THE STUDY OF ELECTRONIC STRUCTURE AND COMPUTATION OF TRANSITION PHASE PARAMETERS IN HIGH TEMPERATURE SUPERCONDUCTORS

BY

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Being a thesis submitted to the Postgraduate School, Ahmadu Bello University, Zaria in Partial fulfilment of the requirement for the award of Master of Science in Physics.

AUGUST, 2000

DECLARATION

I hereby declare that:

(i) the report presented in this thesis is the result of my original research

(ii) this thesis has not been submitted to any other institution, organisation or body for any award other than Ahmadu Bello University; and

(iii) all inclusions from works other than this have been duly referenced and acknowledged.

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CERTIFICATION

The thesis entitled "**The Study of Electronic Structure and Computation of Transition phase Parameters in High Temperature Superconductors**" by **IBEH, Godwin Joseph** meet the regulations governing the award of the degree of Master of Science (MSc.) of Ahmadu Bello University, Zaria and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This work is dedicated to my family

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ABSTRACT

Investigations on the electronic structure of high temperature superconductors are studied. This work showed that there have been tremendous efforts devoted to developing suitable theories and mechanisms of the high temperature superconductivity. Many of these theories are BCS-based even though certain behaviour of the high T_c oxide superconductors such as: the linear dc resistivity with temperature, a Hall coefficient that is temperature dependent, the presence of short coherence lengths etc., suggest that the normal state cannot be described by a Fermi-liquid.

The study also covers details of possible applications of the devices using high-T_c superconductors, which are mostly based on the Josephson junction of the high-T_c oxide superconductors.

An attempt has been made to evaluate the two- and three - dimensional phase transition temperatures of some of the known high-temperature superconductors, based on a recent phenomenological theory of cuprate oxides. The theory assumes two criteria used to calculate the superconducting transition temperatures. One is that the quantum wavelength is of the order of the electron pair spacing. The other is that the fraction of the normal carriers exists as Cooper pairs at T_c. Thus, the model provides a self-consistent condition that the number of pairs that Bose-Einstein condenses is approximately equal to T_c itself. The results of this calculation are found to agree reasonably well with the available experimental data.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 GENERAL INTRODUCTION

Kammerlingh Onnes (1911) observed that resistance of mercury varnishes abruptly beyond the limit of measurement, below the critical temperature T_c = 4.16 K. Struck by this totally unexpected vanishing of the electrical resistance when a metal was cooled towards zero Kelvin, he wrote (Onnes, 1911) "Mercury passes into a new state of matter as its temperature falls below T_c" He called this electrically non-resistance state "SUPERCONDUCTING STATE" and he named the phenomenon as SUPERCONDUCTIVITY. Since then, superconductivity has been observed in several elements, intermetallics and alloys. The highest reported T_c in these so-called conventional metallic systems is close to 23 K in thin films of Nb_3Ge (Testardi, *et al.*, 1974) and bulk YPdBc (Gupta *et. al.*, 1994). Of all the elements, Nb has the highest T_c. The best known semi-conductors Si and Ge become superconducting under pressure, ~ 2 Kbar at T_c = 7 K and 5.3 K respectively (Cyrot and Pavuna, 1992). Using a new form of carbon, C_{60}, superconductivity compounds, such as A_3C_{60} (A = an alkali atom), have been prepared (Kroto, 1988; Iqbal, *et. al.*, 1991).

Soon after J. Georg Bednorz and K. Alex Muller (1986) published their pioneering work "possible conductivity" in La-Ba-Cu-O system ($T_c \approx$ 30 K), M. K. Wu *et al.* (1987) and J. M. Tarascon *et al.* (1987) announced superconductivity with T_c in excess of 77 K in the system Y-Ba-Cu-O. This discovery was a very great surprise. Despite the fact that these materials are oxides, they superconduct with T_c far exceeding those observed in the best known non-oxide metallic superconductors.

Ever since the discovery of high-T_c superconductivity, many reports (Huang, 1988) have appeared claiming observation of extra-high T_c. The highest reproducible and stable T_c, reported thus far in a single material is 125 K in $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Sheng and Hermann, 1988). Table

1.1, taken from Thomas *et al*., (1991), gives T_c of many cuprate superconductors with $T_c > 77$ K. This table also includes two new high-T_c cuprates (with onset temperature = 94 K and 133 K) which contain mercury as one of their constituents.

As was pointed out above the field of high-T_c superconductors has generated tremendous interest leading to several thousand publications. The first part of this dissertation is a short review, wherein a modest attempt is made in describing the current progress achieved in the theoretical understanding of the phenomenon and the applications of the various devices developed.

This dissertation is organized as follows: Chapter One is basically an introduction of the subject matter; the types of Superconductors, thermodynamics and microscopic theories of conventional superconductors are discussed. Chapter two is on the structural properties of high-T_c superconductors. Chapter three is a review of current theories on high-T_c superconductors with emphasis placed on their electronic structures and properties. Chapter four is on the application / Devices of high-T_c superconductors. In chapter five an attempt has been made to evaluate some characteristic parameters, mainly the transition temperatures, T_c of some known high temperature superconductors based on a recently developed phenomenological theory and comparison is made with the available experimental data. Chapter six is on discussion of results, summary, and assessment of the progress made so far in the field of high – T_c superconductivity and its future.

Table 1.1: Structure and T_c data of the known high T_c oxides

Compound	T_c, K	Crystal Structure	Lattice Parameter Å			Lattice Sequence
			a	b	c	
$YBa_2Cu_3O_7$	90	Orthorhombic	3.823	3.886	11.681	-CuO-BaO-CuO_2-Y-CuO_2-BaO-
$Bi_2Sr_2CaCu_2O_8$	80	Orthorhombic	5.408	5.413	30.871	-BiO-SrO-CuO_2-Ca-CuO_2-SrO-BiO-
		Tetrahedral	3.812	-	30.66	
$Bi_2Sr_2Ca_2Cu_3O_{10}$	110	Tetrahedral	5.39	-	37.10	-BiO-SrO-CuO_2-Ca-CuO_2-Ca-CuO_2-SrO-BiO-
$Tl_2Ba_2CaCu_2O_8$	105	Tetrahedral	3.85	-	29.30	-TlO-BaO-Cu_2O-Ca-CuO_2-BaO-TlO-
$Tl_2Ba_2Ca_2Cu_3O_{10}$	125	Tetrahedral	3.85	-	35.58	TlO-BaO-CuO_2-Ca-CuO_2-Ca-CuO_2-BaO-TlO-
$Pb_2Sr_2(Ca, Ln)Cu_3O_8$	70	Tetrahedral;	3.813	-	15.76	-PbO-Cu-PbO-SrO-CuO_2-Y/Ca-CuO_2-SrO-
		Orthorhombic	5.402	5.433	15.74	
$YBa_2Cu_4O_8$	80	Orthorhombic	3.841	3.872	27.24	-CuO_2-BaO-CuO-CuO-BaO-CuO_2-Y
$HgBa_2CuO_{4-8}$	94	Tetrahedral	3.8797	-	9.509	CuO_2-BaO-HgO-BaO-CuO_2
Hg-Ba-Ca-Cu-O	> 130	-		-	-	-

1.2 TYPES OF SUPERCONDUCTORS

There are basically two types of Superconductors. Type I and Type II. In type-I Superconductors, which consists of basically pure metals, the magnetic field is screened from the interior of the sample until a critical field H_c is reached, above which the superconductivity quenched and the field penetrates uniformly into the material. This behaviour, illustrated in Fig. 1.1, is called Meissner effect, it was discovered by W. Meissner and R. Ochsenfeld (1933). The value of the critical field is of the order of few hundred gauss. A qualitatively different behaviour is exhibited by type-II superconductors, which are mostly alloys, at sufficiently small applied fields the system is again in the Meissner state, where the field is screened from the interior bulk of the material. Above a critical field, H_{c1}, called the lower critical field, there is partial penetration of the field while the material remains superconducting. The field increasingly penetrates the system as the applied field is increased, until finally above a second critical field H_{c2} (called upper critical field) the superconducting state is destroyed. The superconducting region between H_{c1} and H_{c2} is called Vortex State.

The basic mechanism responsible for the superconductivity is the same for both type-I and type-II materials, and many type-I materials can be converted to type-II behaviour by the addition of impurities, but the behaviour in a magnetic field is qualitatively different.

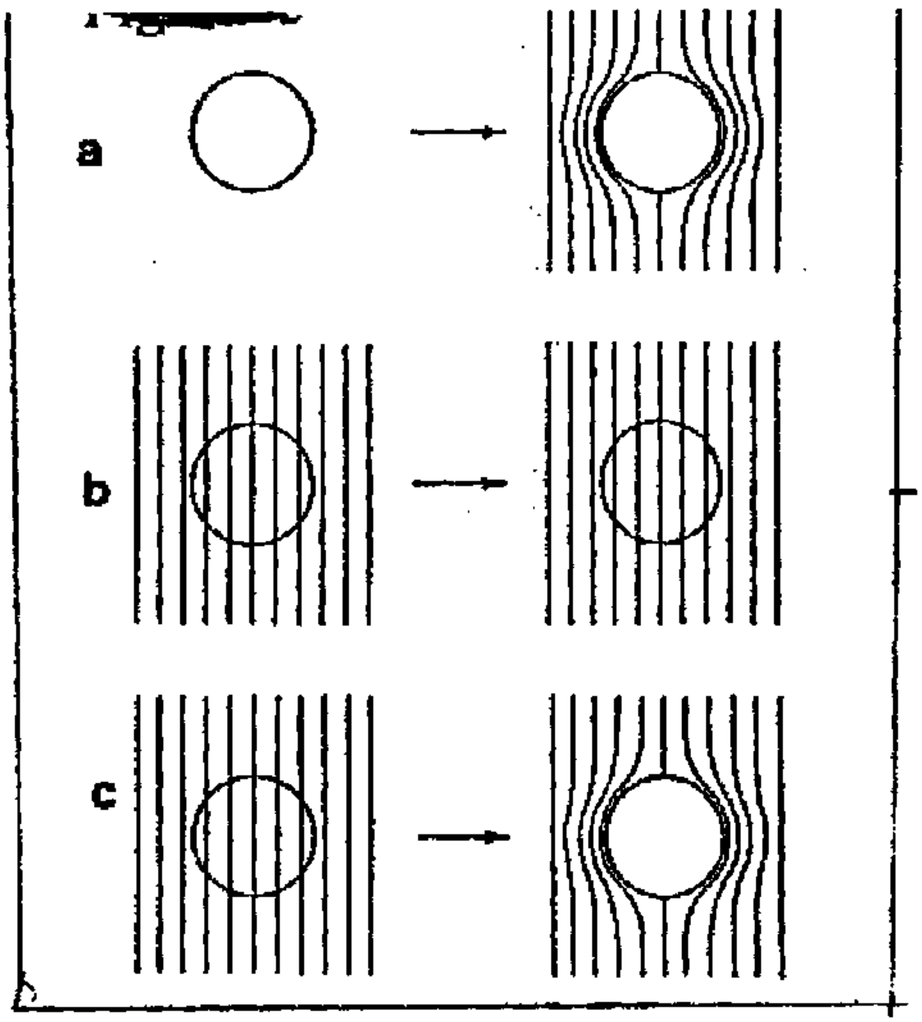

Fig. 1.1, Meissner effect. Shows the magnetic field distribution in the Superconductive State: (a) for zero -field-cooled experiment, (b) for field –cooled experiment as expected for perfect conductor, (c) for field cooled as found by Meissner and Oschsenfield, (1933)

For type-II systems the penetration of the field above H_{c1} is non-uniform, to find what controls the spatial range over which the properties of the superconducting state, such as Cooper Pair wave function, can vary, consider that a Cooper consists of one-electron wave function with momentum ± $\vec{k}$. To modulate this wave function in the superconductiong state, use is made of the fact that only states within ~kT_c of the Fermi energy can be employed to avoid excessive kinetic energy cost. For free electrons this gives a spread in energy.

$$\Delta E \cong kT_c = \frac{P_F}{m}\Delta P \quad \text{...1.1}$$

The range of acceptable momentum values is then:

$$\Delta P \cong \frac{kT_c}{\upsilon_F} \quad \text{.................................1.2}$$

From Heisenberg uncertainty principle, we obtain:

$$\Delta\chi \equiv \xi_o = c\frac{\hbar\upsilon_F}{kT_c} \quad \text{...1.3}$$

where ξ_o is the Coherence length (Pippard, 1953).

The Coherence length apart from being the effective size of a Cooper pair, also depends on the mean free path l of the electrons in the normal state, with ξ given by:

$$\frac{1}{\xi} = \frac{1}{\xi_o} + \frac{1}{l} \quad \text{...1.4}$$

where ξ_o is the intrinsic coherence length,

and ξ is the effective coherence length.

Abrikosov (1957) showed that at an upper critical field,

$$H_{C2} = \sqrt{2}KH_2,\ i.e.\ \mu_o H_{C2} = \phi/(2\pi\xi^2) \quad \text{........................1.5}$$

Where $K = \frac{\lambda_L}{\xi}$, ...1.6

called dimensionless Ginzburg – Landau parameter (Ginzburg and Landau, 1950) and λ_L is the London Penetration depth (Fritz and Heinz London, 1935), there occurs a second-order phase transition from the normal phase to a flux-line lattice with exactly one flux quantum ϕ_o through each lattice cell, and at the lower critical field H_{C1}, which for K >> 1 is given by:

$$H_{C1} \cong H_C \ln(1.08K)/(\sqrt{2}K) \qquad 1.7$$

a transition into the Meissner phase.

Finally, combining eqs. (1.5) and (1.7), we obtain:

$$H_{C1}H_{C2} \equiv H_C^2 \qquad 1.8$$

which implies that the higher H_{C2}, is the lower H_{C1} is.

All the new oxide materials are strong type-II superconductors. The three distinct phases in the phase diagram (Fig. 1.2) of a type-II superconductor are called: For field smaller than H_{C1} – Meissner phase, between H_{C1} and the upper H_{C2} – Shubnikov phase, Mixed state or Vortex State, and above H_{C2} – normal phase.

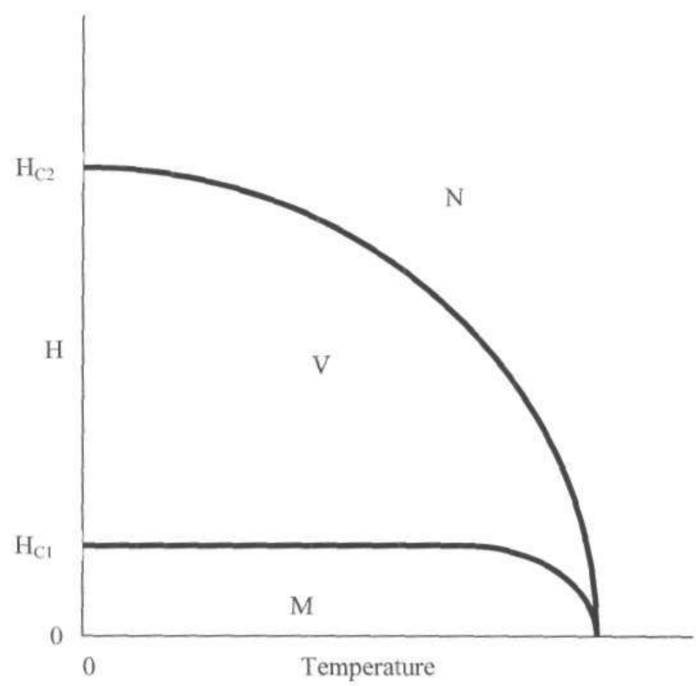

Fig. 1.2: Phase diagram of Type-II superconductor showing the Meissner (M), Vortex (V), and normal (N) regions

1.3 THERMODYNAMICS OF SUPERCONDUCTIVITY

Gorter (1933) and Gorter and Casimir (1934) developed a thermodynamic theory of superconductivity, by characterizing the superconductivity phase by a thermodynamic potential G_s as a function of temperature T and external magnetic field $\vec{H}_{ext}$.

$$G_s (T, H_{ext}) = F_s + W \qquad 1.9$$

Where F_s is the free energy.

$$F_s = \int f_s(T)dV + \frac{1}{2}\int\left(\vec{B}.\vec{H} - \mu_o H_{ext}^2\right)dV \qquad 1.10$$

Here: f_s (T) = intrinsic energy density

$\vec{B}.\ \vec{H} - \mu_o H_{ext}^2$ = change in magnetic energy due to the presence of the superconductor, and

$$W = \mu_o \int \vec{M}.\vec{H}_{ext} dV \qquad 1.11$$

is the interaction energy with the external magnetic circuit.

