CHAPTER – I

INTRODUCTION

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1.1 Introduction

Progress in science is characterized by many great discoveries both in theory and experiment. In particular 'Physics' has gained shapes and shrines out of ground braking inventions and innovations. On superficial observation, these sudden advances may look like a series of accidental occurrences. But in most cases, such impression would be wrong, even totally misleading in many cases. Very often, discoveries occur when the time is ripe, i.e. when certain preconditions have been met, such as adequate technical capability, or attainment of a necessary intellectual and theoretical level. The discovery of superconductivity – the property of certain conductors to display zero DC electrical resistance – by Heike Kamerlingh Onnes and co-workers in 1911 illustrates the point [1]. The necessary technical basis and opportunity for the discovery had been solidly established by him in his own laboratory by the liquefication of the inert gas helium in 1908. In those days, the leading physicists were working on both experimental and theoretical research of the electrical conductivity of metals at temperatures approaching the absolute zero. Mercury was the choice of Onnes for the study of electrical conductivity at liquid helium temperature because it offers the most ideal conditions for the study of intrinsic properties of metals at low temperatures due to the purity at which it could be obtained. Gold was found to have almost immeasurably low resistance in the liquid helium range; but mercury became the first substance found to be superconducting at a temperature near 4K. The distinctive feature was a sudden drop of resistance by several orders of magnitude on lowering the temperature below what appeared to be a sharply defined temperature called as *transition temperature or critical temperature* (T_c). Lead and tin were soon added to the list. In Onnes's experiment, a current flowing through a loop of lead wire cooled to 4 K, for long period of time, continued to flow without current loss known as persistent current. The fact that the atomic nucleus was discovered the same year, 1911, makes this a truly remarkable year in the history of scientific discovery.

1.2 Historical Background of Superconductivity

For the first four decades after Kammerlingh Onnes discovered the superconductivity, research was mainly confined to a few elements and alloys [2] major advancement in the field of superconductivity was the discovery of Meissner effect [3] in 1933. Meissner and Ochsenfeld discovered another fundamental property of exclusion of magnetic field by the superconductor. A superconductor does not allow magnetic field to penetrate its interior. This effect is called Meissner effect. However with further research it is observed that, this effect occurs relatively at small magnetic field. If magnetic field becomes too high it penetrates the interior of metal and the metal loses its superconductivity. Not long 1933, F. London and H. London [4] proposed a phenomenological theory of the electromagnetic properties in which diamagnetic aspects were resolved. F. London, again in 1935, suggested a quantum theoretical approach to a hypothesis in which it was assumed that by some means there occurs a coherence or rigidity in the superconducting state such that wave functions get modified much when magnetic field is applied [5]. The concept of coherence has been emphasized by Pippard in 1953 [6].

The time, at which the Ginzburg–Landau theory [7] was formulated in 1950, superconductors were only the laboratory curiosities and limited in number. Of course, important work had been done since then and much of the basic thermodynamic and electromagnetic properties of what are now known as type I superconductors had been established [8]. There was no basis for predicting the occurrence of superconductivity, and there was little apparent connection with the normal metallic state, although the later was quite well described by the quantum theory of electrons in metals. Outstanding physicists including Einstein, Bohr, Bloch, and Heisenberg tried but were unable to find a satisfactory microscopic theory of superconductivity until BCS theory by Bardeen, Cooper and Schrieffer in 1956 on the basis of the experimental findings of early fifties [9]. According to this theory, an electron moving through the vibrating crystal lattice distorts the lattice. Such a lattice then acts upon another incoming electron having an opposite momentum and spin. This causes the two electrons to form a bound state known as *Cooper pair* and move without resistance. Hence the effective coulomb repulsion is subsidized by the phonon mediation caused due to lattice vibration.

