Chapter 1

Introduction

Immense potentialities for the application and unusual nature of the phenomenon had fascinated the imagination of scientists, engineers and technologists ever since superconductivity was discovered in 1911. The discovery of high $T_C$ superconductivity, therefore, can be considered as the biggest breakthrough in the history of condensed matter Physics. Among all the superconductors intensive studies on high - $T_C$ cuprate superconductors is going on at present. The compounds of the type $R_{2-x}M_xCuO_4$ ( $R =$ rare-earth and $M=$Ce, Th, Sr, Ba....) exhibit strong electron correlation and interesting properties. Some of these compounds are electron doped and others are hole doped. They exhibit a complex interplay of anti-ferromagnetism and superconductivity. These classes of high-$T_C$ cuprate systems are the subject of study in the present work.

1.1 Strongly Correlated Electron Systems

One of the most important problem in the solid state Physics is to find out the relation between the microscopic nature of the electrons which are in the outer most orbitals of the constituent atoms or molecules of the crystal and the macroscopic properties of the solids. The macroscopic properties of the solids
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(such as electric, magnetic and optical properties) which differ from one crystal to another is mainly due to the difference of the microscopic nature of the valence electrons in each crystal. The microscopic behavior of the outermost electrons in a solid is governed mainly by (i) the itinerary of the electron (ii) the inter-electron Coulomb repulsion and (iii) the electron-phonon interaction. The first of these manifestations is a quantum characteristic. Quantum mechanics describes the electron motion in terms of waves. Since electrons are Fermions the interference between identical wave packets is destructed, leading to Pauli exclusion principle. So even if an electron is confined to the outermost orbital of an atom in a solid it can hop from this orbital to the neighbouring ones provided Pauli’s exclusion principle is not violated. This free motion of an electron is generally modulated in many electron systems, since the Coulomb repulsive energy increases, when two electrons happen to be in the same orbital. The standard model of metals and insulators on which the early evolution of condensed matter Physics is founded ignored this electric repulsive force between electrons. Recent superconductivity, superfluidity, anti-ferromagnetism, heavy fermion electron Physics lies at the core of correlated electron. Electron correlation are strong when the on-site electron electron repulsions $U$ are much larger than the energies associated with the hybridization of atomic orbitals belonging to different atoms. The latter are characterized in a solid by the width $W$ of the energy band under consideration.

Large class of physical systems which are recognized as correlated electron are rare-earths, transition metals and its compounds, liquid helium, organic superconductors, fullerites and fullerides and recently discovered borocarbides. Strong electron correlation signified by a large ratio $\frac{U}{W}$ is expected in systems involving $4f$ are $5f$ electrons i.e. rare-earth and actinide atoms. Heavy Fermion systems are rare-earth (usually Ce,Yb etc. ) and Uranium and $Np$ based intermetallic compounds [1].

Normal liquid $^3He$ is a strongly interacting liquid of high density [2]. It stays liquid for $T \rightarrow 0$ and solidifies only under a pressure of 34 bars. As $^3He$ atoms
are Fermions, normal $^3\text{He}$ constitutes a Fermi liquid below the degeneracy temperature $T_p \rightarrow 0.5\,\text{K}$. Its properties are governed by Fermi-Dirac quantum statistics. At very low temperatures $T \sim 0.001 - 0.0027\,\text{K}$ it becomes superfluid.

Fullerene molecule is a highly stable structure of 60 carbon atoms. The discovery of fullerene $C_{60}$ [3, 4] has attracted much interest, especially in connection with the occurrence of high temperature superconductivity in alkali doped fullerides [5]. Recently discovered family borocarbides $R\,Ni_2B_2C, (R = \text{Er, Ho, Tm, Ln etc.})$ [6] are much interesting compounds. The borocarbides show co-existence of anti-ferromagnetism and superconductivity [7].

