ALGEBRA OF COUPLED ELECTRONS IN THE CO-EXISTENCE OF SUPERCONDUTIVITY AND FERROMAGNETISM

BY

MURUNGA GODFREY S.W.,

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DECLARATION

Declaration by the candidate

This thesis is my original work and has not been presented in any University. No part of this thesis may be reproduced in any form or by any means without my permission in writing from the author and/ or University of Eldoret.

Murunga Godfrey S. W,
Signature ……………………………………Date…………………………………..

Declaration by supervisors

This thesis has been submitted for examination with our approval as University supervisors.

Prof. Khanna M. Kapil
Signature …………………………………………Date…………………………………

Prof. Rotich K. Samuel
Signature …………………………………………Date………………………………….

Department of Physics,
University of Eldoret,
P. O Box 1125
Eldoret, Kenya

DEDICATION

This piece of work is dedicated to my ever loving caring parents Mr. Mark Wakoli Murunga and Mrs. Anna Nakhumicha Wakoli through whose invaluable financial and moral support, I developed the right attitude and value for education. Mother and Father may God bless you abundantly.

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Finally, I must appreciate the support, care, encouragement and enabling environment created and accorded to me by my family, led by my wife, Mrs. Rose Murunga followed by all our children.

ABSTRACT

Superconductivity is a phenomenon in which the d.c electrical resistance of a material vanishes completely and instantly rather than gradually when it is cooled below a certain temperature called the superconducting transition or critical temperature, T_c

Both experimental and theoretical studies have been carried out in the last few years on materials that exhibit co-existence of superconductivity and magnetism. The compounds that exhibited such properties included $MgCNi_3$ and Mo_3Sb_7 among others.. In the conventional superconductivity theories, such a co-existence was ruled out, Since superconductivity depends on the nature of electron-electron coupling, weak coupling leading to BCS theory, and strong coupling leading to high-T_c superconductivity, it is necessary to understand the nature of electron-electron coupling that can lead to the co-existence of superconductivity and ferromagnetism. In BCS theory no attempt was made to study the commutation laws that the operator, $a_k^+ \ a_{-k}^+$, that constitutes Cooper pair, should obey. It was also not pointed out as to the kind of statistics that the Cooper pairs will obey. These inconsistencies were pointed out latter. It was, therefore, felt necessary to look into the algebra of coupled electrons that lead to superconductivity and to see simultaneously if such an algebra can lead to the understanding of superconductivity and ferromagnetism. Isolated electrons obey anti-commutation laws, whereas Cooper pairs ($a_k^+ a_{-k}^+$) will behave as bosons that obey commutation laws for Bose particles. The algebra developed correlates the operators associated with the electrons (Fermions) to the operators associated with the bi-linear electron operators that correspond to a pair of electrons. Effect of spin-fluctuation λ_{sf} and electron-phonon coupling λ_{e-ph} on the transition temperature T_c has also been studied, and it has been established that T_c is finite and it increases as the values of λ_{sf} and λ_{e-ph} increase showing thereby that superconductivity and ferromagnetism can co-exist.

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LIST OF SYMBOLS AND ABBREVIATIONS

The following symbols have the defined meaning associated with them, unless otherwise defined in a particular section of this thesis.

$\uparrow, \downarrow$ - Is the spin index ($\uparrow$- spin up; $\downarrow$ -spin down)

μ - Chemical potential

T_c - Transition temperature

n_k - Is the number of electrons which may be bound into Cooperons in the state labelled k

φ_k -Parameter that minimizes energy

Δ - Energy gap parameter

$W_{p,q}$ - The electron-phonon-electron interaction

f- Fermion annihilation operator

b- Boson annihilation operator

i - Site label

E - Particle energy

χ - Generalized susceptibility

M - Magnetization

U - Coulomb energy

T - Absolute temperature

ξ_o - Coherence length

H – Hamiltonian

χ_s - Spin susceptibility

ε_F -Fermi energy

V - Pairing potential

RVB - Resonance Valence Bond

BCS - Bardeen, Cooper, Schrieffer

σ - Spin quantum number

ω - Angular frequency

ρ - Resistivity

f_s - A fermion spinon

Δ_{ij} -Pairing amplitude which is a measure of the energy required for the spinons to form a pair.

F - Phenomenological free energy

λ - Penetration depth of the superconducting state

.*h* - Planck's constant = 6.626176×10^{-34} Js

$\hbar = \frac{h}{2\pi}$

B - Magnetic flux

J - Current density

C - Heat capacity

c -Velocity of light = 3.0×10^{8} m/s

k - Boltzmann constant =1.380662 x 10^{-23}JK^{-1}

a - Coefficient of attenuation

v - Desired filling of energy states

NMR – Nuclear Magnetic Resonance.

T_n - Neel Temperature

N_e – Number of electrons

CHAPTER ONE

INTRODUCTION

1.0 Summary

This chapter focuses on definitions, existing concepts and discoveries as a basis of my work leading to the present state of knowledge about the various theories of superconductivity, problem statement, constraints, and approach to solve the problem

1.1 Superconductivity and its Discovery

Superconductors are materials showing zero resistance and perfect diamagnetism below a certain temperature known as the critical/transition temperature T_c.

Superconductivity was discovered by (Kamerlingh, 1911) while studying the variation with temperature of the DC electrical resistance of mercury within a few degrees of absolute zero. He observed that the resistance dropped sharply to an immeasurably small value at a temperature of 4.2K as illustrated below. The temperature at which the superconducting state appears is known as the transition temperature or critical temperature T_c .

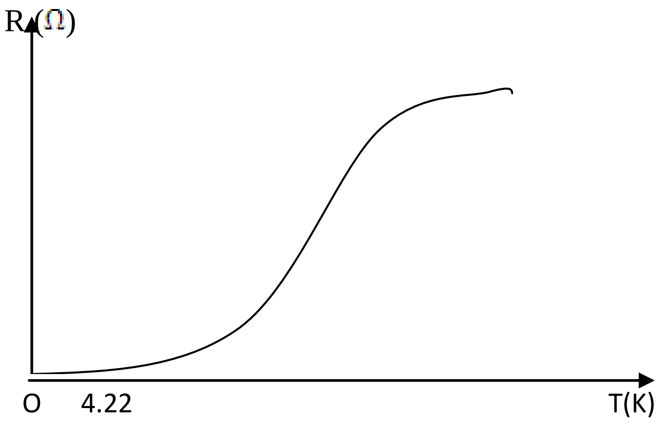


Fig 1.1 Illustration of a graph of variation of DC, electrical resistance with absolute Temperature (Subraanyain & Raja, 1989).

where T_c = 4.22 K

Superconductivity is associated with the formation of a quantum condensate states by pairing conduction electrons, the pair being called a Cooper pair. A Cooper pair is composed of two electrons, one with spin up and momentum up, and the other with spin down and momentum down.

The critical temperature T_c, is a characteristic constant of the superconducting material. At T $> T_c$, the material is in its normal state while at T < T_c, it is in the superconducting state. Thus superconductivity is a reversible phenomenon. Several pure metal alloys and doped semiconductors were discovered (Kamerlingh, 1911) to exhibit this property, which is inevitably accompanied by some spectacular magnetic properties.

The two properties viz: zero d.c electrical resistance coupled with peculiar magnetic properties of the superconductor have led to the development of new technologies and inventions which include zero resistance power lines, electric motors, powerful electromagnets used in medical diagnostic machines, large accelerators for heavy ions, magnetically levitated train and so on.

However, conventional superconductors have not found a much wider range of application owing to the fact that their T_c values are very low, and the use of expensive liquid helium to achieve sufficient cooling to the desired T_c values. As a step towards reversing this unpleasant trend, immense and frantic efforts have been invested to produce substances with higher T_c - values with a maximum value of about 25K being achieved half a century after the initial discovery (Kamerlingh, 1911). The superconducting materials with T_c up to this value (T_c = 25K) are referred to as conventional superconductors, and their properties are explained by the BCS theory (Bardeen, 1950).

In (Bednorz & Muller, 1986) discovered superconductivity in *La-Ba-Cu-O* and *La-Ba-Sr-Cu-O* compounds with 30K < T_c < 40K, and in Y- Ba – Cu-O compounds at T_c ≈ 90K. Other compounds such as *Bi – Ca – Sr – Cu – O* have a value of T_c ≥ 110K, where Ba = Barium, La=Lanthanum, Sr=Stronthium, Cu=Copper, O=Oxides, Y=Yttrium. Such compounds are called high T_c superconductors where liquid nitrogen is commonly used as the refrigerant to obtain high T_c superconducting state and it is much cheaper than liquid helium (4He). Research is on (Tinkham, 2004) to obtain superconductors at room temperature. It will be a major scientific breakthrough in this field if it can be achieved, since it will usher in landmark revolution when such superconductors that perform at room temperature will replace conventional metallic conductors in everyday situations

1.2 The Superconducting State

The most important property of a superconductor is the vanishing of its d.c. electrical resistance when it is cooled below T_c. This means that the conductivity

$\sigma \to \infty$ for T< T_c

From Ohm's law;

$$J = \sigma E \quad \text{.(1.1),}$$

where E is the electric field, J is the current density. Thus, for finite J and $\sigma = \infty$,

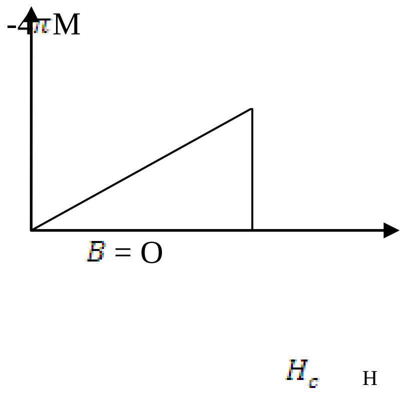
$$\vec{E} = \frac{\vec{J}}{\sigma} = \frac{\vec{J}}{\infty} = 0 \quad \text{.(1.2),}$$

Hence, $\vec{E}$ = 0, i.e. the electric field inside a superconductor is zero. From Maxwell's equation,

$$\frac{\partial \vec{B}}{\partial t} = -c\vec{\nabla} \times \vec{E} \quad (1.3)$$

where c = velocity of light. When E = 0, $\frac{\partial \vec{B}}{\partial t}$ = 0 or B = constant.

This implies that the magnetic field intensity B does not change with time inside a superconductor. B could as well be zero, as shown in figure 1.2



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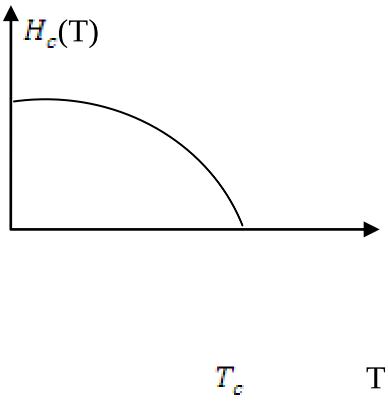
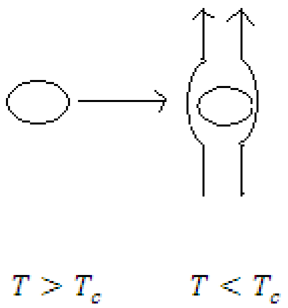


(ii)

Fig 1.2 (i): Meissner effect in type I superconductors, Magnetization curve. (Meissner & Ochenfield, 1933)

Fig 1.2 (ii): Meissner effect in type I superconductors, critical magnetic field curve (Meissner & Ochenfield, 1933)



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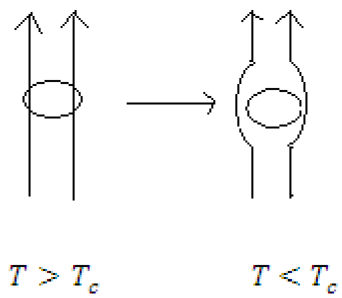

(iv)

Fig 1.2 (iii): Meissner effect in type I superconductors, sample cooled below T_c before Magnetic field is applied (Meissner & Ochenfield, 1933)

.

Fig 1.2 (iv): Meissner effect in type I superconductors, sample put in magnetic field then cooled below T_c (Meissner & Ochenfield, 1933)

The nature of the reversible superconducting state was obtained when (Meissner and Ochenfeld, 1933) demonstrated that at least for low external magnetic fields, all magnetic flux B is in fact expelled from the interior of a superconductor, whether or not there was a magnetic field inside the material before it is cooled below T_c. (Fig1.2).This result does not contradict the earlier conclusion of B constant in time, when $\sigma \rightarrow \infty$. It indicates that the constant value could as well be zero: the superconducting state does not depend on the prehistory of the amount of magnetic field present inside before cooling below T_c.

Since, $\vec{B} = \vec{H} + 4\pi \vec{M} = \vec{H}\,(1 + 4\pi\chi_m)$________________________________ (1.4)

Where $\chi_m = \frac{\vec{M}}{\vec{H}}$

Vanishing of $\vec{B}$ inside the material implies that the magnetic susceptibility,

$\chi_m = {}^{-1}/_{4\pi}$ for low fields, which is the fundamental requirement for a material to be diamagnetic. The magnetic susceptibility measurement below T_c is a bulk measurement, and the ratio of its experimental value to ${}^{-1}/_{4\pi}$ usually gives an idea about the percentage of the bulk of the material which is superconducting.

A rod shaped sample of a superconductor held parallel to a weak applied magnetic field H_o has the property that the field can penetrate only a short distance λ into the surface of the sample. This distance is known as the penetration depth, and is typically of the order of 10^{-5}cm, the field decays rapidly to zero in the superconducting layer. If the strength of the magnetic field is increased, the superconductivity is destroyed and this can happen in two ways:

In type I superconductor, a magnetic field H_0 applied parallel to a large rod shaped sample is completely excluded from the interior of the specimen so long as $H_0 < H_C$ the critical field, and completely penetrates the sample when $H_0 > H_C$ see graph in Fig 1.3 (a)

In type II superconductors, there is a partial penetration by the magnetic field into the sample when the applied magnetic field H_0 lies between the field values H_{C_1} and. H_{C_2} Small surface super currents may still flow up to an applied field, H_{C_3} , or a thin surface layer may remain superconducting up to the field H_{C_3} as shown in Fig 1.3 (b) below.

