CHAPTER 1

OVERVIEW ON HIGH TEMPERATURE SUPERCONDUCTORS

1.1 GENESIS OF HIGH TEMPERATURE SUPERCONDUCTORS

Superconductors are materials usually metals that undergo a remarkable transformation at extremely low temperatures. They have a number of unique characteristics but their most notable property and the origin of their name is their ability to conduct electrical current with absolutely no loss of energy. Nothing else in nature can perform this feat.

The era of superconductivity began with the discovery of zero resistance by Kamerlingh Onnes in 1911. Before 1986, superconductivity was a phenomenon restricted to metals, occuring only at very low temperatures and requiring liquid helium as a refrigerant. The highest known critical temperature, T_c, was 23K for the intermetallic compound Nb_3Ge. In the early part of 1986, Bednorz and Muller [1] found, that a mixed oxide of lanthanum, barium and copper became superconducting at a critical temperature of about 30K. This work, for which they received the Nobel prize for

Physics in 1987, heralded the high T_c explosion. Later, Chu et al [2] showed that the T_c of La-Sr-Cu-O could be raised from 35K to 50K by applying pressure. Then, as an attempt to mimic the effect of increased pressure by chemical substitution, a rare earth ion, namely yttrium was used, which is smaller than lanthanum and thus a higher T_c was obtained owing to the induced internal pressure. This resulted in the discovery of a new compound, subsequently confirmed as $YBa_2Cu_3O_7$, with a T_c of 90K [3]. The intense research effort thus unleashed has led to the discovery of further compounds: Bi-Sr-Ca-Cu-O with T_c upto 120K [4] and Tl-Ba-Ca-Cu-O with T_c as high as 130K [5], including the remarkable C_{60} based fullerene compounds [6] in which T_c in Rb-Tl-C has been claimed at 42.5K. The C_{60} based superconductors provide another totally new arena for studies of novel superconducting organic materials with great future promise for even higher T_c's. In March 1993, the mercury based layered copper oxides $HgBa_2CuO_{4+x}$ (Hg-1201) [7] came to light, the latest of the brood has set a record of 133K for the superconducting transition temperature. Recently, Chu et al [8] have shown that the mercury based systems have a T_c of 160K and this is believed to be the highest critical temperature achieved so far. Although the majority of high temperature superconductors (HTSC) are p-type, involving hole-doping of the planes, a number of n-type electron-doped HTSC such as $Nd_{2-x}Ce_xCuO_4$ [9] have also been discovered.

1.2 PHENOMENON OF SUPERCONDUCTIVITY

Superconductivity, the complete loss of electrical resistance, is destroyed by the application of a magnetic induction,B. The magnitude of B necessary to achieve this is the critical induction, B_c, and is a function of temperature rising from zero at T_c to a value $B_c(0)$ at T=0K. In the so called Type I superconductors, the magnetic flux is completely expelled from the interior of the superconductor if B is greater than B_c. This is called the Meissner effect. The passage of an electrical current greater than a critical value I_c also destroys superconductivity. In a Type I superconductor, I_c is just that current which results in the critical induction occuring at the surface of the superconductor and is therefore a function of temperature, applied magnetic field and conductor size. Critical inductions, and therefore currents, are low in Type I materials, and their practical utility is limited. However, many alloy and compound superconductors have much higher critical inductions, in the range from 1-40 Tesla. These materials are termed as Type II superconductors and they have an incomplete Meissner effect. Magnetic flux enters the body of the superconductor in the form of localised flux lines, each carrying a single quantum of magnetic flux, Φ_0 . When a current, of density J flows in a Type II superconductor in a magnetic induction B, the flux lines experience a Lorentz force F_L = JXB. The critical Lorentz force is equal to the total pinning force per unit volume F_p, which is a function of both temperature and magnetic induction.

