Srinivasan, Physica B, 148, 417, (1987).

[42] G Xiao, F H Streitz, A Gavrin , Y W Du and C L Chien, Phys. Rev. B, 35, 8782, (1987).

[43] C V Narasimha Rao, S K Agarwal, B Jayaram and A V Narlikar, Pramana - J. Phys., 31, L323, (1988).

[44] C N R Rao (ed) "Chemistry of Oxide Superconductors", (Oxford: Blackwell Sci. Publ.- IUPAC) 1, (1988).

[45] E M Engler, V Y Lee, A I Nazzal, R B Beyers, G Lim, P M Grant, S S P Parkin, M L Ramirez, J E Vazquez and R J Savoy, J. Am. Chem. Soc., 109, 2848, (1987).

[46] M B Maple, Y Dalichaouch, J M Ferreira, R R Hake, S E Lambert, B W Lee, J J Neumeier, M S Torikachvili, K N Yang, H Zhou, Z Fisk, M W McElfresh and J L Smith, Novel SC, 839, (1987).

[47] J M Tarascon, L H Greene, B G Bagley, W R McKinnon, P Barboux and G W Hull, Novel SC, P705, (1987).

[48] K Kishio, K Kitazava, S Kanbe, I Yasuda, N Sugii, H Takagi, S I Uchida, K Fueki and S Tanaka, Chem. Lett., (Japan), 429, (1987).

[49] O Smrckova, D Sykorova, J Dominec, K Jurek and L Smrcka, Phys. Stat. Sol., 103, K33, (1987).

[50] S H Kilcoyne and P Cyiwnski., J. Phys.D ., 20, 1327, (1987).

[51] J G Bednorz A K Müller and M Takashige, Science, 236, 73, (1987).

[52] Z Qi-rui, C Lie-zhao, Q Yi-tai, C Zu-yao, G Wei-yan, Z Yong, P Guo-Gang, Z Han, X Jian-sheng, Z Ming-Jian, Y Dao-Qi, F Ming-hu and Z Tao, Sol.St. Commun. 63, 535, (1987).

- G 5344 -

[53] M K Wu, J R Ashburn, C J Forng, G L E Peng, F R Szofran, P H Hor and C W Chu, MRS Anaheim symposium, P69, (1987).

[54] B W Veal, W K Kwok, A Umezawa, G W Crabtree, J W Jorgensen, J W Downey, L J Nowicki, A W Mitchell, A P Paulikas and C H Sowers, Appl. Phys. Lett., 51, 279, (1987).

[55] S B Oseroff, D C Vier, J F Smyth, C T Salling, S Schultz, Y Dalichaouch, B W Lee, M B Maple, Z Fisk, J D Thompson, J L Smith and E Zirngiiebl, Novel SC, 679, (1987).

[56] Y Maeno, T Tomita, M Kyogoko, S Awaji, Y Aoki, H Hoshino, A Minami and T Fujita, Nature, 328, 512, (1987).

[57] I Felner, I Nowik and Y Yeshurun, Phys. Rev.B, 36, 3923, (1987).

[58] P Strobel, C Paulsen and J L Tholence, Sol. St. Commun., 65, 585, (1988).

[59] K Csach, P Diko, V Kavecansky, J Miskuf, M Reifers and P Batko, Czech. J. Phys. B, 37, 1207, (1987).

[60] I K Gopalakrishnan, J V Yakhmi, L C Gupta, A M Umarji, A K Rangarajan, R M Iyer and R Vijayaraghavan, Jpn. J. Appl. Phys. Suppl., 26, 1085, (1987).

[61] J M Tarascon L H Greene, P Barboux W R McKinnon, G W Hull, T P Orlando, K A Delin, S Foner and E J McNiff, Phys Rev B, 36, 8393, (1987).

[62] J M Tarascon, P Barboux,B G Bagley, L H Greene, W R McKinnon and G W Hull, ACS Symp., P198, (1987).

[63] Chin Lin, Zun - Xiao Liu and Jian Lan, Phys. Rev. B, 42, 2554, (1990).

[64] J Thiel, S Song, J B Ketterson and K Poepplemeier, ACS Symposium, P173, (1987).

[65] Tsuyoshi Kajitini, Jpn. J. Appl. Phys., 27, L1307, (1988).

[66] T N Yuen, C L Lin, J E Crow, G N Myer, R E Salomon and P Sclottmann, Phys. Rev. B, 37, 3770, (1988).

[67] Y L Chen, B R Li, A Chen and B F Xu, Hyperfine interactions, 55, 1249, (1990).

[68] G Xiao, M Cieplak, A Gavrin, F H Streitz, A Bakhshai and C L Chien, Phys. Rev. Lett., 60, 1446, (1988).

[69] S K Malik, C V Tomy, A M Umarji, D T Adroja, R Prasad, N C Soni, A Mohan and C K Gupta, J Phys C, Sol. St. Phys. 20, L417, (1987).

[70] D Pavuna, H Berger, M Affronte and J van der Maas, J J Cappni, M Gullot, P Lejay and J L Tholence, Sol. St. Commun., 68, 535, (1988).

[71] M K Malik, V D Nair, A R Biswas, R V Raghavan, P Chaddah, P K Mishra, G Ravikumar and B A Dassanacharya, Appl. Phys. Lett., 52, 1525, (1988).

[72] R G Sharma, Y S Reddy, S R Jha, K D Kundra and D K Suri, Pramana - J.Phys., 30, L75, (1988).

[73] C V Tomy, A M Umarji, D T Adroja, S K Malik, R Prasad, N C Soni, A Mohan and C K Gupta, Sol. St. Commun., 64, 889, (1987).

[74] K K Pan, H Mathias, C M Rey, W G Moulton, H K Ng L R Testardi and Y L Wang, Phys. Lett. A, 125, 147, (1987).

[75] J H Kung, H H Yen, Y C Chen, C M Wang and P T Wu, MRS Boston Symp. 785 (1987) and Jpn. J. Appl. Phys., 26, L657, L832, (1987).

[76] K N R Taylor, D N Mathews and G J Rusell, J. Crystal Growth, 85, 628, (1987).

[77] I Felner and B Barbara, Phys Rev B, 37, 5820, (1988).

[78] S R Ovshinsky, R T Young, D D Allred, G DeMaggio, and G A Vander Leeden, Phy. Rev. Lett., 58, 2579, (1987).

[79] M Xian-Ren, R Yang-Ru, L Ming-Zhu, T Qing-Yun, L Zhen-Jin, S Li-Hua, D Wei-Qing, F Min-Hua, M Qing-Yun, Li Chang-Jiang, L Xiu-Hai, Q Guan-Liang and C Mou-Yuan, Sol. St. Commun., 64, 325, (1987).

[80] R M Iyer, P V P S S Sastry, G M Phatak, I K Gopalakrishnan, K Gangadharan and M D Sastry, Physica C, 152, 505, (1988).

[81] A G Lee, "The Chemistry of Thallium" (ElSevier, Amsterdam 1971) and references therein.

[82] Tomogi Kawai, Takeshi Horiuchi, Katsutoki Mitsui, Kiyoshi Ogura, Sadao Takagi and Shichio Kawai, Physica C, 161, 561, (1989).

[83] M O Figueiredo, F Costa, J M Vielra, J M Alves and M M Godinho, Physica C, 159, 273, (1989).

[84] I Felner, M Kowitt, Y Lehavi, D Edery, L Ben-dor, Y Wolfus, and I Nowik, Mod. Phys. Lett. B, 2, 713, (1988).

[85] I Felner, M Kowitt, Y Lehavi, L Ben-dor, Y Wolfus, B Barbara and I Nowik, Physica C, 153, 898, (1988).

[86] Y Nishi, S Moriya and S Tokunaga, J. Mater. Sci. Lett., 7, 359, (1988).

[87] Y Nishi, S Moriya and S Tokunaga, J. Mater. Sci. Lett., 7, 596, (1988).

[88] Y Nishi, S Moriya and S Tokunaga, Phys. Lett. A, 126, 55, (1987).

[89] I Felner and B Barbara, Sol. St. Commun., 66, 205, (1988).

[90] Y Khan, J Mater. Sci. Lett., 7, 53, (1988).

[91] J D Doss, D W Cooke and C W Mc Cabe and M A Maez, Rev. Sci. Insrum., 59, 659, (1988).

[92] V Vidyalal and C P G Vallabhan (to be published).

[93] M A Beno, L Soderholm, D W Copone II, D G Hinks, J D Jorgensen J D Grace, I K Shuller, C V Segre and K Zhang, Appl. Phys lett., 51, 57, (1987).

[94] Cao Ning , Duan Zhanguo, Shao Xiuyu, Zheng Jiaqi, Ran Qize, Liu Jinxiang, Chang Yingehuan, Hou Desen, Fan Hui, Chen Xichen, and Guan Weiyan, Solid St. Commun., 63, 1125, (1987).

[95] Yoshitake Nishi, Kazuo Nozaki, Takuya Kurotaki, Yuichiro Kita and Kazuya Oguri, Phys. Lett. A, 163, 465 (1992).

[96] N M Tallan and I Bransky, J Electrochem Soc., 118, 345, (1971).

[97] Yoshitake Nishi, Kazuya Oguri, Hideo Ohinata, Kenji Tanioka, Yuichiro Kita and Nabuyuki Ninomiya, Phys. Rev. B, 41, 6520, (1990).

[98] N F Mott, Philos Mag. 19, 835, (1969).

[99] V Vidyalal, K Rajasree and C P G Vallabhan (to be published).

[100] J C Maxwell, "A treatise on electricity and magnetism" (Oxford Univ. N York), 441, (1904).

[101] J R Clem, Physica C, 50, 153, (1988) and references therein.

CHAPTER 6

CRITICAL CURRENT DENSITY MEASUREMENTS IN HTSC SAMPLES

ABSTRACT

This chapter describes the measurement of critical current density (J_c) in HTSC materials. Different techniques employed, methods to enhance the J_c and the effect of sodium doping in Bi based HTSC materials are included.

6.1 INTRODUCTION

The critical current density J_c is an important parameter for the characterisation of high temperature superconductors. The current - carrying capacity of superconductors is determined by J_c, which is essential for the design of devices or transmission lines for power system applications. Several proposed electronic devices using high temperature superconductors such as logic gates or current - triggered superconducting switches, require the knowledge of the critical current for their proper design [1-5].

The different critical parameters of superconductivity; J_c (critical current), H_c (critical field), and T_c (critical temperature) are related to each other. When the current density J in a superconductor exceeds a certain value (J_c), superconductivity is destroyed. This is called the Silsbee effect. J_c of high temperature superconductors remain at a low value compared to conventional (low T_c) superconductors. It also falls dramatically in applied magnetic fields [6]. This has raised doubts about the future use of high T_c materials in various potential high magnetic field applications like superconducting machines, magnets, and related systems.

6.2. MEASUREMENTS OF CRITICAL CURRENT (J_c)

The critical current I_c of a superconductor can be defined as the maximum current that a superconductor can carry at a particular temperature and applied magnetic field. However as noted by many workers [7] this definition is very difficult to apply to measurements in actual practice since the sudden reverting back to 'normal' state (also called 'quenching') produces a large amount of joule heating and hence sample burnouts. This difficulty is overcome by defining I_c as the current at which the voltage across the superconductor is equal to a selected value determined primarily by the sensitivity of the instrument.

There are several measurement techniques available for the determination of J_c viz. DC transport, pulse and magnetisation techniques [8].

The simplest and direct method is the DC transport technique for measuring J_c. In this method J_c is determined by the 4 probe resitivity arrangement [9] (fig.6.1). The transport current through a sample (with a well defined geometry) is gradually increased until the superconducting characteristics are destroyed (Quenching). A finite voltage then appears across the sample, the magnitude of which is measured which generally depends on the sensitivity and range of the instrumentation available and the experimenters decision on the magnitude of the voltage drop (generally ~ 1μV) for the measurement. Thus some ambiguity exists in reported values due to the selection of this criterion. The transport method is preferable for determining the characteristics of a bulk superconductor sample and is the most appropriate method for determining the values of J_c for a variety of practical applications. This method eventhough widely used has the following drawbacks:- 1) I^2R heating of the sample and contacts (with total resistance R) can give a misleading low value for J_c, 2) No information is obtained on the rest of the superconducting to normal transition, but gives only the onset of resistance and 3) the necessity for heavy gauge wires for transporting large currents involved while measuring J_c of bulk samples.

The above drawbacks can be avoided by using the pulse method [10-14]. A short duration current pulse is applied to the superconductor and the voltage across it is amplified and fed to a Boxcar averager. The amplitude of the current pulse is increased until the voltage across the superconductor equals a selected voltage and the corresponding current is then the critical current. Since this method uses low frequency current

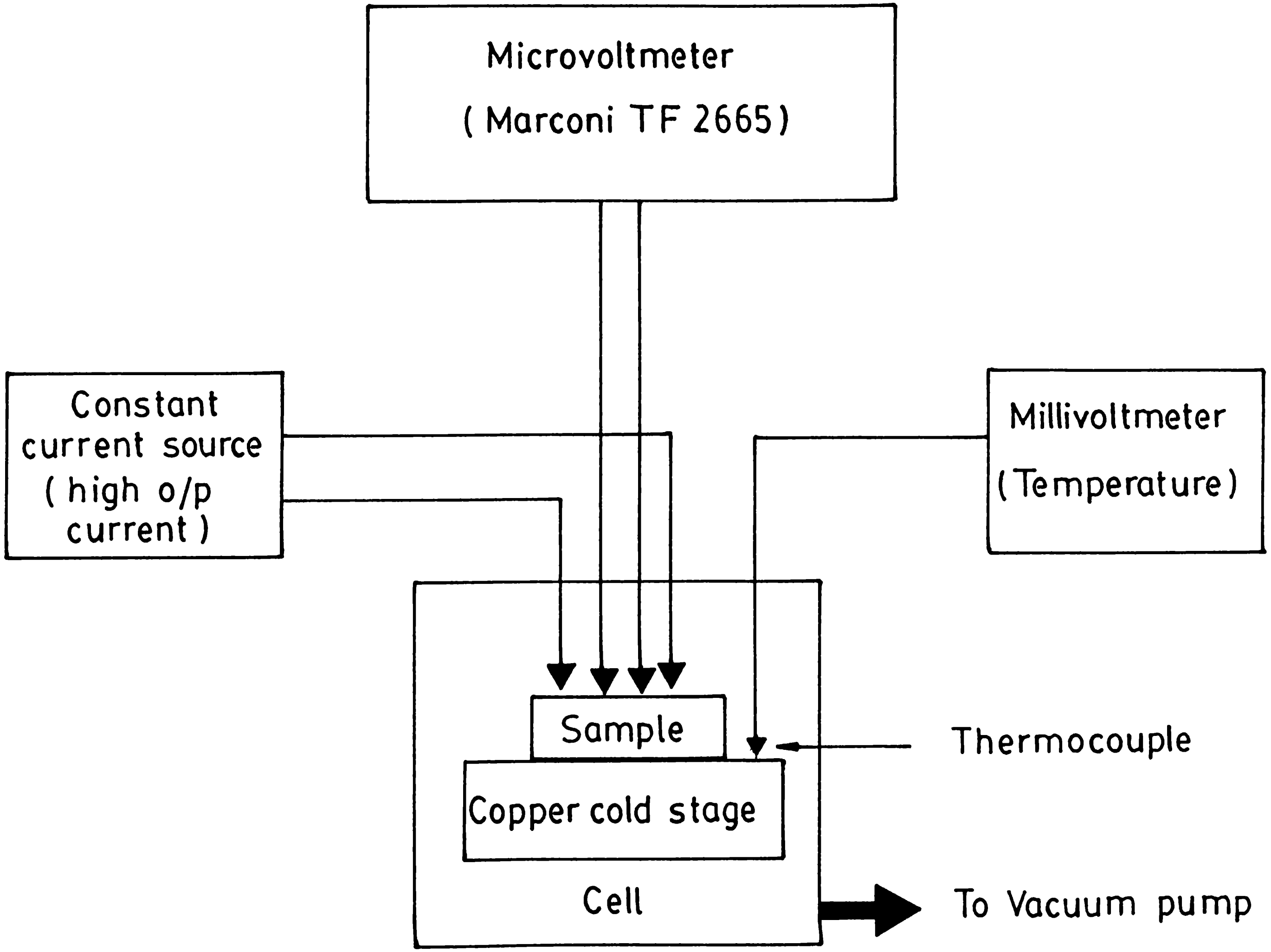


Fig. 6.1. Setup for determining J_c by the transport method.

pulses of variable duty cycle factor, joule heating is less (reduction of I^2 part in I^2R) and also there is sufficient time for the sample to thermally equilibriate with the cool head between pulses (when no current flows through the sample).

However measurement of J_c by the above methods are difficult and they even produce uncertain results whenever the attachment of test leads to a sample is not straightforward. Lead attachment can be quite difficult on very small samples such as single crystals. Similarly in the case of thin structured films, attachments of contacts to accommodate the electrical leads may significantly modify the films characteristics both chemically as well as electrically.

The critical current can also be estimated from magnetic measurements on a superconductor based on the Bean critical state model [15, 16]. J_c obtained by magnetic methods are generally defined as "magnetisation J_c" [17]. Inorder to employ magnetic measurements to determine J_c a suitable "critical state" model must be invoked, the commonly used one being the Bean's model. Within the Bean model formulation, J_c can be determined from both AC [18,19] and DC magnetisation measurements [17]. This method (fully non contact in nature), involves interpretations of the screening currents associated with measurements of the Meissner effect. Indirect measurements of J_c are typically applied to small single - crystal samples where it is rather difficult to attach electrical leads for direct measurements. Predicted large values for J_c (eg. in $YBa_2Cu_3O_{7-\delta}$), are obtained when this method is applied to single crystal samples. Also, intergrain and intragrain supercurrent density can be separated by ac inductive techniques, since there is a large difference in the penetration of flux into the specimen as a function of field amplitude [20]. Using critical field H_c and penetration depth λ, the maximum theoretical critical current density is given by

$$J_c = \left[\frac{H_c}{3\sqrt{6}\pi\lambda} \right] \qquad (6.1)$$

Using the above expression, J_c values of the order of 5 x 10^6 A/cm^2 have been obtained by using measured values of H_c and λ. Typical values for J_c in $YBa_2Cu_3O_x$ single crystals, representing the upper - limit value that one would expect to see in a bulk or thin film samples are of the order of 2 x 10^4 A / cm^2 at 77K in zero magnetic field [21]. The variation of J_c with an applied magnetic field (0.5T-6T) at 1.5K and 15K is given in fig. 6.2 [24]. Similar results have been obtained for HTSC ceramics by others [14, 22, 23].

Magnetization current can be related to the magnetic hysteresis by the basic relation for magnetization current density J_M ($J_M \simeq J_c$) by

$$J_M = \left[\frac{2 \, \Delta M}{\mu_o D} \right] \qquad (6.2)$$

where ΔM is the width of a major hysteresis in the M / H curve [21] and D is the thickness of the specimen. When the applied magnetic field H is more than the lower critical field H_{c1}, penetration of flux lines into the sample takes place and results in hysteresis of the isothermal magnetisation curves. The magnitude of the magnetisation difference $\Delta M = (M^+ - M^-)$ diminishes at high temperatures where M^+ and M^- are the magnetisation of the decreasing and increasing branches (Fig. 6.3). According to the Bean critical state model, ΔM(H,T) is directly proportional to the J_c of the material. Therefore J_c is proportional to the width ΔM of the hysteresis loop. A typical diamagnetic magnetisation curve for a type II superconductor ($TlBa_2Ca_2Cu_3O_y$) is shown in fig 6.4 [24].

In the AC measurement, from an analysis of the imaginary or out of phase fundamental susceptibility component χ'', one can estimate J_c, since χ'' is proportional to the hysteretic losses

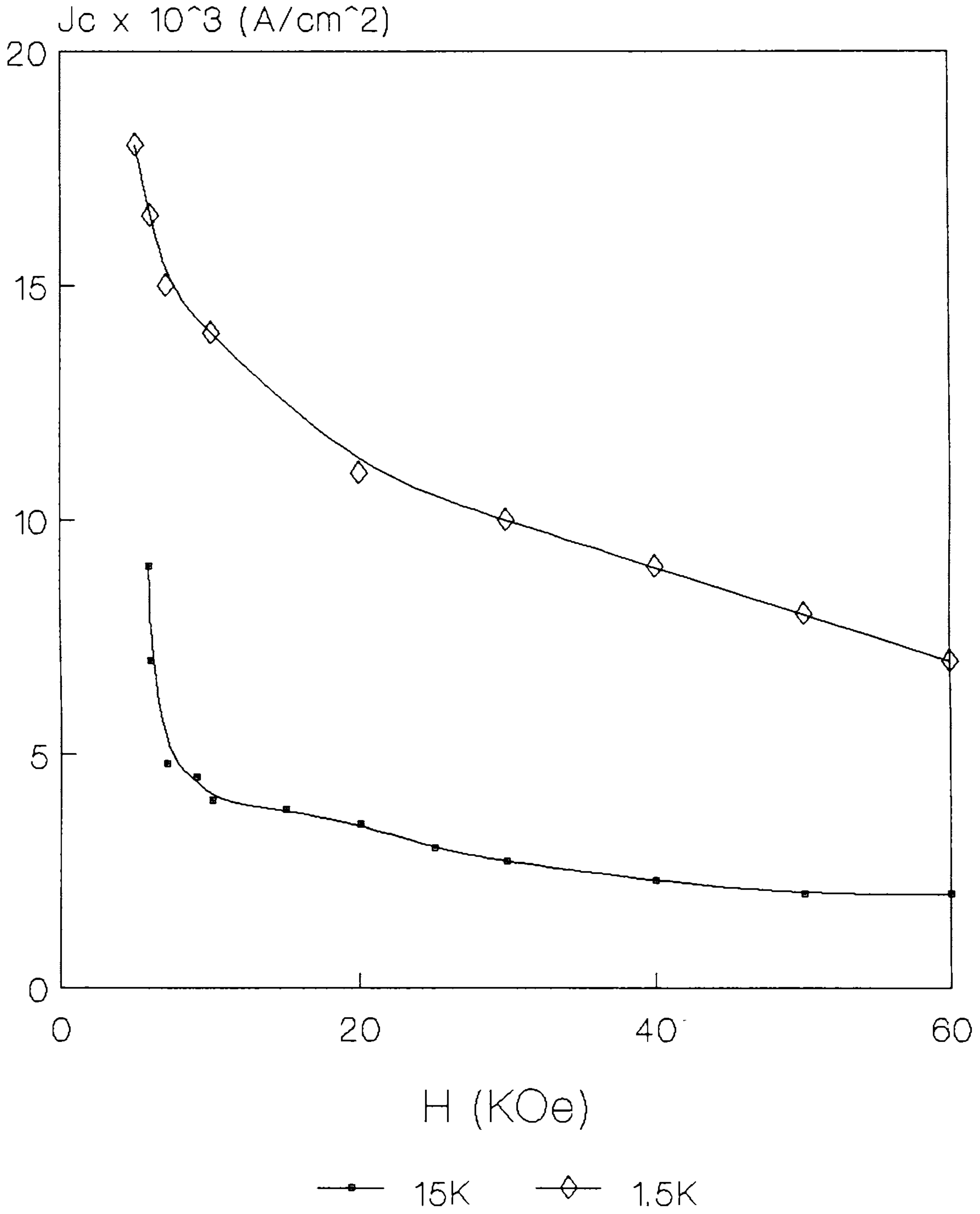


Fig. 6.2. Variation of J_c with an applied magnetic field at 1.5K and 15K (After C D Wei etal [24].

