Synthesis and Characterization of $YBa_2Cu_3O_{7\pm\delta}$ Superconductor

M.Sc. Thesis

By

MD BALAL

DISCIPLINE OF PHYSICS

INDIAN INSTITUTE OF TECHNOLOGY INDORE

JUNE, 2015

Synthesis and Characterization of $YBa_2Cu_3O_{7\pm\delta}$ Superconductor

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree
of
Master of Science

by
MD BALAL

DISCIPLINE OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY INDORE

JUNE, 2015

ACKNOWLEDGEMENTS

First and foremost, I would like to thank my Guide Dr. P. R. Sagdeo and Co-guide Dr. Rajesh Kumar. It has been an honor to do my M.Sc. one year project under them. They have taught me, both consciously and un-consciously, how good experimental physics is done. I appreciate all their contributions of time and ideas to make my M.Sc. experience productive and stimulating. The joy and enthusiasm they have for their research is contagious and motivational for me. I am also thankful for the excellent example they have provided as a successful physicists and professors.

My special thanks to all the members of Material Science Research Laboratory group (Mr. Ravi kiran Late, Mr. Hari Mohan, Mr. Shailendra Saxena, Mr. Md Kamal Warsi, Mr. Vikash Mishra, Miss Priyanka Yogi and Mr. Suryakant Mishra, IIT Indore, who have contributed immensely to my personal and professional time. The group has always been a source of encouragement as well as good advice and collaboration. I am especially grateful and very much appreciated for the enthusiasm, intensity and willingness to help me in the process of literature survey, sample preparation and the conduction of experiments related to my research.

I am particularly indebted to RRCAT Facility and Dr. Archna Sagdeo, Scientific Officer-E (SOE), RRCAT Indore, for the X-ray Diffraction of my sample by Synchrotron Radiation Source. I sincerely thank Dr. Rajeev Rawat of UGC DAE CSR Indore for providing the low temperature resistivity measurements on our samples up to 5K. I would also like to acknowledge my PSPC members Dr. Preeti A. Bhobe and Dr. Sanjay kumar Singh for their gentle support and encouragement. I cannot forget to acknowledge the special comments by Dr. Krushna R. Mavani ma'am during my Research Progress Presentations, which helped me a lot in my improvement.

I would also like to thank all the rest of the PhD seniors, teaching and non-teaching staffs at IIT Indore, who made my stay very enjoyable in a large part of my life due to their friendly behavior that became a part of my life.

There is still a group of people for whom I have to search for a special word to thank them. They were always with me, supporting encouraging and teasing me in all my endeavors. With whom I have spent a quality time at IIT Indore. In one line all I am today is, because of them. The name includes, Rohit Gupta, Ashish Sehrawat, Rupnayan Borah, Uttiya Sarkar, Anupriya Aggarwal, Sourav Solanki, Jigar Choudhary, Ravi Gupta, Sahidul Mondal, Pradeep Kundu, Deepali Arora, Twinkle Yadav, Nazimuddin Khan, Aradhna Singh, Aparna Rai and Camelia Sarkar.

I would like to thank my family and friends for all their love and encouragement. For my parents, who raised me with a love of science and supported me in all my pursuits. And most of all for my loving, supportive and encouraging elder brother Mohammad Ali, whose faithful support till this stage of my M. Sc., is so appreciated.

MD BALAL
M.Sc. II Year
Discipline of Physics
IIT Indore

DEDICATION

Every challenging work needs self-effort as well as guidance of elders specially those who were very close to our heart,

My M.Sc. Physics Thesis, I dedicate to my sweet and loving

Father and Mother,

Whose affection, love, encouragement and pray of the day and night make me able to reach up to this stage of my life.

along with my all hardworking and respected seniors and Teachers.

ABSTRACT

Present report summarizes the work on synthesis and characterization of one of the high temperature superconducting materials i.e. $YBa_2Cu_3O_{7\pm\delta}$ (YBCO). The said superconducting samples were prepared by solid state reaction route. The phase purity of the prepared sample is verified using powder x-ray diffraction (XRD) measurement and found to be pure. The Meissner effect was demonstrated through an experiment using liquid nitrogen (at T = 77K) with the pellet to reveal its *diamagnetic* property below its critical temperature (T_c). Resistivity-temperature (R-T) measurements have been carried out by means of an *in house developed set-up*. Our result revealed that even though the sample successfully demonstrates the Meissner effect but initially the temperature dependent resistivity did not show the zero resistance below T_c, this may be due to the presence of resistive in-homogeneity in the prepared sample. The further heat treatment with controlled heating and cooling rate of ~0.5 ^{0}C/min results in high quality superconducting materials as reveled from sharp drop in temperature dependent of resistivity measurements. The obtain temperature dependence of the resistivity data was investigated using polaronic and bi-polaronic models. It appears that the bipolaronic model may be more suitable for the $YBa_2Cu_3O_{7\pm\delta}$.

MD BALAL
M.Sc. II Year
Discipline of Physics
IIT Indore

List of Publication

Collaborated Publication

DAE SSPS 2014 poster presentation on “Effect of Hafnium Substitution on Optical and Dielectric Properties of $CaCu_3Ti_4O_{12}$”

Table of Contents

List of figures

List of Nomenclature

T	Temperature
K	kelvin
H_c	Critical Magnetic Field
I_c	Critical Current
T_c	Critical Temperature
ρ	Resistivity
T	Temperature
m_e	mass of electron
$\vec{v}$	Velocity of electron
$\vec{E}$	Electric field
$\overrightarrow{J_s}$	Supercurrent density
n_s	Density of the super-electrons
e	Electronic charge
$\vec{B}$	Magnetic field
μ_0	Magnetic permeability
λ	Penetration depth
λ_L	London Penetration depth
E_g	Energy band gap
K_β	Boltzmann constant
H_0	Maximum field
A	Atomic Mass
M	Isotopic Mass

d	Inter-atomic distance
θ	Angle
λ	Wavelength
^{0}C	degree centigrade
$\rho(T)$	Resistivity at temperature T
ρ_0	Residual resistivity
ω_s	Average frequency of the softest optical mode
E	Constant proportional to mass of polaron
ħ	Planks Constant
R_0	Fitting Parameter
σ_b	Relative boson-boson scattering cross section
b	Related to hall coefficient
v_0	Volume of unit cell
R_H	Hall Coefficient

Chapter 1.

Introduction and Motivation

Since the discovery of superconductivity, this field has really been the center of scientific interest and technological applicability. What motivated me the most to work in this field was its amazing property to conduct the electricity i.e. without any loss below transition temperature which have really given us a “super-opportunity” to excel in the field of energy-technology in every aspects of modern day life.

Initially I went through the history of first insight of its discovery by Onnes which was really interesting and motivating [1]. The most compelling thing happened when I studied the Nobel lectures of Bednorz and Muller [2] about the high temperature superconductor and I realized that this amazing property of nature which was initially found by cooling the materials at very low temperature can also be produced by just assembling some different elements or compound into a proper ratio and their proper heat treatment. This discovery of superconductivity was really superb and people named this material as superconductor as it has the remarkable “Super” ability to “conduct” electricity (although there were other properties too discovered later which make it super like perfect diamagnetism). This single discovery by a Dutch Physicist Heike Kamerlingh Onnes[1] attracted the scientists of all over the world and people started thinking of the practical applications of this type of material which can almost solve most of our energy problem by minimizing the loss while its transportation. But there was a major problem in the way of the practical application, as the most of the material discovered at the time was superconducting at very low temperature (near liquid Helium temperature 4.2 K) and transportation at that much low temperature was practically very costly and dangerous too, as production and handling of liquid helium itself requires some expertise for this work.

Even after the seventy five years of the discovery the various researches could reach critical temperature only up to 30K and the need of the hour was for the high temperature superconductor for the more practical use. In the year 1986, there occurred a major breakthrough in the discovery of cuprates high temperature superconductor which eventually led to the discovery of $YBa_2Cu_3O_{7\pm\delta}$ (YBCO) superconductor. $La_{1.85}Ba_{0.15}CuO_4$ (LaBaCuO) was discovered with the critical temperature of 36 K by Johannes Georg, Bednorz and Karl Muller and they got Nobel Prize for this breakthrough discovery [3].

This discovery leads to the search of similar materials containing copper oxide layer. YBCO was discovered by Wu, et al., after one year with critical temperature of 93 K [4]. Since this critical temperature was above the boiling point of liquid nitrogen (77K), this discovery of YBCO superconductor really broke the psychological and technical barrier and opened the doors of possibility and people started thinking hopefully for the practical application of this High Temperature Superconductors (HTSC).

This YBCO being a High-Temperature superconductor is of great technological importance as being superconducting at really high temperature it can carry high density current and thus producing high magnetic fields. There are a range of possible applications of these high temperature superconductors will discuss in later chapters.

Keeping in view the above discussed importance of YBCO in the present thesis I aim to learn the basic sample preparations and its characterization and to understand the field of superconductivity in greater details.

Chapter 2.
Overview of Superconductivity

2.1 Discovery and First insight

It was the first time in 1908, when we reached the lowest temperature in the laboratory ever by one of the Physics graduate student named Heike kamerlingh Onnes[1]. He was basically liquefying helium and was studying the properties of mercury at low temperature and in the process of all these, what he found was of a great interest and started a new era in Physics that is the Physics of superconductivity.

At 4.2 K, the resistivity of mercury suddenly dropped to zero which was never observed before [5]. In this pioneer discovery he realized to have reached in the presence of a new state of matter where the material shows absolute zero resistance to the flow of current. However, in his experiment both superconductivity and super fluidity happened but he could only recognize the superconductivity phenomena well. Further he also established that the material regain its normal state property by applying a magnetic field greater than a certain field called the critical magnetic field $H_{c.}$ Also a critical current I_c will give the same effect.

Onnes studied these low temperature properties of material not because anybody had expectation or any other kind of prediction of the occurrence of this unusual phenomena [6]. The only motivation was to answer the present time controversy over the property of material at low temperature. On one hand, the resistance of metal will completely vanish in accordance with Drude theory [7] as Drude predicted that the electron scattering by lattice vibrations will be unaffected and the resistivity of the material will decline with lowering the temperature and whether if it will increase with lowering temperature as per the speculative theory of Lord Kelvin[5], a very influential scientist, where the freezing of electrons to the material will happen.

Finally, Kamerlingh Onnes received a widespread recognition for his exemplary work and received the 1913 Nobel Prize in Physics for his search in the low temperature investigations on the properties of matter which led, inter alia, to the production of liquid helium [5].

2.2 Introduction to Superconductivity

Superconductivity is a relatively modern phenomenon, discovered by Dutch Physicist Heike Kamerlingh Onnes in 1911 while working at low temperature [5].

Superconductivity is a property exhibited by certain materials, compounds and alloys at certain temperature called transition or critical temperature (T_c), where electrical resistivity vanishes completely and the sample becomes perfectly diamagnetic i.e. expels all the external magnetic fields and shows the Meissner effect. The critical temperature is unique to each element or compound.

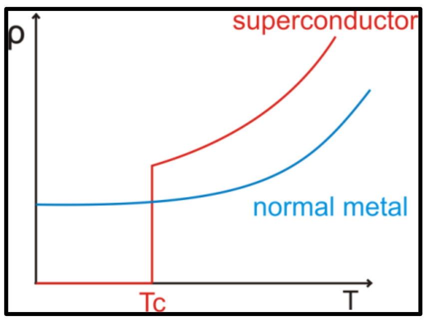


Figure 2.1 Resistivity v/s temperature diagram of normal metal and superconductor [8]

Following physical changes are observed at the transition temperature.

1. The electrical resistivity suddenly drops to zero.
2. There is exclusion of magnetic field lines from the bulk of the material.
3. Discontinuous change in specific heat is observed.
4. There are also a small change in thermal conductivity and the volume of the material.

However the phenomenon of superconductivity was observed long before in early 20s but till the date the we do not have universal theory of superconductivity to explain the origin of superconductivity in type-I and type-II superconductors. There are many theories which seek to explain the properties of the recently discovered high-temperature superconductors but the actual mechanism of the phenomenon of superconductivity has been still remained an open problem. However, the BCS theory [9] successfully explained the microscopic theory of low temperature superconductivity or type-I superconductivity, but it failed to explain the superconductivity in high-temperature as observed in copper oxide superconductors.

2.3 Theory of Superconductivity

Many theories have been proposed since the discovery of superconductivity but BCS theory has gain most of the fame to propose the most relevant theory successfully [9]. In the following we have listed the important theories in brief.

London Theory, 1935:

This is one of the simple but useful descriptions of the electrodynamics of superconductivity proposed by the two brothers Fritz and Heinz London in 1935[10], shortly after the discovery that magnetic fields are expelled from superconductors. Their proposed equations are consistent with the Meissner effect and can be used with Maxwell's equations to predict how the magnetic field and surface current vary with distance from the surface of a superconductor. This theory also predicted the exponential decay of the magnetic field within the superconductor as discussed below.

