AN ABSTRACT OF THE THESIS OF

Show-Jye Cheng for the degree of Doctor of Philosophy in Physics presented on October 18, 1995.

Title: Cu NQR and NMR Study of Metal-Substituted YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_4$O$_8$

Abstract approved: Redacted for Privacy

William W. Warren, Jr.

Pulsed nuclear quadrupole resonance (NQR) and nuclear magnetic resonance (NMR) have been used to investigate the effect of metal-substitution for copper in YBa$_2$Cu$_3$O$_7$ (YBCO123) and YBa$_2$Cu$_4$O$_8$ (YBCO124). Among many metal substitutions, Zn has an especially dramatic effect in suppressing the superconducting temperature $T_c$, and hence superconductivity. More interesting is that Zn and Fe have the same $T_c$ suppression effect in YBCO124. This study focuses on the Zn substitutions in YBCO123 and Zn, Fe, and Co substitutions in YBCO124.

In Zn doped YBCO123, Cu(2), plane site, NQR spectra and the frequency dependence of the spin-lattice relaxation rates have been measured over a temperature range from 77 K to 300 K to study the correlation of the suppression of the relaxation rate with the distance between the probe Cu nuclei and the impurity. It is found that the relaxation rate is insensitive to the variation of the NQR resonance frequency. However, by comparing the results of the Zn doped YBCO124 with those of YBCO123, it can be concluded that the suppression of the relaxation rate for both YBCO compounds in the normal state is caused by destruction of short-range antiferromagnetic correlation with substitution of nonmagnetic ion Zn on the Cu(2) sites.
NQR and NMR measurements were carried out on both Cu(2), plane, and Cu(1), chain sites, for various concentrations of Zn, Fe, and Co dopants in YBCO124 over a temperature range from 77 K to 300 K. A strong correlation of the enhancement of Cu(2) spin lattice relaxation rate and suppression of superconductivity by impurities was found. The temperature dependence of the Cu(2) NMR linewidth exhibits a strong RKKY type exchange interaction below 225 K for Zn and Fe doped samples, which indicates the formation of the local magnetic moment. The enhancement of the relaxation rate is caused by the local magnetic moment Fe$^{+3}$ ion and the moments on Cu(2) neighbors when Zn$^{+2}$ is substituted on Cu(2).

This study gives us a clear picture of the spin pseudogap behavior in the high temperature superconductor cuprates. It also suggests that the magnetic moment on the CuO$_2$ plane may relate to the suppression of $T_c$ in metal-substituted YBCO124.
Cu NQR and NMR Study of Metal-Substituted 
$YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$

by

Show-Jye Cheng

A THESIS

submitted to

Oregon State University

in partial fulfillment of 
the requirements for the 
degree of 

Doctor of Philosophy

Completed October 18, 1995
Commencement June 1996
I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.
ACKNOWLEDGMENT

I am grateful for having professor William. W. Warren, Jr. as my advisor. His constant advice and support helped me conquer the difficulties of my project. I learned a lot not only from his knowledge of physics, experimental techniques, and electronics, but his optimism, kindness, and modest personality.

I enjoyed the experience working with members of Warren group: Wolf-Christian Pilgrim, Andreas Goebel, Neil G. Roberts, Scott E. Fuller, and Susan P. Klein. The working atmosphere blended three different cultures: German, American, and Chinese. We built an efficient research laboratory that was accessible for everyone and explored the boundary of the apparatus. Additionally, Dr. Randy Lundquist and Neil G. Roberts constructed the supreme data analysis program: NMR Utilities which simplified the tedious data extracting procedure.

I would like thank the following people who provided help for my experiments. Mr. Tim Taylor’s suggestion was indispensable for the low temperature setup. Dr. Winyann Jang’s knowledge of electronics helped me fix the instrument – boxcar. Dr. Azmi Gencten and Prof. Ray Dupree provided me with the metallic doped high temperature superconductors.

I would like to thank Robert Paul Botts and Frankie Botts who regard me as a family member, and let me experience the warmth of their family while I was here alone.

Finally, from the deepest of my heart, I thank my wife, Yun-Wei Yu, for her understanding, encouragement, and support of my quest for higher education, and allowing my absence of being a husband and father to my children (Albert and Richard) for almost three years.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1</td>
<td>Motivations</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_4$O$_8$</td>
<td>2</td>
</tr>
<tr>
<td>1.2.1</td>
<td>Crystal Structure</td>
<td>2</td>
</tr>
<tr>
<td>1.2.2</td>
<td>Valence Picture</td>
<td>3</td>
</tr>
<tr>
<td>1.3</td>
<td>Metal Substitution for Cu</td>
<td>6</td>
</tr>
<tr>
<td>1.3.1</td>
<td>Superconducting Transition Temperature $T_c$</td>
<td>6</td>
</tr>
<tr>
<td>1.3.2</td>
<td>Substitution Site: Cu (1) or Cu (2)</td>
<td>7</td>
</tr>
<tr>
<td>1.3.3</td>
<td>Possible Explanations for the Suppression of $T_c$ by Impurity</td>
<td>8</td>
</tr>
<tr>
<td>1.4</td>
<td>Outline of the Project</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>NUCLEAR RESONANCE</td>
<td>12</td>
</tr>
<tr>
<td>2.1</td>
<td>Zeeman Interaction</td>
<td>12</td>
</tr>
<tr>
<td>2.2</td>
<td>Pulsed NMR</td>
<td>15</td>
</tr>
<tr>
<td>2.3</td>
<td>Hyperfine Interaction</td>
<td>17</td>
</tr>
<tr>
<td>2.3.1</td>
<td>Magnetic Hyperfine Interaction</td>
<td>17</td>
</tr>
<tr>
<td>2.3.2</td>
<td>Electric Quadrupole Interaction</td>
<td>18</td>
</tr>
<tr>
<td>2.4</td>
<td>Cu Hamiltonian</td>
<td>19</td>
</tr>
<tr>
<td>2.4.1</td>
<td>Electric Field Gradient</td>
<td>21</td>
</tr>
<tr>
<td>2.4.2</td>
<td>Knight Shift</td>
<td>23</td>
</tr>
<tr>
<td>2.4.3</td>
<td>Spin-Lattice Relaxation Time $T_1$</td>
<td>25</td>
</tr>
<tr>
<td>2.4.4</td>
<td>Spin-Spin Relaxation Time $T_2$</td>
<td>29</td>
</tr>
<tr>
<td>2.5</td>
<td>Spin Pseudogap in Underdoped YBCO</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>EXPERIMENTAL TECHNIQUES</td>
<td>33</td>
</tr>
</tbody>
</table>
### TABLE OF CONTENTS (Continued)

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Apparatus</td>
<td>33</td>
</tr>
<tr>
<td>3.1.1</td>
<td>Pulsed Spectrometer</td>
<td>33</td>
</tr>
<tr>
<td>3.1.2</td>
<td>Probe and Matching Circuit</td>
<td>37</td>
</tr>
<tr>
<td>3.1.3</td>
<td>Temperature Control</td>
<td>38</td>
</tr>
<tr>
<td>3.2</td>
<td>Sample Preparation</td>
<td>41</td>
</tr>
<tr>
<td>3.3</td>
<td>Measurements</td>
<td>42</td>
</tr>
<tr>
<td>3.3.1</td>
<td>Spin-Echo</td>
<td>42</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Spectra</td>
<td>45</td>
</tr>
<tr>
<td>3.3.3</td>
<td>Spin-Spin Relaxation Time $T_2$</td>
<td>46</td>
</tr>
<tr>
<td>3.3.4</td>
<td>Spin-Lattice Relaxation Time $T_1$</td>
<td>46</td>
</tr>
<tr>
<td>4</td>
<td>EXPERIMENTAL RESULTS</td>
<td>49</td>
</tr>
<tr>
<td>4.1</td>
<td>YBCO123:Zn</td>
<td>49</td>
</tr>
<tr>
<td>4.1.1</td>
<td>NQR Spectra: 300 K, 77 K</td>
<td>49</td>
</tr>
<tr>
<td>4.1.2</td>
<td>Temperature Dependence of the $T_1$</td>
<td>52</td>
</tr>
<tr>
<td>4.2</td>
<td>YBCO124:M</td>
<td>53</td>
</tr>
<tr>
<td>4.2.1</td>
<td>NQR</td>
<td>53</td>
</tr>
<tr>
<td>4.2.2</td>
<td>NMR</td>
<td>63</td>
</tr>
<tr>
<td>5</td>
<td>DISCUSSION</td>
<td>73</td>
</tr>
<tr>
<td>5.1</td>
<td>Impurity Occupied Sites in YBCO124:M</td>
<td>73</td>
</tr>
<tr>
<td>5.2</td>
<td>Local Moment in YBCO124:M</td>
<td>77</td>
</tr>
<tr>
<td>5.3</td>
<td>$T_c$ Suppression of YBCO124:M</td>
<td>79</td>
</tr>
<tr>
<td>5.3.1</td>
<td>Static Distortion of Cu(2) Local Structure</td>
<td>79</td>
</tr>
<tr>
<td>5.3.2</td>
<td>Decrease of Carrier Concentration</td>
<td>79</td>
</tr>
<tr>
<td>5.3.3</td>
<td>Change of the Cu(2) Spin Dynamics</td>
<td>80</td>
</tr>
<tr>
<td>5.4</td>
<td>Zn in YBCO123 and YBCO124</td>
<td>87</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
<td></td>
</tr>
<tr>
<td>-----------------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>CONCLUSION</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>92</td>
<td></td>
</tr>
</tbody>
</table>
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Crystal structure of YBa$_2$Cu$_3$O$_7$.</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Crystal structure of YBa$_2$Cu$_4$O$_8$ showing half of unit cell.</td>
<td>4</td>
</tr>
<tr>
<td>1.3</td>
<td>$T_c$ versus impurity concentration in YBCO:M.</td>
<td>6</td>
</tr>
<tr>
<td>2.1</td>
<td>Sketch showing the formation of the spin echo following 90° and 180° pulses.</td>
<td>16</td>
</tr>
<tr>
<td>2.2</td>
<td>Zeeman energy level diagram showing first and second order splitting by nuclear quadrupole interaction when the magnetic field lies along the EFG's principal axis.</td>
<td>22</td>
</tr>
<tr>
<td>2.3</td>
<td>Temperature dependence of $^{63}$Cu(2) magnetic shift for YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_4$O$<em>8$ with magnetic field parallel ($K_c$) and perpendicular ($K</em>{ab}$) to the $c$-axis.</td>
<td>25</td>
</tr>
<tr>
<td>2.4</td>
<td>The $^{63}$Cu(2) NQR spin-lattice relaxation time $T_1$ of YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_4$O$_8$ from Ref. [37],[46], are plotted as $(T_1T)^{-1}$ versus T.</td>
<td>28</td>
</tr>
<tr>
<td>3.1</td>
<td>Block diagram of pulsed NMR spectrometer.</td>
<td>34</td>
</tr>
<tr>
<td>3.2</td>
<td>Resonance circuit of NQR probe.</td>
<td>38</td>
</tr>
<tr>
<td>3.3</td>
<td>Resonance circuit and physical construction of NMR probe.</td>
<td>39</td>
</tr>
<tr>
<td>3.4</td>
<td>Block diagram of variable temperature control setup.</td>
<td>40</td>
</tr>
<tr>
<td>3.5</td>
<td>Block diagram of cool air flow system, 95 to 300 K.</td>
<td>40</td>
</tr>
<tr>
<td>3.6</td>
<td>Pulse sequence of pulse-delay add-subtraction method.</td>
<td>44</td>
</tr>
<tr>
<td>3.7</td>
<td>Pulse sequence of four-phase add-subtraction method.</td>
<td>44</td>
</tr>
<tr>
<td>3.8</td>
<td>Pulse sequence for $T_1$ measurement and block diagram of the boxcar.</td>
<td>48</td>
</tr>
<tr>
<td>3.9</td>
<td>$T_1$ relaxation curve measured by the boxcar.</td>
<td>48</td>
</tr>
<tr>
<td>4.1</td>
<td>$^{63}$Cu(2) NQR spectra and frequency dependence of relaxation rate at 300 K in YBCO123: Zn.</td>
<td>50</td>
</tr>
<tr>
<td>4.2</td>
<td>$^{63}$Cu(2) NQR spectra and frequency dependence of relaxation rate at 77 K in YBCO123: Zn.</td>
<td>51</td>
</tr>
<tr>
<td>4.3</td>
<td>Temperature dependence of $(T_1T)^{-1}$ values for $^{63}$Cu(2) in YBCO123: Zn(2.5%) and (5%).</td>
<td>52</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>4.4</td>
<td>Effect of various metals M on the $^{63}$Cu NQR spectra in $\text{YBa}<em>2(\text{Cu}</em>{1-x}M_x)_4\text{O}_8$ at 300 K.</td>
<td></td>
</tr>
<tr>
<td>4.5</td>
<td>Effect of various metals M on the $^{63}$Cu NQR spectra in $\text{YBa}<em>2(\text{Cu}</em>{1-x}M_x)_4\text{O}_8$ at 77 K.</td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>The decay curve of the spin-echo intensity of the $^{63}$Cu(2) nuclear spin in $\text{YBa}<em>2(\text{Cu}</em>{1-x}M_x)_4\text{O}_8$ at 77 K.</td>
<td></td>
</tr>
<tr>
<td>4.7</td>
<td>The frequency dependence of Cu(2) spin-lattice relaxation rate in YBCO124: Zn, Fe, and Co at 300 K.</td>
<td></td>
</tr>
<tr>
<td>4.8</td>
<td>The frequency dependence of the Cu(2) spin-lattice relaxation rate in YBCO124: Zn, Fe, and Co at 77 K.</td>
<td></td>
</tr>
<tr>
<td>4.9</td>
<td>Temperature dependence of $(T_1T)^{-1}$ in various metallic doped YBCO124.</td>
<td></td>
</tr>
<tr>
<td>4.10</td>
<td>The Cu NMR spectrum of YBCO124:Zn(0.9%) obtained in an external magnetic field 8 T at 300 K.</td>
<td></td>
</tr>
<tr>
<td>4.11</td>
<td>Spin-echo in the time domain measured at 90.105 MHz in YBCO124: Zn (0.9%).</td>
<td></td>
</tr>
<tr>
<td>4.12</td>
<td>$^{63}$Cu NMR spectrum of YBCO124: Zn(1.8%) at 300 K in a magnetic field 8 T for the direction of magnetic field parallel to the $c$-axis.</td>
<td></td>
</tr>
<tr>
<td>4.13</td>
<td>$^{63}$Cu NMR spectrum of YBCO124: Zn(1.8%) at 300 K in a magnetic field 8 T for the direction of magnetic field perpendicular to the $c$-axis.</td>
<td></td>
</tr>
<tr>
<td>4.14</td>
<td>$^{63}$Cu (1) NMR spectra obtained by Fourier transform of the spin-echo measured at 91.7 MHz in YBCO124: Zn(1.8%), Fe(0.9%), and Co(0.75%) with magnetic field ($\text{CuCl } \nu_L = 90.211$ MHz) parallel the $c$-axis.</td>
<td></td>
</tr>
<tr>
<td>4.15</td>
<td>Temperature dependence of $^{63}$Cu(2) central transition ($\pm \frac{1}{2}$) NMR line shapes of YBCO124: Zn(1.8%), Fe(0.9%), and Co(0.75%).</td>
<td></td>
</tr>
<tr>
<td>4.16</td>
<td>The plane $^{63}$Cu(2) magnetic shift versus temperature in YBCO124: Zn(1.8%), Fe(0.9%), and Co(0.75%).</td>
<td></td>
</tr>
<tr>
<td>5.1</td>
<td>$^{63}$Cu NQR integrated intensity ratio at 300 K as a function of atomic concentration x in $\text{YBa}<em>2(\text{Cu}</em>{1-x}M_x)_4\text{O}_8$.</td>
<td></td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>5.2</td>
<td>$^{63}\text{Cu}$ NQR integrated intensity ratio at 77 K as a function of atomic concentration $x$ in $\text{YBa}<em>2(\text{Cu}</em>{1-x}\text{M}_x)_4\text{O}_8$.</td>
<td>75</td>
</tr>
<tr>
<td>5.3</td>
<td>Half linewidth of Cu(2) central $(\frac{1}{2} \leftrightarrow -\frac{1}{2})$ transitions vs. inverse temperature in $\text{YBCO124: Zn(1.8%), Fe(0.9%), and Co(0.75%)$.}</td>
<td>78</td>
</tr>
<tr>
<td>5.4</td>
<td>Spin pseudogap energy $\Delta(\pi, \pi)$ and $^{63}\text{Cu}(2) (T_1T)^{-1}$ at 77 K versus $T_c$ in $\text{YBCO124:M}$.</td>
<td>83</td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>19</td>
</tr>
<tr>
<td>2.2</td>
<td>21</td>
</tr>
<tr>
<td>4.1</td>
<td>58</td>
</tr>
<tr>
<td>4.2</td>
<td>59</td>
</tr>
</tbody>
</table>

2.1 Gyromagnetic ratio $\gamma_n$, quadrupole moment $Q$, and the natural abundance of two Cu isotopes.

2.2 Cu NQR parameters in YBCO123 and YBCO124 at 300 K.

4.1 The Cu(2) spin-spin relaxation time and the spectra intensity corrected ratio (ICR) in YBCO124:M at 300 K, also included are the $T_1$ values of the Cu(1).