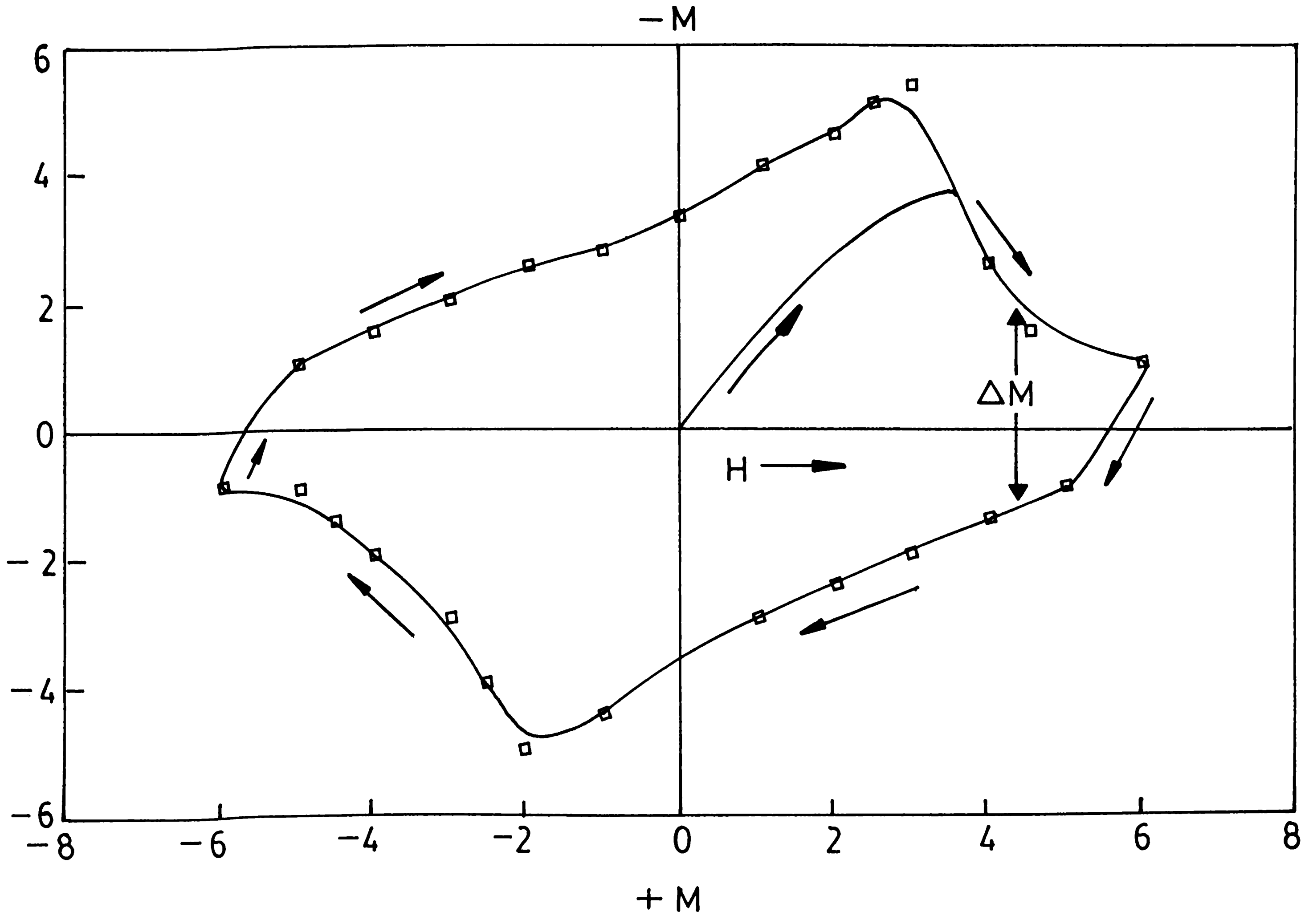


Fig. 6.3. A typical magnetisation curve for type II superconductor showing M^+, M^- and ΔM.

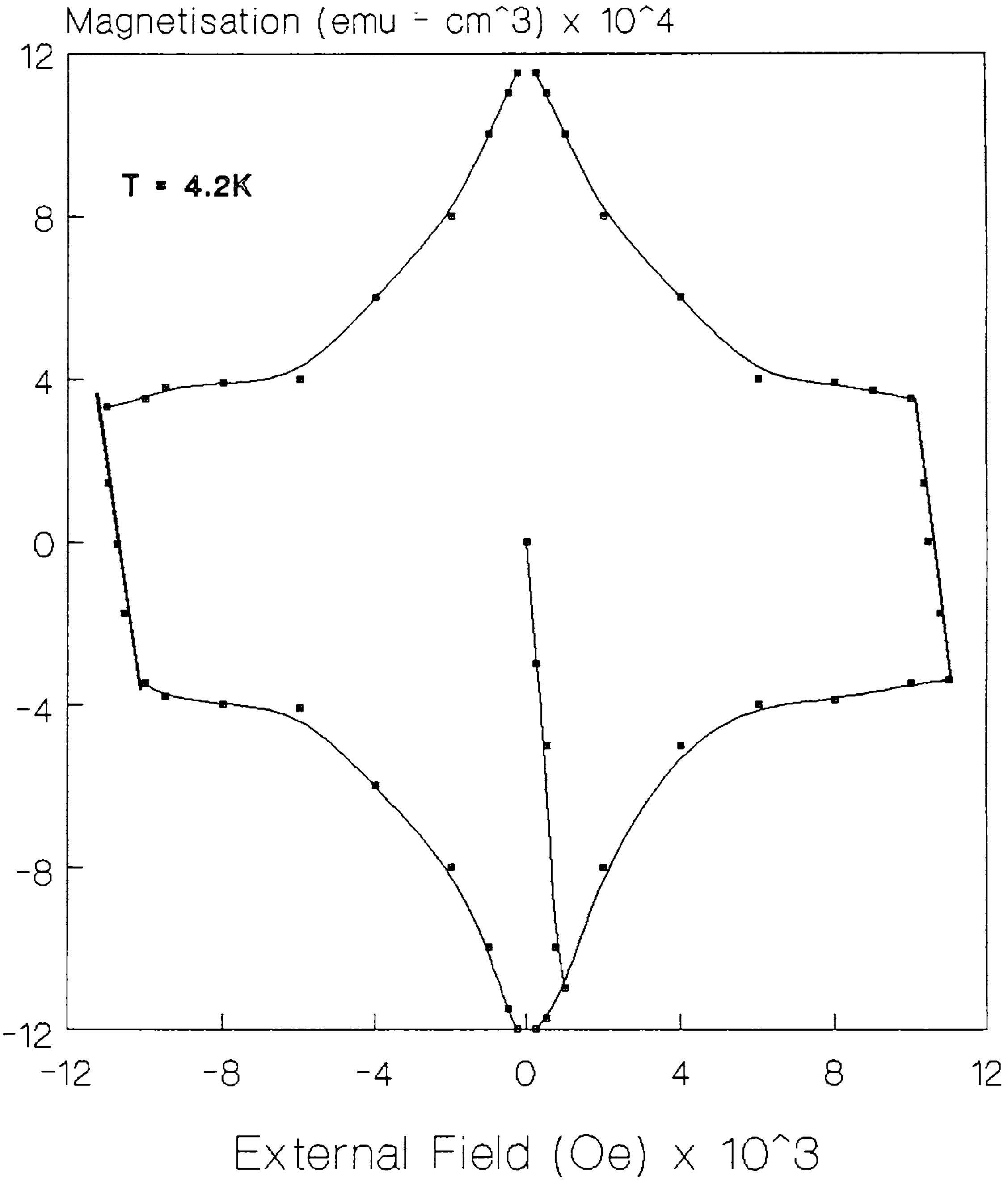


Fig. 6.4. A typical magnetisation curve for $TlBa_2Ca_2Cu_3O_y$ superconductor (After C D Wei etal [24].

i.e. $\chi'' \alpha W \alpha \int HdM$ where M is the magnetisation per unit volume equal to the half width of the hysteresis loop, $\Delta M/2$, and W is the hysteresis loss per unit volume per field cycle. For example in the case of a sample of a slab configuration (thickness 2a, and applied AC field parallel to the slab surface), $J_c = H_p/a$, also H_p is equal to the amplitude of the measuring field H_m at the peak in χ''. This enables one to estimate J_c from an analysis of χ''. In the Bean model H_{c1} is usually taken to be zero, H_a is the applied DC field and H_p is the full penetration field which is a function of the critical current density J_c, and also of the sample geometry. M is the magnetisation per unit volume, which is equal to the halfwidth of the hysteresis loop, (ΔM / 2) for $H_a \geq H_p$. H_m is the maximum field for the hysteresis cycle, *ie.* the amplitude of the AC field.

The equations that relate J_c to DC magnetisation for three common sample geometries are :-

(a) $J_c = 20 \Delta M / D$ ($H_a \parallel$ slab surface) for a slab of thickness D, (b) For a cylinder of radius R, $J_c = 15\Delta M / R$ (H_a axial), and (c) For a flat plate sample $J_c = 10\Delta M / [a - a^2 / 3b]$ ($H_a \perp$ plane, a, b are lateral dimensions of the sample).

Also an equivalent expression to estimate the J_c of single crystals is given by $J_c = 30 \Delta M / d$ A/cm^2, d is the disk radius in cm. [25 - 28].

Even though the T_c of BiSrCaCuO and TlBaCaCuO are high (103K and 125K respectively), the J_c of these compounds are small in external fields at high temperature. The hysteresis observed in the magnetisation versus field curve is much smaller in these compounds than that in $YBa_2Cu_3O_{7-x}$. The single - crystal anisotropy is an important factor whenever single - crystal structures are considered. One effect of this anisotropy is that J_c and the slope of $H_{c2}(-dH_{c2} / dT)$ are dependent on direction of current flow through the crystal. For electric fields aligned with the $YBa_2Cu_3O_x$ single crystal's a - b plane, J_c is at least an order of magnitude higher than that for electric field parallel to c - axis.

The advantages and disadvantages of each technique used for determination of J_c have been discussed in detail by Goodrich and Bray [7]. The value of J_c in epitaxial films range from 10^5- 10^6 A/cm^2. J_c levels in excess of 10^4A/cm^2 at T = $0.9T_c$ have been measured on polycrystalline films, with J_c varying as $\left[(1-T/T_c)\right]^{3/2}$ near T_c and J_c proportional to $\left[(1-T/T_c)\right]^2$ for temperatures below $\approx$ $0.8T_c$ [17]. The value of $J_c(T)$ increases from zero at $T = T_c$ to a maximum value $J_c(0)$ at 0K. The various values of J_c at different temperatures for some common high T_c materials are given in table 6.1. The materials are either sintered compacts, single crystals, thin films or tapes. The transport currents are found to be lower than magnetisation currents in LaSrCuO and YBaCuO systems (table 6.1). Magnetisation derived J_c in bulk single crystal [25] are in excess of 10^6 A/cm^2 in the a-b plane, where as direct transport values are of bulk polycrystals [29 - 31] which are orders of magnitude lower. This difference is attributed to the intrinsic anisotropy of the materials or to the weak-link coupling between the grains [6, 32]. This could be also due to granularity and poor intergrain contact. Improving sample quality brings these values closer to single crystal values [33]. However J_c values of good YBaCuO epitaxial thin films determined by both the methods have almost identical values [34, 35]. Characterization of a high purity, single - phase crystal may at least indicate the possible magnitude of J_c values for a bulk material. However single crystals may not be completely free of impurities and may also present weak links at twinning boundaries. Further, the oxygen concentration gradient across a very small crystal may be sufficient to produce a superconductor with characteristics that vary with depth into the crystal.

A number of reports regarding the measured values of J_c spanning a wide range appear in the literature. The values range from 10 - 10^6A /cm^2. This is mainly due to the difference in measuring techniques, types of samples used (single crystal, bulk or thin film), dopants, synthesising routes etc. The lowest J_c usually is in bulk or polycrystalline samples (10-1000A/cm^2) and these values are usually for low or zero magnetic fields. In sintered samples, superconducting domains are connected by very thin insulating regions which act as tunneling junctions at low temperatures. Similarly the formation of twinning boundaries also limit the J_c. They are formed during synthesis of the HTSC ceramics [36]. These twinning boundaries which have a short coherence length ξ, form effective intragrain weak - link Josephson junctions that severely limit the critical current levels. However this can be minimised in highly textured films.

Synthesising techniques play an important role in determining J_c. One of the improvements made in increasing the transport properties of ceramic High T_c compounds is by a processing technique called the melt - textured growth [21] (see Chap.2). By using the melt textured growth technique, J_c as high as 10^6A / cm^2 or greater have been obtained in epitaxial thin films [34, 35, 37, 38] and single crystals [25, 39, 40]. This high value is not only due to the improvement in connectivity between the grains but also from the alignment of the anisotropic crystallites. Therefore this technique leads to the formation of dense structures, improved connectivity between the grains and to the orientation of the crystalline structure along the preferred superconducting axis, and also removes the impurities or forms cleaner grain boundaries due to the involvement of high processing temperatures. Fig 6.5 represents the various J_c values achieved in $YBa_2Cu_3O_x$ superconductors processed by different routes. A comparison is made with Nb_3Sn.

Several groups have studied the presence of carbon as a contaminant in $YBa_2Cu_3O_x$ [41, 42]. Such factors limit the J_c by

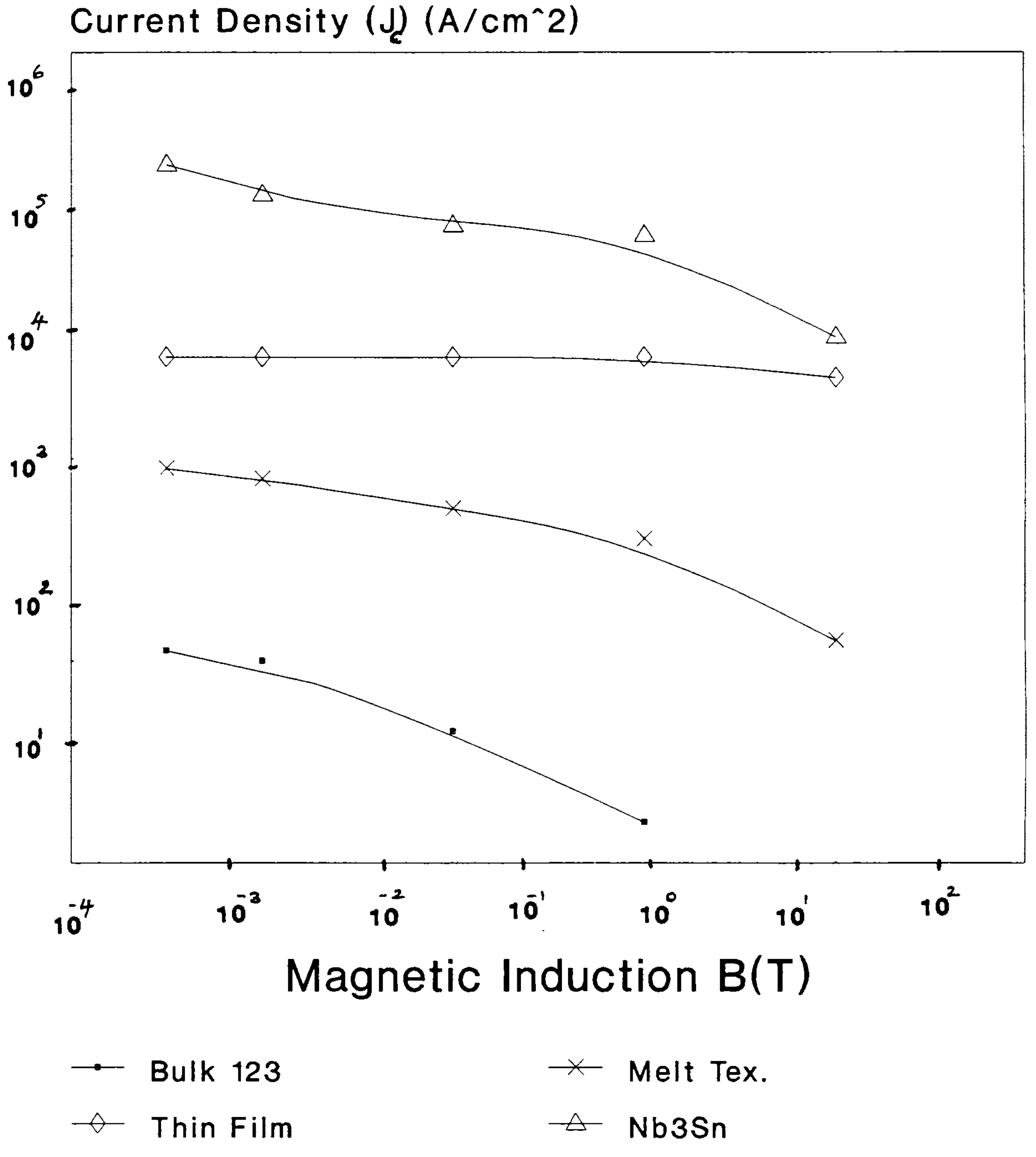


Fig. 6.5. Plot of J_c versus magnetic field for different forms of YBaCuO compared with Nb_3Sn.

acting as a weak link at the interfaces between the grains. Similarly the presence of excess yttrium [43] in YBaCuO, insulating surfaces (can be removed by polishing) [44] etc. limit the J_c in these oxide superconductors.

Grinding and heattreating samples of LaSrCuO and YBaCuO were found to appreciably increase J_c at 4K [45]. High J_c requires efficient flux pinning since J_c increases with pinning force [46]. Weak pinning leads to flux creep and low critical currents [47]. Although the oxide superconductors do not yet compete with the old ones in critical currents, they are superior in their critical field (H_{c2}) capability.

6.3. ENHANCING J_c IN OXIDE SUPERCONDUCTORS

Additions of silver was reported to improve J_c to some extent. J_c was found to depend on the amount of Ag added to the host 123 material :- 4% of Ag_2O increased the J_c to 125A/cm^2(about 5 times), J_c for pure YBaCuO (123) being 40A / cm^2 but reduced to 80A / cm^2 for 6% silver [48]. Possible explanations put forward by the authors is that the Ag improves the connectivity between the superconducting grains and also Ag diffuses into the crystal lattice enhancing J_c.

Improvements in J_c by the use of fluorine in the processing of 123 compounds is also reported [49]. Even though fluorine does not appear to go into the 123 unit cell, it strengthens the weak link connectivity.

From table 6.1 it is clear that the values of J_c at 4.2K is much higher than at 77K. J_c also is anisotropic with higher values parallel to the copper oxide planes. The critical current density is strongly dependent on the direction of the applied field, reflecting the crystallographic anisotropy [25, 50 - 52]. It has been realised that J_c correlates with the physical density of the superconducting oxide ceramics [53]. The low density is thought to be due to the weak links between the grains in the sintered materials. Non - superconducting grain boundaries have a detrimental effect on J_c [54].

Substitution of iron at the copper site enhances J_c due to flux pinning (even though the T_c is reduced). Large intergranular pinning forces have been reported by Wordenweber et al [55] in Y 123 + Fe, the composition being $YBa_2(Cu_{1-x}Fe_x)_3O_{7-y}$, for $x \leq 0.01$ and it is an isostructural layered material.

In Tl based HTSC, the 2223 phase has a higher J_c than 2212. This is due to the fact that the 2223 phase has another Ca and CuO_2 layers inserted into the 2212 phase. This layer must be responsible for the stronger flux pinning in the 2223 phase (larger J_c indicates strong flux pinning in the material) [24]. Also the variation (decrease) of J_c with temperatures above 40K is much more rapid in the case of Tl (2223) than in YBaCuO, probably due to difference in flux pinning mechanism for these systems. It is to be emphasised that pinning sites are different from those seen in low T_c conventional superconductors. A pinning site has to be of the size of coherence length and of the order of 10-20Å. J_c of bulk polycrystalline 123 is very poor (of the order of 100 - 200A/cm^2 as compared to 10^6 A / cm^2 in single crystals of 123 at 77K). The low values of J_c are attributed to the presence of weak links in polycrystalline bulk 123 during synthesis at high temperatures. However, thin films of 123 grown epitaxially on $SrTiO_3$ substrates using laser ablation show J_c's comparable to that of single crystals.

6.4 EFFECT OF Na DOPING ON J_C IN BSCCO SYSTEMS

6.4.a. Introduction

The bismuth based superconductor viz. Bi Ca Sr CuO (BSCCO) at present is the best choice for developing high T_c wires / tapes for various high field magnetic systems which can be operated at 77K. The various advantages of this system are :- a) It has a high $T_c \approx$ 110K well above 77K, b) Non toxic compared to other systems like TlBaCaCuO (TBCCO), c) Better stability and less reactive with humidity and water vapour etc, d) Not sensitive to oxygen stoichiometry (like the 123 systems), and e) A lower sintering temperature (~ 850°C) which is ideal for using a cladding material like silver which has a higher melting point (~ 930°C).

Movement of flux lines by current induced self-field reduces J_c. This field maybe caused either by an external magnetic or electrical field. Therefore if this movement of flux lines are restricted, J_c does not reduce sharply. Stacking faults and lattice distortions along with precipitates of copper and calcium in the BSCCO system are the possible flux pinning sites in this material. It is caused due to rapid solidification and the introduction of extra Ca and Cu in the starting material. Inhomogeneities such as lattice defects, grain boundaries, and fine precipitates etc. in the material act as flux pinning centres and prevent flux line movement until a large J_c is attained. Fine non superconducting phases such as $Sr_2Ca_2Cu_3O_x$, Ca_2CuO_3, and $CaSrPbO_4$, act like flux pinning centres in Ag sheathed BPSSCO tapes having excess of copper [56]. A J_c value of 17400A/cm^2 (77K, 0T) have been reported in these materials. Effect on T_c and Hall effect by doping with Na in the 2212 has been studied extensively by Koike et al [57]. They reported a small increase in T_c (due to increase in hole concentration), even though there is no mention about the Na entering the lattice or getting evaporated. However, EDS studies by others have shown that Na gets evaporated and does not enter into the lattice [58]. Therefore the introduction of dopants such as Na in the material (which does not alter T_c drastically upto a certain stoichiometry) seem to be the right step to be investigated in the BPSSCO systems.