The critical current density is the most important parameter of the superconductor for the majority of applications. In the case of a normal conductor, resistance arises because electrons lose momentum which they have acquired from the electric field, by scattering collisions with defects of the crystalline lattice. In the superconducting state, these collisions still occur but pairs of electrons act in a co-operative manner to ensure that there is no net change in momentum. In conventional superconductors, the motion of the two electrons in a pair is correlated by a lattice phonon. The behaviour of these pairs is described by the Bardeen, Cooper and Schrieffer

(BCS) theory of superconductivity. BCS theory predicts an energy gap, k_bT_c of about 10^{-3}eV, in the band structure of a superconductor at the Fermi surface. When two metals are separated by a thin (~nm) insulating barrier, electrons can tunnel from one to the other. If the metals are superconducting, single electrons cannot tunnel through the barrier unless a voltage sufficient to break up the pairs is applied. However, at zero volts, electron pairs can tunnel and give rise to a critical tunneling current I_o. This is the Josephson effect. The tunneling device is called a Josephson junction and forms the basis of several electronic devices.

1.3 SUPERCONDUCTING OXIDES

The normal state and superconducting properties are believed to arise from the strongly correlated motion of the electronic charge carriers (electrons or holes) in the CuO_2 planes that essentially define the layered cuprate HTSC. The other cations and oxygen atoms in the structure provides structural stability and control the number of charge carriers in the CuO_2 planes. Literally, hundreds of novel superconducting CuO_2 planar compounds have already been synthesised, most of which are substitutional variants of about a dozen basic chemical structures. All of the high T_c oxides (i.e T_c>50K) so far reported contain copper together with two or three other metal oxides. A brief but up-to-date account of some known superconducting materials with special emphasis on the nature of crystal structure and physical properties are given below:

The material which has received the most attention to date is $YBa_2Cu_3O_7$. Its crystal structure is orthorhombic, with a=b and c=3a. This gives rise to extreme anisotropy in the superconducting properties. A detailed study by Chu et al [2] in $RBa_2Cu_3O_{6+x}$ system with R=La,Nd,Sm,Eu,Gd,Ho,Er,Lu,and Y suggests that the unique square-planar copper atoms, each surrounded by four or six oxygen atoms are crucial to the superconductivity of oxides in general. Specifically, superconductivity above 90K can be associated to the quasi two-dimensional assembly of the CuO_2-Ba-CuO_{2+x}-Ba-CuO_2 layers interrupted by R layers only along the c-axis, with particular emphasis on CuO_{2+x} layers while the CuO_2 layers provide the shielding from the R layers. The ordering of R and Ba atoms may also play a role in the high T_c. Compounds with more CuO_2 layers coupled by more Ba atoms may offer an avenue to even higher T_c. T_c is very sensitive to oxygen content and it is also known from neutron diffraction studies that T_c is maximum when the oxygen vacancies are ordered. Depending on the value of x in $YBa_2Cu_3O_{7-x}$, the structure and physical properties including superconductivity are drastically affected. All of these observations are consistent with the defective copper-oxygen layers being responsible for superconductivity in these materials.

Some interesting systematics emerged from the studies of the bismuth and thallium compounds. In 1988, superconductivity was reported in oxide systems based on Bi,Cu and alkaline-earth ions. These compounds do not contain rare-earth elements like the earlier ones. They belong to a structural family with the ideal formula $Bi_2Sr_2Ca_{n-1}Cu_nO_{4n+2+8}$ containing variable number, n, of copper ($Cu-O_2$) layers. Three superconducting phases have been identified so far. They are often referred by their superconducting transition temperature T_c or by their atomic ratio, e.g., i) the 110K or 2223 phase, ii) the 80K or 2212 phase and iii) the 10K or 2201 phase. The structure studies by x-ray, high resolution electron microscopy and neutron diffraction indicated that, the compound exhibits pseudo tetragonal structure with large c-axis due to the varying number of Cu-O planes. The 110K phase has three Cu-O planes, 80K phase has two Cu-O planes and 10K phase, only one.