4.2 The Cu(2) spin-spin relaxation time and the spectra intensity corrected ratio (ICR) in YBCO124:M at 77 K, also included are the $T_1$ values of the Cu(1).
Cu NQR and NMR Study of Metal-Substituted YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_4$O$_8$

1. INTRODUCTION

1.1. Motivations

Since the discovery of high-temperature superconductors (HTSC) in 1986 [1], the origin of superconductivity is still not understood completely. One of the most practical methods of elucidating the mechanism of superconductivity is trying to understand the effects on superconductivity due to substitutional impurities for copper. Among many metal substitutions, Zn has an especially dramatic effect in suppressing the superconducting transition temperature ($T_c$) of La$_{2-x}$Sr$_x$Cu$_{1-x}$Zn$_x$O$_4$ [2], YBa$_2$(Cu$_{1-x}$Zn$_x$)$_3$O$_7$ [3], and YBa$_2$(Cu$_{1-x}$Zn$_x$)$_4$O$_8$.

Many experiments suggest that the magnetic correlations and fluctuations of the Cu$^{+2}$ spins may relate to the superconductivity in the high-$T_c$ cuprates. The nuclear resonance methods, Nuclear Quadrupole Resonance (NQR) and Nuclear Magnetic Resonance (NMR), have been regarded as powerful techniques to study the microscopic magnetic character of HTSC. This is because these methods can investigate the static and dynamic electronic spin properties on an atomic scale, even for the same atom at different lattice sites.

This study uses Cu NQR and NMR to probe the local structure and spin dynamics in an effort to understand the microscopic effect of metal substitution (Zn in YBCO123, Fe, Co, and Zn in YBCO124) and the means by which it suppresses superconductivity. It will also give the test of a proposed phenomenological model (spin-fluctuation-induced superconductivity).
1.2. $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$

1.2.1. Crystal Structure

$\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO123) and $\text{YBa}_2\text{Cu}_4\text{O}_8$ (YBCO124) are the $n=0$ and $n=2$ members of the homologous series $\text{Y}_2\text{Ba}_4\text{Cu}_{6+n}\text{O}_{14+n}$. The transition temperature of the former is 90 K and the latter is 80 K. They have similar crystal structures except that YBCO124 has an additional CuO chain layer. The YBCO124 has higher thermal stability and precise oxygen stoichiometry.

The crystal structure of YBCO123 is shown in Figure 1.1, taken from Mattheiss et al. [4]. The unit cell is orthorhombic with lattice constants $a = 3.8282$, $b = 3.8897$, and $c = 11.6944$ Angstroms, at 300 K [5]. There are two distinct Cu sites, Cu(1) and Cu(2). The Cu (1) and O(4) form the CuO chain layer with the oxygen lined up in chains along the b-direction. The Cu(2), O(2), and O(3) form the CuO$_2$ plane layer which is actually buckled, with the four oxygen atoms around the plane Cu displaced away from the chain layer with respect to the Cu. The O(1) and Ba form the BaO layer. The O(1) which links the Cu(1) and Cu(2) is called apical oxygen. It is believed that the superconductivity originates from the CuO$_2$ plane. The CuO chain layer sandwiched by both the BaO layers serves as a charge reservoir which provides the carriers to the plane layer. Study of oxygen deficient YBa$_2$Cu$_{3-\delta}$O$_{7-\delta}$ shows that the compound undergoes a phase transition from superconductor ($0 \leq \delta \leq 0.4$) to insulator ($0.4 \leq \delta \leq 1$) at a low temperature [6]. This is caused by the removal of the O(4) in the chain layer resulting in a decrease of the charge carrier on the CuO$_2$ plane. Neutron diffraction and X-ray diffraction indicate that the structure undergoes an orthorhombic to tetragonal transition ($\delta = 0.4$) and the buckling of the plane decreases as the oxygen is removed.

The crystal structure of YBCO124 is shown in Figure 1.2, taken from Boolchand et al. [7]. The crystal has two CuO chains between both the BaO layers. The position of the Cu in adjacent CuO chains differs by $b/2$ along the b-axis.
The YBCO124 has an orthorhombic unit cell with the lattice constants \( a = 3.8405 \), \( b = 3.8711 \), and \( c = 27.232 \) Angstroms, at 300 K \([8]\). This compound is chemically and thermally more stable than YBCO123.

1.2.2. Valence Picture

The formal valence picture of \( \text{YBa}_2\text{Cu}_3\text{O}_7 \) is the following: assign a valence charge of 1+ to the Cu(1), 2+ to the Cu(2) and Ba atom, 3+ to the Y, and 2− to each O atom. The monovalent Cu (1) which has 3d\(^{10}\) close shell configuration is nonmagnetic. The divalent Cu(2) which has 3d\(^8\) electronic configuration is magnetic with a spin \( S = \frac{1}{2} \) resided in 3d\(_{x^2-y^2}\) orbitals. When the temperature is less than
FIGURE 1.2. Crystal structure of YBa$_2$Cu$_4$O$_8$ showing half of unit cell. Taken from Boolchand et al. [7].

the Néel temperature, the spins of Cu$^{+2}$ ion on the CuO$_2$ layers order antiferromagnetically in the plane [9]. The YBa$_2$Cu$_3$O$_6$ is an antiferromagnetic insulator.
In case of YBa$_2$Cu$_3$O$_{7-\delta}$, the main effect of adding oxygen is to convert Cu$^{+1}$ ion on the chain to Cu$^{+2}$ ion. Therefore, the additional valence charges increase the holes in the CuO$_2$ plane's oxygen 2p$_x$ or y orbitals, and this disturbs the antiferromagnetic arrangement of the Cu$^{+2}$ spins in the CuO$_2$ plane. The YBa$_2$Cu$_3$O$_{7-\delta}$ moves continuously from the insulating antiferromagnetic state to the metallic superconducting state as $\delta$ changes from one to zero.

There are two band pictures to describe the relation between the hole in the Cu$^{+2}$ d-shell and the extra hole in the O-2p orbital in the CuO$_2$ plane. The first one, called two component picture, regards the Cu d-hole as a permanent magnetic moment uncoupled with the mobile p-hole on the oxygen. The second one is called "one component picture", in which the holes of Cu-3d$_{x^2-y^2}$ and O-2p$_{x,y}$ are hybridized together giving one spin degree of freedom per CuO$_2$ unit cell. Although most NMR results of YBCO are interpreted and consistent with one component picture, there is still some question about its application on the La$_{1-x}$Sr$_x$CuO$_4$ system [10]. Nevertheless, the Cu NMR shift and nuclear relaxation show that the 3d-electrons start pairing below $T_c$. It indicates that the 3d-spins have the itinerant character.
1.3. Metal Substitution for Cu

1.3.1. Superconducting Transition Temperature $T_c$

The effect of substitution for Cu in $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_7$ has been intensively studied [11], [12]. All substitutions reduce the $T_c$, but with different rates. The largest decrease rate is 10 K/at.% for zinc substitution, as seen in the $T_c$ vs. impurity concentration plot in Figure 1.3, data provided from Dr. Dupree [12]. A single-phase $\text{Yba}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$ can be maintained up to a solubility limit of about $x = 0.1$ [13]. Cobalt and iron which result in orthorhombic-tetragonal ($O - T$) structure transition at $x = 0.02 - 0.04$ [14] have a rate of about $-5$ and $-3$ K/at.%, respectively. The solubility limit for Co is $x = 0.33$ and for Fe is $x = 0.27$ [13].

Metallic doped samples of YBCO124 have been synthesized by using a high oxygen pressure technique at higher temperatures (about 900 K) [15] and by reaction with ambient oxygen pressure at lower temperatures (about 800 K) in the presence of a catalyst such as alkali-metal carbonates [16]. Both Zn and Fe have the same $T_c$ suppression rate of about $-23$ K/at.% and the largest effect on $T_c$.
synthesized with those two methods [17], [18], [19]. The solubility limit for Zn is \( x = 0.037 \) and Fe is \( x = 0.02 \). As in the case of YBCO123, Fe causes the O – T structural phase transition at \( x = 0.02 - 0.05 \). The structure of Zn doped YBCO124 remains macroscopically orthorhombic up to the highest dopant concentration. There are contradicting results about the \( T_c \) in Co doped YBCO124. Kodama et al. [18] claimed that Co and Fe doped samples which were synthesized under high oxygen pressure without a catalyst have the same rate of about \(-20\) K/at.%. Our Co doped samples which were synthesized with the catalyst exhibit a small effect on \( T_c \), with a rate of about \(-8\) K/at.%. We think that the discrepancy is probably related to differences in the sample preparation process.

### 1.3.2. Substitution Site: Cu (1) or Cu (2)

Due to the fact that YBCO has two distinct Cu sites, the question arises “where is the impurity substituted?” The answer is often controversial. Neutron diffraction, Extended X-ray Absorption Fine Structure (EXAFS), High Resolution Transmission Electron Microscope (HRTEM), \(^{89}\text{Y}\) NMR, and Mössbauer spectroscopy [17] have been used to investigate this problem. In fact, the different synthesis procedures of the material, the impurity concentration, and the limitation of the experimental techniques affect the interpretation of the site occupancies.

For YBCO123, it can be concluded from most research groups’ results that the trivalent ions, \( \text{Co}^{+3}, \text{Al}^{+3}, \) and \( \text{Ga}^{+3} \), substitute for Cu in the Cu(1) site accompanying the orthorhombic-tetragonal crystal structure phase transition with an increase in the impurity concentration. In case of Fe, most substitutions occur in the Cu (1) site; however, at higher concentrations Fe substitutes on both sites. The divalent ions, \( \text{Zn}^{+2} \) and \( \text{Ni}^{+2} \), preferably occupy the Cu(2) site with less effect on the crystal structure.
There are opposite conclusions regarding Fe substitution sites in material synthesized by different methods, although the materials show the same decrease in the rate of $T_c$ and are investigated by the same experimental technique, i.e. $^{57}$Fe Mössbauer spectroscopy. The Mössbauer spectra show a single quadrupole doublet at room temperature. It is not clear that the discrepancy comes from the different process methods or simply the different interpretation of the same quadrupole doublet. The impurity Fe in YBCO124 synthesized by the method with higher oxygen substitutes Cu in the Cu (2) site, although at a higher concentration ( > 1 %) Fe occupied both sites [20]. The samples synthesized by the method with ambient oxygen pressure substitute Cu in the Cu(1) site, but at a higher concentration ( > 2 %), Fe distributes on both sites [17]. With HRTEM, Yanagisawa et al. [21] showed that Fe substitutes on Cu(1) sites for samples synthesized by high pressure method. Nevertheless, the Zn occupied Cu(2) sites [22], [19] and Co occupied the Cu(1) sites [18], [21] as synthesized by both methods.

1.3.3. Possible Explanations for the Suppression of $T_c$ by Impurity

The suppression of $T_c$ by impurity doping in YBCO may be related to the (1) decrease of carrier concentration, (2) change of the electronic density of states, and (3) pair-breaking effects due to magnetic scattering, potential scattering, and direct suppression of the pairing interaction [23]. Since Zn has the strongest effect in suppressing $T_c$ and has been intensely studied by many groups, the discussion will focus on the Zn impurity.

The carrier concentration can be obtained by Hall effect [24] and thermopower measurement. The studies show that for Cu(1) substitution, such as Co, the profile of the temperature dependence of Hall coefficient ($R_H \sim \frac{1}{n_H}$, $n_H$ concentration of hole) increases substantially with increasing impurity concentration. For Cu(2) substitution, such as Zn and Ni, the impurity has negligible effect on the profile
of the Hall coefficient. In addition, the thermopower measurement of Zn doped YBCO124 shows that Zn does not affect the carrier concentration [25].

$^{89}$Y NMR measurement indicates that the $T_c$ suppression for impurity substitution of Cu(1) in YBCO123, such as Fe, Co, Al, and Ga, correlates with the change in the density of states near the Fermi surface $N(E_F)$ [12]. For Cu (2) substitutions (Zn and Ni), the above effect is small. Studies of Co, Fe, and Zn doped YBCO124 do not show that correlation [19]. Therefore, the strong suppression of $T_c$ by Zn doping in YBCO should not be caused by the reduction of $N(E_F)$.

In Zn doped YBCO, a Curie-Weiss-like behavior of magnetic moment was observed from the temperature dependence of the normal-state susceptibility [26] and NMR line-width of $^{89}$Y NMR [12], [27] and $^{63}$Cu NMR [28]. That was attributed to the nonmagnetic Zn$^{+2}$ substitution disrupting the antiferromagnetic fluctuation background of the CuO$_2$ planes, inducing magnetic local moments near the spin vacancies Zn. This indicates that the magnetic pair breaking is a possible explanation for the strong $T_c$ suppression. However, Ishida et al. [29] conducted a series of NMR studies for Zn doped YBCO123 prepared from oxalates (BaO) and carbonate (BaCO$_3$), and the samples prepared by the oxalates had no trace of the local moments but both the samples had the same effect on $T_c$. They remarked that the large reduction of $T_c$ was correlated to "the combined effect of the local collapse of antiferromagnetic fluctuation near Zn impurities and the occurrence of gapless superconductivity". Walstedt et al. [28] had found that the magnetic pair breaking was inadequate in the YBCO123 system and suggested the strong potential scattering may be a possible explanation. On the contrary, Mahajan et al. [30] argued that a simple RKKY analysis of the $^{89}$Y NMR line broadening and the application of Abrikosov-Gorkov pair-breaking formulation [31] could account for the large suppression of $T_c$ by th local moments induced by Zn.
Zheng et al. [32] have studied the magnetic properties in Zn doped YBCO124 by $^{63}$Cu NMR and NQR. Their results showed that suppression of the spin fluctuation spectral weight which was observed in YBCO124 was removed by Zn substitution. From $^{63}$Cu NMR in YBCO124:Zn, they argue for the formation of local moments on the orbitals orthogonal to the Cu$_{3d_{z^2-r^2}}$ – O$_{2p_z}$ orbitals.

On the whole, metal substituted for Cu(1) has a large effect on the crystal structure, charge carrier, and electronic density state but less effect on the $T_c$ than Zn does. Zn has a strong effect on the Cu spin fluctuation spectrum. This indicates that the magnetic mechanism on the CuO$_2$ plane may have a correlation with the superconductivity of HTSC.

1.4. Outline of the Project

Since high-$T_c$ cuprates have anomalous behaviors in the normal state, this project focuses on normal state study in metallic doped YBCO compound. Two YBCO systems are studied in this work. The first is YBCO123:Zn. A careful measurement of $^{63}$Cu spin lattice-relaxation versus temperature in YBCO123:Zn taken by Dr. William W. Warren, Jr. showed that there is a distribution of relaxation times in these materials. Speculating that the distribution of relaxation rates correlates with the location of Cu(2) nuclei with respect to the Zn impurity, leads us to perform the measurements of $^{63}$Cu(2) spin-lattice relaxation versus NQR frequencies. The idea is that those sites close to the impurities will experience the largest shift of their NQR frequencies with respect to the frequency observed in the undoped YBCO. From the comparison of relaxation rate at different frequencies, one may conclude the impurity effect on the relaxation rate of the Cu nuclei near the Zn impurity.

The second is the metallic doped YBCO124. The samples studied have impurities Co, Fe, and Zn with different concentrations. The striking properties of this
compound are that the nonmagnetic doped Zn and the magnetic doped Fe have the same significant effect on $T_c$ which is very different from their corresponding dopants in YBCO123. Our Co doped samples have less effect on $T_c$ which is different from the result of the other group with other synthetic techniques.