6.4.b. Experimental

The effect on J_c by substituting a monovalent alkali metal such as sodium in the BSCCO system has been investigated here [59]. The composition chosen is $Bi_2Na_xCa_{1-x}Sr_2Cu_2O_y$. Other samples studied include $GdBa_2Cu_3O_{7-x}$, $GdBa_2Cu_3O_{7-x}$+K, BiCaSrCuO, $Bi_{1.7}Pb_{0.3}Ca_2Sr_2Cu_3O_{10-x}$ and laser ablated thin film of $GdBa_2Cu_3O_{7-x}$. Narrow rectangular bars about $1mm^2$ in cross section were cut from sintered pellets of these materials using a diamond saw. The details of sample preparation etc. are given in chapter 2. Intermediate cold pressing technique [60] was also adopted during synthesis. Room temperature X-ray diffraction data were obtained with a Phillips powder diffractometer using CuK_α radiation. The J_c of the samples were determined by the transport current method described earlier fig.(6.1). A constant current source capable of delivering high current was used to bias the HTSC samples. Low contact resistance to the samples was ensured by applying a thin layer of silver paint in the 4 probe electrode pattern. The sample is then heated in the furnace for around 1hour at a temperature below the original sintering temperatures. The electrical leads were spark - bonded to the samples by the capacitor discharge technique [61]. Such a method provide reliable electrical contacts with merits such as good mechanical strength, a small and well defined contact area, low contact resistance and usability from low to very high temperatures. The samples were bonded on to the copper cold finger using GE - varnish. A DC microvoltmeter (Marconi instruments, T F 2655, 100nV resolution) was used to measure the voltage derived from the samples. The temperature of the samples were monitored using a precalibrated chromel - Alummel thermocouple. All measurements was carried out at liquid nitrogen temperatures under vacuum conditions. Critical current I_c was determined at 77K as per the 1μV/cm criterion by the four probe method. J_c values were then calculated by dividing I_c values by the area of cross section of the samples. The results obtained are tabulated in table 6.1.

6.4.c. Results and discussion

From the table it is clear that the Na doped samples have a lower J_c than the pure BSCCO or the Pb/Ag doped BSCCO systems. Possible explanation is that the pinning mechanisms is altered adversely in Na doped BSCCO. It is also likely that these mechanisms are all quite different in the various systems compared.

Oxide superconductors with excellent superconducting properties can carry, however, only small transport currents [6], while closed currents with fairly high density are known to flow inside grains [26,62 63]. This suggests a percolative behaviour of the current caused by imperfections such as insulating layers, voids, cracks, and normal phases.

The observed transport and magnetic properties of these ceramics materials basically depend on two types of vortices:- Intragrain vortices and intergrain vortices. The former is based on large intragrain current densities, while the latter is based on josephson vortices which rely on the reduced intergrain current densities J_j.

The evaluation of intergrain and intragrain J_c of $Tl_2Ca_2Ba_2Cu_3O_{10-\delta}$ and $Tl_2Ca\,Ba_2Cu_2O_{8+\delta}$ materials have been done by transport as well as extensive magnetic measurements. It has been found that Intragrain J_c is large and greater than the transport values [64].

Therefore the two mechanisms which put an upper limit on J_c are a) depinning of intergrain vortices, and b) suppression of the effective grain coupling by the magnetic field. The most significant property of these materials, from a technical point of view, is their very high H_{c2} at low temperatures. For example, it has been shown that in the case of YBaCuO, after an initial sharp drop J_c remains roughly constant with field, for T <60K at fields upto 20T or higher [65]. The exceptional high upper critical fields of these new materials invite speculation about their possible application in high field magnets. The conventional superconductors when used for heavy current applications, are unlikely operated at temperatures > 20% of T_c. In the newer materials, at present, the highest confirmed T_c values are $\gtrsim$ 125K, and therefore the operating temperatures will be $\gtrsim$ 25K.

J_c (in the present ceramics) also depends on sample geometry and self field limitation. In the case of granular superconductors, assuming a grain mean size, the coupling energy E_j can be written as

$$E_j = \left[\phi_o / 2\pi c\right] I_j \qquad (6.3)$$

where ϕ_o= hc / 2e is the flux unit and I_j is the maximal Josephson's current flowing between the adjacent grains. The grains themselves are considered superconducting with a condensation energy $E_g = H^2_{cg}\ (a)^3/8\pi$; which is much larger than the coupling energy E_j between the grains. (H_{cg} is the thermodynamic critical field of the grains). In this limit which applies well to the oxide superconductors, the current in the ceramic is limited by the coupling E_j and not by the suppression of the order parameter in the grains [66].

6.5.REFERENCES

[1] S K Dhali and M Mohsin, Rev. Sci. Instrum, 63, 220, (1992).

[2] B Chelluri, J Barber, N Clements and D Johnson, J. Appl. Phys., 69, 4910, (1991).

[3] K E Gray, T Lenihan and J Tarczon, IEEE Trans. Magn. MAG - 15, 175, (1979).

[4] A Frenkel , T Venkatesan , C Lin , X D Wu, M S Hegde, A Inam and B Dutta, Appl. Phys. Lett., 53, 2704, (1988).

[5] Q Y Ma and E S Yang, Cryogenics, 30, 1146, (1990).

[6] J W Ekin, A I Braginski, A J panson, M A Janocko, M Hong, J Kwo, S H Liou, D W Capone II, N J Zaluzec and B Flandermeyer, J. Appl. Phys., 62, 4821, (1987).

[7] L F Goodrich and S L Bray, Cryogenics, 30, 667, (1990).

[8] L F Goodrich and S L Bray, Cryogenics, 31, 720, (1990).

[9] A F Clark and J W Ekin , IEEE Trans. Magn., 13, 38, (1977).

[10] T E Jones and W C McGinnis, Vol., EA-11, P235, "Extended abstracts : High Temperature Superconductors", ed. D U Gubser and M Schuler (Materials Research Society, Pitsburg), (1987).

[11] W C McGinnis, T E Jones, E W Jacobs, and R D Rees and J W Schindlerr, IEEE Trans. Magn., 25, 2138, (1989).

[12] W C McGinnis, E W Jacobs, C D Rees and T E Jones, Rev. Sci. Instrum., 61, 3, (1990).

[13] Lei Wang and Shirshak K Dhali, Supercond. Sci. Technol., 6, 199, (1993).

[14] T E Jones and W C McGinnis, MRS Anaheim Symp., 225, (1987).

[15] Charles P Bean, Rev. Mod. Phys., 36, 31, (1964),

[16] W A Fietz and W W Webb, Phys. Rev., 178, 657, (1969).

[17] D M Kroeger, C C Koch and J P Charlesworth, J. Low. Temp. Phys., 19, 493, (1975).

[18] S D Murphy, K Renouard, R Cittenden and S M Bhagath, Sol. St. Commun., 69, 367, (1989).

[19] J R Clem, Physica C, 153, 50, (1988).

[20] B T Ni, T Munakata, T Matsushuta, M Iwakuma, K Funaki, M Takeo and K Yamafuji, Jpn. J. Appl. Phys., 27, 177, (1988).

[21] S Jin, T H Tiefel, R C Sherwood, R B van Dover, M E Davis, G W Kammoltt and R A Fastnacht, Phys. Rev. B, 37, 7850, (1988).

[22] A J Panson, A I Braginski, J R Gavaler, J K Hulm, M A Janocko, H C Pohl, A M Stewart, J Talvacchio and G R Wagner, Phys. Rev. B, 35, 8774, (1987).

[23] J W Ekin, A J Panson, A I Braginski, M A Janocko, M Hong, J Kwo, S H Liou, D W Capone II and B Fladermeyer, MRS Anaheim Symp., 223, (1987).

[24] C D Wei. C Lin, Z H Shen, Z X Liu, J Lan, K Wu, L X Xie, Y D Dai, Z Z Gan, Mod. Phys. Lett. B, 3, 157, (1989).

[25] T R Dinger, T K Worthington, W J Gallagher and R L

Sandstorm, Phy. Rev Lett., 58, 2687, (1987).

[26] H Kumakura, M Uehara and K Togano, Appl. Phys. Lett., 51, 1557, (1987).

[27] J Z Sun, D J Webb, M Naito, K Char, M R Hahn, J W P Hsu, A D Kent, D B Mitzi, M R Beasley, T H Geballe, R H Hammond and A Kapitulnik, Phy. Rev. Lett., 58, 1574, (1987).

[28] G Xiao ,F H Streitz, A Gavrin, M Z Cieplak, J Childress, M Lu, A Zwicker and C L Chien, Phy. Rev.B, 36, 2382, (1987).

[29] J W Ekin, Adv. Ceram. Mater 2, 586, (1987).

[30] R J Cava , B Batlogg, R B Van Dover, D W Murphy, S Sunshine, T Siegrist, J P Remeika, E A Rietman, S Zahurak and G P Espinosa, Phys. Rev. Lett., 58, 1676, (1987).

[31] G R Wagner, J Talavacchio and A J Panson, Mater. Lett., 6, 390 (1988).

[32] D E Farrell, M R DeGuire, B S Chandrasekhar, S Alterovitz, P Aron and R Fagaly, Phys. Rev. B, 35, 8797, (1987).

[33] H Wuhl, I Apfelstedt, M Dietrich, J Ecke, W H Fietz, J Fink, R Flukiger, E Gering, F Gompf, H Kûpfer, N Nûker, B Obst, C Politis, W Reichardt, B Renker, H Rietschel, W Schauer and F Weiss, MRS Anaheim Symp., P189, (1987).

[34] P Chaudhari, R H Koch, R B Laibowitz, T R Mcguire and R J Gambino, Phy. Rev Lett., 58, 2684, (1987),

[35] B Oh, M Naito, S Arnason, P Rosenthal, R Barton, M R Beasley, T H Geballe, R H Hammond and A Kapitulnik, Appl. Phys. Lett., 51, 852, (1987).

[36] J G Bednorz and K A Müller, Rev. Mod. Phys., 60, 585, (1988).

[37] J Kwo, T C Hsieh, R M Fleming, M Hong, S H Liou, B A Davidson and L C Feldman, Phys. Rev B, 36, 4039, (1987).

[38] S X Dou, H K Liu, A J Bourdillon, N T Tan, J P Zhou, C C Sorell and K E Easterling. Mod. Phys. Lett., B1, 363, (1987).

[39] G W Crabtree, J Z Liu, A Umezawa, W K Kwok, C H Sowers, S K Malik, B W veal, D J Lam, M B Brodsky and J W Downey, Phy. Rev B, 36, 4021, (1987).

[40] T K Worthington, W J Gallagher and T R Dinger, Phys Rev Lett., 59, 1160, (1987).

[41] F Parmigiani, G Chiarello, N Ripamonti, H Goretzki and U Roll, Phys. Rev. B, 36, 7148, (1987).

[42] J D Verhoeven, A J Bevolo, R W McCallum, E D Gibson and M A Noack, Appl. Phys. Lett., 52, 745, (1988).

[43] Z Mai, L Chen, X Chu, D Dai, Y Ni, Y Huang, Z Xiao, P Geand Z Zhao, Phy. Lett. A, 127, 297, (1988).

[44] Clarke J, Nature, 333, 29, (1988).

[45] M Suenaga, A Ghosh, T Asano, R L Sabatini and A R Moodenbaugh, MRS Anaheim Symp., 247, (1987).

[46] R P Huebener, Magnetic flux structures in superconductors, Springer Verlag, New York, (1979).

[47] C Giovannella, G Collin, P Rouault and I A Campbell, Europhys. Lett., 4, 109, (1987).

[48] M K Malik, V D Nair, A R Biswas, R V Raghavan, P Chaddah, P K Mishra, G Ravikumar, and B A Dasannacharya, Appl. Phys. Lett., 52, 1525, (1988).

[49] Hakuraku Y, F Sumiyoshi and T Ogushi, Appl. Phys. Lett., 52, 1528, (1988).

[50] S Hagen, T W Jing, Z Z Wang, J Horwath and N P Ong, Phys. Rev. B, 37, 7928, (1988).

[51] S Martin, T Finoy, R M Fleming, L F Schncemeyer and J V Waszczak, Phys. Rev. Lett., 60, 2194, (1988).

[52] Z Z Wang and N P Ong, Phys. Rev. B, 38, 7160, (1988).

[53] N McN Alford, W J Clegg, M A Harmer, J D Birchall, K Kendell and D H Jones, Nature, 332, 58, (1988).

[54] S X Dou, H K Liu, A J Bourdillon, J P Zhou, N T Tan, X Y Sun and C C Sorell, J. Am. Cerami. Soc., 71, 127, (1988).

[55] R Wordenweber, G V S Sastry, K Heinemann and H C Freyhardt, J Appl. Phys., 65, 1648, (1989).

[56] T Hikata, T Nishikawa, H Mukai, K Sato and H Hitotsuyanagi, Jpn. J. Appl. Phys., 28, L1204, (1989).

[57] Y Koike, T Kamo and S Matsuda, Jpn. J. Appl. Phys., 28, L551, (1989).

[58] S V Suryanaryana, B Gopala Krishna, Ravichandra Gundakaram and S Venkat Reddy, Bull. Mater. Sci., 14, 303, (1991).

[59] V Vidyalal, K Rajasree and C P G Vallabhan, (to be published).

[60] T Asano, Y Tanaka, M Fukutomi, K Jikihara, J Machida and H Maeda, Jpn. J. Appl. Phys., 27, L1652, (1988).

[61] Yasuhiro Iye, Tsuyoshi Tamegai, Hiroyuki Takeya and Humihiko Takei, Jpn. J. Appl. Phys., 27, L658, (1988).

[62] I Apfelstedt, R FlÜkiger, H KÜpfer, R Meier - Hirmer, B Obst, C Politics, W Schauer, F Weiss and H WÜhl, Proc 18th Int. Conf. Low Temperature Physics, Kyoto, (1987), Jpn. J. Appl. Phys., 26, Suppl. 26 - 3, 1181, (1987).

[63] K Funaki, M Iwakuma, Y Sudo, B Ni, T Kisu, T Matsushita, M Takeo and K Yamafuji, J. Appl. Phys., 26, L1524, (1987).

[64] J R Thompson, J Brynestad, D M Kroeger Y C Kim, S T Sekula, D K Christen and E D Specht, Phys. Rev. B, Condens. Matter., 39, 6652, (1989).

[65] H KÜpfer, I Apfelstedt, W Schauer, R Flukiger, R Meier - Himex and H WÜhl, Z. Phys. B, 69, 159, (1987).

[66] John R Clem, B Bumble, S I Raider, W J Gallagher and Y C Shih, Phys. Rev. B., 35, 6637, (1987).

Table 6.1 :- Shows the various values of J_c obtained in some copper oxide high temperature superconductors. The materials are either in the form of sintered compacts, single crystals, thin films, wires or tapes.

Compound	T(K)	H (T)	Expt. method	Sample	J_c (A/cm^2)	Ref
LaSrCuO	4	0	Mag.	Bulk	10^5	[1]
LaSr(0.05)	4.2	0.025	Trans	Bulk	2	[2]
LaSr(0.05)	4.2	10^{-3}-3	Trans	Bulk	1	[2]
LaSr(0.05)	4.2	7	Trans	Bulk	0.75	[2]
YBaCuO	4.2	0	Mag.	Epi. film	$>10^6$	[3]
YBaCuO	4.2	0	Mag	Epi. film	$>10^5$	[3]
YBaCuO	77	0	Mag	Epi. film	10^5	[4]
YBaCuO	5	0-1	Mag	Crys.	1.4×10^6 ($\perp$)	[5]
YBaCuO	77	0.1	Mag	Crys.	1.1×10^4 ($\perp$)	[5]
YBaCuO	4.5	0	Mag	Crys.	4×10^5	[6]
YBaCuO	4.5	>4	Mag	Crys.	$>10^6$	[6]
YBaCuO	77	0	Trans.	Rod	620	[7]

Compound	T(K)	H (T)	Expt. method	Sample	J_c (A/cm^2)	Ref
YBaCuO	4.2	1-10	Trans.	Epi film	$1.5-2\times10^4$ (bc plane)	[8]
YBaCuO	78	0	Mag	Epi film	$1-5\times10^4$	[9]
YBaCuO	5	0.4	Mag	Sinter forged	9.4×10^4 (⊥)	[10]
YBaCuO	5	0.4	Mag	Sinter forged	5.9×10^4 (‖)	[10]
YBaCuO	4.2	0.2	Mag	Sinter forged	8×10^3 (⊥)	[11]
YBaCuO	4.5	0	Mag	Crys.	3.2×10^6 (⊥)	[12]
YBaCuO	4.5	0	Mag	Crys.	1.6×10^5	[12]
YBaCuO	4.2	0	Trans. (Pul.)	Film	2800	[13]
YBaCuO	77	0	Trans. (Pul.)	Film	650	[13]
YBaCuO	77	0	Trans.	Bulk	336	[14]
YBaCuO	4.2	0	Trans.	Bulk	85	[15]
$YBaCuO_{9-x}$	77	0	Trans.	Bulk	1100	[16]
YBaCuO	77	0	Trans.	Film (Rf Sp.)	5×10^9 (‖)	[17]

Compound	T(K)	H (T)	Expt. method	Sample	J_c (A/cm^2)	Ref
YBaCuO	77	0	Trans.	Pel.	204	[18]
YBaCuO	77	0	Trans.	Pel.	40	[19]
YBaCuO +4% Ag	77	0	Trans.	Pel.	125	[19]
YBaCuO +6% Ag	77	0	Trans.	Pel.	80	[19]
YBaCuO	77	0	Trans.	(Ag.enc wires)	4000	[20]
YBaCuO	77	0	Trans.	(Wire, 0.72mm) dia.	3900	[21]
Gd123	77	0	Trans	Bulk	175	[22]
Gd123+K	77	0	Trans	Bulk	100	[22]
Gd123LA	77	0	Trans	Film	250	[22]
DyBaCuO	4.2	20(KOe)	Mod. Tech.	Crys.	8×10^4 ($\parallel$)	[23]
DyBaCuO	4.2	40(Koe)	Mod. Tech.	Crys.	7.5×10^4 ($\parallel$)	[23]
DyBaCuO	4.2	60(Koe)	Mod. Tech.	Crys.	7×10^4 ($\parallel$)	[23]
DyBaCuO	4.2	20(Koe)	Mod. Tech.	Crys.	5×10^4 ($\perp$)	[23]

Compound	T(K)	H (T)	Expt. method	Sample	J_c (A/cm^2)	Ref
DyBaCuO	4.2	40(Koe)	Mod. Tech.	Crys.	3×10^4 ($\perp$)	[23]
DyBaCuO	4.2	60(Koe)	Mod. Tech.	Crys.	2×10^4 ($\perp$)	[23]
HoBa	77.3	0	Mag.	Film (RF Sput.)	2.54×10^6	[18]
HoBa	77.3	1	Mag.	Film (RF Sput.)	1.5×10^6	[18]
ABCO*	4.2	25	Mag	Bulk	10^6	[24]
BPbCS*	4	0	Trans (Pul)	Bulk	3390	[25]
BPbCS*	60	0	Trans (Pul)	Bulk	1370	[25]
BPbCS*	80	0	Trans (Pul)	Bulk	590	[25]
BPbCS*	120	0	Trans (Pul)	Bulk	4.9	[25]
YBDyCuO	77	15	Mag.	Pellets	560 ($\parallel$)	[26]
BiCS*	61	0	Trans.	Film	10^5	[27]
BiCS*	6	0	Trans.	Film	10^7	[27]

Compound	T(K)	H (T)	Expt. method	Sample	J_c (A/cm^2)	Ref
BiCaS*	4.2	0	Mag	Bulk	6×10^3	[28]
BiCaS*	4.2	0.01	Mag	Bulk	10^3	[28]
BiCaS*	4.2	0.02	Mag	Bulk	5×10^3	[28]
BiCaS*	4.2	0	Mag	Bulk (Ag powder in tube)	15×10^3	[28]
BiCaS*	4.2	2	Mag	Bulk (Ag powder in tube)	12×10^3	[28]
BiCaS*	4.2	8	Mag	Bulk (Ag powder in tube)	8×10^3	[28]
BiCaS*	4.2	12	Mag	Bulk (Ag powder in tube)	7×10^3	[28]
BiCaS* +Pb	4.2	10	Mag	Bulk (Tape)	10^4	[28]
BiCaS* +Ag	4.2	10	Mag	Bulk (Tape)	5×10^3	[28]
BiCaS* +Ni	4.2	10	Mag	Bulk (Tape)	4×10^3	[28]
Ag/BiCaS* +Pb	4.2	0	Trans	Bulk (Tape)	1.49×10^5	[29]
Ag/BiCaS* +Pb	77	0	Trans	Bulk (Tape)	6.14×10^3	[30]

Compound	T(K)	H (T)	Expt. method	Sample	J_c (A/cm^2)	Ref
Ag/BiCaS* +Pb	77.3	0	Trans	Wire	6930	[30]
Ag/BiCaS* +Pb	77.3	0.1	Trans	Wire	1660 I(⊥)H,a-b(∥)H	[30]
Ag/BiCaS* +Pb	77.3	0.1	Trans	Wire	900 I(⊥)H,a-b(⊥)H	[30]
BPCS*	77	0	Trans	Bulk	1070	[31]
BPbCS*	77	0	Trans	Bulk	10-20	[32]
BPbCS*Na	77	0	Trans	Bulk (LA)	15	[33]
BCP*S*	77	0	Trans	Bulk	20	[33]
BPbCS*	100	0	Trans	Bulk	3.5	[34]
BPbCS*	77	0	Mag	Bulk	360	[35]
TlBa	77	0	Mag	Film	10-11x10^4	[36]
TlBa	77	1	Mag	Film	5-6x10^4	[36]
TlBa	77	6	Mag	Film	15 x10^2	[36]
TlBa	78	0	Mag	Bulk	1630	[37]
TlBa*	90	0	Trans	Sputt	10^4	[38]
TlBa**	90	0	Trans	Sputt Film	10^5	[38]
Tl(2212)	77	0	Mag	Bulk	600	[39]

Compound	T(K)	H (T)	Expt. method	Sample	J_c (A/cm^2)	Ref
Tl(2212)	1.5	4	Mag	Bulk	1600	[40]
Tl(2212)	15	4	Mag	Bulk	160	[40]
TlMgCuO	1.5	4	Mag	Bulk	1618-2790	[40]
Tl(2223)	15	4	Mag	Bulk	2164	[40]
Tl(2223)	1.5	4	Mag	Bulk	9385	[40]

In the above table, T(K) = Temperature at which J_c is measured, H (T) = applied field Mag. = Magnetisation method, Trans. = transport measurement, Epi.film = epitaxial film, Cryst. = Crystals, Sint. Forged = sinter forged, RF Sputt. = RF sputtered thin film, Mod. Tech. = Modulation technique, Gd123 L A = laser ablated thin film of $GdBa_2Cu_3O_{7-x}$, YBaCuO = $YBa_2Cu_3O_{7-x}$, YBDyCuO = $Y_{1-x}Ba_2Dy_xCu_3O_{7-y}$, BPCS* = $(Bi_{0.9}Pb_{0.1})_2Ca_2Sr_2Cu_3O_{10+x}$, BPbCS* = $Bi_{1.6}Pb_{0.4}Ca_2Sr_2Cu_3O_{10}$, BiCS* = $BiSrCaCu_2O_x$, BiCaS* = $Bi_2Sr_2Ca_1Cu_2O$, Ag/BiCaS* + Pb = tape, silver added = $Ag/Bi_{1.4}Pb_{0.4}Sr_{1.8}Ca_2Cu_{3.5}O_x$, TlBa = $Tl_2CaBa_2Cu_2O_y$, Tl(2212) = $Tl_2Ba_2\ Ca\ Cu_2O_y$, TlMgCuO = $Tl_2Ba_2(Ca_{1-x}\ Mg_x)_2Cu_3O_y$, BPbCS*Na = $Bi_2Na_xCa_{1-x}Sr_2Cu_2O_y$, Gd123 = $GdBa_2Cu_3O_{7-x}$, Gd123+K = $GdBa_2Cu_3O_{7-x}$+K, BiCaSrCuO, $Bi_{1.7}Pb_{0.3}Ca_2Sr_2Cu_3O_{10-x}$, BCP*S* = $Bi_{1.7}Pb_{0.3}Ca_2Sr_2Cu_3O_{10-x}$, ABCO* = $ABa_2Cu_3O_{7-x}$ (where A = Y, Eu, Gd, Dy, Er), LaSrCuO = $(La_{0.925}Sr_{0.075})_2Cu\ O_4$, HoBa = $HoBa_2Cu_3O_x$, DyBaCuO = Dy $Ba_2Cu_3O_{7-x}$, Tl Ba * = $Tl_2Ba_2Ca_1Cu_2O_8$, and Tl Ba ** = $Tl_2Ba_2Ca_2Cu_2O_{10}$.