In the thallium system, there are two series of compounds, $Tl_1Ba_2Ca_{n-1}Cu_nO_{2n+3}$ and $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4}$ (n=1 to 5) which can be modelled as an interleaving of rock salt and defective perovskite layers. For example, $TlBa_2CuO_5$ can be thought of as a layer of copper oxide sandwiched between two layers of barium oxide which is in turn sandwiched between two layers of thallium oxide. This compound, 1201, is not superconducting. A second copper layer can be inserted into the sandwich provided, it is separated from the first by a calcium layer. This gives the 1212 compound which has a T_c of approximately 90K. A second calcium layer allows the insertion of a third copper layer giving the 1223 compound with T_c increased to 116K. The corresponding series of compounds with double thallium layers have somewhat higher values of T_c, for 2223 ,the highest T_c is at 128K.

The increase in T_c as more copper layers are introduced into the structure, fuelled speculation that the route to room temperature superconductivity is to add more copper layers to the structure. These hopes were dashed when the 1245 and the 2234 compound were prepared and found to have T_c of less than 120K and 102K respectively. Thus, it would appear that T_c is maximised in the Tl_1 compounds at four layers, and in the Tl_2 compounds at three copper layers. But there is considerable difficulty in preparing the pure form of each structure. In all of these compounds, intergrowths are common in the form of alternating regions of the different variants. The three layer variants, which give the highest T_c, can be stabilised by replacing some of the bismuth or thallium with lead.

In late 1988, Cava et al [10] discovered a new family of copper-oxide based HTSC with superconducting onset temperature near 77K. The system can be expressed as $Pb_2Sr_2(R,Ca)Cu_3O_{8+x}$ where R=Y,Eu,Sm and Pr. The crystallographic structure of these oxides is slightly different from the Bi or Tl based superconducting layered oxides. That is, there exist two $Cu\text{-}O_2$ planes which are located between two PbO-Cu-PbO stacking layers in the Pb based layered copper oxides. These oxides are thought to be quite promising candidates for new high T_c superconductor which have T_c's higher than 110K. The structure is orthorhombic with space group $C_{mmm}(D_{2h})$. The oxygen ordering in the PbO-CuO-PbO plays an important role for the occurrence of superconductivity.

The 23K superconductor $Nd_{2-x}Ce_xCuO_4$ known as 214 T' structure superconductors discovered by Tokura et al [9] attracted interest since transport measurements indicate that the charge carriers are electrons and not holes as in all previously discovered HTC superconductors. For all the possible Ce concentration ,the material has the tetragonal, body-centered T' structure, similar to the La_2CuO_4 T structure but differing from it by the shift of the apical oxygen atoms to a position with D_{2d} site symmetry.

The recent discovery of superconductivity at 94 K [7] in the single CuO_2 layer compound $HgBa_2CuO_{4+x}$ (Hg-1201) and at 133K in its two and three copper layer analogues (Hg-1212 and Hg-1223) have renewed interest in the search for new high T_c superconductors. Structurally they contain n=1,2 or 3 adjacent copper oxide sheets, forming a compositional series $Hg_1Ba_2Ca_{n-1}Cu_nO_{2n+2+d}$. As in the similar thallium and bismuth based materials, the superconductivity undoubtedly originates in the electronically (hole) doped copper oxide layers. And like the earlier families, the mercury based counterparts have a T_c that increases with layer number n, with values of 95K, 115K and 133K for n=1,2 and 3 respectively. These high values especially for the n=1 end member(Hg-1201) which can be readily and reproducibly synthesized, account in part for the current excitement in this field.Another potential attraction is their relatively simple tetragonal structure which lacks the complexity of Cu-O chains in Y-123 or superstructural modulations as in Bi-Sr-Ca-Cu-O.Moreover, the relatively close spacing between the sets of Cu-O layers make the superconductor more isotropic and improve its properties relative to the highly anisotropic thallium and bismuth based materials.This material also possess some sobering aspects showing that applications are unlikely to be easy. The supercurrent conduction between randomly oriented grains is poor. This weak-linkage between grains with random orientation seem ubiquitous in the HTSC that have very short superconducting coherence length.