This part of the project focuses on using NQR and NMR techniques to investigate the impurity effect on the environment around the Cu nuclei at the atomic level. Comparing the experimental results, we may determine whether the distortion of the Cu(2) local atomic structure has direct relation with the superconductivity or whether the magnetic fluctuations play a major role in the formation of the superconducting pair. The study includes the static properties of Cu(1) and Cu(2) NQR and NMR spectra at different temperature with different impurity concentrations. The spin dynamics are mainly investigated by measuring the Cu NQR spin-lattice relaxation time and spin-spin relaxation time at different temperatures. In addition the frequency dependence of the relaxation time for various samples is also measured.
2. NUCLEAR RESONANCE

NQR and NMR use nuclei as microscopic probes for exploring the hyperfine interactions between the nuclei and electrons. Nuclear resonance methods examine the large modification of resonance frequency, the line shape and the relaxation behavior of the nuclear resonance which arise from the static as well as dynamic hyperfine interactions. How those measurable parameters are changed by the hyperfine interactions will be described in this chapter, with copper (Cu) nuclei in YBCO compound as an example. The content of the NMR and NQR in HTSC is referred from [33], [34], [35].

2.1. Zeeman Interaction

Using a quantum mechanical description, the nuclear magnetic dipole moment \( \vec{\mu} \) is associated with the nuclear spin angular momentum operator \( \vec{I} \) in units of \( \hbar \), through the relation as follows:

\[
\vec{\mu}_n = \gamma_n \hbar \vec{I}
\]  \hspace{1cm} (2.1)

where \( \gamma_n \) is the gyromagnetic ratio for a specific nucleus, and \( \hbar = \frac{\hbar}{2\pi} \) is Planck’s constant. Different nuclei have their own gyromagnetic ratios. A free magnetic dipole moment is placed in a constant magnetic field \( \vec{H} = H_0 \hat{z} \). The nuclear moments will be quantized along the z-direction. That means nuclei in the magnetic field can only populate discrete energy levels. The interaction Hamiltonian, i.e. Zeeman interaction, for a single nucleus is described as

\[
H_{\text{zeeman}} = -\mu_n \cdot \vec{H} = -\gamma_n \hbar H_0 I_z
\]  \hspace{1cm} (2.2)

The nucleus’s eigenstates can be represented by two quantum numbers, nuclear spin \( I \) and magnetic quantum number \( m = -I, -I + 1, \ldots, I \), for the nuclear operators
The nuclear spin $I$ is either integer or half-integer. Atomic nuclei in their ground states which have even and odd value of mass number ($A$) have integer and half-integer value of nuclear spin, respectively. An exceptional case is that in which both the mass number and the atomic number ($Z$) are even in which the nuclear spin is zero. For example the element Cu has two isotopes $^{63}$Cu ($A = 63, Z = 29$) and $^{65}$Cu ($A = 65, Z = 29$) for which the nuclear spin of each equals $\frac{3}{2}$. The nuclear spin of $^{16}$O ($A = 16, Z = 8$) is zero.

The eigenvalues of the operators can be expressed as:

\[ I_z|I, m\rangle = m|I, m\rangle, \quad I^2|I, m\rangle = I(I + 1)|I, m\rangle, \]

\[ I_\pm = I_x \pm iI_y, \]

\[ I_\pm|I, m\rangle = \sqrt{I(I + 1) - m(m + 1)}|I, m\pm 1\rangle, \]

where $I_+$ and $I_-$ are called raising and lowering operators, respectively, because of the effect they induce on $m$ when they operate on a state $|I, m\rangle$. The angular momentum operator $I_z$ has $2I + 1$ possible eigenvalues of $m$. Therefore the allowed energies for the nuclei are

\[ E_m = -\gamma_n \hbar H_0 m, \quad m = -I, -I + 1, ..., I. \]

The levels are equally spaced by an energy $\hbar \omega_0 = \gamma_n \hbar H_0$ (where $\omega_0$ is the Larmor frequency). The $\omega_0$ resides in radio frequency (rf) range 1 - 42.85 MHz (proton) for 1 Tesla magnetic field. The expectation value of the magnetic moment $\langle \mu \rangle$ behaves like a vector, making a fixed angle with the $z$ axis and precessing in the $x$-$y$ plane.

In thermal equilibrium the ensemble of nuclei unequally populates the Zeeman levels. The population may be represented by a Boltzmann distribution,

\[ P(E_m) = P(0)\exp(-E_m/k_BT). \]

The population of the energy levels exponentially decreases from the lowest energy level to the highest. Thus a macroscopic nuclear
magnetization $M(T)$ results from the sum of the individual components $\mu_z$ along the magnetic field. The magnetization can be expressed as

$$M = \frac{N\gamma_n^2\hbar^2H_0I(I+1)}{3k_BT}$$

(2.5)

where $N$ is the number of nuclei per unit volume. The relative intensity of $M$ and the Larmor frequency $\omega_0$ can be found by spectral absorption.

A time dependent perturbing Hamiltonian:

$$H_{pert} = -\gamma_n\hbar H_{1z}I_x \cos \omega t,$$

(2.6)

where $H_{1z}$ is the magnitude of the perturbation field, can cause nuclei to make a transition from one state to the adjacent one by magnetic dipole process. The operator $I_x, \langle I,m|I_x|I,m'\rangle \neq 0$, has nonzero matrix elements between states $m$ and $m'$ only when $m' = m \pm 1$, restricting the magnetic transition. Accordingly, the transition can be induced by applying a time dependent magnetic field with a component $H_{1z}$ rotating in the plane perpendicular to the $z$-axis. The electromagnetic wave with frequency $\omega = \omega_0$ provides the required energy.

The above situation is achieved experimentally by placing a sample in a coil with its axis perpendicular to the static magnetic field. This coil of inductance $L$ is tuned at a resonance frequency $\omega$ with a parallel or a series capacitor of capacitance $C$. When a sinusoidal alternating current with frequency $\omega$ is applied in this tuned circuit, a linearly polarized magnetic field $H_{1z}I_x \cos \omega t$ is produced in the coil. As the magnetic resonance condition $\omega = \omega_0$ is met, the equilibrium population of the nuclei among the Zeeman energy levels is disturbed by an rf induced transition. NMR can be detected either by the energy loss from the external circuit with an application of low level rf power, known as continuous wave (c.w.) method, or by the weak current induced in the coil by the magnetization of the nuclei precessing at frequency $\omega_0$ after applying a intense rf pulses, known as the pulsed method.
2.2. Pulsed NMR

Pulsed NMR has many advantages over the c.w. method and has become a standard laboratory technique. For instance, a single pulse can excite all the lines in the region of the pulse power spectrum. In the c.w. method it is necessary to scan the whole frequency region to get the same spectrum. The spin dynamics can be studied directly by the pulsed method. In the c.w. method it might be indirectly extracted from analyzing the line shape.

The concept of pulsed NMR can be easily described in a rotating frame. The rotating frame has the same z-axis as the laboratory frame but is rotating at the frequency $\omega$, under the condition of resonance $\omega = \omega_0$. Figure 2.1 shows the response of the magnetization to 90° and 180° pulses. The applied perpendicular field $H_{1z} \cos \omega t$ behaves as a static field $H_{1z}$ along the -x'-axis, in the rotating frame. Just like the case in which spin precesses in the static field, the magnetization will precess around the x'-axis in the rotating frame with the precession angle given by $\phi = \gamma \rho H_1 t_{pw}$, where the $t_{pw}$ is the duration time of the pulse. Thus by controlling the time $t_{pw}$, the direction of magnetization in the rotating frame can be chosen. For example, a 180° pulse inverts the magnetization. A 90° pulse brings the magnetization $M_z$ into the - y'-axis in the rotating frame which corresponds to magnetization $M_{x,y}$ rotating with frequency $\omega_0$ in the x-y plane. After the 90° pulse the magnetization $M_{x,y}$ will perform a free precession in the x-y plane and finally return to the equilibrium via relaxation processes. The observation of the precession is done by recording the tiny voltage about few $\mu V$ to $mV$ induced on the sample coil by the motion of the magnetization. This is called the free induction decay (FID) and its decay time, $T_2^*$. The spin-echo method is a standard technique in pulse NMR. It can eliminate the short $T_2^*$ problem of the FID caused by the static inhomogeneous field. After a 90° pulse, the spins which feel higher (lower) magnetic field precess faster (slower)
FIGURE 2.1. Sketch showing the formation of the spin echo following 90° and 180° pulses. The applied oscillating field \( H_1 \) lies along the \(-x'\) axis. The four isochromats, numbering them 1, 2, 3, 4, represent groups of spins which have particular frequencies.

than the average. They dephase with time resulting in a decaying of the transverse magnetization. If a 180° pulse is applied at some time \( \tau \), the spins will flip 180° with respect to the \( x' \)-axis. The fast precessing spins are left behind the average and the slow ones ahead. After another time \( \tau \) the fanned out spins coalesce, i.e. the macroscopic transverse magnetization is restored, and then the dephasing process starts again. Accordingly, the spin echo is formed at the time \( 2\tau \) after the 90° pulse, assuming \( t_{pw} \ll \tau \). It is just like two free induction decays placed back to back.

The spin-spin relaxation time \( T_2 \), is measured by varying the delay time \( \tau \) between the 90° and the 180° pulses. By manipulating the pulse sequence the spin-lattice relaxation time \( T_1 \) can be measured directly. Pulsed NMR is a valuable method in the study of the static and dynamic nuclei hyperfine interactions and many other local interaction in condensed matter.
2.3. Hyperfine Interaction

The interactions between the nuclei and electrons, except for the coulomb interaction, are called the hyperfine interactions. The two most important hyperfine interactions are the nuclear magnetic dipole and nuclear electric quadrupole interaction.

2.3.1. Magnetic Hyperfine Interaction

The hyperfine coupling between the nuclear magnetic dipole moment and the electronic spin and orbital magnetic moments is

\[
H_{mhfs} = -\gamma_e \hbar \sum_k \gamma_e \hbar \left[ \frac{\mathbf{L}_k}{r_k^3} + \frac{\mathbf{S}_k}{r_k^3} - \frac{3(r_k \cdot \mathbf{S}_k)r_k}{r_k^5} + \frac{8}{3} \pi |\Psi_k(0)|^2 \mathbf{S}_k \right] \tag{2.7}
\]

where \( \gamma_e \) is the electronic gyromagnetic ratio, \( r_k \) is the distance between the nucleus and the \( k \)th electron, \( |\Psi_k(0)|^2 \) is the electron wave density at the nucleus site, and \( \mathbf{S}_k \) and \( \mathbf{L}_k \) are the \( k \)th electronic spin and orbital angular momentum operators, respectively. The first term in equation (2.7) is the orbital hyperfine coupling due to the field produced by the electronic currents. The next two terms describe the dipolar field generated by the electronic spin magnetic moment. The last one is called the Fermi contact term which has no correspondence to a classical interpretation. The time-dependent part of \( H_{mhfs} \) provides an efficient source for nuclear spin relaxation.

The static part of \( H_{mhfs} \) gives rise to a NMR line shift which is proportional to the external magnetic field. Thus the equation (2.7) can be simplified by introducing a magnetic shift tensor, \( \mathbf{K} \).

\[
H_{mhfs} = -\gamma_n \hbar \mathbf{I} \cdot \mathbf{K} \cdot \mathbf{H} \tag{2.8}
\]

The NMR resonance frequency \( \nu \) can be expressed (in the absence of nuclear electric quadrupole effects) by:
\[ \nu = \gamma_n H_0 (1 + K), \tag{2.9} \]

where \( K \) is the total magnetic shift. The total magnetic shift is composed of three quantities \( K = \sigma + K^L + K^S \). The first term \( \sigma \) is the shift caused by the diamagnetism of the closed shell electron orbits. The second term \( K^L \) is the chemical (orbital) shift resulting primarily from the unquenching of orbital angular momentum. The third term \( K^S \) is the Knight shift resulting from the spin paramagnetism of conducting electrons. Generally, the unshifted resonance frequency \( \gamma_n H_0 \) is taken to be the resonance frequency of the nucleus in a closed shell diamagnetic salt. Thus the magnetic shift in equation (2.9) consists of the chemical shift and the Knight shift.

### 2.3.2. Electric Quadrupole Interaction

A nucleus with a nuclear spin \( I \) greater than 1/2 possesses an electric quadrupole moment which is caused by a nonspherical nuclear charge distribution. The quadrupole moment can interact electrostatically with an asymmetrical electric field at the nuclei sites generated by the electrons outside the nucleus. This interaction splits the degenerate nuclear magnetic eigenstates. The Quadrupole Hamiltonian can be simply written [36]:

\[
H_Q = \frac{eQV_{ZZ}}{4I(I-1)} \left\{ 3\tilde{P}_z^2 - I(I+1) + \frac{\eta}{2} (\tilde{P}_+^2 + \tilde{P}_-^2) \right\}, \tag{2.10}
\]

where \( Q \) is the nuclear electric quadrupole moment, the electric field gradient (EFG) tensor, \( V_{\alpha\beta} = \frac{\partial^2 V}{\partial \alpha \partial \beta} \) (\( \alpha \) or \( \beta = x,y,z \)), is expressed with respect to its principal axes OXYZ. The principal components of the EFG tensor are denoted by \( V_{aa} \) with the convention \( |V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}| \), \( \eta = \frac{(V_{XX} - V_{YY})}{V_{ZZ}} \), \( \eta \in [0,1] \) where \( \eta \) is the asymmetry parameter of the EFG. For cylindrical or tetragonal symmetry, \( \eta = 0 \). The EFG at the nuclei site is zero when the nuclei occupy cubic or higher symmetry sites, thus \( H_Q \) equals zero.

The direct detection of the splitting of the nuclear eigenstate by quadrupole interaction in the absence of a magnetic field is called NQR. The theoretical concept
and experimental apparatus for NQR and NMR are the same except the nuclear energy splitting for the former is determined only by atomic structure and the latter is related to the strength of the applied magnetic field and the quadrupole interaction. In low magnetic fields, \( H_{\text{zeeman}} \ll H_Q \), the Zeeman interaction splits the quadrupole levels, called Zeeman-perturbed NQR. In high magnetic fields, \( H_{\text{zeeman}} \gg H_Q \), the NMR frequency may be shifted by the quadrupole interaction.

### 2.4. Cu Hamiltonian

Cu has two naturally occurring stable isotopes, \(^{63}\text{Cu}\) and \(^{65}\text{Cu}\), with the same nuclear spin (\( I = \frac{3}{2} \)) but different quadrupole moments and gyromagnetic ratios. They are presented in Table 2.1.

In the presence of the an applied magnetic field, \( \vec{H} \), the Hamiltonian of Cu nuclei consists of the following terms:

\[
H = H_{\text{zeeman}} + H_{\text{mhf}} + H_Q.
\]  

(2.11)

In YBCO, due to symmetry, the permutation of the EFG principal axes \( XYZ \) coincides with the crystalline axes \( abc \). We can use the same set of axes \( XYZ \) to diagonalize both the magnetic tensor \( K \) and EFG tensor \( V_{\alpha\beta} \). The energy level splitting of Cu in an applied magnetic field can be obtained by diagonalizing the Hamiltonian matrix with values of each component of the tensor. By the following definitions:

<table>
<thead>
<tr>
<th>( \gamma_n (\text{MHz/T}) )</th>
<th>( Q (10^{-24}\text{cm}^2) )</th>
<th>abundance(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{63}\text{Cu})</td>
<td>11.285</td>
<td>-0.16</td>
</tr>
<tr>
<td>(^{65}\text{Cu})</td>
<td>12.089</td>
<td>-0.15</td>
</tr>
</tbody>
</table>

TABLE 2.1. Gyromagnetic ratio \( \gamma_n \), quadrupole moment \( Q \), and the natural abundance of two Cu isotopes.
\[
\nu_0 = \gamma_n H_0, \quad \nu_{Qzz} = \frac{eQV_{ZZ}}{2\hbar}
\]
(2.12)

\[
\zeta = \frac{\nu_0}{\nu_{Qzz}}
\]

\[
A = \zeta (1 + K_{ZZ}) \cos \theta
\]

\[
B_1 = \zeta [(1 + K_{XX}) \sin \theta \cos \phi - i(1 + K_{YY}) \sin \theta \sin \phi]
\]

\[
B_2 = \zeta [(1 + K_{XX}) \sin \theta \cos \phi + i(1 + K_{YY}) \sin \theta \sin \phi]
\]

\[
C = \frac{\eta}{\sqrt{3}}
\]

the matrix (with the indices given by the magnetic quantum numbers \(-\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}\)) is [37]

\[
H = \hbar \nu_{Qzz}
\]

\[
\begin{pmatrix}
1 - \frac{3}{2}A & \frac{\sqrt{3}}{2}B_1 & C & 0 \\
\frac{\sqrt{3}}{2}B_2 & -1 - \frac{1}{2}A & B_1 & C \\
C & B_2 & -1 + \frac{1}{2}A & \frac{\sqrt{3}}{2}B_1 \\
0 & C & \frac{\sqrt{3}}{2}B_2 & 1 + \frac{3}{2}A
\end{pmatrix}
\]
(2.13)

where \(\theta\) and \(\phi\) are the polar and azimuth angles, respectively, of \(\vec{H}\) in the axes XYZ.

