CHAPTER 1
INTRODUCTION

The discovery of superconductivity in La-Ba-Cu-O system [Bednorz, J. G., and Muller, K.A., 1986] with superconducting transition temperature (T_c) above 30K, and subsequent discovery of Y-Ba-Cu-O system [Wu, et al., 1987] with T_c above 90K led to a spurt in the research activity in this class of materials. Later a T_c of 110K was found in Bi-Sr-Ca-Cu-O system [Maeda et al., 1988], 125K in the Tl-Ba-Ca-Cu-O system [Sheng et al., 1988; Parkin et al., 1988], and 127K in HgBa_2CaCu_2O_{6.22} system [Loureiro, S.M., et al., 1993].

The breakthrough of T_c above liquid nitrogen temperatures makes the Y_1Ba_2Cu_3O_{6.65} Bi-Sr-Ca-Cu-O, Tl-Ba-Ca-Cu-O and other high temperature superconducting systems very promising candidates for technological applications such as magnetic levitation, power transmission and storage, and devices based on Josephson junctions. Extensive research work has been carried out in the areas of (1) fundamental understanding of the properties of the materials and (2) improvement of the properties through optimisation in processing for practical purposes.

T_c In the superconducting oxides is dependent upon doping, although the exact mechanisms are not well known [Beyer and Shaw, 1989]. In Y_1Ba_2Cu_3O_{6.65} the oxygen ordering plays a very important role in superconductivity. Therefore, the transport properties associated with the motion of oxygen have been one of the major focuses in the literature [Rothman et al., 1989a; 1989b; Tu et al., 1989; and Bakker et al., 1989].
The structure of $Y_1Ba_2Cu_3O_{6+x}$ is identified by X-ray diffraction to be related to a cubic perovskite structure (ABO$_3$) with one of the cube axes tripled [Hinks et al., 1987] and both Y and Ba in A sites and Cu in B sites (Figure 1.1). The structure is highly anisotropic. It is known that rare earth elements can be substituted in Y and Ba sites depending on the ionic radius and charge state [Zhang et al., 1987] and transition elements in the Cu sites [Beyers and Shaw, 1989].

Figure 1.1 The Idealised Perovskite Structure.
Figure 1.2 Crystal structures of YBCO.

(a) Fully oxygenated $\text{YBa}_2\text{Cu}_3\text{O}_7$.
(b) Completely oxygen depleted $\text{YBa}_2\text{Cu}_3\text{O}_{6}$.
(c) Disordered $\text{YBa}_2\text{Cu}_3\text{O}_{6-}\delta$. 

Oxygens

02, 03, 01, 05

When disordered $\text{YBa}_2\text{Cu}_3\text{O}_{5-\delta}$.
High temperature processes are controlled by diffusion of cations, which are believed to have much slower diffusion rates than oxygen. A complete study of diffusion including all the cations and oxygen as a function of composition, temperature, oxygen partial pressure etc., is required for better understanding of diffusion mechanisms, and their relations to high-temperature processes, and the associated defect structures in this material.

1.1 THE STRUCTURE OF Y$_1$Ba$_2$Cu$_3$O$_{6+x}$.

Figure 1.2 shows the crystal structures for (a) fully oxygenated Y$_1$Ba$_2$Cu$_3$O$_7$, (b) completely oxygen depleted Y$_1$Ba$_2$Cu$_3$O$_6$ and (c) disordered Y$_1$Ba$_2$Cu$_3$O$_{6-x}$ samples as determined from the X-ray diffraction studies. In Y$_1$Ba$_2$Cu$_3$O$_{6-x}$ (0 ≤ x ≤ 0.92), the
oxygen non-stoichiometry $x$, plays a key role in determining the various physical properties of the material. The nominally fully oxygenated sample $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6.92}$ is orthorhombic in crystal structure (O1) and is superconducting with superconducting transition temperature ($T_c$) around 92K. The widely accepted lattice parameters of this fully oxygenated sample are $a = 3.818$, $b = 3.886$ and $c = 11.680 \text{ Å}$ with a space group $\text{Pmmm} (\# 47)$. It is interesting to note that, as the oxygen content $x$ reduces, the ‘$a$’ and ‘$c$’ lattice parameters of the orthorhombic structure increase with simultaneous decrease in the ‘$b$’ lattice parameter, ultimately resulting in a tetragonal crystal structure (T). A typical lattice parameter variation versus oxygen concentration is shown in figure 1.3.