Voogd and de Haas at Leiden [2] in 1928 started the superconductivity research on binary alloys such as SbSn, Sb_2Sn, Cu_3Sn, and Bi_5Tl_3. They found that the combination of a superconducting element and a non-superconducting one gives rise to the binary superconductor. In Bi_5Tl_3, T_c was raised by a factor of 2–3 compared to pure Tl. More interestingly, the magnetic threshold for destruction of superconductivity in these materials was much higher than in any of the elements known to be superconducting at that time. The material would remain superconducting up to 0.5T at 3.4K, and by extrapolation it was predicted to tolerate 0.9T at 1.3K. But soon, they found an even more promising material; a Pb–Bi eutectic alloy with a critical field B_c = 2.3T at 1.9K. Unfortunately, the substance was so difficult to make and to handle that it never was to fulfil its promise as a material for wires, which might otherwise have made it an important material for superconducting electromagnets.

After an intense period of research on binary alloys around 1930, not much happened in the materials area until Bernd T. Matthias and John K. Hulm started a new programme in the early 1950s. Their 'materials approach' to superconductivity would bear rich fruit. A number of new compounds were made, with impressively high transition temperatures and high critical fields. Throughout 1950s, the materials that were developed for use as superconductors included: solid solutions of NbN and NbC with T_c = 17.8K; V_3Si with T_c = 17 K; Nb_3Sn with T_c = 18 K; NbTi with T_c = 9K. Later (1973) Nb_3Ge

was added to this list with the highest T_c of all, at 23.2K, a record that lasted until 1986.

Research on electronically conductive organic materials dates back to 1940s. High electrical conductivity was first discovered in 1954, in Perylene bromine complex. Much later the discovery of a pronounced conductivity peak in (TTF)(TCNQ) near 60K in 1973 [10] stimulated a lot of effort in the direction of low-dimensional systems, so-called charge transfer salts. Superconductivity in a polymer material was first found in (Sn)x in 1975. This was followed by the discovery in 1979 of superconductivity in a molecular salt, $(TMTSF)_2$ FF_6 under 1.2Gpa pressure, and with a T_c of 0.9K [11]. Since then, a long list of organic superconductors have been synthesized, some of them are $(TMTSF)_2ClO_4$ - 1.4 K, β_L – $(ET)_2I_3$ - 1.5 K, κ – $(ET)_2Cu(NCS)_2$ - 10.4 K, κ – $(ET)_2Cu[N(CN)_2]Br$ - 11.8 K. T_c remains low, although it has increased by a factor of more than 10 since the first discovery. In this sense, a remarkable progress has been made. In another sense, it has been disappointing, since the predictions had been made for room temperature superconductivity in stacked organic structures. This prediction was set forth in 1964 by Little [12], where he suggested the possible existence of superconductivity in an organic substance consisting of a long unsaturated polyene chain, called the 'spine', with an array of side chain molecules attached at regular intervals. He showed that even if the spine was initially an insulator because the valence band was full and the conduction band was empty, the addition of side chains could increase the effective electron–electron attraction to the point where it became energetically favourable to enter the superconducting state by mixing in states of the conduction band. It was concluded that superconductivity at room temperature could result.

The breakthrough to a new era in higher superconducting transition temperatures came in 1986 by the discovery of superconductivity in the

$La_{2-x}(Ba,Sr)_xCuO$ compounds by two scientists at the IBM Zurich laboratory, J. George Bednorz and K. Alex Muller [13]. In their article published in *Zeitschrift f'ur Physik*, they cautiously announced: 'Possible high T_c superconductivity in the Ba-La-Cu-O system.' As their material showed onset of superconductivity at about 30 K, well above previous records. Initially, the reaction of the scientists from the community was somewhat hesitant, but this changed to intense interest and competition, as soon as their results were confirmed by other groups from the corners of world. The next important development occurred when the Houston group led by Chu showed that external pressure could raise the T_c substantially, going above 40K under 13 kbar pressure [14]. An effect which is equivalent to application of high pressure is achieved by replacing some of the ions with smaller ones having the same chemical properties. Thus, replacing Ba with the smaller ions like Sr yielded a T_c of 38 K. Naturally, one would think that a similar procedure ought to be tried at the La-site. The Huntsville group led by Wu proceeded in collaboration with the Houston group to replace both La and Ba, with Y and Sr, respectively. This suddenly brought T_c above 90K [15]. The news spread quickly all over the world. Soon, the successful new compound turned out to be $YBa_2Cu_3O_7$. The discovery was made almost simultaneously in several laboratories, in Tokyo, Beijing and at Bell Labs in the US. This breakthrough was of historic proportions. T_c had now moved well above the boiling point of liquid nitrogen (N_2) at 77 K. The best values of T_c turned out to be in the range of 91–93K in $YBa_2Cu_3O_{7-\delta}$, depending on the value of δ. The ensuing response from the scientific community was without parallel in the history of science. Suddenly, the efforts were joined by thousands of scientists and students around the world, trying to understand $YBa_2Cu_3O_{7-\delta}$ and the other newly discovered compounds, and to push T_c even higher.