In a NQR experiment (without the external magnetic field) the terms \(B_1\), \(B_2\), and \(A\) are zero. The remaining terms (Quadrupole term) in matrix (2.13) give two doubly degenerate \(\pm \frac{1}{2}\) and \(\pm \frac{3}{2}\) energy levels. The NQR resonance frequency is the difference between those two levels. The value is

\[
^{63,65}\nu_Q = \frac{^{63,65}QeV_{ZZ}}{2\hbar} \sqrt{1 + \frac{1}{3}\eta^2}.
\]
(2.14)

The resonance frequency of the isotope \(^{63}\text{Cu}\) is higher than that of isotope \(^{65}\text{Cu}\) by about 7% according to the ratio of their quadrupole moment. The NQR parameters for YBCO123 and YBCO124 at 300 K list in Table 2.2 from Ref. [37], [38] with error less than 5%.

In the presence of a large magnetic field the quadrupole interaction shifts the Cu NMR resonance lines into central lines arising from the central transition, \((\pm \frac{1}{2}, -\frac{1}{2})\), and two satellite lines from the \((\pm \frac{1}{2}, \mp \frac{3}{2})\) transitions. The components
TABLE 2.2. Cu NQR parameters in YBCO123 and YBCO124 at 300 K.

<table>
<thead>
<tr>
<th></th>
<th>YBa$_2$Cu$_3$O$_7$</th>
<th>YBa$_2$Cu$_4$O$_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu_Q$ (MHz)</td>
<td>22.16</td>
<td>20.022</td>
</tr>
<tr>
<td>$\eta$</td>
<td>0.984</td>
<td>0.951</td>
</tr>
<tr>
<td>$^{63}$Cu(1) $\Delta \nu_Q$ (KHz)</td>
<td>90</td>
<td>66</td>
</tr>
<tr>
<td>$\nu_Q$ (MHz)</td>
<td>31.19</td>
<td>29.71</td>
</tr>
<tr>
<td>$^{63}$Cu(2) $\eta$</td>
<td>0.012</td>
<td>0.015</td>
</tr>
<tr>
<td>$\Delta \nu_Q$ (KHz)</td>
<td>200</td>
<td>170</td>
</tr>
</tbody>
</table>

of the tensor $K$ and $V_{\alpha\beta}$ can be determined by comparing the resonance lines with the magnetic field along different crystalline axes and the eigenvalues of equation (2.13) with an appropriately chosen parameter $K$ and $V_{\alpha\beta}$. Figure 2.2 shows the energy level diagram of the first and second order splitting by nuclear quadrupole interaction when the magnetic field is parallel to the EFG principal axis.

2.4.1. Electric Field Gradient

The EFG tensor depends on the electron charge distribution around the nucleus site. It is an important static property of a solid, and not only reflects structural aspects of the compound but also provides information about ionicity and bonding. Accurate values of the EFG tensor components are obtained from NMR or Zeeman-perturbed NQR by rotating a single crystal in the magnetic field. Since sufficiently large crystals are not always available and present problems of skin depth and tuning the sample coil for conducting samples, measurements of a oriented powder are used in cuprate superconductors. Because of the anisotropic magnetic susceptibility property of the high $T_c$ cuprate, partially aligned samples ( where the crystallographic
FIGURE 2.2. Zeeman energy level diagram showing first and second order splitting by nuclear quadrupole interaction when the magnetic field lies along the EFG's principal axis. To include magnetic shift $v_0$ is replaced by $v_0(1 + K_{zz})$.

$\sigma$-axes of all the crystallites are parallel to each other can be obtained by mixing the powder with a slow curing epoxy, then letting the mixture harden in magnetic field.

In a semiempirical assumption, the tensor can be written as the sum of two terms, a lattice and a valence contribution:

$$V_{\alpha\beta} = V_{\alpha\beta}^{\text{lat}} + V_{\alpha\beta}^{\text{val}}.$$  \hspace{1cm} (2.15)

The first term arises from all charges of other ions or electrons outside the ion under consideration. Using the point-charge model it is written \cite{39}

$$V_{\alpha\beta} = (1 - \gamma_{\infty}) \sum_k q_k \left( \frac{3x_i^k x_j^k - \delta_{ij} |\vec{x}|^2}{|\vec{x}|^5} \right),$$  \hspace{1cm} (2.16)

where $\gamma_{\infty}$ is the Sternheimer antishielding factor, $q_k$ and $x_k$ are the charge and the position of $k$th charge, respectively. The antishielding factor is a correction value to include the distortion effect of the closed shell electrons caused by the external charges.
The second term in equation (2.15) arises from the non-filled shells of the subject ion. In the case of the $\text{Cu}^{+2}$ ion with a hole in the 3-d orbitals, the valence contribution can be written as [40]:

$$V_{zz}^{val} = A < r^{-3} >_{3d} \left[ n_{3d(z^2-r^2)} - n_{3d(x^2-y^2)} - n_{3d(xy)} - \frac{1}{2} n_{3d(xz)} - \frac{1}{2} n_{3d(yz)} \right], \quad (2.17)$$

where $A$ is a constant, $< r^{-3} >_{3d}$ is the expectation value of $r^{-3}$ for the 3-d wave function, and $n_{3d(x,y,z)}$ are the number of holes in different 3d orbitals.

At the Cu(2) site the lattice and valence contribution of EFG, in equation (2.15), have opposite signs, because the positively charged $n_{3d(x^2-y^2)}$ holes predominantly reside on the $3d_{x^2-y^2}$ orbitals extending towards the negatively charged neighbor oxygen ions [41].

### 2.4.2. Knight Shift

The Knight shift is the shift of the resonance frequency caused by the polarized conduction electron spins together with the nuclear magnetic hyperfine interaction. It is defined as the displacement of the resonance frequency in the metal with respect to the frequency of a diamagnetic reference compound. A paramagnetic metal is characterized by the generalized electron spin susceptibility $\chi_s(q, \omega) = \chi'_s(q, \omega) + i\chi''_s(q, \omega)$, which is a response function of time- and space-varying magnetic fields with corresponding variable frequency and wave vector, respectively. Its real part $\chi'_s(q, \omega)$ and imaginary part $\chi''_s(q, \omega)$ are related by the well known Kramers-Kronig relation [42].

The NMR magnetic shift tensor $K$ of the Cu nuclei has spin and orbital components $K_{aa} = K_{aa}^L + K_{aa}^S$ in the $x,y,z$ reference frame, which can be expressed by the respective magnetic hyperfine interaction tensor and the static, uniform limit of the real part of the generalized electronic spin and orbital susceptibilities:

$$K_{aa}^S = \frac{1}{g\mu_B} \sum_j (A_j)_{aa} \chi_{aa}^S(0,0), \quad (2.18)$$
where $\alpha$ is the direction along the applied magnetic field, $g$ is the Landé factor, $\chi_{aa}^L(0,0)$ is the Van Vleck orbital paramagnetism, and $A_{jaa}$ ($B_{aa}$) is the magnetic hyperfine coupling constant between the nuclei and the electron spin (orbital moment). Generally, the orbital shift is temperature independent because it results from bonding electrons. The Knight shift may be temperature dependent because of the change of the electron states near the fermi surface, i.e. electron pairing in the superconducting state.

For noninteracting electrons, real part of the uniform, static susceptibility is just the Pauli susceptibility:

$$\chi_{aa}^{S\prime}(0,0) = \frac{1}{2}(\gamma_e \hbar)^2N(E_F),$$

where $N(E_F)$ is the density of states at the Fermi energy. The Pauli susceptibility is constant as the temperature is much less than the Fermi temperature, which is about $10^4$ K for an ordinary metal.

For a classical superconductor with s-wave singlet pairing picture in BCS theory, the Knight shift is approximately constant in the normal state, declines exponentially in the superconducting state and approaches zero with zero slope.

In the HTSC compound, the orbital shift ($K_{aa}^L$) is temperature independent, whereas the Knight shift ($K_{aa}^S$) is temperature dependent and expected to vanish as $T = 0$ K due to the singlet spin pairing. Thus the residual magnetic shift near the 0 K is assigned to be the orbital shift in the HTSC compound. Figure 2.3 shows the $c$-axis ($\alpha = c$) and in-plane ($\alpha = ab$) NMR shifts versus temperature for planar Cu(2) sites in both YBCO123 [43] and YBCO124 [37]. The results for $K_{ab}$ in YBCO123 illustrate the loss of the spin-paramagnetic shift for $T<T_c$ due to the spin pairing. In YBCO124, $K_{ab}$ declines smoothly at a value less than the YBCO123 as $T$ decreases, which is similar to the underdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6.64}$ (60 K)
FIGURE 2.3. Temperature dependence of $^{63}$Cu(2) magnetic shift for YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_4$O$_8$ with magnetic field parallel ($K_c$) and perpendicular ($K_{ab}$) to the c-axis. A replot of the data from [37],[43].

phase. The orbital components of $K_{ab}$ (T → 0) are 0.28% and 0.26% for YBCO123 and YBCO124, respectively. The change of $K_c$ below $T_c$ is anomalously small for YBCO. The $K_{ab}$ results indicate that the superconductivity in YBCO involves carrier spin pairing in the CuO$_2$ plane.

2.4.3. Spin-Lattice Relaxation Time $T_1$

The spin-lattice relaxation time "$T_1$" is the characteristic time for a disturbed nuclei spin system to relax back to thermal equilibrium with the surrounding environment, i.e. lattice. This process contains energy transfer from the nuclei system to the lattice. The longer the $T_1$ the weaker the coupling between the nuclear spins and lattice.

In metals the dominant mechanism of spin relaxation is the nuclear-electron magnetic hyperfine interaction, equation (2.7). Moriya showed that $1/T_1 T$ probes
the q-averaged imaginary part of the dynamical electron spin susceptibility \( \chi''(q, \omega_n) \) \[44\],

\[
\left( \frac{1}{T_1 T} \right)_\alpha = \frac{k_B}{\gamma_e^2 \hbar^4} \sum_q F'_\alpha(q) \left[ \frac{\chi''(q, \omega_n)}{\omega_n} \right]_{\omega_n \to 0},
\]

\[
F'_\alpha(q) = \left| \sum_k A^k_{\perp \alpha} \exp(i \mathbf{q} \cdot \mathbf{r}) \right|^2,
\]

where \( \omega_n \) and \( \gamma_e (\gamma_n) \) are the resonance frequency and nuclear (electronic) gyromagnetic ratios, respectively. The \( \alpha \) denotes the axis of quantization, i.e., the magnetic field direction for NMR or electric field gradient tensor principal axis for NQR, and the \( \alpha' \) is the direction perpendicular to \( \alpha \). The weight factor \( F(q) \) is the transverse part of the Fourier transform of the nuclear-spin interactions' strength \( (A^k_{\perp \alpha}) \).

Since the nuclear resonance frequency is much less than the electron fluctuation frequency, the temperature dependence of the spin-lattice relaxation rate can only give information about low frequency spin excitations.

From a quantum chemical analysis of the Cu(2) anisotropic Knight shift and spin-lattice relaxation time in YBCO123, Mila and Rice \[45\] proposed the Cu (2) hyperfine Hamiltonian under the assumption of one electron spin per CuO_2 unit cell as

\[
H_i = \sum_\alpha I_{i \alpha} A_{\alpha \alpha} S_{i \alpha} + I_i B \cdot \sum_j S_j,
\]

where \( A \) is the anisotropic on-site term coupling to local Cu^{+2} electronic spin, \( B \) is the isotropic transfer term from the second neighbor Cu(2) spins. For Cu(2) the relaxation rate can be expressed as

\[
\left( \frac{1}{T_1 T} \right)_{\text{Cu(2)}} = \frac{k_B}{\gamma_e^2 \hbar^4} \sum_q \left[ (A_x + 2B f(q))^2 + (A_y + 2B f(q))^2 \right] \frac{\chi''(q, \omega_n)}{\omega_n} \bigg|_{\omega_n \to 0},
\]

where \( A_{x,y} \) are the on-site hyperfine components. Because the isotropic hyperfine field \( B \) couples the Cu nuclei to spin fluctuations on the neighboring Cu(2) sites,
it is necessary to include the geometric form factor \( f(q) \). Since the sum over \( q \) is taken over all \( q \) values, the spin correlations of quite short wavelength (comparable with interatomic dimensions) can make important contributions to spin-lattice relaxation. Generally, the relaxation rate depends on two factors [33]. One factor is the effective number of spins interacting with the nucleus, which is proportional to the \( \chi'(0,0) \). The second factor is the spin fluctuation correlation time \( \tau_c \). Thus the rate can be expressed as

\[
\left( \frac{1}{T_1T} \right)_{\text{Cu(2)}} = \frac{k_B}{\gamma_n^2 \hbar^2} \cdot \omega_{hf}^2 \cdot \chi'(0,0) \cdot \tau_c, \tag{2.23}
\]

where \( \omega_{hf} \) is the strength of the hyperfine interaction.

In an ordinary metal of weakly interacting electrons, both \( \chi'(0,0) \) and \( \tau_c \) are independent of temperature. The correlation time relates to the density states at the Fermi level, \( \tau_c = \hbar N(E_F) \), which leads to the Korringa relation between the rate and the Knight shift.

\[
(T_1T K^2)^{-1} = \frac{4\pi k_B \gamma_n^2}{\gamma_e^2 \hbar} = S, \tag{2.24}
\]

where \( S \) equals \( 2.67 \times 10^5 \) (K sec\(^{-1}\)) for \(^{63}\)Cu nuclei. The \( T_1T \) and Knight shift for Cu metal are 1.27 sec K and 0.239 \%, respectively.

For YBCO\(_{123}\) in the normal state, the relaxation rate of Cu(2) shows strong antiferromagnetic spin correlation, which \( 1/T_1T \) increases with decreasing temperature down to the \( T_c \), see Figure 2.4, a replot from [46], [37]. Nuclear relaxation rates for the \(^{89}\)Y and planar \(^{17}\)O(2,3) nuclei show an Korringa temperature dependence (\( T_1T = \text{constant} \)). Millis, Monien, and Pines proposed a phenomenological model (in short MMP) [47] to accommodate the extreme different temperature dependence of relaxation rate of Cu and O in the CuO\(_2\) plane with the application of the Mila-Rice
around the $q(0, 0)$, and an antiferromagnetic fluctuation part peaked at $q_{AF}(\pi, \pi)$.

The imaginary part of the dynamical spin susceptibility can be expressed

$$\chi''(q, \omega_n) \propto \frac{\pi \hbar \chi'(0, 0)}{\Gamma} [1 + g(q)], \quad (2.25)$$

where $\chi'(0, 0)$ is the susceptibility of the quasiparticles, $\Gamma$ is the characteristic spin fluctuation energy for the quasiparticles, and $g(q)$ is enhanced at wave vector $q_{AF}(\pi, \pi)$ by a peak whose width varies inversely as the square of the antiferromagnetic correlation length $\xi(T)$. The temperature dependence and enhancement of $T_1 T$ for the Cu(2) can be solely simulated by the variation of $\xi(T)$. The nearly constant $T_1 T$ of O(2,3) and Y can be explained with the same dynamic susceptibility using the quadratically vanishing of their hyperfine form factor $F_{\alpha}(q)$ in equation (2.20) as $q$ approaches the $q_{AF}(\pi, \pi)$ point. The model, called by the inventor a "nearly antiferromagnetic Fermi liquid picture", can explain most anomalous behavior of the low frequency spin excitation spectrum measured either by NMR or NQR with different nuclei $^{89}\text{Y}$, $^{17}\text{O}$, and $^{63}\text{Cu}(2)$. However, the inelastic neutron scattering
experiment which also can probe the $\chi''(\omega)$ showed that an incommensurate anti-ferromagnetic peak exists with no temperature dependence of the width [48]. This raises a serious question about the assumption of a temperature dependent spin-spin correlation length $\xi(T)$. Nevertheless, the model along with its variations is used to claim that superconductivity in the HTSC originates in spin-fluctuation-induced interactions of the quasiparticles: $T_c$ increases as the hole doping increases.