6.1.a. REFERENCES OF TABLE

[1] M Suenaga, A Ghosh, T Asano, R L Sabatini and A R Moodenbaugh, MRS Anaheim Symp., 247, (1987).

[2] D C Larbaleister, M Daeumling, P J Lee, T F Kelly, J Seuntjens, C Meingast, X Cai, J McKinnel, R D Ray, R G Dillenburg and E F Hellstorm, Cryogenics, 27, 411, (1987).

[3] P Chaudhari, R H Koch, R B Laibowitz, T R Mcguire and R J Gambino, Phy. Rev. Lett., 58, 2684, (1987).

[4] P Chaudhari, R T Collins, P Freitas, R J Gambino, J R Kirtley, R H Koch, R B Laibowitz, F K LeGoues, T R Mcguire, T Penney, Z Schlesinger, A P Segmuller, S Foner and E J McNiff Jr., Phy. Rev. B, 36, 8903, (1987).

[5] G W Crabtree, J Z Liu, A Umezawa, W K Kwok, C H Sowers, S K Malik, B W veal, D J Lam, M B Brodsky and J W Downey, Phy. Rev. B, 36, 4021, (1987).

[6] T R Dinger, T K Worthington, W J Gallagher and R L Sandstorm, Phy. Rev. Lett., 58, 2687, (1987).

[7] S Jin, R. C Sherwood, R B van Dover, T H Tiefel and D W Johnson Jr., Appl. Phys. Lett., 51, 203, (1987).

[8] J Kwo, T C Hsieh, R M Fleming, M Hong, S H Liou, B A Davidson and L C Feldman, Phys. Rev. B, 36, 4039, (1987).

[9] B Oh,M Naito, S Arnason, P Rosenthal, R Burton, M R Beasley, T H Geballe, R H Hammond and Kapitulink, Appl. Phys. Lett., 51, 852, (1987).

[10] S N Song, Q Robinson, S J Hwu, D L Johnson, K R Poeppelmeier and J B Ketterson, Appl. Phys. Lett., 51, 1376, (1987).

[11] K Togano, H Kumakura, K Fukutomi and K Tachikawa, Appl. Phys. Lett., 51, 136, (1987).

[12] T K Worthington, W J Gallagher and T R Dinger, Phys. Rev. Lett., 59, 1160, (1987).

[13] T E Jones and W C McGinnis, MRS Anaheim Symp., 235, (1987).

[14] Ji Chunlin, Wang Kuihan, Fan Zhanguo, Liu Sulan, Cui Chuanmeng, Zhang Guofan, Zeng Guiyi, Quian Cuenfu and Wang Shilan, Sol. St. Commun., 65, 863, (1988).

[15] S X Dou, A J Bourdillom, C C Sorrell, S P Ringer, K E Easterling, N Savvides, J B Dunlop, and R B Roberts, Appl. Phys. Lett., 51, 535, (1987).

[16] R J Cava, B Batlogg, R B Van Dover, D W Murphy, S Sunshine, T Siegrist, J P Remeika, E A Rietman, S Zahurak and G P Espinosa, Phys. Rev. Lett., 58, 1676, (1987).

[17] J S Satchell, R G Humphreys, N G Chew, J A Edwards and M J Kane, Nature, 334, 331, (1988).

[18] J V Yakhmi, I K Gopalakrishnan, M A Vaidya and R M Iyer, Pramana, 29, L597, (1987).

[19] M K Malik, V D Nair, A R Biswas, R V Raghavan, P Chaddah, P K Mishra, G Ravikumar, and B A Dasannacharya, Appl. Phys. Lett., 52, 1525, (1988).

[20] D Swinbanks, Nature, 327, 356, (1987).

[21] O Kohono, Y Ikeno, N Sadakata, and K Goto, Jpn. J. Appl. Phys., L2., 27, 77, (1988).

[22] V Vidyalal, K Rajasree and C P G Vallabhan (To be

published).

[23] N E Alekseevskii and S F Kim, Physica C, 178, 89, (1991).

[24] K Nakao, K Tatsuhara, N Mivra, S Uchida, H Takagi, T Wada and S Tanaka, J. Phys. Soc., JAP., 57, 2476, (1988).

[25] W C McGinnis, E W Jacobs, C D Rees and T E Jones, Rev. Sci. Instrum., 61, 3, (1990).

[26] K Noto, H Morita, K Watanabe, T Murukami, Y Kogangi, I Yoshi, I Sato, H Sugawara, N Kobayashi, H Fugimori and Y Muto, Physica B&C, 148B+C, 239, (1987).

[27] M Hong, J Kwo and J J Yeh, J Cryst.Growth, 91, 3, 383, (1988).

[28] Y Tanaka, T Asano, M Fokutomi and H Maeda, Bull. Mater. Sci., 14, 227, (1991).

[29] S R Shukla, Y S Reddy and R G Sharma, Pramana, 38, 179, (1992).

[30] T Hikata, K Sato and H Hitotsuyanagi, Jpn. J. Appl. Phys. 2 Lett., 28, L82, (1989).

[31] V Plechacek, H Hedjova and Z Trejbalova, Cryogenics, 30, 11, (1990).

[32] M Matsuda, Y Iwai and M Takata, Jpn. J. Appl. Phys. Lett., 27, 1650, (1988).

[33] V Vidyalal, K Rajasree and C P G Vallabhan (To be published).

[34] K Togano, H Kumakura, H Maeda, E Yanagisawa and K Takahashi,

Appl. Phy. Lett., 53, 1329, (1988).

[35] K Togano, H Kumakura and D R Dietderich, Cryogenics, 29, 286, (1989).

[36] E L Venturni, R J Baughman, B Morosin and D S Ginley, Physica C, 156, 103, (1988).

[37] Cui Chang - Geng, Li Shen - Lin, Zhang Jin - Long, Wang HuiSheng, Li Lin, xie Si- Shen, Zhang Yu - Ling, Che Guang - Lan, Wang Rong - Shu and Long Pei-Jin, Supercond. Sci. Technol., 2, 59, (1989).

[38] M Hong , S H Liou, D D Bacon, G S Grader, J Kwo, A R Kortan and B A Davidson, Appl. Phys. Lett., 53, 2102, (1988).

[39] K Togano, H Kumakura and D R Dietderich, Cryogenics, 29, 286, (1989).

[40] C D Wei. C Lin, Z H Shen, Z X Liu, J Lan, K Wu, L X Xie, Y D Dai, Z Z Gan, Mod. Phys. Lett. B, 3, 157, (1989).

CHAPTER 7

DEGRADATION AND AGING BEHAVIOUR OF COPPER OXIDE SUPERCONDUCTORS

ABSTRACT

Degradation of HTSC materials, the decomposition equations of 123 based HTSC and the possible ways of preventing aging are described in this chapter. The influence of synthesising routes on resistivity and aging characteristics of Bi cuprate superconductors prepared by two main synthesising routes is discussed. A possible method to revive T_c and J_c of aged superconductors is also discussed.

7.1 INTRODUCTION

Applications of high T_c superconductors require a thorough investigation of the stability of these materials with respect to external influence. The oxide superconductors are not inert materials, but rather they are sensitive to exposure to certain gases and to surface contact with specific materials. These ceramics are catalytic to oxygenation reactions, and these factors result in the occurrence of various chemical and other interactions, especially at elevated temperatures. The porous and granular nature has an accelerating effect on such reactions.

Soon after the discovery of high T_c materials, deterioration of the superconducting properties due to the interactions with water, water vapour, moisture and other aqueous medium was investigated [1-10]. It was shown that storage and thermorecycling of $YBa_2Cu_3O_7$ ceramics can lead to a decrease or increase in T_c [11,12]. For Bi-Sr-Ca-CuO ceramics doped with Pb and Sn, degradation of the properties of unidentified phases and anomalously high T_c (>120K) were observed during thermal cycling [13] and storage [14]. Nakada *et al.* [4] discovered that $YBa_2Cu_3O_7$ (black - I phase as denoted by them) gets decomposed by warm water at temperatures above 35°C, but was inert to water at 22°C and below. Dominec *et al.* [5] discovered that there was no change of χ - T curve when the temperature of water was below 30°C. Yan *et al.*[2] reported that if $YBa_2Cu_3O_7$ powder was soaked in deionised water at room temperature for 3 days, the height of the $YBa_2Cu_3O_7$ X - ray diffraction peaks decreased to 1/4 of the original height and the diffraction lines of CuO, Y_2BaCuO_5 and some unidentified amorphous material appeared. Later Kariosis and Vance [7] obtained similar results. Thompson *et al.* [10] reported that after 24 hrs exposure to atmosphere at room temperature, following immersion in liquid N_2 showed no corrosion. They pointed out that if care was not taken to avoid frosting as the specimen warms to room temperature after immersion in liquid N_2, surface corrosion accelerated significantly.

It has been reported that after the initial quenching the transition temperature in oxygen deficient crystals like $YBa_2Cu_3O_{7-\delta}$ increases with aging time at room temperature by as much as 10K [15,16]. An increase in critical current density upon storage is also reported [17]. However transport properties subsequently degrades as time progresses.

Measurements of T_c, and the Meissner effect on a crystal at room temperature in helium enviornment reveal that T_c increases by 10K and Meissner fraction increases as much as 2% due to the aging of samples. The fact that the Meissner fraction and T_c follow approximately the same time dependence suggests that they have a common origin. The reduction of the oxygen vaccancy disorder with aging inorder to explain the increase in Meissner effect reflects a decrease in pinning. For the unaged crystal the quenched disorder has a tendency to trap many flux lines which leads to a relatively small Meissner fraction. As the oxygen vacancy order increases during aging, the ability to pin flux is reduced and the Meissner fraction increases. As monitored through Meissner fraction data, the majority of the ordering occurs quickly after initial quenching followed by a progressively slower ordering as the final equilibrium T_c is reached. The pattern of the time dependence of the pinning and T_c can be naturally explained by an increasing oxygen vacancy order. This implies that pinning decreases with aging, as would be expected if the oxygen vaccancy ordering is the mechanism behind the aging effect [18].

Similarly samples quenched in a controlled oxygen - nitrogen atmosphere, show a rise in T_c as much as 10K, when aged in ambient atmosphere for few days. The sample composition does not change but structural changes occur with an increase in orthorhombicity. This shows that significant atomic motion occur and under these conditions ie internal ordering occurs. These effects are attributed to oxygen - vaccancy ordering that occurs in the chain region of the structure. The rise in T_c with aging (ordering) is attributed to increased hole doping in the planes that results from an increased population of two - coordinated monovalent copper atoms. Increase in T_c results from charge distribution in the structure that increases the hole content in the planes. That is, the variable chain disorder directly affects the electronic properties in the plane region of the structure. Compositional variations in the chains alter the overall charge balance in the 1:2:3 system and produce changes in the carrier concentrations in the planes thereby affecting T_c [19-26]. However T_c changes also occur without change in composition so that charge variation in the planes occurs simply as a consequence of oxygen atom redistribution. Charge redistribution occurs also as a consequence of changes in the coordination of chain copper atoms [27]. The valence state of copper bounded to oxygen is closely associated with its coordination number [28]. Two coordinated copper is monovalent. The shift of oxygen atoms from their normally vacant chain cites to their normally occupied chain cites increases the population of two coordinated (monovalent) copper atoms. In becoming monovalent, these copper atoms acquire an additional electronic charge which comes from the planes. The charge redistribution is reflected in the clearly observed bond length changes [29]. Theoretical results [25,26] appear to be consistent with this picture. Calculations show that as oxygen is removed from $YBa_2Cu_3O_{7-\delta}$, the carrier concentration in the planes symmetrically falls. Importantly, however, when the chain region of the structure is ordered there is a corresponding rise in the in-plane carrier concentration. These variation of the in - plane carrier density directly affects T_c.

Neutron diffraction results on polycrystalline samples showed that there is no change in oxygen site occupancy during the aging process. [29]. Also, similar studies on the process of aging show significant changes in line - width and diffuse scattering background when the samples are kept in open environment. Deterioration of structural parameters are reduced when the samples are kept in sealed quartz enclosures.

A structurally well ordered material degrades in air at ambient temperature and exhibits basal plane faulting. Basal plane faulting has also been observed in ion - beam thinned material [30] and attributed to response of the structure to changes in oxygen contents, whereas others [31] have linked this faulting to the method of sample preparation.

The effect of moisture on $YBa_2Cu_3O_{7-\delta}$ leading to structural modifications such as promotion of slow crack growth etc. has also been discussed [9]. The possible structural modification on aging maybe due to strain field and concommitant excess oxygen and its migration to the grain boundary region, formation of non superconducting and possibly amorphous phases at the grain boundaries and also due to formation of peroxide ions [32]. Formation of oxygen depleted grain boundaries due to absorption of moisture and carbon dioxide from the environment has also been postulated [33].

Interaction of $YBa_2Cu_3O_{7-\delta}$ with water has been studied using Auger electron and X - ray photoelectron spectroscopy [34]. Such studies have revealed that at the initial period of decomposition of this compound, $Ba(OH)_2$ deposits on the ceramic grain surface and partial reduction of copper to Cu_2O occurs in the oxide. Subsequently barium diffuses to free surfaces of the ceramic grains and migration of barium atoms from the depth of the ceramic grains to the surface takes place. A change of composition of the grain surface layers occurs near their free surfaces (pores, cracks and outer sides of the samples) and in sintered contacts of grains the possibilty of initial deviation from stoichiometry and impurity localisation results.

These studies also showed that in the degenerated layer of all the samples which underwent the water vapour effect, copper was partially reduced to Cu^{1+}. Thus the Cu^{1+} content in the degenerated layer of a fresh break of the ceramics with the density of 4.9 g/cm^3 was upto 50% of the total amount of copper. Heating of such degenerated samples at 920°C for 5 hrs in air or in oxygen saturated atmosphere restores the composition of the grain surface to the initial $YBa_2Cu_3O_{7-\delta}$. The characteristics of the transition are also partially restored.

$YBa_2Cu_3O_{7-\delta}$ in the powdered form has been observed to react vigorously at room temperature with water producing a non-superconducting cuprate with copper in oxidation state +2. The other products being O_2 , CuO and $Ba(OH)_2$. Similar reactions will also occur with nearly equal rapidity in all cuprate superconductors. Specimens react slowly with humid air at room temperature and rapidly in air at 85°C and 85% relative humidity, the standard conditions used for acclerated humidity testing. The resultant end products are nonsuperconducting phases formed in hours to days, depending on conditions.

The decomposition reaction of $YBa_2Cu_3O_7$ proposed by M F Yan et al [2] is as follows :-

$$2YBa_2Cu_3O_7 + 3H_2O \longrightarrow 5CuO + 3Ba(OH)_2 + Y_2BaCuO_5 + \frac{1}{2} O_2 \qquad (7.1)$$

Y_2BaCuO_5 is a semiconducting "green phase" originally thought to be superconducting [35].

The phases thus formed in (7.1) are non superconductors with high room temperature resistivities higher than $YBa_2Cu_3O_7$. Another reaction formula of $YBa_2Cu_3O_7$ with water proposed by Zhuang *et al.* [36] is

$$2YBa_2Cu_3O_7 + 7H_2O \longrightarrow 6CuO + 4Ba(OH)_2 + 2Y(OH)_3 + gas \qquad (7.2)$$

All compounds in the right side of the formulas (7.1) and (7.2) are insoluble in water except barium hydroxide. Dominec et al [5] obtained a similar result by the atomic absorption analysis of water in which the $YBa_2Cu_3O_7$ was soaked.

The possible loss of O_2 by decomposition reaction can also be by a decomposition reaction represented as

$$YBa_2Cu_3O_7 \longrightarrow YBa_2Cu_3O_6 + \frac{1}{2} O_2 \qquad (7.3)$$

It has been shown that when x in $YBa_2Cu_3O_x$ goes from 7 to 6, the superconducting orthorhombic phase undergoes a transition to the nonsuperconducting tetragonal phase at $x = 6.63$ [37].

$YBa_2Cu_3O_7$ decomposes in water more readily at low pH but at high temperatures eventually even in strongly basic solutions. The material is stable enough in alcohol (and other nonaqueous solvents) so that it can be used for cleaning specimens, however at high temperatures decomposition occurs in alcohol even under normal conditions.

The effect of acetone and other organics [38] has been determined and stable carboxyl groups have been found in the $YBa_2Cu_3O_7$ lattice [39]. Reactivity with electrolytes such as NaCl is low at room temperatures in 24h and thus changes to a slight reaction at $300^{\circ}C$ in a few days. The products were identified as $CuO + Y_2BaCuO_5$.

Similary the degradation process of $Tl_2Ba_2Ca_1Cu_2O_x$ ceramics has been investigated, and it was found that Tl based ceramics degrades both after short time exposure to water vapour and after weeks of storage in a desiccator [40]. Studies on Bi based materials show that low temperature thermocycling of these ceramics leads to a decrease of the temperature of diamagnetic response onset, T_{on}. The degradation is displayed in lowering of the grain superconducting transition temperature. A shift of $\varkappa'(T)$ and R (T) dependence to low temperatures on thermocycling is observed. Single phase samples are more resistant to thermocycling than multiphase samples [41]. Aging also depends on the synthesising routes/techniques adopted reflecting on the phase purity as well as the density of the samples [42].

The foregoing evidence for the reactivity of the oxide superconductors makes it necessary to consider methods of passivation or protecting them from long term degradation. An epoxy coating was found to provide some protection [1]. Coating the surface with metals can be deleterious since metals such as Fe [43-45] and Ti [46] react with the surface of LaSrCuO or YBaCuO. There are examples for the passivation of the surface of La based HTSC with gold [47].

Degradation of samples in ordinary ambient in a matter of days makes it unwise to use unprotected specimens for serious measurements for many applications. Epoxy coating greatly inhibits reaction with water but does not eliminate it completely. Consequently, metallised plastic or glass encapsulation will be required for many applications and measurements.

It is also reported that a plastic encapsulant considerably slowed such reactions, but did not eliminate them [1]. An ideal water resistive plastic solution to protect $YBa_2Cu_3O_7$ from humidity for laboratory use should have the following features.

1) Both the solute (plastics) and solvant should cause only minimum degradation of superconductivity in $YBa_2Cu_3O_7$.

2) The film formed on the surface of $YBa_2Cu_3O_7$ (after being coated and dried of the solution) should enhance the resistance of $YBa_2Cu_3O_7$ to water and moisture corrosion as much as possible.

3) The protective film should be easily removable (easily dissolvable in the solvent) and the superconducting properties basically should remain unchanged.

4) It should be cheap and easy to handle.

A solution satisfying the above conditions to a good extent is a mixture of butadiene and styrene copolymer (SBSC) with the solvant being carbon tetrachloride [48]. The solution can be easily smeared on the $YBa_2Cu_3O_7$ superconductor and left to dry in the shade.

7.2. INFLUENCE OF SYNTHESISING ROUTES ON RESISTIVITY AND AGING CHARACTERISTICS OF Bi - CUPRATE SUPERCONDUCTORS

The dependence of synthesising routes on aging in Bi - Cuprate superconductors were studied by preparing the material by two main popular solid state reaction routes viz. solid state diffusion reaction [49-52] (Designated as sample A) and the matrix method (sample B) [53, 54] (The details of preparation are given in chapter 2) Even though both the routes produce single phase materials superconducting at 110K, the resistivity behavior above T_c is found to be different. Aging/degradation behavior was studied in terms of T_c on both sets of samples stored in a desiccator for eight months. Our studies indicate that the synthesising routes play a major role in the preparation of high quality bulk Pb doped Bi - 2223 superconductors which are more resistant to degradation when exposed to humid conditions (42).

7.3. EXPERIMENTAL DETAILS

Electrical resistivity was measured by the usual four-probe technique in the temperature range 300-77K, the details are discussed in chapter 2. Immediately after resistivity measurements, both the samples A and B were stored in the same desiccator. The effect of aging was determined by making the resistivity measurements after a period of 8 months.

7.4. RESULTS AND DISCUSSIONS

The highest T_c (R = 0) for both the batches were 110K (figure

- 7.1). The value of T_c and in general ρ vs T characteristic did not change with I even if the current was increased from 10mA to 25 mA. The values of ρ_{300} was higher for batch A type samples. Extended scale around T_c shows the curves of the A type samples to be more irregular, (Figure - 7.2) which we believe to be due to the difference in synthesing routes. Generally, we find that the onset of superconductivity is at a different temperature in A compared with the same for samples B. Large transition widths shown by sample A could be due to inhomogeneous distribution of the superconducting phases and the presence of phases which may possess different stoichiometry in the sample. However the T_c of the both the samples did not shift downward with increase of current density. This indicates that the samples can endure current density variations.

Figure - 7.3 shows the aging effect of both samples A and B. Even though both the samples show an increase in the slope of the linear part of the ρ vs T plot and in the value of ρ_{300}, along with a broad transition width, sample A exhibits a more prominent variation. The T_c values for both the samples A and B decreased to 82K and 100K respectively from a T_c of 110K. This clearly shows phase segregation with time due to the transformation of the 110K phase to a mixture containing low T_c phases. Enlarging the low temperature region (figure - 7.4) a transition tail is observed, slightly resembling the 2212 phase [50, 53, 55]. It can therefore be concluded that sample B had almost complete 110K phase initially, and does not degrade structurally in a drastic manner compared to A indicating that oxygen losses may be fast. Earlier measurements carried out on $GdBa_2Cu_3O_{7-\delta}$ and in general on 123 systems, showed a marked effect and a transformation into a semiconductor due to the reduction of copper to Cu_2O taking place in the oxide. It was also found that dense ceramics are more resistant to humid atmosphere [34]. However decreasing T_c for both samples when exposed to atmosphere need not be bulk degradation phenomenon but may be due to peripheral deterioration as a result of carbonate/hydroxide formation at the surface.