"The discovery of new superconductors with remarkable properties and higher T_c have much promise but they also have more problems. Perhaps problems and promise are just different perspectives as the same thing - but the real challenge that now remains is to translate the first into the second".

1.4 THEORETICAL MODELS

The discovery of superconductivity at higher temperatures (100K) in oxide materials (mainly cuprates) has thrown serious challenge to theorists regarding the mechanism that may be operative in rather strange systems and the pace of research activity all over the world has been frenetic. Various models have been formulated so far which involve the revival of old theories which have been put forward by theorists in the last 30 years.However, the highlights of few models that have been suggested for cuprate superconductors are presented here.

The antiferromagnetic-insulating to superconducting-metallic transition on doping, appears to be a universal feature of the HTSC. Many theorists are therefore convinced that the anomalous normal state properties and the high critical temperature can be attributed to the same electronic interactions that lead to antiferromagnetism in the parent insulating phase. However, this is not proved. Indeed, an indirect attractive pairing of electrons via some kind of lattice vibration, which is the basis of the highly successful BCS model for conventional superconductors, may yet explain superconductivity in the cuprate superconductors.

There are at least three quite distinct theoretical approaches to the problem of high temperature superconductivity. The first "conventional" approach assumes that, although strong correlations and the essential two dimensionality of electronic conduction in the CuO_2 planes may significantly affect the electronic properties, the charge carriers remain as fermions with unchanged quantum statistics. Superconductivity then involves the BCS-like pairing of electronic fermion quasi-particles at T_c, mediated by an yet undefined indirect attractive interaction via lattice phonons, spin fluctuations or excitonic electron states.

The second approach assumes the pre-existence of paired electron boson states above T_c, as in the formation of bipolarons associated with local lattice distorsions. The search for such a mechanism for superconductivity provided the motivation for Bednorz and Muller's [1] original measurements on the transition metal perovskite structures. In this model, superconductivity results from the Bose-Einstein condensation of these paired states at T_C, closely analogous to the superfluid transition in liquid helium.

The final approach, introduced by Philip Anderson [11], in his resonating valence bond model (RVB), postulates an entirely new exotic state of matter. The charge and spin associated with electron holes in the CuO_2 planes are assumed to dissociate into two quite distinct quasi-particles - a holon with unit charge but no spin and a spinon with no charge but half-integral spin. This separation of charge and spin is a many-body effect and does not violate the familiar rules of single-particle statistics.It has also been shown that two-dimensionality could lead to what are known as anyon charge carriers with statistics that are intermediate between those of fermions and bosons. Superconductivity can be predicted for all such models.The challenge to the experimentalist is to devise experiments that can unambiguously distinguish between the multiplicity of possible theories.

1.5 SUPERCONDUCTING STATE

Although the origin of superconductivity in the HTSC still remains unclear, the early measurements of the flux quantum as h/2e, proved that electrons were paired in the superconducting state. Most experiments seem to imply zero angular momentum s-state pairing. However, many theoretical models predict electron pairing in higher orbital momentum p or d states similar to superfluid liquid ^3He and, very likely, heavy fermion superconductors also. Low temperature NMR measurements of the nuclear relaxation rate via electronic excitations exhibit a power law temperature dependence inconsistent with s-state pairing, though it is not clear whether this is an intrinsic effect. A number of research groups have looked for a rotation in the plane of polarisation of light by HTSC, which could provide a signature for non-s-state pairing. However, the results are confusing.It is not clear whether these differences are sample or optical-frequency dependent. The question of the symmetry of the pairing therefore remains unresolved, though a balanced s-state pairing seems most likely.