2.4.4. Spin-Spin Relaxation Time $T_2$

Spin-spin relaxation, also called transverse relaxation, is a process in which the transverse magnetization $M_{X,Y}$ decays due to time dependent local fields. The spin-spin relaxation time, $T_2$, is a measure of how fast the spins lose their phase memory due to the fluctuating local field. The relaxation arises from nuclear direct spin-spin coupling, nuclear indirect spin coupling, and spin-lattice relaxation. These couplings contribute a homogenous broadening to the linewidth. The different spin-spin coupling mechanisms result in a complex lineshape. However, the transverse magnetization decay curve can often be described as the convolution of a Gaussian line and Lorentzian line,

$$E(2\tau) = E_0 \exp\left\{-\frac{1}{2}(\frac{2\tau}{T_{2G}})^2\right\} \exp\{-2\tau\left(\frac{1}{T_{2L}} + \frac{1}{T_{2R}}\right)\},$$

(2.26)

where $E_0$ is the echo amplitude at $\tau = 0$, $T_{2G}$ and $T_{2L}$ are the characteristic times for Gaussian-like and Lorentzian-like shapes, respectively, and $T_{2R}$ is the time constant describing spin-lattice relaxation. The full width at half maximum (FWHM) for the Gaussian and Lorentzian lines are $\frac{3.34}{2\pi T_{2G}}$ and $\frac{1}{\pi T_{2L}}$, respectively.

Theoretically, the direct spin-spin interaction results in a Gaussian lineshape. The linewidth can be calculated by the "second moment" method. It was estimated that the width for Cu(2) sites in YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_4$O$_8$ are 0.97 and 0.94 kHz, respectively [49].
The indirect spin-spin coupling is a higher order nuclear interaction. It was described as the mutual spin flip between two nuclei mediated by the surrounding electrons, which leaves the total nuclear spin moments and electron states unchanged. This coupling provides an efficient way for a nuclear spin system to approach internal equilibrium. The nuclear spin-spin coupling (direct and indirect) leads to a wide variety of time dependences of echo decay curve. In the case of pure YBCO, it was found that the Cu(2) spin echo decay curve has a Gaussian and an exponential time dependence. The Gaussian term is attributed mainly to the indirect spin-spin coupling mechanism ($T_{2G}$ measured is less than the theoretical calculated $T_{2G}$ from the direct spin-spin coupling mechanism). The exponential term arises from the spin-lattice relaxation process.

Owing to the spin-lattice relaxation process, the spin has a finite lifetime in a Zeeman energy level, which broadens the resonance line by an energy of the order of $\frac{\hbar}{T_1}$. It is also called lifetime broadening. Because of the anisotropic $T_1$ of the Cu(2) nuclei in YBCO, the $T_2$ is also anisotropic. By the Redfield theory [39], the $T_1$ process contributes a decay with a rate constant $\frac{1}{T_{2R}}$,

$$\frac{1}{T_{2R}} = \frac{1}{T_{1ab}} + \frac{2}{T_{1c}},$$

where $T_{1ab}$ and $T_{1c}$ are the $T_1$ values measured in NMR with the magnetic field perpendicular and parallel to the crystalline $\tilde{c}$-axis, respectively.

### 2.5. Spin Pseudogap in Underdoped YBCO

The spin pseudogap behavior was first observed by NMR in the underdoped $YBa_2Cu_3O_{6.7}$. The characteristic of this behavior is the Cu(2) ab plane Knight shift $K_{ab}$ and its temperature dependence. At 300 K the shift is lower than the overdoped YBCO123, which represents a lower hole concentration, and starts a smooth decrease to zero as the temperature approaches 0 K. There is a large reduction of $K_{ab}$ in the normal state as the $T$ is reduced to $T_c$. The antiferromagnetic enhancement of the
Cu (2) $1/T_1 T$ is suppressed and shows a broad peak at a temperature $T^*$ which is higher than the superconducting temperature $T_c = 60$ K. The same characteristic behavior has been observed in the YBCO124, Figure 2.3, 2.4. Thus the YBCO124 is classified as an underdoped HTSC.

The decline of the Knight shift indicates that a gap or pseudogap opens in the spin-density of states at temperatures well above the temperature where the superconducting gap opens in a conventional superconductor. The behavior of $1/T_1 T$ suggests that the spin pseudogap effect competes with the antiferromagnetic fluctuation. Above the $T^*$, where the maximum of $1/T_1 T$ occurs, the antiferromagnetic fluctuations dominate. Below the $T^*$, the spin-gap effect predominates thus $1/T_1 T$ is decreasing in the underdoped structure. Experiments of the YBa$_2$Cu$_3$O$_{7-\delta}$ and Ca doped the YBCO124 show that $T^*$ decreases with increasing $T_c$ which is interpreted as a cause of adding the hole carrier in the system [50]. As more carriers are added, $T^*$ coincides with $T_c$ at the optimal doping and the full doping.

The spin pseudogap is also observed in low energy (40 m eV) inelastic neutron scattering experiments. Tranquada et al. [51] show that the dynamical susceptibility $\chi''(\omega)$ at the point $q_{AF}(\pi, \pi)$ in the normal state measured with the underdoped single crystal YBa$_2$Cu$_3$O$_{6.7}$ can be described by the phenomenological expression

$$\chi''(\omega) = A \left[ \tanh \left( \frac{\hbar (\omega - \omega_g)}{2k_B T} \right) + \tanh \left( \frac{\hbar (\omega + \omega_g)}{2k_B T} \right) \right], \quad (2.28)$$

where $A$ is a constant and $\omega_g$ is the experimental gap frequency. An analytical expression of the NMR relaxation rate and Knight shift data can be deduced by the equation (2.28). To apply the above expression to NMR data where $\hbar \omega \ll k_B T$ and $\omega \to 0$, one obtains

$$\chi''(\omega \approx 0) = BT^{-1} \left[ 1 - \tanh^2 \left( \frac{\Delta_0}{2T} \right) \right], \quad (2.29)$$
where gap energy $\Delta_\pi = \frac{\hbar \omega}{k_B}$ was introduced with the index $\pi$, denoting the zone corner at $q_{AF}(\pi, \pi)$. The relaxation can be expressed as

$$\frac{1}{T_1T} = CT^{-\alpha} \left[ 1 - \tanh^2\left( \frac{\Delta_\pi}{2T} \right) \right],$$

(2.30)

where $C$ is the constant and $\alpha$ is factor introduced to give a flexible fit to the temperature dependence of the rate. The Knight shift can be fit with the following expression:

$$\chi(0) = \chi_o \left[ 1 - \tanh^2\left( \frac{\Delta_o}{2T} \right) \right].$$

(2.31)

The Cu(2) relaxation rates in the normal state of YBCO124 are well described by equation (2.30) with parameters $\Delta_\pi = 280$ K and $\alpha = 1.5$. Fitting the Knight shift data in the same compound by the formula , one obtains a small value of $\Delta_o = 235$ K. Winzek and Mehring [52] applied the same equations for the spin-gap effect of the Tl relaxation and Knight shift in Tl$_2$Ba$_2$CaCu$_2$O$_{8-\delta}$ studied for various values of $\delta$, while the gap energy seems to decrease with increasing $T_c$ which itself increases with increasing hole concentration.

There are conflicting opinions about the relation of the spin pseudogap to superconductivity. Randeira et al. [53] regard the spin pseudogap behavior as a precursor to superconductivity. Monthoux P. and D. Pines [54] think that the pseudogap is a subtle modification of the quasiparticle behavior due to the presence of the holes and strong antiferromagnetic correlation. As the hole concentration increases, that modification becomes less important. The superconductivity, on the other hand, originates in spin-fluctuation exchanges between quasiparticles. Both the strength of the fluctuation spectrum and $T_c$ increase with increased doping. Thus the formation of a spin pseudogap in the normal state acts to reduce superconductivity.
3. EXPERIMENTAL TECHNIQUES

3.1. Apparatus

3.1.1. Pulsed Spectrometer

Two pulsed NMR spectrometers were used to perform NQR and NMR in this study. The basic scheme is the same for both spectrometers. The block diagram of the spectrometer is shown in Figure 3.1. The frequency synthesizer produces a sinusoidal signal at frequency $\omega$. This signal is divided into a reference signal and a signal that is fed into the pulse sequence generator. The function generator sends a Transistor-Transistor-Logic (TTL) signal with rate $f$ to the pulse generator. Each TTL signal triggers the generator to produce the proper sequence of radio frequency pulses. The rate $f$ determines how fast the generator repeats the sequence. The time $(1/f)$ is called the pulse delay $(pd)$. The sample coil will provide a time dependent magnetic field, $H_1 \cos \omega t$, during the pulse and pick up the electromagnetic-force $(\text{emf})$ induced by the precession of magnetization after the pulse. The matching network couples the coil with the transmitter and receiver. A tank circuit is tuned at frequency $\omega$ with the impedance matched at both ends to the transmitter and receiver. The quarter wavelength cable and both the crossed diodes act like a duplexer. When the pulse is on, both crossed diodes conduct, making the quarter wavelength cable a short to ground, so almost no power passes through to the preamplifier. In addition, the preamp has a blanking device which will turn the preamp off during the pulse to protect it. When the transmitter pulse is off, both crossed diodes have a high resistance. The transmitter is isolated from the sample coil and the receiver, so the induced emf signal can only feed to the preamplifier.
FIGURE 3.1. Block diagram of pulsed NMR spectrometer.

The quadrature detection is executed using two receivers with reference signals differing by a phase of 90°. Thus the real and imaginary signals are acquired. The absorption mode and dispersion mode signal can be obtained by adjusting the
phase shifter between the synthesizer and pulse generator. The receiver contains a mixer to mix the emf signal and reference signal, low pass filter to preserve the low frequency part of the beat mixed signal, and an audio amplifier to enhance it. The resultant signal is then digitized and stored. Several thousand acquisitions is typical for solid state NMR measurements. A computer interfaced with the hardware serves as controller.

3.1.1. ATT Spectrometer

The ATT spectrometer was used for the Cu(2) NQR experiments. It is a combination of homemade circuits and commercial components designed and built by Dr. William W. Warren, Jr while at AT&T. The spectrometer is equipped with a 2 Tesla iron-core electromagnet which can sweep the magnetic field. The transmitter has an operational frequency range of 1 MHz – 35 MHz with pulse power in the range of 2 – 3 kW. The pulse sequence was controlled by manually changing the logic and timing components. Quadrature detection was performed by feeding two reference signals with a 90° phase difference to two receivers. Both the absorption and dispersion mode signals can be recorded at the same time. There are two signal-averaging schemes: for spin-lattice relaxation measurements a boxcar integrator and waveform analyzer are used. For the other measurements a transient digitizer and memory averager are used. Using the boxcar, we can get the magnetization recovery curve sweep by sweep with varying T over 256 values. The electronic drift problem in an ordinary T₁ measurement can be greatly reduced.

The digitizer has maximum 30 MHz sampling rate, so the minimum dwell time is 33 nsec. A IBM486 clone with a GPIB controller card interfaces with the waveform analyzer and memory averager. The computer configures these instruments for data acquisition, initiates the measurement process and transfers data to
the hard disk. The non-linear-curve-fitting for the relaxation measurement is carried out by the software program, MicroCal Software, Inc.

3.1.1.2. CMX Spectrometer

The CMX360 is a commercial spectrometer made by Chemagnetics, Inc. It is equipped with a 8 Tesla superconducting magnet built by American Magnetics, Inc. This spectrometer was used for Cu NMR. It was also used to do the Cu(1) NQR study in YBCO124 without the magnet.

The CMX spectrometer has two independent radio-frequency channels each with a frequency range 1 - 500 MHz. Its pulse generator provides sophisticated pulse sequences for both channels, so the spectrometer can perform double resonance and cross polarization. The signal acquisition scheme has a background phase cycling capability to correct the instrumental artifacts resulting from transmitter ringing, DC offset, receiver gain differences, etc., by adding or subtracting the signal in data buffers. The ADC digitizer has a fast sampling rate 2 MHz. The system is software controlled, with almost all of the experiment parameters adjusted by a computer program.

The magnet has a cylindrical 3 inch diameter room temperature clear bore, with the field along its axis. It has a maximum 8 Tesla central field in persistent current mode and about 1 ppm inhomogeneity over 1 cm cubic volume. The central field decay rate is about 0.08 ppm per day as measured by $^{63}$Cu NMR (90.211 MHz) in CuCl diamagnetic powder over a forty day period. Since some NMR experiments are performed over months during which the magnetic field may have been changed, the $^{63}$Cu NMR in CuCl was always measured to calibrate the field.

3.1.2. Probe and Matching Circuit
Two probes have been built in this work: one is the NQR probe and the other is the NMR probe. The NQR probe is designed for a working frequency range of 15–32 MHz and a temperature range of 77–300 K. The NMR probe is designed for 80–130 MHz and 100–500 K.

The NQR probe is a unit made up of heater and the coil. The resonant circuit used for the probe is shown in Figure 3.2. The circuit is tuned to resonance mainly by the variable capacitor ($C_t$) which is in series with the coil. The capacitor ($C_m$) in parallel with the coil adjusts the impedance of the circuit to match the impedance of both the transmitter and the preamplifier. In order to perform the low temperature measurement, the coil is placed in a dewar and connected to the capacitors with an extension cable. The heating element is constructed with 8 feet (2 ohms/feet) of nichrome wire, slid into many ceramic tubes to form a zigzag configuration in order to minimize its magnetic field, and then wrapped around a 3/4” copper tube. This heater is placed on the top of the coil. Also a K-type (Chromel-Alumel) thermocouple is placed at the end of the heater to measure the temperature.

The NMR probe is constructed with the coil and the matching circuit as an integrated unit. Figure 3.3 shows the resonant circuit for the NMR probe. There are two tuning capacitors, the one ($C_{t1}$: 3–0.3 pf) in series with the coil and the other ($C_{t2}$: 10–0.5 pf) in parallel with the coil. The matching capacitor ($C_m$) has capacitance range 10–0.5 pf. This setup can tune a 10 turn coil with an inner diameter of 0.3 inch in a frequency range 80–130 MHz. In addition the coil is made of silver wire rather than copper in order to avoid spurious copper metal signals. The probe is made of 2.85” aluminium tubing with the coil oriented with its axis perpendicular to that of the tubing. The matching circuit is placed just beneath the coil, in order to avoid additional capacitance introduced by long leads.
The timing of the NMR probe is performed by using the directional decoupler which can show the reflected power from the probe on the scope. The tuning is completed by minimizing the reflected power by adjusting the capacitors. The trick is, first adjust the $C_{t1}$ till there is a change of the amplitude of the reflected voltage on the scope and then adjust the $C_{t2}$ and $C_m$ simultaneously.

3.1.3. Temperature Control

The temperature of the sample is controlled by sending electrically heated air over the sealed sample cell. As shown in Figure 3.4, the temperature controller senses the temperature near the sample by a sensor and then regulates the current to the heater which heats the air.

A cool air flow system is used for low temperature experiments, see Figure 3.5. An FTS AD-80 air dryer and XR11851 Air jet cooler are used to bring the
temperature down to 223 K. The air is cooled further to 95 K by sending the air through a heat exchanger made by copper tubing placed in liquid nitrogen.

For NQR study at 77 K, the NQR probe is placed in a dewar filled with liquid nitrogen. For higher temperature the cool air flow system was used without the liquid nitrogen in the dewar. A K-type thermocouple is used as a sensor with a reference temperature at 77 K, see Figure 3.4.

The NMR probe uses the variable temperature accessory provided by CMX and the cool air flow system described above to carry out experiments from 100 to 300 K. The temperature control unit is essentially the same as the one NQR probe used, except that the CMX system uses a resistance temperature device as the temperature sensor so there is no need for a reference temperature.

![FIGURE 3.3. Resonance circuit and physical construction of NMR probe.](image-url)
Cool AirTo Heater
in

Thermocouple: Chromel

Alomel Chromel

Liquid N₂

Reference Temperature (77 K)

Sample Coil

DC Power Supply

FIGURE 3.4. Block diagram of variable temperature control setup.