The first successful explanation of the Meissner-Ochsenfeld effect was achieved in 1935 by Heinz and Fritz London. They assumed that the supercurrent is carried by a fraction of the conduction electrons in the metal. The 'super-electrons' experience no friction, so their equation of motion in an electric field is

$$m_e \frac{\partial \vec{v}}{\partial t} = -e\vec{E}$$

This leads to an accelerated motion. The supercurrent density is

$$\vec{J_s} = -en_s\vec{v}$$

Where n_s is the density of the super-electrons, which immediately yields the equation

$$\frac{\partial \vec{J_s}}{\partial t} = \frac{n_s e^2}{m_e}\vec{E} \qquad equation\ (1)$$

Now one uses the Maxwell equation

$$\vec{\nabla} \times \vec{E} = -\frac{\partial \vec{B}}{\partial t}$$

and takes the curl (rotation) of (1) to obtain

$$\frac{\partial}{\partial t}\left(\frac{m_e}{n_s e^2}\vec{\nabla} \times \vec{J_s} + \vec{B}\right) = 0$$

Since the time derivative vanishes the quantity in the brackets must be a constant. Up to this point the derivation is fully compatible with classical electromagnetism, applied to the frictionless acceleration of electrons. An example might be the motion of electrons in the vacuum of a television tube or in a circular accelerator. The essential new assumption H. and F. London made is that the bracket is not an arbitrary constant but is identical to zero. Then one obtains the important London equation

$$\vec{\nabla} \times \vec{J_s} = -\frac{n_s e^2}{m_e}\vec{B} \qquad equation\ (2)$$

It should be noted that this assumption cannot be justified within classical physics, even worse, in general it is wrong. For instance the current density in a normal metal will vanish when no electric field is applied, and whether a static magnetic field penetrates the metal is of no importance. In a superconductor of type I, on the other hand, the situation is such that Eq. (2) applies. Combining the fourth Maxwell equation (for time-independent fields)

$$\vec{\nabla} \times \vec{B} = \mu_0 \overrightarrow{J_s}$$

and the London equation and making use of the relation

$$\vec{\nabla} \times (\vec{\nabla} \times \vec{B}) = -\nabla^2 \vec{B}$$

(This is valid since $\vec{\nabla}.\vec{B} = 0$) we get the following equation for the magnetic field in a superconductor

$$\vec{B} - \frac{\mu_0 n_s e^2}{m_e} \vec{B} = 0 \qquad equation\ (3)$$

It is important to note that this equation is not valid in a normal conductor. In order to grasp the significance of Eq. (3) we consider a simple geometry, namely the boundary between a superconducting half space and vacuum, see figure below. Then, for a magnetic field parallel to the surface, Eq. (3) becomes

$$\frac{d^2 B_y}{dx^2} - \frac{1}{\lambda_L^2} B_y = 0$$

With the solution

$$B_y(x) = B_0 \exp(- {}^{x}/_{\lambda})$$

Here we have introduced a very important superconductor parameter, the London penetration

depth $$\lambda_L = \sqrt{\frac{m_e}{\mu_0 n_s e^2}} \qquad equation\ (4)$$

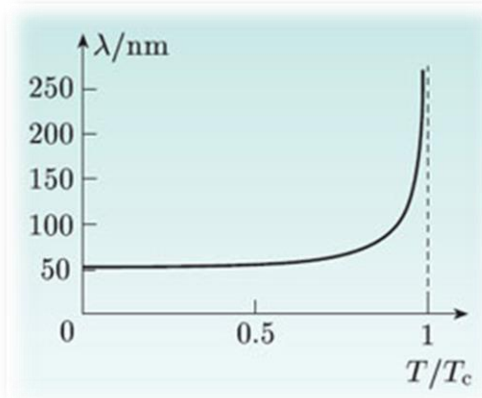
So the magnetic field does not stop abruptly at the superconductor surface but penetrates into the material with exponential attenuation.

The penetration depth has a temperature dependence which can be calculated in the BCS theory.

$$\lambda(\mathrm{T}) = \frac{\lambda(0)}{\left[1 - \left(\frac{\mathrm{T}}{\mathrm{T_C}}\right)^4\right]^{\frac{1}{2}}}$$

When approaching the critical temperature, the density of the supercurrent carriers goes to zero, so λ_L must become infinite:

$$\lambda_L \to \infty \quad for \;\; T \to T_C$$



This is shown in Figure below. An infinite penetration depth means no attenuation of a magnetic field which is just what one observes in a normal conductor.

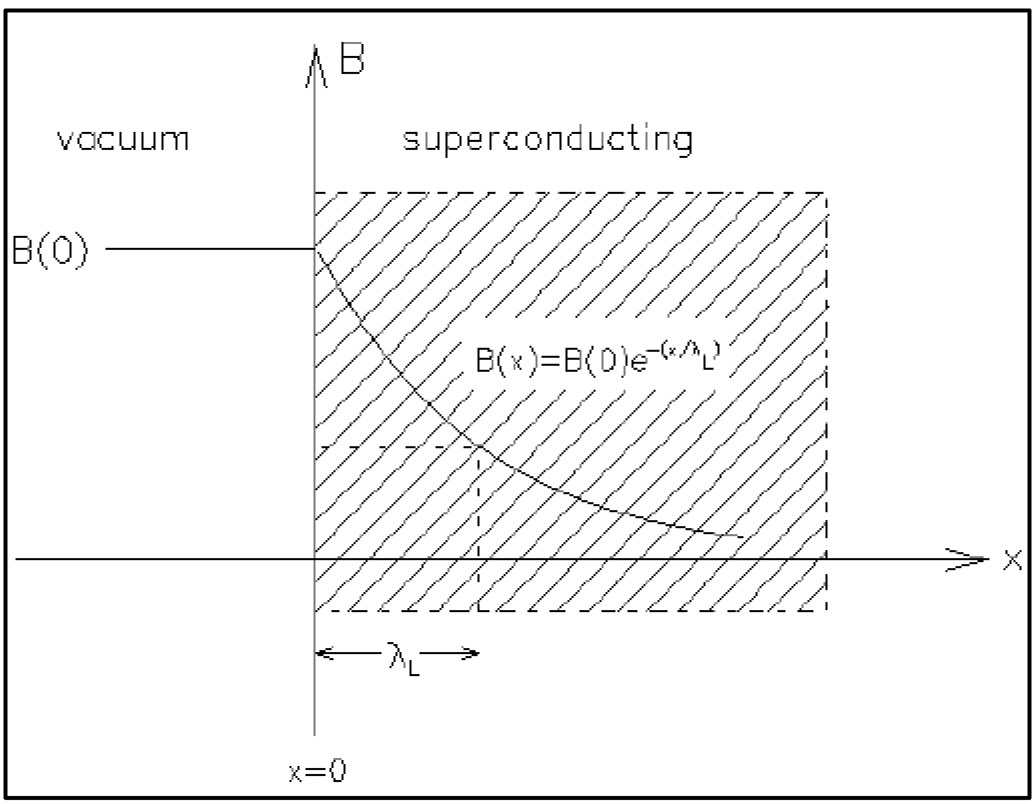


Figure 2.2 left figure showing the magnetic field decaays to $B(0)/e$ at a distance $x = \lambda_L$ and the right showing the λ_L denpendence of T_C.[37]

Ginsburg-Landau Theory, 1950: [11]

It is a mathematical physical theory which gives the idea that the super conducting state is characterized by a single complex wave function. This theory describes the properties of super conducting state such as meissner effect, zero electrical resistance and Type II super conductor.

BCS Theory, 1957:

In 1957 Bardeen, Cooper and Schrieffer proposed a microscopic theory, the BCS-theory, explaining superconductors. It has been shown to be very exact, but unfortunately it can only explain the behavior of metallic and alloy superconductors [11].

The idea behind the BCS-theory are so called Cooper pairs which are created below T_c, and the density of Cooper pairs increases when the temperature decreases.

The BCS theory of superconductivity has successfully described the measured properties of Type I superconductors. It envisions resistance-free conduction of coupled pairs of electrons called Cooper pairs. This theory is remarkable enough that it is interesting to look at the chain of ideas which led to it.

1. One of the first steps toward a theory of superconductivity was the realization that there must be a band gap separating the charge carriers from the state of normal conduction.

$$E_g \approx \frac{7}{2} K_\beta T_C$$

A band gap was implied by the very fact that the resistance is precisely zero. If charge carriers can move through a crystal lattice without interacting at all, it must be because their energies are quantized such that they do not have any available energy levels within reach of the energies of interaction with the lattice.

A band gap is suggested by specific heats of materials like vanadium. The fact that there is an exponentially increasing specific heat as the temperature approaches the critical temperature from below implies that thermal energy is being used to bridge some kind of gap in energy. As the temperature increases, there is an exponential increase in the number of particles which would have enough energy to cross the gap.

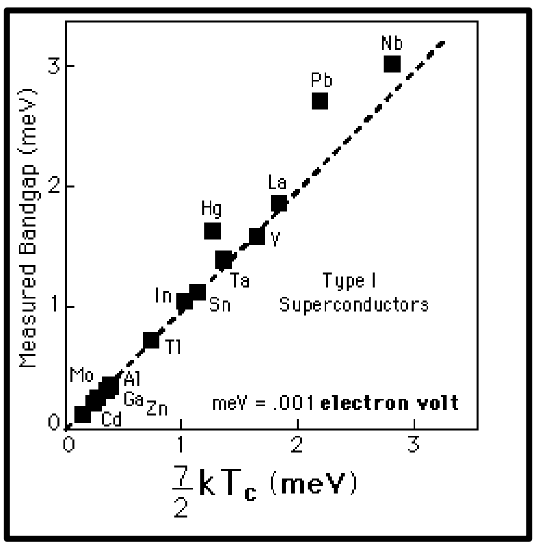


Figure2.3 Measured superconducting band gap of Type-I Superconductors [38]

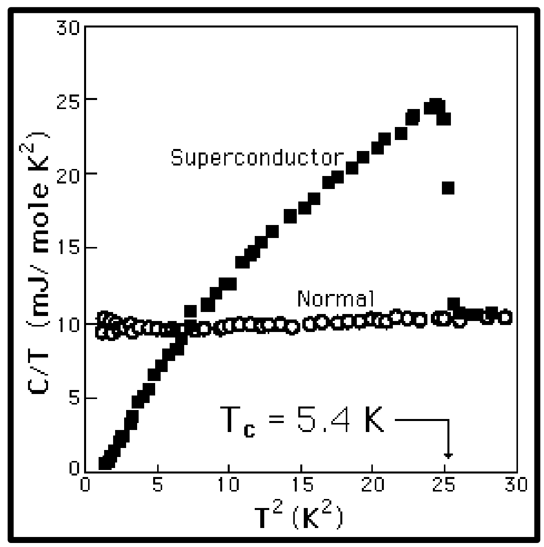


Figure2.4 Exponential heat capacity of vanadium [38]

2. The critical temperature for superconductivity must be a measure of the band gap, since the material could lose superconductivity if thermal energy could get charge carriers across the gap.
3. The critical temperature was found to depend upon isotopic mass. It certainly would not if the conduction was by free electrons alone. This made it evident that the superconducting transition involved some kind of interaction with the crystal lattice.
4. The needed boson behavior was consistent with having coupled pairs of electrons with opposite spins. The isotope effect described above suggested that the coupling mechanism involved the crystal lattice, so this gave rise to the phonon model of coupling envisioned with Cooper pairs.

Principle of Cooper pairs;

According to the BCS theory, electrons experience a special type of attractive interaction while moving through the lattice which is greater than the coulombic interaction between the two electrons; as a result electron pairs of electrons formed due to electron-lattice-electron interaction by overcoming the electron-electron interaction with equal and opposite momentum spin called Cooper Pairs. At low temperature these pair moves without scattering (i.e.,) without any resistance through the lattice points and the material becomes superconductor.

Mechanism for Cooper Pair formation:

An electron moving through the crystal produces a lattice distortion due to the polarization and sets the heavier ions into slow forced oscillation. Meanwhile, another electron happens to pass through this site experiences a huge force of attraction due to the polarization of the lattice. This attractive force lowers the energy of the second electron. The Coulomb's repulsion is instantaneous and thus less than the attractive force meditated by lattice distortion which is highly regarded in time. Therefore, the attraction caused by even a weak lattice distortion can overcome stranger Coulomb's repulsion.

Thus the net effect is the attraction of two electrons via lattice distortion to form a pair of electrons known as the Cooper pair. It is now obvious that the mass of an ion has an important role.

