COMPOSITION DEPENDENCE OF SUPERCONDUCTIVITY
IN YBa$_2$(Cu$_{1-x$A$_x$)}$_3$O$_{6+\delta}$ SYSTEM WITH A = Zn, Ni

by

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Thesis submitted to the Graduate Faculty of
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

Physics

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November, 1987
Blacksburg, Virginia
56.55
58.55
1987
56.25
0.2
COMPOSITION DEPENDENCE OF SUPERCONDUCTIVITY

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(ABSTRACT)

The results of substitution of $\text{A}$ (with $\text{A} = \text{Ni and Zn}$) for Cu are presented in the high Tc superconductors, $\text{YBa}_2(\text{Cu}_{1-x}\text{A}_x)_3\text{O}_{6+\delta}$ where $x < 0.03$ for Zn and $x < 0.10$ for Ni. We have observed that the superconducting temperature in the high Tc $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ system decreases if copper is substituted by Ni and Zn and the substitution of Zn affects Tc much more than Ni. We discuss our results in terms of pair breaking by magnetic impurities and in terms of the Resonance Valence Bond model proposed by Anderson.
ACKNOWLEDGEMENTS

The author would like to thank her thesis advisor Dr. A. L. Ritter for his patient guidance and encouragement during her thesis work.

The author would also like to thank Dr. J. R. Long for providing the nice instruments and Mr. Y. Y. Wang for many useful discussions and help. The author is grateful to Dr. R. L. Bowden for his advice and encouragement, Mr. C. Gao and Mr. Eric Cole for help, and Mr. R. M. Nickell for reading the draft of this thesis.

Finally the author would like to express a special thanks to her husband, Chaoqiang Geng, to whom this thesis is dedicated.
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Chapter 1

INTRODUCTION

Superconductivity, the abrupt fall of electrical resistance at low temperatures, was first discovered by Kamerlingh Onnes\(^1\) in 1911, using mercury at liquid helium temperatures (4.1 K). Since then, superconductivity has been observed in many elemental metals and in a few metal-oxide compounds. In addition to zero resistance, a superconductor also expels magnetic flux below the transition temperature - the Meissner effect. This expulsion of flux is not simply a consequence of infinite conductivity (Lenz law would imply that the flux through the material should not change when the conductivity became infinite), but is a separate phenomena. The superconducting state is characterized by the transition temperature \(T_C\) and by a critical magnetic field \(H_C\) (in a so called type II superconductor, there are two critical fields). The \(H-T\) phase diagram for the normal-superconducting phases indicates that the superconducting transition is a second order phase transition. Finally, several experimental techniques, such as specific heat, normal tunneling, and infrared spectroscopy, indicate there is an energy gap between the ground state and the excited levels.

In spite of a large effort in the past 75 years, the superconducting temperature remained below 23.2 K, the \(T_C\) of \(\text{Nb}_3\text{Ge}\) observed by Gavaler et al. and Testardi et al.\(^2,\,^3\) in 1973. In September 1986, Bednorz and Müller\(^4\) broke through the barrier by reporting the possibility of high \(T_C\) superconductivity in the \(\text{La-Ba-Cu-O}\) system. From this exciting discovery, intensive studies on the superconducting properties of ceramics have been performed with hopes to achieve higher
Tc's and to elucidate the mechanism of superconductivity. The superconducting properties of the metal-oxides is sensitive to the precise balance of metal valence states and oxygen stoichiometry. In a short time, new compounds of Y-Ba-Cu-O have replaced the previously reported ones with higher Tc. Since it was reported that YBa$_2$Cu$_3$O$_{6+\delta}$ definitely exhibits Tc above liquid nitrogen temperature$^5$, most researchers have shifted gears to study the new material. The structure of this 1-2-3 compound$^6,7$ is an orthorhombic, distorted, oxygen, defect perovskite with ordering of yttrium and barium ions. Interestingly, the superconductivity remains essentially unaffected by the substitution of Y with isoelectronic rare-earth elements even if they have large localized moments$^8$. The fact that the rare-earth site is not much involved in the superconductivity process indicates that the superconductivity in this class of materials is confined to the CuO$_2$-Ba-CuO$_2$ layer assembly interrupted by R (R = Y or a rare-earth metal) layers$^9$. At the same time, substitution in Ba site by, for example, 25% Sr does not affect the high transition temperature either$^{10}$. In addition, the expected local density of states at the Fermi level DOS(E$_F$) should be small around the Ba$^{2+}$ and Y$^{3+}$ sites because of the stable Xe and Kr core electron structure. All these facts have led to the conclusion that the main contribution to the high transition temperature superconductivity in the YBa$_2$Cu$_3$O$_{6+\delta}$ compound comes from the Cu and O ions with the d band and spd hybridization states, respectively$^9$.

Substitution of Cu with metallic elements should produce substantial changes in the superconducting properties which in turn allow the nature of the high-Tc superconductivity and electronic structure to be
elucidated. In particular, this thesis will study the effect of substituting the two 3d elements, Zn and Ni, for the Cu ions by different concentrations from 0 to 10%. From the periodic Table, we can see that the ionic size and orbital structure of Zn and Ni are very close to those of Cu (Ni and Zn are the nearest neighbors to Cu on the left and right hand sides, respectively). Especially, Zn ions have no magnetic moment but Cu and Ni do. Therefore, by replacing Cu by Zn and Ni in the 1-2-3 system, it should hint which is the main reason of causing the superconductivity, the electric or magnetic properties of Cu.

This thesis is organized in the following way: Chapter 2 reviews the theories of superconductivity. The preparation and apparatus of the experiments are presented in Chapter 3. Results and analysis of the experiments are given in Chapter 4. Conclusions are in Chapter 5.
Chapter 2
THEORIES OF SUPERCONDUCTIVITY

The theories of superconductivity are classified into four sections: BCS theory, the depression of Tc by magnetic impurities from the BCS theory, the crystal structure of the new type superconductor YBa$_2$Cu$_3$O$_{6+\delta}$ and Anderson's Resonance Valence Bond (RVB) Model.

2.1 BCS Theory

The basic quantum theory of superconductivity was presented by Bardeen, Cooper and Schrieffer (BCS) in 1957$^{11}$, which we will summarize in the following three parts.