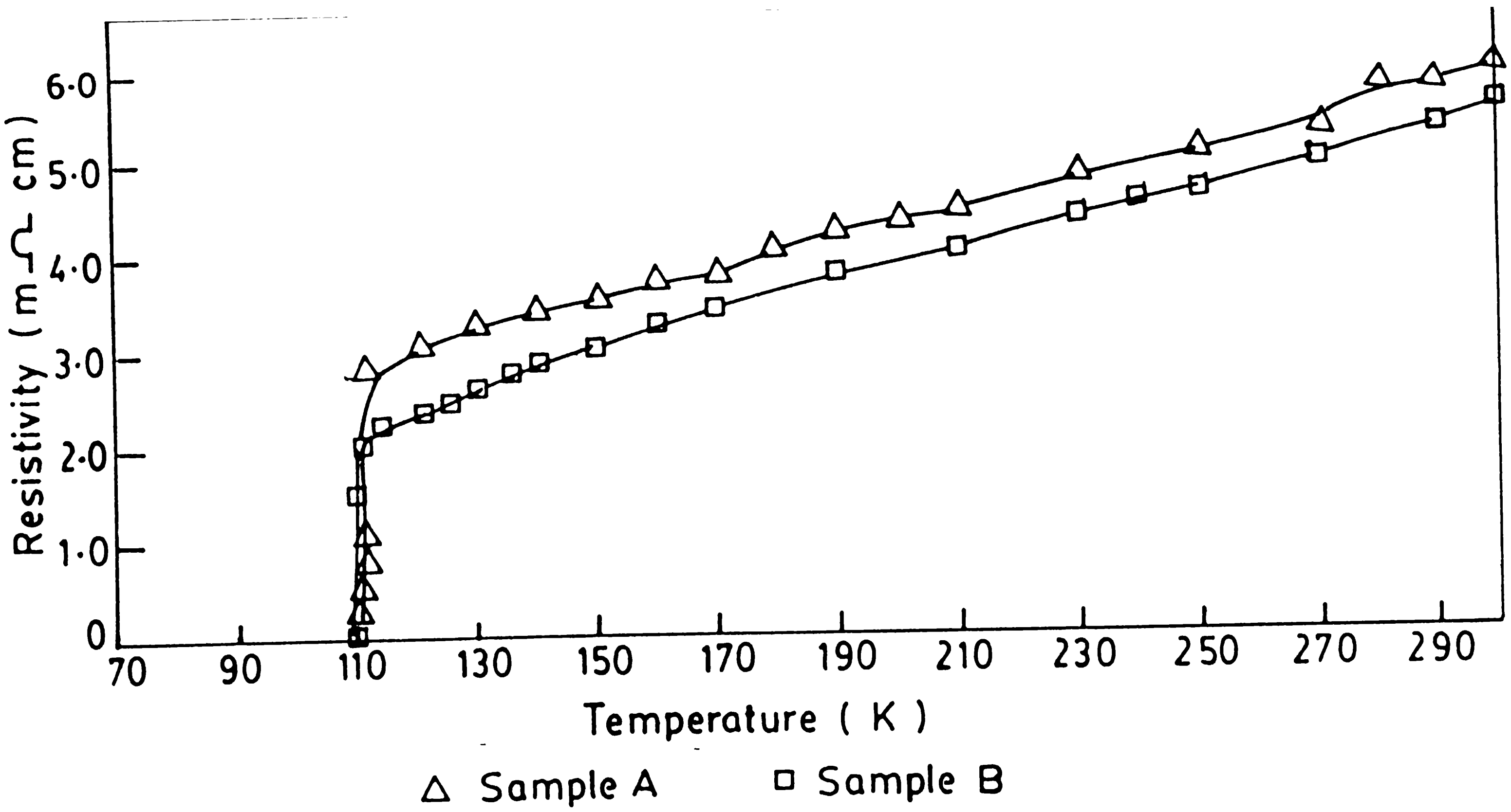


Fig. 7.1. Plot of resistance versus temperature for samples A and B.

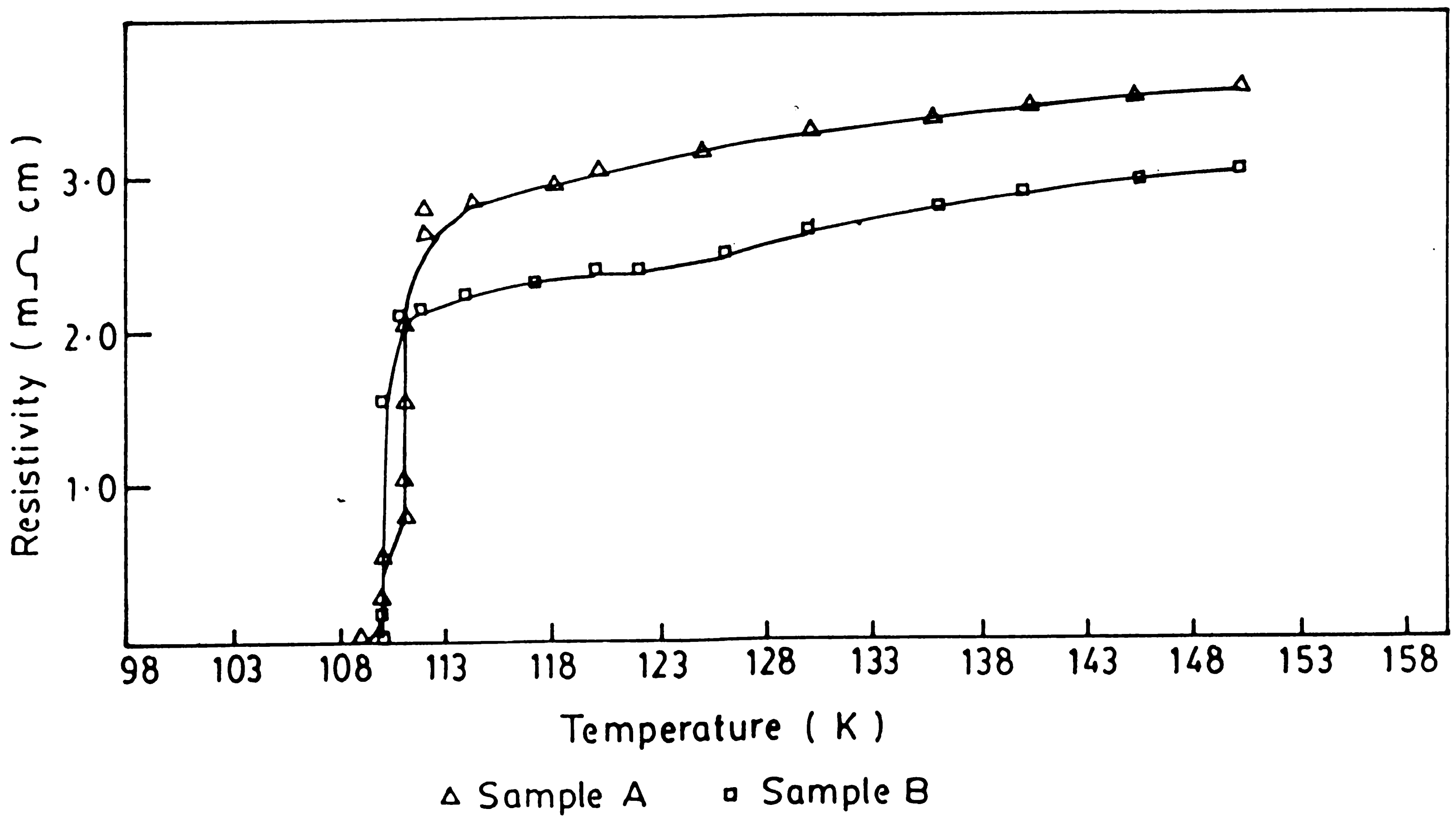


Fig. 7.2. Expanded scale plot of temperature versus resistance for samples A and B.

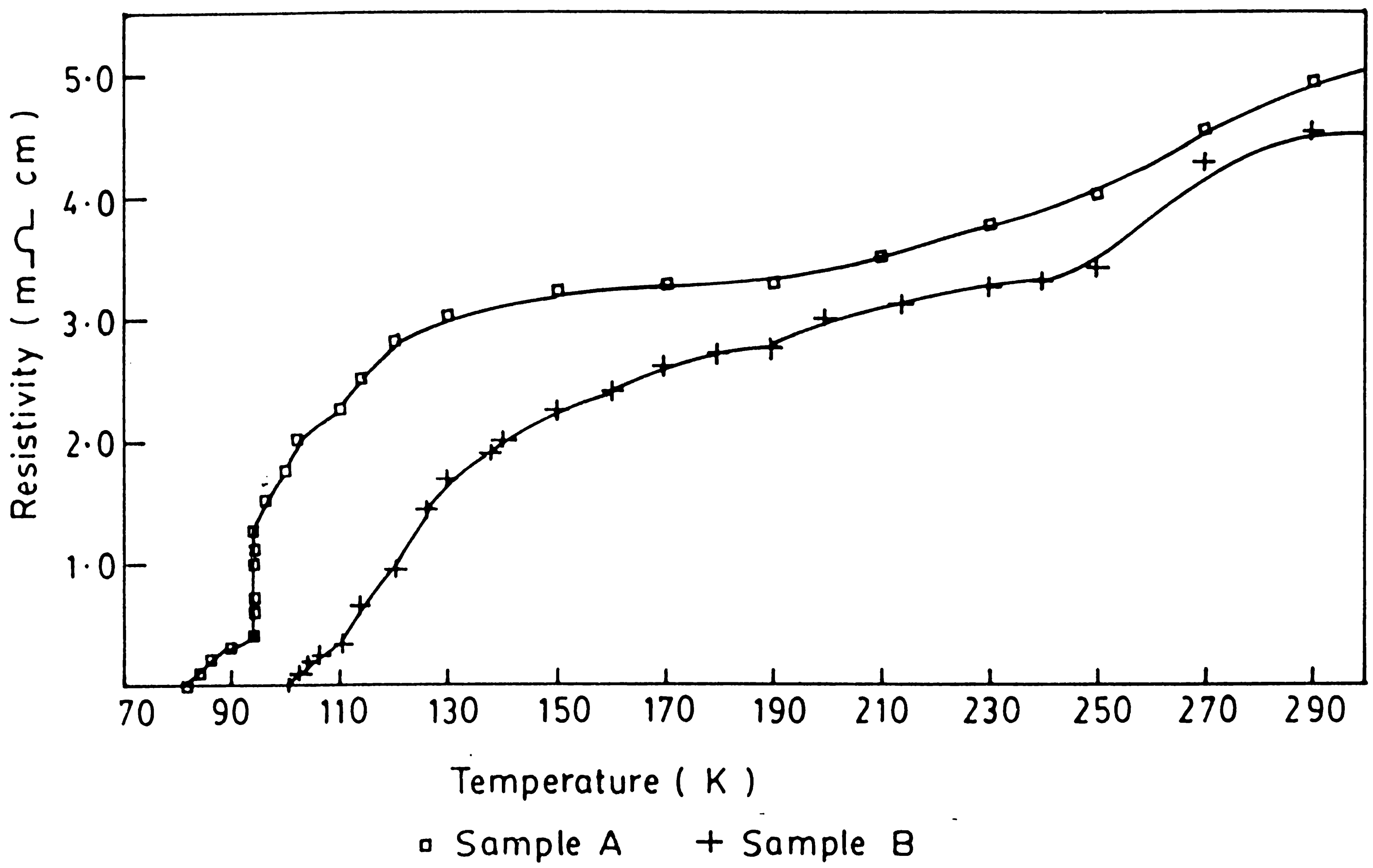


Fig. 7.3. Plot of resistance versus temperature for samples A and B after 8 months.

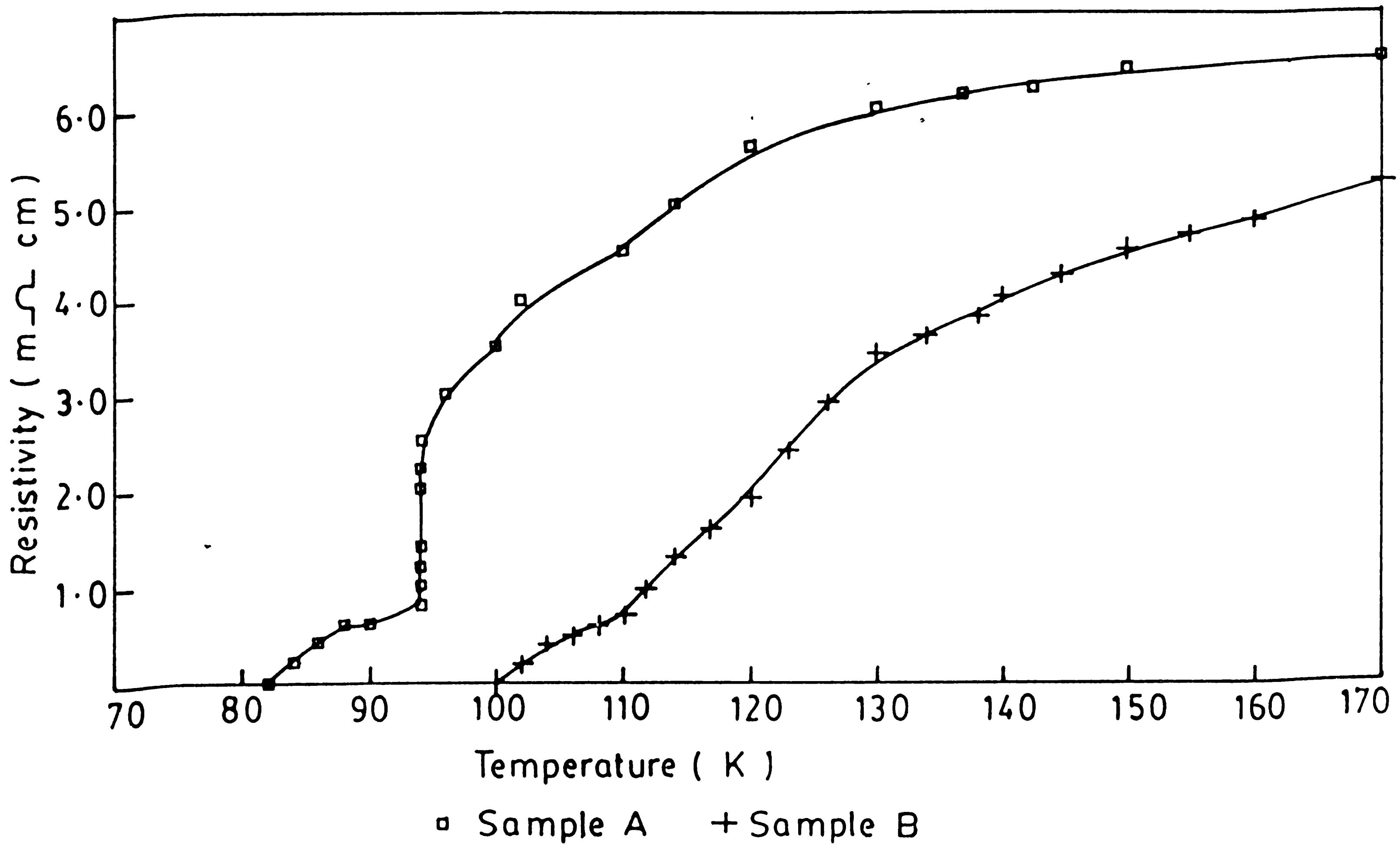


Fig. 7.4. Expanded scale plot of temperature versus resistance for samples A and B after 8 months.

7.5. REVIVING T_c AND J_c OF AGED SUPERCONDUCTORS

In the case of 123 compounds, reheating of the degenerated samples at 920°C for 5 hrs in air or in oxygen saturated atmosphere restores the composition of the grain surface to the initial stoichiometry and the characteristics of the transition are also partially restored to some extent [34]. This is true in the case of Bi and Tl based superconductors. However, it may not be feasile to do the resintering always (for eg. sintering on lead attached samples) and an alternative method is described below :- In the 4 probe arrangement (or in any configuration) one normally uses a DC constant current source (CCS) for biasing while carrying out DC resistivity measurements. In the place of this 'low' CCS, a high current power supply (which is internally protected from overloads and short circuits) is substituted and a high current is passed through the sample which is kept immersed in liquid nitrogen. Special attention is to be paid to the current carrying leads and it should be preferably dipped in the cryogen too. A current density of the order of ~ 40A / cm^2 for 18hrs was found to be appropriate to restore the transport characteristics to a good extent The samples studied were Gd - 123 (93K) and BiPb 2223 (110K). The restored T_c values were Gd 123:- 88K and BiPb2223 :- 100K) [56]. Similar techniques in this line have been reported in samples of Dy - 123 and Tl based materials [57]. One of the possible explanations evidenced from studies on $Tl_2 Ba_2CuO_{6+\delta}$ (transport properties of Tl based materials are sensitive to δ) confirm redistribution and long range electromigration of oxygen ions.

7.6 REFERENCES

[1] R L Barns and R A Laudise, Appl. Phys. Lett., 51, 1373, (1987).

[2] M F Yan, R L Barns, H M O'Bryan, Jr.P K Gallagher, R S Sherwood and S Jin, Appl. Phys. Lett., 51, 532, (1987).

[3] M M Garland, Appl. Phys. Lett., 52, 1913, (1988).

[4] I Nakada, S Sato, Y Oda and T Kohara, Jpn. J. Appl. Phys., 26, L697, (1987).

[5] J Dominec, L Smrcka, P Vasek, and S Geurten, O Smrckova, D Sykorova and B Hajek, Sol. St. Commun., 65, 373, (1988).

[6] B G Hyde, J G Thompson, R L Withers, J G Fitzgerald, A M Stewart, D J M Bevan, J S Anderson, J Bitmead and M S Paterson, Nature, 327, 402, (1987).

[7] F G Kariosis and E R Vance, Mater. Lett., 6, 16, (1987).

[8] A Barkatt, H Hojaji and K A Michael, Advan. Ceram. Mater., 2, 701, (1987).

[9] K G Frase, E G Liniger and D R Clarke, Adv. Ceram. Mat., 2, 698, (1987).

[10] J G Thompson, Mat. Res. Bull., 22, 1715, (1987).

[11] D N Matthews , A Bailey, T Puzzer, G J Russel, J Cochrane, R A Vailey, H B Sun and K N R Taylor, Sol. St. Commun. 65, 347, (1988).

[12] A I Golovashkin , I S Levchenko, G P Motylevich and L M Polykhina, Sov. J. Sol. St. Phys., 30, 2520, (1988).

[13] Lui Hongbao, Cao Liezhao, Zhou Ling, Mao Zhigiang, Li Xiaoxian and Yu Zhilong, Sol. St. Commun., 69, 867, (1989).

[14] A R Zaynulin, E F Makarov, A V Dubovitskii, G G Lazarev and E V Galtseva, Sov. Superconductivity, 3, 446, (1989).

[15] B W Veal, A P Paulikas, Hoydoo You, Hao Shi, Y Fang and J W Downey, Phys. Rev. B, 42, 6305, (1990).

[16] H Claus, S Yang, A P Paulikas, J D Downey and B W Veal, Physica C, 171, 205, (1990).

[17] A Sequeira, H Rajagopal and J V Yakhmi, Sol. St. Commun., 65, 991, (1988).

[18] K G Vandervoort, G W Crabtree, Y Fang, S Yang, H Claus and J W Downey, Phys. Rev. B, 43, 3688, (1991).

[19] J D Jorgensen, B W Veal, A P Paulikas, L J Nowicki, G W Crabtree, H Claus and W K Kwok, Phys. Rev. B, 41, 1863, (1990).

[20] E H Appelman, L R Morss, A M kini, U Geiser, A Umezawa, G W Crabtree and K D Carlson, Inorg. Chem., 26, 3237, (1987).

[21] R J Cava, B Batlogg, C H Chen, E A Rietman, S M Zahurak and D Werder, Phys. Rev. B, 36, 5719, (1987).

[22] B Batlogg, T T M Plastra, L F Schneemeyer, R B Vasdover and R J Cava, Physica C, 153 - 155, 1602, (1988).

[23] Y Tokura, J B Torrence, T C Huang and A I Nazzal, Phys. Rev. B, 38, 7156, (1988).

[24] J K Burdett and G V Kulkarni, Phys. Rev. B, 40, 8908, (1989).

[25] Ph. Lambin, "Oxygen Disorder effects in High T_c Superconductors", P101, (Plenum, New York), (1990).

[26] J Zannen, A T Paxton, O Jepsen and O K Andersen, Phys. Rev. Lett., 60, 2685, (1988).

[27] D deFontaine, G Cedder and J W Morris Jr., Phys. Rev. Lett., 64, 76, (1990).

[28] R D Shannon and C T Prewitt, Acta Crystollogr., B25, 925, (1969).

[29] J D Jorgensen, S Pei, P Lighfoot, H Shi, A P Paulikas and B W Veal, Physica C, 167, 571, (1990).

[30] A Ourmazd, J A Rentschler, J C H Spence, M O Kneefe, R J Graham, D W Johnson Jr. and W W Rhodes, Nature, 327, 308, (1987).

[31] R A Camps, J E Evetts, B A Glowacki, S B Newcomb, R E Somekh and W M Stobbs, Nature, 329, 229, (1987).

[32] C N R Rao, P Ganguly, J Gopalakrishnan and D D Sharma, Mat. Res. Bull., 22, 1159, (1987).

[33] R B Goldfarb, A F Clark, A I Braginski and A J Panson, Cryogenics, 27, 475, (1987).

[34] V P Seminozhenko, V T Zagoskin, Yu G Litvinenko, E T Moghilko, Yu B Poltoratskii and O V Tuchin, Bull. Mater. Sci., 14, 179, (1991).

[35] R J Cava, B Batlogg, R B Van Dover, D W Murphy, S A Sunshine, T Siegrist, J P Remeika, E A Reitman, S Zahurak and G P Espinosa, Phys. Rev. Lett., 58, 1676, (1987).

[36] D X Zhuang, Xiao Mingshan, Zhang Ziqing, Yue Shubinm Zhao Huausui and Shang Shuxia, Sol. St. Commun., 65, 339, (1988).

[37] P K Gallagher, Advanced Ceramic Materials, 2, 3B, Special issue P632, (1987).

[38] T P Mc Andrew, K G Frase, and R R Shaw, A.V.S. Topical conf. on "thin film processing and characteristics of high temp. Sup. cond.", Anaheim California, AIP #165, Nov. (1987).

[39] F Parmigiani, G Chiarello, N Ripamonti, H Goretzki and U Roll, Phys. Rev. B, 36, 7148 (1987).

[40] K D Vernon-Parry, L T Romano, J S Lees and C R M Grovenor, Physica C, 170, 388, (1990).

[41] A M Grishin, V N Corenivski and A N Ul'Yanov, Mod. Phys. Lett B, 5, 1175, (1991).

[42] V Vidylal, K Rajasree and C P G Vallabhan, Mod. Phys. Lett B, 6, 1535, (1992).

[43] Y Gao, T J Wagener, J H Weaver, B Flandermeyer and D W Capone II, Appl. Phys. Lett., 51, 1032, (1987).

[44] D M Hill, H M Meyer III, J H Weaver, B Flandermeyer and D W Capone II, Phys. Rev. B, 36, 3979, (1987).

[45] J H Weaver, Y Gao, T J Wagener, B Flandermeyer and D W Capone II Phys. Rev. B, 36, 3975 (1987).

[46] H M Meyer III, D M Hill, S G Anderson, J H Weaver and D W Capone II, Appl. Phys. Lett., 51, 1750, (1987).

[47] H M Meyer III, T J Wagner, D M Hill, Y Gao, S G Anderson, S D Krahn, J H Weaver, B Flandermeyer and D W Capone II,

Appl. Phys. Lett., 51, 1118, (1987).