Air in, T = 300 K

Dryer

Air Jet Cooler

Liquid N₂

Dewar

FIGURE 3.5. Block diagram of cool air flow system, 95 to 300 K.
3.2. Sample Preparation

The samples studied for $YBa_2(Cu_{1-x}M_x)_3O_7$ are YBCO123:Zn ($x = 2.5\%$, (5\%)). For $YBa_2(Cu_{1-x}M_x)_4O_8$, they are YBCO124: Zn(0.9\%), (1.8\%), (3\%), Fe(0.9\%), (1.8\%), and Co(0.75\%), (1.5\%). All the samples were provided by Dr. Azmi Gencten and Prof. Ray Dupree at Warwick University, Physics department, United Kingdom. The preparation and characterization of these samples are described in Dr. A. Gencten’s Ph. D. thesis [19]. The Zn doped YBCO123 samples were synthesized by a conventional solid state method with stoichiometric amounts of ZnO, Ba$_2$Co$_3$, Y$_2$O$_3$, and CuO. The metallic doped YBCO124 samples were prepared at one atmosphere by a two step process first developed by Cava et al. [16] with sodium carbonate ($Na_2CO_3$) as a flux. No second phase material could be detected by X-ray diffraction (XRD) in these samples. The superconducting transition temperatures determined by A.C. susceptibility are shown in the Figure 1.3. Both Fe and Zn substitutions in YBCO124 cause a dramatic decrease in $T_c$ with a rate of about 20 K/at.\%. The decreases in $T_c$ are much faster than Zn substitution for YBCO123 (10 K/at.\%). Co dopant has less effect on $T_c$, $T_c = 74$ and 70 K for concentration $x = 0.9$ and 1.8\%, respectively. These values are consistent with results from other research groups [17], [23], except for the Co doped YBCO124. Kodama et al. [18] reported that the Co doped YBCO124 had the same temperature decrease rate as the Fe doped sample.

For the Cu NQR studies, in order to improve penetration of the radio frequency field into the sample and prevent changes of the sample characteristics in ambient environments, each sample was finely ground and sealed in glass ampoules. The same amount of doped YBCO124 (0.4 gram) with the largest grain diameter 43 $\mu$m (obtained by sifting through a No.325 mesh screen) was sealed under vacuum (about 50 mtorr). For Zn doped YBCO123, fine powder samples were sealed under one atmosphere of oxygen to prevent possible oxygen loss.
Cu NMR study of aligned YBCO powder samples will give important information about the anisotropic properties of the compound. To make a good $\bar{c}$-axis oriented metallic doped YBCO124, fine powder, low viscosity epoxy, and special mixing process was needed. The sample was finely ground before and after baking in an oven at 400 K for about 2 hours with flowing oxygen gas. A low viscosity epoxy (Duro master mend TM-81505, viscosity: resin 7000 osi, hardener 9000 osi), was used. The starting volume ratio for the epoxy and the powder was 7 : 3. The mixing procedure is as follows: first brush the the premixed epoxy on a flat disk, secondly sift the powder through the mesh till a layer of powder forms on the epoxy, then stir it. Repeat the above procedure until all of the powder is in the mixture. Thus the powder should be uniformly distributed in the epoxy. The resulting material is then loaded into a teflon sample container, inserted into the NMR coil, and cured in an 8 T field for 12 hours.

The $\bar{c}$-axis alignment was confirmed by the sharp features in Cu NMR spectrum. With this method alignment can be achieved for Co(0.75%), Fe(0.9%) and all the Zn doped YBCO124, but not for higher doping concentration of Fe and Co. Probably the large amount of magnetic impurity destroys the anisotropic magnet susceptibility. The one main drawback of the Duro epoxy is that the hardened epoxy will melt around 600 K.

3.3. Measurements

3.3.1. Spin-Echo

The Cu FID signal in YBCO only lasts for about 7 - 10 $\mu$s. In such a short time the preamplifier is still paralysed by the applied pulse. Therefore, the spin-echo method is used both in Cu NQR and NMR. The pulse sequence for a 90-180 echo, called chemical echo, is $(t_{90} - \tau - t_{180} - \text{echo} - t_{pd})$. The pulse width ($t_{pw}$) and the pulse separation time ($\tau$) vary for different spectrometers. Generally the time
between the two pulses can be chosen greater than the deadtime of the receiver and smaller than the spin-spin relaxation time, $T_2$. Since the echo signal decreases with increasing $\tau$ due to $T_2$ process, $\tau$ is chosen to be just greater than the deadtime to get the biggest symmetric echo. To avoid saturation, the $t_{pd}$ was usually chosen to be greater than $7T_1$.

### 3.3.1.1. ATT Spectrometer

The $t_{pw}$ of the $90^\circ$ and $180^\circ$ was adjusted separately to optimize the echo signal. The $t_{pw}$ is determined by the power transmitted to the coil, $H_1$. Because the ATT spectrometer has a high power amplifier, the optimal pulse width for Cu (2) nuclei was $t_{90} = 1.1 \mu\text{sec}$ and $t_{180} = 2.1 \mu\text{sec}$. The $\tau$ was chosen to be $25 \mu\text{sec}$. Since the echo signals are quite weak, a signal averaging of 64,000 echos is typically needed to get a good signal to noise ratio. With this much averaging, coherent noise such as the electronic ringing of the coil the intense rf pulse, can mask the signal. A two pulse-delay add-substraction sequence was used to eliminate these problems, illustrated in Figure 3.6. Two different $\tau$ values led to two echos. The modulus of both the echos was integrated separately to represented the echo intensity for different value of $\tau$. Since the real and imaginary mode signals were recorded by two independent receivers, the different gain of the receivers was corrected by a factor obtained from comparing the intensity ratios between those without the $90^\circ$ phase shifter.

### 3.3.1.2. CMX Spectrometer

The Cu(1) NQR spin echo was carried out with parameters: $t_{90} = 3 \mu\text{sec}$, $t_{180} = 5.5 \mu\text{sec}$, $\tau = 45 \mu\text{sec}$, $t_{pd} = 12 \text{msec}$, and acquisition = 33024 at 300 K in CMX spectrometer. For 77 K measurement, the $t_{pd}$ changed to 30 msec owing to the increase of $T_1$. Since the CMX has less pulse power, a larger $t_{pw}$ was needed to
The transient signal results from the coherent noise which has the same phase as the pulse. Using this toggle sequence and add-subtract method, one can remove this coherent noise. The FID after the pulse has been omitted in this plot.

FIGURE 3.6. Pulse sequence of pulse-delay add-subtraction method.

This pulse sequence can remove the coherent noise resulted from both $90^\circ$ and $180^\circ$ pulses. The FID after the pulse has been omitted in this plot.

FIGURE 3.7. Pulse sequence of four-phase add-subtraction method.
optimize the echo. The larger $t_{pu}$ increases the deadtime of the system. Thus a long $\tau$ is needed to form a echo. Because the Cu(1) nuclei in YBCO124 has relatively long $T_2$, about 250 $\mu$sec, we can still get good signal-to-noise ratio with a longer $\tau$.

For Cu NMR spectra study, the $t_{90}$ used was between 1.5 - 3 $\mu$sec depending on the probe nucleus studied, i.e. $^{63}$Cu and $^{65}$Cu. The $\tau$ used was 20 $\mu$sec and the $t_{pd}$ was 20 msec.

Coherent noise was eliminated from the echo signal with phase cycling between the 90° and 180° pulse for each echo acquisition. The phase cycling is a commonly-used four-phase add-subtraction method [55], see Figure 3.7. The two receivers' gain difference was compensated by a four-step phase cycling [56]. To sum up, the total background phase cycling requires 16 steps.

3.3.2. Spectra

The resonance spectrum can be obtained by Fourier transform of the second half of the spin echo, provided that the width of the pulse's power spectrum ($\sim \frac{2.8}{\pi t_{pu}}$) is larger than that of the line shape. In high-$T_c$ material the true line is often too broad to be seen by Fourier transform of the FID. Plotting the integrated values of the spin echo point by point against frequency is used to represent the broad line.

Both the Cu NQR spectra and NMR spectra were constructed by plotting the integrated values of the magnitude of the spin echo using the modulus of the absorption mode and dispersion mode signals to avoid cumbersome adjustment of the phase of the echo at each individual frequency. The frequency stepsize of the measurement was as small as possible (about 50 kHz) to represent the sharpest feature of the spectrum.
3.3.3. Spin-Spin Relaxation Time $T_2$

Spin-spin relaxation was measured by evaluating the spin echo intensity at various $\tau$ values. The integrated echo is plotted against the time $2\tau$. The Cu(2) decay curve could be fitted by the equation

$$E(2\tau) = E_0 \exp\left(-\frac{1}{2} \left(\frac{2\tau}{T_{2G}}\right)^2\right) \exp\left(-\frac{2\tau}{T_{2R}}\right)$$

(3.1)

using the $T_{2R}$ which is calculated by the equation (2.27) and the $E_0$ and $T_{2G}$ as the free parameters. The Cu(1) echo decay curve in YBCO124 exhibited a long decay time with a sinusoidal modulation on the echo envelope. However, the curve can be fitted using two Lorentzian functions described as

$$E(2\tau) = E_0 \exp\left(-\frac{2\tau}{T_{2L}}\right) \exp\left(-\frac{2\tau}{T_{2R}}\right).$$

(3.2)

In order to compare the impurity effect on the spectra, the ratio of $\frac{E(0)}{E(2\tau)}$ is used to correct the echo intensity, which was measured with fixed value $\tau$, for samples with different $T_2$.

3.3.4. Spin-Lattice Relaxation Time $T_1$

The spin-lattice relaxation was measured by using an inversion recovery method. A $180^\circ$ pulse inverts the equilibrium spin magnetization $M(\infty)$ to the $-z$ axis. After a time $t$, the magnetization $M(t)$ was measured using the standard NMR method, either by a $90^\circ$ pulse or a spin-echo. The dependence $M(t)$ on time may often be described by an exponential time constant [57], $T_1$:

$$M(t) = M(\infty)(1 - 2A \exp\left\{-\frac{t}{T_1}\right\}),$$

(3.3)

where $A$ is an adjustable factor which compensates for incomplete inversion of the $180^\circ$ pulse.

In the NMR experiment the quadrupole interaction splits the degenerate Zeeman levels. The relaxation has a multiple-exponential time dependence for each transition level. For Cu ($I = \frac{3}{2}$) the central transition line has a function
\[ M(t) = M(\infty) \{ 1 - 2A[0.1 \exp(-\frac{t}{T_1}) + 0.9 \exp(-\frac{6t}{T_1})] \} \]  \hspace{1cm} (3.4)

For the satellite transitions,

\[ M(t) = M(\infty) \{ 1 - 2A[0.1 \exp(-\frac{t}{T_1}) + 0.5 \exp(-\frac{3t}{T_1}) + 0.4 \exp(-\frac{6t}{T_1})] \} \]  \hspace{1cm} (3.5)

The \( T_1 \) obtained from NMR is three times that of the NQR \( T_1 \) [57].

For the CMX spectrometer, the inversion recovery curve was carried out by measuring the \( M(t) \) at several different values of \( t \). The pulse sequence is

\[(t_{180} - t - t_{90} - \tau - t_{180} - echo - t_{pd}).\]

For the ATT spectrometer the magnetization was measured by the quadrupole-echo method. The pulse sequence is

\[(t_{180} - t - t_{90} - \tau - t_{90} - echo - t_{pd}).\]

The magnetic recovery curve was measured by the boxcar, see Figure 3.8. The boxcar integration aperture is positioned at time \( \tau \) after the tail of the second pulse. The \( t_{pd} \) is chosen to be greater than 7 \( T_1 \). A quadrupole spin echo was used to measure the equilibrium magnetization \( M(\infty) \) attained for very long \( t \). Figure 3.9 shows the magnetization recovery curve performed by boxcar. The total 256 values of \( t \) were measured sweep by sweep about 4 minutes per sweep. For relative small signal difference between \( M(\infty) \) and \( M(0) \) in impurity doped YBCO, each \( T_1 \) measurement was carried out about 70 - 128 sweeps to get good signal to noise ratio. The range of the \( t \) is set to be about 15 \( T_1 \) in order to check for the suspected long \( T_1 \) process in the doped compounds.
F(t_A) - F(t_B) \propto \text{magnetization value at time } t.

FIGURE 3.8. Pulse sequence for T_1 measurement and block diagram of the boxcar.

FIGURE 3.9. T_1 relaxation curve measured by the boxcar. The dots represent the measured value for each increment of t. The line is fitted with a single exponential function.
4. EXPERIMENTAL RESULTS

4.1. YBCO123:Zn

In order to investigate the distribution of the Cu relaxation time with respect to the distance from Zn impurities, the Cu spectra and the frequency dependence of the relaxation rate in YBCO123: Zn (2.5%) and Zn (5%) were measured at the temperatures 300 K and 77 K. In addition, the temperature dependence of Cu (2) relaxation rate in both samples were measured at the temperature above T_c in order to look at the correlation of impurity dopant and the relaxation rate.

4.1.1. NQR Spectra : 300 K , 77 K

The $^{63}$Cu(2) NQR spectra and the relaxation rate at frequencies in the range $30.8 \leq \nu_Q \leq 31.6$ MHz at 300 K are shown in Figure 4.1 for $x = 0$, 2.5%, and 5% in YBa$_2$(Cu$_{1-x}$ Zn$_x$)$_3$O$_7$. Compared to the spectrum of pure sample, Zn dopant substantially broadens the Cu(2) line and suppresses the Cu(2) intensity. The FWHM for $x = 0$, 2.5%, and 5% are 450, 850, and 900 kHz, respectively. With dopant Zn, the center of gravity of the line moves up about 200 kHz, but the shift is within the linewidth of the pure sample. There are about 10 % and 40 % decreases of the integrated intensity (I.I.) with respect to the pure YBCO123 for Zn(2.5%) and Zn(5%), respectively. This indicates that the Cu(2) nuclei near the Zn impurity will experience the largest shift of their NQR frequency, which either renders no contribution to the spectra or increases the intensity of high frequency part of the line with respect to the pure sample. The relaxation rate was extracted from using one single exponential time function to fit the magnetization recovery curve. The result represents the average relaxation rate $1/T_1$ for the sample with a distribution of relaxation time, i.e. Zn doped YBCO123. As seen in Figure 4.1, the rate, which
FIGURE 4.1. $^{63}$Cu(2) NQR spectra and frequency dependence of relaxation rate at 300 K in YBCO123:Zn.

is about $3.63 \pm 0.07 \text{ k sec}^{-1}$, is frequency independent in the pure sample. In the case of Zn(2.5%), the rate at the peak is significantly suppressed to a value of $3.08 \pm 0.07 \text{ ksec}^{-1}$. Scattering values of relaxation rates are observed with varying the NQR frequency, about $\pm 6\%$ with respect to the peak value. Nevertheless, a correlation is found that the relaxation rates are a little bit higher at the high frequency end of the spectra, about 3\% higher than the low frequency end. In the case of Zn (5\%), the rates are more suppressed, to about $2.80 \pm 0.05 \text{ ksec}^{-1}$. A same correlation of the rate and frequency is found as the Zn(2.5%).

The spectra and its relaxation rate at 77 K for Zn(2.5\%) and Zn(5\%) doped YBCO123 are shown in Figure 4.2. The general feature of the graph is the same as the one measured at 300 K in Figure 4.1. At 77 K, the linewidth is about 1 MHz for both samples. The I.I. only decreased by 5\% as the Zn concentration increased. Owing to the large NQR signal of $^{63}$Cu(2) at 77 K, measurement of isotope $^{65}$Cu(2) spectra and spin lattice relaxation time is feasible. The relative NQR peak ratio of
the two isotopes is the same as their quadrupole moment ratio ($\frac{Q_{63}}{Q_{65}} = 1.0806$), and this indicates that there is no internal magnetic field occurring on the Cu nuclei site at 77 K.

$$Zn(2.5\%): \frac{63\nu_{Q}}{65\nu_{Q}} = \frac{31.54}{29.22} = 1.079$$

$$Zn(5\%): \frac{63\nu_{Q}}{65\nu_{Q}} = \frac{31.63}{29.3} = 1.08$$

The relaxation rate ratio of two isotopes indicates that the suppression of the relaxation rate is caused by magnetic hyperfine interactions ($\frac{T_{1}^{-1}}{T_{1}^{-1}} = \frac{\frac{63T_{1}^{-1}}{65T_{1}^{-1}}}{\frac{63T_{1}^{-1}}{65T_{1}^{-1}}} = 0.8696$).

$$Zn(2.5\%): \frac{63T_{1}^{-1}}{65T_{1}^{-1}} = \frac{1550 \pm 20}{1730 \pm 20} = 0.896 \pm 0.016$$

$$Zn(5\%): \frac{63T_{1}^{-1}}{65T_{1}^{-1}} = \frac{1380 \pm 30}{1590 \pm 30} = 0.868 \pm 0.029$$

**FIGURE 4.2.** $^{63}$Cu(2) NQR spectra and frequency dependence of relaxation rate at 77 K in YBCO123:Zn.
4.1.2. Temperature Dependence of the $T_1$

Values of $1/T_1T$ of $^{63}$Cu(2) for Zn(2.5%) and Zn(5%) samples are compared with the results for the pure sample data cited from Ref. [46] in Figure 4.3. These data show that $1/T_1T$ is reduced significantly in both Zn doped materials and the reduction increases with an increase in Zn concentration. But the rate-reduction between the 2.5% and 5% Zn doped samples is much smaller than that between 2.5% Zn doped and pure sample. The $T_c$ reduction rate in Zn doped samples is about 13 K/at.%. This indicates that there is little quantitative relationship between the suppression of $1/T_1T$ and the reduction of the $T_c$. There is no change in the general character of the normal-state $T_1$ curve by the Zn doping. That is completely different from the observation in the oxygen-deficient YBCO123(60 K) phase which shows the spin pseudogap behavior having a relaxation rate greater than that of YBCO123 (90 K) at 300 K [58].