Apart from these there are also a number of other physical systems where electron correlation plays an important role. However, the present discussion will be centered mainly on the transition metals and high-$T_c$ cuprates. The system with d-electrons i.e. transition metal compounds are strongly correlated too. These materials also exhibit the most diverse range of electronic and magnetic behaviour such as metallic, insulating with disordered magnetic moments, insulating with magnetic order. This arises from the competing nature of the itinerant and local behaviour of the d-electrons in these class of materials, owing to an interplay between the strong intra-atomic coulomb strength and a large hopping interaction strength. Due to the presence of large electron-electron interaction effects, independent electron approximations normally failed to yield correct ground state. In order to understand the insulating nature of the partially filled 3d-shell as in those oxides Mott pointed out the crucial role played by electron-electron coulomb interaction that suppresses the charge fluctuations induced by hopping leading to a localized behaviour. After the discovery of high temperature superconductivity, these considerations received renewed interest. The pure high-$T_c$ materials such as the 214 compounds $La_2CuO_4$, $Nd_2CuO_4$ and the 123 compounds $Y\,Ba_2\,Cu_3O_6$ are magnetic insulators. The electronic structure and the phase diagram of these compounds are discussed in subsequent sections.
1.2 Discovery of High $T_c$ Cuprates:

Two properties of superconductivity namely resistance less current flow and perfect diamagnetism, have tremendous technological implications. But two major obstacles in implementation were as follows. (1) Extremely cold temperature were required two achieve the superconducting state. Although liquid Helium could serve as a coolant, Its scarcity and processing costs made it expensive. And sophisticated equipments were required to handle it. (2) The superconducting state of the elemental metals was easily destroyed by the application of modest external magnetic fields or electrical transport currents. As a consequence, their use in electromagnetic applications was made impractical. Because of these problems, an intensive search for new materials that would become superconducting at higher temperature and retain their superconductivity in the presence of large magnetic fields and electrical currents, is required. Liquid Nitrogen boiling point is 77 K. Its processing cost is low.Liquid Nitrogen is also easy to handle. So scientists dreamt of achieving superconductivity by using liquid Nitrogen as the coolant.Until recently, the materials that are used for superconducting technology are alloys of Niobium (particularly $Nb - Tn$). These alloys remain in the superconducting state while supporting large j electrical currents. Hence they are used in the construction of powerful magnets. Transition-metal alloy compounds of $A15(Nb_3Sn)$ and $(NbN)$ structure have so for shown the highest superconducting temperature. In 1973, Gavalev et al.[8] observed superconductivity at 20K was disappointed that they do so only at low temperatures (nearly that of liquid Helium). Most of the simple alloys or compounds based on combining two or three elements also required disappointingly low temperature for superconductivity. So there is a feeling of despair among some scientists perhaps superconductivity at 77K was simply not possible.

In 1986, two scientists George Bednortz and K.Alex Muller[9], working at the IBM facility in Zurich reported a startling result. They found superconductivity in the (214) class of ceramic oxides $La_{2-x}Ba_xCuO_4$ (Doping
La$_{2-x}$CuO$_4$ with divalent Barium) with transition temperature in the range of 30K to 40K. After this discovery a whole new family of materials, ceramics, was ripe for investigation, and the pace of research accelerated. In early 1987, groups, at the University of Houston and University of Albana, headed by physicists Pauli Chu and M.K. Wu, Jr, respectively found superconductivity with transition temperature in the range 90–100K in the (123) compounds $YBa_2Cu_3O_7$-$\delta$ [10] (creating oxygen excess in $YBa_2Cu_3O_{6.5}$).

In the present work, we attempt to study the doped cuprates of the form $R_{2-x}M_xCuO_4$.