$\vec{B}$ and $\vec{H}$ are the magnetic induction and magnetic field, respectively, in the presence of the superconductor, and $\vec{M} = \mu_o^{-1}\ \vec{B}.\ \vec{H}$, is the magnetization due to the Meissner screening current.

At constant pressure and temperature, the thermodynamic potential G_s of the superconductor as a function of magnetic is obtained from:

$$G_s(H) - G_s(O) = -\int M dH_{ext} \qquad 1.12$$

The normal state of most superconductors is paramagnetic and the magnetization is small compared with that of the superconducting state shown in Fig. (1.2) for fields below H_C or H_{C2}. Therefore, neglecting the normal state magnetization,

$$G_N(H) - G_N(O) = 0 \qquad 1.13$$

where G_N is the thermodynamic potential of the normal state. At the critical field, the thermodynamic potential of the normal and superconducting state must be equal for two-phase equilibrium:

$$G_N(H_c) = G_s(H_c) = G_s(0) - \int_0^{Hc} MdH \qquad 1.14$$

from equation (1.12), Combining equations (1.14) and (1.13), the thermodynamic potential difference ΔG between the two states becomes:

$$\Delta G = G_N(0) - G_s(0) = -\int_0^{H_c} MdH \qquad 1.15$$

The thermodynamic potential is just the area under the magnetisation curve. The type II magnetisation curves are drawn to give the same thermodynamic potential difference: the areas under the curve are equal. For a Type I superconductor,

$$\Delta G = \int_0^{H_C} MdH = \frac{1}{2} H_C^2 \qquad 1.16$$

The term thermodynamic critical field H_c of a Type II superconductor is defined by setting the right-hand of equation (1.16) equal to the area under the Type II magnetisation curve.

1.4 MICROSCOPIC THEORY

Considering Superconductivity to be some kind of co-operative phenomenon, Welker (1938) showed that the assumption of a gap Δ of the order of kT_c in the electronic excitation spectrum of a superconductor would explain the perfect diamagnetism, the behaviour of the specific heat, the temperature dependence of the critical field $H_c(T)$, and to some extent also the infinite conductivity. Daunt and Mendelssohn (1946) obtained the first experimental indication of a gap in the electronic spectrum from a measurement of the Thomson effect. Further evidence for an energy gap was obtained from a variety of experiments.

Maxwell (1950) and Reynolds, *et. al.*, (1950) discovered the isotope effect which indicated that the electron-lattice interaction is involved in the superconductive mechanism. Frohlich (1950) pointed out that the same electron-lattice interaction which describes the scattering of conduction electron by lattice vibrations gives rise to an indirect interaction between the electron. He proposed this to be the interaction responsible for superconductivity.

Schafroth (1954) noted that an ideal gas of charged bosons below its condensation point shows superconductive behaviour. He concluded that superconductivity should occur in a metal if the total effective interaction between the electrons, including the indirect interaction via lattice vibrations, gives rise to the formation of resonant states of electron pairs. Chemical equilibrium between these pairs and single electrons was proposed to lead to a Bose Condensation (Schafroth, *et. al.*, 1957).

1.4.1 **Cooper Pairs**

Cooper (1956) discovered that two electrons with an attractive interaction in the presence of a filled Fermi sphere always form a bound pair (and not just a resonance), no matter how small the interaction, with a wave function decaying exponentially at large distances. He showed that the energy gap

$$\Delta \approx 2\hbar\omega_D e^{-1/FN_F} \qquad \text{1.17}$$

Where N_F is the density of states at the Fermi level (for one spin state), $\hbar\omega_D$ is the Debye energy of the phonon. F is the interaction strength.

1.4.2 BCS Theory

Because the size of a Cooper pair is large compared to the average electron distance, the electronic state cannot realistically be described as a gas of Cooper pairs, but involves complicated many body correlations. Bardeen, Cooper and Schrieffer, (1957) succeeded in constructing a variational wave function for the superconducting ground state which takes many body correlations into account, and which is separated from the band of single-particle excitations by an energy gap.

The theory contains a number of approximations, but it works very well for simple metals and contains all the essential elements of superconductive phenomenon in weak-coupling superconductors.

The BCS theory also makes a predication for the ordering temperature in terms of the parameters of the theory.

The transition temperature is given by:

$$k_B T_C \doteq 1.13\hbar\omega_D e^{-1/FN_F} \qquad \text{1.18}$$

where k_B is the Boltzmann's constant. Since the phonon frequency is inversely proportional to the square root of the mass for simple metal, this prediction is in agreement with the isotopic effect.

Finally, the theory gives a relationship between the zero temperature energy gap and the ordering temperature:

$$\frac{\Delta(0)}{k_B T_c} = 1.764 \qquad 1.19$$

1.4.3 **ODLRO**

The essence of BCS theory is the pairing instability and the formation of a coherent pair condensate (Allen, 1990). Yang (1962) conjectured that off-diagonal long-range order (ODLRO) is the minimal essence of superconductivity.

CHAPTER TWO

2.0 STRUCTURAL PROPERTIES OF HIGH-T_c SUPERCONDUCTORS

2.1 INTRODUCTION

Physical properties of high-T_c materials are intimately connected with their crystal structure. The study of the crystal structure have been done using X-ray and neutron diffraction techniques. However, neutron powder diffraction data is employed for almost all structural refinement of superconductors because unlike the X-ray, the neutron scattering amplitudes of light and heavy atoms are comparable, also neutrons have higher penetrating power than X-rays. Rietveld method (1969) is used in the profile analysis of the structures.

All high-T_c superconductors are either tetragonal or nearly tetragonal, with the lattice parameters a, b, and c such that c >> a, b and a ~ b. A common and essential ingredient of the structure of all high-T_c Superconductors is the presence of Cu-O planes, normal to the c-axis. Each copper atom in such a plane is strongly bonded to four oxygens, forming a nearly planar square, at a distance of ~ 1.90 Å (Vijayaraghavan and Gupta, 1995). Existence of the CuO planes is crucial since they carry electrical conduction and therefore are responsible for Superconductivity. These Cu-O planes are arrange in stacks. Each of these stacks, called the Conduction Layer (Jorgensen, 1991), contains a specific number n of immediately neighbouring Cu-O planes spaced from each other by about 3.2 Å. Each stack is separated from the neighbouring one by a much larger distance. The region between the two stacks is filled with extended insulating sheets of La-O, Ba-O, Sr-O, Cu-O, Tl-O, Bi-O or Pb-O (depending upon the particular material of interest). This insulating layer is known as the Charge Reservoir Layer (Jorgensen, 1991). Because of their higher anisotropic structure, high-T_c systems are intrinsically 2D-Conductors (Vijayaraghavan and Gupta, 1995).

In the remainder of this Chapter we shall review the structure of some particular high-T_c compounds, starting with a brief discussion of the structure of Perovskite which is the structure to which $BPb_{1-x}Bi_xO_3$ and related compounds belong.

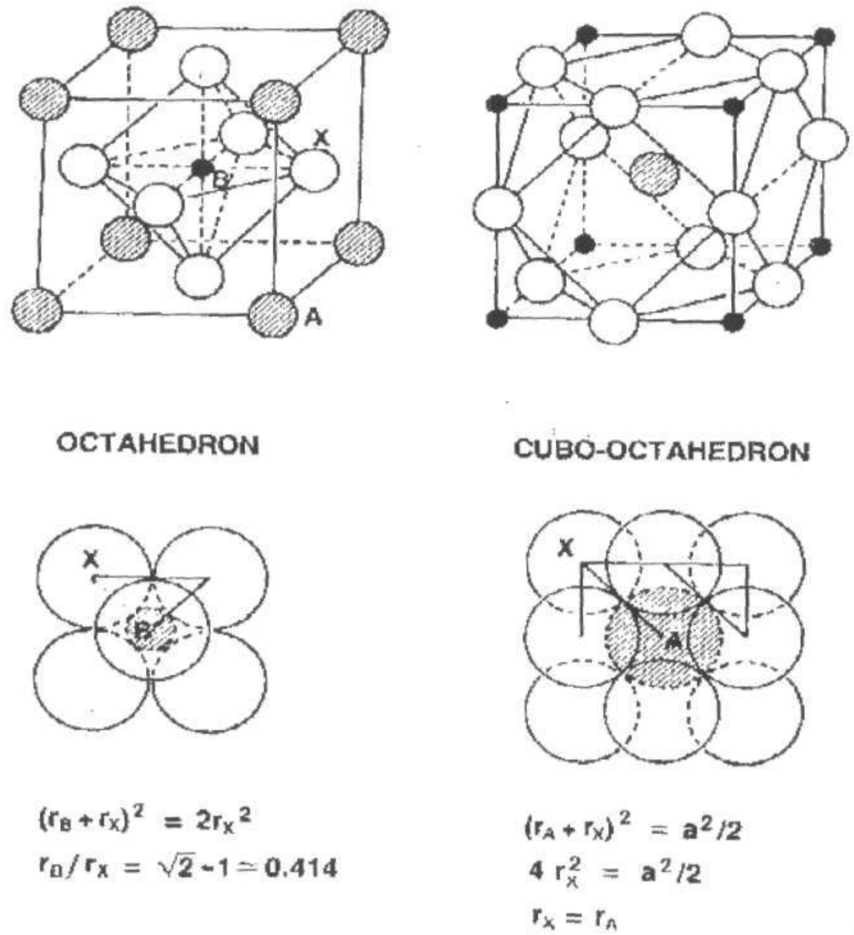

Fig. 2.1: Idealized structure of perovskite ABX_3

2.2 THE STRUCTURE OF PEROVSKITE

Many high-T_c Superconductors have a close relationship with structure of Perovskite ($CaTiO_3$) this structural type is common to a great variety of compounds of general formula ABX_3 (Ashcroft and Mermin, 1976). A Perovskite is a highly symmetrical arrangement of atoms (the A and B atoms have Cubo-octahedral and octahedral co-ordination, respectively, see Fig. 2.1) which imposes rather severe limitations on the size of the ions present in the structure. If r_A, r_B, and r_X are the ionic radii (Shannon, 1976) of A, B, and X respectively then

$$r_A + r_x = (r_B + r_x)\sqrt{2} \qquad \text{2.1}$$

It has been found that the structure of Perovskite exits whenever the condition

$0.75 \leq P \leq 1.0$ is satisfied (Santoro, 1990), where

$$P = \frac{(r_A + r_x)}{\sqrt{2}\,(r_B + r_x)} \qquad \text{2.2}$$

However, distortions in the structure may be present with consequent lowering of the symmetry (tetragonal, trigonal, and orthorhombic). Because the ions A and X are nearly equal in size, the structure of Perovskite contains close packed layers of composition AX_3. The atoms X are linked to four ions A and two ions B and are close to eight other ions X (Fig. 2.1). It is to be noted that the size of the ions is a more important factor than the valence of the atoms in determining the atomic arrangement of compound having the Perovskite type structure.

2.3 THE SYSTEM $BaPb_{1-x}Bi_xO_3$

Sleight *et al.*, (1975) first detected high-T_c Superconductivity in the system $BaPb_{1-x}Bi_xO_3$, and soon after this discovery structural studies were carried over the entire range of composition, including the end members $BaPbO_3$ and $BaBiO_3$ (Cox and Sleight, 1976A; Cox and Sleight, 1976B; Cox and Sleight, 1979; Shannon and Bierstedt, 1970; Thorton and Jacobson, 1976; Thorton and Jacobson, 1978). The solid solution in this system extends from x = 0 to x = 1, and the degree and type of distortions present in the basic structure vary with x. At room temperature, the symmetry of the material changes according to the following sequence (Cox and Sleight, 1976A):

Orthorhombic $0 \leq x \leq 0.05$

Tetragonal $0.05 \leq x \leq 0.35$

Orthorhombic $0.35 \leq x \leq 0.90$

Monoclinic $0.90 \leq x \leq 1.0$

Superconductivity exists only for values of x between 0.05 and 0.35. The value of the critical temperature T_c increases with x, reaches a maximum $T \approx 13$ K for $x \approx 0.25$, and then decreases in the range $0.25 < x < 0.35$. For $x > 0.35$, the material becomes a semiconductor.

The relationship between the structure of $BaPb_{0.75}Bi_{0.25}O_3$ (Fig. 2.2) and Perovskite is so simple and direct that there is no change in the co-ordination of the Ba and R (R = 0.75 Pb + 0.25 Bi) cations, the first being twelve-fold co-ordinated with a distorted cubo-octahedron as co-ordination Polyhedron, and the second octahedrally co-ordinated. Also, the oxygen anions remain bonded to four Ba and two R cations in the same way as the X anions of the Perovskite-type structure.

Two formulations are possible for $BaPb_{1-x}Bi_xO_3$, depending on the oxidation state assigned to the bismuth cations, i.e., $Ba^{2+}Pb^{4x}{}_{1-x4}Bi_x{}^{4x}O_3$ and $Ba^{2+}Pb^{4+}{}_{1-x}(Bi^{3+}{}_{0.5}Bi^{5+}{}_{0.5})_xO_3$ and a number of structure studies have been carried out to determine the values of bismuth in this system. Most of this research has been done on the compound $BaBiO_3$ which is monoclinic (Cox and Sleight, 1976B; Thorton and Jacobson, 1978).