1. The BCS interaction pairing$^{12,13}$

In the BCS theory, a weak attractive interaction between electrons can lead to a ground state separated from the excited states by an energy gap $E_g$. The ground state is a correlated state of zero-momentum, singlet electron pairs $(k\uparrow, -k\downarrow)$ (neglecting all other electron-electron interactions). The pair with opposite spin and moment is called a Cooper pair which has many boson attributes. One of the key predictions of this theory is that a minimum energy should be required to break a pair creating two quasi-particle excitations. That the effective charge of the quasi-particle is 2e rather than e can be seen in tunneling experiments and from the quantization of magnetic flux. The zero resistance in the superconducting state is also due to the energy gap, to break a Cooper pair by scattering from an impurity or defect would destroy the many electron correlated state and cost the full gap energy.
2. The BCS electron-phonon interaction

In the BCS theory, the electron-electron coupling is mediated in second order perturbation theory by the electron-phonon interaction. Fig. 1 shows the simplified process in lattice and Fig. 2 shows the electron-phonon-electron interaction in momentum space. The contribution of phonons to the superconducting state is demonstrated by the isotope effect. In many elemental superconductors, the transition temperature is proportional to $M^{-1/2}$ where $M$ is the mass of the atom. This follows naturally from the BCS theory where $T_c$ is proportional to the Debye frequency of the solid which in turn is proportional to $M^{-1/2}$. In the high temperature superconductors, the transition temperature is weakly dependent on $M$ in the La$_2$CuO$_4$ compounds ($T_c = 40K$) and independent of $M$ in the Y-Ba-Cu-O compounds ($T_c = 90K$). This experimental observation suggests that the BCS theory may not apply to the high $T_c$ materials.

3. Density of states in BCS

The criterion for the transition temperature of an element or alloy involves the electron density of orbitals $D(E_F)$ at the Fermi level, i.e., $DOS(E_F)$ and the electron-lattice interaction $U$, which can be estimated from the electrical resistivity:

$$k_B T_c = 1.14 \hbar \omega_D \exp[-1/D(E_F)U]$$

(2.1)

According to this theory, one could observe an interesting correlation: The higher the resistivity at room temperature (larger $U$), the more likely it is that a metal will be a superconductor when cooled.

The experimental results for non-oxide superconductors over the
Fig. 1. The electrons interaction via the lattice deformation.
Fig. 2. The process of the electron-electron scattering mediated by a phonon.
past twenty years are in excellent agreement with the BCS theory. However, many phenomena observed in the high Tc oxide superconductors, particularly the weak isotope effect, do not appear to be consistent with the BCS theory and several new theories have been presented. We will only consider the RVB model.

2.2 Depression of Tc by Magnetic Impurities from the BCS Theory

It is necessary to briefly review the theory of the interrelation between superconductivity and magnetism which has been studied in the last thirty years. It was noticed years ago that superconductivity was absent in metals which had localized magnetic moments from magnetic impurities. The mechanism of their destructive effect on the superconducting state might be understood within the framework of the BCS theory if one took into account the exchange interaction of conduction electrons with localized magnetic impurities. In fact, in the superconducting state the electrons of the metal are coupled into Cooper pairs. If one of the electrons of such a pair is scattered by a paramagnetic atom, there is a large probability that its spin will change orientation due to the exchange interaction. As a result, the pair will collapse. These conclusions were essential for explaining the experimental results in a number of rare-earth superconducting compounds. As an example, Fig. 3 shows superconducting transition temperature Tc vs Gd concentration for the La$_{1-x}$Gd$_x$.system (from Ref. 15) which is a straight line with slope:

$$\frac{\Delta T}{\Delta C} = \frac{5K}{0.01} = 500 \text{ K}$$  (2.2)
Fig. 3 Superconducting transition temperature vs concentration of magnetic impurity in La-Ga system (from Ref. 15).
and the normalized slope:

\[
\frac{1}{T_c} \frac{\Delta T_c}{\Delta C} = 109.
\]  

(2.3)

2.3 The Crystal Structure of the New Type Superconductor YBa$_2$Cu$_3$O$_{6+\delta}$

It has been found in a number of investigations$^6,7$ that the superconducting phase has the composition YBa$_2$Cu$_3$O$_{6+\delta}$ (with $\delta = 1$) and that the structure of the compound can be described as a distorted oxygen deficient perovskite which is orthorhombic (cf. Fig. 4). The superconducting properties of these compounds are very sensitive to the oxygen concentration. If $\delta = 0.8$, the material is not a superconductor. Whereas, if $\delta = 1.0$, then $T_c = 90K$. The different oxygen conditions in the preparation process can cause the sites of the oxygen atoms to be occupied in a different way. According to Beech et al.$^{16}$, for compounds YBa$_2$Cu$_3$O$_{6+\delta}$, the O(4) sites are fully occupied in the samples annealed with Oxygen and only 80% of the O(4) sites are occupied in the samples annealed without oxygen, which correspond to the compositions YBa$_2$Cu$_3$O$_{7.0}$ and YBa$_2$Cu$_3$O$_{6.8}$, respectively. As shown in Fig. 4, for the oxygen-annealed phase, the copper atom Cu(1) atoms are at a distance of 1.846Å$^{17}$ apart. These rectangle are connected by vertices and form chains along the b-axis. The copper atom Cu(2) is also surrounded by four oxygen atoms with distances Cu(2) - O(2) = 1.929Å, Cu(2) - O(3) = 1.962Å, and Cu(2) - O(4) = 2.295Å. This pyramidal configuration is shown in Fig. 4. The relevant data are given in Table 1$^{17}$. In the non-oxygen annealed compound, all the crystal sites are the same as the oxygen annealed phase except that about 20% of the O(4) sites are
Fig. 4. Perspective view of the unit cell of YBa$_2$Cu$_3$O$_{6+x}$ (from Ref. 16).
<table>
<thead>
<tr>
<th>Bond</th>
<th>Calculated</th>
<th>Observed</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y-02</td>
<td>2.369</td>
<td>2.415</td>
<td>+0.048</td>
</tr>
<tr>
<td>Y-03</td>
<td>2.369</td>
<td>2.378</td>
<td>+0.009</td>
</tr>
<tr>
<td>Ba-01</td>
<td>2.820</td>
<td>2.879</td>
<td>+0.059</td>
</tr>
<tr>
<td>Ba-02</td>
<td>2.820</td>
<td>2.976</td>
<td>+0.156</td>
</tr>
<tr>
<td>Ba-03</td>
<td>2.820</td>
<td>2.970</td>
<td>+0.150</td>
</tr>
<tr>
<td>Ba-04</td>
<td>2.820</td>
<td>2.743</td>
<td>-0.077</td>
</tr>
<tr>
<td>Cu1-01</td>
<td>1.890</td>
<td>1.943</td>
<td>+0.053</td>
</tr>
<tr>
<td>Cu1-04</td>
<td>1.890</td>
<td>1.850</td>
<td>-0.040</td>
</tr>
<tr>
<td>Cu2-02</td>
<td>2.000</td>
<td>1.929</td>
<td>-0.072</td>
</tr>
<tr>
<td>Cu2-03</td>
<td>2.000</td>
<td>1.962</td>
<td>-0.038</td>
</tr>
<tr>
<td>Cu2-04</td>
<td>2.000</td>
<td>2.303</td>
<td>+0.303</td>
</tr>
</tbody>
</table>