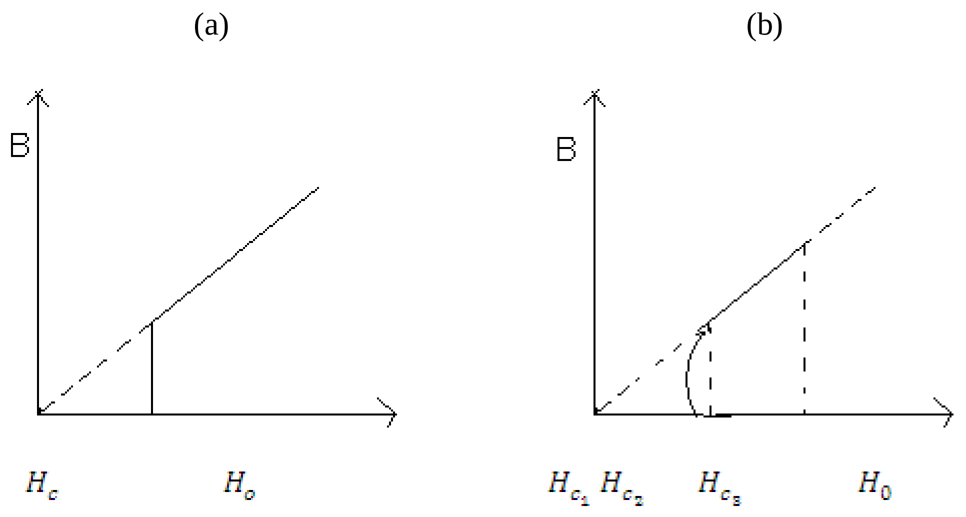

Fig 1.3 (a) Type 1 superconductor, magnetic field H_o is completely excluded from the interior of the specimen when $H_0 < H_C$ and the magnetic field completely penetrates the sample when $H_0 > H_C$ (Meissner & Ochenfield, 1933).

Fig 1.3. (b) Type II superconductors, there is a partial penetration by the magnetic field into the sample when the applied magnetic field H_0 lies between the field values $H_{c_1}$and, H_{c_2}.Small surface super currents may still flow up to an applied field H_{c_3} , or a thin surface layer may remain superconducting up to the field H_{c_3} (Meissner & Ochenfield, 1933).

For applied fields between H_{c_1} and H_{c_2} the sample is in a mixed state (Subraanyam & Raja, 1989). It consists of superconductor penetrated by threads of magnetic flux, and a normal (state) phase. Some ingenious experiments have confirmed that these threads or filaments form a regular two dimensional array in the plane perpendicular to. H_0

The existence of an attractive interaction between electrons in a metal leads to the existence of a phase transition in the electron gas at low temperatures. However, it would have been a phenomenon as startling as superconductivity if there was no already familiar experimental evidence (London & London, 1935). The nature of this evidence is illustrated in Fig 1.4 in which the resistivity ρ, the specific heat C, and the co-efficient of attenuation α, are plotted as functions of the temperature for a superconductor.

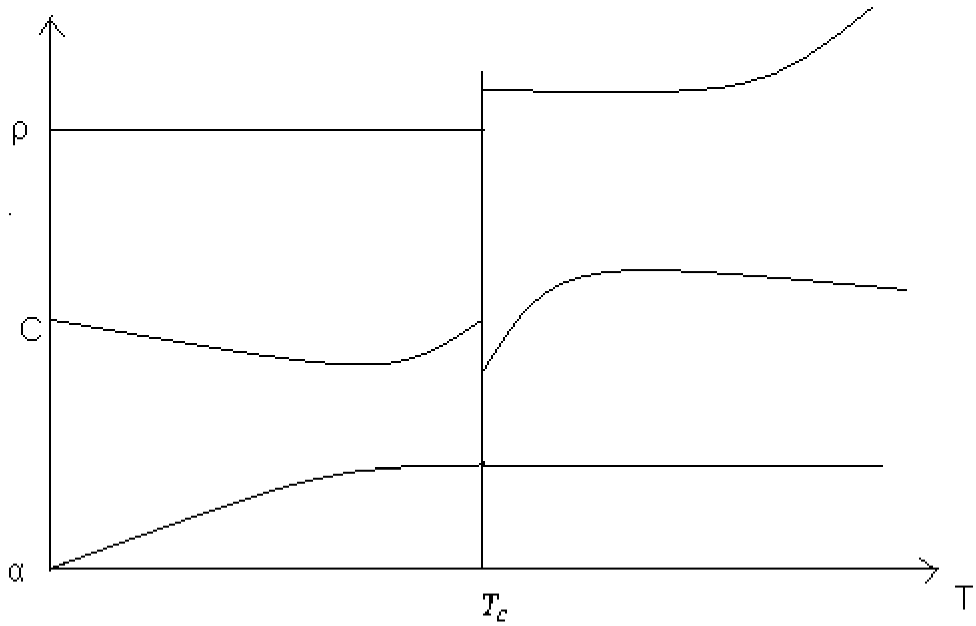

Fig 1.4 variation of ρ, C and α with T for a superconductor (Khanna, 2008)

At the transition temperature, T_c , a second order phase transition occurs in dozens of metals and many alloys, the most important consequence being the apparent disappearance of resistance to weak steady electron current. The contribution of the electrons to the specific heat is found no longer to be proportional to the absolute temperature, as it is in normal (non-superconducting) metals and superconductor when $T > T_c$, but to vary at lowest temperature as $e^{\frac{-\Delta}{kT}}$, where Δ is the energy of the order of κT_c. This leads us to suppose that there is an energy gap in the excitation spectrum; an idea that is confirmed by the absorption spectrum for electromagnetic radiation. Only when the energy $\hbar\omega$ or $h\omega$ /2π of incident photons is greater than about 2Δ, does absorption occur, and this suggests that the excitations that give the exponential specific heat are created in pairs.

In many cases it is possible to predict whether a superconductor will be type I or II from measurements of Δ and λ. One defines a coherence length, ξ_0, equal to $hv_f/2\pi\,\Delta$ where v_f is the Fermi velocity. (This length is of the order of magnitude of ε_f/Δ times the lattice spacing). Superconductors for which $\lambda \gg \xi_0$ tend to exhibit properties of type II superconductors. With the availability of isotopes of many elements from a nuclear reactor, it became possible to test whether the isotopic mass of the elements of the metal had any effect on T_c. in many metals, It was found that the $T_c \approx M^{-\alpha}$. where α was close to 0.5. For an elemental metal, this implies that the phonons (ionic vibrations) whose frequencies vary as $M^{-0.5}$ may be somehow involved in the superconducting transition.

1.3 The Theory of Superconductivity

The theory of superconductivity deals with the study of the behavior of electrons in metals and alloys, and more recently even the behavior of electrons in non-metals like ceramics that show superconducting behavior at high temperature of the order of 100K and above. The main facts which a theory of superconductivity must explain are:

i) The order of phase transition at T_c.

ii) An electronic specific heat as $e^{(-T_0/T)}$ near $T = 0K$ and other evidence for an energy gap for individual particle – like excitations

iii) The Meissner effect ($B = 0$)

iv). Effects associated with infinite conductivity, $E = 0$, and

v) The dependence of T_c on isotopic mass,$T_c\sqrt{M}$ =constant

Not very long afterwards (London & London, 1935) proposed a phenomenological theory of electromagnetic properties in which the diamagnetic aspects were assumed basic. (London, 1948) suggested a quantum- mechanical approach aspects were to a theory in which it is assumed that there is somehow a coherence or rigidity in the superconducting state such that the wave functions are not modified very much when a magnetic field is applied. The concept of coherence was emphasized by (Pippard, 1953), who, on the basis of experiments on penetration phenomena, proposed a non-local modification of the London equations in which a coherence length, ξ_0, is introduced.

The Sommerfeld- Bloch individual particle model (1928) gives a fairly good description of normal metals but fails to account for superconductivity. Early theories based on electron – phonon interactions were not successful either. Froehlich's theory, which makes use of a perturbation theory approach, does give the correct isotopic mass dependence for, T_c, but does not yield a phase with superconducting properties and further, the energy difference between what is supposed to correspond to normal and superconducting phases is far too large.

A variational approach by (Bardeen, 1951) ran into similar difficulties. Both theories are based on the self-energy of the electrons in the phonon field rather than on the true interaction between electrons, although it was recognized that the later might be important (Bardeen, 1950).

1.4 Statement of the Problem

To establish the role of different types or nature of electron-electron coupling in determining the properties of high - T_c superconductors. The effect of electron-electron coupling and electron-phonon coupling on the properties of high - T_c superconductors coupled with conventional beliefs held that superconductivity and ferromagnetism could not co-exist, and this laid the ground to study the co-existence of strong ferromagnetic and spin fluctuations. It is also studied as to how the spin fluctuation coupling constant, λ_{sf} as well as electron phonon interaction contribution λ_{e-ph} affect specific heat, C and T_c.

1.5 Objectives of the study

1. To investigate the co-existence of superconductivity and ferromagnetism in Mo_3Sb_7 compound.
2. To calculate transition temperature T_c for a superconductor spin fluctuation system.

3. To study how the spin fluctuation coupling constant λ_{sf} as well as the electron-phonon interaction contribution factor λ_{e-ph} affect specific heat, C and T_c.

1.6 Justification

Over time, both theoretical and experimental efforts were made in understanding temperature dependences of the magnetic susceptibility, specific heat C, and electrical resistivity ρ on materials which not only undergo superconducting transition but also exhibit rather unconventional properties in their normal and superconducting state, among them being the heavy-fermion systems and intermetallic actinides such as UPt_3 or UCo_2 with spin fluctuation behaviour. Only a few materials without any actinide element exhibit both superconductivity and spin fluctuation behaviour. However, the nature of the electron coupling that describes the properties of such system is still unknown. Therefore it is necessary to formulate a high T_c superconductivity theory describing the nature of the electron coupling that is responsible for the co-existence of superconductivity and ferromagnetism which does not confine itself to materials that contain any actinide element as a crucial feature, on the basis of which one can construct an appropriate quantitative description.

1.7 Significance of the study

The study provides useful information about the electron coupling in the co-existence of high - T_c superconductivity and ferromagnetism in Mo_3Sb_7 compound.

CHAPTER TWO

LITERATURE REVIEW

2.1 The BCS Theory

The first successful microscopic theory of superconductivity was given by (Bardeen, Cooper and Schrieffer, 1957) and is called BCS theory. This theory was built using the concept of what is called "Cooper pairs" which are a pair of electrons, mediated by a phonon such that the pair of electrons is considered to be bound and the energy of the phonon $\hbar\omega$ is greater than the energy difference between the states of the two electrons that constitute the Cooper pair. The assembly of Cooper pairs can undergo a transition akin to Bose-Einstein condensation i.e the electron pairs behave essentially as bosons and undergo condensation to the lowest energy state at the critical temperature, T_c. The formation of electron pairs can best be understood by considering conduction mechanism in metals. The repulsive Coulomb force between any two particles of the same charge is small compared with the overall potential of the lattice. As a result, the net interaction of electrons in a metal is attractive and arises from lattice vibrations or phonons that accompany the moving electrons. As the electrons pass near the positive lattice ions, phonons propagate as a result of the mutual electrical attraction. (Formation of nucleon pairs leading to superfluidity and phase transition in atomic nuclei was emphasized by (Khanna, 1962)

Superconductivity requires that the conducting material must be cold. At temperatures near absolute zero, atoms, electrons and molecules tend to be near their quantum-mechanical ground state. They are not in a state of zero energy when in their lowest energy. Only in the unique conditions of lower energy of a lattice, can electron pairing take place. The coupling or attraction of electron pairs is very weak, and normal temperatures can cause thermal motion so large that any attraction is destroyed.

The pairing interaction between electrons occurs because the motion of electron 1 influences and modifies the vibration of the ion and this in turn interacts with electron 2 which is Frohlich's interaction as illustrated below (fig 2.1).

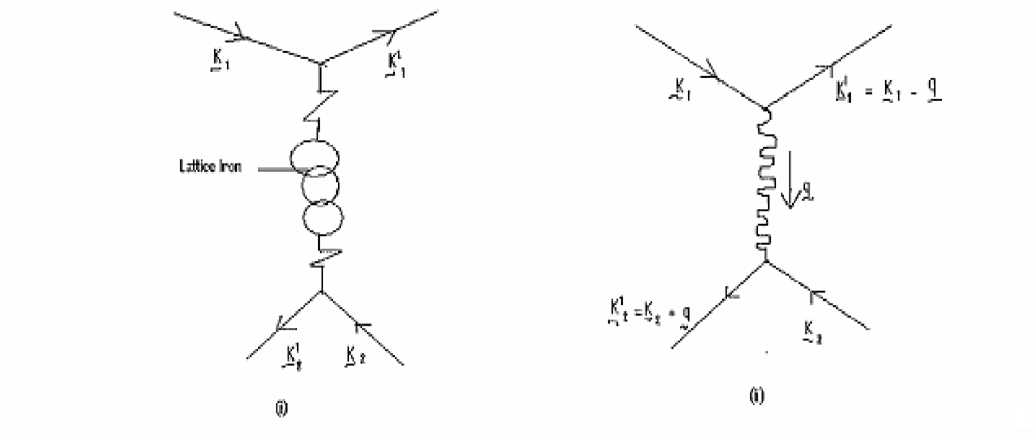

Fig 2.1 illustrates the electron pairing via electron-phonon interaction.

Suppose an electron travelling with momentum k_1 encounters a lattice ion as shown in Fig 2.1. The momentum of the electron will be reduced to k_1 – q due to Coulomb interaction and local lattice vibration will be set up, characterized by the remainder of the momentum q. A second electron of momentum k_2 entering the locality of this lattice vibration may be influenced by it. The precise effect will depend very much on the phase of the vibration at that time, but it is possible that the whole of the momentum has been transferred between electrons. The net effect of these two interactions is that there is an apparent attractive force between the two electrons resulting in the formation of Cooper pairs when the energy difference, $\Delta\varepsilon$, between the involved states of the two electrons, that constitute pair, is less than the energy $\hbar\omega$ of the phonon which would not have been there if the ion had not been present. In field theory the interaction is said to be due to the exchange of a virtual phonon with momentum *q* between the two electrons. In terms of wave vectors *k* of the first and second electrons, the process can be formally written as:-

$k_1 - q = k_1'$ or $k_1 - k_1' = q$ ____(2.1)

and

$k_2 + q = k_2'$ or $k_2' - k_2 = q$ ____(2.2)

Combining equations (2.1) and (2.2) gives $k_1 - k_1' = k_2' - k_2$ ______________(2.3)

The net wave vector of the pair is conserved.