Several new compounds with higher T_c were soon synthesized. With one exception, $Ba_{1-x}K_xBiO_3$ [16], all had one common feature: a quasi-2D network of

CuO_2 i.e. they were all cuprate perovskites. The new materials are very different from traditional metals, being doped oxides. Their normal state properties are different from metals, and they are so strongly anisotropic that they could be shown in some cases to possess metallic like conductivity in directions parallel to the CuO_2 planes although not free-electron like while behaving like semiconductors along the *c*-axis, normal to CuO_2 planes. This profound anisotropy essentially affects all the physical properties [17].

In the subsequent years, huge efforts were spent on achieving superconductivity at still higher temperatures, even with the hope of reaching room temperature. This did not happen, but the efforts resulted in a long list of new superconducting compounds with complex structures and intriguing properties i.e $Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+2}$ [18], $Tl_mBa_2Ca_{n-1}Cu_nO_{2n+m+2}$ [19] and $HgBa_2Ca_{n-1}Cu_nO_{2n+2}$ [20] (where m=1,2 and n=1,2,3 and 4). A superconducting transition temperature as high as 163 K was eventually reported in the Hg-based ($HgBa_2Ca_2Cu_3O_8$) compound under high external pressure. Figure 1.1 summarizes the main historical development of T_c versus time.

In the framework of the BCS theory, the low mass elements results in higher frequency phonon modes which may lead to enhanced transition temperatures. Hence there has been renewed interest in intermetallic superconductors which incorporates light elements, after the discovery of superconductivity in borocarbides, an intermetallics (Y-Ni-B-C) with T_c = 15 K and Y-Pd-B-C exhibits T_c as high as 23 K [21]. Finally in 2001, the announcement of BCS limit breaking, 40 K superconductivity in MgB_2 [22], proved to be catalyst for the discovery of several superconductors. Magnesium diboride, MgB_2 is a intermetallic compound known since 1950. It is a hardest but brittle material with a hexagonal structure, having magnesium located in the external corners and in the face centre positions of the upper and lower hexagon, and with boron located in the inner hexagon, rotated by 60° with respect to the Mg hexagons.

The recent discovery in the field of superconductivity is the invention of rare-earth iron oxypnictides with the generic formula $REFeAsO_{1-x}F_x$ [23]. It has now been established that the iron oxypnictides can be superconducting when doped (with $x \sim 0.05–0.2$) and that they can have transition temperature T_c above 40 K when La is put as a rare earth element [24]. It is also increased above 50 K by replacing La by Pr, Nd, Sm and Gd [25–28].

Some of the important events in the field of superconductivity are listed below;

1. 1911-Discovery of phenomenon by H. K. Onnes; Persistent currents, and critical magnetic fields. (Nobel Prize 1913)
2. 1933-Meissner - Ochsenfeld effect: diamagnetism and superconducting state.
3. 1935-London phenomenological theory and London`s Proposal that superconductivity is a quantum phenomena on a macroscopic scale.
4. 1950-Discovery of isotope effect, importance of electron phonon interaction was emphasized by Frohlich.
5. 1950-Discovery of vortex lattice and flux pinning by Alexi Abrikosove and Vitali Ginzberg. (Nobel Prize 2003)
6. 1953-Experimental evidence for superconducting energy gap.
7. 1957-Microscopic theory of J. Bardeen, L. N. Cooper and J. R. Schrieffer based on paring hypothesis. (Nobel Prize 1972)
8. 1960-Tunnel effect was discovered by Giaever, Experimental measurement of energy gap.
9. 1961-Flux quantization was discovered by Deaver and Fairbank, Doll and Nabuer.
10. 1962- Tunneling of Supercurrent -Josephson effect (Nobel Prize 1973)
11. 1986 - Discovery of high T_c [44] superconductivity in La_2CuO_4 doped with Ba. (Noble Prize 1987)