### 1.3 Structure of High $T_c$ Cuprates

The lattice structure of three representative, so-called undoped parent compounds of the high temperature superconductors (HTSC) are shown in the Fig.1.2(a,b,c). In essence all the high temperature superconductors (HTSC) consist of two dimensional $CuO_2$ planes which are sandwiched between the intervening atomic layers. All the cuprate superconductors have two dimensional character. In these cuprate superconductors the lobes of $P_{xy}$ orbits of oxygen overlaps with that of the $d_{x^2-y^2}$ orbitals of copper planes. This low dimensionality is confirmed from the following experimental observations: (1) The band structure calculations indicates that the bands show very little dispersion along the crystal axis. This implies the two dimensional nature of electron states. (2) The structure measurements show that the distance between copper and oxygen atoms at the apexes of the $Cu-O$ octahedron is large compared to that in the $CuO_2$ plane. This confirms their two dimensional character. It is experimentally well established that the parent compounds $La_2CuO_4$, $Nd_2CuO_4$ and $YBa_2Cu_3O_{6.5}$ [11, 12, 13] are insulators and ordered anti-ferro-magnetically (AFM) below the Neel temperature $T_N$. In $La_2CuO_4$ the Lanthanum ion is $La^{3+}$ and Oxygen ion is $O^{2-}$. For electrical neutrality of the compound copper must appear as $Cu^{2+}$. In $Nd_2CuO_4$ the Neodymium ion is $Nd^{3+}$ and Oxygen is $O^{2-}$.
For electrical neutrality of the compound copper must appear as $Cu^{2+}$. Similarly in $YBa_2Cu_3O_{6.5}$ Yttrium ion is $Y^{3+}$, Barium ion is $Ba^{2+}$. Therefore for electrical neutrality of the compound copper must appear as $Cu^{2+}$. From these discussions, it is clear that when these compounds are formed all the ions except for $Cu^{2+}$ have a closed shell structure. The electronic configuration of copper is $1s^2\; 2s^22p^6\; 3s^23p^63d^{10}\; 4s^1$. $Cu^{2+}$ remain in $1s^2\; 2s^22p^6\; 3s^23p^63d^9$. Therefore, in compounds discussed above there is a partially filled d-band. From the band theory of solids, one may predict these compounds to be metals. But because of crystal field effect, anti-ferromagnetic long range order and intra-atomic electron correlation these compounds behave as insulators. In these materials the $Cu^{2+}$ ions are surrounded by the $O^{2-}$ ions in an octahedral co-ordination (Fig.1.1). Due to this arrangement of ions an electric field is created which will split the energy levels. This is known as the crystal field effect. The crystal field splits the ten fold degenerate d-level into a six fold degenerate lower $t_{2g}$ level and four fold degenerate upper $e_g$ level. In copper ($Cu^{2+}$) the $t_{2g}$ level is completely filled and $e_g$ level is partially filled with three electrons (Fig.1.1). Because of anti-ferromagnetic long range order the periodicity of the lattice is doubled and hence the Brillouin zone is reduced to half of its original value. At the new zone boundary gap is opened. Thus the $e_g$ band is split into two sub-bands. The lower sub-band is completely filled, while as the upper sub-band is half filled. Upper sub-band is occupied by one electron per copper site (Fig.1.1). The band structure of solids is determined by a one body calculation, where intra-atomic electron correlation effect is ignored. In the oxide superconductors it is necessary to consider the correlation effect. Because of this intra-atomic electron correlation, the upper sub-band splits by a large energy gap. So, the material becomes a Mott-Hubbard insulator.
Since the discovery of high temperature superconductivity in copper oxide compounds [15], there has been much effort to understand what is required for a compound to have a high transition temperature ($T_c$). Up to now, all of the families of high $T_c$ copper oxide superconductors have contained two dimensional sheets of $Cu-O$ pyramids or octahedra, and the carriers of the superconducting have been electron vacancies, or, 'holes'. By contrast, there is a family of superconducting copper oxides in which the carriers are electrons.
The superconductors are Ce$^{4+}$-doped compounds, with the formula $R_{2-x}Ce_xCuO_{4-y}$, where $R$ stands for lanthanide i.e. Pr, Nd or Sm. The compounds have the Nd$_2$CuO$_4$(T') structure, which is composed of sheets of Cu–O squares (Fig.1.2.a), this structure has no apical oxygen atoms, in contrast to the T phase structure with Cu–O octahedra (Fig.1.2.b.), as observed in La$_{2-x}$Sr$_x$CuO$_4$ [15], and the T"-phase structure with Cu–O pyramids (Fig.1.2.c), as in Nd$_{2-x}$Ce$_x$Sr$_x$CuO$_4$[15].