$k_1 + k_2 = k_1' + k_2'$ ____. (2.4)

The exchange of phonons between electrons can give rise to an effective electron-electron interaction which is most strongly attractive when the momenta and spins of the two interacting electrons are equal and opposite, i.e., $k_2 = -k_1$, The two electrons at the Fermi surface can lower their energy by vibrating in phase with zero point oscillation.

2.2 Consequences of Electron Pairing

Pairing energy depends on the strength of the interaction between the electrons and the ions and since the energy involved is quite small, the pairs can be broken by thermal activation. Pairs will begin to form at transition temperature T_C. As the temperature is further reduced, more pairs will be able to remain stable until at 0 *K* all possible electron pairs would be formed.

It is worth noting that even when the material is superconducting, there will always be some unpaired electrons (called quasi-particles or normal electrons) present. The idea of two types of electronic states was the basis of the two fluid model of superconductivity.

Since an electron pair has a lower energy than two normal electrons, there is an energy gap between the paired and two single electron states. This energy is often denoted as 2Δ. Thus, the net energy to excite each electron is Δ, although, of course both must be exited at the same time.

In principle, any two electrons can pair up provided that their net wave vector is conserved before and after the exchange of the virtual phonon. All pairs are in condensed state.

In the BCS theory, the pairing of electrons and condensation of pairs with centre of – mass momentum occurs at precisely the same temperature T_c. However, rather than performing a “tango” in the superconducting state, the electron pairs participate in a “square dance” exchanging partners in a time scale of the order.

$$\tau_c = h / k_B T_c \qquad (2.5)$$

The characteristic separation is the coherence length given by

$$\xi = V_F \tau_c \qquad (2.6)$$

where V_F is the Fermi velocity. Below T_c the electron pair wave function Ψ has non zero amplitude and serves as an order parameter analogous to the spontaneous magnetization of Fe below the Curie temperature.

Since electrons repel in free space, the pairing "glue" must arise from the solid state. The BCS model assumes that the virtual exchange of phonons mediates the electron attraction.

The picture is that an electron moving through the lattice virtually polarizes the positively charged ionic background, which in turn attracts another electron moving through it at a later time. The characteristic length scale for this interaction is small, of the order of lattice spacing. However, the characteristic time scale – the interval before one electron passes through a region polarized by its partner − is long $\frac{1}{\omega_o} \gg \frac{1}{E_F}$, where E_F is the Fermi energy and ω_o is the maximum vibration frequency of the lattice. This temporal separation effectively reduces the Coulomb repulsion.

The BCS theory predicts (Bardeen, Cooper & Schrieffer, 1957) a simple exponential relation between T_c and the strength of the attraction interaction, *V*. Taking the normal state Fermi – energy density of state to be N(o), and the time averaged Coulomb repulsion to be, U^*, T_c is given by

$$k_B T_c \approx 1.13\hbar\omega_o \exp\left[\frac{-1}{N(o)[V-U^*]}\right] \qquad (2.7)$$

From this equation, it can be deduced that:

i) An arbitrarily weak net attraction ($V - U^* < O$) will yield superconductivity

ii) T_c is exponentially sensitive to input values of model parameters, rendering any T_c estimate only within an order magnitude,

iii) Naively, $T_c \propto M^{-0.5}$, where M is the mass of atoms forming the lattice. Thus, BCS theory describes very successfully the superconducting properties of conventional

Superconductors. The isotope effect verified the Frohlich hypothesis that the electron phonon Interaction caused superconductivity. Infact, BCS theory was the first to explain Superconductivity in metals and also to make a number of remarkable predictions.

2.3 High Temperature Superconductivity

In spite of the successful discoveries and demonstrations of superconductivity, its full impact on our technological advances remained elusive for some time, a limitation which was attributed to the so called temperature barrier, which refers to the unusually low temperature at which superconductivity, occurs. Until 1986, it was believed that the BCS theory forbade superconductivity at temperatures above 30 *K*. In that year, (Bednorz et.al., 1986) discovered superconductivity in Lanthanum – based cuprate which had a transition temperature, $T_c = 35K$ for which they won Nobel Prize in 1987. It was later discovered by (Wu & Chu, 1988) that by replacing the Lanthanum with yttrium, i.e. making YBCo, raised the critical temperature to $T_c = 92\ K$, which was important because liquid nitrogen could then be used as a refrigerant since its boiling point, is 77K at atmospheric pressure. Thus, high - T_c superconductor was defined as the one whose critical transition temperature T_c, is greater than 90K and the superconducting state can be reached by cooling in liquid nitrogen.

The discovery of possible high temperature superconductivity in Lanthanum-barium-copper oxide (La – Ba – Cu – O) compound (Bednorz et.al., 1986) with T_c = 30K was an important and decisive break through in the high- T_c superconductivity research. The great success with La – Ba – Cu – O and La – Sr – Cu – O compound led to the discovery of multilayered compounds whose transition temperatures were more than

90K. The three main families of mixed oxides that had shown high T_c superconductivity properties included:

i) Yttrium – Barium – Copper – Oxide (Bednorz & muller, 1986) with T_c =90K

ii) Bismuth – Srontium – Calcium – Copper Oxide (Maeda et.al., 1988) T_c = 105K

iii) Thallium – Barium – Calcium – Copper – Oxide (Ruvalds et. al., 1987) with T_c = 110K

By March 2007, the best high - T_c superconductivity was exhibited by a ceramic superconductor consisting of Thallium, Mercury, Copper, Barium, Calcium, Strontium and Oxygen (T_c= 138K). A patent has also been applied for material with T_c = 150K. Many other cuprate superconductors have been discovered and some of which together with their corresponding values of T_c are shown in table 2.1:

Table 2.1 High - T_c super conducting Copper Oxides (Khanna, 2008)

Compound	T_c **(K)**
$(NdCeSr)CuO_4$	30
$(La_{2-}\ x\ - Sr_x\ )CuO_4$	37
$(La_{2-x} - Sr_x)CaCuO_4$	60
$YBa_2\ Cu_4\ O_8$	81
$Bi_2\ Sr_2CaCu_3\ O_8$	90
$Tl_2\ Ba_2\ CuO_6$	90
$YBa_2\ \ Cu_3\ O_7$	92
$Tl_2\ Ba_2\ CaCu_3\ O_8$	110
$Bi_2\ S_{r2}\ Ca_2\ Cu_3\ O_{10}$	110
$Tl_2\ Ba_2\ Ca_2\ Cu_3\ O_{10}$	122
$Tl_2\ Ba_2\ Ca_2\ CuO_{10}$	127
$HgBa_2\ \ Ca_2\ Cu_3\ O_8$	135

Since the discovery of high -T_c superconductors in 1986 – 87, the mechanism of high - T_c superconductivity has never been obvious and continues being elusive since some experimental data on high - T_c cannot be explained by the BCS theory, and the high - T_c theories so far proposed.

While these materials share a number of common features with conventional low-temperature superconductors, they possess distinguishing characteristics which justify their inclusion in a separate section. It should be emphasized at the outset that the properties to be described are not attributable to all superconductors with T_c >30K, and we will consider their general characteristics in order to bring out their special scientific attributes.

2.4 Characteristics of high - T_c Superconductors.

Common high T_c superconductors are predominantly cuprates or copper oxides which exhibit three main characteristics:

i) Strong correlations on copper,

ii) The well-known anisotropy, and,

iii) Large electron – phonon coupling

2.5 Strong correlations on copper

In the structure of superconducting copper oxide, the valence state of copper is Cu^{2+} .the copper ion has one hole with spin S = ½ in the 3 – D shell and this hole is localized since the energy barrier prevents the transfer of the hole to the neighbouring oxygen site. The magnetic moments associated with spin ½ of Cu^{2+} are coupled by super- exchange interaction to a given anti-ferromagnetic ground state with Neel Temperature, $T_n \geq 300K$. When the oxygen content is increased, additional holes mainly of oxygen P_α character are transferred into $O_{(2p)}$ states in CuO_2 planes. These holes form a band of states within energy gap for the copper excitation.

When the number of holes increases further, they tend to align adjacent spin in a parallel configuration that leads to Mott insulator metal transition and the material becomes superconductor.

Thus, the only motion possible is the alternating spin:

$$\alpha = [½ , - ½] \qquad (2.8)$$

where the energy band splits into two narrow Hubbard bands separated by 2U, where U is the on-site Coulomb energy, the lower band being fully occupied by anti-ferromagnetically aligned electrons and the upper band being empty.

Anderson (Anderson, 1987) argued that the strong correlations in the CuO_2 planes are best described by a Single – band Hubbard model with on-site repulsion. Strong Coulomb repulsion and hole correlation play a crucial role in the 2 dimensional CuO_2 sub -lattice. It is essential here that the charge carriers are confined to CuO_2 planes.

2.6 The Well known Anisotropy

Due to the layered structure (quasi – two dimensional nature of structure), high -T_c superconductors exhibit a strong anisotropic superconducting behavior which favours superconducting currents flowing in CuO planes. This implies that the coupling between adjacent conducting layers is in the form of tunneling process.

2.7 The Algebra of Large Electron – Phonon Coupling

According to BCS theory, the critical transition temperature, T_c, is given by

$$kT_c \approx 1.134\hbar\omega_D \exp\left[-\frac{1}{V\rho(\epsilon_F)}\right] \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_} (2.9)$$

where k is the Boltzmann constant, $\hbar = \frac{h}{2\pi}$, h is the Planck's constant, V is the coupling constant and $\rho(\epsilon_F)$ is the density of states at the Fermi surface. In the weak coupling limit, $V\rho(\epsilon_F)$ «1. Thus, with the Debye temperature $\hbar\omega_D \leq 450$K, where ω_D is the Debye frequency, upper limit on $T_c \approx 68$ K. Equation (2.9), therefore cannot be used to predict the high - T_c values found in the high - T_c superconducting copper oxide compounds

According to BCS theory, the energy gap $\Delta(T)$ in the energy spectrum can be expressed as

$$\Delta(T) = 3.2\kappa T_c\left[1 - \frac{T}{T_c}\right]^{\frac{1}{2}} \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_} (2.10)$$

and

$$\frac{2\Delta(T)}{\kappa T_c} = 3.5 \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_} (2.11)$$

Whereas, the experimental measurements (Vedeneev et.al., 1994) indicate that in copper oxide superconducting components the ratio,

$$\frac{2\Delta(T)}{\kappa T_c} = 5 \rightarrow 8 \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_} (2.12)$$

(where 5→ 8 means 'ranges from 5 to 8')

Equation (2.9) shows that for T_c to be large, electron-phonon coupling constant, *V*, should be large. (Doglov et.al., 1997) observations showed an evidence for strong electron-phonon coupling. Also, the self-consistent band structure calculation (Newns et.al., 1992) gave large values of *V*.

2.8 Theories for High T_c Superconductivity

A number of theories have been proposed as possible explanation for high - T_c superconductivity. Most of which require that there should be an attractive interaction between the charge carriers resulting in the formation of pairs which act as Bosons, and can undergo Bose-Einstein condensation. The proposed theories fall into the following three main categories.

i) Interaction through phonons (lattice vibrations)

ii) Interaction through charges (charge fluctuations)

iii) Interaction through unpaired spins (spin fluctuations)

2.9 Bipolaron Theory

Polaron is defined as a self- trapped electron, and bipolaron is a bound pair of electrons with a cloud of phonons. The assembly of these bound pairs can undergo superconducting transition at temperatures below the Bose-Einstein condensation temperature, T_c, given by the equation.

$$\kappa T_c = 3.3\frac{\hbar n^{\frac{2}{3}}}{m} \qquad (2.13)$$

where *n* is the density of pairs, and *m* is the effective mass of each pair.

2.10 Exciton Theory

Excitons are bound states of electron-hole pair created by electrostatic interaction between an electron in the excited state and a hole in the ground state. Oxide superconductors have a layered structure and thus a multiband nature of electron spectrum. It is, therefore, highly probable to have excitons. Since, here the energy responsible for coupling is of the order of electron energies, much higher T_c can be obtained. Some of the exciton models include:

i) Plasma excitations which have a quasi – two – dimensional electronic spectrum which give rise to the appearance of weakly damped acoustic plasmons. (Wu et.al., 1987).

ii) Collective electron excitation connected to copper-oxygen charge transfer (Anderson, 1987).

2.11 Spin Bag Theory

(Schrieffer et.al., 1989) proposed a model in which boson excitations are responsible for superconducting pairing in copper oxide high T_c compounds. When a mobile charge carrier or hole passes through the CuO_2 lattice, it creates a region of local depression in which copper spins are aligned anti-ferromagnetically when another hole passes through this region; it gets attracted to this region of lower potential energy resulting in the appearance of a magnetic polaron that moves with a deformed cloud. High -T_c and wave pairing are conditioned by a strongly anisotropic energy region due to anti-ferromagnetic spin fluctuations.

2.12 Fredel's Theory of Van-Hove Anomaly and its Algebra

(Friedel, 1989) proposed that superconductivity was due to electron –phonon coupling of delocalized carriers. Since the carriers are confined to the CuO_2 plane, high T_c superconductors exhibit quasi-two-dimentional Fermi surface. The band structure for holes leads to electronic density of states at or very near the Fermi surface which has Van Hove singularity. This logarithmic density of states is defined as,

$$D(\epsilon)=D\,(\epsilon_F)\,\log\left[\frac{w}{\epsilon}\right] \qquad (2.13)$$

where the width, *w*, is the characteristic energy for two dimensional bands. According to (Newns et.al. 1992) the critical temperature T_c, is given by,

$$\kappa T_c=1.36\omega\,\exp\left[-\sqrt{\frac{2}{\lambda}}\right] \qquad (2.14)$$

where

$$\lambda = VD\,(\varepsilon_f) \qquad (2.15)$$

Thus, the temperature, T_c, increases because the width ω is of the electronic nature which is greater than the phonon energy. The Van Hove anomally in electronic spectrum leads to anomalous isotope effect.

2.13 Resonating Valence Bond (RVB) State Theory

A quantum spin liquid or singlet state is called a Resonating Valence Bond state. (Anderson, 1987) found that the whole wealth of experimental results on the so called high-T_c superconducting compounds could not fix exactly to conventional BCS theory. The departures were in two fronts. The first one was that high - T_c superconductivity was not due to phonon-induced pairing of electrons. The second and perhaps the most important one is that in high T_c superconductor, superconductivity arises not from

Cooper pair condensation but of new quasi particles of positive charge which are called holons.