The completely oxygen deficient sample, $\text{Y}_1\text{Ba}_2\text{Eu}_3\text{O}_{6.0}$ is tetragonal in crystal structure and non-superconducting. The lattice parameters of the tetragonal structure are $a = b = 3.858$ and $c = 11.839 \text{ Å}$ and the space group in $\text{P4/mmm} (\#123)$.

There are two copper atoms per unit cell located in the conduction layer of the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6-x}$. It is the number of carriers in this layer, measured approximately by the oxidation state of copper atoms, that appears to control superconductivity. A third copper atom is located in the charge reservoir layer (basal plane of the orthorhombic unit cell). The unusual co-ordination of oxygen atoms around this copper atom, forming a one-dimensional Cu-O-Cu-O-... chain like structure along the $b$ direction, is popularly termed as “Cu-O chains”. These oxygen atoms are ordered between the chain copper atoms. For this reason, $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6-x}$ lattice with orthorhombic crystal structure is known as the ordered structure. As the sample temperature is raised the oxygen atoms present in the Cu-O chains become mobile, and finally come out of the lattice above 350°C. At low temperatures, however, the behaviour is more complex, because of the interactions between the oxygen atoms along the chain and interchain sites leading to
various ordered structures. Several calculated phase diagrams [de Fontaine, D., et al., 1990; Khatchaturyan, A.G., et al., 1988] can be found in the literature for Y$_1$Ba$_2$Cu$_3$O$_{6-x}$ and a typical phase diagram for Y$_1$Ba$_2$Cu$_3$O$_{6-x}$ is shown in figure 1.4. The OI and T are the basic orthorhombic and tetragonal structures already discussed. The OII phase is an ordered orthorhombic structure characterised (at the ideal $x = 0.5$ composition) by alternating full and empty chains, giving rise to a supercell doubled along the $a$ axis. This OII phase is known to exhibit a plateau at 60K in the $T_c$ versus oxygen concentration curve. The calculations that yield this phase diagram also predict a number of additional ordered phases corresponding to more complex ordering patterns. The OII phase and many of the more complex ordered phases have been observed in diffraction experiments on oxygen deficient samples at room temperatures [Beyers, R., et al., 1989]. However, sluggish kinetics results in the formation of ordered structures only on a microscopic scale preventing a full experimental verification of the calculated phase diagram. At the other end of the oxygen concentration ($x = 0$) no oxygen atoms are present in the chains also. This would result in Cu-$\cdot$-Cu-$\cdot$- type of ordering, where $\cdot$ is a vacancy, along the $b$ direction.

1.2 DIFFUSION OF OXYGEN IN Y$_1$Ba$_2$Cu$_3$O$_{6+x}$.

The normal-state and superconducting properties of the Y$_1$Ba$_2$Cu$_3$O$_{6-x}$ depend strongly on the oxygen concentration [Jorgensen, D., et al., 1987; Kwok, K., et al., 1988; Cava, R.J., et al., 1987; Park, S.I., et al., 1988]. The control of oxygen concentration and in turn the variation of the conducting behavior in a systematic manner is an important issue. It means more than just varying the amount of $x$ in Y$_1$Ba$_2$Cu$_3$O$_{6-x}$ i.e., the oxygen content, but also having a clear picture of the distribution of $x$ in the oxide, which must include the ordering of the oxygen vacancies as well as the spatial
Figure 1.4 Phase diagram of Y$_1$Ba$_2$Cu$_3$O$_{6+x}$ system.
gradient or inhomogeneity of oxygen. When the parameter $x$ is varied by a moderate annealing, the variation of the oxygen concentration only occurs in $O(1)$ sites, i.e., in the CuO chains. The driving force of the intercalation can be monitored by the partial pressure of oxygen in the annealing ambient atmosphere, and the kinetics can be changed by changing the annealing temperature. Hence, it is of paramount importance to perform a systematic study of oxygen intercalation in the oxide by a proper selection of the ambient and the temperature of annealing.