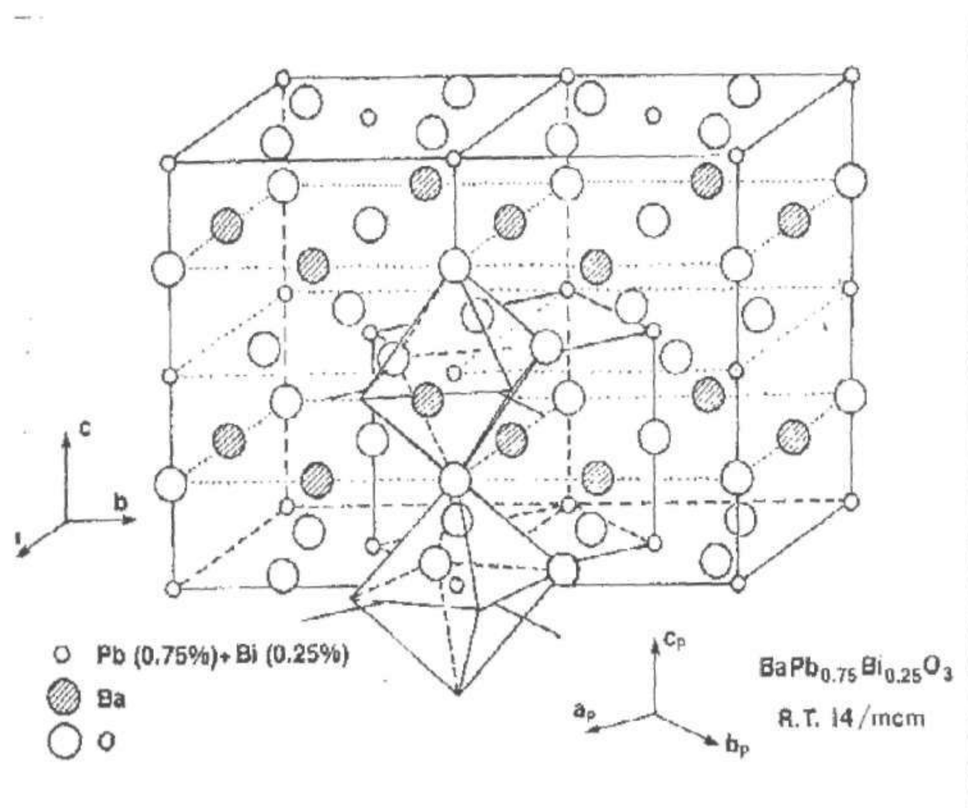

Fig. 2.2: $BaPb_{1-x}BiO_3$ Structure

2.4 THE $La_{2-x}M_xCuO_4$ (M = Ba, Sr) SYSTEM

The first high-T_c Copper oxide Superconductor $La_{2-x}Ba_xCuO_4$ discovered (Bednorz and Muller, 1986; Uchida *et al.*, 1987; Takagi *et al.*, 1987; Beno *et al.*, 1987; Capponi, *et al.*, 1987) belong to the $K_2NiF_4^-$ structure at room temperature. The structural type is pictured as containing alternate layers of Perovskite (ABX_3) and rock salt (AX) units (Fig. 2.3). The value of T_c in the system $La_{2-x}B_xCuO_{4-y}$ is a function of x and has a maximum value of about 35 K for x ≈ 0.15. Jorgensen *et al.*, (1987) determined the structural composition by powder-neutron diffraction.

Cava, Santoro *et al.*, (1987) and Francois, *et al.*, (1987) carried out the structural analysis of the system $La_{2-x}Sr_xCuO_{4-y}$, this has also T structure (fig, 2.3). In the compound, the CuO_2 planes are ~ 6.6 Å apart, separated by LaO planes which form the charge reservoir that captures electrons from the conducting planes upon doping. The atomic configurations of the elements forming this compound are Cu:[Ar]$(3d)^{10}(4S)$; La:[Xe]$(5d)(6S)^2$; O:[He]$(2S)^2(2P)^4$; and Sr:[Kr]$(5S)^2$. Each copper atom in the conducting planes has an oxygen (belonging to the charge reservoir) above and below in the c direction. These are, the apical O atoms or just O_z. Then, in this compound, the copper ions are surrounded by Octahedral of oxygen as in a perovskite structure. However, the distance Cu-O_z is ~2.4 Å, which is considerably larger than the distance Cu-O in the planes (~1.9 Å).

Upon doping La^{3+} are randomly replaced by Sr^{2+}, thus fewer electrons are donated to the CuO_z planes. Metallic behaviour has been observed for very small doping concentration, $x \geq 0.04$. The sign of the Hall Coefficient shows that the carrier are holes (Dagotto, 1994). The actual phase diagram of this material is shown in Fig. 2.4, according to results obtained by Keimer *et al*., (1992) and Birgeneau (1990). Near half-filling, anti-ferromagnetic order is clearly observed. Experimentally, Aeppli *et. al*., (1989) and Hayden *et. al*., (1991) showed that spin wave theory with only first neighbour interactions accounts for the spin dynamics of La_2CuO_4. A small residual interaction between planes leads to a finite Neel critical temperature of about 300 K. The spin-glass phase of Fig. 2.4 was considered by Harshman *et al*., (1988). For Sr dopings at low x ~ 0.05 and ~ 0.30, a superconducting phase is found at low temperatures.The maximum value of Tc is observed at the "Optimal" doping x # 0.15 (Cava, van Dover et al., 1987). A structural phase transition was also found in this compound, as shown in Fig. 2.4. At high temperature the structure is tetragonal, but at low temperatures the copper atoms and the six oxygens surrounding them slightly deviate from their positions forming an orthorhombic structure (Burns, 1992).

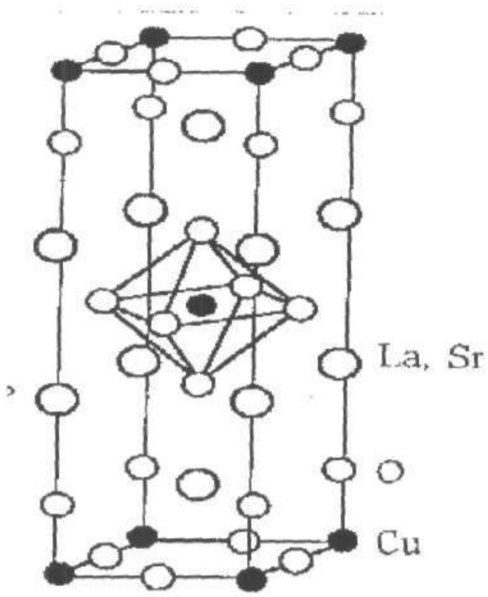

Fig. 2.3: Crystal structure of $La_{2-x}Sr_xCuO_4$ (T phase). Taken from Almasan and Maple (1991).

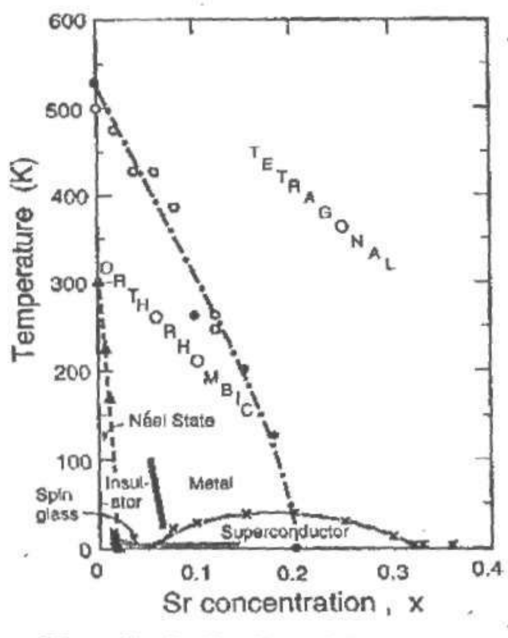

Fig. 2.4: Phase diagram of $La_{2-x}Sr_xCuO_4$ (from Keimer *et al.*, 1992).

Another compound similar to $La_{2-x}Sr_xCuO_4$ is the $Nd_{2-x}Ce_xCuO_4$ which is body-centred tetragonal (Fig. 2.5). The difference between the two lies in the position of the oxygen atoms of the charge reservoir. The structure corresponding to $Nd_{2-x}Ce_xCuO_4$ is called T′ structure. Note that the T structure can only be easily hole doped, while the T′ structure can be easily electron doped, the reason for this asymmetry is unknown (Dagotto, 1994). The atomic configurations of the elements forming the compound are Nd: $[Xe](4f)^4(6s)^2$ and Ce: $[Xe](4f)(5d)(6s)^2$, while Cu and O have been described before. In the crystal, copper becomes Cu^{2+}, oxygen is O^{2-}, and Neodymium is in a state Nd^{3+}. After doping , i.e., when a Nd ion is replaced by Ce^{4+}, the CuO_2 planes get an excess of electrons. This is confirmed by the experimentally observed sign of the Hall Coefficient.

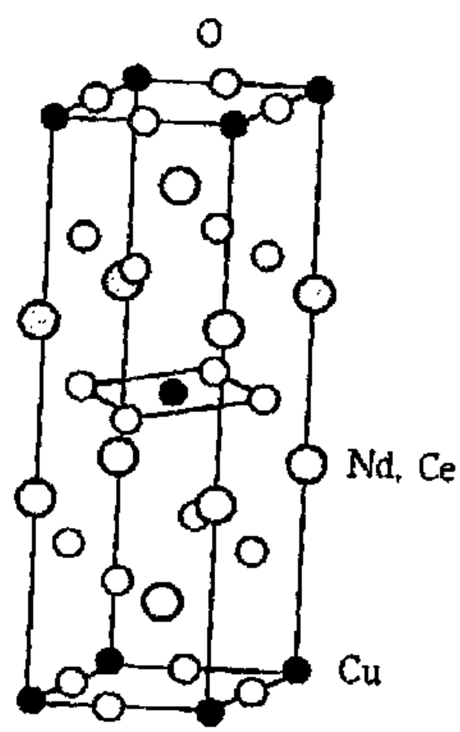

Fig. 2.5: Crystal structure of $Nd_{2-x}Ce_xCuO_4$ (T′ phase). Taken from Almasan and Maple (1991).

2.5 THE $YBa_2Cu_3O_{6+x}$ (YBCO) SYSTEM

Wu *et al.*, (1987) discovered superconductivity with T_c above 90 K in the YBCO system. Following this discovery several laboratories established that the superconductivity compound is $YBa_2Cu_3O_{6+x}$ (Cava, Batlogg, *et al.*, 1987; Grant *et al.*, 1987; Hinks *et al.*, 1987; Kadowaki *et al.*, 1987; Ganguly *et al.*, 1987). The profile analysis of neutron powder data was carried by Beno *et al.*, (1987); Greedan *et al.*, (1987); Capponi *et al.*, (1987); David *et al.*, (1987); Beech *et. al.*, (1987); Katano *et al.*, (1987). The (Primitive tetragonal) structure of this compound is shown in Fig. (2.6). In YBCO, there are two CuO_2 planes per unit cell approximately 3.4 Å apart, separated by yttrium ions. The figure shows that these pairs of CuO_2 planes are themselves separated by layers of atoms containing barium, oxygen and copper, which form the charge reservoir.

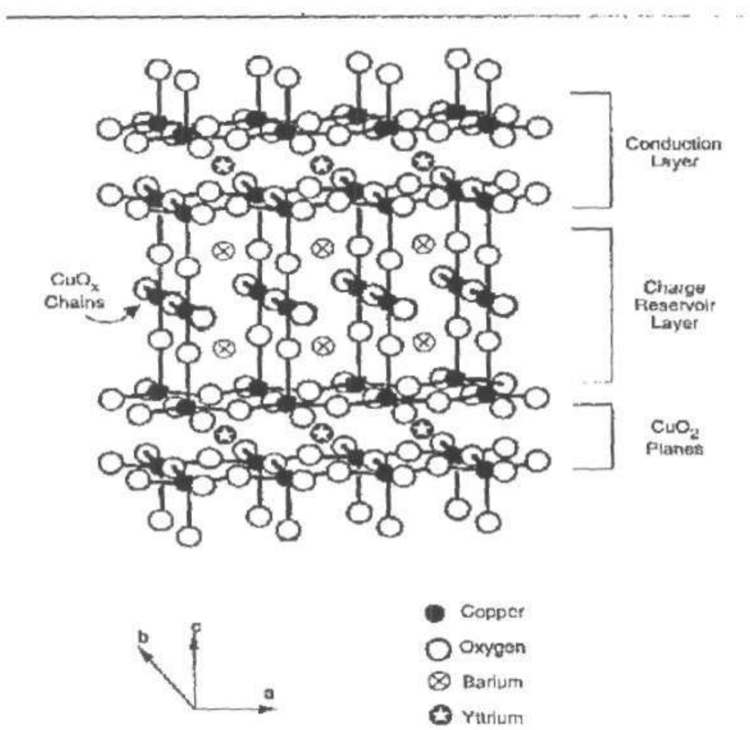

Fig. 2.6: Crystal structure of $YBa_2Cu_3O_{6+x}$ (taken from Jorgensen, 1991).

The atomic configurations of Y and Ba are [Kr]$(5s)^2(4d)$ and [Xe]$(6s)^2$, respectively, while those of Cu and O have been described before for the lanthanum compound. The Cu atoms in the charge reservoir, in combination with oxygen atoms, form one-dimensional structure along the b direction which are called the Cu-O chains. The presence of the structure affects such measurable properties of the material, as the optical conductivity. The distance Cu-O in the chains is ~1.9 Å as it is in the planes. The chains are well defined for $YBa_2Cu_3O_7$, but at the minimum oxygen concentrations they have defects. Actually, at the minimum oxygen concentration ($x = 0$), no Cu-O chains exists (Dagotto, 1994).

In this material, the number of carriers depends on the oxygen content in the formula $YBa_2Cu_3O_{6+x}$. In the case $x = 1$, the oxygen atoms are structurally ordered and form the Cu-O chains shown in Fig. (2.6); when x is reduced, oxygen atoms are taken from the chains. Increasing the oxygen content is equivalent to adding holes to the conducting planes (Burns, 1992).

In Fig. (2.7), the phase diagram of $YBa_2Cu_3O_{6+x}$ is shown. The range of defect concentrations (oxygen excess) in this compound is large, allowing the properties to change from insulating to superconducting. For x close to 0, an antiferromagnetic phase is observed with a Neel temperature over 500 K. This spin order is caused by the spin- ½ holes in the *d*-shell of the in-plane coppers, as in other compounds (the copper of the chains is not magnetic). At $x_c \sim 0.3$ ($\delta_c \sim 0.7$ in the notation of the figure), antiferromagnetic long-range order disappsears and the superconductivity phase starts developing. The "Optimal" composition (i.e., the one that gives the largest T_c) is slightly below $x \sim 1$ ($\delta \sim 0.0$). A structural phase transition occurs in this material near x_c~0.3 from a tetragonal to an orthorhombic phase, similar to that found for $La_{2-x}Sr_xCuO_4$. In this structural transition the conduction planes CuO_2 are slightly affected.

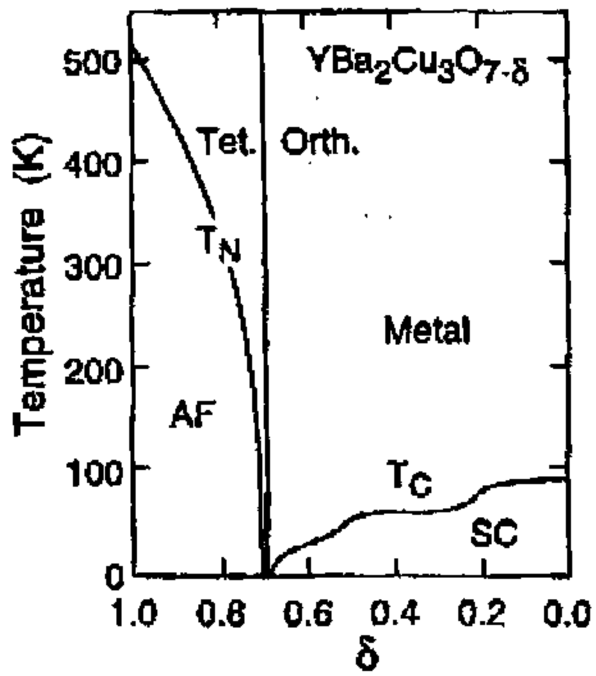

Fig. 2.7: Phase diagram of $YBa_2Cu_3O_{6+x}$ (taken from Burns, 1992; Koike *et al.*, 1989).

2.6 Bi - AND Tl – BASED COMPOUNDS

Bi- based copper oxide materials with T_c onsets over 100K were discovered by Maeda *et al.*, (1988) and Chu *et al.*, (1988) in the Bi-Sr-Ca-Cu-O system and have been verified by several other (Subramanian, Torandi, Calabrese *et al.*, 1988; Sunshine *et al.*, 1988; Tarascon *et al.*, 1988). The introduction of Bi- into $La_{2-x}M_xCuO_{4-x}$ materials by Michel, Provost, *et al.*, (1987) earlier had found a slight enhancement of T_c (to 42 K), and Michel, Hervieu *et al.*, (1987) had also investigated the Bi-Sr-Cu-O system and found T_c onset near 30 K.