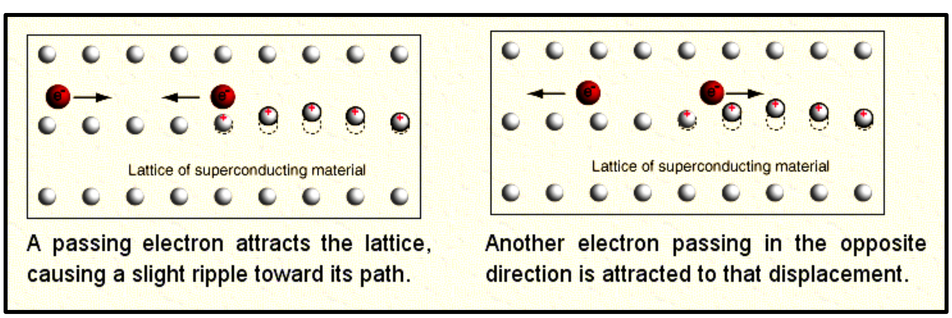


Figure 2.5 A model for Cooper pair attraction.[43]

2.4 Properties of Superconductors

The Superconductors are characterized by the following properties;

Zero electrical Resistance – The superconductors show zero dc electrical resistivity at a temperature below its critical temperature. They can maintain a current inside it for an infinite period of time without any loss giving a persistent current. This property is exploited to make high field electromagnets for MRI (magnetic resonance imaging) and NMR (Nuclear Magnetic Resonance) NMR to maintain the magnetic field constant etc.

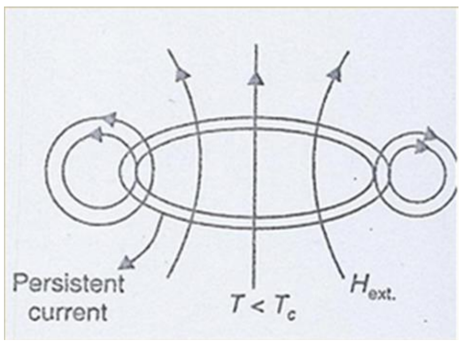


Figure 2.6 Persistent current in superconducting ring.[39]

Diamagnetic Property & Meissner Effect – Superconductors have a special ability apart from that zero resistivity which differentiates it from the perfect conductor is its ability to expel external magnetic field when it is cooled below the critical temperature. They are perfectly diamagnetic below T_c.

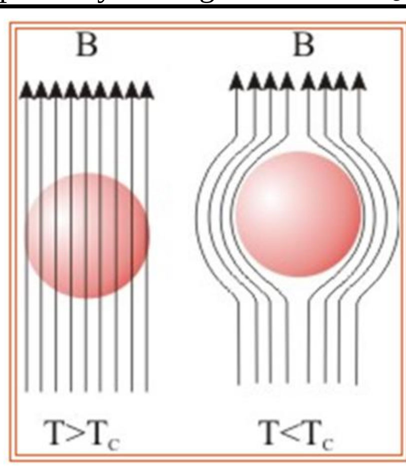


Figure 2.7 Meissner effect: exclusion of magnetic field below T_C [40]

Critical Temperature T_c – All the materials loose its superconductivity above a certain critical temperature called critical temperature. This critical value varies for different materials.

Critical Magnetic Field H_c – Like the critical temperature, the superconductors also lose their ability to super conduct above a limited range of applied magnetic field. Superconducting state of a metal exists only in a particular range of field strength. This critical value is known as Critical Magnetic field of superconductors.

$$H_C = H_0 \left[1 - \left(\frac{T}{T_C}\right)^2\right]$$

Where H_c is the maximum critical field strength at the temperature T. H_o is the maximum critical field strength occurring at absolute zero and T_c is the critical temperature the highest temperature of superconductivity.

Critical Current I_c – The magnetic field that causes a superconductor to become normal from a superconducting state is not necessarily by an external applied field. It may arise as a result of electric current flow in the conductor. The superconducting properties of conductors disappear when a sufficiently heavy current is passed through them. The minimum current that can be passed in a simple without disturbing its superconductivity, is called critical current I_c.

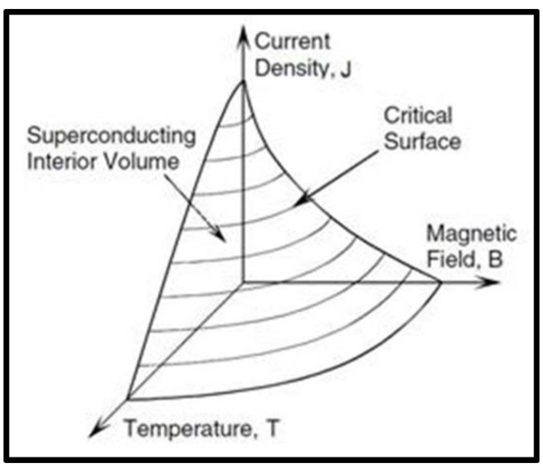


Figure 2.8 Schematic diagram of Critical value of magnetic field, current density and temperature. [40]

Isotope Effect – The critical temperature of the superconductors also depends greatly upon the isotopic mass of the material as confirmed by Maxwell and others, who used mercury isotopes. T_c of mercury varies from 4.185 K to 4.146 K as the isotope mass M varies from 199.5 to 203.4[12].

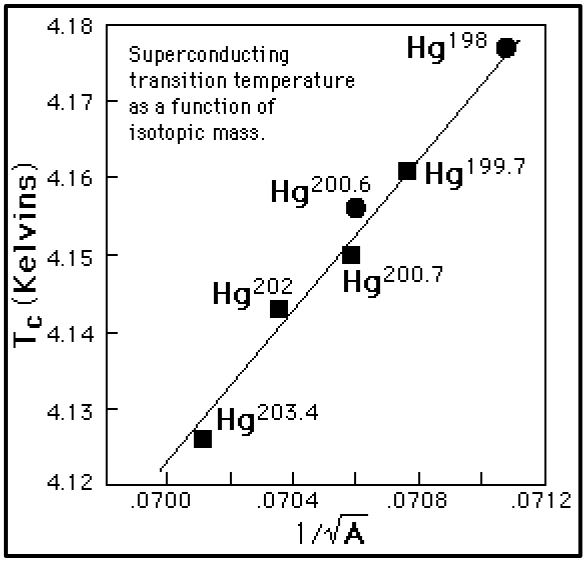


Figure 2.9 Isotope effect in Hg.[38]

Mathematically,

$$T_c \ M^{\alpha} = Const.$$

Where T_c is the critical temperature, M is the isotopic mass and α is the constant whose value is approx. 0.5.

Penetration Depth – According to F. London and H. London the applied magnetic field does not suddenly drop to zero at the surface of the superconductor, but decays exponentially according to the equation,

$$H = H_0 \, e^{\left(-\frac{x}{\lambda}\right)}$$

Where H_0 , the value of magnetic field at the surface and λ is the characteristics length known as the penetration depth.

2.5 Types of superconductors

On the basis of their response to the external magnetic field superconductors are divided into two categories.

Type I superconductors

Type I superconductors possess only one critical magnetic field H_c, below which the superconductor produces shielding currents that flow on the surface of the material expelling the magnetic field from its interior. In this condition the superconductor is in the Meissner state. Above H_c, the applied magnetic field penetrates completely into the interior of the material, disrupting the superconductivity.

Type II superconductors

Type II superconductors are characterized by two critical fields: a lower critical field, H_{c1}, and an upper critical field, H_{c1} .Figure shows the magnetic phase diagram for a type II superconductor. Below H_{c1} the superconductor behaves likes a type I superconductor and it is the Meissner state, Meissner currents flowing at the surface disabling the magnetic field to penetrate into the sample. As the magnetic field is increased above H_{c1} but still below the H_{c2}, the magnetic field penetrates the superconductor in the form of tiny quantized microscopic filaments called vortex. A vortex consists of a normal core where the Cooper pair density is zero and this core is surrounded by a superconducting region in which flows a persistent supercurrent. Further increasing the magnetic field, the number of vortices inside the sample increases and the upper critical field H_{c2}, the cores of the neighboring vortex overlap and the sample goes to the normal state. Between H_{c1} and H_{c2} the superconductor is said to be in the mixed state.

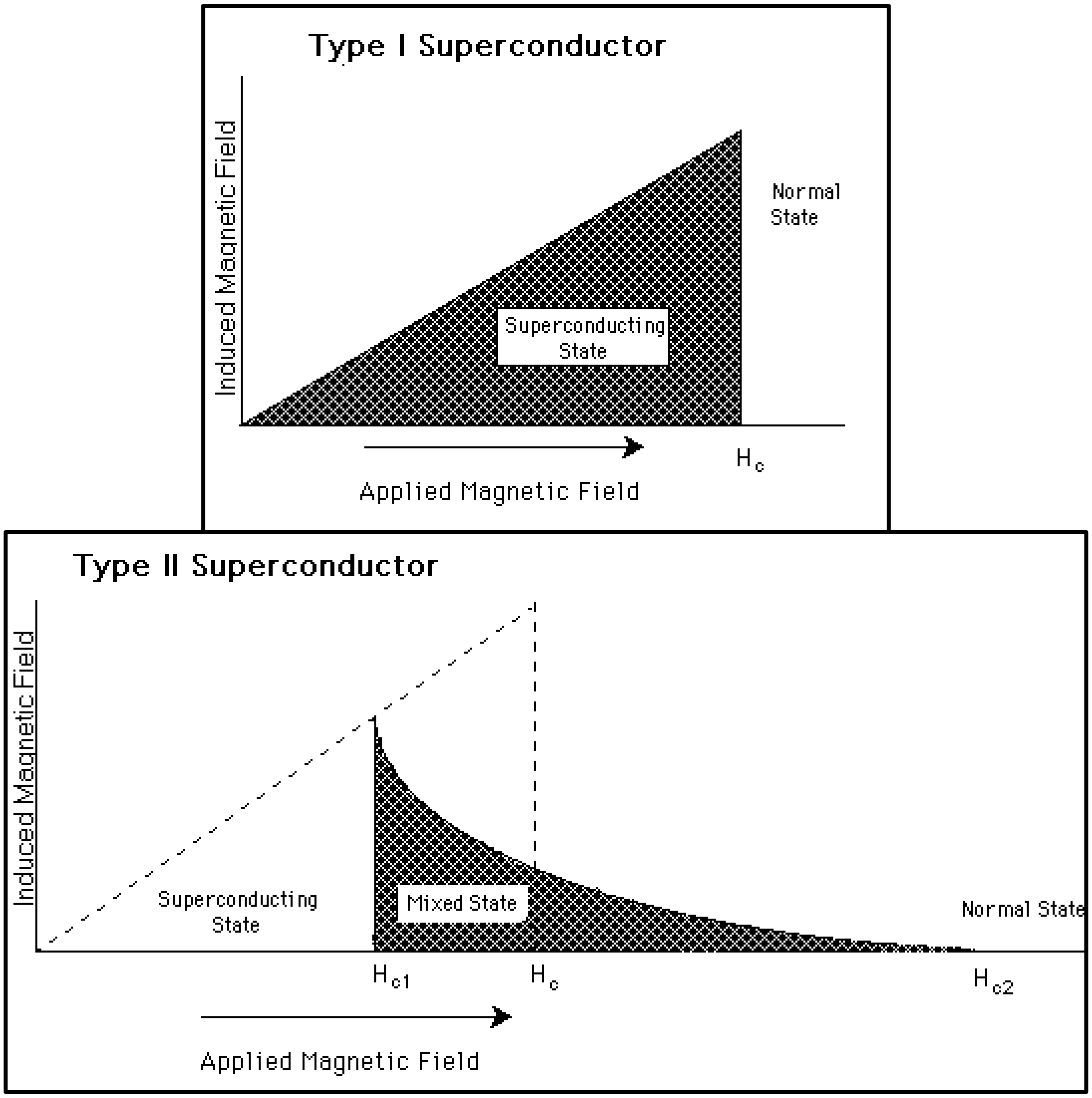


Figure 2.10 graphs showing the different state of a type-I and type-II superconductor [13]

2.6 High Temperature Superconductors

Until 1986, the highest T_c recorded was 23.2K [14] for an Nb_3Ge thin film, and this value had remained stagnant for about 12 years. Bednorz and Müller's (1986) exciting announcement of a T_c of around 30 K for a ceramic sample of $La_{1.85}Ba_{0.15}CuO_4$ was most unexpected [15]. The excitement was not due to the high T_c alone, although in itself this was a remarkable feat. More than that, this was also a breakthrough in the type of materials that were being investigated. The ceramic oxides are generally insulators, and no one had ever thought of cuprates as potential candidates for superconductivity, let alone for high T_c. Within months of Bednorz and Müller's discovery, $YBa_2Cu_3O_{7-\delta}$ was found [4] as the first superconductor with $T_c \approx 90$ K, well above the boiling point of liquid nitrogen at about 77 K. Clearly, a new family of high-temperature superconductors, commonly termed HTS, in the form of cuprates was emerging. Those materials with T_c in excess of 30 K are generally considered as high T_c superconductors (HTS), while lower-T_c materials are termed as low-temperature superconductors (LTS) [16].