Electron doped superconductivity is not restricted to Nd-based compounds, but is also evident in the T'-phase of Pr- and Sm-based copper oxide compounds Ce-doped.
1.4 Phase Diagram of Cuprates

Parent compounds can be doped which eventually leads to metallic behaviour and superconductivity. Doping is achieved by heterovalent substitution as in $La_{2-x} Sr_x CuO_4$ and $Nd_{2-x} Ce_x Cu O_4$ or by a variation of total oxygen content as in $Y Ba_{2-x}Cu_x O_{6+x}$. Doping introduces additional charge carriers into the $Cu O_2$ planes. In $La_2Cu O_4$ the formal valency of Lanthanum is $La^{+3}$. When Lanthanum is doped with di-valent $Sr^{2+}$, in plane Oxygen atoms change from $O^{2-}$ to an $O^{2-}$ state leaving additional holes in the planes. In $Nd_{2-x} Ce_x Cu O_4$ the neodymium $Nd^{+3}$ state is replaced by a $Ce^{+4}$ state yielding an excess electron which enters the planes. The sign of the measured Hall co-efficient supports the picture of hole carriers in $La_{2-x} Sr_x CuO_4$ and of electron carrier in $Nd_{2-x} Ce_x Cu O_4$ [14]. In $Y Ba_{2-x}Cu_x O_{6+x}$ doping amounts to the addition of oxygen atoms in between out-of-plane copper atoms. This leads to formation of $Cu - O$ chains. It is believed that these oxygen atoms form $O^{2-}$ states by absorbing electrons from the rest of the materials and to a certain extent from out-of-the $Cu O_2$ planes. This process is still controversial. In particular, it introduces the possibility of hole-type carriers in the $Cu - O$ chains, it is certainly responsible for the non-linear relation between dopant concentration and the in-plane carrier density in $Y Ba_{2-x}Cu_x O_{6+x}$. In (Fig.1.3), we show the phase diagrams of $La_{2-x} Sr_x CuO_4$, $Nd_{2-x} Ce_x Cu O_4$ and in $Y Ba_{2-x}Cu_x O_{6+x}$ in the temperature ($T$) vs. dopant concentration. Evidently depending on $T$ and $x$ the cuprate HTSC can be varied continuously between an $AFM$ insulator, a spin glass phase, a high temperature superconductor and a 'normal' metal. Since apparently, none of this is accompanied with any major structural change of these materials, it is quite natural to expect electronic correlation to play a significant role in these systems [16]. However, recent measurements from high resolution thermal expansion measurements on different HTSC, clearly exhibits the strong influence of lattice instability on superconducting transition [17]. These measurements while demonstrating the insensitivity of structural distortion to charge carrier doping clearly exhibits
that the highest superconducting transition temperature is limited by the occurrence of lattice instability.

![Phase diagram of Nd$_{2-x}$Ce$_x$CuO$_{4-y}$ and La$_{2-x}$Sr$_x$CuO$_{4-y}$](image)

\[ \text{Metallic} \leftarrow \text{Insulating} \rightarrow \text{Metallic} \]

- **Electron-doped** Nd$_{2-x}$Ce$_x$CuO$_{4-y}$
- **Hole-doped** La$_{2-x}$Sr$_x$CuO$_{4-y}$

**Fig. 1.3** Phase diagram of \( Nd_{2-x} \) Ce$_x$ CuO$_4$ and \( La_{2-x} \) Sr$_x$ CuO$_4$ (for comparison)

Obviously, holes and electrons doped into the AFM insulators are very efficient in destroying the AFM order. In \( La_{2-x} \) Sr$_x$ CuO$_4$ only \( \sim 2 \% \) of holes are sufficient to achieve this, while \( \sim 12 \% \) of electrons are required in \( Nd_{2-x} \) Ce$_x$ CuO$_4$. Therefore, charge carriers seem to couple very strongly to
the spin systems. However, there is an apparent asymmetry between the elec-
tron and hole doped systems regarding the stability of anti-ferromagnetism as
well as that of superconductivity. The $AFM$ regime is broader where as the
$SC$ regime is narrower for electron doped case compared to the hole doped
system-this being one of the important differences to be noted.

Different experimental data for Cuprates like, the photo- emission, nuclear mag-
netic resonance(NMR), muon spin relaxation rate ($\mu$sr), Andreev reflections, Ra-
man scattering, Infra-red(IR) absorption, inelastic neutron scattering, optical
reflectivity, ultrasonic attenuation, thermo power, thermal conductivity, ther-
mal expansion, Hall effect, specific heat etc. clearly show that the behaviour of
cuprate materials is quite different from the normal metals. As a result metal
oxides have attracted the attention of solid state physicists and chemists for last
several years.