The combination of a large pairing energy $\Delta \sim kT_C$ and a small Fermi velocity v_f results in an extremely small superconducting coherence length $\xi \sim v_f / \Delta$. For YBCO, ξ is 20 - 30 Å in the CuO_2 planes and only~1.5-3 Å in the perpendicular direction. Such values can be determined by the upper critical field, $H_{c2} \sim h/2e\,\xi^2$, which are much higher (typically > 100 T) than for conventional superconductors. The short coherence length means that superconductivity can be destroyed by defects even on an atomic scale - by departures in exact stoichiometry, oxygen vacancies, dislocations, etc. It also results in very small pinning energies ($\sim \mu_0 H_c^2 \xi^3$, where H_c is the thermodynamic critical field) for flux lines associated with flux penetration in the superconducting state. The small pinning energy means that flux lines can be relatively easily unpinned by intrinsic thermal fluctuations. This is the main challenge for high-temperature, high current power applications of HTSC.

The short coherence length also creates problems because of the difficulty of retaining atomic perfection at surfaces, as required for the measurement of superconducting properties by the powerful characterisation tools of surface science, and across interfaces in device structures. Any degradation close to an interface may lead to the measurement of superconducting properties that are not representative of the bulk. This is the major source of irreproducibility in published values for the energy gaps. The final consequence of the short coherence length is the ubiquitous "weak-link" problem. Weak-links are simply localised regions of the superconductor where the properties are degraded by structural defects - variations in chemical stoichiometry, vacancies, lattice defects, or even grain boundaries within otherwise perfect single crystls.

1.6 RAMAN SPECTROSCOPY OF HTSC

The role played by the phonons in the mechanism of superconductivity in the perovskite family of superconductors is not fully understood although a large series of experimental results has shown considerable coupling of some phonons to electronic excitation in these systems [12]. Optical spectroscopy and especially Raman and infrared spectroscopy revealed a strong direct influence of the changes in the electronic states to the phonon at the centre of the Brillouin zone. And also, HTSC in all their morphologies (ceramics, twinned and untwinned single crystals, oriented and partially oriented thin films) have been investigated by Raman spectroscopy.

It is well established that Raman scattering is a powerful tool to observe phonon instabilities caused by structural distortion. In $RBa_2Cu_3O_7$ systems, this technique has been employed to study oxygen vacancy effects on the Cu-O chains, phase properties by microanalysis technique, the dependence of phonon spectra upon the oxygen content, temperature dependence of phonon peaks, energy gap, impurity phase and structural phase transition above T_c. All Raman scattering studies mentioned above had a common aim at clarifying the nature of the phonon structures of such compound, which are directly or indirectly related to the mechanism of superconductivity.

1.7 TOWARDS APPLICATIONS

Inspite of the numerous difficulties, the improvement in the superconducting properties has opened the door to a host of futuristic applications. The basic properties of superconductors, (viz., zero electrical resistance, Meissner effect, Josephson effect etc.) have been successfully exploited for their practical applications. The three fundamental parameters that determine the economic feasibility for the applications are: i) critical temperature (T_c) , ii) critical current (J_c) and iii) critical magnetic field (H_{c2}). The higher the above three values, the better will be the practical applications.

The discovery of HTSC has created a unique challenge for the electric power industry. It holds the promise of a new technology which becomes economically viable only in the area of large scale power generation and distribution. The large scale application of superconductors in power industry depends on two basic properties:

i) its ability to carry very high current with no or very little loss

ii) its ability to produce medium to high magnetic field.

The first property is used in power transmission while the second in power generation and storage.

1.7.1 Power Transmission

Since superconductors exhibit zero resistance below T_c, there is no energy dissipation (I^2R loss) associated with the flow of current through it. Hence, superconductors have been proposed for power transmission cables for loss-less transmission. Many superconductors can carry, without energy loss, 100 to 1000 times larger current densities compared to normal conductors like copper. The need for cryogeneic apparatus for cooling effectively excludes them for small scale transmission due to high costs. It becomes economically viable at very high power levels of transmission. Economic feasibility now exists for power transmission and in electronic circuitary employing liquid nitrogen as the coolant.