The diffusion coefficient for an arbitrary direction in an orthorhombic crystal is given by [Nye, J.F., 1975]

$$D = D_a \cos^2 \Theta_a + D_b \cos^2 \Theta_b + D_c \cos^2 \Theta_c$$

where the $D_a$, $D_b$, and $D_c$ are the diffusion coefficients, in the three principal crystal directions and the $\cos \Theta$ are the direction cosines of the arbitrary direction with respect to the three principal axes. The large variation in the values of $D_a$, $D_b$, and $D_c$ indicates the anisotropy in the oxygen diffusion. This explains the neutron diffraction results that the mobile oxygen ions occupy $O(1)$ sites by moving along the basal plane but not along the $c$ axis which is too long for a jump to take place easily [Jorgensen, J.D., et al., 1987].

1.3 DEPENDENCE OF SUPERCONDUCTING PROPERTIES ON OXYGEN ORDERING.

The superconducting properties are strongly affected by the oxygen stoichiometry $x$, as well as by the defect ordering on a short length scale. It is known from the studies of Jorgensen, J.D., et al., 1990, that the superconducting and structural properties of oxygen-deficient $Y_1Ba_2Cu_3O_{6-x}$ undergo a change while the oxygen atoms diffuse
towards an ordered configuration at room temperature. The diffusion lengths involved are short - on the order of 10 Å, while the times required are of order 24 hours; thus, structural ordering can occur only on a short length scale, perhaps over a few unit cells. Nevertheless, the effects on the superconducting transition properties are dramatic.

Quenching experiments were conducted by Viel, B.W, et al, 1990, on single crystal of Y_{1}Ba_{2}Cu_{3}O_{6+x} at 500°C in appropriate partial pressure of oxygen to establish optimum oxygen concentration. The sample was then quenched to LN_{2} temperature (freezing in the configuration of oxygen atoms that existed). The T_{c} of the sample was measured. The sample was then warmed to room temperature, annealed for a specified amount of time and cooled for measurement of a new T_{c}. The structural measurements confirm that the systematic increase in T_{c} resulted from the ordering of oxygen atoms on a short length scale as these atoms diffused to achieve a configuration more consistent with the equilibrium phase diagram at room temperature. These observations show that the defect ordering influences the superconducting properties. This ordering leads to a charge transfer because the oxidation state of the chain copper atoms is a function of the co-ordination geometry as well as co-ordination number [Burdett, L.K., et al, 1990]. The electronic band structure calculations also lead to the same conclusion - that the formation of Cu-O-Cu-O-... chain fragments or ordered configurations in the charge reservoir layer enhances the carrier concentration in the conduction layer [Poulsen, H.F., et al., 1991].

The oxygen vacancies in YBCO have a clear tendency to order in quite elaborate patterns, showing superstructures of the basic orthorhombic cell, itself a perovskite ( a_{c} ≈ 3.8Å ) superstructure. The oxygen stoichiometry of this material crucially depends on the oxygen atoms present in the basal plane of the lattice.
In-situ neutron diffraction study [Jorgensen et al., (1987)] revealed that the observed changes in lattice parameters and oxygen content as functions of temperature are accompanied by the changes in oxygen ordering in the basal plane (between the Ba layers). It is known that the oxygen arrangement changes from fully ordered at room temperature in the orthorhombic phase, to partially ordered at high temperature in the same phase, and then to completely disordered at even higher temperatures in the tetragonal phase. Evidence of additional oxygen ordering has been observed by numerous electron diffraction studies [Beyers, et al., 1987; Van Tendeloo, et al., 1987; Alario-Franco, et al., 1989].
Alario-Franco, M.A., et al., 1989 have shown pictorially the possible mapping of the oxygen atoms in the basal plane to arrive at different stoichiometries (figure 1.5). Figure 1.5a corresponds to a fully ordered lattice with oxygen stoichiometry $x = 7$. In figure 1.5b an oxygen atom is eliminated from every fourth Cu-O row in the basal plane structure, which gives an oxygen stoichiometry of 6.875. Similarly, by properly eliminating oxygen atoms from the basal plane of the YBCO lattice, various oxygen non-stoichiometric phases can be pictured. The diagonal cells correspond to $2(2)_a * 2(2)_a * 3a_c$. In general $0 \leq x \leq 1$, it is possible to divide into five structurally
monophasic subregions that can be characterized by a general formula $Y_{1}Ba_{2}Cu_{3}O_{6-0.125m}$ with $m$ having only even values between 0 and 8 with structures characterized by unit cells corresponding to perovskite superstructures.