(This Table is from Ref.17.)
vacant, resulting in a significantly defective structure along the chains Cu(1) - O(4). Apparently, superconductivity is suppressed in these materials by the defective structure.

2.4 Anderson's Resonance Valence Bond (RVB) Model

It is generally believed that the quasi-two-dimensional nature of the copper-oxide system is responsible for the occurrence of high temperature superconductivity in the new high Tc materials\(^4,5,6\). From neutron scattering\(^18\), it is observed that in the La\(_2\)CuO\(_4\) systems (which also have two dimensional copper-oxide sheets), the magnetic moments on the copper atoms form an anti-ferromagnetic liquid. That is, there is long range, anti-ferromagnetic correlations between the spins, but the system never goes into the Neel state. Based heavily on this experimental observation, Anderson resurrected a model he proposed in 1973 called the resonating valence bond (RVB) model\(^19\) which is equivalent to the Heisenberg s = 1/2 antiferromagnetic and the Mott insulating half-filled Hubbard models. The model predicts four excitations from the ground state: a spin 1/2 chargeless soliton called a spinon, a spin zero charged (+e) soliton called a holon, and real electrons and holes. There is no clear prediction at this time of how the superconducting state is formed. Originally, Anderson suggested that the holons undergo a Bose condensation (like superfluid He\(^4\)) into the superconducting state. In his latest preprint\(^20\) he suggests that electrons tunneling between the Cu-O layers maybe coupled by the exchange of holons just as electrons in the standard BCS theory are paired by the exchange of phonons. In this thesis, it is assumed that the holons and spinons are involved in the
formation of the superconducting state, in a way which is not clear at this time, and consider how these quasi-particles might be affected by the substitution of Ni and Zn for Cu.

To understand this theory, one would like to start from the chemical picture of Cu-O plane. From Table 2, note that oxygen atom can get two electrons from the cations (Y, Ba, or Cu atoms) to form a closed shell $O^{2-}$ while the copper atom loses 2 electrons and becomes $Cu^{++}$ with a closed shell + $3d^9$ electrons. For the $Cu^{2+}$ ion, eight electrons are paired in the 3d orbitals and the 9th unpaired electron is a spin 1/2 moment in the hybrid (dx²–y² hybridized with O 2p orbitals) bond between Cu and O. These half filled bonds form antibonding molecular orbitals with the neighbor Cu-O bonds, thus creating the half-filled Hubbard band. Comparing the photoemissions of CuO crystal and Y-Ba-Cu-O system shown in Fig. 5, we conclude that the 2p3d hybridization is very strong.

By writing the Y-Ba-Cu-O as

$$Y^{+3}Ba^{+2}_2Cu^{+2}_3O^{2-}_y.$$ 

one finds that for $y = 6.5$, the Y-Ba-Cu-O is defect free and each Cu-O has reverse charge-spin properties, i.e.,

$$Cu^{2-} \leftrightarrow O^{2-}$$

has charge q=0 and spin=1/2. The 2-D lattice corresponds to a sea of spins which couple strongly to form the valence-bonded pairs giving
<table>
<thead>
<tr>
<th>Atomic Number</th>
<th>Atomic Symbol</th>
<th>K</th>
<th>L</th>
<th>M</th>
<th>N</th>
<th>Electronic Shell</th>
<th>Ground State</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>O</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td></td>
<td>$^3\text{P}_2$</td>
</tr>
<tr>
<td>26</td>
<td>Fe</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td>6</td>
<td>$^5\text{D}_4$</td>
</tr>
<tr>
<td>27</td>
<td>Co</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td>6</td>
<td>$^4\text{F}_{9/2}$</td>
</tr>
<tr>
<td>28</td>
<td>Ni</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td>6</td>
<td>$^3\text{F}_4$</td>
</tr>
<tr>
<td>29</td>
<td>Cu</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td>6</td>
<td>$^2\text{S}_{1/2}$</td>
</tr>
<tr>
<td>30</td>
<td>Zn</td>
<td>2</td>
<td>2</td>
<td>6</td>
<td>2</td>
<td>6</td>
<td>$^1\text{S}_0$</td>
</tr>
</tbody>
</table>
FIG. 5. Comparison of photoemission spectra from Y$_1$Ba$_2$Cu$_2$O$_7$ and CuO. The O 2$p$ and Cu 3$d$ valence states nearly coincide in the high-$T_c$ material leading to resonantly enhanced Cu-O interaction. The dotted spectrum is from a contaminated sample after oxygen loss caused by irradiation (from Ref. 21).
short range anti-ferromagnetic ordering as observed by neutron scattering. The magnetic fluctuations of the system are called spinons in RVB theory.

For $y > 6.5$, there must be defects which we might picture either as

$$\text{Cu}^{++} \rightarrow \text{O}^-$$

or

$$\text{Cu}^{+} \rightarrow \text{O}^-$$

with charge $= +e$ and spin $= 0$. These holes in the lattice are the charged spinless bosons.