[48] Sui-Geng Jin, Lin-Gmei Liu, Zheng - Zhong Zhu and Yun-Lian Huang, Sol. St. Commun., 69, 2, 179, (1989).

[49] H Maeda, Y Tanaka, M Fukutomi and T Asano, Jpn. J. Appl. Phys., 27, L-1839, (1988).

[50] J M Tarascon, Y Le Page, P Barboux, B G Bagley, L H Greene, W R McKinnon, G W Hull, M Giroud and D M Hwang, Phys. Rev. B, 37, 9382, (1988).

[51] C N R Rao, L Ganapathi, R Vijayaraghvan, G Rangorao, Kumari Murthy and R A Mohan Ram, Physica C, 156, 827, (1988).

[52] L Hongbao, C Liezhao, Z Lieg, M Zhiquiang, Y Zhidong, X Bai, M Xianglei, Z Guien, R Yaozhong, C Zhaojiu and Yuheng Z, Sol. St. Commun., 69, 867, (1988).

[53] P V P S S Sastry, J V Yakhmi and R M Iyer, Sol.St. Commun., 71, 935, (1989).

[54] P V P S S Sastry, I K Gopalakrishnan, A Sequeira, H Rajagopal, K Gangadharan, G M Pathak and R M Iyer, Physica C, 156, 230 (1988).

[55] S M Green, C Jiang, Yu Mei, H L Luo and C Politis, Phys. Rev. B, 38, 5016 (1988).

[56] V Vidyalal, K Rajasree and C P G Vallabhan, (to be published).

[57] A V Mitin, N E Alekseevskii and E P Khlybov, Physica C, 199, 351, (1992).

CHAPTER 8

MICROWAVE AND LASER ABLATION THRESHOLD STUDIES OF SOME HTSC MATERIALS

ABSTRACT

This chapter is divided into two parts. The first part discusses the behaviour of HTSC materials at microwave frequencies. Determination of surface resistance and the fabrication of a HTSC device *viz.* a ring resonator are included. The second part describes the determination of laser ablation thresholds of doped Bi based HTSC materials by pulsed photothermal deflection technique. Striking correlation of the laser ablation threshold with T_c variation has been observed in these studies.

SECTION A : HTSC MATERIALS AT MICROWAVE FREQUENCIES

8.1 INTRODUCTION

Microwaves and far infrared sources are useful tools for the study of superconductivity even when a superconducting path of the material is not established for DC measurements. Microwave absorption studies provide unique information regarding the nature of superconductors in a high T_c material [1]. It is also a powerful non contact technique in the detection and elucidation of the normal to superconducting transition in the high T_c materials [2-6]. The phenomenon of non resonant absorption of electromagnetic radiation in the superconducting state of $YBa_2Cu_3O_7$ was also reported by various groups [7, 8] and this has been confirmed by others as a unique feature of granular superconductors. Such studies at RF, microwave and mm wave frequencies give detailed information regarding the gap parameter, the density of states and the nature of quasi particle excitations. In addition to this, information regarding the potential applications of devices at these frequencies can also be obtained from such studies [9, 10].

Microwave measurements and electron spin resonance (ESR) methodologies [11-15] can also determine whether a high T_c phase co-exist with lower temperature superconducting phase which is difficult to differentiate by conventional resistivity measurements. These studies can be used to monitor the normal to superconducting phase transition [16, 17]. It has the unique advantages over conventional methods particularly with regard to the following :-

1) There is no need for physical continuity between the superconducting (SC) phases in the sample enabling the detection of onset of SC even in a dilute phase with concentration of the order of a few percentage.

2) It is sensitive to stoichiometry of constituents and

3) There is no necessity for fixing electrodes as in the case of resistivity and reverse Josephson measurements.

The importance of the study of superconductors at microwave frequencies, arises from the fact that these measurements especially the surface resistance determines the suitability of these materials as microwave devices and components.

8.2 DETERMINATION OF SURFACE RESISTANCE

Surface resistance R_s is an important parameter to be considered when designing low loss components. Zero resistance at T_c is somewhat misleading since the losses in a superconductor increase rapidly with frequency. For a normal metal, loss increases as the square root of the frequency but for a superconductor it increases as the square of the frequency. A superconductor has much lower losses than copper upto several GHz. At the higher frequencies, the figure of merit for a superconductor is the microwave surface resistance (R_s).

Measurement of the surface resistance of a superconductor at high frequency is an important parameter, both for theoretical and for practical reasons. This may be accomplished by a variety of microwave techniques, but one of the most popular methods is to load a resonant structure with a superconducting sample and to study the variation of the Q factor with temperature (with and without the sample in place). Buravov *et al* [18] adopted the cavity perturbation method to determine microwave conductivity and dielectric constant of highly conducting substances. Cavity losses $\Delta(1/Q_m)$ is given by

$$\Delta Q_m = \mu'' \int_{v'} H^2 dV = \frac{2\alpha\mu'' V'}{V} \qquad (8.1)$$

$$\text{Here } \alpha = \frac{3.09}{(1+0.672r^2/b^2)}$$

where V′ is the volume of the sample , V is the volume of the cavity, μ'' is the imaginary part of the permeability and r and b are the radius and height of the cylindrical cavity respectively.

The resonant superconducting niobium cavity method has been used by several investigators to determine the characteristics of $YBa_2Cu_3O_x$ [19-22]. Others have introduced a "disk resonator method" for the measurement of R_s which consists of a pair of disks separated by a dielectric spacer out of which one is the high temperature superconductor sample, which dominates the loss of the system [23].

The precise geometry of the configuration will determine how cavity losses are related to superconductor - sample R_s. The basic approach is as follows :-

The general relationship between the cavity (or sample) parameters and surface resistance is

$$R_s = G \left[\frac{Z_o}{Q_o}\right] \qquad (8.2)$$

Here Z_o is the characteristic impedance of free space (377Ω), Q_o is the unloaded cavity Q, and G is the cavity geometric factor [24]. G must be modified when a sample is inserted, to take the field perturbation caused by the sample into account. Superconducting samples are generally compared to the samples of normal conductor that have the same size and shape.

The relation to determine the unloaded cavity quality factor (Q_o) from bandwidth measurements is

$$Q_o = \left[\frac{F_r}{F_H - F_l}\right] = \left[\frac{F_r}{\text{bandwidth}}\right] \qquad (8.3)$$

The bandwidth is measured in the usual manner by determining the upper and lower frequencies (F_H and F_l) at the half - power locations around resonance (F_r), [where field is peak field $/\sqrt{2}$].

The two - fluid relationship for surface impedance of a superconductor is approximated by the expression [25,26]

$$Z = R_s + j X_s \approx \frac{\omega^2 \mu_o^2 \lambda^3 n_n \sigma_n}{2n_s} + j \omega \mu_o \lambda \qquad (8.4)$$

where, σ_n is the conductivity component due to normal electrons, λ is the London penetration depth. From the above equation it is clear that $R_s \propto \lambda^3$.

In the case of 123 materials, anisotropy plays an important role (For the unit cell, $\lambda_{ab} \approx 270$Å while λ_c is ≈ 1800Å), and that must be taken into account when considering how the films should be constructed to minimise the surface resistance (R_s). It has been observed that the surface resistance determined by the microwave technique depends on the surface roughness, material preparation, oxygen stoichiometry etc [27, 28].

8.3 EXPERIMENTAL

In the present experiment, the surface resistance R_s was measured in a cylinderical copper TE_{011} transmission type cavity at different resonance frequency such as 3, 5, 9, and 11 GHz. Rectangular samples of HTSC material viz. Bi (2212) were cut out from a circular pellet and was mounted at the bottom plate of a X-band wave guide and irradiated with highly stabilised microwave radiation.

The microwave power was maintained at a precise adjusted low value during the frequency sweep to obtain power independent data. The quality factor (Q) was determined using a network analyzer (HP 8510B) and a S parameter test set in the above frequency range. A personal computer automatically measured the quality factor (Q). The experiment was repeated with standard copper samples of similar dimensions. The experimental R_s was determined from the relation

$$R_s = R_{cu} \left[\frac{Q_{cu}}{Q_{sc}} \right], \qquad (8.5)$$

where R_{cu} is the surface resistance of copper at the resonant frequency.

8.4. RESULTS AND DISCUSSION

The plot of $-\Delta 1/Q$ versus temperature for Bi-2212 is given in fig. 8.1. The sharp changes around 80K and 108K correspond to the superconducting transition temperatures. In the normal state, the microwave field does not penetrate the sample entirely as its thickness is greater than the skin depth in the normal state. Thus only a limited portion of the sample (thin shell) indeed is absorbing. In superconducting (SC) composites of this type which consists of clusters of SC grains each of the order of the penetration depth, the SC properties are controlled by the effects of percolation and frustration in analogy with the well known behaviour of spin glasses [29]. The SC grains are weakly coupled together either by the proximity effect for a metallic host or by the Josephson tunneling for an insulating host. Josephson junctions are naturally formed between the grains of HTSC samples [30-45].

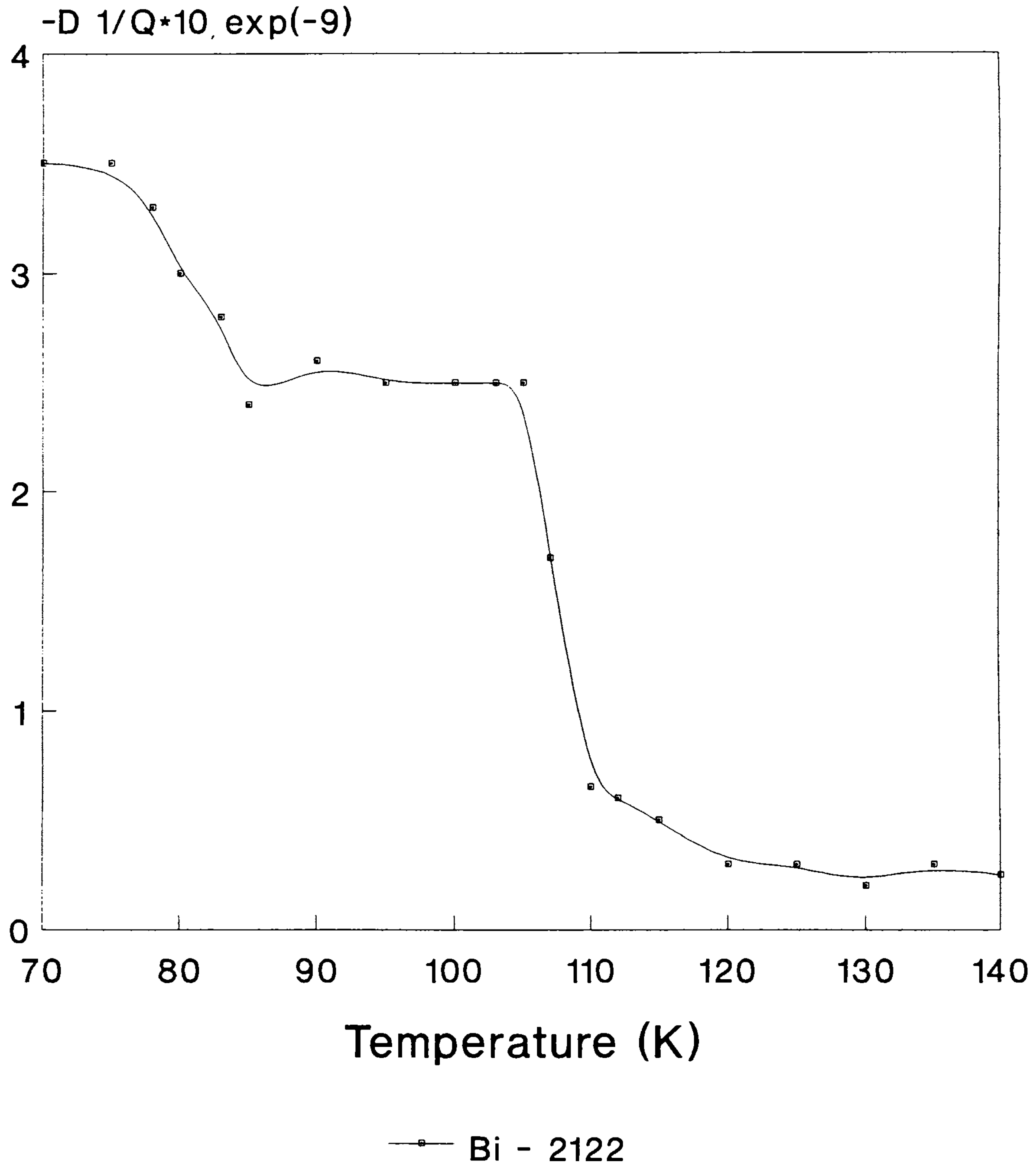


Fig. 8.1. Plot of $-\Delta(1/Q)$ versus temperature for Bi-2122 HTSC samples.

The various values obtained for R_s (fig. 8.2) is compared with reported values [46]. The discrepancy with the reported values are due to the following reasons 1] Localised superconductivity in the sample and 2] Structural defects, deformations, surface roughness and inhomogeneity of the pellets giving rise to large surface resistances and 3] since the cavity used is a non superconducting type, lower values of cavity Q results in a reduced sensitivity to the presence of the relatively small superconducting sample losses.

8.5. FABRICATION OF A HTSC DEVICE : RING RESONATOR

8.5.1. Introduction

Recent researches in microwave electronics employing HTSC materials are mainly concerned with boosting up system performance by exploiting its potential characteristics and also by tapping the reduced cost of low temperature environment. Also the large energy gap (Δ) of high T_c superconductors compared with the microwave energy spectrum make these suitable to be employed in microwave circuits.

Thin film high T_c devices find various applications in the electronics industry, specifically for microwave devices in communications, instrumentation, radio astronomy, and surveillance. Such devices are free of the problems faced by conventional devices such as noise figure, loss and size. The discovery of high temperature superconductors has made a new class of microwave devices. Performance of high T_c superconductors at microwave frequencies is well established in Microwave Integrated Circuit (MIC's) and transmission lines [46-49]. The high T_c superconductors find applications in passive microwave devices particularly in filters and resonators. In such circuits, the surface resistance is extremely low and hence better performance is achieved, compared to systems employing normal conductors. These types of circuits are useful in satellite communication systems, where high efficiency is

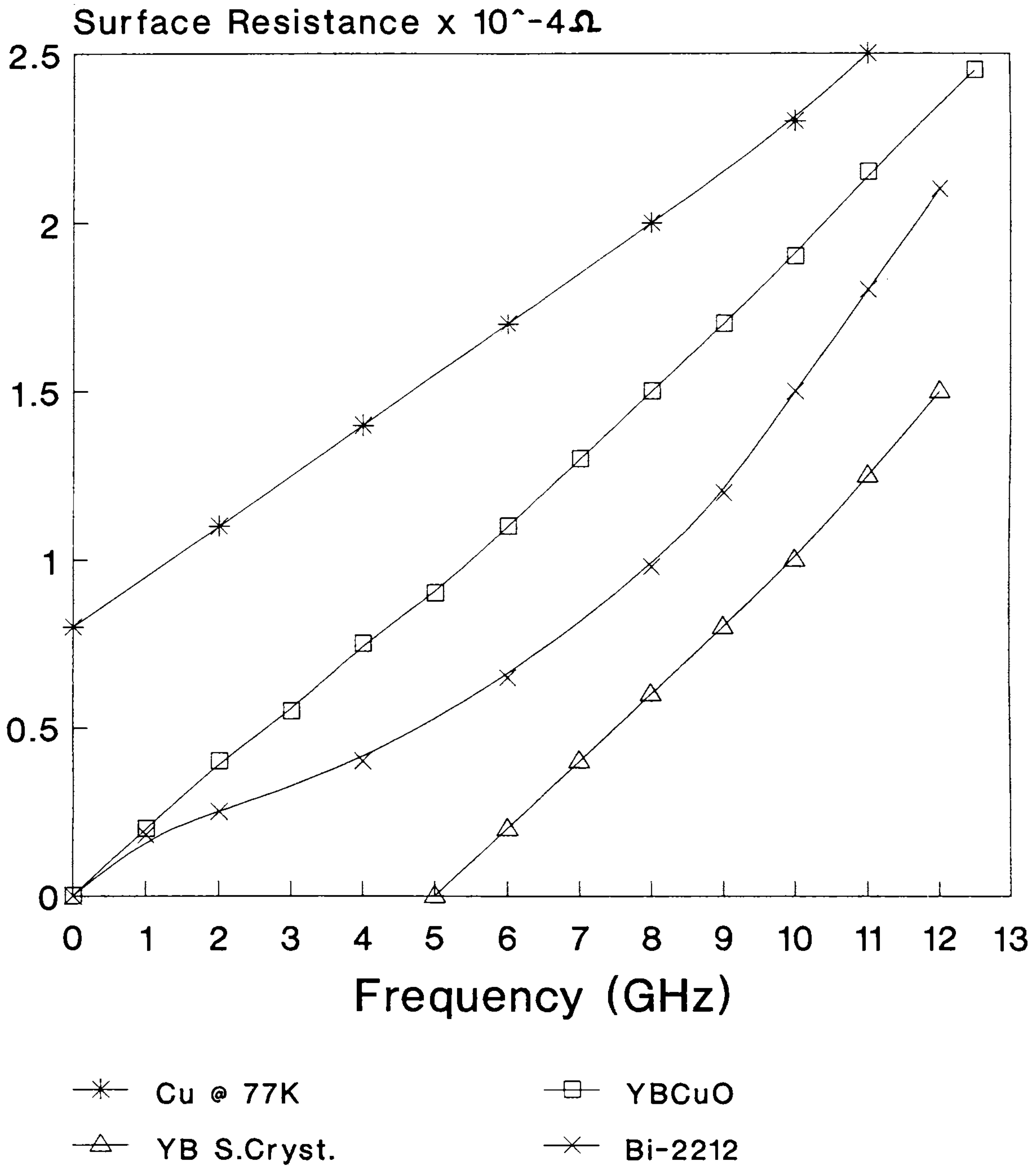


Fig. 8.2. Plot of surface resistance versus temperature for samples Bi-2212 sample compared with reported values.

required.

The low - loss, low - dispersion properties of HTSC offer great promise for application in passive microwave circuits. As the quality of the material improves surface resistance decreases. Measurements on patterned films at 77K have shown that an improvement of a factor of 10 over conventional films at 10GHz is achievable [50], although extrapolation of the data from higher frequencies suggests a factor 100 is possible [51].

Superconductors when substituted for normal metals will result in lower insertion losses, higher Q's, and much smaller physical size for the circuits.

Various fabrication procedures have emerged recently for successful coating of high T_c superconducting thick films and the development of bulk microwave components. Film deposition by coevaporation and the annealing process are difficult. Moreover, the repeatability of the production of SC films is poor.

This also prevents the use of ordinary substrates like alumina for the fabrication of SC films because all devices produced are on single crystal substrates such as MgO, La Al_2O_3 or on buffered substrates. Badhari *et al* [52] have produced high T_c superconducting films on alumina substrate by screen printing method. Though the T_c of these films found to be high, none of these films showed zero resistance state at their lowest measurement temperature. Mongro - Campero and Turner [53] have reported the zero resistance film on alumina substrate using zirconia as buffer. Yoshiko *et al* [54] reported the development of superconducting devices on alumina substrate, prepared by printing method with buffer treatment. In this context, it is necessary to try to develop high T_c superconducting devices in ordinary substrates like alumina, without making use of any buffer layer. The performance of the rare earth based ceramic substrate has been evaluated [55], and it is found that this substrate is useful for fabrication of MIC's.

In this following section, the design and fabrication of SC circular resonator of GdBaCuO on alumina substrate without any buffer layer is discussed.

8.5.2. Methodology and Experimental results

The resonator is fabricated in a microstrip configuration consisting of superconducting transmission lines. A thick copper block is used as the ground plane. Gadolinium based oxide ceramic material has been synthesised using the melt textured growth discussed in chap. 2. Resistivity and susceptibility measurements carried out on these samples show that the samples superconduct (R = 0) at 93K.

The resonator having a radius of 5mm, fabricated from the bulk sample was connected to a 50 ohm feed line on an alumina substrate (ε_r = 9.8) of thickness 0.635mm. The feed lines are designed in such a way that it makes 180° with each other as shown in fig 8.3. After the optimisation of this design, another resonator was fabricated using copper with the same parameters. The performance of these two resonators were compared at room temperature and at liquid nitrogen temperatures.

The schematic diagram of the resonator with metallic housing is shown in figure 8.4.

The microstrip resonator is connected to the ports of the HP8510 B Network analyzer. The network analyzer is calibrated to full two port with 401 frequency points. The operating frequency band is chosen as 50MHz to 20GHz. The cryogenic arrangements are made in such a way that, it will not affect the performance evaluation of the circuit.

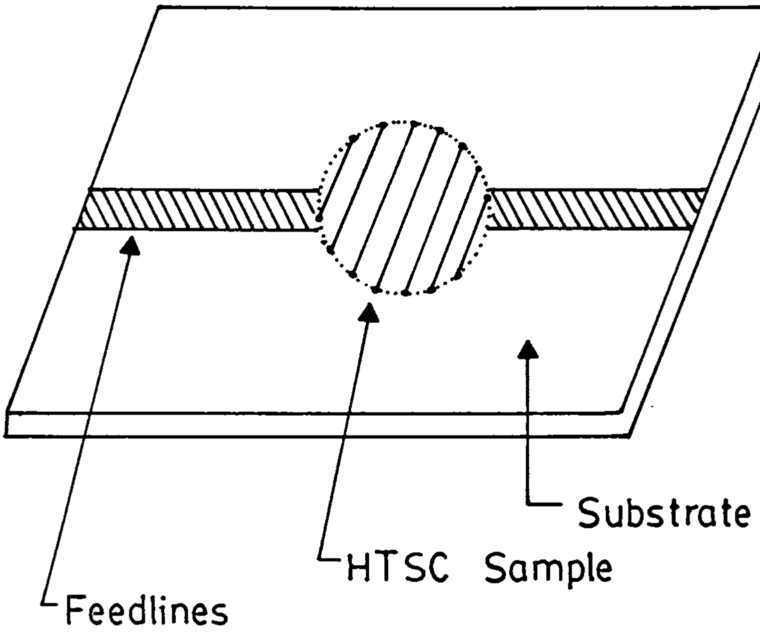


Fig. 8.3. Schematic diagram of the resonator.