The subsequent discovery of high-temperature superconductivity in Tl-based materials by Sheng *et al.*, (1988) was related to that of the Bi-based materials both because of the high-

T_c values and because of the structure, which was determined thereafter to be similar to that of the Aurivillius (1950a, 1950b, 1950c) phases.

Subramanian, Torardi, Gopalakrishnan *et al.*, (1988) identified the structure of $Tl_2Ba_2CaCuO_8$ (Tl2212) as slightly distorted from a body centred-tetragonal). The unit cell contains two CuO_2 layer separated by Ca ions, and two TlO layers separated from each of the CuO_2 layers by a BaO layers. The structural data suggest that the true structure involves a subtle rearrangements of atoms in the TlO planes (FitzGerald *et al.*, 1988).

The general formulas of these complex compounds are $Bi_mSr_2Ca_{n-1}Cu_nO_{2n+m+2}$ and $Tl_mBa_2Ca_{n-1}Cu_nO_{2n+m+2}$ (where m and n are integers), and are typically identified by the shorthand notation Bi(or Tl) m2(n-1)n, e.g., Bi 2212. In particular Tl 2223 has one of the highest confined critical temperatures, $T_c \sim 125$ K, of the high-T_c family. It contains three CuO_2 planes per unit cell, which are separated by Ca atoms ~ 3.2 Å apart. The sets of three planes are ~11.6 Å apart (Halder *et al.*, 1988; Parkin *et al.*, 1988; Subramanian, Torandi, Gopalakrishnan, *et al.*, 1988; Torardi *et al.*, 1988; Torrance *et al.*, 1988; Siegrist *et al.*, 1988; Jorgensen 1991; Burns, 1992).

The $Bi_2Sr_2CaCu_2O_8$ (Bi 2212) material has a structure that is closely related to that of Tl 2212. Formal valence counting leads to a Cu^{2+} assignment and Vaknin *et al.*, (1989) reported that the material is antiferromagnetic insulator with Neel temperature, $T_N = 540$ K and have plane Cu moment ordering similar to the previously known Copper-oxide antiferromagnets.

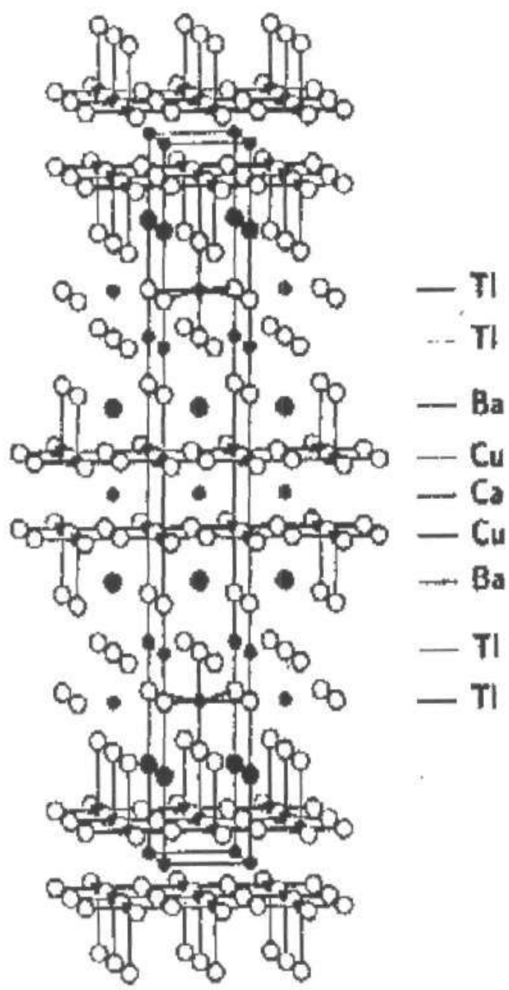

Fig. 2.8: Structure of $Tl_2Ba_2CaCu_2O_8$

In 1993 Putilin *et al*., (1993) and Schilling *et al*., (1993) found superconductivity at 133 K in some Copper oxides that include Hg (See Table 1.1).

CHAPTER THREE

3.0 THEORETICAL MODEL OF HIGH - T_c SUPERCONDUCTIVITY

3.1 INTRODUCTION

The superconducting oxides exhibits a variety of Co-operative phenomena, including metal-insulator transitions, antiferromagnetism and superconductivity. From the standpoint of superconductivity the central issue is to identify the nature of the superconducting state. One aspect concerns the basic character of the superconducting state itself that is, whether it develops in the usual Bardeen, Cooper, Schrieffer (BCS) way as a result of an instability of the Fermi liquid, or perhaps entails a different mechanism such as resonating valence band (RVB). The second basic question involves the identification of the interaction which is responsible for the electron – pairing (Lynn, 1990).

Theories that combine the pairing ideas with the presence of strong antiferromagnetic correlations include:

i. Spinbag theories: Schrieffer, *et al.*, (1988, 1989); Kampf and Schrieffer, (1990); Levin *et al.*, (1992).

ii. Antiferromagnetic Fermi – liquid theories: Millis, *et al.*, (1990).

iii. The $d_{x^2-y^2}$ theories: Bickers, *et. al.* (1989); Mouthoux, *et al.*, (1991).

iv. Interchange of Magnons may produce the attractive force needed to pair the charge carriers: Miyake, *et al.*, (1986); Scalapino *et al.*, (1986); Bickers, *et al.*, (1987); Monthoux and Pines, (1993).

v. van Hove singularity scenario: Markiewicz, (1991); Newns, *et al.*, (1991); Pattnaik *et al.*, (1992).

vi. Hole mechanisms: Hirsch and Marsiglio, (1989).

vii. Nested Fermi-liquid Virosztek and Ruvalds, (1990).

viii. Antiferomagnetic van Hove scenario: Dagotto, *et al.*, (1994).

ix. and others.

Non-Fermi – liquid theories are:

i. Resonating valence bond (RVB) theories: Anderson, (1987, 1990a, 1990b).

ii. Anyon superconductivity: Laughlin, (1988a, 1988b); Chen *et al.*, (1989); Wen, *et al.*, (1989).

iii. Marginal Fermi-liquid theories: Varma *et al.*, (1989).

iv. Gauge theories: Nagaosa and Lee, (1990).

v. and several others.

3.2 ELECTRONIC STRUCTURE

Many questions about the normal state properties of the high temperature superconductors can be answered based on the results of band structures calculations. For example the unusual superconducting transition phase diagram of $YBa_2Cu_3O_{7-X}$ as a function of oxygen vacancy concentration (Fig 2.7) can be understood from (1) the hole count on the $Cu\text{-}O_2$ layer which modifies the electron-electron correlations, (2) the metallic nature of the chain layers near E_F which control the interlayer coupling between the CuO_2 layers. Similar arguments can also be applied to the bismuth - and thallium - based copper oxides, where T_c increase with increasing number of $Cu\text{-}O_2$ layer. In addition, the Hall coefficient and fermi surfaces predicted by band theory have been confirmed by experiment (Wang, 1990).

3.2.1 Electronic Structure of $La_{2-x}(Ba, Sr)_xCuO_4$

$La_{2-x}(Ba, Sr)_xCuO_{4-y}$ crystallizes in the tetragonal phase when $x > 0.2$ and undergoes an orthorhombic distortion for $x \leq 0.2$, due to rotation of the oxygen octahedra (Jorgensen *et al.*, 1987). The superconducting transition temperature depends critically on the amount of Sr or

Ba doping and oxygen vacancy concentration. In particular, T_c reaches a maximum value near x = 0.15. For x > 0.15, detailed neutron powder diffraction data indicates that the oxygen vacancy concentration increases sharply and more than compensates the effects of the Ba or Sr doping so that T_c drops rapidly to zero. Fermi surface were observed by Tanigawa *et al.* (1988) in orthorhombic La_2CuO_{4-y} in position 2D-ACAR measurements on sample which exhibit semi-conducting behaviour in their resistivity.

Mattheiss (1987) and Yu *et al.*, (1987) were the first to report the band structure of La_2CuO_4 in which the energy bands showed 17 bands that are centred at -3 eV below Fermi energy E_F having two bands, the antibonding and the bonding states of the Cu_{3d} orbital x^2-y^2 symmetry and the O_{2p} orbital of x and y symmetry along the nearest neighbour Cu-O bonds in the xy plane. The antibonding band, being exactly half filled, play important role in superconducting and magnetic properties of the system. The band structure of La_2CuO_4 is quasi-two-dimensional in character (Yu *et al.*, 1987).

Pickett *et al.*, (1987) used the simple rigid band model (in this model it is assumed that the changes in the density of states are negligible and E_F can be shifted to accommodate the extra charge) to calculate the band structure of $LaBaCuO_4$. They found that the Ba doping leads to a substantial downward shift of E_F in $LaBaCuO_4$. There is a van Hove singularity in the density of state which occur very near the concentration of Ba or Sr doping where T_c reaches its highest value (x = 0.15) (Schwarz, 1987). The model is similar to the exciton model of Varma *et al* (1987) which emphasizes the charge fluctuations between Cu and O ions.

The Fermi surface of $La(Ba, Sr)_xCuO_4$, for x = 0 consists of hole like cylinder along the z – axis (Xu *et al*, 1987). At the concentration x = 0.17, at which E_F touches the van Hove singularity, the fermi surface undergoes a change from hole like cylinders to electron cylinders. There is a near perfect fermi surface nesting which suggests the possibility of charge density wave or spin density wave instability.

3.2.2 Electronic Properties of $YBa_2Cu_3O_{7-x}$

The $RBa_2Cu_3O_{7-x}$ (R = Y, Gd, Eu, etc.) compounds are superconducting in the orthorhombic phase but are insulating in the tetragonal case. The orthorhombic phase is superconducting due to the formation of ordered chains that acts as dopants for the two – dimensional CuO_2 planes. The band structure of $YBa_2Cu_3O_7$ was first reported by Mattheiss and Hamann (1987) and by Massidda *et al* (1987) and Yu *et al*., (1987). Mattheiss and Hamann found that away from E_F the electronic structure of $YBa_2Cu_3O_7$ consists of occupied O_{2s} bands centred at 15 eV, Ba_{5d} bands centred at – 10 eV, as well as unoccupied Ba_{5p} and Y_{4d} bands above 3.4eV. The band structure of Krakauer and Pickett (1987) showed close agreement with calculations of Massidda *et al*., (1987) and Ching *et al*., (1987). They found that among the four bands that Cross E_F, two of them have the majority of their charge on the $Cu\text{-}O_2$ plane corresponding to one band for each layer.

Results of Gupta and Gupta (1993) on electronic structure calculations, for the ordered tetragonal crystal structure for the $RbaCu_3O_7$ Superconductors they proposed, showed that the hole density and the fermi level in this tetragonal crystal structure are practically identical to those found in the orthorhombic phase.

In the band structure of tetragonal $YBa_2Cu_3O_6$, by Yu *et al*., (1987), the two $Cu\text{-}O_2$ bands remain the same as in $YBa_2Cu_3O_7$, but there is an upward shift of E_F due to the ionicity of the missing oxygen atoms. Accordingly there are significant changes in the fermi surface and the hole count in the CuO_2 bands (Wang, 1990).

3.2.3. Electronic Structure of the Bismuth and Thallium Superconductors

The band structure of Sterne and Wang (1988) for the high-T_c $Bi_2Sr_2CaCu_2O_8$ compound is similar to the calculations of Hybertsen and Mattheiss (1988), Krakauer and Pickett (1988) and Massidda *et al.*, (1988). There are two Cu-O_2 pdσ antibonding bands extending from about 1 eV below E_F to 1.5 eV above, E_F, equally important is the presence of two bismuth *p* electron bands which dip below E_F by about 0.7 eV around a point. These interact with the Cu-O_2 antibonding bands producing a complicated band structures around the point, it was also found that the bismuth oxide layers are metallic.

In the band structure of the low T_c $Bi_2Sr_2CuO_6$ compound the Copper – Oxygen antibonding band looks essentially identical to the corresponding bands in the $Bi_2Sr_2CaCu_2O_8$ compound. Around the point mentioned above, the two Bi *p*-bands barely cross and extend less than 0.1 eV (Wang, 1990).

Present in the band structures of the two and three layer thallium compounds, reported by Yu *et al*., (1988), and that of the one layer compounds by Hamann and Mattheiss (1988), is the antibonding Cu-O_2 band, whose filling factor is controlled by charge transfer to the Tl-O band that crosses E_F. Kasowski *et al.,* (1988) calculated the electronic structures of the one-to-four-layer Tl compounds. They found narrow Cu-O bands that lie very close to and sometimes overlaps E_F.

3.3 Normal – State Transport properties

The strange normal state properties of high T_c oxides, which are not characteristic of other materials, is most vividly displayed in their transport properties. The conductivity is extremely anisotropic, with metallic – like behaviour along one direction and semiconducting – like or insulating behaviour along the other (Wolf and Krezin, 1987; Tachiki *et al*., 1987; Muller and Olsen, 1988). We shall briefly review results of transport property studies, measured as a function of temperature and the level of doping, which show that anomalous temperature dependence of the resistivity and the Hall Coefficient of the high T_c materials and their anisotropy are indication of an exotic electronic state.

3.3.1 **Hall effect**

A central issue on the normal state transport properties of the high T_c oxides is whether normal Fermi liquid theory can account for the observed transport properties. Hall effect measurements (Iye, 1992; Ong, 1990; Kitazawa, *et al.*, 1989) lead to some results which point out complex Fermi surface even if the Fermi liquid picture should apply to the High T_c oxides.

In the low doping regime, Hall coefficient, R_H, gives a good measure of the carrier density. Sign of R_H and the relation $1/R_H \propto x$ for low doping are regarded as a strong support to the doped Mott-Hubbard parent insulator picture (Uchida *et al.*, 1989; Sleight, 1989). In the system $La_{2-x}Sr_xCuO_{4-y}$ and $Nd_2.xCe_xCuO_{4-y}$, R_H changes its sign on going from light doping, to heavy doping (these are the region where superconductivity disappears and the system attains the lowest resistivity) implying that the sign of the carriers changes in the region of overdoping (Tajima and Kitazawa, 1991; Sleight, 1989; Uchida, *et al.*, 1989). In that region of doping, the material behaves like a Fermi liquid, Hall coefficient is rather low.

Sleight (1989) pointed out and discussed a remarkable symmetry of the phenomenon of high T_c superconductivity which Hall effect measurements bring out. Either of the two ways, reduction of Cu^{2+}- ions by adding electrons (*n*-type carriers) or oxidation of Cu^{2+}- ions by removing electrons (*p*-type carriers), leads to super- conductivity.

R_H of the high – T_c superconductors is anisotropic. This behaviour has been observed in $Bi_2Sr_2CaCuO_8$ and $Bi_2Sr_2CuO_6$ (Forro *et al.*, 1990) and $La_{2-x}Sr_xCuO_{4-y}$ (Kitazawa, *et al.*, 1989).

The most remarkable feature of the Hall Coefficient R_H is its temperature dependence (Vijayaraghavan and Gupta, 1995). Not only is the magnitude of R_H temperature dependent, in certain cases the sign of R_H also may change at certain temperature (Ong, 1990; Wang *et al.*, 1991). R_H in $YBa_2Cu_3O_{7-y}$ exhibits a sharp temperature dependence: $1/R_H = T$, Iye, (1992) pointed out that this temperature dependence becomes weaker in sample with reduced T_c. There exist a strong correlation between the temperature dependence of R_H and the occurrence of superconductivity. R_H follows a linear temperature dependence in $YBa_2Cu_3O_{7-y}$, $Bi_2Sr_2CaCuO_{8+y}$ and $Tl_2Ba_2CuO_6$ (Iye, 1992). In some cases, such as over doped $TlSr_2CaCu_2O_{7-y}$ and $Tl_2Ba_2CuO_{6+y}$ (Forro, *et al.*, 1990) inverse Hall mobility $\mu_H^{-1} = \rho/R_H$ has been observed to have simple T^2-dependence.