1.5 Electron Phonon Interaction

1.5.1 The Role of Phonon

It has been well established that conventional metallic superconductivity, i.e.
superconductivity in Pb, Sn, In, Al, Nb$_3$Sn, etc., can be adequately described
by the B.C.S. theory with phonon mediated pairing. However it is not clear
that all the superconducting systems known prior to the discovery of high tem-
perature superconductivity in the oxides were a result of phonon mediated pair-
ing [18]. This controversy has primarily centered around the highly correlated
heavy electron system, [19, 20, 21, 24, 25] and the possibility of supercon-
ductivity in low dimensional organic systems [26] and layered semiconductor -
metal systems. [27]. The possible division of superconductors into classes of sys-
tems each resulting from a different pairing mechanism is best illustrated in the
Fig.1.4, where $T_c$ is plotted against the density of electronic states as measured
by $\gamma$, the electronic specific heat coefficient.
Referring back to the B.C.S. expression, $T_c$ should be exponentially related to $\gamma$ leading to broad bands of $T_c$ vs. $\gamma$ reflecting the varied pairing strengths within each class of superconductors. It would be expected that different classes of superconductors would group in separate or nearly separate regions of the Fig. 1.4. This is dramatically reflected by the heavy electron systems which appear in the lower right corner removed from the bulk of the phonon mediated superconductors which have been highlighted by the somewhat arbitrarily defined lines. The oxide superconductors are located at the upper edge or just above the band of $T_c$ vs. $\gamma$ for the phonon mediated superconductors. Are these oxide systems just highly coupled phonon mediated superconductors or are these candidates of a new class of high $T_c$ materials which will populate the upper left corner of Fig. 1.4 Approaches to new theories of superconductivity divide into two general classes. Those that propose an alternate pairing mechanism into a B.C.S. framework [22, 23, 27, 28] and those which rely on an alternate pairing mechanism and construct the ground state through a non-B.C.S. approach [29]. This section primarily focuses on exploring the role played by phonon in the oxide superconductors. Most realistic strong coupling extensions of the B.C.S. theory seem to exclude phonons as the sole mechanism leading
to pairing at 100K or higher. However these models do not exclude a partial but important role being played by the phonons. In the search for evidence of phonon participation in the pairing for the recently discovered superconducting oxides, the isotope effect as provided the direct evidence.

1.5.2 Experimental Evidence of Electron-Phonon Coupling

The isotope shift in $La_{2-x}Sr_xCuO_4$ gives an indication of phonon mediated pairing [30, 31, 32]. The high energy tunneling experiments in the electron doped system $Nd_{2-x}Ce_xCuO_4$ indicate that phonon mediated pairing is important in the superconductors. The structural phase transition in the system from high temperature tetragonal to low temperature orthorhombic phase gives rise to a soft mode. However, other experimental evidences like optical spectroscopy [33], Raman scattering [34], infrared scattering, neutron scattering [35], velocity of sound and ultrasonic measurements [36] indicate strong connection between phonon states and superconductivity. These results appear to point towards phonon mediated pairing and strong coupled superconductivity. So the exact mechanism of superconductivity is not known at present. The experimental data on velocity of sound and Raman scattering are discussed in detail in chapter -3 and -4 respectively.

1.6 Unsolved Problems in Cuprate Systems

The normal-state phases of the high-temperature superconductors exhibits a host of important phenomena, including anti-ferromagnetism, charge density waves, strong correlations among the conduction electrons, and variable range hopping. Some of these properties remind us of the organic superconductors [44], and the heavy fermion superconductors [45]. How can we explain the
interesting normal state properties of the new materials? Fundamental con­siderations are involved. For example, do the electrons form a Fermi Liquid in the normal state, so that a Fermi surface would be observable? We learn much from the metal-insulator transition, which appears to be characteristic of the high temperature superconducting materials as their stoichiometry is changed slightly from that which optimizes $T_c$. What are the effects of strong magnetic coupling seen by neutron scattering and by resonance experiments? Why are magnetic transitions frequently induced by slight doping? What roles do anti-ferromagnetism and magnetic frustration play? Are the magnetic properties and the electronic transport properties affected primarily by different types of excitations? What effects the twin boundaries or phase boundaries have on the electronic properties? Why do the high temperature superconductors have normal state resistivities which are both high and temperature dependent? Why do they have temperature dependent Hall coefficients? The normal state will have to be explained before the superconducting properties can be fully understood.