Anderson refers to ceramic superconductors as, strange insulators, strange metals and strange superconductors. Superconducting transition temperature T_c is generally large, of the order of 92K and above. There are indications of unstable superconductivity even at room temperatures. The superconductor- normal metal tunneling is anomalous. There is a strong ultrasonic attenuation and velocity of sound anomaly. The infrared absorption is very different from the BCS compounds. Wide discrepancies are there in the gap measurements obtained from different experiments such as tunneling infrared absorption.

The remarkable fact is the vicinity of the insulating phase to the superconducting phase. At very low temperatures the system directly goes from an insulator to a superconductor.

It was the inelastic neutron scattering in La_2CuO_{u-y} that had shown a clear indication for the presence of a quantum spin (called a RVB state) liquid. (Anderson, 1987) generalized Pauli's theory of resonant valence bond to make it relevant to high -T_c oxide compounds. In this model, valence electrons are bounded singlet anti-ferromagnetic pairs (magnetic singlet pairs) which become mobile as in a liquid in the presence of mobile holes.

2.14 The RVB State Algebra

RVB is characterized by a system of singlet for pairs of electrons on the lattice sites i and j; described by the order parameter for holons.

$$B_{ij} = \langle b_i^+, b_j \rangle \qquad (2.16)$$

where b_i^+ , and b_j are the creation and annihilation operators for the bosons

The order parameter for spinons is given by the equation

$$\Delta_{ij} = \langle C_{i\alpha}^+ C_{j-\alpha}^+ - C_{i-\alpha} C_{j\alpha} \rangle \qquad (2.17)$$

where α and – α are the spin indices $C_{i\alpha}^+$and $C_{j\alpha}$are the fermion creation and annihilation operators, Δ_{ij} is the spinon pairing amplitude, while $b_i^+$and b_j are the creation and annihilation operators for the bosons, and these are charged quasi – particles without spin, called holons.

Superconductivity is assumed to be occasioned by:

i) Condensation of holons with $\langle b_i^+, b_j \rangle \neq 0$. Pairing is by interlayer tunneling of holons.

ii) Tunneling of pair of electrons between the layers under the condensation of spinon pairing amplitude $\Delta_{ij} \neq 0$

2.15 The Theory and Algebra of Electron – Paring in Exotic Superconductors – The Theory of Anharmonic Apical Oxygen Vibration in High – T_c Superconductors

This theory established that most of the high - T_c superconductors had Cu – O layers sandwiched between layers of other materials (Tinkham, Plackida & Hazen, 1990). The charge carriers are electrons and the pairing mechanism between the electrons is exotic. The electronic pairing in exotic superconductors is such that three electrons take part in the superconducting current and that they interact with each other through harmonic forces (Khanna & Kirui, 2002). Two of these electrons form a bound pair while the third one is a polarization electron which hops from one lattice site to another lattice site of similar symmetry. Studies based on photo induced Raman scattering (Freund & Kaplansky, 1976) have shown that there exist strong an-harmonic nature of apical oxygen vibrations. When the spectral function of electron phonon interaction is compared with the phonon spectrum in bismuth compounds, it is noted that both low frequency vibrations (buckling mode) and high frequency vibrations (breathing mode) contribute to the electron-phonon coupling (Cava, Dover, Bathlogg & Rietinann, 1987).

It is therefore assumed (Khanna & Kirui, 2002) that the polarization electron causes perturbation with respect to the apical oxygen vibration leading to the contraction of $Cu_p - O_3$ bond.

This perturbation is assumed to be of the form.

$$H = \beta x^3 + \gamma x^3 \qquad (2.18)$$

where β and γ may or may not depend on temperature.

Using the an-harmonic perturbation, and the non-degenerate many body perturbation theory, we can obtain the expression for the total energy, the specific heat and the critical transition temperature for both the buckling and breathing modes (Khanna & Kirui, 2002).

2.16 The Algebra based on section 2.15

The eigenvalues and eigenfunctions of the unpertubed harmonic oscillator Hamilltonian, H_o are given by:

$$H_0|n,0\rangle = \epsilon_n^0|n,0\rangle \qquad (2.19)$$

where

$$\epsilon_n^0 = \left(n+\frac{1}{2}\right)\hbar\omega, n = 0,1,2 \qquad (2.20)$$

$$|n,0\rangle = N_n H_n(\xi)\exp\left(-\frac{1}{2}\xi^2\right) \qquad (2.21)$$

$H_n(\xi)$ are the Hermite polynomials such that,

$$N_n = \left[\frac{\alpha}{n!2^n\sqrt{\pi}}\right]^{\frac{1}{2}} \quad (2.22)$$

$$\xi = \alpha x \quad (2.23)$$

$$\alpha^2 = \frac{\mu\omega}{\hbar} \quad (2.24)$$

where ω is the phonon frequency and μ is the reduced mass of the pair of electrons interacting harmonically.

When the system is perturbed, the eigenvalue to be solved is

$$H|n\rangle = \epsilon_n|n\rangle \quad (2.25)$$

Where *H* is the perturbed Hamiltonian of the entire system such that:

$$H = H_0 + H' = \frac{\hbar^2}{2\mu}\nabla^2 + \frac{1}{2}\mu\omega^2 x^2 + H' \quad (2.26)$$

To solve equation (2.25), the creation and annihilation operators for the harmonic oscillator are defined as:

$$a^+ = \frac{1}{\sqrt{2}}\left[\alpha x - \frac{1}{\alpha}\frac{\partial}{\partial x}\right]; a = \frac{1}{\sqrt{2}}\left[\alpha x + \frac{1}{\alpha}\frac{\partial}{\partial x}\right] \quad (2.27)$$

Such that

$$a^+|n\rangle = \sqrt{n+1}|n+1\rangle; a|n+1\rangle\sqrt{n+1}|n\rangle \quad (2.28)$$

From equation (2.27), we obtain

$$x = \frac{1}{\alpha\sqrt{2}}(a + a^+) \quad (2.29)$$

substituting for *x* from equation (2.29) in equation (2.18), the value of H becomes

$$H = \frac{\beta}{\alpha^3\sqrt{8}}(a + a^+)^3 + \frac{\gamma}{4\alpha^4}(a + a^+)^4 \quad (2.30)$$

To obtain an expression for the total energy of the system due to perturbation, the non-degenerate many-body perturbation theory has been used to calculate the correction to the energy eigenvalue. These corrections are given by (Khanna & Kirui, 2002).

$$\epsilon_n = \langle n,0|H|n,0\rangle + \sum_m \frac{|\langle m,0|H|n,0\rangle|^2}{\epsilon_n^0 + \epsilon_m^0} \qquad (2.31)$$

Knowing that $\langle m,0|n,0\rangle = \delta_{mn}$" and substituting for H from eqn (2.30) to eqn (2.31) we get,

$$\epsilon_n = \frac{15\hbar^2\beta^2}{4\mu^3\omega^4}\left(n^2+n+\frac{11}{30}\right) + \frac{3\gamma h^2}{2\mu^2\omega^2}\left(n^2+n+\frac{1}{2}\right) \qquad (2.32)$$

Now the total energy ϵ_n .of the superconducting system is given by,

$$\epsilon_n = \epsilon_n^0 + \epsilon_n'. \qquad (2.33)$$

Substituting from equation (2.20) and equation (2.32), we get

$$\epsilon_n = \left(n+\frac{1}{2}\right)\hbar\omega + \frac{3\gamma\hbar^2}{2\mu^2\omega^2}\left(n^2+n+\frac{1}{2}\right) - \frac{15\hbar^2\beta^2}{4\mu^3\omega^4}\left(n^2+n+\frac{11}{30}\right) \qquad (2.34)$$

At the transition temperature, it is necessary to consider the energy difference between states in which hopping electron is on one site and then when it is on another site of similar symmetry. The difference in energy levels of two sites gives the probability amplitude Green's function, which according to quantum treatment of lattice vibrations, is equivalent to the thermal activation factor, exp $\left(-\frac{\Delta\epsilon}{\kappa T}\right)$. Now the systems of the ensemble are distributed over the states with probability, P_n such that

$$P_n = exp\left(-\frac{\Delta\epsilon}{\kappa T}\right), with \sum_n P_n = 1 \qquad (2.35)$$

Thus, equation (2.34) becomes

$$\epsilon_n = \left(n+\frac{1}{2}\right)\hbar\omega + \left[\frac{3\gamma\hbar^2}{2\mu^2\omega^2}\left(n^2+n+\frac{1}{2}\right) - \frac{15\hbar^2\beta^2}{4\mu^3\omega^4}\left(n^2+n+\frac{11}{30}\right)\right]\exp\left(-\frac{\Delta\epsilon}{kT}\right)$$

$$\approx A_{10} + [A_{11}\gamma + A_{12}\beta^2]exp\left(-\frac{\theta}{T}\right) \_\_\_\_\_\_\_\_\_\_\_\_ (2.36)$$

where

$$A_{10} = \left(n+\frac{1}{2}\right)\hbar\omega$$

$$A_{11} = \left[\frac{3\hbar^2}{2\mu^2\omega^2}\left(n^2+n+\frac{1}{2}\right)\right.$$

$$A_{12} = \frac{-15\hbar^2}{4\mu^3\omega^4}\left(n^2+n+\frac{11}{30}\right)$$

$$\theta = \frac{\Delta\epsilon}{\kappa} \_\_\_\_\_\_\_\_\_\_\_\_ (2.37)$$

In this study, three special cases have been considered while considering the values of β and γ.

i) β and γ are not functions of temperature

ii) β and γ are linear functions of temperature

iii) β and γ are quadratic functions of temperature

In each case, the expression for the specific heat, C, has been derived as

$$C = \frac{\partial \epsilon_n}{\partial T} \_\_\_\_\_\_\_\_\_\_\_\_ .(2.38)$$

The critical temperature of transition, T_c has been calculated from condition

$$\left(\frac{\partial C}{\partial T}\right)_{T=T_c} = 0 \_\_\_\_\_\_\_\_\_\_\_\_ (2.39)$$

2.17 Results

Since βx^3 and γx^4 must have the same dimensions of energy (ML^2T^{-2}), the dimensions of β and γ should be $ML^{-1}T^{-2}$ and $ML^{-2}T^{-2}$, respectively.

Thus, a parameter with dimensions of length has been introduced, which is fundamental to the perturbation parameter β and γ.

This parameter in terms of length is denoted by a_0, and it is defined as the distance between the vibrating apical oxygen atom O, and the conduction plane. The high – T_c oxide planar superconductors have different number of immediate adjacent planes separated from each other by about 3.2 Å. thus, it was proposed that,

$$a_0 = Cu_p \rightarrow O_3 + \sqrt{3}.2Å\,(n-1) \qquad (2.40)$$

where $Cu_p \rightarrow O_3$ stands for the distance between the vibrating apical oxygen atom, O_3 and the conduction Cu_p plane and the quantity.

$$\sqrt{3}.2Å\,(n-1) \leq Cu_p \rightarrow O_3$$

It should be understood that other superconducting parameters are correlated with structural parameters such as Cu_p to apex –O bond, pair density and coherence length (Cava, Dover, Bathlogg & Rietinann, 1987).

2.18 Buckling and breathing modes

This arrangement in which oxygen atoms are above and below the Cu atoms is called apical. These are called apical oxygen atoms. The distance between the copper atoms and an apical oxygen atom is around 2.4Å, whereas the distance between Cu and O (Cu-O) in the plane is around 1.9 Å , which is the intra layer distance. The apical Oxygen atoms can vibrate with a high frequency called breathing mode, or low frequency called buckling mode.

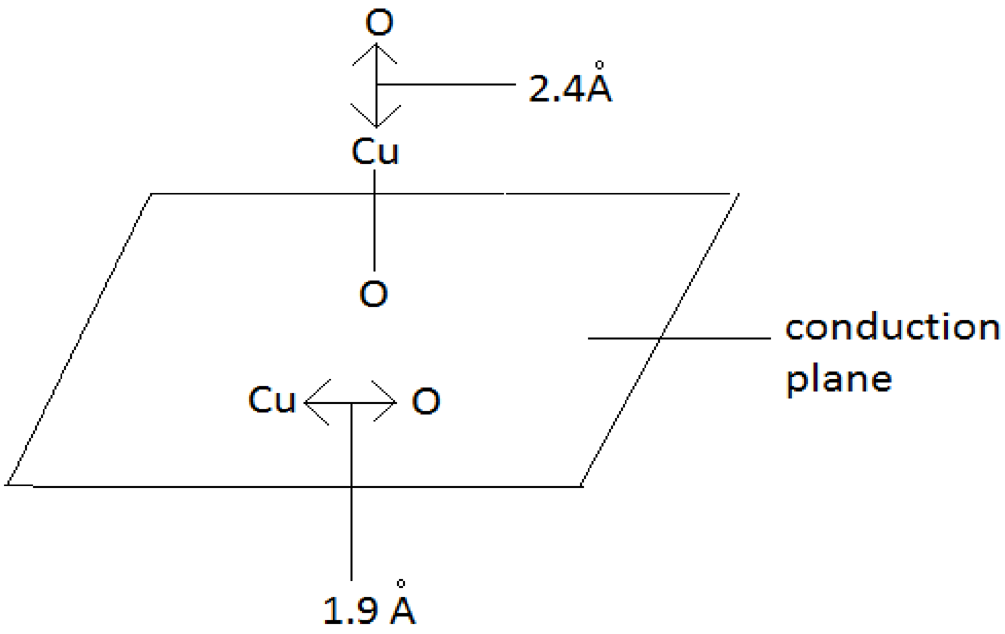

Figure 2.2 the apical arrangement

For numerical calculations, the following optical phonon energies have been used (Khanna & Kirui, 2002).