Since there are an infinite number of equivalent bonding arrangements such as

the system can resonate between these configurations.

Many experimental consequences are compatible with the idea\textsuperscript{20} that conduction in the normal state is mediated by hole solitons and that the magnetic fluctuations are spinons (Fermion solitons) with a pseudo-Fermi surface (pseudo-Fermi surface because the ordinary Fermi surface is calculated from charge neutrality and therefore it does not apply to chargeless objects). Both of the excitations involve rearrangements of the entire layer wave functions in the two-dimensional Cu-O layers, and cannot tunnel from one layer to another. The charged carriers, hole
solitons of charge e, are scattered effectively by the spinon. The scattering process leads to the in-plane conductivity (cf. Fig. 6). The only three-dimensional objects are real electrons, which can tunnel between layers but must then break up into soliton-spinon pairs of excitations. In this tunneling process, a boson is scattered not within the layer but from layer to layer, again with the emission and absorption of a pair of spinons, one in each layer. Namely, the electron spin is carried by the spinon and the electron charge is formed into the condensate (cf. Figs. 7,8). The Bose condensation might give rise to electron-electron pair amplitudes \( \langle C_{k+'} C_{-k+'} \rangle \) leading to "conventional" superconductivity. Therefore, it is suggested that the observed superconductivity might be a result of the electron-holon-electron tunneling between the layers.
Fig. 6. Spinon-holon scattering process with the matrix element $t$ (from Ref. 20).
Fig. 7. Interplane scattering process: a holon grabs a spinon forming an electron (from Ref. 20).
Fig. 8. Electron tunneling process: (a) before the tunneling and (b) after the tunneling. Here, it is supposed that in Layer I there is a hole with charge +e and spin zero which may come from the Cu$^{++}$O$^-$ chain. As the electron tunnels from Layer II to the hole in Layer I, a new hole and soliton are created in Layer II and a new spinon in Layer I.
Chapter 3

PREPARATION AND APPARATUS

3.1 Preparation

Samples at various compositions were prepared by solid state reaction from the powders of pure (99.99%) yttrium oxide (\(Y_2O_3\)), barium carbonate \(BaCO_3\), cupric oxide CuO, zinc oxide ZnO and nickel oxides NiO. These powders were mixed in appropriate atomic ratios of \(Y/Ba/Cu_{1-x}A_x\) with \(A = Ni\) or Zn and well grounded via mortar and pestle to form the desired compounds. (The parent sample \(YBa_2Cu_3O_{6+\delta}\) was also made for the comparison.) Then they were pressed into pellets of 1.2 cm diameter and 1.5 mm thick at 1.5 K bar and sintered for 24 hours at 930°C under 1 atm of flowing oxygen in a tubular furnace. In the last heat treatment the samples had been kept at 500°C in the oxygen atmosphere for 5 hours to be annealed (oxygen is used as opposed to air or other gases to improve the superconducting properties). After being slowly cooled down to room temperature, the samples were ready. The sample \(YBa_2(Cu_{1-x}A_x)_3O_{6+\delta}\) with \(x = 0\) prepared by this procedure showed a symmetric superconducting transition temperature at about 900K.

The compounds \(YBa_2(Cu_{1-x}Zn_x)_3O_{6+\delta}\) were prepared in six compositions, with \(x = 0, 0.25\%, 0.5\%, 1.0\%, 2.0\%\) and 3.0\%. The compounds \(YBa_2(Cu_{1-x}Ni_x)_3O_{6+\delta}\) were prepared in three compositions, with \(x = 1\%, 5\%\) and 10\%. As an example, the menu of the parent sample \(YBa_2Cu_3O_{6+\delta}\) is given in Table 3 with the molecular weights of \(Y_2O_3, BaCO_3, CuO, ZnO\) and NiO.

In a careful study of \(YBa_2(Cu_{1-y}Ni_y)_3O_{6+\delta}\), Maeno et al. found from
Table 3. YBa$_2$Cu$_3$O$_{6.5}$ menu

<table>
<thead>
<tr>
<th>Compound</th>
<th>Filter Paper</th>
<th>Paper+W(g)</th>
<th>W(g)</th>
<th>Mole</th>
<th>Atomic Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>YO</td>
<td>0.7939</td>
<td>2.2539</td>
<td>1.4600</td>
<td>$6.50 \times 10^{-3}$</td>
<td>1</td>
</tr>
<tr>
<td>BaCO</td>
<td>0.8523</td>
<td>5.9562</td>
<td>5.1039</td>
<td>$2.59 \times 10^{-2}$</td>
<td>2</td>
</tr>
<tr>
<td>CuO</td>
<td>0.8077</td>
<td>3.8935</td>
<td>3.0858</td>
<td>$3.88 \times 10^{-2}$</td>
<td>3</td>
</tr>
</tbody>
</table>

$W(\text{Y}_2\text{O}_3) = 88.905 \times 2 + 15.994 \times 3 = 225.792$

$W(\text{BaCO}_3) = 137.34 + 12.011 + 15.994 \times 3 = 197.333$

$W(\text{CuO}) = 63.546 + 15.994 = 79.540$

$W(\text{ZnO}) = 65.37 + 15.994 = 81.364$

$W(\text{NiO}) = 58.71 + 15.994 = 74.704$
electron probe micro-analysis that the Ni did substitute for the Cu up to
a concentration $y = 0.25$. A similar study by Xiao et al., in which they
substituted 10% Ni and Zn for Cu, also indicated that both Ni and Zu
substituted freely with the Cu atoms. This conclusion was based on x-
ray diffraction data on the samples which showed they were the same
single phase perovskite structure as the undoped Y-Ba-Cu-O. What is
uncertain is the influence of Ni and Zn on the oxygen concentration.
Since $T_c$ is sensitive to the amount of oxygen in the structure, it is
possible that the depression of $T_c$ by doping with Ni and Zn is due to a
systematic correlation between the impurity and oxygen concentration.
Given the similar size and electronic structure of Ni, Cu, and Zn, this
correlation seems unlikely, but need to be explored by measuring the
oxygen content as a function of doping.