1.3 Ideal High Temperature Superconductor (HTSc)

1) Higher T_c to facilitate the testing of some theoretical models and to make application more thermodynamically efficient.
2) Reduced anisotropy to facilitate the testing of the 2D-criterion adopted presently by most models and simplifies the preparation of quality material and high performance devices.
3) Non-cuprates or non-oxides to determine if cuprate is synonymous with HTSc and make the development of devices with a significant commercial impact.

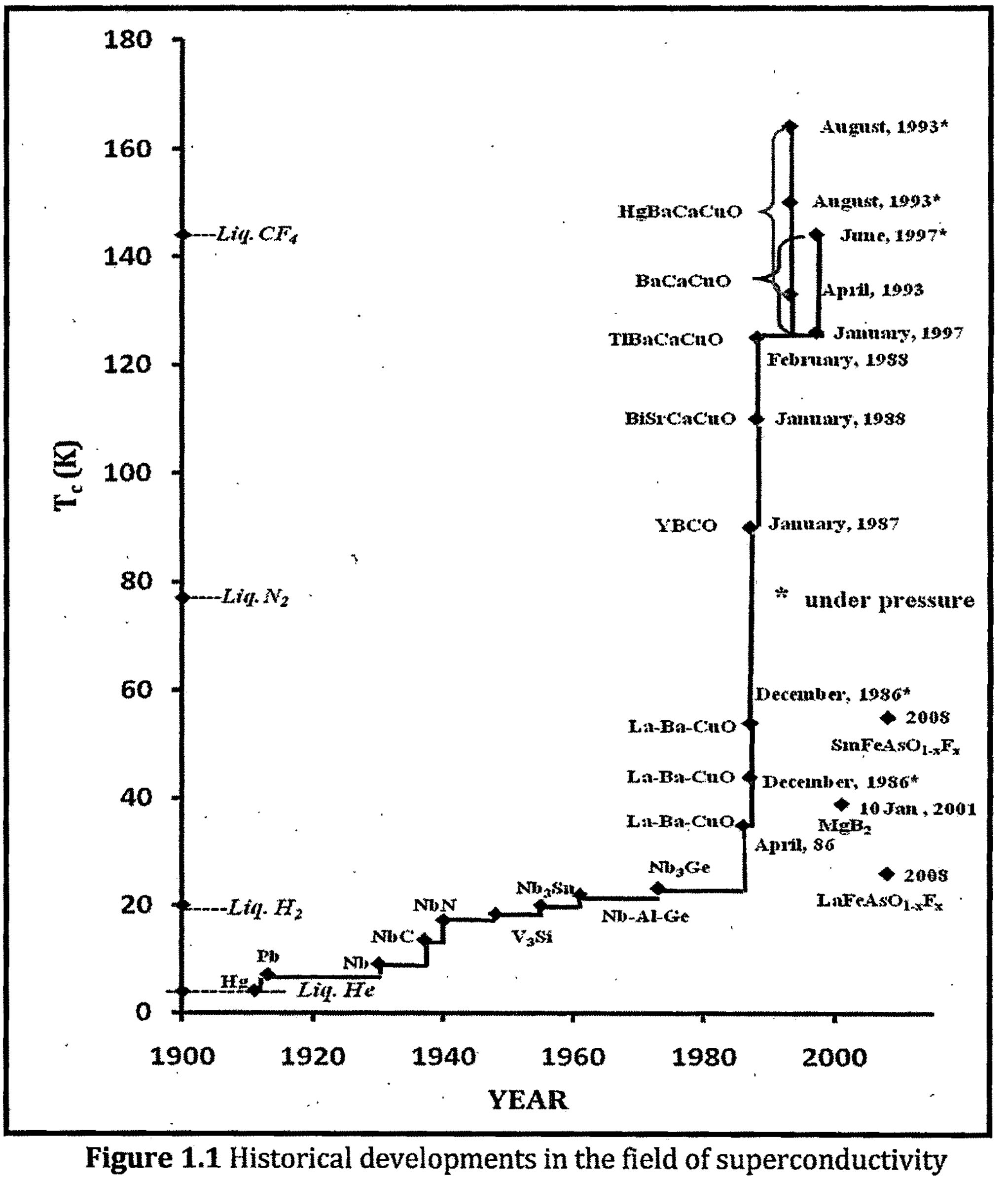

Figure 1.1 Historical developments in the field of superconductivity

1.4 Statement of Problem

The large area, uniform HTS thin films with high transition temperature T_c, high critical current density J_c and low surface resistance R_s value provide the benefit of reducing power consumption, size and weight as well as enabling devices with improved sensitivity and speed to be fabricated. High J_c values and low R_s values can be achieved in both yttrium based and thallium based superconductors, but Tl based superconductors have the advantage of exhibiting significantly higher T_c values than the more commonly used YBCO superconductors. This is particularly important for satellite applications where essentially the reduced size and weight of the cooling systems is necessary. Unfortunately, Tl based superconducting films are particularly difficult to process due to the volatility of thallium. Also, since Tl is one of the most toxic elements, it has to be handled very carefully. In addition to the risks from ingestion and inhalation, water soluble Tl compounds can be absorbed through unbroken skin. Dedicated processing facilities are therefore required and this has limited the number of research groups working on Tl HTSc phases. The aim of the present investigation is to develop the easy way of processing the Tl-2223 ceramics so that it can be used in the applications like tapes and microwave devices. The work is planned to develop the processes for the synthesis of thin films of Tl-based superconductor for their future applications in tapes and passive devices.