Buckling mode

$\hbar\omega = 8.01 \times 10^{-21}$ J,θ = 580.43K ________________________________.(2.41)

Breathing mode

$\hbar\omega = 1.602 \times 10^{-20}$ J, θ= 1160.87K-________________________________ (2.42)

β and γ are not functions of temperature

The parameters of perturbation are defined as,

$$\beta = \frac{\hbar\omega}{a_0^3}, and \;\; \gamma = \frac{\hbar\omega}{a_0^4} \qquad (2.43)$$

equation (2.36) on substituting β and γ becomes,

$$\epsilon_n = A_{10} + (A_{21} + A_{22}) exp\left(-\frac{\theta}{T}\right) \qquad (2.44)$$

where

$$A_{21} = A_{11}\frac{\hbar\omega}{a_0^3} \; ; and \; A_{22} = A_{12}\frac{\hbar^2\omega^2}{a_0^6} \qquad (2.45)$$

Thus, the expression for the specific heat, C, becomes

$$C = \frac{\partial\epsilon_n}{\partial T} = A_{23}\frac{\theta}{T^2}\, exp\left(-\frac{\theta}{T}\right) \qquad (2.46)$$

where $A_{23} = A_{21} + A_{22}$

We shall now calculate the transition temperature for the compound

$La_{2-x}Sr_xCuO_4[La(n = 1)]$ for which

$a_0 = 2.41 \times 10^{-10} m.$

The expression for the critical transition temperature is T_c obtained from equation (2.39). Substituting from equation (2.46) in equation (2.40) we get,

$$\left(\frac{\partial C}{\partial T}\right)_{T=T_c} = \left[\frac{2A_{23}\theta}{T_c^3} + \frac{A_{23}\theta^2}{T_c^4}\right] exp\left(-\frac{\theta}{T}\right) = 0 \qquad (2.47)$$

From equation (2.29), the expression for T_c Buckling and Breathing modes for the compound

$La_{2-x}Sr_xCuO_4[La(n=1)]$ and $a_0 = 2.41 \times 10^{-10} m$ were obtained as follows:

Buckling mode

For this

$$\frac{A_{21}}{A_{22}} = -9.42K$$

Therefore equation (2.37) becomes,

$T_c^3 + 580T_c^2 + 168200T_c - 158444 = 0$ and this gives, T_c= 9.1K

Breathing mode

For this. $\frac{A_{31}}{A_{32}} = -37.7K$, and equation (2.36) becomes,

$T_c^3 + 1160T_c^2 + 672800T_c - 25386664 = 0$ and this gives T_c= 35.5K

which is close to the experimental value of, T_c= 38K

Similar calculations can be done for other compounds. Thus, one can find the detailed calculations where β and γ are quadratic functions of temperature (Khanna & Kirui, 2002).

2.19 Discussion of the results in section 2.17

To study the properties of the high -T_c superconductors, it has been assumed in this study that three electrons are responsible for superconducting current. Two of these electrons form an exotic bound pair and the third electron is a polarization electron that hops from one site to another site of similar symmetry. It was assumed that the pairs of electrons are interacting through a harmonic oscillator potential while the polarization electron acts as a perturbation on the apical oxygen ions. Time independent many-body perturbation theory had been used with the perturbation.

$$H = \beta x^3 + \gamma x^4$$

to obtain the expression for the energy ϵ_n of the system. The specific heat, C, and the transition temperature, T_c were calculated for three special cases. For linear temperature dependence β and γ when the calculated and experimental values of T_c are compared, it is found that the breathing mode (high frequency vibrations) contribute to the electron-phonon coupling. This means that the high frequency vibrations contribute to the exotic pairing.

On the other hand for quadratic temperature dependence of β and γ, the comparison between calculated and experimental values of T_c shows that buckling mode (low frequency vibrations) contributes to the electron – phonon coupling and, therefore the exotic pairing.

However, the present study has clearly confirmed the effect of exotic pairing and hopping electron on the phenomena of transition to superconductivity. It has been established that both the linear and quadratic temperature dependence of the perturbation parameters play an important role in the theory of high -T_c superconductivity. It is well known that other parameters like depolarization rate, penetration depth, coherence length and critical current density are all temperature dependent (Hott et.al., 1999).

It can therefore be concluded that the anharmonic perturbation of phonons with perturbation parameters depending on temperature for both high and low frequency modes significantly increase the value of the transition temperature T_c.

CHAPTER THREE

METHODS OF THE STUDY

The algebra developed correlates the operators associated with the electrons (fermions) to the operators associated with the bilinear electron operators that correspond to a pair of electrons as follows

From the Physics of the second quantization;

$a_{\uparrow}^{+}$ ≡ Creation operator,

$a_{\uparrow}^{-}$ ≡ annihilation or destruction operator,

Corresponding operators with spin down are;

$a_{\downarrow}^{+}$ and $a_{\downarrow}^{-}$

Such operators belong to an algebra, keeping in mind the spin of the particles. In the absence of pairing, these operators define normal electrons. Hence they should generate two unrelated operators say $h_{-\sigma}$ and h_{σ} such that

$h_{-\sigma} = a_{\sigma}^{+},\ a_{\sigma}^{-}$ ____(3.1)

$(a_{\sigma}^{\pm})^2 = 0$ ____(3.2)

$[h_{\sigma}, a_{-\sigma}^{\pm}] = 0$ ____(3.3)

Where the following anti-commutators have values,

$\{a_{\uparrow}^{+},\ a_{\downarrow}^{+}\} = \{a_{\uparrow}^{-},\ a_{\downarrow}^{-}\} = 0$ ____________________________________(3.4)

$\{a_{\uparrow}^{+},\ a_{\downarrow}^{-}\} = \{a_{\sigma}^{+},\ a_{-\sigma}^{-}\} = 0$ ____________________________________(3.5)

$\{a_{\sigma}^{-},\ a_{-\sigma}^{+}\} = 0$ ____(3.6)

Since creation and annihilation operators for different spins are assumed to anti-commute,, BCS theory has to use products of operators in order to describe Cooper pairs. Products of operators in the BCS theory are not part of the algebra described in equations (3.1) to (3.6).

Consequently this is one of the features from which the algebraic inconsistencies of the BCS theory arise. The only way out of such inconsistencies is resorting to an alternative algebraic structure that will more clearly describe electron-electron pairing. To this aim, it should be observed that a coherent scheme should further include in the algebra, creation and annihilation operators b^+ and b^- for the particles (of integer spin) generated by binding pairs of electrons. If the two electrons with spin up and down are bound, then the net speed is zero ($\frac{1}{2} - \frac{1}{2} = 0 = spin \longrightarrow S$); and if two electrons spin the same direction are bound, then S=$\frac{1}{2} + \frac{1}{2} = 1$ or S=-$\frac{1}{2} - \frac{1}{2} = -1 = |1|$

Such operators have to be by bilinear in the electron operators, i.e. they have to be in the form $a^+a^+ \ or \ a^-a^-$; and because of the statistics requirement (pairs of fermions) must give rise to bosons, they should belong to the even sector of the graded algebra. The only way it can be achieved is to replace the ant-commutators

$\{a_\uparrow^\pm, \ a_\downarrow^\pm\}$ = 0 by the relation

$\{a_\uparrow^\pm, \ a_\downarrow^\pm\} = b^\pm$ ____(3.7)

where $b^\pm = (a_\sigma^\pm)^2$ ____________________________________(3.8)

or $b^+ = a^+a^+$____(3.9)

$b^- = a^-a^-$ ____(3.10)

If there exists pairing, the b's are finite; but in the absence of pairing $(a_\sigma^\pm)^2$ = 0, And hence b's will be zero.

The new anti-commutation relations given in equation (3.7) formalize the physical requirement that, due to the interaction, electrons belonging to a pair should lose their fermionic nature, allowing for Cooperons to have unlimited occupation numbers in an energy state.

Thus, the Physics of superconductivity requires a super-algebra with 8 generators, 4 of them odd $(a_\uparrow^+, a_\downarrow^+, a_\uparrow^-, a_\downarrow^-)$ and 4 of them even $(b^+, b^-, h_\downarrow, h_\uparrow)$, and the relations given by the equations (3.1), (3.2), (3.3), and (3.7).

Hence the following relations must hold,

(i) Odd-odd

$$\{a_\uparrow^\pm,\ a_\downarrow^\pm\} = \{a_\sigma^\pm,\ a_{-\sigma}^\pm\} = 0 \tag{3.11}$$

(ii) Even –odd

$$[h_\sigma, a_{-\sigma}^\pm] = \pm\, a_{-\sigma}^\pm \tag{3.12}$$

$$[b^\pm, a_\sigma^\pm] = 0 \tag{3.13}$$

$$[b^\pm, a_\sigma^\mp] = \mp\, a_{-\sigma}^\pm \tag{3.14}$$

(iii) Even-even

$$[h_\uparrow, h_\downarrow] = 0 \tag{3.15}$$

$$[b^-, b^+] = 4(h_\uparrow + h_\downarrow) \tag{3.16}$$

$$[h_\sigma, b^\pm] = \pm\, b^\pm \tag{3.17}$$

Using equations (3.8), (3.9), (3.10) and (3.11), the results given in equations (3.12), (3.13), (3.14), (3.15), (3.16) and (3.17) can be proved.

CHAPTER FOUR

THEORETICAL DERIVATIONS

4.1 The Algebra of coupled electrons in Superconductivity

The question whether electron pairs could give rise to a complete Bose-Einstein Condensation in the theory of superconductivity is yet to be answered (Piekarz, Konior, Blatter, Blatt & Bill, 1999). However, it is generally believed that superconductivity may be viewed as the Bose condensation of weakly bound Cooper pairs (Noziers et.al., 1985), but the superconducting instability is induced by the weak attraction when the bound pairs have strong overlap and fermion exchange becomes dominant.

In this picture

$$\left(\frac{N}{V}\right) a_0^3 \geq 1$$

where N is the number of charge carriers in volume V, and a_0 is the characteristic length of the order of the linear size of a bound pair. Now, due to saturation imposed by the Pauli Exclusion Principle, the wave function is assumed to extend in *k*-space in such a way as to accommodate in the ground state the largest number of pairs compatible with *N*. This implies that the Cooper pairs can be treated as “hardcore bosons” of integer spin and the square of their creation operator is equal to zero, i.e.

$$(b_k^+)^2 = (a_k^+ a_{-k}^+)^2 = 0 \qquad (4.1)$$

Infact, the attractive interaction due to phonons can be considered as a perturbation such that it does not change the space of states, and for this reason Cooper pairs can be treated as “hardcore bosons” of integer spin and the square of their creation operator is equal to zero, i.e. keeping this in mind, it is observed that a coherent scheme should include in the algebra creation and annihilation operators $a_k^{\pm}$ for the particles of integer spin generated by binding pairs of electrons. Such operators should be bilinear in the electron operators and because of statistics requirement (pair of fermions must give rise to bosons) they should belong to the even sector of the graded algebra in which scheme anticommutators,

$$\{a_{\uparrow}^{\pm}, a_{\downarrow}^{\mp}\} = 0 \qquad (4.2)$$

will be replaced by

$$\{a_{\uparrow}^{\pm}, a_{\downarrow}^{\pm}\} = b^{\pm} \qquad (4.3)$$

As such there could be two systems:-

i.) One in which there are only Cooperons, and

ii.) The second could be several Cooperons and one extra electron.

System (i) in which there are only Cooperons refers to the BCS theory which is not able to explain the main features of high -T_c superconductivity, while system (ii) in which there could be several Cooperons and one extra electron such that is a two electron system and a third electron. The new anticommutation relation in equation (4.3) formalizes the physical requirement that due to the interaction, electrons belonging to a pair should lose the fermionic nature, allowing for the Cooperons to have unlimited occupation numbers (Bose condensation).

Hence, Physics appears to look for a super algebra with eight generators, 4 of them odd $\{a_{\uparrow}^{+} a_{\downarrow}^{+}, a_{\uparrow}^{-}, a_{\downarrow}^{-}\}$ and 4 even $\{b^{+}, b^{-} h_{\uparrow}, h_{\downarrow}\}$ for relations (4.1) and (4.3).

An investigation among simple Super algebras of small dimensions (Mihailovic et.al., 1990) indicates that there exists only one super algebra whose Jordan products, besides relations (4.1) and (4.3) are the following:

i.) Odd – Odd

$$\{a_{\uparrow}^{\pm}, a_{\downarrow}^{\mp}\} = 0$$

ii.) Even –Odd

$\lfloor h_\sigma, a_\sigma^\pm \rfloor = \pm a_\sigma^\pm$

$\lfloor b^\pm, a_\sigma^\pm \rfloor = 0$

$\lfloor b^\pm, a_\sigma^\mp \rfloor = \mp a_{-\sigma}^\pm$

iii.) Even – Even

$[h_\uparrow, h_\downarrow] = 0$

$(b^-, b^+) = 4(h_\uparrow + h_\downarrow)$

$[h_\sigma, b^\pm] = \pm b^\pm$; $h = h_\uparrow + h_\downarrow$

$2h = \{a^+, a^-\}$

Cooperons are represented in the even sub-algebra generated by $\{b^+, b, h = h_\uparrow + h_\downarrow\}$ in agreement with (Celeghini, Rasetti & Vitiello, 1995). From system (ii) which is a two electron system and a third electron, the function associated with the third electron may be written as:-

$a^+ |0\rangle$

The total wave function of the three electrons system involved in the superconducting current can be written as:

$$\Psi = \prod_k (U_k + V_k b_k^+) a_k^+ |0\rangle \qquad (4.4)$$

where $b_k^+ = a_k^+ a_{-k}^+$.(4.5)

and U_k and V_k are constants such that for fermions,

$$U_k^2 + V_k^2 = 1 \qquad (4.6)$$

It can be shown that:

$$(\Psi,\Psi) = (1 - n_e)\prod_k (U_k^2 + V_k^2) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ (4.7)$$

Here n_e refers to the density of the third electron, and is given by

$$n_e = \frac{1}{e^{\beta(\varepsilon_i - \mu)} + 1} \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ (4.8)$$

Thus,

$$(\Psi,\Psi) = \left[\frac{e^{\beta(\varepsilon_i - \mu)}}{1 + e^{\beta(\varepsilon_i - \mu)}}\right]\prod_k (U_k^2 + V_k^2) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ (4.9)$$

Since (Ψ, Ψ) = 1 and $U_k^2 + V_k^2 = 1$,

$$e^{\beta(\varepsilon_i - \mu)} \gg 1 \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ (4.10)$$

If we write

$$\beta(\varepsilon_i - \mu) = \alpha \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_. (4.11)$$

then for $e^{\alpha} \gg 1$, the transition temperature T_c at which this may happen is given by

$$\beta(\varepsilon_i - \mu) = \alpha = \frac{1}{KT_c}(\varepsilon_i - \mu) \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ (4.12)$$

For e^{α} to be large, α can be chosen arbitrarily as α = 5 or more; whereas $(\varepsilon_i - \mu)$ is known to be 0.05*eV* (Khanna, 2008).