3.3.2 Resistivity

Takagi, *et. al.*, (1989) and Uchida, *et al.*, (1989) found that the room temperature resistivity $\rho(300\ K)$ of the polycrystalline samples decreases drastically as x, the level of doping increases. The carriers that are produced due to doping tend to get localized at low temperatures, thereby resulting in an upturn in the resistivity at low temperatures. On further doping, $\rho(300\ K)$ decreases systematically and the localization of the carriers is pushed to still lower temperatures and, eventually superconductivity appears in the material with $x > 0.07$. With still higher doping, T_c decreases; $T_c \to 0$ for a sample with $x = 0.3$. The system however, retains its metallic character up to $x = 0.35$.

Temperature dependence and anisotropy of resistivity $\rho(T)$ of high-T_c superconductors are rather Unusual. Iye (1992) and Gurvitch and Fiory (1987) have given the temperature dependence of resistivity $\rho(T)$ of several high T_c Cuprate systems. These shows that $\rho(T)$ varies linearly with temperature in critically doped systems over a range of temperature which is too wide for phonon scattering induced resistivity. This large linear T – dependence suggests that the normal state is physically different from that of a conventional metal.

3.4 **MAGNETIC PROPERTIES.**

Cu-atoms carry a magnetic moment in all the undoped high-T_c materials and exhibit antiferromagnetic ordering. This has been established by a variety of microscopic measurements, for $La_2CuO_{4-\delta}$ by Susceptibility (Johnson, *et al.*, 1987), neutron scattering (Vaknin, *et al.*, 1987; Mitsuda, *et al.*, 1987, Freltoft, *et al.*, 1987; Shirane, *et al.*, 1987; Freltoft, *et al.*, 1988; Stassis *et al.*, 1988; Kastner *et al.*, 1988; Endoh *et al.*, 1988; Shirane, *et al.*, 1989), and Muon precision (Uemura et al., 1987; Harshman, Aeppli, *et al.*, 1988) experiments. And for $RBa_2Cu_3O_{6-x}$ (R = rare Earth) systems by Muon spin precession experiments (Nishida, *et al.*, 1987; Brewer *et al.*, 1988) and neutron scattering experiments (Tranquada, Cox *et al.*, 1988; Li, *et al.*, 1988; Kadowaki, *et al.*, 1988; Lynn, *et al.*, 1988; Tranquada, Moudden, *et al.*, 1988; Petitgrand and Collin, 1988, Burlet, *et al.*, 1988; Lynn and Li, 1988; Moudden *et al.*, 1988; Lynn, *et al.*, 1989). Undoped high-T_c materials are called Mott – Hubbard systems because they have insulating and magnetic ground states (Hubbard, 1964). Anderson (1988; 1989) regards high-T_c ssuperconductivity to be essentially a magnetic Mott – Phenomenon.

The system of Cu-spins in La_2CuO_4 undergoes an antiferromagnetic transition at a fairly high temperature, that is the magnetic ordering temperature $T_N \sim 300$ K (Jhonston, *et al.*, 1988). Both magnetic as well as electrical properties of La_2CuO_{4-y} exhibit a strong dependence on the oxygen stoichiometry. Jhonston, *et al.*, (1988) observed a drastic drop in T_N in an oxygen deficient sample ($T_N \sim 100$ K for $y \sim 0.05$).

The dynamics of Cu-spins exhibits several interesting features because of the structural anisotropy, coupling among the Cu-spins is highly anisotropic. At temperatures $T > T_N$, the spin system behaves as though it were a 2D – magnet, i.e., there are strong correlations among Cu – spins in the *ab*-plane but no significant correlations between layers. As the temperature get close to T_N the in-plane correlation length ξ increases rapidly and becomes sufficiently large; ~ 50 Å at 500 K and 500 Å at $T > T_N$ (Endoh, *et al.*, 1988). As the Spins become ordered within a layer (2D – ordering) the layer also get properly matched so that every spin is correctly paired with the spins in the adjacent layers. This ensures minimum magnetic energy and results in a 3D – magnetic ordering in the spin system.

Magnetic properties arising due to the Cu-moments in the Cu-O planes of other high-T_c cuprates are quite similar to those described above. Tranquada, Cox, *et al.*, (1988) observed that the ground state of $YBaCu_3O_6$ is antiferromagnetic (T_N ~ 500 K) with a large magnetic anisotropy. Similarly, Yang, *et al.* (1989), de Renzi, *et al.*, (1989). Nishida, *et al.*, (1988); Tamegai, and Iye (1989) found that $Bi_2Sr_2Ca_xY_{1-x}Cu_2O_y$ exhibits a magnetic ground state for $x = 0$, as inferred from the muon spin resonance (mu-SR) spectroscopic studies.

Magnetic properties of La_2CuO_{4-y} depend very sensitively on the concentration of holes sensitively (Takagi, *et al.*, 1989; Uchida, *et al.*, 1989) which may be introduced into the system by partially substituting trivalent La-atoms by divalent metal ions Ca, Sr and Ba. The superconductivity – magnetism phase diagram, evolution of superconductivity out of magnetism in the system $La_{2-x}Sr_xCuO_{4-y}$ as x varies from zero onwards shows that T_N decreases rapidly as the concentration x increases. Another important conclusion drawn from the phase diagram is that substantial Cu-moment persists even in the superconducting state. This results from the movement of carriers against the background of the localized Spins.

Resonance (Watanabe, *et al.*, 1987; Kitaoka, *et al.*, 1987; Kitaoka, *et al.*, 1989; Budnick, *et al.*, 1988) and neutron scattering Studies (Pinto, *et al.*, 1992), taken together suggest that the magnetic ordering becomes more and more short – ranged as the level of doping increases initially. For low level of doping, magnitude of the local moment is nearly unaffected but T_N is depressed rapidly. This depression of T_N is caused by the weakening of the effective magnetic interaction among the Cu – Spins rather than by a reduction in the magnetic moment itself. Spin-glass like magnetic behaviour is observed for certain level x of hole – doping before the sample becomes superconducting (Birgeneau and Shirane, 1989).

Doping of holes in other system leads to similar variations in the magnetic properties due to the Cu – moments. The system $YBa_2Cu_3O_{6+x}$ goes over from an antiferromagnetic to a superconducting state (Tranquada, Moudden, *et al.*, 1988) as x increases and holes are doped (T_c = 90 K). The magnetic ground state of $Bi_2Sr_2Ca_xY_{1-x}Cu_2O_y$ transforms into a superconducting sate as doping level x increases, T_c = 95 K for x = 1 (Tamegai and Iye, 1989). Tl based materials $TlSr_2Ca_xNd_{1-x}Cu_2O_y$ becomes superconducting for $x > 0.3$. Similarly, the material $TlBaLaCuO_5$ is insulating; Superconductivity is observed when La is partially replaced by divalent Ba – ions (Sundaresan, *et al.*, 1991).

Electrons can be doped only in materials RE_2CuO_4 (RE = Nd, Pr, Eu, Sm). Electrons are doped in these systems on substituting trivalent RE ions by tetravalent Ce/Th-ions. As doping level x is increased T_N (Cu) gets depressed and eventually superconductivity appears (Tokura, *et al.*, 1989; Takagi, *et al.*, 1987; Tokura, Torrance, *et al.*, 1989; James, *et al.*, 1989).

3.5 THE SUPERCONDUCTING STATE.

The unusual properties such as the linear behaviour of the d.c. resistivity with temperature, a Hall coefficient that is temperature dependent, the presence of short coherence lengths, etc., suggest that the normal state of the High – T_c cuprate oxide superconductors cannot be described by a Fermi liquid. However, the BCS or pairing theory is a broader concept and describes Fermions in which an effective attractive interaction produces a condensate, with large overlaps between pairs. The source of the attraction is not crucial for this theory to hold, and thus BCS ideas are not excluded as a possible explanation of the behaviour of the High-T_c superconductors.

3.5.1 **Pairing of charge carriers**

Gough *et al.* (1987) established pairing of charge carriers in high-T_c superconductivity, they showed that the flux Φ trapped in a ring of the ceramic high-T_c material $YBa_2Cu_3O_7$ at helium temperature, was quantized in units of $\phi_o = (0.97 \pm 0.4)hc/2e$. Koch *et al.*, (1987) obtained similar results. Keene *et al.*, (1989) demonstrated the quantization of flux in a composite ring containing sections of high-T_c and conventional superconductors.

Shapiro steps have been seen in high-T_c material (Yamashita *et al.*, 1987; Witt, 1988). Shapairo steps are voltage steps with a spacing $h\upsilon/2e$ (1 μV for 484 MHz) when exposed to a microwave radiation of frequency υ,. These are exhibited in the I – V characteristics of a Josephson tunnel junction

A microscopic probe which provides an evidence of pairing is the Andreev scattering (Andreev, 1964; Blonder *et al.*, 1982). van Bentum *et. al.*, (1989) and Ong,.
et al., (1989) observed Andreev reflection in single crystals of $YBa_2Cu_3O_7$.

Associated with pairing, there exists an energy gap Δ (k) in the superconducting state; a minimum energy Δ_{min} is required to break up a Cooper pair. No electronic excitations are possible for energies less than Δ_{min}. Many measurements (Batlogg, 1990; Annett, 1990) provide information on the magnitude and the T – dependence of the gap function Δ (k,T), using techniques such as tunneling spectroscopy, optical spectroscopy, photo-emission spectroscopy, Raman scattering, infrared reflectivity, low temperature specific heat, electromagnetic penetration depth and NMR and NQR spectroscopy.

Nuclear quadrupole/magnetic resonance and relaxation measurements (MacLaughlin, 1976) provide information about the characteristics of the normal state as well as the superconducting state. These studies have played a crucial role towards our understanding (Takigawa, 1992a; Takigawa, 1992b; Pines, 1991; Asayama *et al.*, 1991; Asayama, 1993) of the spin dynamics in the normal state and the nature of pairing in the superconducting state of high-T_c materials. Also, in many high-T_c superconductors, specific heat is observed to vary linearly with temperature as $T \rightarrow 0$ (Junod, 1990, Annett, *et al.*, 1990). One of the implications of this observation is that the gap function vanishes on certain regions of the Fermi surface.

From the above measurements, it follows that the energy gap in high-T_c super conductors is highly anisotropic and possibly has zero on the Fermi surface.

3.5.2 **Nature of Pairing**

The pair wave function $\psi(r_1, S_1, r_2, S_2)$ is anti-symmetric with respect to an exchange of two electrons in a cooper pair. Therefore there can be two types of pairing: those with S (= $S_1 + S_2$) = 0; Spin part anti-symmetric and orbital part symmetric (the relative angular momentum L and even integer) called the singlet pair wave functions and those with S = 1; Spin part symmetric and orbital part anti-symmetric (L an odd integer) called the triplet pair wave function. Note that the above classification is valid only if there is rotational symmetry in spin space, e.g., if we ignore spin-orbit coupling (Annet, *et al.*, 1990; Fulde, *et al.*, 1988). Conventional phonon-mediated attractive interaction lead to an S = 0, L = 0 (S-waves) pairing. In high-T_c superconductors, other models are considered, such as S = 0, L = 2 (*d*-wave, even parity) and S = 1, L = 1 (*p*-wave, odd-parity) of pairing.

Experimental data, from NMR Knight shift (KS) (MacLaughlin, 1976; Pennington and Slichter, 1990; Takigawa, *et al.*, 1989; Barrett, *et al.*, 1990; Alloul *et al.*, 1989). Temperature dependence of the penetration depth in high-T_c material, which support *s*-wave pairing (Batlogg, 1990; Batlogg, 1991), Temperature dependence of nuclear magnetic relaxation rate and its anisotropy (Takigawa, 1992a; Takigawa 1992b) favour very strongly *d*-wave pairing, all rule out odd-parity (*p*-wave) pairing.

Pan, *et al.* (2000) introduced a zinc into the copper site of a bismuth-strontium-calcium-copper oxide (BSCCO) superconductor and observed using a specially developed scanning tunnelling microscope (STM), (Hudson, *et al.* 1999), an image that provided visual confirmation of the d-wave nature of the electron pairing state in such materials (Levi, 2000).

3.5.3 **Fermi Surface in High-T_c Materials**

The Fermi surface is defined as the locus in momentum space where the occupation of the electronic states drops abruptly and where the energy required to create particle-hole excitations vanishes.

Pickett *et al.* (1992) have critically reviewed experimental results obtained using the three experimental techniques employed to measure Fermi surface in high-T_c superconductors, namely: de Haas-van Alphen effect (dHυA), angular correlation of annihilation radiation (ACAR) from positions annihilating electrons and the angle resolved (direct and inverse) photoelectron spectroscopy (ARPES and ARIPES, respectively), and emphasized that they are consistent with the band calculations which Krakauer *et al.* (1988) and Pickett, *et al.* (1990) have carried out in $YBa_2Cu_3O_7$. As is clear from the result, the topology of the surface is quite complicated. It is electron-like in some regions and hole-like in others (Hamada, 1992). Existence of Fermi surface implies that doping the parent Mott-Hubbard insulating and magnetic material weakens the charge transfer gap and transforms it into a band-metallic state.

Specific heat measurements (Junod, 1990) in the normal state suggest that the density of states N (E_F) at the Fermi level is rather small in high-T_c materials.

3.5.4. Coherence Length and Penetration Depth

Coherence length, which is a measure of the spatial extent of the cooper pairs, is highly anistropic (Cyrot and Pavuna, 1992). ξ_c (0)is much smaller than the thickness of the charge reservoir layer. Along the *c*-axis cooper pairs are confined between the immediately adjacent Cu-O planes and they extend only to a few unit cells in the *ab*-plane (Vijayaraghavan and Gupta, 1995). Therefore superconduction along the *c*-axis is essentially a tunneling process. Coherence lengths in three superconductors $YBaCu_3O_7$ (T_c = 90 K), $La_{2-x}Sr_xCuO_4$ (T_c = 38 K) and $Bi_2Sr_2Cu_3O_{10}$ (T_c = 110 K) are ξ_{ab} = 15 Å, 35 Å and 13 Å, and ξ_c = 4 Å, 7 Å and 2 Å respectively.

According to the BCS theory (de Gennes, 1989), $\xi_o = h\upsilon_F/\pi\Delta\,(o)$

The short coherence lengths are consistent with this relation as (i) the carrier density is small in these materials and therefore the Fermi velocity is small (~ 10^7 cm/sec.) and (ii) the energy gap is large, ~4 – 5 kT_c. Low carrier concentration and small coherence volume further imply that there are only a few Cooper pairs within the coherence volume.

Using the Ginzburg-Landau expression (Cyrot and Pavuna, 1992)

$\xi\,(T) \sim [T_c\,/\,(T_c - T)]^{1/2}$, for the temperature dependence of the coherence lengths, the temperature T^+ at which the coherence lengths, becomes equal to the thickness of charge reservoir layer is for $YBa_2Cu_3O_7$ ~ 70 K. The significance of this temperature is that superconductivity exhibits a crossover from a 3D behaviour at $T > T^+$, to a 2D behaviour $T < T^+$. In the case of Bi- and Tl - compounds, T^+ is very close to T_c. This is essentially due to the large separation between the two conducting layers, in these materials compared to that in $YBa_2Cu_3O_7$. Thus at low temperatures, Bi- and Tl- compounds can be approximated as a superconductor - insulator multi-layer structure with weak Josephson coupling between the superconducting planes.

Penetration depth λ, a characteristic length that governs the flux expulsion behaviour of superconductors have been measured using muon spin resonance, nuclear magnetic resonanes, magnetization of thin crystals and the inductance (due to sample) of a coil as a function of an applied magnetic, techniques. λ(T) is highly anisotropic and is very large as compared to the coherence length (Cyrot and Pavuna, 1992).