It is realized that the normal state as well as superconducting state in these systems are considerably influenced by the strong electronic correlations. As a result there have been many proposals involving purely electronic mechanisms of pairing for superconductivity: the resonating valence bond state (RVB) [16], the spin bag model [37], the anti-ferromagnetic exchange model [38], the correlated metallic state and the correlation bag model of superconductivity [39]. Therefore, it is clear from the discussions of the prominent theories of high temperature superconductors that there exists large number of competitive theories each of them have merits and demerits of their own. There are so many questions unanswered in cuprate systems in their normal as well as in superconducting states. In the present thesis we address some of the problems on velocity of sound [40], Raman spectra [41] and anomalies in Raman active phonons in the normal state of the cuprate systems. In an attempt to study the interplay of anti-ferromagnetism and superconductivity, we use Fulde model [42] in presence of a phonon mediated pairing interaction. It is realized that the normal state as well as superconducting state in these systems are considerably influenced
by the strong electronic correlations.

1.7 Contents of the Thesis

We have given an overview of the strongly correlated electron system. The discovery, the electronic structure and the phase diagram of the cuprates are discussed in detail. Then the role of phonons in pairing mechanism and the unsolved problems in high-$T_c$ cuprates are outlined. In the present section we summarize the content of the thesis.

The chapter - 2 of the thesis starts with a brief summary of the experimental findings of the electron doped and hole doped $R_{2-x} M_x CuO_4$ (R=rare-earth, $M=\text{Ba, Sr, Ce, ...}$). The electronic and the phonon softening of the system are highlighted. A model Hamiltonian [42] is formulated for the cuprate systems taking into account the sub-lattice magnetization of the copper sites. This takes care of strong electron correlation in $\text{CuO}_2$ plane. The hybridization between the carriers (f-electrons) and Cu - d electrons is expected to explain the new prototype heavy fermion behaviour. The phonon coupling to the hybridization is considered to explain the phonon softening and elastic properties of the cuprates. This provides a base for the microscopic theory of phonon softening and hardening. The Green function of zubarev type [43] is used to calculate phonon Green functions and hence phonon self energy.

At the out set, the chapter - 3 contains a brief review of the anomaly in sound velocity and ultrasonic attenuation in the doped cuprate system. We developed microscopic theory to derive an expression for the velocity of sound of the doped cuprate system in normal state. The numerical computation is carried out and the sound velocity anomalies are explained with the aid of the computer plots.

The chapter - 4 contains the detailed calculation of phonon spectral density based on the electronic model in presence of electron-phonon interactions considered in chapter - 2. The Raman intensities due to scattering of phonons has been calculated at zero phonon wave vector and finite temperatures. The origin
of Raman phonon peaks in normal state of doped cuprates are investigated. The phonon anomalies of each peak is discussed in details.

The chapter - 5 of the thesis deals with the phonon anomaly in the Raman spectra in dynamic limit. The phonon peaks appearing in Raman spectra at different frequencies exhibit anomalies. The anomalies are explained on the basis of microscopic theory developed in the chapter - 2 and - 4. Soon after the discovery of the high temperature superconductivity, it was realized that the normal state as well as the superconducting state in the systems of the type $R_{2-x}M_xCuO_4$ (cuprate system) are considerably influenced by strong electron correlation. The exact mechanism of superconducting pairing in these compounds is not known at present. As an attempt to analyze the interplay between the superconductivity and anti-ferromagnetism, we consider the phonon mediated BCS type pairing mechanism as well as the sub-lattice magnetization of the same copper in presence of the hybridization between the carriers (t-electrons) and the Cu - d electrons and investigate the co-existence. The inter sub-lattice cooper pairing in presence of anti-ferromagnetism is investigated in the final chapter - 6. In the chapter-7 we summarize the main results and conclude.
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Introduction


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