Thus,

$$T_c = \frac{\varepsilon_i - \mu}{\alpha K} = 115.94\text{K} \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_. (4.13)$$

And this value of T_c falls in the range of transition temperatures for high - T_c superconductors.

In this picture the Cooperon acquires the nature of true Bose particles as far as statistics is concerned, but the theory does not distinguish otherwise between a Cooperon and a pair of non-interacting electrons. However, the question remains open whether this exactly replaces physical phenomena or should rather be considered as an approximation

(Tinkham, 2004) or approximate description. However, in this description, Cooper pairs are true bosons which can occupy each state, and their number is limited to the number (½ N_e), and the corresponding Hamiltonian will deal with multi Cooperon states. Assuming that the total number of electrons is even, the ground state is written as

$$|\Psi_{g.s}\rangle = \prod_{k} |\Psi_{g.s}\rangle_k \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_(4.14)$$

where $|\Psi_{g.s}\rangle$ is a super position of all possible states with all electrons coupled in pairs of total momentum zero. Contrary to BCS theory, where only states, with zero or one Cooperon, can be mixed, here we realize the mixing of the infinitely many accessible states. The Hamiltonian for such an assembly will be

$$H = \sum_{k} \epsilon_k \, n_k + \sum_{p,q} W_{p,q} \, b_p^{+} b_q^{-} \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_(4.15)$$

(Here $W_{p,q}$ is the electron – phonon interaction) or electron – electron interaction. Due to the phonon field; this interaction is negative or attractive. The number of electrons is given by

$$N_e = \sum_{k} n_k \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_(4.16)$$

Where $\epsilon_k = \varepsilon_k - \mu$

Here n_k counts the electrons that may be bound into Cooperons in the state labeled by *k*. Now the following can be calculated;

$$\langle \Psi_{g.s} | H | \Psi_{g.s} \rangle,$$

which will give ground state energy; and also

$$\langle \Psi_{g.s} | N_e | \Psi_{g.s} \rangle = vN \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_(4.17)$$

Where *v* stands for desired filling.

The infinitely many accessible states can be mixed by introducing the unitary Bogoliubov operator (Celeghini, Rasetti & Vitiello, 1995)

$$U = \prod_k U_k \,; U_k = e^{-i\Phi_k(b_k^+ + b_k^-)} \qquad (4.18)$$

where $|\Psi_{g.s}\rangle$ can be straightforwardly obtained in a variational way, by introducing first the trial state vectors

$$|\Psi_{g.s}\rangle_k = U_k(\Phi_k)|0\rangle \qquad (4.19)$$

and finding then the set of parameters { Φ_k} which minimize the energy expectation value

$$\langle \Psi_{g.s}|H|\Psi_{g.s}\rangle$$

Together with this, the equation (4.17) must exist in order to obtain the consistent value of μ necessary to impose the desired filling v. Solution to the system of the resulting N+1 equations, N for the k states {Φ_k } and one for μ. have to be obtained.

The algebra of free electrons is assumed to be influenced by the interaction induced by phonons. This theory has to be reformulated in such a way as to capture all the features described within the algebra based on Cooper pairs such that superconductivity is a result of the Bose condensation of weakly bound pairs.

$$H = \sum_k \epsilon_k a_k^+ a_k + \sum_{p,q} W_{p,q} a_p^+ a_{-p}^+ a_q a_{-q}$$

where

$$\left\langle 0 \left| \sum_k \epsilon_k a_k^+ a_k \right| 0 \right\rangle = \sum \epsilon_k n_k$$

is an expression where the condition for the overlapping states is not applicable.

Now $|\Psi_{g.s}\rangle = \prod|\Psi_{g.s}\rangle_k$ and $U_k = e^{-i\Phi_k(b_k^+ + b_k)}$

where Φ_k is a parameter that is used to minimize energy $\langle\Psi_{g.s}|H|\Psi_{g.s}\rangle$ and we write

$$|\Psi_{g.s}\rangle_k = \mathrm{U}_k\,|0\rangle_k = e^{-i\Phi_k(b_k^+ + b_k)}\,|0\rangle_k$$

Thus,

$$|\Psi_{g.s}\rangle = \prod_k e^{-i\Phi_k(b_k^+ + b_k)}|0\rangle_k$$

where $b_k^+ = a_k^+ a_{-k}^+$ and $b_k = a_k a_{-k}$

I can calculate,

$\langle\Psi_{g.s}|H|\Psi_{g.s}\rangle$, which will give ground state energy, and also $\langle\Psi_{g.s}|N_e|\Psi_{g.s}\rangle = \nu N$,

where ν stand for desired feeling.

$$N_e = \sum_k n_k$$

and n_k counts electrons possibly bound into Cooperons in the state labeled by *k*.

The expression, $e^{-i\Phi_k(a_k^+ a_{-k}^+ + a_k a_{-k})}$, can be expanded and when it operates on $|0\rangle$, due to Pauli exclusion principle, only the first two terms in the expansion will give finite values.

Hence, $e^{-i\Phi_k(a_k^+ a_{-k}^+ + a_k a_{-k})} \approx 1-\Phi_k(a_k^+ a_{-k}^+ + a_k a_{-k})$, and

$$\langle\Psi_{g.s}|H|\Psi_{g.s}\rangle = \left\langle 0\left|\prod_k(1-\Phi_k(a_k^+ a_{-k}^+ + a_k a_{-k}))H\right|\left[\prod_k(1-\Phi_k(a_k^+ a_{-k}^+ + a_k a_{-k}))\right]|0\rangle\right\rangle \quad (4.20)$$

The first term in equation (4.20) will be,

$$\left\langle 0\left|\prod_k[1-\Phi_k(a_k^+ a_{-k}^+ + a_k a_{-k})]\left(\sum_k \epsilon_k\, a_k^+ a_{-k}\right)\prod_k[1-\Phi_k(a_k^+ a_{-k}^+ + a_k a_{-k})]\right|0\right\rangle \ldots (4.21)$$

The first term in equation (4.21) is

$$\langle 0| \prod_k \left(\sum_k a_k^+ a_k \in_k \right) \prod_k |0\rangle$$

When the system is in a single ground state, the condition for the overlapping of states given by

$$\prod_k |0\rangle$$

will not be required and hence

$$\langle 0| \prod_k \left(\sum_k a_k^+ a_k \in_k \right) \prod_k |0\rangle$$

can be written, knowing that $\langle 0||0\rangle$ =1 as

$$\left\langle 0 \left| \sum_k \epsilon_k a_k^+ a_k \right| 0 \right\rangle = \sum_k \in_k n_k$$

and this is the first term of H in equation (4.15). The rest of the terms in equation (4.21) will correspond to second term of H in equation (4.15).

4.2 The Algebra of High - T_c Superconductivity due to a Long – Range Electron – Phonon Interaction

In the superconducting state $(T < T_c)$ single particle excitations interact with the pair-condensate via the same short range attractive potential which forms the pairs (Candolfi et.al., 1995). Now on the basis of the long-range electron – phonon interaction mechanism, the expression for specific heat C is

$$C = \frac{\partial \in_n}{\partial T}$$

and the critical temperature T_c is obtained from the condition

$$\left(\frac{\partial C}{\partial T}\right)_{T=T_c} = 0$$

The Hamiltonian describing the interaction of excitations with pair Bose-condensate is written as

$$H = -\sum_{sm,n,}[t(m-n)+\mu\delta_{m,n}]C_{sm}^{+}C_{sn} + \sum_{m}[\Delta(m)C_{\uparrow m}^{+}C_{\downarrow m} + HC]\_\_\_\_\_\_(4.22)$$

where $s = \uparrow, \downarrow$ stands for the spin, μ is the chemical potential, $\Delta\,(m)$ is the off-diagonal potential in the strong-coupling regime and is mainly determined by the pair Bose condensate, and $t(m-n)$ is the kinetic energy difference between the two sites,m and n.

Using Bogoliubov transformation, the old and the new operators, a_k, $\alpha_k$and β_k are related to each other by the following relations,

$$a_{k,1/2} = U_k\alpha_k + V_k\beta_k^{+} \text{ and } a_{-k,-1/2} = U_k\beta_k - V_k\alpha_k^{+}\_\_\_\_\_\_\_\_\_\_\_\_(4.23)$$

According to Heisenbberg's representation, the time development of an operator (which is also called the equation of motion of the Heisenberg operator) is,

$$a(t) = a(t=0)e^{-i\hbar\omega t} = a(t=0)e^{i\epsilon_k t}\_\_\_\_\_\_\_\_\_\_\_\_\_\_. (4.24)$$

where $\epsilon_k$refers to the band dispersion energy of a polaron or an electron. Thus, combining the Bogoliubov transformation and Heisenberg's operators, the operators $C_{\uparrow m}$and $C_{\downarrow m}$

can be expressed as;

$$C_{\uparrow m}(t) = \sum_{j}[U_j(m)a_j e^{-i\epsilon_j t} + V_j^{*}(m)\beta_j^{+}e^{-i\epsilon_j t}]\_\_\_\_\_\_\_\_\_\_\_\_(4.25)$$

$$C_{\downarrow m}(t) = \sum_j \left[U_j(m)\beta_j e^{-i\epsilon_j t} - V_j^*(m)\alpha_j^+ e^{-i\epsilon_j}\right] \_\_\_\_\_\_\_\_ (4.26)$$

Substituting equations (4.25) and (4.26) into equation (4.22), the single particle excitation spectrum equations become,

$$\epsilon U(m) = -\sum_n \left[t(m-n) + \mu\delta_{m,n}\right] U(n) + \Delta(m) + \Delta(m)V(m) \_\_\_\_\_\_\_\_ (4.27)$$

$$-\epsilon U(m) = -\sum_n \left[t(m-n) + \mu\delta_{m,n}\right] V(n) + \Delta(m)U(m) \_\_\_\_\_\_\_\_ (4.28)$$

In this superconducting state, the excitation wave function is a superposition of plane waves, such that we can write.

$$U(m) = U_k e^{ik.m} + U_k^+ \_\_\_\_\_\_\_\_ \quad (4.29)$$

and

$$V(m) = V_k e^{j(k-g).m} + V_k^+ e^{j(k-g_y).m} \_\_\_\_\_\_\_\_ .. \ (4.30)$$

where $g_x = (\pi, 0)$; $g_y = (0, \pi)$and $g = (\pi, \pi)$ are reciprocal double lattice vectors. Substituting equations (4.29) and (4.30) into equations (4.28) and (4.27), one obtains four coupled algebraic equations,

$$\epsilon_k U_k = \varsigma_k U_k - \Delta_c(V_k + V_k^+) \_\_\_\_\_\_\_\_ (4.31)$$

$$+\epsilon_k U_k^+ = \varsigma_{k-g} U_k^+ + \Delta_c(V_k - V_k^+) \_\_\_\_\_\_\_\_ (4.32)$$

$$-\epsilon_k V_k = \varsigma_{k-g_x} V_k + \Delta_c(U_k - U_k^+) \_\_\_\_\_\_\_\_ (4.33)$$

$$-\epsilon_k V_k^+ = \varsigma_{k-g_x} V_k^+ - \Delta_c(U_k - U_k^+) \_\_\_\_\_\_\_\_ (4.34)$$

where

$$\varsigma_k = -\sum_n t(n) e^{ik.n} - \mu$$

The determinant of the system of equations (4.31) to (4.34) gives the following equations for the energy spectrum

$$(\epsilon_k + \varsigma_k)(\epsilon_k - \varsigma_{k-g})(\epsilon_k + \varsigma_{k-g_x})\left(\epsilon_k + \varsigma_{k-g_y}\right) = \Delta_c^2\left(2 \in_k + \varsigma_{k-g_x} + \varsigma_{k-g_y}\right)(2\epsilon_k - \varsigma_k - \varsigma_{k-g}) \quad \text{4.35)}$$

Equation (4.35) has two positive roots for $\in_{k,}$ and these will describe the single particle excitation spectrum. When the pair binding energy $2\Delta_p$ is large compared with the energy gap Δ_c, and with the single particle band width *w* the chemical potential in this limit is,

$$\mu = -\left(\Delta_p + \frac{w}{2}\right) \quad (4.36)$$

Thus, μ is negative and its magnitude is large compared with Δ_c. The right hand side of equation (4.35) gives the spectrum, i.e.

$$\in_{1k} \cong \varsigma_k - \frac{\Delta_c^2}{\mu} \quad (4.37)$$

$$\in_{2k} \cong \varsigma_{k-g} - \frac{\Delta_c^2}{\mu} \quad (4.38)$$

Knowing the values of the parameters in equations (4.37) and (4.38), the energy spectrum could be obtained. However, if we decide to choose ς_k and ς_{k-g} in such a manner that they are equal, then the two equations will correspond to the same energy spectrum. Thus we can write,

$$\in_k \cong \varsigma_k - \frac{\Delta_c^2}{\mu} \quad (4.39)$$

Now Δ_c as a function of temperature is given by,

$$\Delta_c(T) = \frac{1}{2}\sum_{k^1} V_{kk^1}\frac{\Delta_{k^1}}{\left(\in_{k^1}^2 + \Delta_{k^1}^2\right)^{1/2}}\ tanh\frac{\left(\in_{k^1}^2 + \Delta_{k^1}^2\right)^{1/2}}{2kT} \quad (4.40)$$

Substituting for $\Delta_c(T)$ from equations (4.40) in the equation (4.39), we get an expression for $\in_k$ as a function of *T*. Numerical methods can be used to calculate $\in_k$ as a function of *T*.

The specific heat C can be obtained as,

$$C = \frac{\partial \in_k}{\partial T} \qquad (4.41)$$

And this can also be calculated numerically as function of temperature T. Similarly the transition temperature T_c can be obtained from the following equation,

$$\left(\frac{\partial C}{\partial T}\right)_{T=T_c} = 0 \qquad (4.42)$$

4.3 The Algebra of Coupled Electrons in High –T_c Superconductivity based on Spin Fluctuation Mechanism

Under spin fluctuations mechanism in superconductivity, the value of the critical temperature $\boldsymbol{T_c}$ depends on such factors as governed by the equatioian, (Junod, et.al, 1983),

$$T_c = \frac{\theta_D}{1.45} exp\left[-\frac{1.04(1+\lambda_{eff})}{\lambda_{eff} - \mu^*_{eff}(1+0.62\lambda_{eff})}\right]$$

where θ_D= 310K is the Debye temperature, λ_{eff} and μ^*_{eff} are the normalized parameters which can be expressed as [14,16,17];

$$\lambda_{eff} = \lambda_{e-ph}(1+\lambda_{sf})^{-1} and\ \mu^*_{eff} = (\mu^* + \lambda_{sf})(1+\lambda_{sf})^{-1}$$

where λ_{sf} is a contribution arising from spin-fluctuations, λ_{e-ph} the electron – phonon coupling constant and μ* = 0.08 is renormalized Coulomb parameter (Mcmillan & Daams, 1981).