1.7.2 Power Storage

Another area, where large scale application of superconductors are conceptualised is in the area of superconducting magnetic energy storage. Here one utilizes the property of a superconductor to sustain very high magnetic field. With d.c. operating the current in a superconducting coil short-circuited at its ends, flows indefinitely so that superconductive coils can be used as an inductive storage device. The most attractive application of such a device will be in load balancing in existing power grids.

1.7.3 Superconducting Magnets

The most important application of superconductors is in magnets. The success of superconductivity started with small laboratory magnets and extended through NMR to whole body magnetic resonance medical imaging (MRI). Superconducting magnets are also used in nuclear physics for the acceleration and focusing of particle beams and in particle detecting bubble chambers. Fusion reactors will require superconducting magnets for plasma containment.They are also used for mineral separation and magnetic levitation transport systems. High-speed ground transportation based on magnetic suspension has received considerable attention particularly in Japan. Magnetically suspended rail systems appear superior to all other forms of tracked transportation. The forward motion of the vehicle induces Eddy currents in the track which set up a repulsive levitating force between vehicle and track. The repulsive system is inherently stable.

1.7.4 Motors, Generators and Alternators

Homopolar dc motors and generators, and alternators have been successfully demonstrated using superconducting windings. The advantage of superconductivity in all of the above applications lies in the reduction in size for a given power over a conventional machine. The lower cost of refrigeration to nitrogen rather than helium temperatures, counted with the greater reliability of nitrogen refrigerators over helium refrigerators will inevitably make machines based on 77K superconductors more attractive economically than those using existing commercial materials.

1.7.5 Electronic Applications

Though currents in electronic devices are small, due to restricted dimensions, current densities are similar to those in large machines. However, magnetic fields are generally small. In thin film form, ceramic superconductors can have adequate critical current densities. It seems reasonable to suggest that the first applications of ceramic superconductors will be in electronic circuits and devices. The use of superconductors, with high current densities and absence of dissipation, implies the possibility of higher packing density on a circuit board or chip. Conventional superconductivity is not very attractive in these applications as the associated semiconductor elements do not operate well at helium temperatures. However, nitrogen temperatures are beneficial to semiconductor operation as carrier mobilities are often maximised in this temperature range. Thus the possible use of ceramic superconductors as passive circuit elements can confer a double advantage. All of the above applications require the production of high current density superconducting films which can be processed in compatibility with the semiconducting components, a goal which has not yet been proven to be readily achievable. Large passive electronic devices which can profit from the use of superconductivity include RF cavities and antennae. The absence of dissipation improves efficiency. The Meissner effect allows superconductors to be used for magnetic shielding.

The largest class of active superconducting devices are two terminal devices based on the Josephson effect. This two junction device, called a SQUID can be used as a sensitive detector and very accurate meter for magnetic flux. It can also be used as amplifiers, magnetometers and as digital components.

1.8 FUTURE PROSPECTS

Continuing advances in the experimental and theoretical understanding of HTSC can be expected confidently, particularly as sample quality improves. Superconductivity at higher temperatures, even at room temperature via as yet unrevealed mechanism, may still remain a possibility. The next significant breakthrough is likely to come from a totally unexpected direction, combining the skills of the synthetic chemist with the now familiar element of serendipity, as in the latest discovery of supercoductivity in the fullerenes.

HTSC marks the beginning of a new era of material science. Researchers are looking beyond the simple metals, their alloys, binary annd ternary compounds to the almost limitless range of complex molecular solids, many of which will be based on the rich chemistry of the transition metals. These new materials can be expected to have interesting and technologically important electronic and magnetic properties as the familiar materials of modern day technology. The important legacy has been the major investment in new research equipment and the powerful range of theoretical, experimental and material processing techniques developed primarily for HTSC but equally applicable to a much wider range of materials of potential importance to future material scientists.

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