1.4 PSEUDOGAPS AND PHASE DIAGRAM OF HIGH-$T_{c}$ CUPRATES.

The $Y_{1}Ba_{2}Cu_{3}O_{6.8}$ is isomorphic to $Y_{1}Ba_{2}Cu_{4}O_{8}$ system, possesses an essentially identical $T_{c}$, $^{63}$Cu-spin-lattice relaxation rate in NMR, bulk susceptibility, and displays a magnetic behavior which is strikingly different from that measured for $Y_{1}Ba_{2}Cu_{3}O_{7}$. The $Y_{1}Ba_{2}Cu_{3}O_{6.8}$ system is generally considered as the optimally doped system, where the dopant is a hole. The $Y_{1}Ba_{2}Cu_{3}O_{6.63}$ is generally considered as underdoped and $Y_{1}Ba_{2}Cu_{3}O_{7}$ is overdoped. Though the $T_{c}$ depends on the oxygen concentration, what determines the $T_{c}$ is the hole doping concentration in the planes. $T_{c}$ is maximum for optimally doped material and decreases for either the underdoped or the overdoped material.

In the underdoped side of high-$T_{c}$ cuprate systems, anomalies now called "pseudo gaps" or "spin gaps" are observed in the normal state well above $T_{c}$. The first observation of this phenomenon was made with the NMR measurements [Yasuoka, H., et al., 1989] in 1988, where the $1/(T_{1}T)$ (where $T_{1}$ is the $^{63}$Cu spin-lattice relaxation rate, $T$ is sample temperature) was not constant above $T_{c}$ but rather kept increasing with increasing temperature until it saturated around $T^{*}$, the pseudogap temperature. This implies that the spin degree of freedom is gradually released, by thermal activation over a possible "gap" or binding energy characterised by $T^{*}$. Subsequently neutron scattering measurements [Rossat-Mignod, J., et al., 1992] have shown that the inelastic scattering response is reduced to zero below $T^{*}$ and below the corresponding energy transfer,
further suggesting the "gap". Recently, it has been suggested that: (1) the ab-plane dc conductivity of underdoped cuprate deviates from the linear-T behavior and becomes better below $T^*$ [Tagaki, H., et al., 1992]; (2) the c-axis dc conductivity shows reduction below $T^*$, as if the system crosses over from metallic to insulating behavior in terms of the interplanar conduction [Nakamura, Y., and Uchida, S., 1993; Takenaka, et al., 1994]; (3) the c-axis optical conductivity $\sigma_{ac}(\omega)$ at $T > T^*$ shows a reduction below the frequency $\omega$ corresponding to $T^*$ [Homes, C.C., et al., 1993]. These three observations indicate that the "pseudo gap" is related not only to the spin phenomena, but also to the charge transport.

The pseudo gap temperature $T^*$ is defined as the point where the temperature dependence of the conductivity departs from the linear-T behavior. This is, of course, the crudest way to estimate $T^*$. With increasing doping and increasing $T_c$ in the underdoped region, $T^*$ decreases, approaching $T_c$ in the optimum $T_c$ region. There is no signature of the pseudo gap behavior in the optimum $T_c$ and overdoped regions. If it is assumed that fermionic carriers form the so called "pre-formed pairs" in the normal state above $T_c$ in the underdoped region, then in this picture, $T^*$ can be viewed as the binding energy of a fermion pair. The reduction of in-plane dc-resistivity below $T^*$ occurs because spin-flip scattering is eliminated when the pair is formed. The reduction of c-axis conductivity can be explained if it is assumed that interplanar charge conductivity is much higher for a single fermion carrier than for the pre-formed pair, i.e., the tunnelling between adjacent CuO$_2$ planes for unpaired carriers occurs with much higher probability than for pairs.