In view of the above problems associated with Tl HTS film deposition, in the present investigation, it is decided to study the two different processing techniques viz. spray pyrolysis technique and soft electrochemical processing technique. Two step approach was followed for the deposition of thin films by spray pyrolysis method. The first step consists of optimization of the spray parameters like spraying solution concentration, temperature of substrate, period to get uniform deposit of Ba-Ca-Cu-O alloy films onto buffered Al_2O_3

substrate having the cation composition 2:2:3. Further, the effect of post treatment parameters such as annealing temperature and the pressure of the oxygen on the phase formation are studied.

In the second technique, thin films of aluminum on different substrates such as silver, copper, stainless steel and glass are deposited with the help of vacuum evaporation technique. The electrochemical cell used for the deposition of Tl-Ba-Ca-Cu-O alloy film consists of the heterostructure substrate as working electrode, graphite as counter and saturated calomel electrode as reference electrode. This three electrode cell is connected to Princeton Perkin-Elmer Applied Research Versa Stat-II; Model 250/270 with PC interface, which is used to control the deposition process. Electrode electrolyte kinetics of the bath containing the nitrates of Tl, Ba, Ca and Cu has been studied by means of cyclic voltammetry. These alloyed films are post heat-treated to form the Tl-2223 ceramic. The resultant films are then studied for their structure, morphology and composition by different characterization techniques like x-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and energy dispersive x-ray analysis (EDAX) to confirm the phase formation and to analyze the film quantitatively. Electrical resistivities of these films at low temperature are measured for the validation of superconductivity.

Finally, the room temperature microwave absorption studies are carried out by using the microstripline overlay technique. The PNA-L N5320A vector network analyzer is used to record S21 parameter for the samples under investigation in the frequency range 1 GHz to 10 GHZ. The Q values obtained from the energy loss calculations are used to determine Rs values. The effect of microstructure on the Rs is studied for samples with different morphology. Low temperature microwave measurement is carried out for the selective sample.

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