Over the last more than two decades, both experimental and theoretical studies were made on materials that not only undergo superconducting transition but also exhibit rather unconventional properties in their normal and superconducting states. There are materials that contain rare-earth ions or the heavy fermion, $CeCu_2Si_2$ compound, which display an intimate, interplay of superconductivity and magnetism (Lynn, Jarlburg & Steghich, 1985). There are also intermetallic actinides such as Upt_3 or UCo_2 with spin fluctuation behavior (Stewart & Frings, 1985) that contribute to superconductivity. Only a few materials are without any actinide element fluctuation behavior (Junod, et.al, 1983).

There has been great attention on the intermetallic Perovskite superconducting $MgCNi_3$ (He et. al., 2001) where strong ferromagnetic spin fluctuations have been observed by NMR measurements (Singer et. al., 2001). These fluctuations could either suppress superconductivity or induce an exotic pairing mechanism (Rosner et.al., 2001). In general, spin fluctuation effects usually manifest themselves at low temperatures as a T^2 term in the electrical resistivity, a parabolic temperature dependence of the magnetic susceptibility, and for some compounds, in an upturn of the specific – heat temperature dependence (Stewart & Frings, 1985).

Recently, a type II superconductor, Mo_3Sb_7 which crystallizes with a Ir_3Ge_7 type structure, was identified as being a Pauli paramagnet with superconducting transition temperature, T_c = 2.1K and an upper critical field of 17kwb (Bukowski et.al., 2002).

In another experimental observation (Dmitriev et.al., 2006) on a Mo_3Sb_7 polycrystalline sample, measurements were made for the first time on electrical resistivity, magnetic susceptibility and heat capacity. The result suggested that Mo_3Sb_7 could be classified as a co-existent superconductor – spin fluctuation system.

CHAPTER FIVE

RESULTS AND DISCUSSIONS

5.1 Results

Low temperature behavior shows sharp specific heat discontinuity, ΔC, occurring at T_c= 2.3K, thus showing specific heat jumps at the transition temperature to the superconducting state. (figure 5.1)

The normal state heat capacity data can be generally recovered by using an expression of the form, (Candolfi et.al., 2007)

$$C_c = \gamma_n T + \beta_n T^3 + \alpha_n T^5 \quad (5.1)$$

where γ_n = electronic specific – heat co-efficient.

β_n = Lattice specific – heat co-efficient

α_n = a term to account for the anharmonicity of the lattice.

Numerical methods are applied to equation (4.41) to yield equation (5.1). If there is a characteristic anomaly in the specific heat, then a term $T^3 log\left(\frac{T}{T_{sf}}\right)$ due to spin fluctuation is added (Moriya, Doniach, Brinkman & Berk, 1979), where T_{sf} is the spin fluctuation temperature. A rough estimate of this characteristic temperature (T_{sf}) is obtained by making measurements on magnetic susceptibility. For Mo_3Sb_7 it turns out to be T_{sf}= 180K (fig. 5.3) (Brodsky, 1974). The values of the co-efficients are, (Subraanyam & Raja, 1989)

γ_n = 34.2*mJ/mol.K*^{2}

β_n = 0.65*mJ/mol.k*^{4}

α_n= 2.65 x $10^{-3}{}_k$ *mJ/mol.K*^{6}

The value of the specific heat jump.

$\Delta C = 80.\ mJ/mol\ K$

and the ratio at T_c= 2.25K

$$\frac{\Delta C}{\gamma_n T_c} = \frac{80.\ mJ/mol\ K}{(34.2mJ/mol.K^2)(2.25k)} = \frac{80}{76.95} = 1.24$$

.

This value for the ratio $\frac{\Delta C}{\gamma_n T_c}$ is much lower than the BCS value which is1.43 (Kresin et.al., 1975). The ratio $\frac{A}{\gamma_n^2}$ = 0.55x10^{-5} *molcm*$\left(K.\frac{mol}{mJ}\right)^2$ and this relation can be explained in terms of the spin fluctuation theory (Kadowaki et.al., 1986). This is thus another evidence of the possibility for, Mo_3Sb_7 to be considered as a spin fluctuator.

Now for Mo_3Sb_7 the specific heat jump.

$\Delta C = \frac{80.mJ/mol}{K}$ is a measured value, and thus its magnitude is under no dispute.

T_c = 2.25K is also a measured quantity. If the ratio $\frac{\Delta C}{\gamma_n T_c}$ has to correspond to the BCS value of 1.43, then the only quantity that must change is γ_n; rather γ_n should be less than

$$\frac{34.2mJ/mol}{K^2}$$

Hence, γ_n which is the electronic specific heat co-efficient must be smaller than the value used earlier (Kadowaki et.al., 1986). To get the new value γ_n that should be smaller, we write,

$$\frac{\Delta C}{\gamma_n T_c} = 1.43$$

or

$$\gamma_n = \frac{\Delta C}{1.43 \times T_c} = \frac{80.mJ/mol}{K \times 1.43 \times 2.25K} = \frac{80.mJ/mol}{3.2175K^2} = \frac{24.86mJ/mol}{K^2}$$

This means that the electronic contribution to the specific – heat may be smaller than the value usually anticipated. This reduction points to spin fluctuations.

Thus, the measurements on the electrical, magnetic and thermal properties along with the characteristic specific – heat anomaly at T_c of a polycrystalline Mo_3Sb_7 sample clearly confirm the bulk nature of the superconductivity, and that Mo_3Sb_7 can be classified as a co-existent superconductor-spin fluctuation system. The above mentioned properties of such a system could possibly be studied within the frame work of spin fluctuation theory.

The calculations presented above regarding the value of γ_n such that the value of the ratio $\frac{\Delta C}{\gamma_n T_c}$ conforms to the BCS value, leads to the assertion that Mo_3Sb_7 is a co-existent Superconductor-spin fluctuation system. Using the well-known BCS value for

$$\frac{\Delta C}{\gamma_n T_c} = 1.43$$

Table 5.1 Variation of Specific heat with temperature

Specific heat, C (J $mol^{-1}K^{-1}$)	**Temperature, T(K)**
0.00	0.60
0.028	0.75
0.084	1.00
0.112	1.50
0.140	1.75
0.168	2.00
0.028	2.00
0.056	2.50
0.112	3.75
0.168	4.25
0.196	4.75
0.252	5.50
0.364	6.25
0.504	7.25
0.616	8.00
0.980	9.25

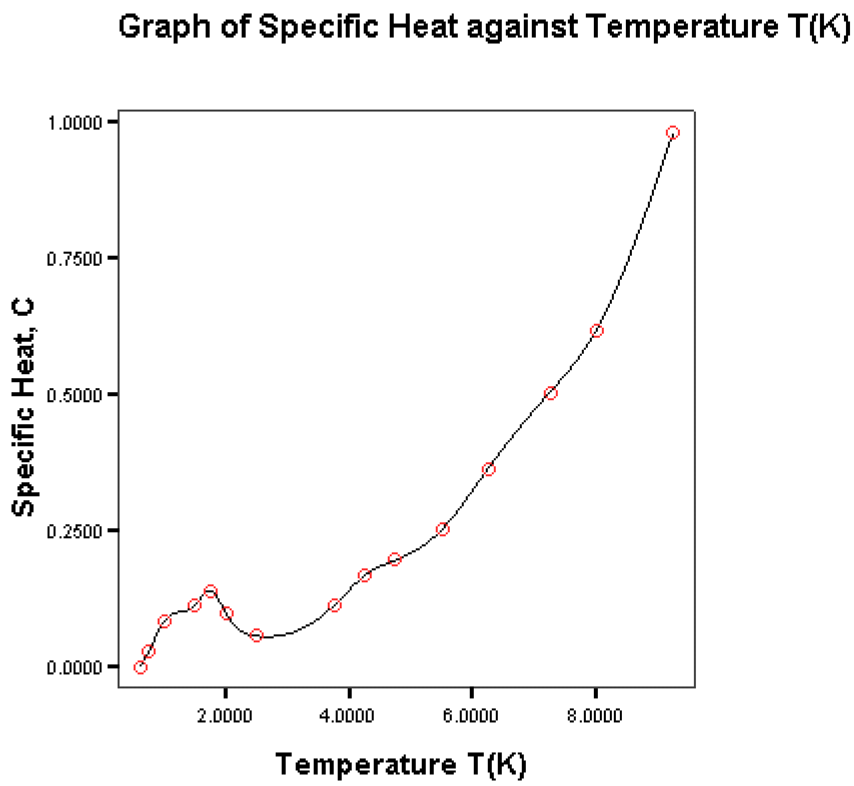

Figure 5.1 A graph of Specific heat, C (J mol^{-1}K^{-1}) against Temperature, T (K)

The electrical resistivity drops to zero at about 2.25K with a transition width of 0.1K, (Figure 5.2)

Table 5.2 Variation of resistivity with temperature.

Resistivity, ρ (Ωcm)	**Temperature, T(K)**
0.00	1.90
0.00	1.95
0.00	2.00
0.00	2.05
0.00	2.10
0.00	2.15
0.00	2.20
40.00	2.25
105.00	2.30
105.00	2.35
105.00	2.40
105.00	2.45
105.00	2.50

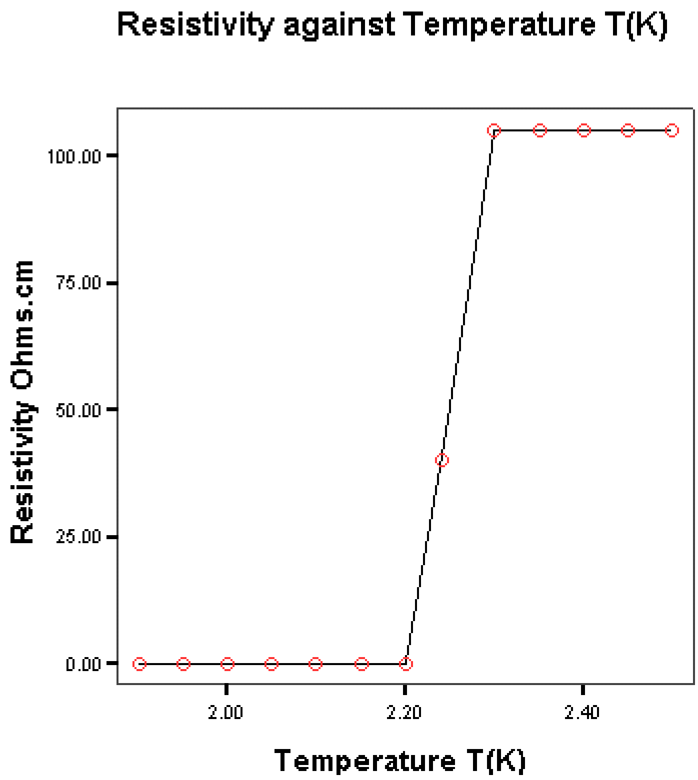

Figure 5.2 A graph of Resistivity, (Ωcm) against Temperature, T(K)

There is strong evidence indicating that Mo_3Sb_7 is a spin fluctuation system. Its electrical resistivity, ρ, at low temperatures (T<50K), can be fitted by $\rho(T) = \rho_0 + AT^2$ (Figure 5.2) and fitting parameters, ρ_0 and A are ρ_0 = 104 mol.cm A= 6.5 x 10^{-3} mol.cmK^{-2}. This quadratic dependence, associated with both a large increase and a saturation tendency of the electrical resistivity in going up to the room temperature (Figure 5.2), is often attributed to spin fluctuation (Frings & Dmitriev, 2007).

These results are in agreement with previous studies (Bukoswki & Dmitriev, 2006) and they indicate that the superconducting state is not due to the presence of any secondary phase but is clearly a bulk property.

Important evidence indicating that Mo_3Sb_7 is a spin fluctuation system is the temperature dependence of the magnetic susceptibility temperature dependence of magnetic susceptibility has been experimentally measured for the Mo_3Sb_7 compound in the 0.6 – 350K range whose results are shown below.