Technologically, the HTS cuprates, owing to their higher T_c, are of particular interest for practical applications. However, they are inherently brittle and are highly anisotropic systems, both of which are serious handicaps. Also, with their very small range of coherence, their grain boundaries manifest a pronounced *weak-link effect* that drastically lowers their current densities. In addition, their functioning at liquid nitrogen temperatures is seriously impaired by flux creep effects. All of these factors have constituted major challenges for the development of these materials as conductors, in the form of wires and tapes, for high-field electromagnets and transmission cables functioning at liquid nitrogen temperatures. These challenges are being effectively met, however, and the overall progress that has been achieved with these materials has been truly impressive.

Despite numerous attempts, the mechanism behind the high values of T_c has to date remained elusive. This is mostly because the cuprates have turned out to be most unusual materials with intriguing properties even above T_c; that is, even their *normal state* remains to be fully understood.

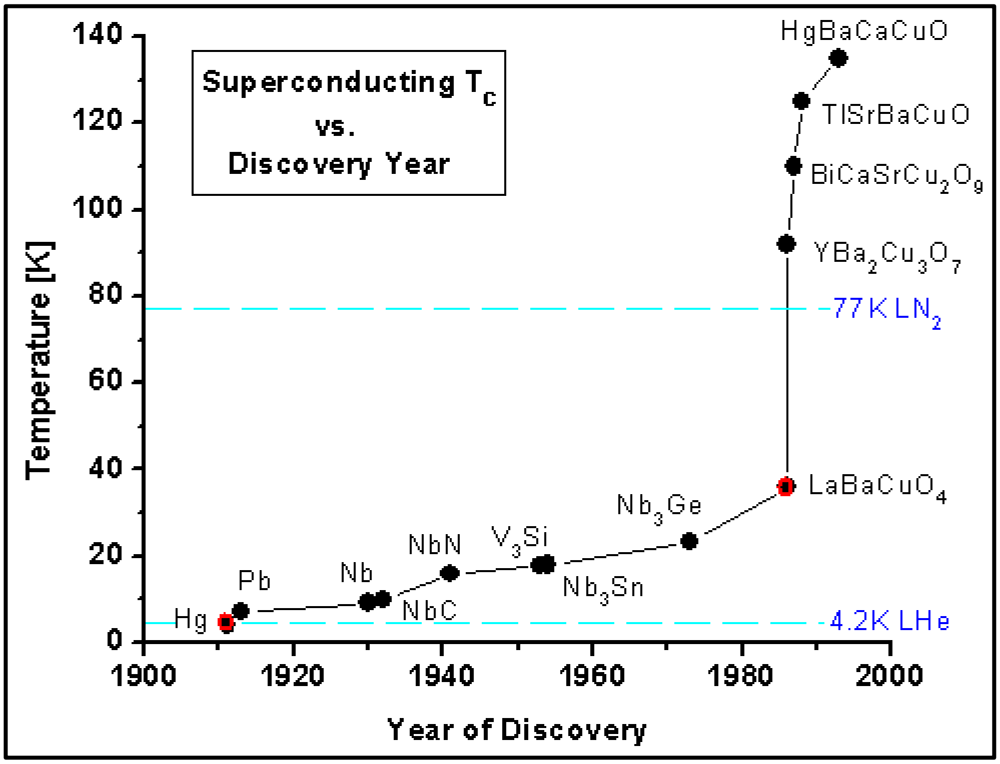


Figure 2.11 Discovery of materials with successively higher T_C's over the last century.[41]

2.7 High-T_C Superconductors: $YBa_2Cu_3O_{7\pm\delta}$ Material

Yttrium barium copper oxide, often abbreviated as YBCO, is a crystalline chemical compound with the chemical formula $YBa_2Cu_3O_{7\pm\delta}$. This material, a famous Type-II "high-temperature superconductor", achieved prominence because it was the first material to achieve superconductivity above the boiling point of nitrogen. YBCO was the first material to become superconducting above 77 K, the boiling point of nitrogen [17]. All materials developed before 1986 became superconducting only at temperatures near the boiling points of liquid helium or liquid hydrogen (T_c =20.28 K) - the highest being Nb_3Ge at 23 K. The significance of the discovery of YBCO is the much lower cost of the refrigerant used to cool the material to below the critical temperature. Superconductivity in YBCO triple perovskite structure resides in the Cu-O planes [18]. It has crystallographically two distinct Cu sites i.e., Cu (1) site in Cu-O chains and Cu (2) in CuO_2 planes. It is known that CuO_2 layers play an important role in transferring of the charge carriers, whereas Cu-O chains are non-superconducting and acts as "charge reservoir". Many experiments have shown that, the CuO_2 sheet in the YBCO structure is a superconducting layer(S) whereas the Cu-O chain layer is a non-superconductor (N) [19].

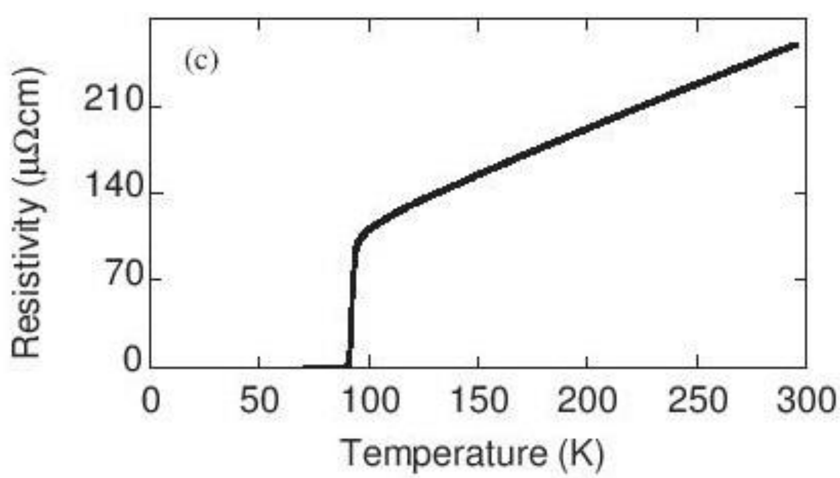


Figure 2.12 Temperature dependent resistance of $YBa_2Cu_3O_{7-\delta}$ Superconductor [17]

2.8 Applications of Superconductors

Superconductors are of great technological importance. In fact, they are the real solutions of most of the energy related problem of this modern worn. They have very vast areas of applications.

- ✓ Power transmission – As most of the electricity (almost 10-20%) is dissipated in resistive losses during the transmission lines. So, Loss less power transmission is one of the most cost effective applications of these high temperature superconductors.

- ✓ Maglev Trains – By utilizing the diamagnetic property or Meissner effect property of the superconductors, making high speed maglev trains are also one of the possible applications of superconductors.

- ✓ Superconducting Magnet – These high temperature superconductors can carry high current density thus giving rise to a high magnetic field. This property can be utilized to build high electromagnet producing field in the range of several Teslas. Most of the high energy accelerators like LHC and Fermi Lab use these high superconducting electromagnets made of type-II superconductors. Applications of superconducting magnets can be found in nuclear magnetic resonance (NMR) magnets, they are used in a powerful method in chemistry and biology to identify and study the structure of complex molecules.

- ✓ Josephson Devices – Using the concept of tunneling of Cooper pair across the Superconductor-Insulator-Superconductor junction Josephson made a device which is used as the standard measure of the voltage.

- ✓ MRI Images – Superconducting magnets are also used as magnetic resonance imaging (MRI) magnets in hospitals where inner parts of the body are imaged, without any surgery. As these superconducting magnet fulfills both the criteria for the better measurement by producing high magnetic field in the range of several teslas and the keeping uniform magnetic field over a large space over the subject and extremely stable over the time.

- ✓ SQUID Magnetometer – A major application of the Josephson effects is the SQUID (Superconducting Quantum Interference Device), which is an extremely sensitive magnetometer as it can measure the field as low as 10^{-14} T.

- ✓ Electric Motors – We can also reduce the size as well as weight of the motors and generators at a great extent by use these superconducting for specialized purposes.

Chapter 3.

Experimental Works

3.1 Sample Preparation

We have prepared our sample by the solid-state reaction route which is the most widely used method for the preparation of polycrystalline ceramic samples. In general most of the solids do not react together at room temperature over normal time scales and it is necessary to heat them to much higher temperatures, often to 1000 to 1500 °C in order for the reaction to occur at an appreciable rate. The factors on which the feasibility and rate of a solid state reaction include, reaction conditions, structural properties of the reactants, surface area of the solids (grain size), their reactivity and the thermodynamic free energy change associated with the reaction.

Making yttrium-barium-copper-oxide ($YBa_2Cu_3O_{7\pm\delta}$) superconductors requires the following raw materials:

- Yttrium Oxide (Y_2O_3)
- Barium Carbonate ($BaCO_3$)
- Cupric Oxide (CuO)
- A Laboratory Furnace
- Labware made of alumina
- Pelletizer

Safety Note: Before handling of these chemical compounds we must go through their Material Safety Data Sheets (MSDS) to have the prior knowledge of their proper uses and the precautions to be taken. And if hazard happens, these sheets also provide the proper remedy. As per MSDS of Barium Carbonate, it is found to be a toxic substance. It can be safely handled with ordinary laboratory procedures. It is imperative, however, that (especially during the grinding and mixing of the chemicals) a good-quality dust mask is worn during the procedure. It is also important to wear laboratory gloves, such as disposable latex surgical gloves, while working with these chemicals.

Experimental procedure:

i. **Reagent;** Taking the primary compounds called as reactants in a definite proportion. Here, for making of $YBa_2Cu_3O_{7-\delta}$, we take Yttrium Oxide (Y_2O_3), Barium Carbonate ($BaCO_3$) and Cupric Oxide (CuO). The selection of reactant chemicals depends on the reaction conditions and expected nature of the product. The reactants are dried thoroughly prior to weighing.
The proper weight ratios for our **5 grams** sample are:

- ✓ **Yttrium Oxide, Y_2O_3 1.69478 grams**
- ✓ **Barium Carbonate, $BaCO_3$ 5.92659 grams**
- ✓ **Cupric Oxide, CuO 3.58208 grams**

In the compounds taken, the Y_2O_3 is a hygroscopic compound, so we first kept it in the furnace at a temperature of 200 ^{0}C for 4-5 hours, and then weighed.

We must choose the chemicals to be mixed in the proper proportions so that the atomic ratios of yttrium, barium, and copper are 1:2:3.

ii. **Mixing of Chemicals:** After the reactants have been carefully weighed out in the required amounts, they are mixed. For the mixing of the reactants, we have used an agate mortar and pestle. Sufficient amount of some volatile organic liquid preferably Isopropyl alcohol is added to the mixture to aid homogenization. This forms a paste which is mixed thoroughly. During the process of grinding and mixing, the organic liquid gradually volatilizes and has usually evaporated completely after 30 minutes to 1 hour. The grinding is done for 5-6 hours continuously. The ultimate purpose of this entire process is to make the homogenous mixture of the starting compounds.

iii. **Container material:** For the subsequent reaction at high temperatures, it is necessary to choose a suitable container material which is chemically inert to the reactants under the heating conditions used. Here we employ Alumina (Al_2O_3) crucibles as they have a wide application due to its versatility and low material cost. Alumina possesses a high melting point, strong hardness, and good chemical stability, making it a good material to withstand high temperature and chemical corrosion.

iv. **Calcination:** For the initial heat treatment, called calcination, the gray powder mixed sample was first heated at 940 degrees Celsius for about 24 hours. This first heat treatment forms the basic crystal structure of $YBa_2Cu_3O_{7\pm\delta}$, and gets rid of the carbon dioxide from the barium carbonate. (Barium carbonate is used instead of barium oxide because barium oxide of any reasonable purity is difficult to obtain. Also, exposing barium oxide to air tends to quickly convert much of it to barium carbonate and barium hydroxide.) The result of this first firing is a porous black or very dark gray clump.

v. **Pelletizing:** We used the hydraulic press in which, the powdered sample is pressed to make pellet or disk before the final oxygen annealing. This has definite advantages over just sintering the loose powder. Generally a pressure of 15 to 16 ton is applied to make these pellets.

vi. **Final sintering:**

After making the pellet final sintering of the sample is done at a temperature slightly higher temperature than the calcination temperature.

We sintered our sample at a temperature of 950^0 C.

3.2 Characterization of Sample by X-ray diffraction

The crystal structure and impurity levels of the samples are measured via powder X-ray diffraction. When x-rays are scattered from a crystal lattice, peaks of scattered intensity are observed. This is given by the Bragg's law.