Identification of the pseudo gap energy scale $T^*$ with the pair formation temperature $T_p$ allows us to directly map to the phase diagram of high-$T_c$ cuprates [Uemura, Y.J., 1995]. The underdoped side is then characterised by predominantly
Bosonic features. This explains why $T_c$ is proportional to $n_*/m_*$, (where $n_*$ is the superconducting carrier density and $m_*$ is the effective mass, and $n_*/m_*$ is the supercurrent density) with the universal ratio common to various different series of cuprates: the Bose condensation temperature is determined only by the density and mass of the condensing particles, regardless of detailed differences in the pairing interactions. This may also explain why the universal relation in cuprates can be extended to many other exotic superconductors.

Batlogg, B., et al., 1994, while carrying out studies on the normal state phase diagram of (La, Sr)$_2$CuO$_4$ using quantitative charge dynamics methods (resistivity and Hall effect) observed the characteristic temperature $T^*$ which depends strongly on the hole concentration, especially in the underdoped regions. In the underdoped regions $\rho_{ab}(T)$ shows weak localisation at lowest temperatures, increases superlinearly at intermediate $T$'s and finally grows less rapidly with a near-linear $T$-dependence at highest temperatures (figure 1.6). The knee at high $T$ is identified as the characteristic temperature $T^*$. This $T^*$ in LSCO is found to be $\sim 700 K$ for $x = 0.5$. The $T^*$ is found to be decreasing with $x$. This feature was found to be similar to the YBCO case. Starting with the double chain analogue YBa$_2$Cu$_4$O$_8$, which is chemically stable at high temperatures, $T^*$ is 200 - 250 K and $\rho(T)$ is very close to linear from $T^*$ to 900 K [Bucher., B., et al., 1993]. The results of YBCO$_{6.78}$ from two sets of data belonging to Bucher., B., et al., and Ito et al., are indistinguishable (figure 1.7) and highlight that the double chain compound is intrinsically underdoped. To estimate $T^*$ for other underdoped Y$_1$B$_2$Cu$_3$O$_{6-x}$ crystals, a $d\rho/dT$ versus $T$ for various compositions of $x$ are plotted. These curves show similar nature $T^*$ is then determined by the increase of $d\rho/dT$ upon cooling. Since a simple relationship appears to hold between $T^*$ and the maximum in $d\rho/dT$, $T^*$
Figure 1.6 Resistivity of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ multiplied by $x$ covering the wide span of the hole concentration from under to overdoping.

Figure 1.7 Two $\rho(T)$ curves typical for the underdoped region.
can be estimated for various values of $x$, and ranges from 500 (±50) K for $x = 0.45$ to -200 K for $x = 0.85$. Figure 1.8 shows a $T^*$ (K) versus Sr content ($x$) in normal state phase diagram $T^*$ - $x$ for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. The $T^*$'s for underdoped $\text{YBa}_2\text{Cu}_3\text{O}_y$ are superimposed for comparison. This indicates that the optimal hole concentrations coincide and that the increase of $T^*$ roughly follows the LSCO trend.

In this thesis an account of the various experiments carried out to grow ordered regions of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6-x}$ on a macroscopic scale is discussed. Several methods were adopted for the preparation of pure $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6-x}$ sample, and the samples thus prepared were characterised using high temperature X-ray diffraction, high temperature resistivity and $T_c$ measurements. For the purpose of measurement of high temperature resistivity of sintered samples, a new apparatus was designed and fabricated. A few innovations, such as (1) development of Si(911) single crystal wafers for use as the sample holder plates in X-ray diffraction studies, (2) precision alignment of X-ray powder diffractometer etc., were done to enhance the data quality. While carrying out X-ray diffraction studies of the samples prepared, a few batches of samples showed several Bragg peaks in addition to the normal reflections, which could be attributed to a super structure lattice. All these points, are discussed in detail in this thesis.
Figure 1.8 Normal state phase diagram $T^* - x$ for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with $T^*$'s for YBCO superimposed.
1.5 REFERENCES