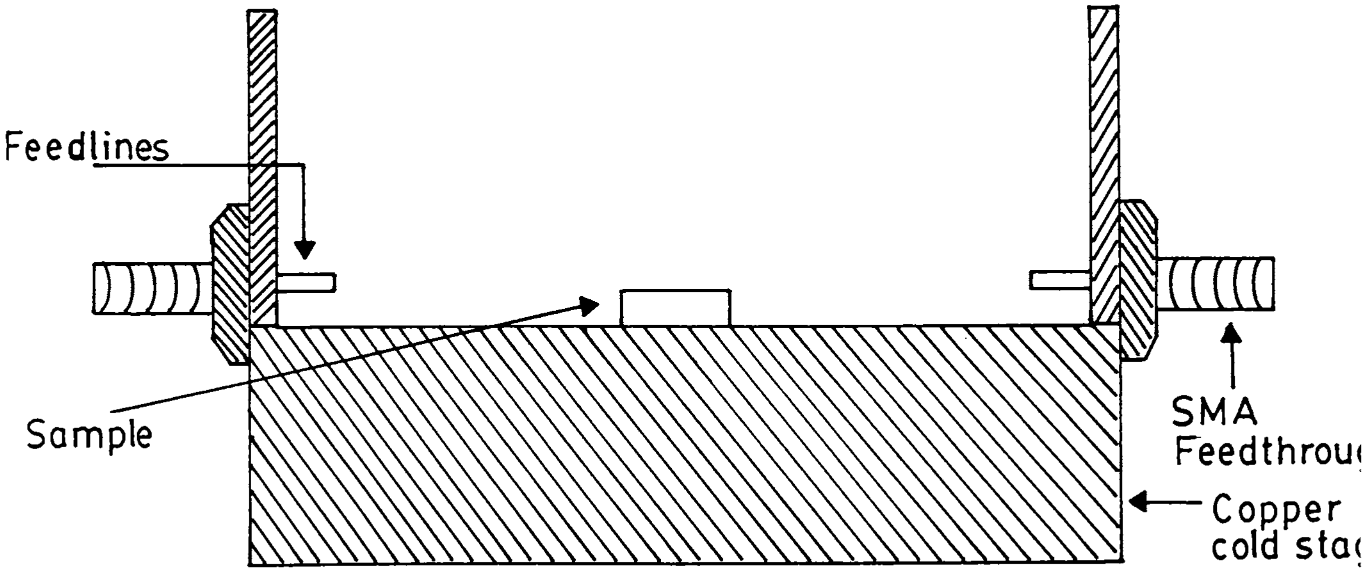


Fig. 8.4. Schematic diagram of the resonator with metallic housing and connectors.

The transmission characteristics of the superconducting resonator at liquid nitrogen temperature is shown in figure 8.5 [56]. Above T_c the resonator behaves as a resistive conductor and the resonance peaks are buried in the noise and poorly resolved. At liquid nitrogen temperatures much below T_c, the resonator is found be having good resonance characteristics at 4.75GHz. The resonance behaviour of similar resonator using copper is also shown in fig 8.5.

SECTION B : DETERMINATION OF LASER ABLATION THRESHOLD OF DOPED BiSrCaCuO HTSC BY PULSED PHOTOTHERMAL DEFLECTION TECHNIQUE

8.B.1 Introduction

Studies on pulsed laser induced ablation from solid targets have recently gained great importance because of its potentiality for use as an alternative tool for the deposition of high temperature superconducting thin films [57, 58]. There exists a number of parameters such as the nature of the target, wavelength of laser radiation and laser power which control the ablation process. Accurate knowledge of ablation threshold is essential in controlling the laser power for a given target in order to get good quality thin films.

Various techniques are used to characterise the ablation process thereby yielding precise information regarding the etching rate, the velocity of ablation products, the threshold of ablation etc. [59, 60]. Thermo-optic deflection (mirage effect) has recently been shown to be one such technique to measure the laser induced damage threshold of a variety of targets including optical materials and polymers [61, 62].

Photothermal deflection technique essentially consists of measuring the deflection of an optical beam (probe) due to the refractive index gradient in the vicinity of a sample surface

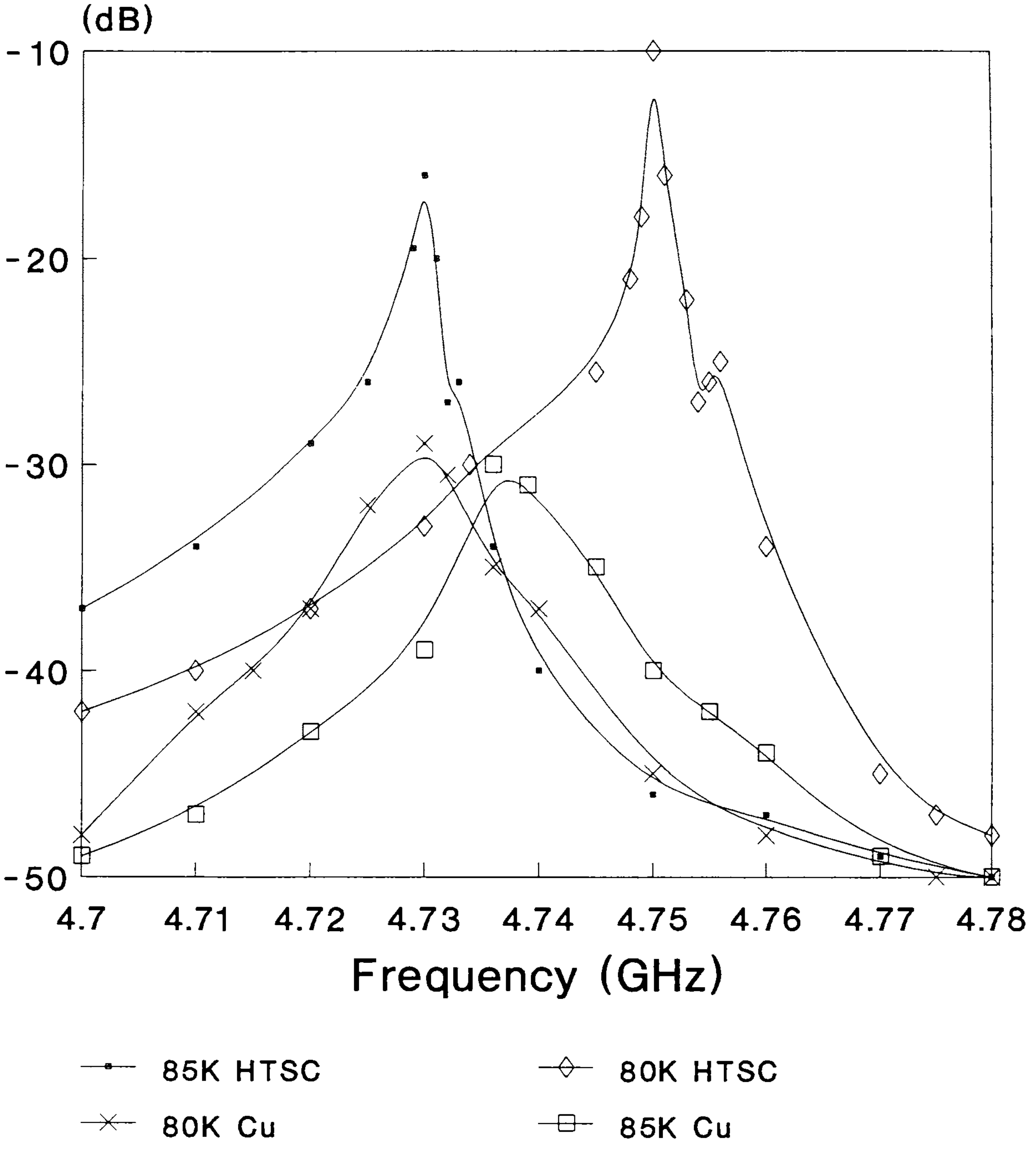


Fig. 8.5. Performance of the HTSC resonator at two different temperatures compared with a copper resonator.

generated by a pulsed/modulated pump beam. In the present case the technique employed viz. photothermal deflection, exploits the signal due to the deflection and/or distortion of the probe beam caused by the thermal wave which occurs near the ablated sample. This technique has been used by Sell *et al* [63] to measure the ablation threshold of high temperature superconducting bulk YBaCuO samples using pulsed UV excimer laser. In this chapter the results of laser induced ablation threshold measurements carried out on high temperature superconducting samples of $Bi_2 (Sr Ca)_x Cu_3 O_y$ (x = 2, 2.2, 2.6, 2.8, 3) and $Bi_{1.6} (Pb)_x Sr_2 Ca_2 Cu_3 O_y$ (x = 0, 0.1, 0.2, 0.3, 0.4) by irradiating the target with Nd - YAG laser beam at 1.06 μm wavelength are presented. The objective of this study was to correlate the ablation threshold with the variation of the quantity x in these samples and to see whether this has any relation to the other physical parameters of the samples such as T_c.

8.B.2 EXPERIMENTAL

Samples of superconducting materials with varying Sr, Ca and Pb concentrations were prepared by the well known solid state reaction matrix method [64, 65] and is described in chapter 2. The specimens were made into pellets of 1cm diameter and the T_c values were measured using the four probe technique under vacuum conditions.

The experimental set-up to determine the laser induced damage and ablation threshold of the samples is shown in fig-8.B.1. The ablation beam is a focused output of pulsed Nd-YAG laser (DCR - 11, Quanta Ray) operating at 1.06 μm (Pulse width = 10 nsec). The refractive index gradient (RIG) generated in the gas surrounding the sample following the irradiation is probed by a stabilized 5-mw He-Ne laser (Spectra Physics) beam. A converging lens (f= 25cm) focuses the probe beam so that in the interacting region, the probe beam diameter is smaller than that of the ablation beam. The probe beam which is at right angles to the pump beam causing ablation, is allowed to pass grazing the sample surface.

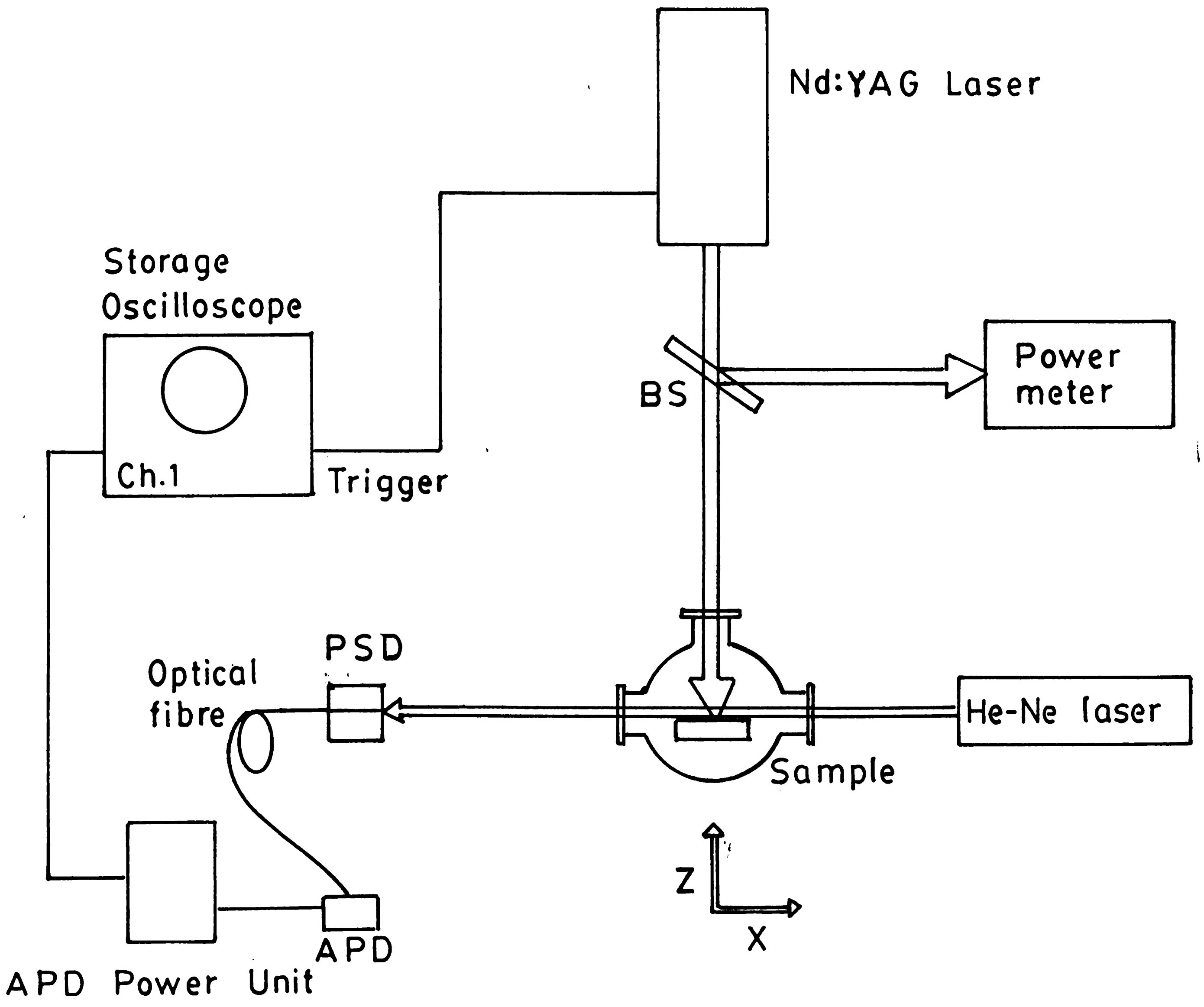


Fig. 8.B.1. Schematic diagram of the experimental setup for the photothermal measurement of laser ablation.

A position sensitive detector located at about 50cm away from the sample measures the deflection of the probe beam due to the transient refractive index gradient generated above the laser heated sample. The position sensitive detector consists of the polished tip of a multimode optical fiber (200/380μm) at one end and the other end is coupled to an avalanche photodiode [66]. The deflection signal amplitude was monitored with a CRO (Tektronix Model 466) for different pump energy densities. The incident laser power was measured using an on-line power meter (Delta Developments).

8.B.3 RESULTS AND DISCUSSION

A plot of the incident energy density versus the signal amplitude is shown in figures 8.B.2 and 8.B.3. As the energy density is increased, an abrupt change in the deflection signal amplitude occurs corresponding to the onset of surface damage in the sample. At still higher fluences the signal amplitude keeps on increasing till it reaches a point where another abrupt change of slope occurs. This region, evidently corresponds to the threshold of ablation.

Variations in the damage as well as ablation threshold values were determined for various values (x) of the concentration of the Pb and Sr - Ca in the superconducting samples (fig-8.B.4 and 8.B.5). Results obtained in various samples are given in Table 8.b.1. It is observed that with increasing Sr, Ca concentration, both thresholds increase linearly. But in the case of Pb doped samples, ablation and damage thresholds initially increase, reach a maximum value and then begins to decrease with increase in Pb concentration. These results imply that incorporation of Sr, Ca with increasing concentration enhances the optical strength and or thermal stability of the material while for Pb doped samples there is an optimum concentration for which the ablation and damage thresholds attain maximum values. It is really striking to note that an exactly similar variation is observed in T_c values also in the case of Pb doped samples in which the stabilization

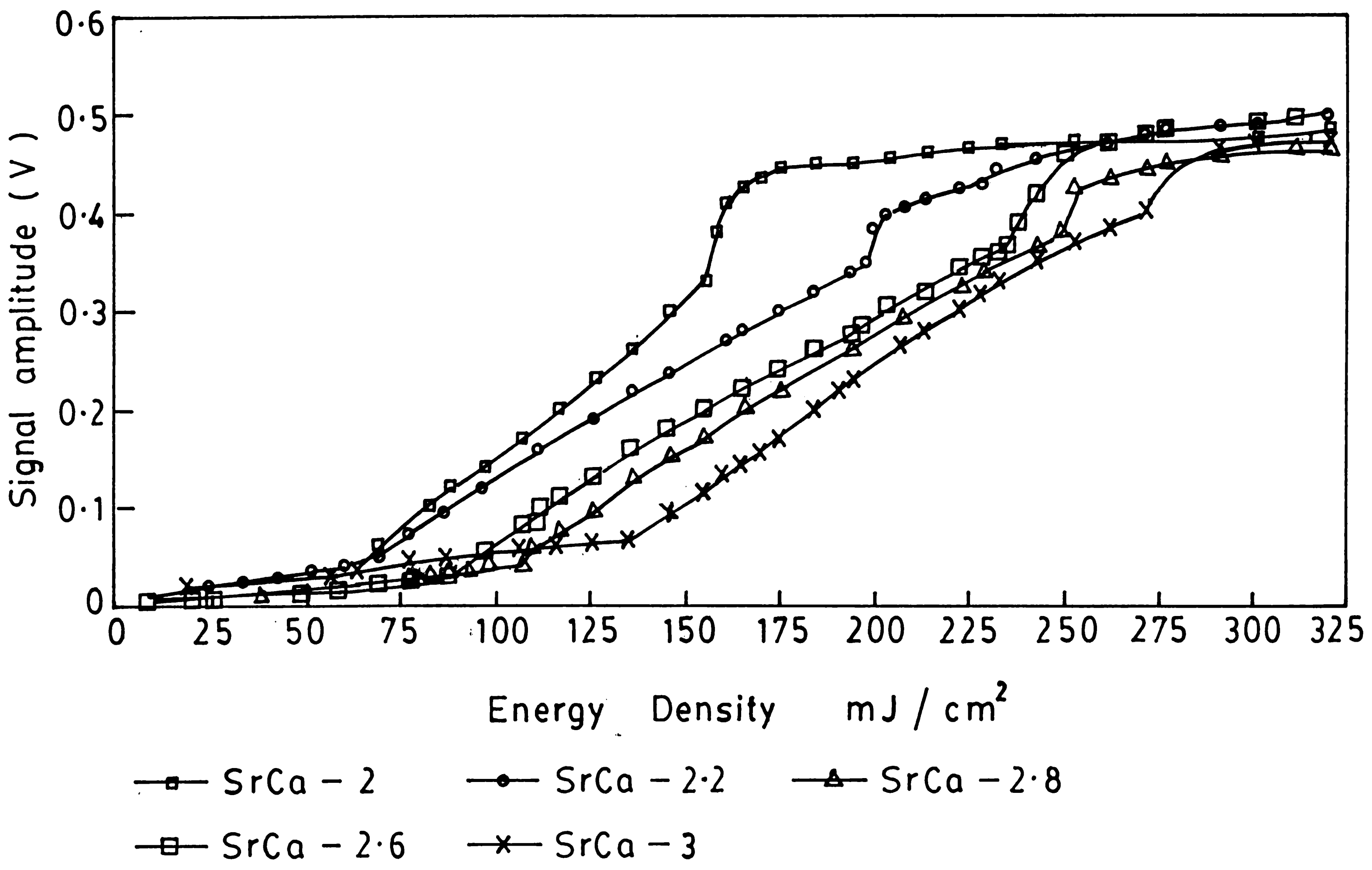


Fig. 8.B.2. Plot of the laser energy density versus PTD signal amplitude for $Bi(SrCa)_xCuO$ for various x values.

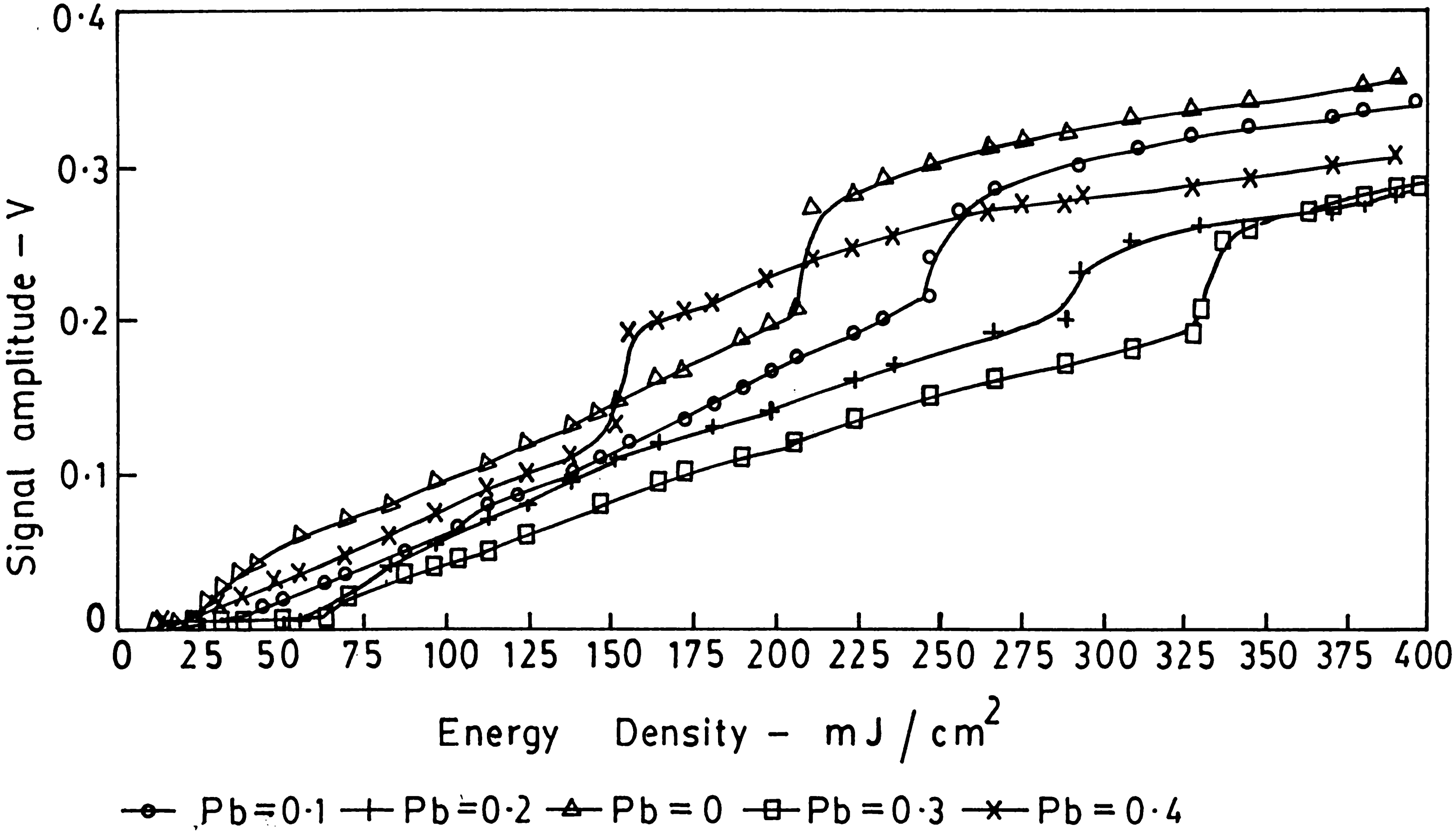


Fig. 8.B.3. Plot of the laser energy density versus PTD signal amplitude for Bi(Pb)$_x$SrCaCuO for various x values.