Temperature dependence of the penetration depth λ(T) has been measured, for example, in $YBaCu_3O_7$ (Fiory, *et al.*, 1988; Pumpin, *et al.*, 1989; Harshman, *et al.*, 1989). From the measured values of the penetration depth $\lambda(T)$ $[= (mc^2 / 4\pi n_s(T)e^2)^{1/2}]$, one obtains $n_s(T)$, the density of superconducting electrons in the superconducting state at a temperature T. Pines (1991) argued that a careful analysis of the penetration depth data has led to the conclusion that the data do not provide a convincing evidence for or against either S-wave or d-wave pairing, since the data was regarded to favour BCS theory and *s*-wave pairing.

3.6. THEORETICAL MODELS

This section, reviews some of the various models that have been proposed to understand the mechanism giving rise to superconductivity with transition temperature as high as 100 K or above. In section (3.5) it was stated that the central core of BCS theory is the pairing instability of the Fermi liquid in the presence of an attractive interaction, with the source of this interaction inconsequential. This implies that this theory, despite its several inadequacies as applied to high - T_c materials, is still employed as the mechanism of superconductivity. However, besides phonons, other bosonic excitations, such as magnetic and electronic excitations, may also provide essential attractive force among electrons to form Cooper pairs.

3.6.1. **Spin Fluctuations**

Experimental support as to the existence of antiferromagnetic fluctuations comes from NMR (Horvatic, *et al.*, 1993; Kitaoka, *et al.*, 1991; Rajarajan, *et al.*, 1992) and neutron scattering (Rossat-Mignod, 1993) measurements in underdoped samples. Spin fluctuations provide a very effective channel of nuclear relaxation in the normal as well as the superconducting state. Rajarajan *et al.*, (1992) carried one such study on $TlBa_{2-x}La_xCuO_y$. They found that the nuclear relaxation rate R(T) deviates from the high temperature behaviour below a certain temperature T* much higher than T_c. Further, there is no noticeable anomaly in R(T) across T_c. This has been interpreted to suggest, and has been corroborated by neutron studies (Rossat-Mignod, 1993) that (i) antiferromagnetic spin fluctuations are responsible for the nuclear relaxation (Beal-Monod *et al.*, 1986; Scalapino *et al.*, 1986; Miyake, *et al.*, 1986) and (ii) a gap develops in the low frequency region of their fluctuation spectrum at $T < T^*$ and causes R(T) to slow down below T*. T* is sensitive to the level of doping. *d*-wave pairing is the natural consequence of the attractive interaction mediated by antiferromagnetic spin fluctuations (Moriya *et al.*, 1992).

3.6.2. **Oxygen Holes and Copper Spins**

Various experiments suggest that carriers in Cu-O superconductors are located primarily on oxygen atoms, rather than in hybridized Cu (3d) oxygen (2p) anti-bonding bands as suggested by band theory. Tranquada *et al.*, (1987) find that pure La_2CuO_4 has the finger-print of the $Cu^{2+}(3d^9)$ ion, and does not evolve toward Cu^{3+} as carriers are introduced by Sr doping ($La_{2-x}Sr_xCuO_4$ with $0 \leq x \leq 0.2$). The oxygen 1*s* to 2*p* transitions have been explored by Nucker *et al.*, (1988) using electron energy-loss spectroscopy in $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-y}$. Their spectra seem to show a filled O (2p) - shell for values of *x*, *y* in the insulating region, but holes in this shell, roughly proportional to *x* and *y*, for conducing samples. This leads to the view that the Cu sublattice remains insulating with S = ½Cu(d^9) correlations even in samples, which are metallic. Long range antiferromagnetic (AF) order is lost, short-range spin order of some kind is presumed to remain.

Two models proposed which treat the oxygen holes as a conventional Fermi liquid and achieve BCS pairing by an attractive interaction caused by Cu spins, are the Birgeneau, Kastner, and Aharony (BKA, 1988) and Emery and Reiter (ER, 1988) models.

Birgeneau *et al.*, (1988) require that superconducting samples should exhibit fluctuation AF order with a correlation length of several planar Cu-Cu spacings. The BKA model says that the oxygen hole (carrying S = ½) tends strongly to orient its two neighbouring Cu spins into a S = 3/2 ferromagnetic cluster. A second such cluster of opposite S will then prefer to be close because the pair of clusters is less disruptive to fluctuating AF order than either one individually. The source of the ferromagnetic alignment energy is Hund's rule energy (from ordinary Coulomb exchange energy) which dominates over AF exchange because the oxygen hole is assumed to lie in a p_y-orbital (where x is the Cu-O-Cu bond axis and x–y is the CuO_2 plane). This orbital is orthogonal to Cu ($d_{x^2-y^2}$)) and the hopping matric element t vanishes by symmetry. The p_y-orbital is assigned the highest energy based on an electrostatic calculation (Guo *et al.,* 1988).

Emery and Reiter (1988) assign the oxygen hole to the p_x-orbital, which is favoured by antibonding covalency as in band theory. The ER mechanism is the enhanced Superexchange. The Cu-Cu exchange J is only partly given by t^2/U, because the hopping parameter t to go from Cu to Cu is small. Instead, the principal route is to hop indirectly via the intervening oxygen ion using a larger matrix element t'. The process which is fourth order, showed that the effect is bigger than the additive energy changes of two single oxygen satellite holes, and causes attraction of oxygen holes located at second neighbour sites. It was found that this interaction is more effective for anti-parallel spins and this favours singlet BCS pairing.

3.6.3. Theories that combine the pairing ideas with the presence of strong antiferromagnetic correlations.

3.6.3.a. The Spin-bag Theories

Schrieffer *et al.*, (1988, 1989) presented a detailed spin-bag approach to the high-temperature superconductivity. The general argument that the local suppression of the electronic pseudogap lead to an attractive interaction of the quasi-particles is substantiated by the detailed calculation of the pairing potential mediated by the collective modes of the spin-density-wave background. In the low-dopping limit, different shapes of the Fermi surface give rise to a superconducting gap which formally has d-wave or p-wave like symmetry, however the gap has no nodes on the Fermi surface. Therefore, the superconducing properties of the spin-bag model are analogous to those of a conventional *s*-wave (i.e., nodeless) BCS superconductors.

Kampf and Schrieffer (1990) observed the precursors of the split bands of the pseudogap in the electronic spectrum of doped high-T_c. superconductors, as "shadow bands" in angle resolved photoemission spectra.

3.6.3.b. Antiferromagnetic Fermi-liquid Theories

Millis, *et al.*, (1990) showed that a phenomenological model of a system of antiferromagnetically correlated spins give a good quantitative description of NMR, nuclear - quadrupole - resonance, and Knight - shift measurements on yttrium, planar copper, and planar oxygen sites in $YBa_2Cu_3O_7$. The antifermagnetic correlation length was estimated to be ~ 2.5 lattice constants at T = 100 K. The temperature dependence of the correlation length ceases at

$T_x \approx 100$ K. The enhancement of the observed relaxation rates over what is expected for weakly interacting electrons was shown to be large.

3.6.3.c. $d_{x^2-y^2}$ Theories

Bickers, *et al.*, (1989) developed a technique for investigating phase transitions and dynamics in interacting electron systems, this technique is based on the derivation and self-consistent solution of infinite-order conserving approximation. It provides an approach to the study of two-particle correlations with strong frequency and momentum dependence. Bickers *et al.*, (1989) used this technique to derive a low-temperature phase diagram and dynamic correlation functions for the two-dimensional Hubbard model.

Monthoux, *et al.*, (1991) showed that the retarded interaction between quasi particles on a 2D square lattice induced by the exchange of antiferromagnetic paramagnons leads uniquely to a transition to a superconducting state with $d_{x^2-y^2}$ symmetry. With a spin-excitation spectrum and a quasiparticle paramagnon coupling determined by fits to normal state experiments, Monthoux, *et al.*, (1991) obtained high transition temperatures and energy-gap behaviour comparable to those measured for $YBa_2Cu_3O_7$, $YBa_2Cu_3O_{6.63}$, and $La_{1.85}Sr_{0.15}CuO_4$.

3.6.3.d. van Hove Singularity Scenario

Markiewicz (1991) describes a Fermi liquid picture of high-T_c superconductivity in which a density of states (dos) peak associated with the CuO_2- plane van Hove singularity causes a peak in T_c as a function of hole doping. Strong correlation effects drive a Mott transition a half-filling. For intermediate doping, the electronic system is unstable against phase separation, with one phase near the insulating state, the other near the T_c peak.

The large density of states leads to competition between superconductivity and structural instability, in analogy with the A15 compounds. The superconductivity appears to be driven by strong electron phonon coupling, enhanced by fluctuation effects (Markiewicz, 1991). Newns, *et al.*, (1991) found that the Fermi level, of the realistic $U = \infty$ models for oxide superconductor solved in slave-boson mean-field approximation, lie very close to the nearly logarthmic van Hove singularity in the density of states over a substantial range of doping. This makes it possible without large Fermi liquid parameters to reconcile the light mass found in photoemission experiments with the high density of states deduced from thermodynamic data.

Pattnaik *et al.*, (1992) found that provided the Fermi level lies near the van Hove singularity in the quasi-two dimensional band structure, a large life time broadening from electron scattering, with the characteristic linear dependence on energy from the Fermi energy seen in high-temperature superconductor is obtained.

3.6.3.e. **Hole Mechanisms**

Hirsch and Marsiglio (1989) studied within BCS theory the properties of an effective Hamiltonian to describe conduction by holes through an oxygen anion network. The Hamiltonian contains an on-site repulsive interaction U_p and a modulated hopping interaction Δt that yields a larger hopping amplitude sites when other holes are present on those sites. The superconducting state was found to be *s*-wave with an energy dependent gap. Superconductivity is restricted to low hole densities and the critical temperature increases with the hopping amplitude. The particular form of the interaction allow for superconductivity even in the presence of large Coulomb repulsion, up to $U_p/\Delta t = 30$. This model provides a natural explanation for the spread in gap values observed in different experiments, for the observed broadening of the resistive transition in a field, and for the observed superconducting glass behaviour.

3.6.3.f. **Nested Fermi Liquid Theory**

The susceptibility and quasiparticle self-energy are found to exhibit anomalous behaviour in nested Fermi liquid (NFL) systems (Virosztek and Ruvalds, 1990) that have nearly parallel sections of the Fermi surface. Electron - electron scattering yields damping much stronger than the conventional electron-gas result and predicts a linear temperature variation of the resistivity. Virosztek and Ruvalds (1990) calculated the susceptibility $\chi_{NFL}(\bar{q}, \omega)$ for nested fermions at $\bar{q} = \bar{Q}$, where $\bar{Q}$ is a typical nesting wave vector. The NFL susceptibility is linear in frequency up to a cross-over region near $\omega \approx 4T$ where a saturation to a constant value occurs. The above features, as well as various theoretical constraints, are highly sensitive to the strength of the electron-electron coupling and to the degree of nesting.

3.6.4 **Non-BCS Based Theories**

3.6.4.a. **Bipolarons**

The solution of the Cooper (1956) problem in the dilute limit showed that electrons form mobile bound pairs provided the attractive interaction is strong enough to support a bound state (which requires a critical strength in three dimensions). The <u>bipolaron</u> is such a mobile bound pair of electrons, bound by electron phonon interactions. Chakraverty and Schlenker (1976) showed that the metal-insulator transitions seen in Ti_4O_7 at 140 K and 150 K could be described as bipolaric. Specifically it is assumed that as T is reduced, Ti atoms form dimers of Ti^{3+}. At 150 K the dimers form in a disorganized, liquid form, and at 140 K these pre-formed dimers crystallized into a relatively normal insulating phase. In the "liquid" phase between 140 and 150 K one has pairs of electrons bound to pairs of Ti^{3+}- ions and free to move by breaking bonds and forming new ones neighbouring undimerized Ti^{4+} atoms which then form new dimer bonds. Chakraverty (1979) proposed that in the liquid state the bipolarons could Bose condense to form a new kind of superconductor.

Leggett (1980) worked out a model showing the crossover from BCS condensation to Bose condensation of molecular pairs. A case closely related both to Ti_4O_7 and to CuO-based superconductors is $Ba(Pb_{1-x}Bi_x)O_3$ which is insulating when $x > 0.35$ and superconducting for $x < 0.35$ with a high $T_c \sim 15$ K occurring close to the phase boundary. Rice and Sneddon (1981) proposed that the superconducting phase was normal BCS and electron-phonon driven, but with increasing x and increasing electron-phonon coupling, "real-space pairing" took over and created an insulator. The real-space pairs are hypothesized to consist of pairs of electrons bound to pair of Bi atoms making Bi^{3+} - Bi^{5+} frozen dimers, i.e. another kind of bipolaronic crystal. Scalapino *et al.*, (1987) argue that CuO-based superconductivity may be electron - phonon driven, and on the border between bipolaronic and BCS like.

A related notion is the Anderson (1975) "negative-U center", an isolated but immobile bipolaron. Simanek (1979) and Ting *et al.*, (1980) suggested that if the bond sites proposed by the above idea, occurred in a superconducting metal, T_c would be enhanced by the additional binding available if cooper pairs temporarily fell into negative-U centres. Schuttler *et al.*, (1987) claim to have made some progress by numerical methods and to verify that the enhancement is significant.

Gyorffy *et al.*, (1991) found that, unlike the case of the BCS solution, the formation of pairs and their condensation into a superconducting ground state take place at two different temperatures. They calculated the condensation temperature T_c for all U and discussed the nature of the normal state, which, for large enough U, features a macroscopically large number of pairs. They argued that the model has relevance for high - T_c superconductors.

3.6.4b. **Resonating Valence Bond (RVB) Theory**

The best evidence that superconductivity in CuO based superconductors has something to do with the Hubbard model comes from diffraction experiments showing ordered antiferromagnetism in La_2CuO_4 (Vaknin *et al.*, 1987) and $YBa_2Cu_3O_{6+x}$ (Tranquada *et al.*, 1988). Anderson (1987) claimed that the version of the Hubbard Hypothesis which generates "strong" superconductivity, by first condensing into a new state (Allen, 1990; Hubbard, 1963; 1964) is a "resonating valence bond" (RVB) state. This new state is not a conventional Fermi liquid, so the low T superconducting condensate is not conventional BCS.

According to RVB theory (Anderson, 1987), for insulating La_2CuO_4, neighbouring spins combine to form a spin-paired singlet and the ground state of the system is a coherent super-position of these singlet spin-paired bonds extending over all the pairs of bonds.

3.6.4c. **Anyon Superconductivity**

Chen, *et al.*, (1989) suggested the Anyon theory as possible mechanism of high T_c superconductivity. This suggestion is based on the proposal that the ground state of the frustrated Heisenberg antiferromagnet in two dimensions, which is considered to be a good starting point for high T_c, may be similar to the ground state of an anyon gas (which is a charged superfluid, i.e. a superconductor) (Wilczek, 1991).