Diffraction of an x-ray beam occurs when the light interacts with the electron cloud surrounding the atoms of the crystalline solid. Due to the periodic crystalline structure of a solid, it is possible to describe it as a series of planes with an equal inter-planer distance. As an x-ray's beam hits the surface of the crystal at an angle theta, some of the light will be diffracted at that same angle away from the solid. The remainder of the light will travel into the crystal and some of that light will interact with the second plane of atoms. Some of the light will be diffracted at an angle theta, and the remainder will travel deeper into the solid. This process will repeat for the many planes in the crystal. The x-ray beams travel different path-lengths before hitting the various planes of the crystal, so after diffraction, the beams will interact constructively only if the path length difference is equal to an integer number of wavelengths as given by the equation

$$\boldsymbol{2d\ Sin\theta = n\ \lambda}$$

- n is an integer determined by the order given,
- λ is the wavelength of x-rays.
- d is the spacing between the planes in the atomic lattice, and

θ is the angle between the incident ray and the scattering planes.

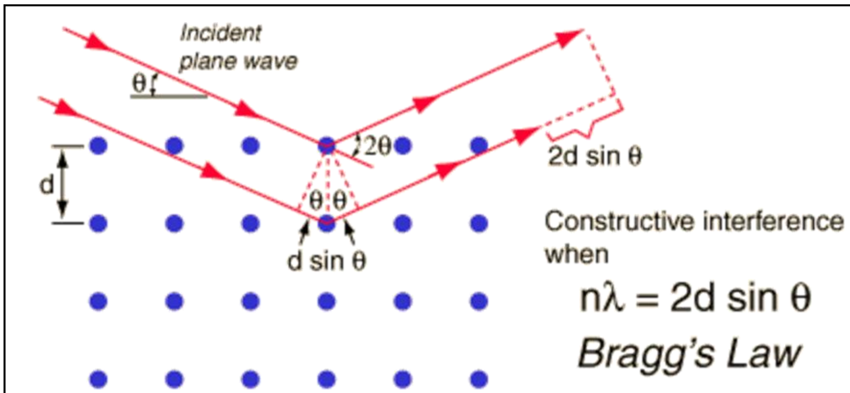


Figure 3.1 Schematic of Bragg's reflection from atomic plane. [42]

3.3 **Failures and successes in sample preparation and confirmed by x-ray diffraction**

The very first sample which we prepared was not successful as it shows the peaks due to impurity phases in the XRD pattern. As the X-ray data of the sample prepared did not match well with the standard (The International Centre for Diffraction Data: Joint Committee on Powder Diffraction Standards ICDD JCPDS) data of $YBa_2Cu_3O_{7\pm\delta}$ (see figure 3.2-a). In order to understand this failure we have revisited the literature on the sample preparation of $YBa_2Cu_3O_{7\pm\delta}$ and modified the heating and cooling conditions. In some of the sample preparation studies it is shown that rate of the cooling plays very crucial role [20]. Keeping this in the view we have modified the rate of cooling to 1 ^{0}C/min against the initial 2 ^{0}C/ min. We observed that the sample prepared with cooling rate of 1 ^{0}C/min is chemically pure and did not show the other phases of Y_2O_3, $BaCO_3$ and CuO etc. (see figure 3.3).

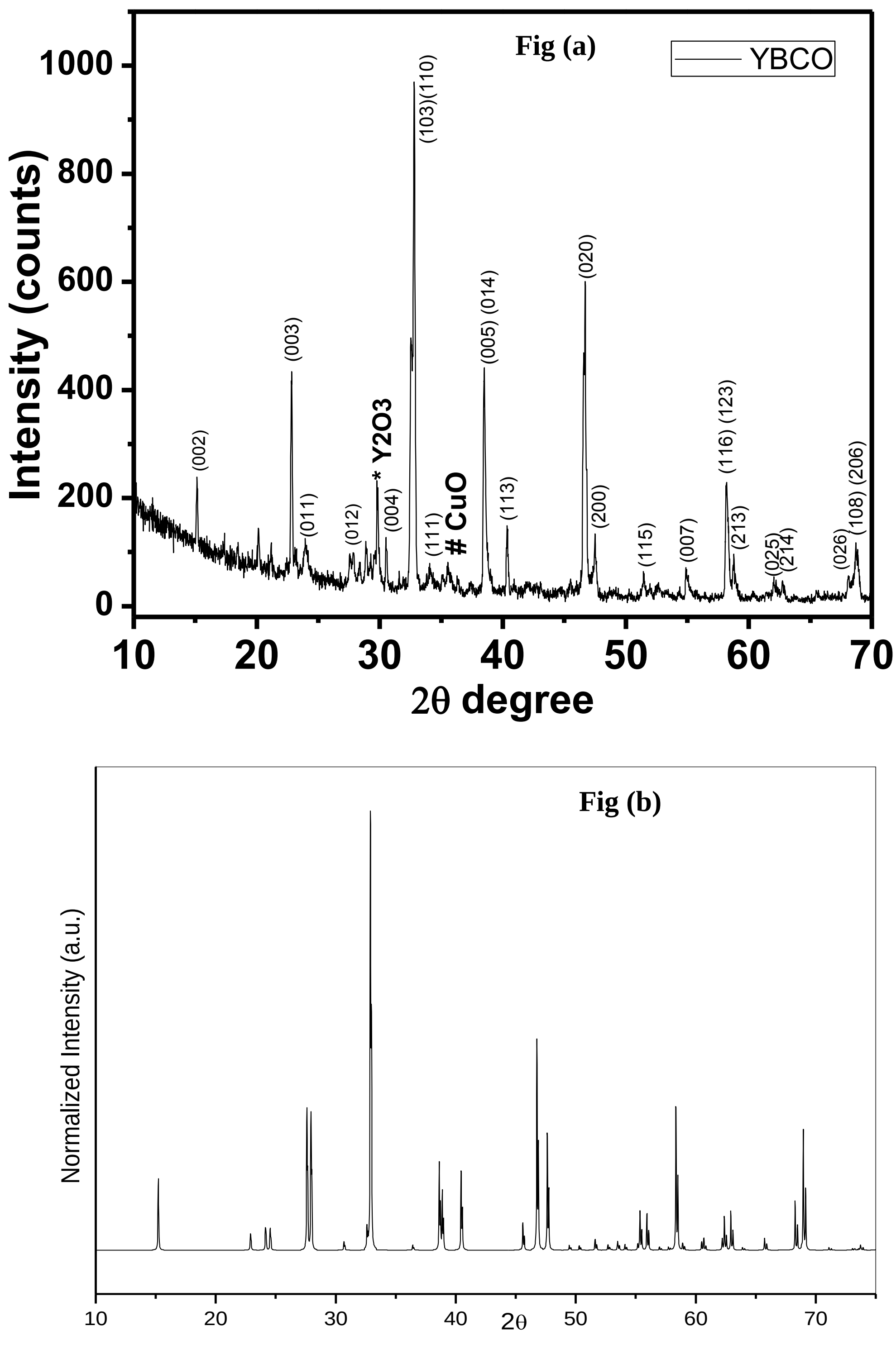


Figure 3.2 XRD pattern in fig (a) is for synthesized sample of YBCO showing impurity peaks of (*) Y_2O_3 and (#) CuO and fig (b) showing the standard XRD Pattern of YBCO Sample.

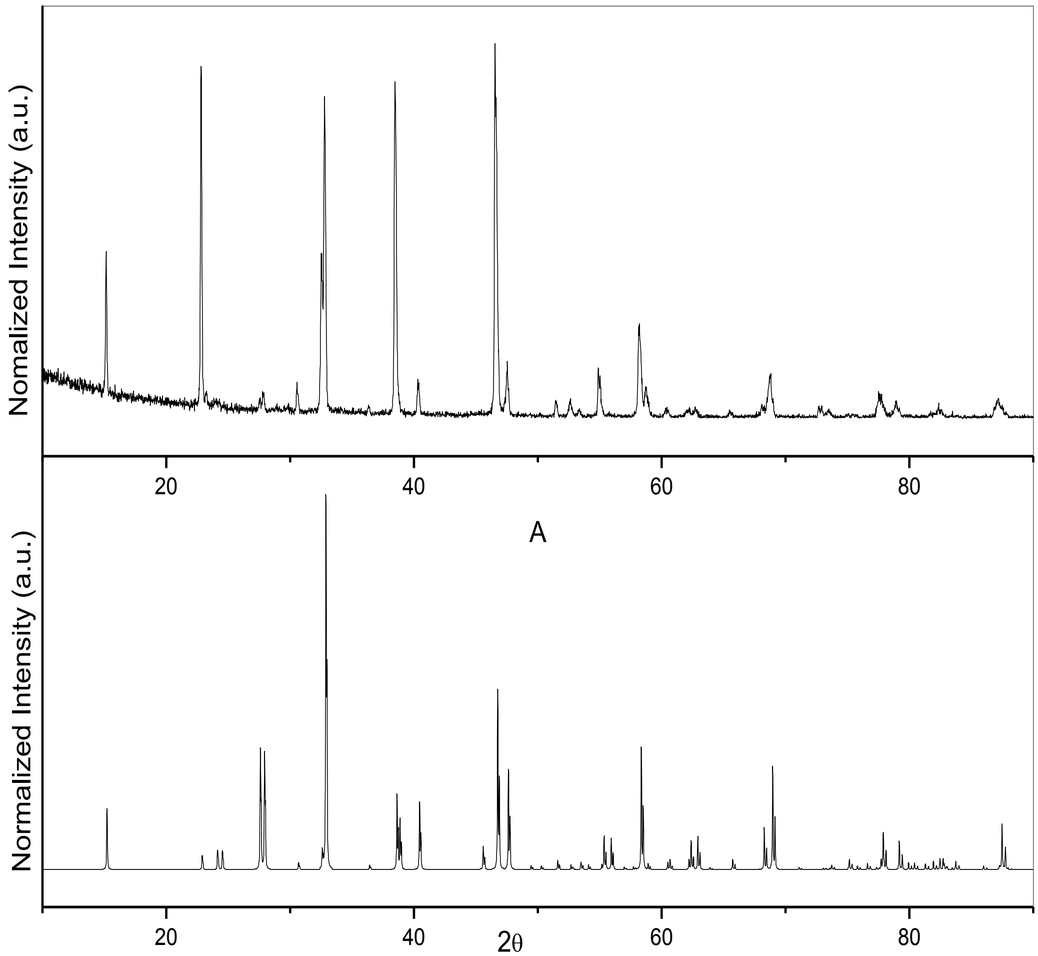


Figure 3.3 XRD pattern of sample prepared by solid state reaction route with cooling rate of 1 ^{0}C/min. No peaks due to other chemical/crystallographic phase have been observed.

3.4 Meissner Effect Demonstration

After the confirmation of the phase purity of our sample we have confirm the perfect diamagnetic nature of the prepared superconducting sample. The same is done by performing the Meissner effect experiment with our pelletized sample.

The materials used for the Meissner Effect Demonstration

Liquid Nitrogen, pellet sample of prepared $YBa_2Cu_3O_{7\pm\delta}$ Samarium cobalt magnet, a petri dish, safety hand gloves etc.

Experimental procedure and results:

Initially we kept the disk shaped superconducting pellet in the petri dish. Then the samarium cobalt magnet was kept on the top of the disk, we saw no levitation as the whole system was at room temperature and as from the literatures we know the sample to be superconducting, the temperature must be below its critical temperature. So we can understand that the field lines of the magnet were initially passing through the superconducting sample at room temperature. We started pouring the liquid nitrogen inside the petri dish. As the sample is in direct touch with the liquid nitrogen, hence the temperature of the sample starts decreasing till it reaches the Liquid nitrogen temperature. Once the temperature of the pellet reached ~90 K [17] the sample is expected to become the superconductor and hence perfect diamagnetic [17]. The same has been observed here (See figure 3.4 below).

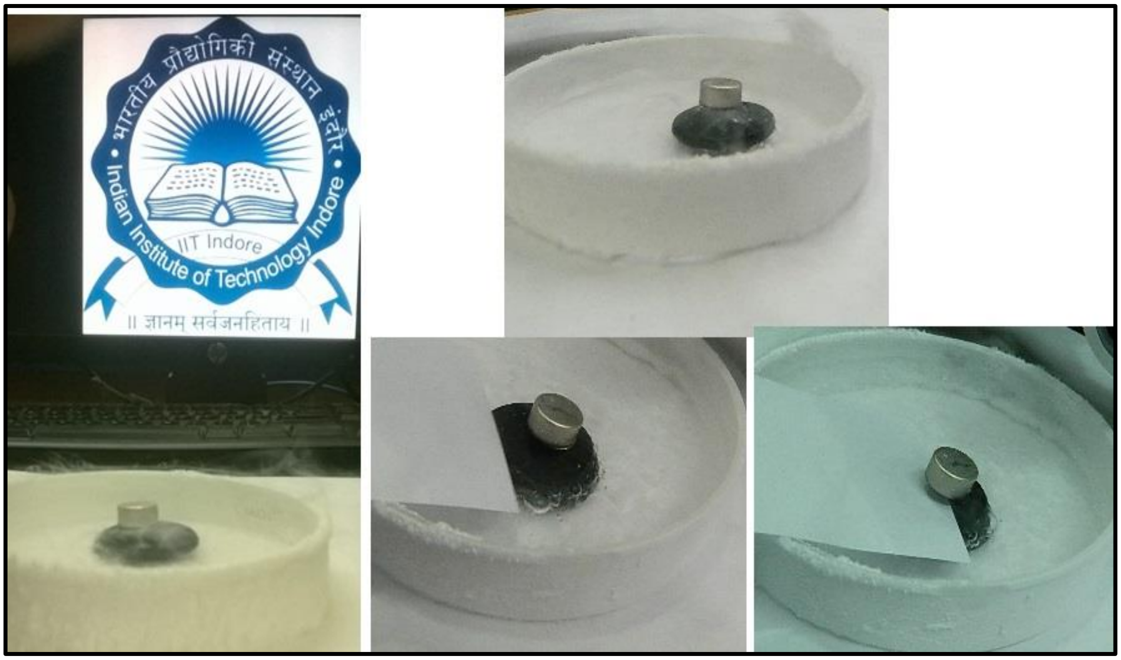


Figure 3.4 cobalt-samarium magnet levitating over $YBa_2Cu_3O_{7-\delta}$ superconductor at liquid nitrogen temperature.