FIGURE 4.3. Temperature dependence of $(T_1T)^{-1}$ values for $^{63}$Cu(2) in YBCO123: Zn(2.5%) and (5%). The solid lines represent values in undoped YBCO123 from Ref. [46].
4.2. YBCO124:M

4.2.1. NQR

4.2.1.1. Spectra: 77 K and 300K

Figure 4.4 shows the concentration dependence of various metallic doped YBCO124 $^{63}$Cu NQR spectra for Cu(1) and Cu(2) sites at 300 K. To show the substantial line broadening due to the impurity, each Cu spectra are superimposed with a Gaussian line with the peak and the width of pure YBCO124, $\nu_{Cu(1)}^{63} = 20.0$ MHz, $\Delta \nu_{Cu(1)}^{63} = 66$ kHz and $\nu_{Cu(2)}^{63} = 29.7$ MHz, $\Delta \nu_{Cu(2)}^{63} = 170$ kHz, cited from Ref. [37]. Because the isotope $^{65}$Cu NQR lines, ($\nu_{Cu(1)}^{65} = 18.5$ MHz , $\nu_{Cu(2)}^{65} = 28.5$ MHz ), are well separated and relatively small compared with those of the isotope $^{63}$Cu, only the $^{63}$Cu lines were measured. All the spectra have been corrected for the $T_2$ effect on the echo intensity. Therefore, the result shown is proportional to the initial value of the magnetization $M(0)$.

The comparison of line shape and integrated intensity of each site between different dopants is valuable. Because the spectrometers are not calibrated, the relative intensity comparison between Cu(1) and Cu(2) spectra has no meaning. Additionally, both Cu(1) and Cu(2) spectra are scaled in order to show both spectra on the same plot.

The peak positions of Cu(1) and Cu(2) in the spectra were almost the same as those of the undoped YBCO124. The impurities have a different effect on the Cu line shape and integrated intensity. The Zn (0.9%) line width of Cu(2) and Cu(1) are 380 and 190 kHz, respectively. Both lines are broader by a factor of about 2.2 and 2.9 than those of the pure YBCO124, respectively. Also, these lines are much broader than the predicated homogenous line width calculated by the Gaussian term and Lorentzian term of the spin-spin relaxation time ($\Delta \nu_{Cu(2)}^{Zn(0.9\%)} = \frac{3.34}{2\pi T_2G} = 6$ kHz , $\Delta \nu_{Cu(1)}^{Zn(0.9\%)} = \frac{1}{\pi T_2L} = 1.2$ kHz, Zn(0.9%) ). So the broadening is caused by the
static inhomogeneous EFG's distribution at the Cu nuclei sites. Comparing with Zn(0.9%), the main features of the spectra were that most of the Cu signal was wiped out because of a large distribution of EFG caused by the dopant.

For Zn dopant, the Cu(2) integrated intensity decreases with increasing impurity. On the contrary, Zn has less effect on the Cu(1) signal. Zn asymmetrically distorted the Cu(2) line shape, and the Cu(1) line showed a symmetric broadening.

Co strongly suppressed both Cu(1) and Cu(2) intensity by about 50% and 30%, respectively, but the effect had less dependence on the Co concentration. Also the additional Co, from impurity concentration 0.75% to 1.5%, has less effect on the line width of both sites.

The Cu(2) line shape of Fe(0.9%) is similar to that of Zn(1.8%). The Cu(2) intensity is strongly suppressed for Fe(1.8%). There is a low frequency tail on the Cu(1) line which increases with increasing Fe concentration.

Figure 4.5 shows the NQR spectra at 77 K. Cu spectra are superimposed with a Gaussian line with the peak and the width of pure YBCO124, $\nu_{Cu(1)}^{63} = 19.95$ MHz, $\Delta\nu_{Cu(1)}^{63} = 77$ kHz and $\nu_{Cu(2)}^{63} = 29.8$ MHz, $\nu_{Cu(2)}^{63} = 195$ kHz, measured at 100 K from Ref. [37]. The overall characteristics of the spectra were about the same as measured at 300 K with the following exceptions: for Zn dopant the Cu(2) line moves to higher frequency with increasing Zn concentration, and Fe has the strongest wipe out effect on the Cu (2) site. The linewidths for Cu(1) and Cu(2) sites in Zn (0.9%) were 280 kHz and 620 kHz, respectively. The predicted homogeneous linewidths by the $T_2$ mechanism were $\Delta\nu_{Cu(2)}^{63} = 11$ kHz and $\Delta\nu_{Cu(1)}^{63} = 1.3$ kHz. Therefore, the impurities contribute an inhomogeneous line broadening for both Cu(1) and Cu(2) sites and this effect magnifies as the temperature decreases.

According to the observation of the above spectra, Zn mainly affects the Cu(2) site, Fe affects both Cu(1) and Cu(2) sites, and Co wipes out the signal on both sites without changing the line shape.
FIGURE 4.4. Effect of various metals M on the $^{63}$Cu NQR spectra in $YBa_2(Cu_{1-z}M_z)_4O_8$ at 300 K. The solid lines are guides to the eye. The dot points are the Gaussian line shape with the width and peak position of undoped YBCO124.
FIGURE 4.5. Effect of various metals M on the $^{63}$Cu NQR spectra in YBa$_2$(Cu$_{1-x}$M$_x$)$_4$O$_8$ at 77 K. The solid lines are guides to the eye. The dot points are the Gaussian line shape with the width and peak position of undoped YBCO124 at 100 K.
4.2.1.2. Spin-Spin Relaxation Time $T_2$

![Diagram](image)

**FIGURE 4.6.** The decay curve of the spin-echo intensity of the $^{63}$Cu(2) nuclear spin in YBa$_2$(Cu$_{1-x}$M$_x$)$_4$O$_8$ at 77 K.

The spin echo decay $M(2\tau)$ observed at 29.8 MHz for Cu(2) at 77 K is plotted against $2\tau$ in Figure 4.6, where $\tau$ is the time between the 90° and 180° pulses. The lines are the best fit to equation (3.1) with $\frac{1}{T_{2G}}$ and $M(0)$ as fitting parameters. The $\frac{1}{T_{2R}}$ was determined by the equation (2.27) with the measured relaxation rate by NQR of each sample and the anisotropic relaxation ratio $R = 3.3$ [37] of pure YBCO124 (assuming that the impurities will not change the ratio). The fitted value of $T_{2G}$ is rather insensitive to the choice of the value $T_{2R}$ since $T_{2R} \geq 200 \mu$s. These values of $T_{2R}$ and $T_{2G}$ were used to extrapolate decay curves to obtain $M(0)$ at the peak frequency of the NQR line. Assuming $T_2$ to be independent of frequency, this result was used to correct spin-echo spectra obtained with fixed $\tau = 25 \mu$s. The $T_{2G}$ and intensity corrected ratio can be found in Table 4.1 at 300 K and Table 4.2 at 77 K.

The Cu(1) spin-echo decay is not followed by equation (3.1). However it can be fitted with equation (3.2). The intensity corrected ratio is about the same for all
TABLE 4.1. The Cu(2) spin-spin relaxation time and the spectra intensity corrected ratio (ICR) in YBCO124:M at 300 K, also included are the T1 values of the Cu(1).

<table>
<thead>
<tr>
<th></th>
<th>Cu(2)</th>
<th>Cu(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>@ 300 K</td>
<td>T2G(μsec) ICR</td>
<td>T2L(μsec) ICR</td>
</tr>
<tr>
<td>Zn(0.9%)</td>
<td>87±3 1.61</td>
<td>260±12 1.28</td>
</tr>
<tr>
<td>Zn(1.8%)</td>
<td>— —</td>
<td>280±10 1.22</td>
</tr>
<tr>
<td>Zn(3%)</td>
<td>109±3 1.48</td>
<td>260±20 1.23</td>
</tr>
<tr>
<td>Fe(0.9%)</td>
<td>89±3 1.8</td>
<td>280±10 1.14</td>
</tr>
<tr>
<td>Fe(1.8%)</td>
<td>77±4 2</td>
<td>240±20 1.2</td>
</tr>
<tr>
<td>Co(0.75%)</td>
<td>80±5 1.8</td>
<td>250±13 1.27</td>
</tr>
<tr>
<td>Co(1.5%)</td>
<td>93±4 1.8</td>
<td>246±25 1.39</td>
</tr>
</tbody>
</table>

That is because Cu (1) has rather long T2 about 250 μsec, which is five times larger than the τ value used in spin-echo measurements of the Cu(1) spectra.

4.2.1.3. **Frequency Dependence of T1**

Figures 4.7 and 4.8 show the $^{63}$Cu(2) spin-lattice relaxation rate versus frequency in the range of 29.5 – 30.0 MHz at 77 K and 300 K, respectively. T1 was measured by the spin-echo inversion recovery method. The magnetization recovery curve could be fitted with a single exponential function, i.e. equation (3.3). The large error bar for certain relaxation rates was caused by either the lower signal to noise ratio or the deviation of the single exponential of the magnetization recovery curve.

At 300 K, the spin-lattice relaxation rates for Zn doped samples at the peak (29.7 MHz) were reduced significantly compared with those of the pure YBCO124,
TABLE 4.2. The Cu(2) spin-spin relaxation time and the spectra intensity corrected ratio (ICR) in YBCO124:M at 77 K, also included are the T₁ values of the Cu(1).

<table>
<thead>
<tr>
<th></th>
<th>Cu(2)</th>
<th>Cu(1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>@77 K</td>
<td>T₂C(μsec) ICR</td>
<td>T₂L(μsec) ICR</td>
</tr>
<tr>
<td>Zn(0.9%)</td>
<td>45±2</td>
<td>240±10</td>
</tr>
<tr>
<td>Zn(1.8%)</td>
<td>—</td>
<td>240±10</td>
</tr>
<tr>
<td>Zn(3%)</td>
<td>49±2</td>
<td>252±10</td>
</tr>
<tr>
<td>Fe(0.9%)</td>
<td>38±2</td>
<td>230±10</td>
</tr>
<tr>
<td>Fe(1.8%)</td>
<td>33±1</td>
<td>250±10</td>
</tr>
<tr>
<td>Co(0.75%)</td>
<td>42±2</td>
<td>240±10</td>
</tr>
<tr>
<td>Co(1.5%)</td>
<td>42±2</td>
<td>240±10</td>
</tr>
</tbody>
</table>

FIGURE 4.7. The frequency dependence of Cu(2) spin-lattice relaxation rate in YBCO124: Zn, Fe, Co at 300 K. The lines are drawn to guide the eye.

4300 msec⁻¹ [37]. When the frequency increased or decreased relative to the peak position, the rate was suppressed more, and this resulted in a concave-down relationship between the rates and the NQR frequencies. The relaxation rate and
FIGURE 4.8. The frequency dependence of the Cu(2) spin-lattice relaxation rate in YBCO124: Zn, Fe, and Co at 77 K. The lines are drawn to guide the eye.

the curvature decreased with increasing Zn concentration. For Co doped samples, the rate was the same as that of the pure sample within experimental error, and the frequency dependence of relaxation rate exhibited a convex-like shape. For Fe doped samples, the relaxation rate increased with increasing Fe concentration. Their relaxation rates were constant throughout the broad NQR lines.

At 77 K, the rates for Zn doped samples were enhanced substantially compared with the pure sample, i.e. about 2.5 times the value of the pure compound, $1/T_1 = 700 \text{ sec}^{-1}$ [37]. The rates increased with increasing Zn concentration. There was no significant frequency dependence of the relaxation rates, which suggested an uniform enhancement of the spin-correlation time. In the case of Co, the relaxation rate was enhanced to about twice the pure compound’s rate. For 0.75% Co, the rates were not changed at different frequencies. But as one increases Co concentration, the frequency dependence of the relaxation exhibited an s-like shape with small amplitude. In the case of Fe, the rates were enhanced 3.4 times and were independent of the frequency for small concentration 0.9%. For 1.8% Fe, the rates were enhanced
more and showed a concave curve of frequency dependence. Generally speaking, the rates showed less frequency dependence at lower impurity concentration. For spins far away from the impurities to be observed by NQR, the change of the relaxation rate is uniform.

4.2.1.4. Temperature Dependence of $T_1$

From the spectra studied at 77 K and 300 K, we found that the peak position for each sample was in the range of 29.7 and 29.8 MHz. The frequency dependent measurement showed that the variation of the rate within that frequency range was small. Thus the $T_1$ measurements at temperatures between 77 K and 300 K were carried out at the frequency 29.7 MHz. They are plotted as $\frac{1}{T_1T}$ versus T in Figure 4.9, where they also compared with data for pure YBCO124 [37]. The lines were the results of data points applied to the spin gap equation (2.30). As seen in Figure 4.9, the Cu(2) $1/T_1T$ of undoped YBCO124 shows a broad peak around $T^* = 150$ K which is well above the $T_c = 81$ K. For Co doped YBCO124, $1/T_1T$ has the same temperature dependence as the pure YBCO124 except with higher values of $1/T_1T$ and the broad peak at a lower temperature, about 125 K. The rate of 0.75% and 1.5% Co is the same within the experimental error. The 0.9% Fe doping results in the progressive increase of the rate with decreasing temperature and movement of the $T^*$ to 100 K. With further increase of the Fe concentration to 1.8%, an enhancement of $1/T_1T$ emerges with the same temperature dependence as the 0.9% Fe and shows a maximum at about 100 K. The relaxation rates of the Zn doped YBCO124 show complex behavior. At room temperature the rates have a larger suppression than that of the pure material and decrease with increasing dopant concentration. At lower temperatures, the suppression becomes smaller; a crossover occurs at a temperature around 150 K. Then the rate becomes more
FIGURE 4.9. Temperature dependence of \((T_1T)^{-1}\) in various metallic doped YBCO124. The pure YBCO data was cited from Ref. [37]. The error bar shown are typical for corresponding compounds.

enhanced than that of the pure compound and the rate increases with increasing dopant concentration.
4.2.2. NMR

4.2.2.1. Powder Spectrum

Figure 4.10 shows the Cu powder spectrum of YBCO124: Zn(0.9%) at 300 K in an 8 T magnetic field (the Larmor frequency, $\nu_L$, of CuCl is $\nu_L = 90.291$ MHz). Because of the random distribution of the crystallites with respect to the applied magnetic field, the observed spectra correspond to the three dimensional powder patterns of the quadrupolar split Zeeman transition. Figure 4.10 consists of two equivalent spectra of isotopes $^{63}$Cu and $^{65}$Cu which are well separated by the difference of their gyromagnetic ratios. Furthermore, both spectra consist of a superposition of two distinct spectra coming from different Cu sites, because those sites have distinct quadrupole coupling constant $\nu_{Qzz}$ and asymmetry parameters $\eta$. The set with more intense peaks is due to $^{63}$Cu which is 2.2 times more abundant than $^{65}$Cu. The peaks in the spectrum correspond to the singularities in the Cu ($I = \frac{3}{2}$) line shape distribution function derived by second-order perturbation theory [59]. The line shape function in the case of spin-$\frac{3}{2}$ central transition has two-peak structures: when $\eta = 0$, the two peaks have maximum separation. As $\eta$ increased from zero to unity the peaks shift toward the center of the shape function. The Cu(2) sites have a small asymmetry factor ($\eta = 0.015$) in the pure YBCO124; the two peaks at 88.0 and 92.5 MHz which are further apart come from the Cu(2) sites. The central peaks which have a small separation come from Cu(1) site ($\eta = 0.95$). The amplitude of the Cu(2) lines is much less than that of Cu(1) lines because Cu(2) has a wide spread range of transition frequency and a relatively small $T_2$. A huge signal found at 90.105 MHz, which is not shown on the spectra of the chemically identical isotope $^{65}$Cu, can not be the Cu signal. Checking on the nuclei gyromagnetic table, it was found that the peak originates from sodium (Na) nuclei.
The Cu NMR spectrum of YBCO124:Zn(0.9%) obtained in an external magnetic field 8 T at 300 K. A symbol like $^{63}\text{Cu}(1)$ denotes the assignment of the respective peak to the $^{63}\text{Cu}$ ions in Cu(1) sites.