3.2 Apparatus

The superconducting transition temperatures of the samples were
measured by the standard D.C. four-probe technique with 1 mm diameter Cu
wire held to the sample surface with small indium tip. The instrument
is described in the thesis of R. Mattozzi (Ph.D. 1982, Virginia
Polytechnic Institute and State University). The current used for the
measurement was 1 mA and the resolution of the voltage measurement was 1
x $10^{-5}$ V. Sample temperature was determined by using a calibrated
platinum resistor. The samples with four-probe and thermal resistor
were in a vacuum system of 100 Torr when they were cooled down to low
temperature. The value of $T_c$ was chosen as the main value of the
temperatures at the 10% and 90% values (denoted by $T_{co}$ and $T_{ce}$,
respectively) of the normal-state resistivity. The superconducting transition width ($\Delta d_T$) is taken as the difference between the temperatures $T_{co}$ and $T_{ce}$, namely

$$\Delta d_T = T_{co} - T_{ce}$$

(3.1)

The geometry of the samples is irregular and the ceramic samples do not perfectly have homogeneous density causing the absolute values of the resistivity measurement to have error. However, the relative changes in $\rho$ can be measured more precisely.
Chapter 4

RESULTS AND ANALYSIS

4.1 Results

1. The compounds $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$

A typical superconducting resistivity-temperature curve is shown in Fig. 9 which is the parent sample $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ made for comparison. The curve is from an x-y chart recorder. The voltage across a calibrated Pt resistor is proportional to temperature and drives the x-axis. The voltage across the sample is proportional to the resistance of the sample (the current through the sample is constant) and drives the y-axis. In this figure, the resistance $R$ initially drops almost linearly with the temperature $T$, a symmetric transition starts at 92 K, and a "zero-$R$" state is achieved at 79 K.

According to the notations given in Chapter 3, one has:

$$T_{co} = 91 \text{ K},$$

$$T_{ce} = 89 \text{ K},$$

$$T_c = \frac{T_{co} + T_{ce}}{2} = 90 \text{ K},$$

and

$$\Delta d_T = T_{co} - T_{ce} = 2 \text{ K}.$$ (4.4)

The slope of the normal state is given by:
Fig. 9. Temperature dependences of the resistivity of the compounds YBa$_2$Cu$_3$O$_{6+\delta}$.
\[ \beta = \frac{1}{R} \frac{\Delta R}{\Delta T} \quad (4.5) \]

The characteristic temperatures associated with superconducting transitions are also shown in Fig. 10.

2. The compounds \( \text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{6+\delta} \)

Figure 10 shows the temperature dependence of the resistances of the various compositions of \( \text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_{6+\delta} \) with \( x = 0 \), \( x = 0.25\% \), \( x = 0.5\% \), \( x = 1.0\% \), \( x = 2.0\% \) and \( x = 3.0\% \). The resistance decreases linearly with temperature in the normal state. The superconducting transition temperature as a function of Zn content is shown in Fig. 11. (Data for the curves in this section and the resistances at room temperature are given in Tables 4 and 5, respectively.)

3. The compounds \( \text{YBa}_2(\text{Cu}_{1-x}\text{Ni}_x)_3\text{O}_{6+\delta} \)

In Fig. 12, the variations of resistivity with temperature of the compounds \( \text{YBa}_2(\text{Cu}_{1-x}\text{Ni}_x)_3\text{O}_{6+\delta} \) are displayed, where \( x = 1\% \), 5\% and 10\%. In Fig. 13, the onset temperature \( (T_{co}) \), mid-point temperature \( (T_c) \) and end-point temperature \( (T_{ce}) \) are plotted versus Ni content. (The variation of the mid-point of superconducting transition temperature \( T_c \) with the A-content \( x \) for the compounds \( \text{YBa}_2(\text{Cu}_{1-x}\text{A}_x)_3\text{O}_{6+\delta} \) with \( A = \text{Ni} \) and \( \text{Zn} \) is shown in Fig. 14.)
Fig. 10. Temperature dependences of the resistivity of the compounds \( \text{YBa(Cu}_{1-x}\text{Zn}_x)\text{O}_{6} \) with concentrations \( x=0, 0.25\%, 0.5\%, 1.0\%, 2.0\% \) and 3.0\% of Zn.
Fig. 11. Variation of the mid-point of superconducting transition temperature $T_c$ with the Zn-content.
<table>
<thead>
<tr>
<th>A</th>
<th>x%</th>
<th>Tco(K)</th>
<th>Tce(K)</th>
<th>Tc(K)</th>
<th>ΔdT(K)</th>
<th>Slope $\beta = \frac{1}{R} \frac{\Delta R}{\Delta T}$ (K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>91</td>
<td>89</td>
<td>90</td>
<td>2</td>
<td>3.67x10⁻³</td>
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<tr>
<td></td>
<td>0.25</td>
<td>87</td>
<td>84</td>
<td>86</td>
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<tr>
<td></td>
<td>0.5</td>
<td>82</td>
<td>80</td>
<td>81</td>
<td>2</td>
<td>5.29x10⁻³</td>
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<tr>
<td></td>
<td>1.0</td>
<td>67</td>
<td>60</td>
<td>64</td>
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<tr>
<td></td>
<td>2.0</td>
<td>60</td>
<td>54</td>
<td>57</td>
<td>6</td>
<td>3.83x10⁻³</td>
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<tr>
<td></td>
<td>3.0</td>
<td>46</td>
<td>42</td>
<td>44</td>
<td>4</td>
<td>2.42x10⁻³</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>89</td>
<td>84</td>
<td>87</td>
<td>5</td>
<td>6.71x10⁻³</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>81</td>
<td>75</td>
<td>78</td>
<td>6</td>
<td>2.19x10⁻³</td>
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<tr>
<td></td>
<td>10.0</td>
<td>71</td>
<td>66</td>
<td>69</td>
<td>5</td>
<td>3.99x10⁻³</td>
</tr>
<tr>
<td>A</td>
<td>x %</td>
<td>Io (mA)</td>
<td>Vo (mV)</td>
<td>Ro=Vo/Io (Ω)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
<td>---------</td>
<td>---------</td>
<td>--------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0.468</td>
<td>0.468</td>
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<tr>
<td>0.25</td>
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<tr>
<td>1.0</td>
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<td>0.015</td>
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</tr>
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<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>1</td>
<td>0.250</td>
<td>0.250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0</td>
<td>1</td>
<td>0.029</td>
<td>0.029</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10.0</td>
<td>1</td>
<td></td>
<td></td>
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</table>
Fig. 12. Temperature dependences of the resistivity of the compounds YBa$_2$(Cu$_{1-x}$Ni$_x$)$_3$O$_{6}$ with concentrations $x=1\%$, 5\% and 10\% of Ni.
Fig. 13 Variation of the mid-point of superconducting transition temperature Tc with the Ni-content.
Fig. 14. Variation of the mid-point of superconducting transition temperature $T_c$ with the A-content dopant concentration.
4.2 Analysis