Table 5.3 Variation of susceptibility with Temperature

Susceptibility (EMU mol^{-1} x 10^{-6})	**Temperature, T(K)**
362.25	0
340.625	30.76
362.25	46.14
431.25	69.21
475.00	84.79
525.00	107.66
548.75	130.73
558.25	146.11
568.25	176.87
565.75	192.25
550.00	223.01
531.25	238.39
500.75	276.84

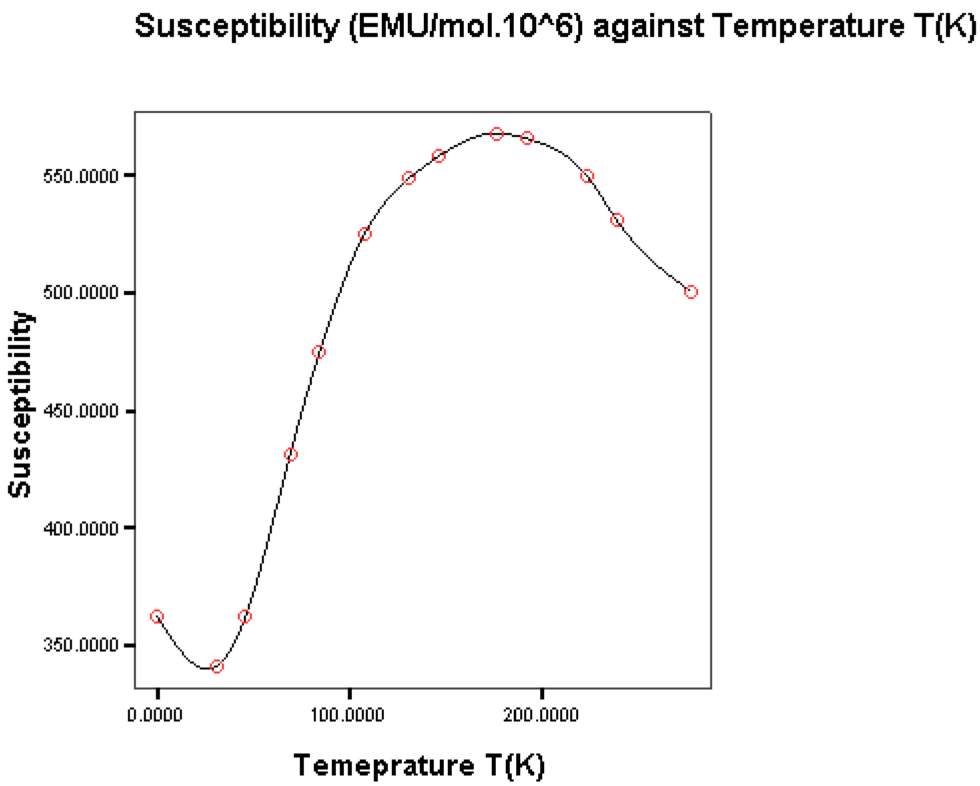

Figure 5.3 A graph of Susceptibility (EMU mol^{-1} x 10^{-6}) against Temperature, T (K)

For Mo_3Sb_7, the susceptibility displays a parabolic dependence at low temperatures (0 – 40K), then increases as the temperature increases, and at higher temperatures becomes maximum around 180K and obeys a Curie – Weiss law, the critical temperature, T_c can be calculated using the modified McMillan

expression (Junod et. al., 1983),for $\boldsymbol{T_c}$ i.e.

$$T_c = \frac{\theta_D}{1.45} exp\left[-\frac{1.04(1+\lambda_{eff})}{\lambda_{eff} - \mu^*_{eff}(1+0.62\lambda_{eff})}\right] \quad (5.2)$$

where θ_D= 310K is the Debye temperature, λ_{eff} and $\mu^*_{eff}$are the normalized parameters which can be expressed as; **(**Junod et. al., 1983),

$$\lambda_{eff} = \lambda_{e-ph}(1+\lambda_{sf})^{-1} \quad (5.3)$$

$$\mu^*_{eff} = (\mu^* + \lambda_{sf})(1 + \lambda_{sf})^{-1} \qquad (5.4)$$

where λ_{sf} is a contribution arising from spin – fluctuations, λ_{e-ph} the electron phonon coupling constant and μ = 0.08 is renormalized Coulomb parameter.

Here λ_{sf} is 0.088 ≤ λ_{sf} ≤0.97 and λ_{e-ph} values span the range .0.56 – 0.62 i.e. (0.56≤ λ_{e-ph} ≤0.62)

Substituting different values of λ_{sf} and λ_{e-ph}, and μ*, we can get different values for λ_{eff} from equation (5.4). Substituting these values in equation (5.2), different values for T_c against λ_{sf} and λ_{e-ph} are obtained, and the graph will show how the value of T_c change with these parameters. For λ_{sf} and λ_{e-ph} the following values are used (Junod, Orlando & Clogston, 1981)

λ_{sf} = 0.088/0.090/0.092/0.094/0.096

λ_{e-ph} = 0.56/0.57/0.58/0.59/0.60/0.61/0.62

Table 5.4 Variation of T_c with λ_{sf} and λ_{e-ph}

T_c (K)	0.2020	0.2187	0.2367	0.2555	0.2742
λ_{sf}	0.0880	0.0900	0.0920	0.0940	0.0960
λ_{e-ph}	0.5600	0.5700	0.5800	0.5900	0.6000

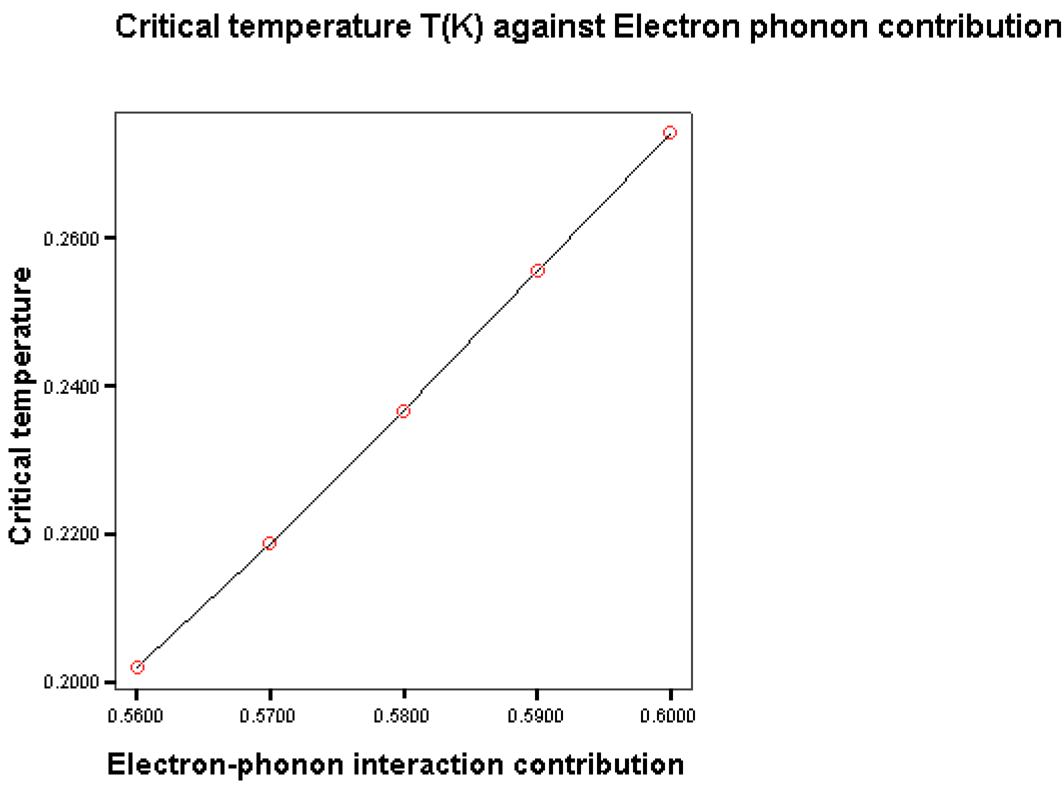

Figure 5.4 A graph of T_c against λ_{e-ph}

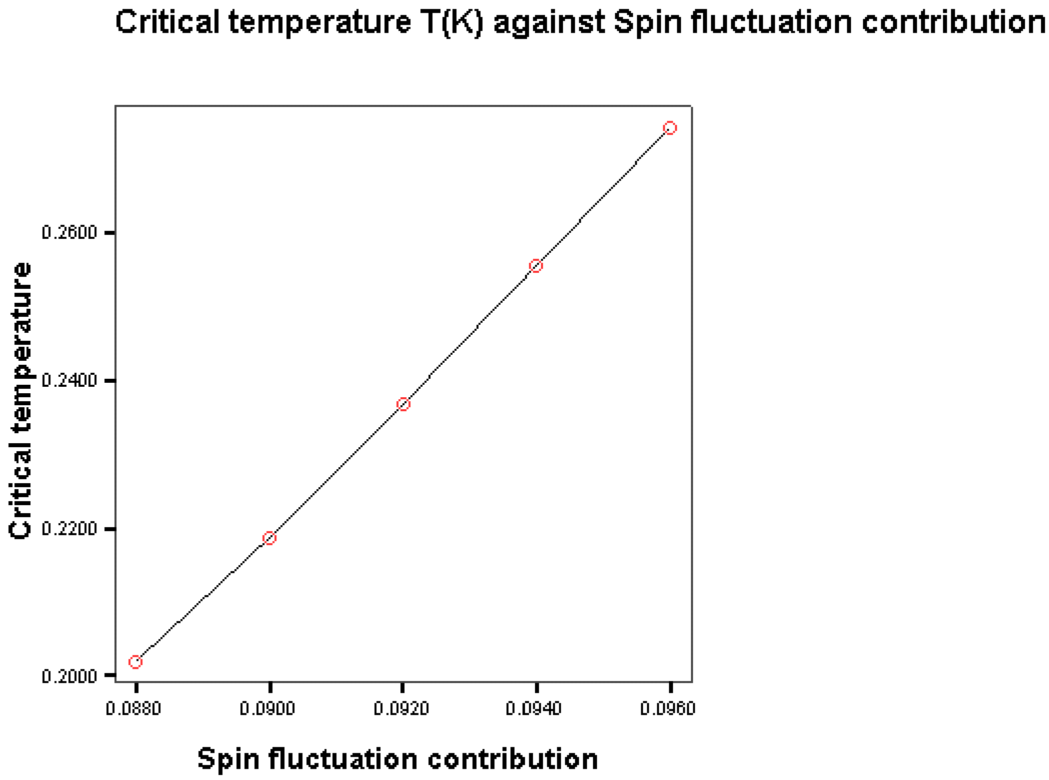

Figure 5.5 A graph of T_c against λ_{sf}

5.2 Discussions

Different types of electron coupling that may lead to the study of high T_c superconductivity have been presented in this Thesis. The emphasis was on the type of coupling that can result in the co-existence of superconductivity and spin fluctuation. The sharp specific- heat discontinuity, ΔC of Mo_3Sb_7 occurring at 2.5K strongly suggests that this compound undergoes a superconducting transition, as shown in (figure 5.1) This observation is corroborated by the electrical resistivity curve which shows a drop to zero resistance at about 2.20K with a transition width of approximately 0.1K, as shown in (figure 5.2.)

(Figure 5.3) shows the temperature dependence of the magnetic susceptibility, in which the susceptibility displays a parabolic dependence at low temperature, then increases with temperature, and at a higher temperature becomes maximum around 180K. This is another piece of evidence indicating that Mo_3Sb_7 is a spin fluctuation system in which the temperature depends on the magnetic susceptibility. These results are consistent with the theoretical predictions made by Beal- Monod et.al. (Beal-Monod et.al., 1968) on the spin fluctuation contribution to the low temperature dependence of the magnetic susceptibility. The obtained coefficients from the fit being 34.2 mJ/mol.K^2, 0.65 mJ/mol.K^4, and 2.6 x 10^{-3} mJ/mol.K^6 for γ_n, β_n and α_n respectively. These results create a deeper insight into the superconducting properties of the Mo_3Sb_7 compound through estimating the ratio, $\Delta C/\gamma_n T_c$ which yields 1.04 with ΔC = 80mJ/mol.K and T_c = 2.20K (figure 5.1). This value is much lower than the well- known BCS value of 1.43(Kresin et.al., 1975). Moreover, the ratio A/γ_n^2 is equal to 0.55x 10^{-5}$\mu\Omega$.cm(K.mol/mJ)^2 which is in fairly good agreement with the Kadowaki-Woods relation A/γ_n^2 = 1.0 x 10^{-5}$\mu\Omega$.cm(K.mol/mJ)^2. As this relation can be explained in terms of the spin fluctuation theory (Wada et.al., 1993), the obtained value is another evidence of Mo_3Sb_7 to be considered as a spin fluctuator.

An important thermodynamic quantity, the specific heat C, was chosen for such a study. A term $T^3\log\left(\frac{T}{T_{sf}}\right)$ which is due to the spin fluctuation was added to generally known expression for the specific heat C, to study the effect of the spin fluctuation temperature T_{sf} on C and thereby the phenomena of superconductivity. Similarly, the effect of the spin fluctuation coupling constant λ_{sf} on T_c has been studied. The studies lead to finite changes on C and T_c under the influence of spin fluctuation. These calculations, therefore, confirm possible co-existence of spin fluctuation and superconductivity. Figure 5.4 shows variation of the critical temperature T_c against the electron-phonon interaction represented by λ_{e-ph}. The straight line graph shows that as the value of λ_{e-ph} increases, T_c increases proportionately. Similarly T_c varies proportionately as the value of the spin fluctuation parameter, λ_{sf} increases. Since there is a finite value of T_c , and there is a finite variation of T_c with λ_{sf}, it supports the co-existence of superconductivity and spin fluctuation, as shown in figure 5.5.

CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

6.0 Conclusion

The thesis has led to the following conclusions

1) The electrical, magnetic, and thermal properties of a polycrystalline Mo_3Sb_7 sample having been explored in this Thesis, the characteristic specific-heat anomaly at T_c clearly confirm the bulk nature of the superconductivity which is well corroborated by electrical resistivity measurements. These results, combined with the magnetic susceptibility study, provide a unified picture of both transport and magnetic properties of Mo_3Sb_7 within the framework of spin fluctuation theory. Under spin fluctuations mechanism in superconductivity, the value of the critical

Temperature T_c depends on such factors as governed by the equation.

$$T_c = \frac{\theta_D}{1.45} exp\left[-\frac{1.04(1+\lambda_{eff})}{\lambda_{eff} - \mu^*_{eff}(1+0.62\lambda_{eff})}\right]$$

where θ_D= 310K is the Debye temperature, λ_{eff} and $\mu^*_{eff}$are the normalized parameters which can be expressed as;

$$\lambda_{eff} = \lambda_{e-p^h}(1+\lambda_{sf})^{-1} and\ \mu^*_{eff} = (\mu^* + \lambda_{sf})(1+\lambda_{sf})^{-1}$$

where $\lambda_{sf}$is a contribution arising from spin-fluctuations, λ_{e-ph} the electron – phonon coupling constant and μ* = 0.08 is renormalized Coulomb parameter. Spin-fluctuation system and superconductivity can co-exist or superconductivity and Ferromagnetism can co-exist.

2) The transition temperature T_c for this superconductor spin fluctuation system is given by;

$$T_c = \frac{\varepsilon_i - \mu}{\alpha K} = 115.94\text{K}$$

And this value of T_c falls in the range of transition temperatures for high -T_c superconductors

3) Figures 5.4 and 5.5 show that T_c increases as the value of λ_{eff} and λ_{e-ph} increase. Although the variation is not large, but it is still significant-Straight line graphs show that the variation in T_c is directly proportional to the variation in the coupling constant λ_{eff} and λ_{e-ph}

6.1 Recommendations

It is recommended that experimental observation on Mo_3Sb_7 be undertaken to determine how the number of superconducting electrons in Mo_3Sb_7 can determine the co-existent of superconductivity and spin – fluctuation. What theoretical mechanism could explain these new observations, i.e. co-existence of superconductivity and ferromagnetism could form important future theoretical studies. Further research is also recommended in this area with a view to obtaining superconductors which perform at room temperature. This will effectively reduce the cost in terms of the coolant applied.

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