The magnet kept on the disk started levitating as the sample temperature reached below its critical temperature value and became perfect diamagnetic at this state the sample expels all the external magnetic lines which was initially penetrating above the critical temperature.

This levitation of the magnet over the sample confirms the sample to be perfectly diamagnetic.

3.5 Experimental design for Resistivity v/s Temperature measurements of the $YBa_2Cu_3O_{7\pm\delta}$ sample

To measure the resistivity as a function of temperature for our sample we designed an in house set-up for the same.

The figure below shows the schematic diagram of the set up.

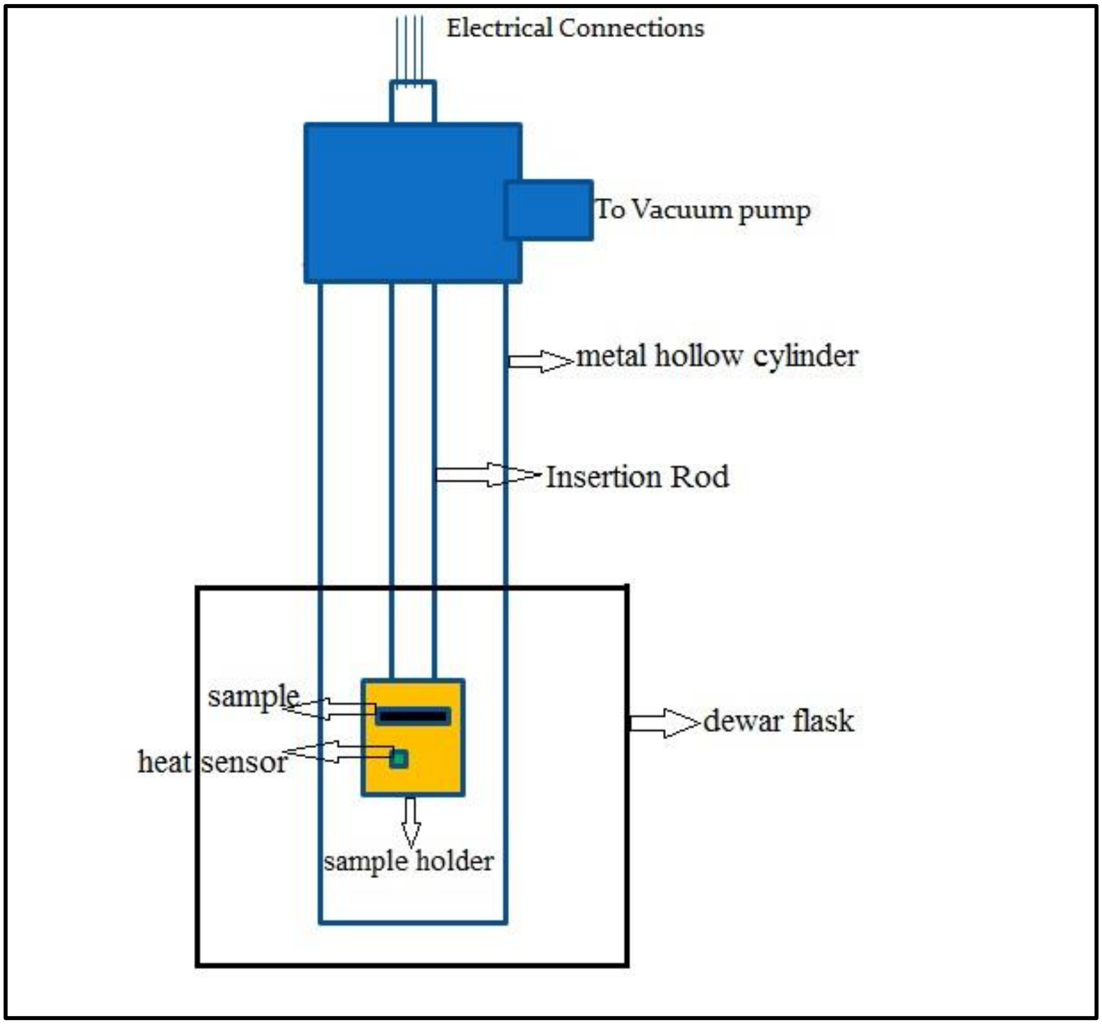


Figure 3.5 Schematic diagram of in house resistivity v/s temperature measurement set up.

Device explanation measurement process:

The device basically consists of long hollow cylindrical pipe made of brass, the insertion rod at the end of which a copper plate is attached called as sample holder where on the front side the sample and the temperature sensor is attached and the back side of this copper plate the heater is connected. There is an electrical connection attached with the insertion rod for the measurement of the voltage and current. The cylindrical pipe is tightly packed from the upper side using O-rings and also the pipe is attached to the vacuum pump to create vacuum inside the pipe at the time of measurement. For the measurement at low temperature, the whole system is dipped into the Dewar flask of liquid nitrogen and exchange gases are used inside the pipe to maintain the temperature of the sample same as the liquid nitrogen.

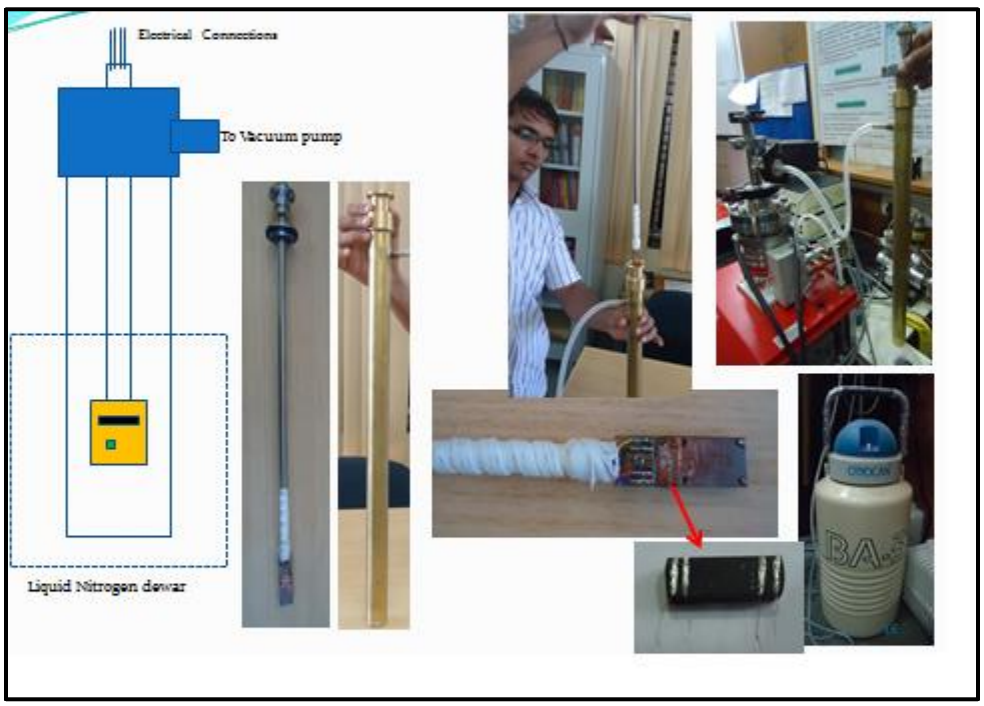


Figure 3.6 Schematic of the varius parts of the experimental set up.

3.6 Four Probe Method for Resistivity Measurement

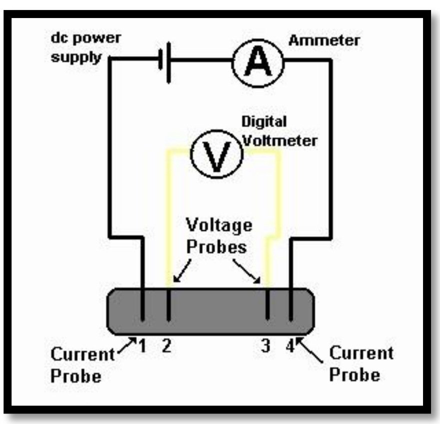
We have applied the four probe method [21] to measure the resistivity as a function of temperature for our sample.

The main advantage of using four probe methods over two probes is that the contact resistance is more in two probe as we measure current and voltage with the same probe. But in case of four probe method we use two additional probes for the voltage measurements, and as the input impedance of voltmeter is very high and hence very few currents flow inside the voltage probes and hence the contact resistance is negligible.

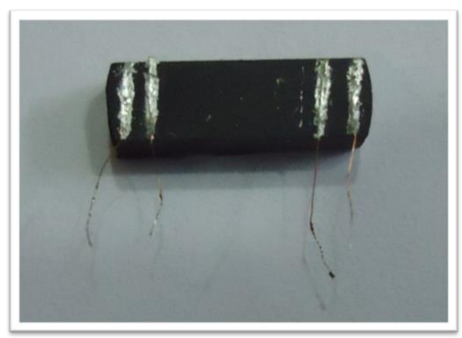
Making contact on the sample

The four contacts are made over the sample using the silver paste. We used the copper wire as a contact wire.

Care must be taken while making contact, as the improper contacts will give rise to contact resistance.



(a)



(b)

Figure 3.7 (a) schematic of four probe set up [22] (b) sample of YBCO on which contacts have been made.

The figure below shows the temperature dependent of resistance data for our sample collected using developed resistivity setup.

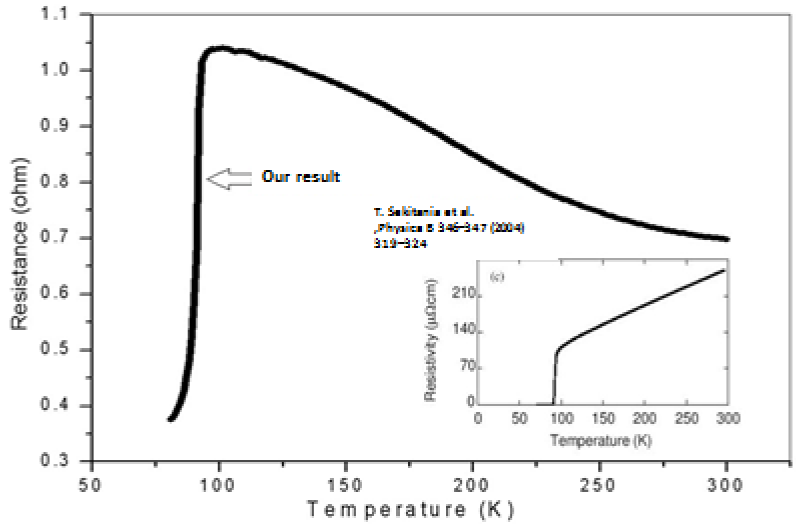


Figure 3.8 Variation of Resistance v/s Temperature curve for the YBCO sample inset; shows the variation of resistivity v/s temperature taken from litrature [17].

From the figure it is clear that even at 80 K the sample did not show the zero resistance. In order to understand this we have carefully examined the structural coherency (peak width of XRD pattern). It is observed that the structural coherency of the sample is only up to ~ 20 nm which may be due to slight variation in the chemical composition from one grain to other or due to oxygen vacancies in the sample. This may lead to the electrically in-homogenous sample and hence no absolute zero resistance. Further experimental effort was needed to confirm the same.

3.7 Further treatment of the sample and the successes in result

We then further re-grinded the sample, made pellet of few powder and kept both pellet and powder in the furnace. This time for a slightly higher temperature of 960^0 C and kept the rate of heating and cooling rate low. The rate of heating was 1^0C per minute and that of cooling we kept at the rate of approx. 0.5 ^{0}C per minute. We soak the sample at 960^0 C for 48 hours this time.

No impurity phase was found this time as confirmed after comparing it from standard XRD data.

The result of XRD pattern and resistance as function of temperature of the sample is shown below.