Because of the similarity of ionic size and electronic structure we expect that the 3d elements such as Ni (on the left hand of Cu in Periodic Table) and Zn (on the right of Cu) will occupy the Cu sites in Y-Ba-Cu system. This work presented the results of fundamental experiments concerning the superconducting properties of the compounds $\text{YBa}_2(\text{Cu}_{1-x}\text{A}_x)_3\text{O}_{6+\delta}$ ($\delta = 1$) $\text{A} = \text{Ni}, \text{Zn}$, with different concentrations as mentioned in Section 4.1.

All the samples studied here show a symmetric superconducting transition in which $T_c$ decreases with dopant concentration. From Figs. 10 and 12, one can see that the depression of $T_c$ is stronger for Zn than for Ni. For YBa$_2$$(\text{Cu}_{0.9}\text{Zn}_{0.1})_3\text{O}_{6+\delta}$, $T_c$ is less than 4.2 K. For the compounds YBa$_2$$(\text{Cu}_{0.9}\text{Ni}_{0.1})_3\text{O}_{6+\delta}$, on the other hand, the transition temperature is 70 K, a modest decrease of 22% from the transition temperature of the undoped compound. From Fig. 14, the normalized slopes of Ni-curve and Zn-curve are

$$k_{\text{Ni}} \equiv \frac{\Delta T}{T_c} \frac{\Delta C}{\Delta C} \bigg|_{\text{Ni} = 2} \quad (4.6)$$

and

$$k_{\text{Zn}} \equiv \frac{\Delta T}{T_c} \frac{\Delta C}{\Delta C} \bigg|_{\text{Zn} = 18} \quad (4.7)$$

respectively, which represent the changes of $T_c$ by the impurity elements and one has $k_{\text{Ni}} \ll k_{\text{Zn}}$. By comparing the slope of the La$_{1-x}$Gdx system in Eq. (2.2) with Eqs. (4.6) and (4.7), it was found that the effect of impurity element Gd which reduced the $T_c$ in the "old" superconducting material is much stronger than that of Zn and Ni in the new 1-2-3 compound.
To explain the Tc suppressions caused by substitutions of Ni and Zn of some of the Cu ions, one should start from the pure copper compound, which gives a maximum Tc 90 K in our experiment. In agreement with high-temperature magnetic data\textsuperscript{22}, the crystal structure suggests that the Cu\textsuperscript{2+} is in an $S = 1/2$, orbitally nondegenerate state, strongly hybridized with the surrounding oxygen p-levels. According to Anderson's theory\textsuperscript{19,20}, pertaining to the process of a boson scattered with emission or absorption of a pair of spinons (cf. Fig. 8), a real electron can tunnel between two-dimensional Cu-O layers. And it is suggested that superconductivity might be a result of electron-holon-electron pairing as described in 2.3. From this point of view, I now consider how doping with Zn and Ni might affect the RVB ground state.

I first consider how the RVB ground state is perturbed by replacing Cu with Zn atoms. The Zn\textsuperscript{2+} ion which occupies a Cu site cannot form antiferromagnetic pairs with other Cu-O chains since it has no magnetic moment $P$ ($P = 2s(s+1)^{1/2}$ with $s = 0$ for Zn\textsuperscript{2+} (cf. Table 6)). Therefore, in the RVB picture, replacing Cu\textsuperscript{2+} by Zn\textsuperscript{2+} creates a spinon and a spinless, chargeless defect as shown in the following way:

\begin{equation}
\begin{array}{c}
\text{Cu}^{2+} \\
\text{Cu}^{2+} \\
\text{Zn}^{2+} \\
\text{s=1/2} \\
\text{s=0} \\
\text{q=0} \\
\text{q=0} \\
\text{spinon defect}
\end{array}
\end{equation}

where Cu\textsuperscript{2+} means Cu\textsuperscript{2+} - O\textsuperscript{2-} bond and Zn\textsuperscript{2+} means the Z\textsuperscript{2+} - O\textsuperscript{2-} bond. The
Table 6. Effective magneton numbers for iron group ions

<table>
<thead>
<tr>
<th>Ion</th>
<th>Configuration</th>
<th>Basic Level</th>
<th>p(calc) = (g[J(J+1)])</th>
<th>p(calc) = (2[S(S+1)])</th>
<th>p(exp)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti(^{3+}, V^{4+})</td>
<td>3d(^1)</td>
<td>(^2)D(_{3/2})</td>
<td>1.55</td>
<td>1.73</td>
<td>1.8</td>
</tr>
<tr>
<td>V(^{3+})</td>
<td>3d(^2)</td>
<td>(^3)F(_2)</td>
<td>1.63</td>
<td>2.83</td>
<td>2.8</td>
</tr>
<tr>
<td>Cr(^{3+}, V^{2+})</td>
<td>3d(^3)</td>
<td>(^4)F(_{3/2})</td>
<td>0.77</td>
<td>3.87</td>
<td>3.8</td>
</tr>
<tr>
<td>Mn(^{3+}, Cr^{4+})</td>
<td>3d(^4)</td>
<td>(^5)D(_0)</td>
<td>0</td>
<td>4.90</td>
<td>4.9</td>
</tr>
<tr>
<td>Fe(^{3+}, Mn^{2+})</td>
<td>3d(^5)</td>
<td>(^6)S(_{5/2})</td>
<td>5.92</td>
<td>5.92</td>
<td>5.9</td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td>3d(^6)</td>
<td>(^5)D(_4)</td>
<td>6.70</td>
<td>4.90</td>
<td>5.4</td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>3d(^7)</td>
<td>(^4)F(_{5/2})</td>
<td>6.63</td>
<td>3.87</td>
<td>4.8</td>
</tr>
<tr>
<td>Ni(^{2+})</td>
<td>3d(^8)</td>
<td>(^3)F(_4)</td>
<td>5.59</td>
<td>2.83</td>
<td>3.2</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>3d(^9)</td>
<td>(^2)D(_{5/2})</td>
<td>3.55</td>
<td>1.73</td>
<td>1.9</td>
</tr>
<tr>
<td>Zn(^{2+})</td>
<td>3d(^10)</td>
<td>(^1)D(_0)</td>
<td>0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(This Table is from Ref.13.)
defect is a break in the RVB sea and strongly scatters holons:

\[ \text{Cu}^{++} \quad \text{Cu}^{-} \quad \text{Cu}^{++} \quad \text{Zn}^{++} \quad \text{Cu}^{++} \quad \text{Cu}^{++} \]

\[ s = 0 \]

\[ q = +e \]

\[ \text{Cu}^{++} \quad \text{Cu}^{++} \quad \text{Cu}^{+++} \quad \text{Zn}^{++} \quad \text{Cu}^{++} \quad \text{Cu}^{++} \]

\[ \text{Cu}^{+++} \quad \text{Cu}^{++} \quad \text{Cu}^{++} \quad \text{Zn}^{++} \quad \text{Cu}^{++} \quad \text{Cu}^{++} \]

The holon cannot "pass through" the Zn\(^{++}\) because the reaction Zn\(^{++}\) + Zn\(^{+++}\) + e \(^{+}\) is energetically too costly, and therefore the holon is scattered with 100% probability. If superconductivity arises from a "condensation" of the holons, this condensation is disrupted by the Zn\(^{++}\). Furthermore, we expect spinons to be strongly scattered by this defect also. Since the d-states filled by ten electrons in Zn are much lower in energy (cf. Fig. 15) than they are in Cu, Zn\(^{++}\) ions will not hybridize as readily with the oxygen 2p states. This means the spinon cannot "get past" the Zn\(^{++}\) either

\[ \text{Cu}^{++} \quad \text{Cu}^{++} \quad \text{Cu}^{++} \quad \text{Zn}^{++} \quad \text{Cu}^{++} \quad \text{Cu}^{++} \]

\[ \text{spinon} \quad + \]

\[ \text{Cu}^{++} \quad \text{Cu}^{++} \quad \text{Cu}^{++} \quad \text{Zn}^{++} \quad \text{Cu}^{++} \quad \text{Cu}^{++} \]

\[ \text{Cu}^{++} \quad \text{Cu}^{++} \quad \text{Cu}^{++} \quad \text{Zn}^{++} \quad \text{Cu}^{++} \quad \text{Cu}^{++} \]

I next consider the effect of Ni impurities on the RVB ground state. By the same arguments applied to Zn impurities, substituting
Fig. 15. The band structure of Zn (from Ref. 23).
Cu$^{++}$ by Ni$^+$ creates a holon and a negatively charged, spin 1/2 defect

\[
\begin{align*}
Cu^{++} & \quad \quad Cu^{++} \\
\downarrow & \\
Cu^{+++} & \quad Ni^+ \\
s=0 & \quad s=1/2 \\
q=+e & \quad q=-e \\
\end{align*}
\]

If the energy difference Ni$^+ \neq Ni^{++}$ is small, then a holon can "pass through" the defect

\[
\begin{align*}
Cu & \quad Cu & \quad Cu^{+++} & \quad Ni^+ & \quad Cu & \quad Cu \\
Cu & \quad Cu & \quad Cu^{++} & \quad Ni^{++} & \quad Cu & \quad Cu \\
Cu & \quad Cu & \quad Cu & \quad Ni^+ & \quad Cu^{+++} & \quad Cu & \quad Cu \\
Cu & \quad Cu & \quad Ni^+ & \quad Cu & \quad Cu & \quad Cu^{+++}. \\
\end{align*}
\]

This energy difference Ni$^+ \neq Ni^{++}$ is non-negligible; there will be some probability of scattering the holon. But it will be less than for Zn. In addition, the d-states of Ni$^+$ are closer in energy to the Cu$^{++}$ d states (cf. Fig. 16 and Fig. 5) and will hybridize more readily with the oxygen 2p electrons. So the Ni defect can participate with the RVB sea and therefore the scattering of spinons by the defect is reduced

\[
\begin{align*}
Cu & \quad Cu & \quad Cu^{++} & \quad Ni^+ & \quad Cu^{++} & \quad Cu & \quad Cu \\
\downarrow & \\
Cu & \quad Cu & \quad Cu^{++} & \quad Ni^+ & \quad Cu^{++} & \quad Cu & \quad Cu .
\end{align*}
\]

Thus, from the point of view of the RVB model, nickel impurities perturb the gas of holons and spinons much less strongly than do zinc impurities, that is, Zn-substitution affects Tc much more strongly than that of Ni.
Fig. 16. Photoemission spectra of NiO (from Ref. 24).
Another possibility for the Tc suppression caused by Zn-substitution may come from the reduction of DOS (E_F), the local density of the states at the Fermi level. Since Cu^{++} ion has 9 electrons, the DOS (E_F) comes mainly from the antibonding dx^2 - y^2 band, which is about half filled in the pure compound. Substitution of Cu sites by Zn provides an extra electron, which fills up the dx^2 - y^2 band and reduces the DOS (E_F) at those sites, thus reducing the superconductivity transition temperature.