CHAPTER FOUR

4.0 APPLICATIONS OF HIGH - T_c SUPERCONDUCTORS

4.1. INTRODUCTION

All electronic should be done at room temperature. The only reason for going to cryogenic temperature is in order to achieve high performance. Traditionally, this label is characterized by very high switching speed (or bandwidth), small size, low electrical power and reliability. These attributes have long been ascribed to superconductive electronics. The first attempt is attributable to Dudley Buck (1956) for the invention of the cryotron switching device for digital computing. This device was demonstrated to work, was later modified and developed into a "manufacturable" form, thus becoming an incipient "technology". As it was being pursued, its advantages were gradually overtaken and overwhelmed by semiconductor technology until the cryotron disappeared from view. Its inherent speed limitations were demolished by the discovery of superconductive tunneling, quasi-particle and coherent (Josephson, 1962; Giaever, 1960), which launched a major attempt to evaluate devices, which exploited these phenomena and then create a technology. Along the way, remarkably high-quality fabrication processes were developed which have allowed very high performance special function electronics to be built: millimeter wave mixers, detectors, amplifiers; picosecond sampling circuit; ultra-precise voltage standards; very sensitive magnetometers; dispersive delay lines and possibly low-power linear A/D converters. Now, with the discovery of "High Temperature Superconductivity" by Bednorz and Muller (1986) and the follow-up work by Chu *et al* (1987), Maeda et *al* (1988), Herman *et al.* (1988), it appears that there is a new opportunity to insert superconductivity into electronic systems, i.e., make it a technology.

4.2 CRYOTRON

The first superconductive electronic switching device for a large application area was induced by Buck (1956) with his invention of the wire-wound cryotron. In this device, the switching was produced by using the magnetic field suppression of superconductivity; the application was in digital computing. The basic operation is straight forward (Fig.4.1). Current inserted into coil A produces a magnetic field within the coil which is sufficient to quench the superconductivity of the "gate" wire, but yet not large enough to cause the driving coil itself to become resistive. This can be accomplished by the proper choice of materials and operating temperature; in the original case the coil was made of niobium (T_c = 9.3 K) and the gate of tantalum (T_c = 4.3K). This control drive current results in all the gate current being shunted to the path controlled by coil B. If these branched lines are themselves electrically connected to coils, then the current steered can be used to control other current paths and thereby one can carry out logical operations such as "OR", "AND". In addition, if the devices are connected as in (Fig.4.2), a memory cell can be made. The input current I_g divides equally between the two legs, since their inductances are the same. Control current into coil A will cause I_g to transfer into the left leg with an L/R time constant. Upon removal of A (first), then I_g, a persistent circulating current is set up, CCW. To "read", one simply reapplies I_g and reads the resistive/superconductive state of sensor R; in this case, with no current through the right leg of the cell, R will be superconductive. Clearly, had coil B been driven at the start, R would be resistive in the read-out state. Notice that there is no power dissipated in the standby state and also that the persistent current will be maintained in the memory loop indefinitely and not be affected by repeated "read-out".

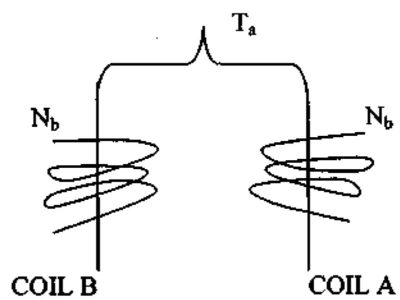

Fig 4.1: Wire Wound Cryotron

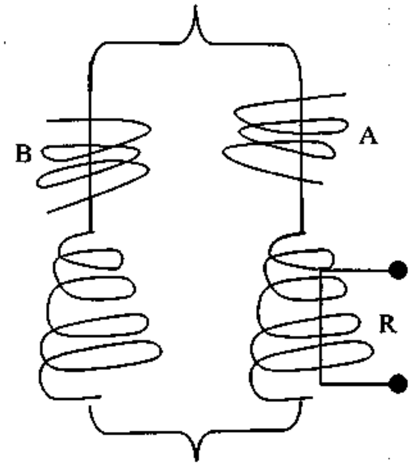

Fig 4.2: Cryotron Memory Cell

For reasons of device and circuit speed and for credibility in large scale fabrication of these devices, A proposal was made (Bremer, 1962) to change the structure from a wire-wound device to a thin film one. The basic concept of the current switch stayed unchanged, but was implemented with a "cross film" control line and gate. The electrical changes were significant, and the performance changes were likewise large.

The attractions of current gain, non-latching behaviour, and speed "offered" by the cryotron device using high T_c materials are as yet not available (Bedard, 1990).

4.3. JOSEPHSON DEVICE

The speed performance limitation which the cryotron device encountered was demolished with the discovery of superconductive Josephson tunnelling (Josephson, 1962; Giaever, 1960).

4.3.1. **Josephson Superconductive Tunnelling**

Josephson (1962) pointed out that the tunnelling current between two superconductors contains, in addition to the ordinary single-particle tunnelling terms, previously neglected contributions due to the tunnelling of Cooper pairs.

At a voltage V applied across the junction there occurs, in addition to the usual dc current, an ac supercurrent of frequency 2 $eV/\hbar$ with an amplitude J_o proportional to an effective matrix element for pair transfer; at zero applied voltage, there occurs a dc supercurrent of up to a maximum of J_o. Theoretically, the value of J is equal to the current flowing in the normal state at a voltage of $\pi/2$ times the energy gap.

Anderson (1963) pointed out that the tunnelling of Cooper pairs gives rise to a coupling of the phases of the superconducting wave functions on the two sides of the junction.

The coupling energy depends on the relative phase (Josephson, 1964) in the form

$$E = -(h/2e)\, J_o \cos\phi \quad \text{.........} 4.3.1a$$

Assocaited with E (ϕ) is the dc Josephson current

$$J = (2e/h)\frac{\partial E}{\partial \phi} = J_o \sin\phi \quad \text{.........} 4.3.1b$$

The ac properties are determined by an equation of motion relating the rate of phase change to the applied voltage V,

$$\frac{d\phi}{dt} = 2eV/\hbar \quad \text{.........} 4.3.1c$$

At constant voltage, V_o,

$$\phi = \frac{2eV_o t}{\hbar} + constant\,(\phi_o) \quad \text{.........} 4.3.1d$$

The ac Josephson current flowing through the junction is

$$J = J_o \sin\phi = J_o \sin\left[\frac{2eV_o t}{\hbar} + \phi_o\right] \qquad \text{4.3.1e}$$

where , $\frac{2eV_o}{\hbar} = \omega$, the frequency of current oscillations.

Devices derived from the Josephson superconductive tunnelling are fabricated from superconducting ring containing a weak-link. Weak links can be formed as thin insulating layers between two superconducting surfaces (an SIS junctions), across a thin normal region between two superconductors (an SNS or proximity junction), across a narrow constriction on a superconducting path (a microbridge) or across a junction made by pressing a superconducting point onto another superconductor (a point contact junction).

The first weak link to be fabricated is the SIS tunnelling device. This device does not have the speed performance limitation of the cryotron device. The detailed behaviour of the device is based on the model created by Stewart (1968) and McCumber (1968).

The Josephson device is the international standard for defining the volt; 2eV = h, where 1 V (DC) applied to a Josephson junction produces a current oscillation in the junction at a frequency of 483.59 MHz. The existence of these oscillations had been inferred very early in superconductive tunnelling research as very prominent steps (Shapiro steps) in the I-V curves of the junctions which were illuminated by microwaves (Shapiro *et al.*, 1964).

4.4. SUPERCONDUCTING QUANTUM INTERFERENCE DEVICE (SQUID)

For many applications the single Josephson junction is used shunted by an inductor to form a SQUID.

The current through the junction of a superconducting ring containing a weak link is often well described by the Josephson current phase relationship (e.g. 4.3.1b). Where J_o is the maximum supercurrent that the weak-link can support and $\phi = (\phi_1 - \phi_2)$ is the phase difference of the superconducting wave function across the weak-link. If a current path is taken well inside the bulk of the superconductor on either side of the junction, continuity of the phase of the superconducting wave function requires that $2n\pi = -\phi + 2\pi\Phi/\Phi_o$, where Φ is the magnetic flux.

The circulating supercurrent can therefore be expressed as $J = J_o \sin \pi\Phi/\Phi_o$. In the absence of an applied field, the flux within the ring is determined by the circulating current, $\Phi = LJ$ (where L is the ring inductance) so that $\Phi = LJ_o \sin 2\pi\Phi/\Phi_o$. The magnetic behaviour of such a ring is determined by the parameter $\beta = 2\pi LJ_o/\Phi_o$.

A weak-link ring can be biased by an externally applied flux Φ_{ext} as produced by a current carrying coil within the ring. The diamagnetic induced shielding current is then given by $(\Phi - \Phi_{ext})/L$. The flux within the ring is then given by $\Phi_{ext} = \Phi + LJ_o \sin(2\pi\Phi/\Phi_o)$.

4.4.1. rf SQUID

The single junction SQUID device has been used very effectively for years as an ultra-high sensitivity magnetometer; it has been the standard against which all magnetometers are measured (Bedard, 1990). The SQUID operates by measuring the hysteretic magnetic energy loses induced when a resonant LC - tank circuit is magnetically coupled to a superconducting ring containing a weak link.

Energy is fed into the resonating tank-circuit through a large resistance, so that the oscillating magnetic field within the rf coil builds up in time. As soon as the magnetic field generated is sufficient to induce a hysteretic transition energy is lost and the stored rf energy is decreased to below that necessary to give hysteresis. The process repeats itself indefinitely so that for a given rf charging current, the rf voltage across the LC circuit assumes an averaged steady value.

In the peak rf voltage across the tank circuit as a function of rf bias current, the first knee occurs when the bias current is just sufficient to take the loop round a single hysteresis loop. On increasing the charging current, the voltage remains nearly constant but the charging rate between hysteresis is decreased. Eventually, one hysteresis loop is traversed every rf cycle, so that further increase of the charging current simply increases the stored energy until the amplitude is sufficient to include 2 transitions/cycle, where upon another plateau in the voltage output is reached (Gough, 1990).

The first successful realisation of rf SQUID behaviour was performed with point contact structures (Silver and Zimmermann, 1965). The SQUID device is also used effectivelv to quantize an analog signal (Hurrell *et al.*, 1980).

4.4.2. DC SQUID

The supercurrent, through a superconducting ring containing two weak-links in parallel, divides along the two paths with the current in each path determined by the phase differences, ϕ_1 and ϕ_2, across the weak-links. The total current assuming identical strength junctions is then given by $I_c[\sin\theta_1 + \sin\theta_2]$. The total current through the ring is given as $2I_c \cos(\pi\Phi/\Phi_o) \sin(\phi_1 + \phi_2)/2$, where Φ is the sum of any flux applied externally plus the flux produced by any supercurrents encircling the ring.

$2I_c \left|\cos\pi\Phi/\Phi_o\right|$ is the maximum supercurrent that can be passed through the ring, which is periodic in Φ_o.

The first evaluation and use of this two-junction configuration was in the design of logic circuitry. It was noted by Zappe (1977) that the conventional Josephson logic device, the magnetically coupled Josephson junction, suffered from being a low impedance device. The junction capacitance presented such a low reactance for high-speed pulses that the loading transmission lines would have to be of very low impedance. A transmission line of such a low impedance would result in extremely slow signal propagation and be too wide for high density microelectronics use. Consequently, one needed a higher impedance switch, which the double weak-link superconducting SQUID provided. A complete logic family evolved from this basic element (Gheewala, 1980) as an example of the versatility of the two junction SQUID.

An unbalanced "interferometer" SQUID was created by Gheewala (1980). This device offered a sizeable transfer of gate current for a given change in control current as well as an operating region to allow for process parameter variances. The basic two-junction SQUID configuration was modified and enhanced by Kotani (1986) in his modified variable Threshold Logic (MVTL) gate design.

The depence of critical current on enclosed flux provides the basic of operation of the DC SQUID magnetometer (Jaklevic *et al.*, 1964; Clarke *et al.*, 1976; Barone and Paterno, 1982; van Duzer and Turner, 1981). DC SQUIDs fabricated from conventional superconductor thin films operating at liquid helium temperatures are by far the most sensitive magnetometers available (Nisenoff, 1988). The sensitivity is sufficient to monitor the miniscule magnetic fields produced by neurological signals inside the brain.

4.5. HIGH-TEMPERATURE SQUIDs

4.5.1. rf and DC SQUIDS

The first observation of rf SQUID behaviour in HT_C superconductors was made by Colclough *et al.*, (1987) using bulk material, where the weak-link rings were the naturally occurring weak-link loops between the grains of the sintered material. The distribution in size of the intergranular supercurrent loops resulted in a quasi-periodic field dependence of the SQUID output with contributions from a number of triangular dependence of different periodicities but with an average field "periodicity" given by Φ_o / A, where A is an effective average area of the intergranular current loops. Similar quasi-periodic field dependence were subsequently observed in the V/I characteristics of a thinned down section of YBCO (Robbes *et al.*, 1988).

SQUID magnetometry has been identified as one of the most likely early applications of HT_c superconductors. Koch, (1989) fabricated a dc SQUID using a Tl-based HT_c film. The noise performance of one such SQUID at liquid nitrogen temperatures was shown to exceed the performance of commercially available hybrid rf SQUIDs. Face *et al.* (1990) used Bi-Sr-Ca-Cu-O thin films to produce thin-film dc SQUIDs. The best SQUID which operated up to 75 K, had an inside loop diameter of $\approx$18 μm and an estimated loop inductance of 30 pH. The detailed noise measurements reported for this SQUID are the first for any Bi-Sr-Ca-Cu-O based SQUID. A dc SQUID was fabricated on an amorphous Y-Ba-Cu-O film. The SQUID showed periodic and symmetric behaviour in the voltage versus magnetic flux curves (Goto *et al.*, 1991; Romaine *et al.*, 1991; Lee *et al.*,1991). Xu *et al.*, (1991) fabricated dc SQUIDs using a Pb-doped BiSrCaCuO superconducting thin film made by mixed evaporation of a single source composed of related components with a resistance heater. These SQUIDs showed perfectly periodic voltage-flux characteristics without magnetic shield. Xu *et al.*, (1991) found out that one of the SQUIDs still was able to operate on flux-locked mode without bias currents and showed voltage flux second harmonic characteristics.

Progress on HT_c rf SQUIDs was rather more immediate. Zirmmermann *et al.*, (1987) was the first to realise an rf SQUID fabricated out of bulk YBCO, which operated at liquid nitrogen temperature. In this device the weak-link was formed by what is known as a break-junction.

In an attempt to circumvent the lack of mechanical and thermal stability of such a structure, Harrop *et al.*, (1988) devised a 2 hole structure with a very small connecting region. The interconnecting region was mechanically filed down to provide a weak-link of the appropriate strength for currents circulating the two holes.

Zhang and Heiden (1990) made Bulk $YBa_2Cu_3O_{7-y}$ rf SQUIDs using different topologies, e.g., two-hole gradiometer type geometry and quasi-toroidal arrangement. Performance tests made with emphasis on the noise behaviour are reproducible at frequencies > 100 Hz. Blinov *et al.* (1992) developed an rf SQUID based on a lead-doped high-T_c superconducting BSCCO ceramic. A comparison of the noise characteristics of this SQUID with those of a YBCO SQUIDs showed that it has excess noise in the low-frequency region.

4.6. OTHER DEVICES

4.6.1. Binary Counter

Hurrell and Silver (1978) proposed and Hamilton (1983) demonstrated that the two-junction SQUID could be used as pulse counting for both the voltage-frequency and flux counting analog/digital converters. The SQUID is biased leading to a very fast binary counter behaviour. Faris (1980) verified the low-speed counting and reading. Preliminary measurements which have scaled the output voltage of a series of such binary stages versus the input current have verified that a factor of two voltage reduction is achieved per stage, consistent with proper operation (Hamilton, 1983).

4.6.2. Sampling Oscilloscope

The most striking demonstration of the speed and timing stability of a Josephson device is given by its use as a gate for a sampling oscilloscope. The original circuit (Faris, 1980; Tuckerman, 1980) was motivated by the need to verify and characterize the operation of Josephson junction logic gates. Connecting room temperature probes not only disturbed the circuits but also presented great difficulty in measuring the low voltage fast rise-time waveforms. Two basic circuit elements are required for the function. The first is a very fast pulser, and the second is essentially an "AND" gate which sums the pulse with the analog wave form and external bias current (Wolf, 1985; Wolf *et al.*, 1985).