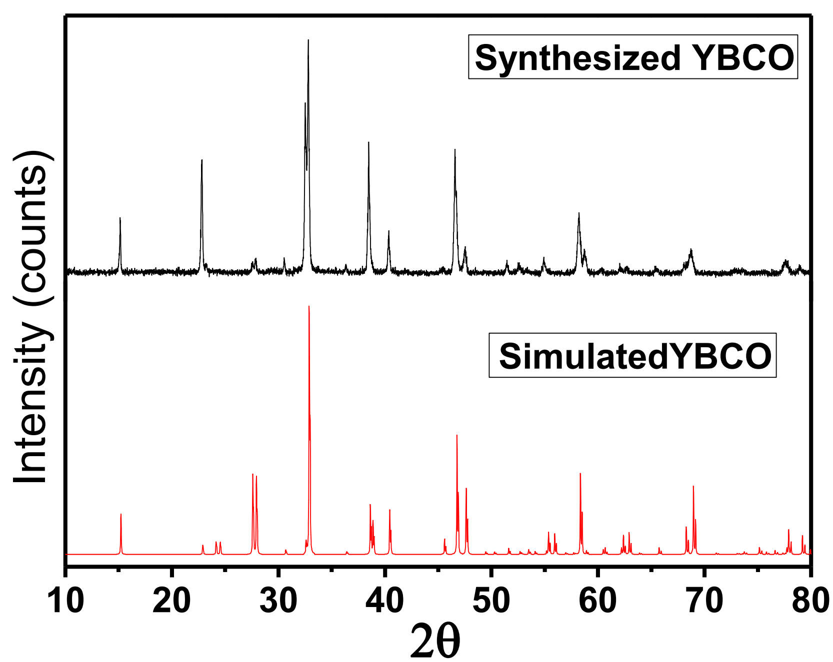


Figure 3.9 The XRD pattern of simulated v/s synthesized YBCO sample for cooling rate of 0.5 ^{0}C/min.

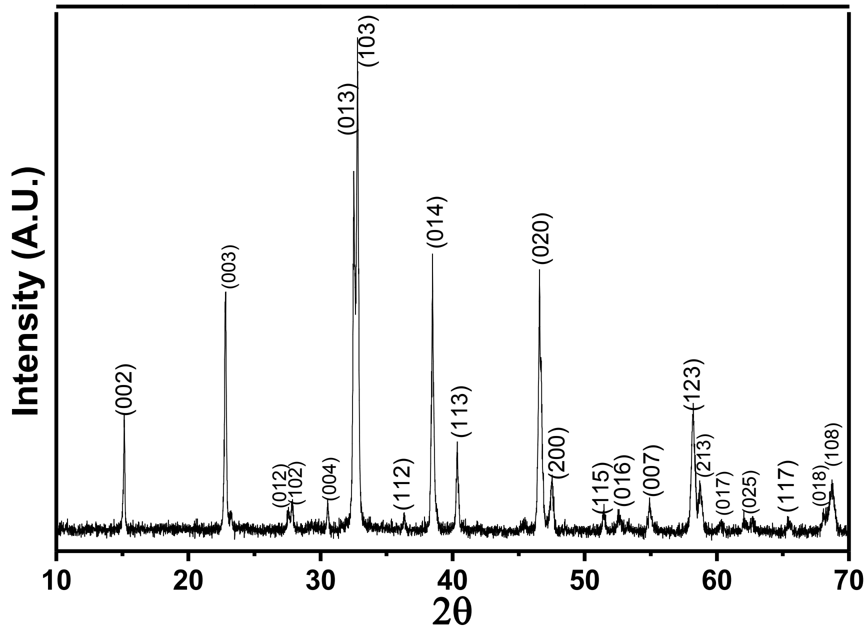


Figure 3.10 Indexing for the YBCO sample.

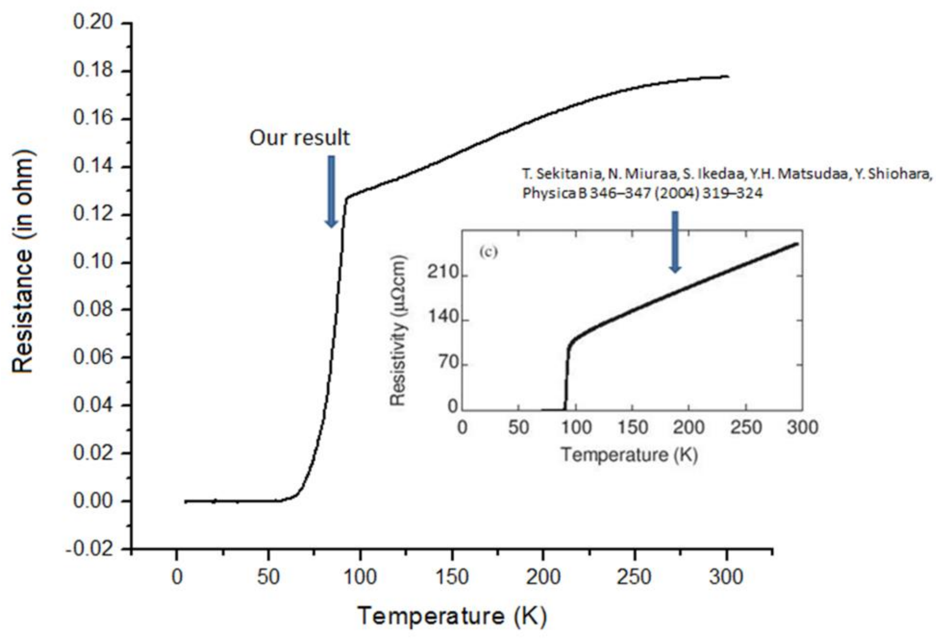


Figure 3.11 Variation of Resistance v/s Temperature curve for the YBCO sample for cooling rate of 0.5 ^{0}C/min. inset; shows the variation of resistivity v/s temperature taken from litrature [17].

Figure 3.10 shows the indexing pattern of the sample prepared and figure 3.11 shows the R-T pattern which matches with the standard sample.

This time the resistivity measurement was carried out for the temperature range of 5K to 300K, in the low temperature laboratory of Dr. Rajeev Rawat at UGC- DAE-CSR Indore.

Chapter 4.

Theoretical works

4.1 Polaron and Bipolaron models for Superconductivity

The discovery of high-temperature superconductors has broken constraints on the maximum T_c predicted by the conventional theory of low-temperature superconducting metals and alloys. Understanding the pairing mechanism of carriers and the nature of the normal state in the cuprates and other novel superconductors has been a challenging problem of the Condensed Matter Physics. A number of theoretical models have been proposed, which rely upon the different non-phononic mechanisms of pairing. On the other hand, increasing evidence for the electron-phonon interaction has been provided by isotope effect measurements, infrared and thermal conductivity, neutron scattering, and more recently by angle resolved photoemission spectroscopy (ARPES). To account for the high values of T_c in the cuprates, one has to consider electron-phonon (e-ph) interactions. So far based on electron-phonon (e-ph) interactions, researchers have proposed some models in which the Polaron model and the Bipolaron model will be discussed here [23].

Lev Landau, Herbert Fröhlich , A.S. Alexandarov and N.F. Mott have given special contribution in the theory of polaron and Bipolaron [26][27][28][30].

Polaron and Bipolaron concepts are important in understanding the superconductivity phenomena. Polaron and Bipolaron are thought to be the important carriers of superconducting current. The electron phonon interactions that form Cooper pairs in type-I superconductors can also be modeled as a polaron, and two opposite spin electrons may form a bipolaron by sharing a phonon cloud. This has been suggested as a mechanism for Cooper pair formation in type-II superconductors. Polarons are also important for interpreting the optical conductivity of these types of materials.

4.2 Polaron

In 1933 Landau set forth the concept of polaron [24][25]. Polaron is basically a quasi-static particle in the condensed matter physics which help us to understand the interaction between the electrons and the atoms in the solid materials. It also gives the idea of the mobility of electrons in the crystal. When an electron moves inside a crystal the coulomb interaction between a conduction electron and the lattice ions result in a strong electron-phonon coupling. In this case, even with no real phonons present, the electron is always surrounded by a cloud of virtual phonons. The cloud of virtual phonons corresponds physically to the electron pulling nearby positive ions towards it and pushing nearby negative ions away. The electron and its virtual phonons, taken together, can be treated as a new composite particle, called a polaron.

The effective mass of a polaron is larger than the mass of the underlying electron. Loosely speaking, the electron must drag the lattice distortion with it as it moves, creating a larger inertia.

The mobility of a large polaron is often limited (at least in certain temperature range) by scattering due to (real) optical phonons, as a result of the strong electron-optical phonon coupling in these materials.

The temperature dependent of resistivity in the case of polaronic model is given by equation [32]

$$\rho(T) = \rho_0 + E\omega_s / sinh^2(\hbar\omega_s / 2k_B T)$$

Where ρ_0 is the residual resistivity ω_s is the average frequency of the softest optical mode , and E is a constant, being proportional to the effective mass of polarons. ħ is the plank constant and k_B is the Boltzmann constant.

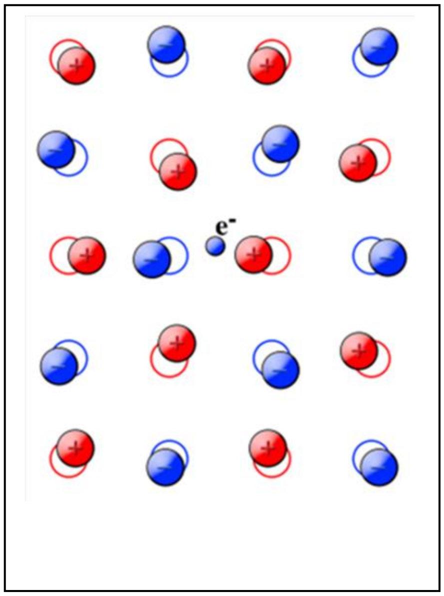


Figure 4.1 Schematic diagram of Polaron. [44]

4.3 Bipolaron

In physics, a bipolaron is basically a bound pair of two polarons[27]. Although two electrons repelled by the Coulomb interaction, two electron polarons can in theory have a net attractive force, due to the attraction of each to the lattice distortion induced by the other. When two polarons are close together, they can lower their energy by sharing the same distortions, which leads to an effective attraction between the polarons. If the interaction is sufficiently large, then that attraction leads to a bound bipolaron. For strong attraction, bipolarons may be small. Small bipolarons have integer spin and thus share some of the properties of bosons. If many bipolarons form without coming too close, they might be able to form a Bose–Einstein condensate. This has led to a suggestion that bipolarons could be a possible mechanism for high temperature superconductivity [30][31].

A bipolaron is similar to a Cooper-pair in the BCS theory of superconductivity, in that two electrons are bound by the exchange of virtual phonons, except that the electrons in a Cooper-pair are paired in k-space, while the electrons in a bipolaron are paired in real space.

The temperature dependent of resistivity in the case of bi-polaronic model is given by equation [31]

$$R = R_0 \frac{T + \sigma_b T^2}{1 + bT}$$

Where $\sigma_b$the relative boson-boson scattering cross section and b is related to hall coefficient

$$R_H = \frac{v_0}{2e(n - n_L)(1 + bT)}$$

With $(n - n_L)(1 + bT)$ being the number of delocalized carriers in the unit cell volumev_0, and R_0 is a fitting parameter.

4.4 Fittings

In order to investigate the applicability of these models for our samples we have carried out the fittings of the temperature dependent resistivity data using equation 1(polaron model) and 2 (bi-polaron model) and the same is shown in the figure-4.2 and 4.3. The inset of the figure shows the value of the fitted parameters for corresponding equation. From the fittings it is clear that both the models equation fit the obtain resistivity data, but the value of the constants and the corresponding error obtain from the polaronic models appears to be unphysical, hence from the fittings of polaronic and bi-polaronic models it appears that the bi-polaronic model is more suitable.