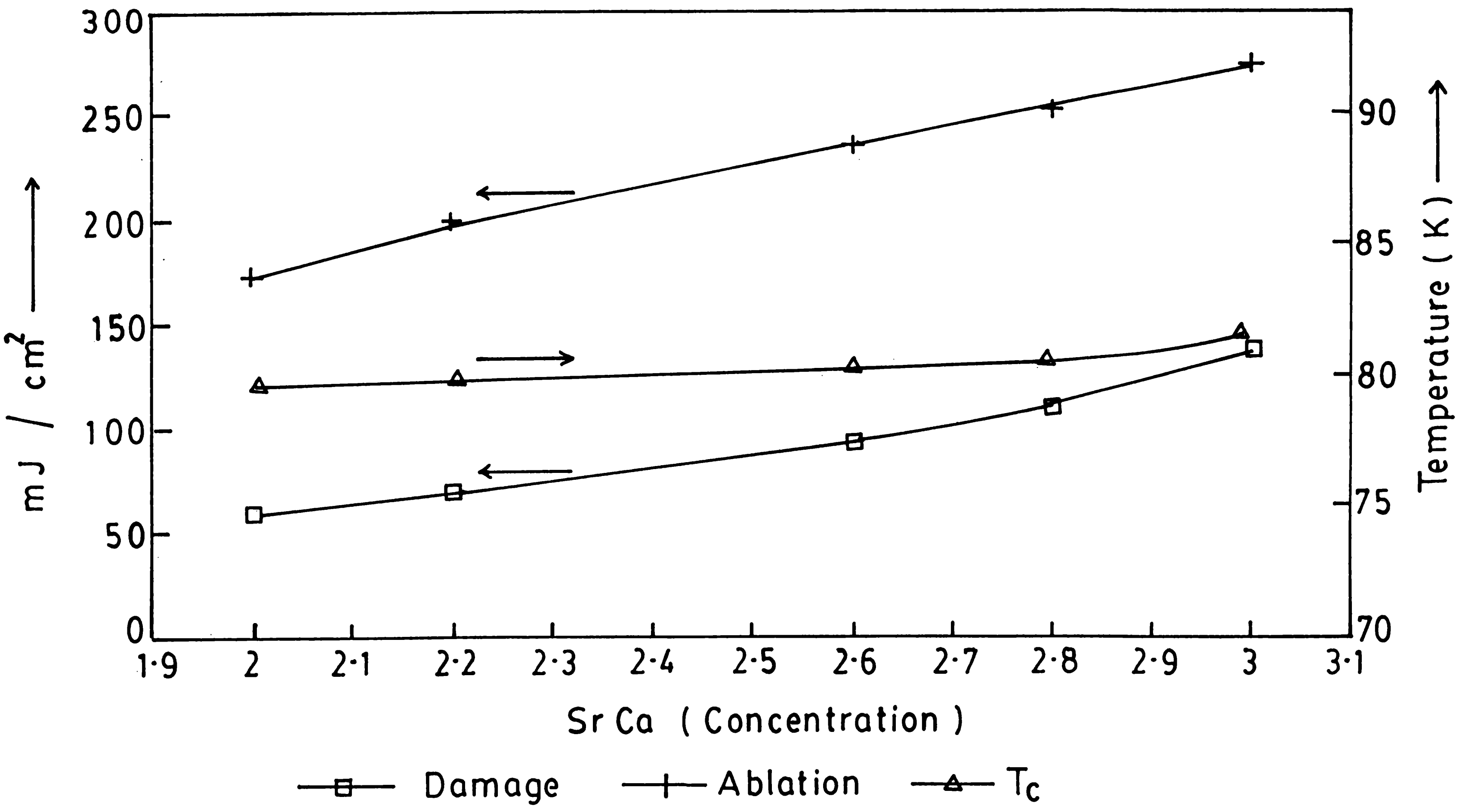


Fig. 8.B.4. Plot of damage and ablation threshold for $Bi(SrCa)_xCuO$ for various x values.

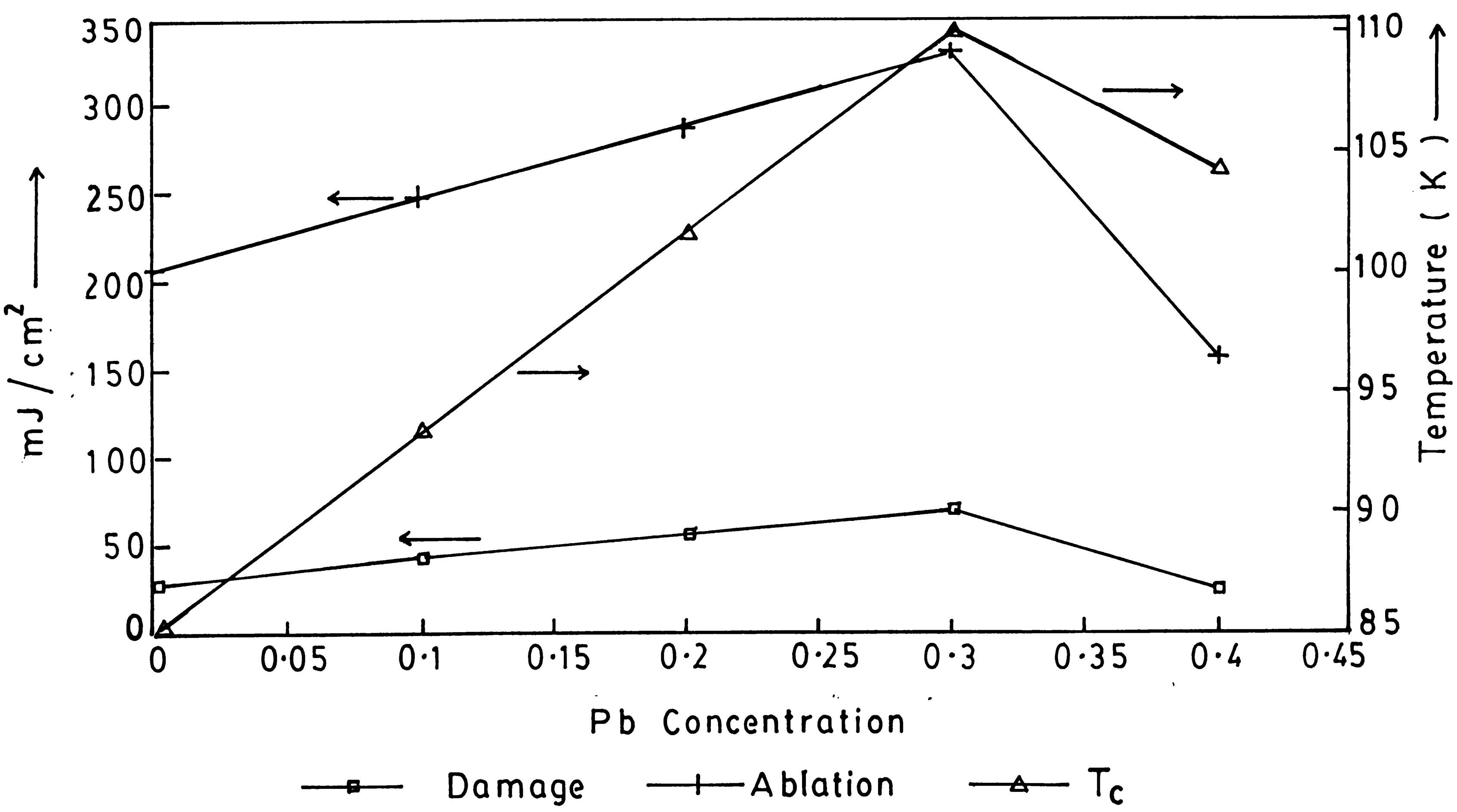


Fig. 8.B.5. Plot of damage and ablation threshold for $Bi(Pb)_xSrCaCuO$ for various x values.

of 110K superconducting phase takes place almost at the same value of x. The variation of laser induced damage and ablation thresholds follow the changes in T_c with x, indicating that structural stabilization occurs at an optimum value of Pb concentration for the superconducting sample of BiSrCaCuO [67]. This observation is in good agreement with the results of X-ray diffraction studies of above samples [68-70].

TABLE 8.B :- Laser induced damage and ablation threshold and T_c values for the superconducting samples.

SAMPLE	Damage Threshold (mJ/cm²)	Ablation Threshold (mJ/cm²)	T_c (K)
$Bi_2Sr_2Ca_2Cu_3O_y$	58.03	172.32	79.2
$Bi_2Sr_{2.2}Ca_{2.2}Cu_3O_y$	68.74	198.2	79.7
$Bi_2Sr_{2.6}Ca_{2.6}Cu_3O_y$	93	235	80
$Bi_2Sr_{2.8}Ca_{2.8}Cu_3O_y$	108.2	250	80.5
$Bi_2Sr_3Ca_3Cu_3O_y$	136	272	81.5
$Bi_{1.6}Pb_0Sr_2Ca_2Cu_3O_y$	26	203	85
$Bi_{1.6}Pb_{.1}Sr_2Ca_2Cu_3O_y$	42	247	93
$Bi_{1.6}Pb_{.2}Sr_2Ca_2Cu_3O_y$	55.1	287	100
$Bi_{1.6}Pb_{.3}Sr_2Ca_2Cu_3O_y$	68.8	329	110
$Bi_{1.6}Pb_{.4}Sr_2Ca_2Cu_3O_y$	23	155	104

8.6. Part A References.

[1] J G Bednorz and K A Muller, Z Phys B, 64, 189, (1986).

[2] K W Blazey, A M Portis and J G Bednorz, Sol. St. Commun., 66, 1153, (1988).

[3] M D Sastry, Y Babu, R M Kadam, A G I Dalvi, I K Gopalakrishnan, J V Yakhmi and R M Iyer, Sol. St. Commun., 66, 1219, (1988).

[4] Anand M Awasthi, John P Carani, Barakat Alavi and George GrÜner, Sol. St. Commun., 67, 373, (1988).

[5] W L Kennedy and S Sridhar, Sol. St. Commun., 68, 71, (1988).

[6] A K Ganguli, K S N Swamy, G N Subbanna, A M Umarji, S V Bhat and C N R Rao, Sol. St. Commun., 67, 39, (1988).

[7] R Durny, J Hautala, S Ducharme, B Lee, O G Symko, P C Taylor, D J Zheng and J A Xu, Phys. Rev. B, 36, 4, (1989).

[8] C Ebner and D Stroud, Phys. Rev. B, 31, 165 (1985).

[9] W H Hartwig and C Passow, "Applied superconductivity" Academic Press, (1975).

[10] M Tinkham, "Introduction to superconductivity", (Mc Graw - Hill, New York,) (1989) and W P Beyermann, B Alavi and G Gruner. Phys. Rev. B, 35, 8826, (1987).

[11] K W Blazey, K A Muller, J G Bednorz, W Berlinger, G Amoretti, E Buluggiu, A Vera and F C Matacotta, Phys. Rev. B, 36, 7241, (1987).

[12] R Jones, R Janes, D J Keeble, K K Singh and P P Edwards, J. Chem. Soc. Faraday Trans, 84, 683, (1990).

[13] S V Bhat, P Ganguly and C N R Rao, Pramana, 28, 425, (1987).

[14] R Durny, J Hautala, S Ducharme, B Lee, O G Symko, P C Taylor, D J Zheng and J A Xu, Phys. Rev. B, 36, 2361, (1987).

[15] S V Bhat, P Ganguly and C N R Rao, Jl. Phys. C : Sol. St. Phys., 20, L559, (1987).

[16] M D Sastry, R M Kadam, Y Babu, A G I Dalvi, I K Gopalakrishnan, P V P S S Sastry and R M Iyer, Physica C, 153, 1667, (1988).

[17] V Vidyalal, C P G Vallabhan, K A Jose, P Mohanan and K G Nair, Proc, APSYM - CUSAT, DEC 29-31, P30, (1992).

[18] L I Buravov and I F Shchegolev, Prib. Tek. Eksp., 4, 171, (1971).

[19] M Hein, N Klein, F M Mueller, H Piel, R W Röth, W Weingarter and J O Willis, Un.Wuppertal pub. WUB 87 - 15h, 1, (1987).

[20] M Hagen, N Hein, A Klein, A Michalke, G Müller, H Piel, R W Röth, F M Mueller, H Sheinberg and J L Smith, Un.Wuppertal pub. WUB 87 - 12h, 1, (1987).

[21] J S Martens, J B Beyer and D S Ginley, Appl. Phys. Lett., 52, 1822, (1988).

[22] S Sridhar and W L Kennedy, Rev. Sci. Instrum., 59, 531, (1988).

[23] A Fathy, D Kalokitis and E Belohoubek, Microwave Journal, 31, 75, (1988).

[24] H Hahn, H J Halama and E H Foster, J. Appl. Phys., 39, 2606, (1968).

[25] T Van Duzer and C W Turner, "Principles of Superconductive devices and circuits", (Elsevier, New York), P68, P129, P138, P317, P319, (1981).

[26] Jeffrey T Williams and Stuart A Long, IEEE Ant. and Prop., 66, Aug,(1990).

[27] M Hein, G Muller, H Piel, U Klein and M Peiniger, J. Less. Comm. Metals., 151, 71, (1989).

[28] A M Portis, K W Blazey and F Waldner, Physica. C, 159, 308, (1989).

[29] P V P S S Sastry, I K Gopalakrishnan, A Sequeira, H Rajagopal, K Gangadharan, G M Phatak and R M Iyer, Physica C, 156, 230, (1988).

[30] Fan Changxin, S Lin, Miao Bocai and Lin Jun, Sol. St. Commun., 64, 689, (1989).

[31] C J Lui, X F Meng, K Shao, Y D Dai, Y Zhang, R P Peng, Z L Bao, C Y Li, K Wu and D L Yin, Sol. St. Commun., 64, 321, (1987).

[32] A I Golovashkin, A L Gudkov, S I Krasnosvobodtsev, L S Kuzmin, K K Likharev, Yu V Maslennikov, Yu A Pashkinm E V Pechen and O V Snigirev, IEEE Trans Magn., 25, 943, (1989).

[33] B Haûser, M Diegel and H Rogalla, Appl. Phys. Lett., 52, 844, (1987).

[34] N D Kataria, V S Tomar, A K Gupta and M Kumar, J. Phys. C,

21, L523, (1988).

[35] R H Koch, W J Gallagher, B Bumble and W Y Lee, Appl. Phys. Lett., 54, 951, (1989).

[36] L Li, D Hong-min and Z Dian-lin, Phys. Rev. B, 37, 3681, (1988).

[37] H Nakane, Jpn. J. Appl. Phys., 26, L1581, (1987).

[38] R H Ono, J A Bealle, M W Gomar, P M Mankiewich, R E Howard and W Skocpol, IEEE Trans. Magn., 25, 976, (1989).

[39] D Robbes, M Lam, Chok Sing, Y Monfort, D Bloyt, J Provosk and B Raveau, Appl. Phys. Lett., 54, 1172, (1989).

[40] N X Shen, P H Wu, S Z Yang, Q H Cheng, Y B Sheng, H Y Luo and J S Kui, IEEE Trans. Magn., 25, 915, (1989).

[41] J Song, P H Wu, Q H Cheng, S Z Yang, J Chen, D Jin, H X Luo and J S Kui, IEEE Trans. Magn., 25, 911, (1989).

[42] A Sugishita, Jpn. J. Appl. Phys., 26, 1472, (1987).

[43] P H Wu, Jpn. J. Appl. Phys., 26, L1579, (1987).

[44] T Yamashita, A Kawakami, S Noge, Weiwei Xu, Masasoke Takada, Takayuki Komatsu and Kazumasa Matusita, Jpn. J. Appl. Phys., 27, L1107, (1988).

[45] T Yang, D Liu, Zi Qiong Sun, Xin Hang Chen, Chunfang Lui, Jianping Li, Xiaozu Wu and Lian Zhou, IEEE Trans. Magn., 25, 970, (1989).

[46] H Piel, M Hein, N Klein U Klein, A Michalke, G Mueller and L Ponto, Physica C, 153, 1604, (1988)

[47] A A Valenzucle and B Daalmans, Electron. Lett., 25, 1435, (1989).

[48] A K Gwarek and C Mroczkowski, IEEE Microwave theory tech., MTT - 39, 1655, (1991).

[49] G D Inzeo, F Gihnnini, M Sodi and R Sorrentono, IEEE Microwave theory tech., MTT - 26, 462, (1978).

[50] A Inam, X Wu, L Nazar, M Hegde, C Rogers, T Venkatesan, R Simon, K Daly, H Padamsee, J Kirichqussner, D Moffat, D Rubin, Q Shu, D Kalokitis, A Fathy, V Pendrik, R Brown, B Brychi, E Belohoubek, L Drabeck, G Gruner, R Hammond, F Gamble, B Lairsom and J Brauman, Appl. Phys. Lett., 56, 1178, (1990).

[51] M Nuss, K Goosen, P Mankiewich, R Howard, B Straughn, G Berkstresser and C Brandle, IEEE Electron Dev. Lett., EDL-11, 200, (1990) and N Klein, G Muller, H Piel, B Roas, L Schultz, U Klein and M Peiniger, Appl. Phys. Lett., 54, 757, (1989).

[52] R C Badhari, Sing-Mo H Tzeng, H J Doerr and R F Bunshah, Appl. Phys. Lett., 51, 1277, (1987).

[53] A Mongro - Campero and L G Turner, Supercondu. Sci. and Tech., 1, 269, (1989).

[54] Yoshiko H Ohashi, Kêisuke Kawabata, Minoru Niwa and Mitsuru Fukuchi, Jpn. J. Appl. Phys., 28, 132, (1989).

[55] J K Thomas, J Kurien, J Koshy, P S Mukkerjee, Y P Yadava, A D Damodaran, K A Jose, K K Narayanan and K G Nair, Proc., APSYM - CUSAT, DEC 29-31, P37, (1992).

[56] V Vidyalal, C P G Vallabhan, K A Jose, K K Narayanan, P Mohanan, K Vasudevan and K G Nair, Presented at the National

symposium on Advances in Microwave, Dept. of Electronics Sciences, Univ. Of Delhi, March 1 - 2, (1993).

Part B. References

[57] T Venkatesan, X D Wu, A Inam and J B Watchman, Appl. Phys. Lett., 52, 1193, (1988).

[58] P E Dyer, R D Greenough, A Issa and P H Key, Appl. Phys. Lett., 53, 534, (1988).

[59] S Lazare and V Granier, J. Appl. Phys., 63, 2110, (1988).

[60] G Koren, Appl. Phys. Lett., 51, 569, (1987).

[61] S Petzodlt, A P Eig, M Reichling, J Reif and E Matthias, Appl. Phys. Lett., 53, 2005, (1988).

[62] K Rajasree, P Radhakrishnan, V P N Nampoori and C P G Vallabhan, Meas. Sci. Technol., 4, 591, (1993).

[63] J A Sell, D M Heffelfinger, P Ventzek and R M Gilgenbach, Appl. Phys. Lett., 55, 2435, (1989).

[64] P V P S S Sastry, J V Yakhmi and R M Iyer, Sol. St. Commun., 71, 935, (1989).

[65] P V P S S Sastry, I K Gopalakrishnan, A Sequeira, H Rajagopal, K Gangadharan, G M Pathak and R M Iyer, Physica C., 156 , 230, (1988).

[66] K Rajasree, A V Ravikumar, P Radhakrishnan, V P N Nampoori, and C P G Vallabhan, J. Acou. Soc. India., 18, 24, (1990).

[67] K Rajasree, V Vidyalal, P Radhakrishnan, V P N Nampoori, and C P G Vallabhan, J. Appl. Phys., 74, 2004, (1993).

[68] J M Tarascon , W R Mc Kinnon, P Bardoux, D M Hwang, B G Bagley, L H Green, G W Hull, Y Le Page, N Stoffel, and M Giround, Phys. Rev. B, 38, 8885, (1988).

[69] M Takano, J Takada, K Oda, H Hitaguchi, Y Miura, Y Ikeda, Y Tomii and H Mazaki, Jap. J. Appl. Phys., 27, L - 1041, (1988).

[70] S M Greene, C Jiang, Yu Mei, H L Luo and C Politis, Phys. Rev. B., 38, 5016, (1988).

CHAPTER 9

SUMMARY AND CONCLUSIONS

The discovery of materials exhibiting superconductivity above liquid nitrogen temperature has initiated a surge of activity in the scientific community. This has made possible even small laboratories to carry out significant work in the area of superconductivity with moderate facilities. The work presented in this thesis has been motivated mainly by the new possibilities offered by high temperature ceramics. This concluding chapter aim to provide a summary of the work done by the author described in the preceding chapters of this thesis.

A brief overview of the history of superconductivity, from the discovery by Kammerlingh Onne s to the revival and rejuvenation by Bednorz and Müller, was given in the first chapter which included an overall view of the important events which took place in this field. A concise account of the theoretical views given by the workers in the field of high temperature superconductors along with the microscopic theory of BCS superconductivity were reviewed. This chapter also included the chemical composition and structure of Y based, Bi based and Tl based superconductors.

In the second chapter, the preparation and characterisation of various HTSC materials were given. Various techniques like solid state reaction, co-precipitation method, freeze drying technique, preparation of single crystals, thin film preparation by laser ablation and melt textured growth were discussed. The samples prepared and studied by the author include Gd - 123, Bi based 2212 and 2223 systems. The details of determination of resistivity, susceptibility and hence the transition temperatures were also discussed.

The instrumentation developed for the determination of the resistivity of HTSC samples was described in chapter 3. The design and realisation of a metallic cryostat, and a precision constant current source was discussed. For precise determination of resistivity these two components play an important role along with supporting instruments (like a DC nanovoltmeter). Due to the unique design of the cryostat it consumes only very little liquid nitrogen. The effectiveness and utility of the designs have been demonstrated by making measurements on some HTSC samples. Electrical characteristics of devices which are sensitive to intrinsic power supply transients and extraneous interfering electromagnetic noise can be determined using these components. The units can be constructed at a very low cost compared to commercially available ones. The chapter concludes with the discussion on the determination of AC electrical resistivity which can throw light on the conductivity behaviour of HTSC materials.

Determination of magnetic susceptibility and transition temperature were discussed in chapter 4. The design of a glass cryostat with which rapid characterisation of samples are possible was described. The glass cryostat has added advantages like reduced consumption of liquid nitrogen and the elimination of offset voltages which appear in cryostats made of metal (where the sensing coils are unbalanced due to the proximity to a metal).

Three methods namely a) self inductance method b) mutual inductance method and c) frequency shift method with necessary instrumentation which can be used to determine T_c were described. The frequency shift method has a higher resolution compared to the other two eventhough supporting electronics are required. A MOSFET based Robinson oscillator (which is highly stable and hence has a very low drift) was used for this purpose.

The chapter concludes with a discussion with the efficacy of EM shields using HTSC materials compared to conventional shielding materials like μ metal, aluminium and copper.

As a prelude to the investigations in stepping up T_c, various dopants and substitutions were tried in Gd based 123 HTSC's. Moreover chemical doping is a crucial investigative tool since it affects the structure. In chapter 5, among the various alkali metals doped, only potassium was found to give positive results. Stable and reproducible transitions between 92K and 100K were observed both resistively and magnetically for certain weight percentages of potassium.

Chapter 6 gives an elaborate discussion on critical current density (J_c). Various techniques used for the measurement of J_c, enhancing J_c in oxide superconductors and effect of Na doping on J_c have been discussed.

Chapter 7 gives an elaborate sketch of the degradation and aging behaviour of copper oxide superconductors. The possible end products due to degradation, methods to prevent ageing with a plastic solution etc. are discussed. The influence of synthesising routes on resistivity and aging characteristics of Bi-cuprate superconductors, and a novel method to revive T_c and J_c of aged superconductors have also been included in this chapter.

In the first part of chapter 8, the behaviour of HTSC materials at microwave frequencies are discussed. Such studies have great importance in the fabrication of devices based on these new materials and hence a thorough investigation of its various electrical properties are necessary. The surface resistance of some HTSC samples were determined by the cavity perturbation method. A HTSC device viz. a ring resonator was designed and fabricated using Gd - 123 HTSC material. It characteristics were studied and compared with a resonator made of copper.

The concluding part of the last chapter deals with the determination of damage and laser ablation thresholds of Bi based systems. Such studies are of immense importance for the preparation of thin films.

* * * * *