The time and amplitude stability of the pulser, stability of the AND gates current operating point, as well as the time stability of the experiment pulser time differences, are such that 5 picoseconds sampling resolution is available in a commercial instrument and 2.1 picoseconds has been demonstrated in the laboratory (Wolf, 1985).

Some of the anticipated benefits that can be obtained using HTS in this sampling circuit are: first, if the room temperature-to-low temperature transmission line could be made with these materials, greater band widths might result. Second, if a Josephson tunnel junction were available with the expected much larger energy gap this would translate into an intrinsically faster device (Bedard, 1990).

4.6.3. Transmission Line

In all high-frequency, high-performance applications of superconductive devices, there is a requirement to transfer signals from one point to another. A unique important advantage of superconductivity is the prospect of doing this via transmission lines of very high bandwidth, which have exceptionally low loss and dispersion. In addition, this seems feasible for physically small and closely packed configurations, which normally would result in unacceptable levels of cross-talk between the lines. Finally, because of these features one can even build long delay lines and deliberately coupled lines in order to perform some important signal processing functions (Bedard, 1990).

A conventional normal-metal delay line is characterized by the usual inductances and capacitance per unit length, with dissipative terms due to the resistance of the line and its return path (ground) plane along with the dissipation of the dielectric medium.

In a superconductor the London penetration depth allows the surface current to descend into the superconductor to a finite depth, on the order of 400 Å for Pb, 600 Å for Nb to 2000 Å for NbN. The new high temperature superconductors have a London penetration depth which is anisotropic, roughly 400 Å in one orientation and 3000 Å in the orthogonal direction. Within this region any electric field associated with the alternating currents will succeed in accelerating the normal electrons and hence result in losses which will increase with frequency. Hence the line will indeed not be lossless, but nevertheless will still have impressively low losses. Another aspect is that the superconducting electrons, lossless, will themselves be accelerated and decelerated by the driving source. Thus, in addition to the magnetic field, and hence stored energy, created by the current, there will be a kinetic energy stored by these electrons. As a consequence, the effective inductance/length will be increased which may significantly alter the impedance and delay characteristics of the line.

The Meissner effect makes an important contribution to the transmission line behaviour in "expelling" magnetic fields from the conductor. The magnetic field distribution between the transmission line and ground plane achieved a high value which is very localized (Zappe, 1983) and is practically frequency independent. The result is to produce a frequency independent phase velocity and a very low inductive coupling between adjacent lines. The latter point permits very close line spacing with consequent small "cross-talk".

The current density requirement in such transmission lines depends upon both the driving voltage level and the desired line characteristic impedance. For low T_c Josephson junction circuits with voltage levels in the 30 - 10 mV range and line impedances of 1-10 Ω the current density is not stressed.

High T_c materials are being evaluated for possible use as interconnection lines between semiconductor chips which are already cooled to cryogenic temperatures for performance reasons: lower noise in the case of receivers, higher speed and higher reliability for digital systems.

One of the most striking and useful exploitation of transmission lines is the development of long dispersive delay lines carried out by Lincoln Laboratories. They construct two spaced transmission lines on the same substrate with a lateral separation which is carefully controlled by the lithography (Ralston, 1985). At selected positions the lines are brought close enough together to cause the driven line to couple energy into the second line. Constructing this coupling section to be a quarter wavelength long results in the maximum transfer of voltage to occur at that frequency. These "taps" are usually chosen so that lower frequency ones are positioned further down the line than those corresponding to higher frequencies. Thus, an input frequency spectrum can be linearly time delay in its passage through the input - output transmission lines. If the input spectrum is itself linearly swept in time with the lowest frequency first such that the time spread matches the time dispersion of the line, an out-put compressed pulse will appear (Bedard, 1990). The line length and its quality determine the frequency resolution and band width of the device.

In considering applications for high temperature superconductors such "chirp transform" filters are very attractive candidates. They require no active superconductive devices, only high quality lithographically determined films with a very low loss at GHz frequencies (Berdard, 1990).

4.6.4. Magnetic Levitation Devices

One of the most fascinating demonstrations of superconductivity is the levitation of a superconducting particle over a magnet (or vice versa). Typically this is done by dropping a particle of one of the high temperature materials in a dish of liquid nitrogen, with a magnet underneath, and watching the particle jump and hover above the magnet when the temperature drops below T_c. In fact one can arrange the system so that the particle jumps out of the liquid nitrogen, warms above T_c drops back onto the magnet, and then repeats the cycle (Lynn, 1990).

Chang *et al.*, (1990; Riise *et al*, 1992; Hull, *et al.*, 1994) measured the Levitation forces between a small permanent magnet and a disk of bulk high-temperature superconductor at 77 K as a function of vertical separation for disks of composition Y-Ba-Cu-O, Ag/ Y-Ba-Cu-O, (Pb, Bi)-Sr-Ca-Cu-O, and Tl-Ba-Ca-Cu-Cu-O. The forces were highly hysteretic; however, for all samples, on the initial descent of the magnet toward the disk, the force was unique, independent of magnet speed, and varied approximately as the negative exponential of the separation distance.

High-T_c superconducting levitation motor have been developed, Weeks (1991) improved and extend this motor with an optical commutator. The primary extension is the development of a heat exchanger that permits high - T_c superconductors to be cooled with liquid nitrogen to 77 K and below in vacuums of 10^{-5} Torr and less. This permits the levitation motor to be operated without the decelerating force of atmospheric drag.

CHAPTER FIVE

5.0 DATA/EVALUATION OF DATA

5.1. METHODOLOGY

The phenomenological theory of cuprate superconductivity developed by Rabinowitz and McMullen (1993) is based on two criteria used to calculate the superconducting transition temperature of known superconductors. One is that the quantum wavelength is of the order of the electron-pair spacing. The other is that a fraction of the normal carriers exists as cooper pairs at T_c.

All known superconductors meet two conditions. One is the existence of bosons. The other is a condensation in momentum space. These led to a consideration that there may be temperatures: T_p, the pairing temperature to form bosons out of fermion pair; and the condensation temperature T_C. If $T_p \leq T_C$ then T_p is the limiting temperature, that is, the transition temperature T_c. However, the difficulty encountered when calculating T_p led Rabinowitz (1987,1988,1989[a], 1989[b], 1990) to consider three possibilities:

(1) That T_c might be less than or equal to T_p in which case $T_c = T_C$.

(2) That a fraction of fermions ~ $k_\beta T_c / E_F$ are incipient cooper pairs at T_c.

(3) Reduced dimensionality effects properly enter into the de Broglie wavelength, λ via the equipartition principle.

To avoid the difficult calculations encountered when the nature of the interaction is known, and which are impossible to do when the pairing interaction is not known, Rabinowitz and McMullen (1993) adopted the point of view that as the temperature is decreased in a gas similar to a Bose - Einsten (BE) gas, particle should start a BE type condensation into the superconducting state when the de Broglie wavelength is of the order of the interparticle spacing for the fraction of carriers that have become cooper pairs (Rabinowitz, 1987; Rabinowitz, 1988; Rabinowitz, 1989a, Rabinowitz, 1989b; Rabinowitz, 1990; Rabinowitz, 1993a; Rabinowitz, 1993b).

The assumption is that a BE type condensation in three dimensions of the free Bose gas involves electron pairs within a shell of energy ~ $k_\beta T_c$ around the Fermi energy, E_F. The number of electrons involved is the number of k values within a shell Δk of energy width $\Delta k T_c$ within the Fermi surface, so that Δk is given by:

$$k_\beta T_c \cong \frac{\hbar^2 k_F^2}{2m} - \frac{\hbar^2 (k_F - \Delta k)^2}{2m} \qquad 5.1$$

where $\hbar$ (h/2π) Planck's constant

k_β is the Boltzmann constant

T_c is the transition temperature

k is the wave vector, and

m is the effective mass of the electron.

Eqn. (5.1) is approximated to:

$$\frac{\Delta k}{k_f} = \frac{k_\beta T_c}{2\left[(\hbar^2/2m)k_F^2\right]} = \frac{k_\beta T_c}{2E_F} \qquad 5.2$$

where $\quad E_F = \dfrac{\hbar^2}{2m} k_F^2 = Fermi\ energy$

The number density of Cooper pairs for a roughly spherical Fermi surface is then

$$n_B = \frac{1}{2} \frac{\Delta k (4\pi k_F^2)}{\frac{4}{3}\pi k_F^3} n = \frac{3\Delta k}{2k_F} n \qquad 5.3$$

Combining Eqns. 5.2 and 5.3, we have,

$$n_B = \frac{3k_B T_C}{4E_F} n \qquad 5.4$$

For some less anisotropic materials Rabinowitz and McMullen (1993) introduced a three dimensional transition temperature, T_{c3}, which is assumed as providing the energy cut off that selects the effective bosons. Thus Eqn. 5.4 becomes

$$n_B = \frac{3k_B T_{C3}}{4E_F} n \qquad 5.5$$

T_{c3} is used to determine the interboson spacing in order to calculate T_{c2}, which is taken as the transition temperature estimate for the cuprates. The choice of two dimensional motion for the cuprates is based on their layered structure and highly anisotropic normal state properties.

Two electron pairs are encompassed by (½)λ when

$$\lambda = 2(n_B)^{-\frac{1}{3}} \qquad 5.6$$

For a pair of electrons of effective mass, $2m$, momentum P, and kinetic energy $(f/2)k_B$T, the de Broglie wavelength is:

$$\lambda = \frac{h}{P} = \frac{h}{\{2(2m)[(f/2)k_B T_c]\}^{\frac{1}{2}}} \qquad 5.7$$

where f is the number of degrees of freedom per particle, and

$$P = \sqrt{2(2m)[(f/2)k_B T_c}$$

For three-dimensional motion of the bosons, $f = 3$. For two-dimensional motion, $f = 2$ (Rabinowitz, 1989a). Combining Eqns. (5.5) and (5.6), we obtain,

$$T_c = 102.0883h^2 \Big/ 2mk_\beta n^{1/3}\lambda^3$$

Substituting for λ from Eqn. (5.7) we have,

$$T_c = \frac{(5.9037)}{f^3}\left\{\frac{h^2 n^{2/3}}{2mk_\beta}\right\} \qquad 5.8$$

For the three-dimensional case, $f = 3$. Hence,

$$T_{C3} = 0.2187\left(\frac{h^2 n^{2/3}}{2mk_\beta}\right) \qquad 5.9$$

To obtain the two-dimensional transition temperature, λ as given by eqn. (5.6) is equated to λ as given by eqn. (5.7) with $f = 2$, as we restrict the kinetic energy to two dimensions by the equipartition of energy principle. This yields the two-dimensional transition temperature.

$$T_{C2} = 0.328\left(\frac{h^2 n^{2/3}}{2mk_\beta}\right) \qquad 5.10$$

5.2. COMPARISON OF EXPERIMENTAL AND CALCULATED VALUES OF T_{C3} AND T_{C2} TRANSITION TEMPERATURES

Table 5.1 shows a comparison of the experimentally observed transition temperatures with T_{c3} and T_{c2}, together with the relevant input data as obtained from Harshman and Mills (1992). Rabinowitz and McMullen (1993) calculated T_{c2} for compounds 1-12 in the table, while we calculated T_{c3} for all the compounds shown and T_{c2} for compounds 13-19.

Table 5.1: Comparison of experimental and calculated values of T_{c3} and T_{c2} transition temperatures

No	Compound	T_{exp} (K)	T_{c3}	T_{c2}	$n/10^{21}/m^3$	m/m_o
1	$La_{1.9}Sr_{0.1}CuO_4$	**33**	30.4	45.8*	0.5	2.0
2	$La_{1.875}Sr_{0.125}CuO_4$	36	37.2	55.9*	1.0	2.6
3	$La_{1.85}Sr_{0.15}CuO_4$	**39**	33.7	50.7*	5.2	8.6
4	$Yba_2Cu_3O_{6.67}$	**60**	39.6	59.6*	1.1	2.6
5	$Yba_2Cu_3O_7$	**92**	53.0	79.8*	16.9	12.0
6	$Yba_2Cu_4O_8$	**80**	50.5	76.0*	2.8	3.8
7	$HoBa_2Cu_4O_8$	**80**	95.9	144.3*	1.3	1.2
8	$Bi_2Sr_2CaCu_2O_8$	89	28.6	43*	3.5	7.8
9	$(Bi_{1.6}Pb_{0.4})Sr_2Ca_2Cu_3O_{10}$	107	28.0	42.1*	3.4	7.8
10	$Tl_2Ba_2CaCu_2O_8$	99	33.2	49.9*	4.9	8.4
11	$Tl_2Ca_2Ba_2Cu_3O_{10}$	125	44.1	66.4*	4.2	5.7
12	$(Tl_{0.5}Pb_{0.5})Sr_2CaCu_2O_7$	80	60.0	90.3**	2.8	3.2
13	$[TMTSF]_2$ ClO_4	1.2	2.5	3.8	0.38	20.0
14	$TaS_2(P_y)_{½}$	3.4	22.0	33.1	12.0	23.0
15	$Ba_{0.6}K_{0.4}Bi\ O_3$	32	27.7	41.6	0.57	2.4
16	$BaPb_{0.75}Bi_{0.25}\ O_3$	11	5.6	8.4	0.12	4.2
17	$PbMo_6S_8$ (Chevrel)	12	37.2	55.9	1.0	2.6
18	UPt_3	0.53	2.8	4.2	7.8	13.5
19	Nb_3Sn	17.9	18.5	278.4	47.0	6.8

* * Calculated T_{c2} by Rabinowitz and McMullen (1993).
Unstarred T_{c3} and T_{c2} results by the author.

CHAPTER SIX

6.0 DISCUSSION OF RESULT, SUMMARY AND CONCLUSIONS

A comprehensive review of the available literature on high temperature superconductivity has been made, mainly concentrating on the electronic structure. The review showed that there have been tremendous efforts devoted to developing suitable theories and mechanisms of the high temperature superconductivity. This can be inferred from the list of publications that have appeared and conferences and workshops conducted since 1986 the year Bednorz and Muller announced their discovery.

The present review also touches upon the potential application of high T_c superconductivity and the various devices that have been built in recent times. The latest device built has been a *d*-wave π-SQUID device using one standard Josephson junction and one π-junction as reported in the April 2000 issue of Physics Today. This latest device has the potential application for superconducting electronics or even superconducting qubits in future quantum computer.

The table in Chapter five (Table 5.1) provides details of the calculated transition temperature both for two-dimensional and three-dimensional systems alongside the experimentally observed values. It is seen that the calculated transition temperatures agree quite well with the experimental values and this is more marked by the two-dimensional transition temperature T_{c2} which is based on the layered structure and highly anisotropic normal state properties of the superconducting materials.

It should be noted here that Rabinowitz and McMullen's theory (Rabinowitz and McMullen, 1993) did not explicitly introduce a pairing mechanism. This according to them is due to the reasoning that T_c itself is a measure of the interaction strength. In their model T_c enters into the relevant equation in two different ways and as such it is possible to solve the equation to arrive at a value for T_c. The model provides a self-consistent condition that the number of pairs that Bose-Einstein condenses is approximately equal to T_c itself. Of course this model works best for short coherence length pairs and not so well for metallics having greatest pair-pair interactions with large overlap and having long coherence length.

It is quite possible that better results may be achieved if a suitable pairing mechanism modified from the *d*-wave pairing mechanism as introduced in the present theory is considered. This is one likely direction in which this work could be extended to provide better results. As noted earlier the two-dimensional transition temperature T_{c2} agree better than the three-dimensional transition temperature T_{c3} with the experimentally observed results, for all the systems evaluated by the earlier workers and by the present work.

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