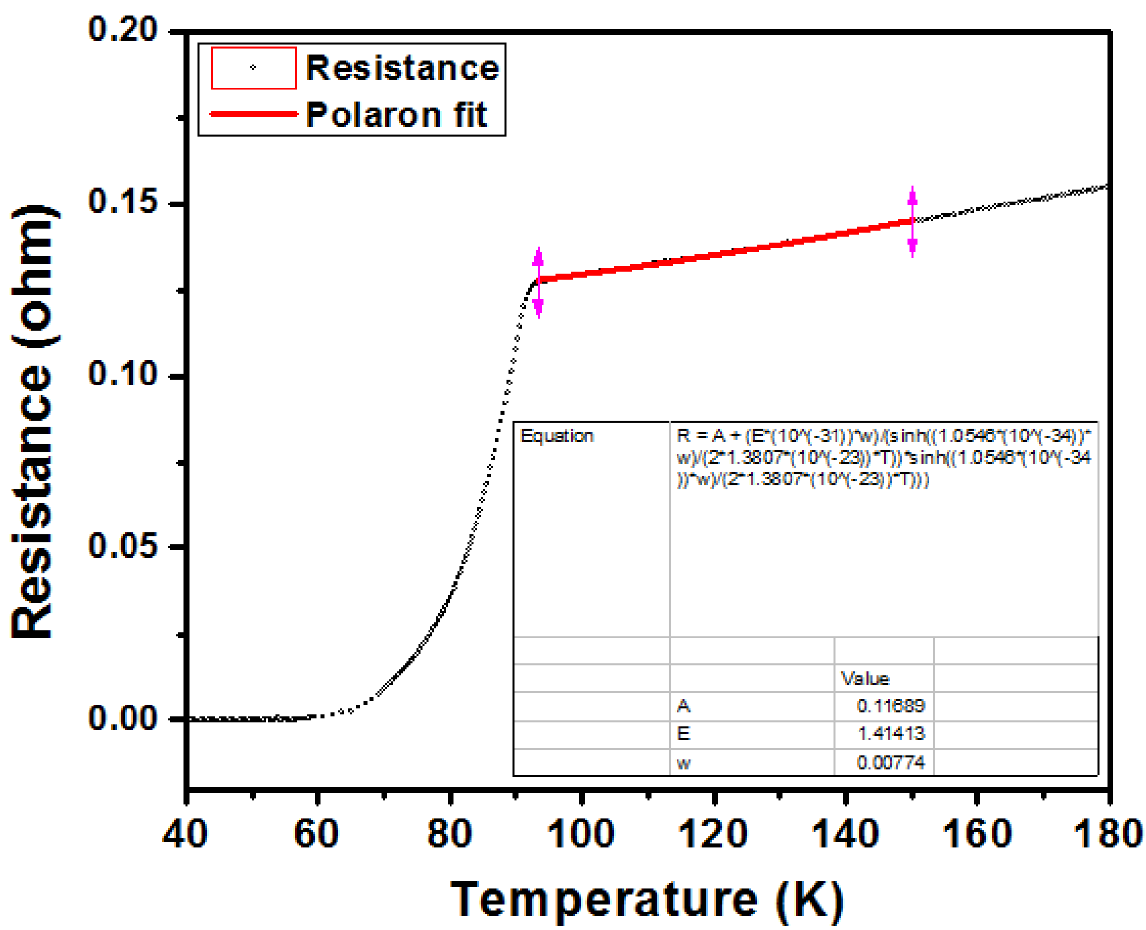


Figure 4.2 Fittings for polaron

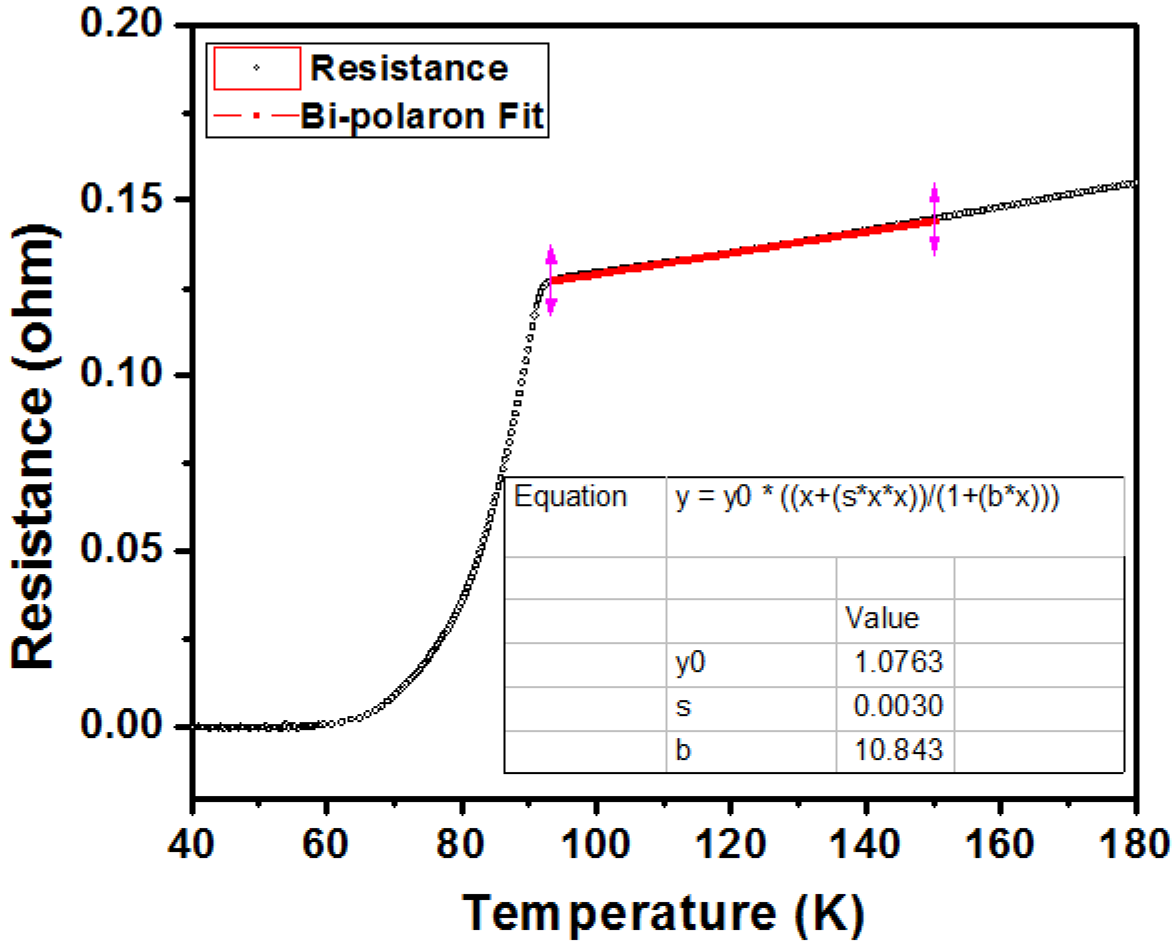


Figure 4.3 Fittings of Resistivity v/s curve by using Bi-polaron model.

Chapter 5.

Conclusion

In conclusion we have prepared single phase samples of high temperature superconductor YBCO. From the experimental work presented here it is clear that the heating and the cooling rate during sample preparation plays a very crucial role in critically controlling the quality of the sample. Further from the levitation experiments confirms that the samples acquire the perfect diamagnetic state below transition temperature. The temperature dependent of resistivity and corresponding fittings suggests that the bi-polaronic model is more suitable to explain the temperature dependent of resistivity data.

Chapter 6.

Scope for future work

From the our experimental results it is clear that the heating/cooling rates and the grinding process plays very crucial role and detects the chemical in-homogeneity in the prepared samples, hence in future I will try to prepare these samples with high quality wet ball mill grinder machine to ensure chemical homogeneity in the prepared samples. Further I will also compare various other theoretical models to explain the temperature dependent of resistivity data. If required we will try to fabricate high quality thin film samples of these materials in order to get rid of effects due to grain boundaries etc.

Chapter 7.

References

References from Journal Article

[1] Onnes H. K., Nobel Lecture, December 11, 1913.

[2] Bednorz J. G., Müller K. A., Nobel lecture, December 8, 1987.

[3] Bednorz J.G. and Müller K.A, Z. Phys. B – Condensed Matter 64, 189-193 (1986). (DOI:10.1007/BF01303701)

[4] Wu et al., 1987, Superconductivity at 93 K in a New Mixed-Phase Y-Ba-Cu-O Compound System at Ambient Pressure. (http://dx.doi.org/10.1103/PhysRevLett.58.908)

[5] Onnes H.K, Commun. Phys. Lab. Univ. Leiden 12, 120 (1911).

[6] Wysoki´nski K.I., Remarks on the first hundred years of superconductivity, Institute of Physics. (doi:http://arxiv.org/pdf/1111.5318.pdf)

[7] Drude, Paul (1900). "Zur Elektronentheorie der metalle". Annalen der Physik 306 (3): 566.

[8] http://www.superconductors.org/type1.htm

[9] Bardeen, Cooper, and Schrieffer, Phys. Rev. 108, 1175 (1957). (doi:http://dx.doi.org/10.1103/PhysRev.108.1175)

[10] London F., Superfluid's, 2d rev. ed. p.10-16 (New York: Dover Publications, 1961).

[11] J. Exptl. Theoret. Phys. (U.S.S.R) 36, 1918-1923 (June, 1959)

[12] Maxwell E., (1950). "Isotope Effect in the Superconductivity of Mercury". Physical Review78 (4). (http://dx.doi.org/10.1103/PhysRev.78.477)

[13] http://web.ornl.gov/info/reports/m/ornlm3063r1/pt3.html

[14] Kunzler J.E., Buehler E., Hsu F.L.S., and Wernick J.H., (1961). Physical Review Letters 6: 89–91. (http://dx.doi.org/10.1103/PhysRevLett.6.89)

[15] Bednorz J.G., and Müller K.A, Z. Phys. B – Condensed Matter 64, 189-193 (1986) (DOI:10.1007/BF01303701)

[16] Mourachkine, Andrei. Room-temperature superconductivity. p.5-7 (Cambridge, UK: Cambridge International Science Pub., 2004).

[17] Sekitania T., Miuraa N., Ikedaa S., Matsudaa Y.H., Shiohara Y., Upper critical field for optimally-doped $YBa_2Cu_3O_{7-\delta}$, Physica B 346–347 (2004).

[18] Sahoo M., Behera D., Study of $YBa_2Cu_3O_{7-\delta}/Al_2O_3$ Composite for Structural and Electrical transport Property, IJSRP, 2, 9 (Sept. 2012 1 ISSN 2250-3153).

[19] Shi D., N., and Li Z., The effect of nonmagnetic doping on high-Tc superconductivity, J Physica C, p 274, 1996. (DOI: 10.1016/S0921-4534(96)00499-6)

[20] Ogale S.B. et. al., Solid State Commun. 89,1, p.1-4, (1994).

[21] Schuetze A.P., Lewis W., Brown C., and Geertsa W.J., A laboratory on the four-point probe technique.

[22] http://www.imagesco.com/articles/superconductors/four-pt-schematic.gif

[23] Byrnes S.J.F., Basic theory and phenomenology of polarons.

[24] Polarons by, Devreese J.T.

[25] Iadonisi G., Cataudella V., Ninno D., Chiofalo M.L., Physics Letters A 196 359-364(1995). (doi:10.1016/0375-9601(94)00922-C)

[26] Alexandrov A.S., Bratkovsky A.M., and Mott N.F., Physica C 235-240 (1994) 2345-2346. (doi:10.1016/0921-4534(94)92394-9).

[27] Esmaeili A., Sedghi H., Golzan M.M., Amniat-Talab M., J Supercond. (2011) 24:2237–2242. (DOI 10.1007/s10948-011-1190-9)

[28] Alexandrov A.S., Bratkovsky A.M., and Mott N.F., Phys. Rev. Lett. 72, 1734 (1994). (http://dx.doi.org/10.1103/PhysRevLett.72.1734)

[29] Prelovsek P, Rice T.M., Zhang F.C., and Klostermann A., Physica 148B 268-270(1987). (doi:10.1016/0378-4363(87)90207-5)

[30] Mott N.F., Physica A 200 127-135(1993). (10.1016/0378-4371(93)90511-2)

[31] Chen W., Frank J.P., and Jung J., Experimental fitting to bipolaronic model of the normal-state resistance of $Bi_2Sr_2CaCu_2O_8$. arXiv:cond-mat/0002206v1 [cond-mat.supr-con] (14 Feb 2000).

[32] Zhao G., M., Smolyaninova V., Prellier W., and Keller H., Electrical Transport in the Ferromagnetic State of Manganites: Small-Polaron Metallic Conduction at Low Temperatures, Phys. Rev. Lett. 84.6086

References from Books

[33] Narlikar A.V., Frontiers in Superconducting Materials. ISBN 3-540-24513-8

[34] Narlikar A.V., (Ed.) High Temperature Superconductivity 2. ISBN 978-3-662-07764-1.

[35] Kittel C., Introduction to Solid State Physics, Eighth Edition, ISBN 0-471-41526-X

[36] Ashcroft N. W., Mermin N. D., Solid State Physics, ISBN-13: 978-0030839931

References from Online images and texts

[37] http://jick.net/theses/Sonier/PhD/node7.html

[38] http://hyperphysics.phy-astr.gsu.edu/hbase/solids/bcs.html

[39] http://www.physics-assignment.com/superconductivity

[40] http://www.lhc-closer.es/1/4/8/0

[41] http://hoffman.physics.harvard.edu/materials/SCintro.php

[42] http://hyperphysics.phy-astr.gsu.edu/hbase/quantum/bragg.html

[43] http://hyperphysics.phy-astr.gsu.edu/hbase/solids/coop.html

[44] https://en.wikipedia.org/wiki/Polaron