It is also possible that the reduction of Tc by Ni-substitution may be due to spin exchange scattering from the localized magnetic impurity associated with the difference between the magnetic moments of Ni^{+} and Cu^{++}, i.e.

\[ P_{Ni^{+}} - P_{Cu^{++}} = 1.73 - 0.22 = 1.51, \quad (4.8) \]

where \( P_{Ni^{+}} = 1.73 \) is from the calculated value of magnetic moment for free Cu^{++} ion (cf. Table 6) and \( P_{Cu^{++}} = 0.22 \) is the effective magnetic moment in the 1-2-3 structure (cf. Table 7). As the Ni^{+} ions couple with the surrounding atoms, the extra magnetic moments may locally scatter or destroy some of the Cooper pairs in Cu - O plane. In this way, the superconductivity might be reduced. If I apply this argument to the other 3d elements with bigger magnetic moments than that at Ni, it would imply the suppression of Tc will reach a maximum at Mn and then follow off (dTc/dC become smaller) going from Mn to Ti. The data of Xiao et al., shows dTc/dC reaching a maximum of Co, not Mn, then decreasing again. So the suppression of Tc by exchange scattering is
Table 7. Tc; measured susceptibility at 100 K; fitted values of $\chi_0$, C, and To; and the deduced values of $p_A$ for YBa$_2$(Cu$_{1-x}$A$_x$)$_3$O$_{6+x}$

<table>
<thead>
<tr>
<th>A</th>
<th>Tc(K)</th>
<th>$\chi_{av}(100K)$</th>
<th>$\chi_0$</th>
<th>C</th>
<th>To(K)</th>
<th>$p_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>75.0</td>
<td>0.419</td>
<td>2.554</td>
<td>0.007</td>
<td>54.0</td>
<td>0-0.45</td>
</tr>
<tr>
<td>Cr</td>
<td>84.5</td>
<td>0.988</td>
<td>0</td>
<td></td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>73.9</td>
<td>1.821</td>
<td>8.187</td>
<td>0.143</td>
<td>-39.3</td>
<td>1.35-2.01</td>
</tr>
<tr>
<td>Fe</td>
<td>38.0</td>
<td>5.004</td>
<td>7.405</td>
<td>0.458</td>
<td>-7.1</td>
<td>3.29-3.61</td>
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<tr>
<td>Co</td>
<td>21.2</td>
<td>4.735</td>
<td>8.786</td>
<td>0.369</td>
<td>3.3</td>
<td>2.87-3.20</td>
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<td>Ni</td>
<td>66.3</td>
<td>1.923</td>
<td>2.395</td>
<td>0.148</td>
<td>9.6</td>
<td>1.40-2.05</td>
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<tr>
<td>Cu</td>
<td>94.1</td>
<td>0.490</td>
<td>2.362</td>
<td>0.017</td>
<td>33.9</td>
<td>0.22</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt;3.0</td>
<td>1.378</td>
<td>1.268</td>
<td>0.083</td>
<td>30.5</td>
<td>0.49*</td>
</tr>
</tbody>
</table>

*This moment is assumed to reside on the copper sites, and was used as the upper limit of the Cu moment.

(This Table is from Ref.8.)
not totally correct. But if we apply it just to Ni and Co and make the assumption:

\[ \Delta T_{Ni} = \alpha_1 (P_{Ni} - P_{Cu}) \]  
\[ \Delta T_{Co} = \alpha_2 (P_{Co} - P_{Cu}) \]

with

\[ \Delta T_{Ni} \equiv T_{Ni}^{Cu} - T_{Ni}^{Ni} \]  
\[ \Delta T_{Co} \equiv T_{Co}^{Cu} - T_{Co}^{Co} \]

where \( T_{Ni}^{Cu} \), \( T_{Ni}^{Ni} \) and \( T_{Co}^{Co} \) correspond to the transition temperatures of pure copper compound, 10\% Ni - substitution compound and 10\% Co-substitution compound. And make the further assumption:

\[ \alpha_1 = \alpha_2. \]

Then,

\[ \frac{\Delta T_{Ni}}{\Delta T_{Co}} = \frac{P_{Ni} - P_{Cu}}{P_{Co} - P_{Cu}} \]

From experimental data (cf. Tables 4 and 7), we have

\[ \frac{\Delta T_{Ni}}{\Delta T_{Co}} = \frac{94.1 - 66.3}{94.1 - 21.2} = \frac{27.8}{72.9} \approx 0.38 \]

\[ \frac{P_{Ni} - P_{Cu}}{P_{Co} - P_{Cu}} = \frac{1.40 - 0.22}{2.87 - 0.22} = \frac{1.18}{2.56} = 0.46 \]
Within experimental error the two values are nearly equal. Thus, our assumption of $\Delta T_A \propto (P_A - P_{Cu})$ appears to be valid for Ni and Co. However, this proportionality breaks down for Fe and Mn so other factors must be playing a role$^{25}$.

Finally, for both Zn and Ni cases, the non-uniform distribution of A (where A = Ni or Zn) ions at the Cu sites suggests that a significant inhomogeneity in the superconducting properties of the samples should exist and a large transition width would be expected. Indeed, as shown in Table 5, the widths of transition temperatures are getting bigger as the concentrations increase.
Chapter 5

CONCLUSIONS

On the basis of the existing data, it appears that there is a strong correlation between the superconducting transition temperature and the magnetic and electronic characteristics of Ni and Zn alloyed with the YBa$_2$Cu$_3$O$_{6+\delta}$ system. We have observed that the superconducting temperature in the high-$T_c$ YBa$_2$Cu$_3$O$_{6+\delta}$ system decreases if copper is substituted by Ni or Zn and the substitution by Zn affects the $T_c$ much stronger than that of Ni. This may simply be the same phenomena of pair breaking by magnetic moments seen in the work of Matthias et al (cf. Fig. 3). But if we take the magnetic moment of the copper atoms to be 0.22 as measured by the experiment, then either the differences between the Ni and Cu moment ($1.73 - 0.22$) is much bigger than the difference between the Zn and copper moment ($0 - 0.22$), in which case Ni would depress $T_c$ more strongly than Zn, or if Ni is in the divalent state, then the difference is the same for Ni and Zn and they should depress $T_c$ by the same amount. Thus, pair breaking by spin exchange scattering does not appear to be a viable explanation for the difference in $dT_c/dC$ between Ni and Zn.

On the other hand, the RVB model predicts that Zn will scatter holons and spinons more strongly than Ni and if the superconductivity arises from a correlation (say, bose condensation) of these excitation, then the RVB model provides a natural explanation for the difference in $dT_c/dC$ for Ni and Zn.
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VITA

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