The powder spectra of Fe(0.9%) and Co(0.75%) were also measured. The main feature of these spectra is the same as those of Zn(0.9%), including the sharp Na peak.

4.2.2.2. Na Impurity

The time domain signal of the spin-echo measurement at 90.105 MHz in Zn(0.9%) is shown in Figure 4.11. A sharp peak on the top of a long transient signal is the echo which corresponds to a wide line in the frequency domain coming from the Cu(1), and the slowly decaying signal corresponds to a sharp line in the frequency domain arising from Na. This sharp line was also observed in all of the metallic doped YBCO124 samples. The sharp line's position and width were the same as that measured for Na in Na$_2$CO$_3$ powder. In addition there is no more than a 6% difference of $T_1$ among the Na in Na$_2$CO$_3$ ($T_1 = 1.296$ sec, at 300 K), Zn(0.9%), Fe(0.9%), and Co(0.75%). This suggests that the Na in the samples has
Spin-echo measured at $\tau = 15 \, \mu\text{sec}$, $t_{pd} = 200 \, \text{ms}$

FIGURE 4.11. Spin-echo in the time domain measured at 90.105 MHz in YBCO124: Zn (0.9%).

The Na signal intensity compared with that of the Na$_2$CO$_3$ indicates that Na is in an impurity phase at a level of 4% maximum by mass. This amount is less than the impurity resolution (5%) of the XRD experiment. That explains why XRD claimed that all the samples were single phase and NMR showed a small amount of Na$_2$CO$_3$. The Na$_2$CO$_3$ which was presumed to evaporate during the synthetic process still remained.

4.2.2.3. Oriented Powder Spectrum

Figures 4.12 and 4.13 show the $^{63}$Cu NMR spin-echo spectra in an 8 Tesla magnetic field taken at 300 K, with $B_0$ parallel and perpendicular to the $\bar{c}$-axis oriented sample Zn(1.8%), respectively. The spectra were taken with $\tau = 40 \, \mu\text{sec}$ between the $t_{90} = 2.5 \, \mu\text{sec}$ and $t_{180} = 4.5 \, \mu\text{sec}$ pulses, $t_{pd} = 20 \, \text{msec}$ and sixteen thousand acquisitions. The Na signal which appears as a slow transient signal in the time domain at the frequency range 90.0 - 90.2 MHz has been removed from
FIGURE 4.12. $^{63}\text{Cu}$ NMR spectrum of YBCO124: Zn(1.8%) at 300 K in a magnetic field 8 T for the direction of magnetic field parallel to the $\bar{c}$-axis.

FIGURE 4.13. $^{63}\text{Cu}$ NMR spectrum of YBCO124: Zn(1.8%) at 300 K in a magnetic field 8 T for the direction of magnetic field perpendicular to the $\bar{c}$-axis.

these spectra. The arrows point to the line position of corresponding nuclei. The subscript $\frac{1}{2}$ and $\frac{3}{2}$ of the symbol Cu(1) means the central and satellite transitions of the Cu ion from the chain sites, respectively. The Al nuclei signal comes from
the aluminum metal in the NMR probe assembly. The Cu lines were first identified by comparing the spectra with the result obtained by diagonalizing the exact Cu Hamiltonian (Section 2.3.1) using the reported magnetic shift, NQR frequency, and \( \eta \) parameter of the pure YBCO124. Then the identifications were further checked by the appreciable difference of \( T_1 \) or \( T_2 \) between the Cu(1) and Cu(2) sites, as known from NQR.

For the Cu (1) sites, the EFG \( \tilde{z} \) principal axis is parallel to the crystallite \( \tilde{a} \)-axis and the \( \tilde{x} \) principal axis is along the \( \tilde{b} \)-axis. In the case when \( \tilde{c} \parallel \tilde{B}_0 \), the polar angle between the field and the \( \tilde{z} \) axis is \( \theta = 90^\circ \) and \( \phi = 0 \). The eigenvalue of the Cu Hamiltonian equation (2.13) gives the two satellite transitions which are close to the central transition because its asymmetry parameter is nearly unity. The \( T_1 \) of the sharp Cu(1) central transition (91.7 MHz), which was measured by the inversion recovery method and then fitted with equation (3.3), was 3.13 msec. This value is 1.5 times larger than that measured by \( ^{63}\text{Cu}(1) \) NQR, and this maybe due to the slightly anisotropic spin-lattice rate on the Cu(1). However, it certainly did not come from the Cu(2) sites.

For the Cu(2) sites, the EFG \( \tilde{z} \) principal axis is parallel to the crystallites \( \tilde{c} \)-axis, and the \( \tilde{x} \) principal axis is along the \( \tilde{a} \)-axis. In the case when \( \tilde{c} \parallel \tilde{B}_0 \), the angles are \( \theta = 0 \) and \( \phi \in [0, 360] \). The central transition and both the satellites are widely separated. No significant Cu(2) peaks emerge on the spectra, because the Cu (2) central transition line which sat between the Cu(1) central and satellite lines was smeared out by the wing of Cu(1) lines. When checking the high frequency Cu(2) satellite lines, it was found at 121.1 MHz. The difference between the observed and predicted satellites in the equation (2.13) is 100 kHz which is about 10% of the satellite linewidth. This indicates that the predicted line positions are correct.

Figure 4.13 shows the spectra for \( \tilde{c} \perp \tilde{B}_0 \). In the Cu (1) case \( \theta \in [0, 180] \) and \( \phi = 90^\circ \). The resonance distribution function \( \nu(\theta, \phi) \) for \( \phi = 90^\circ \) is determined by
diagonalizing the Hamiltonian as described in Section 2.3.1. The distribution of $\theta$ gives a two dimensional powder spectra. The singularities of the spectra occur at the angles $0^\circ$, $45.8^\circ$, and $90^\circ$ at which the function $\frac{d\nu(\theta)}{d\theta} = 0$ [37].

In the Cu(2) case, the angles are $\theta = 90^\circ$ and $\phi \in [0, 180^\circ]$. The singularities should occur at the angles $\phi = 0$ and $90^\circ$, because the sample is only $\overline{c}$-axis oriented. We can not distinguish the difference between the field along the $\overline{a}$-axis and the $\overline{b}$-axis. The Cu(2) line presents the average effect from both axes. The spin-spin relaxation time was measured to be 80 $\mu$sec, which is closer agreement as that found in the NQR experiment.

In short, the significant differences between $^{63}$Cu NMR spectra of magnetic field perpendicular and parallel to the crystalline $\overline{c}$-axis indicated good alignment of our magnetically oriented sample. Among those differences, the most noticeable feature is the sharp and intense chain $^{63}$Cu central transition line with the magnetic field parallel to the $\overline{c}$-axis. Therefore I can check the Cu(1) line to verify the alignment of the samples. There are other undefined peaks that might be due to the unaligned powder or some spurious defect around the Cu nuclei.

4.2.2.4. Cu(1) Spectra

In order to probe the in-plane static electron spin susceptibility on the Cu(2) site, we need to measure the Cu (2) Knight shift with the magnetic field perpendicular to the crystalline $\overline{c}$-axis. First I checked the Cu(1) line to make sure of good alignment of the sample.

Figure 4.14 shows the $^{63}$Cu(1) central transition NMR spectra of the Fourier transform spin-echo measured at spectrometer frequency 91.7 MHz with magnetic field 7.9938 T parallel to the crystalline $\overline{c}$-axis at the temperature 200 and 300 K for Zn(1.8%), Fe(0.9%) and Co(0.75%). The spectra show two peaks. The sharp peak at -100 kHz is identified as the $\pm \frac{1}{2}$ transition of the Cu(1) sites, which indicates
FIGURE 4.14. $^{63}$Cu (1) NMR spectra obtained by Fourier transform of the spin-echo measured at 91.7 MHz in YBCO124: Zn(1.8%), Fe(0.9%), Co(0.75%) with magnetic field ($\nu_L = 90.211$ MHz) parallel the $\bar{c}$-axis.

good alignment of the sample. The broad lump with peak at about 100 kHz comes from the background signal due to the unaligned parts of the sample. The overall
width of the line represents the width of the pulse power spectrum with the FWHM about 200 to 250 kHz. In the Fe and Co doped samples, the relative intensities of the sharp peak and the lump decrease with decreasing temperature. Additional checks of the spectra with longer repetition rate from 25 Hz to 45 Hz at 200 K show the same spectra. It may be that the additional field generated by the temperature dependent polarization of the local magnetic moment from Fe$^{+3}$ and Co$^{+3}$ shifts the Cu resonance frequency and then smears out the sharp peak. In Zn doped compound, the sharp peak feature sustains at lower temperature. The different behavior of the spectra suggests that the Co and Fe substituted on the same sites - Cu(1). There are no significant Cu(1) line shift for all metal doped compounds over the temperature range 130 – 300 K within the experimental error (20 kHz).

4.2.2.5. Cu(2) Knight Shift

Figure 4.15 shows $^{63}$Cu(2) central transition NMR spectra in Zn(1.8%), Fe(0.9%) and Co(0.75%) doped YBCO124 for magnetic field ($\nu_L = 90.211$ MHz) perpendicular to the $c$-axis at a series of temperatures in the range 100 K $\leq$ T $\leq$ 300 K. The lines broaden with lowering temperature. The broadening in the low frequency part of the line is caused by the second order quadrupole broadening which is temperature dependent as observed in NQR spectra. For Zn(1.8%), the peak of the line moves to lower frequency as temperature decrease. The intensity of the line is relative larger than that of Co and Fe, which is consistent with the intensity comparison of the Cu(1) line. In the case of Fe, the spectra show significant line broadening and no appreciable shift. At T = 100 K, the line features at low frequency smear out by quadrupole interaction. As observed in Fe doped NQR spectra, the inhomogeneous distribution of EFG introduced by Fe substantially broadens the Cu(2) line. For the Co doped sample, the line feature is preserved at low temperature.
FIGURE 4.15. Temperature dependence of $^{63}$Cu(2) central transition ($\pm \frac{1}{2}$) NMR line shapes of YBCO124: Zn(1.8%), Fe(0.9%), and Co(0.75%).

FIGURE 4.16. The plane $^{63}$Cu(2) magnetic shift versus temperature in YBCO124: Zn(1.8%), Fe(0.9%), Co(0.75%). The solid-circle represents the data of pure YBCO124 from Ref.[37].
Although the linewidth of the Cu(2) spectra are broader, the temperature dependence of the magnetic shift $K$ in the plane is determined from the relative peak of the broad line. Since there is no appreciable change of the Cu(2) NQR and NMR resonance frequency by doping impurity, the magnetic shift in the Cu(2) plane is extracted by directly diagonalizing the exact matrix as described in sec (2.4) with the known value: magnetic shift along the $\bar{z}$-axis $K_z$, quadrupole resonance frequency $\nu_Q$, and asymmetry parameters $\eta$. The Cu(2) magnetic shifts are plotted versus temperature in Figure 4.16 for metallic doped samples and pure samples [37]. The shift consists of the temperature-dependent Knight shift and temperature-independent orbital shift. The orbital shift value, extrapolated from the magnetic shift as $T \rightarrow 0$ K, is 0.28 % [37]. As seen in Figure 4.16, the shifts of the Co and Zn doped samples show the same temperature dependent as the pure's within the experimental error. It shows that the static spin susceptibility is not changed by doping Zn and Co. In the case of Fe dopants, the shift appears to be constant and the line shows additional broadening as the temperature decreases. It is difficult to resolve the shift from such broad lines.
5. DISCUSSION

5.1. Impurity Occupied Sites in YBCO124:M

The Cu NMR and NQR studies of YBCO124:M show the effect of impurities on the local environment of the Cu host nuclei. Comparing those effects on the static properties (resonance linewidth and intensity) and dynamics (relaxation times $T_1$ and $T_2$), of the Cu(1) and Cu(2) sites, we may determine where the majority of the impurities are substituted. Although these are indirect methods, we can probe the microscopic local atomic structure around Cu nuclei on either the chain or plane sites.

All the NQR lines are substantially broadened by small amounts of impurities. This is caused by the inhomogeneous distribution of the electric field gradient at Cu sites generated by substitutional impurities. It is difficult to make a distinct comparison of linewidth between the two sites with such broad lines. Comparing the concentration dependence of the lineshape, we observed that Zn mainly affects the Cu(2) line and Fe affects the Cu(1). The former are the larger distortion of the Cu(2) lines compared with Cu(1) as Zn concentration increases in the Zn doped samples. The latter is a low frequency tail which emerges on Cu(1) spectra in Fe doped samples; the intensity of the tail increases with increasing Fe concentration.

To compare the effects of metal substitution on the Cu NQR line intensity, I have plotted the logarithm of integrated intensity (I.I.) ratio versus impurity concentration $x$ for both Cu sites. I use the I.I. of Cu(1) and Cu(2) in Zn(0.9%) as the reference for each corresponding site of the rest of the samples. The intensity ratio for $x = 0$ is a value extrapolated from a straight line which is fitted to the ratio of Zn doped samples, and the value is used to rescale each I.I. ratio. Figure 5.1 and 5.2 show the plots for the NQR measurements at 300 K and 77 K, respectively. For
Zn dopant, the ratio of Cu(2) sites decreases with increasing x. On the other hand, the I.I. of Cu(1) sites is independent of the concentration within experimental error. This indicates that Zn occupied mainly the Cu(2) sites.

With a few assumptions, the "wipe-out number" $n$ of the Cu nuclei in the vicinity of the impurity that do not contribute to the Cu(2) NQR spectra can be deduced [60]. First, around each impurity a "wipe-out radius" $r$ can be defined such that inside the circle of radius $r$ centered at the impurity the nuclear quadrupole moments experience an EFG strong enough to shift the Cu(2) resonance frequency beyond the observable range. Outside the circle the nuclei are not affected. Second, $n$ nuclear spins are located inside the circle. The line intensity will be proportional to the probability for a given spin to find $n$ sites around it without an impurity. The probability is $(1 - c)^n$, where $c$ is the concentration of the impurity, if the impurities are distributed randomly. Third, since it is well known that the Cu(2) NQR line
is very sensitive to the disorder of the Cu(1) chain, I assume that the impurity on Cu(1) sites has the same effect on the intensity as it has on Cu(2) sites, which means \( c = 2x \% \). The value \( n \) can be obtained from the slope of the straight line in the logarithm of the intensity versus \( c \) plot. The results give a minimum wipe-out number if the impurities on the Cu(1) sites have a little effect on the EFG of Cu nuclei in the plane. The wipe-out number of Zn doped samples equals 12 at 300 K and 4 at 77 K, which corresponds to \( r = 2a \) and \( a \) (assuming Cu sits on a square lattice with lattice constant \( a \)), respectively. For Fe doped samples, the numbers are about \( n = 29 \) with an effective radius \( 3a \) and \( n = 42 \) with radius \( r = 4a \) at 300 K and 77 K, respectively. For Co dopant, the intensity does not change on increasing the concentration from 0.75 to 1.5\%. The number and the radius are the same for 0.75 and 1.5\%, which are \( n = 40 \) and \( r = 4a \) at 300 K and \( n = 42 \) and \( r = 4a \) at 77 K. In the case of the Fe dopant, all the Cu nuclei will be wiped out with such

![Graph](image_url)

**FIGURE 5.2.** \(^{63}\text{Cu} \) NQR integrated intensity ratio at 77 K as a function of atomic concentration \( x \) in \( \text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_4\text{O}_8 \). M: Zn, Fe, Co. The solid symbol: Cu(1) and the empty symbol: Cu(2).
large n at doping concentration 1.8%. This means the assumption of the random
distribution is not appropriate for the Fe doped sample. The same reasoning applies
to the Co doped sample with a large impurity concentration. However, the result
shows that both Co and Fe have a stronger effect on the Cu(2) local atomic structure
than Zn.

Fe affects the lineshape of the Cu(1) NQR spectra and the Cu(2) intensity
which suggests that Fe may substitute on both sites. This conclusion is also sup­
ported by NMR spectra. The local magnetic moment Fe$^{+3}$ polarized by the external
magnetic field will add an additional field to the surrounding Cu nuclei. In Fe
(0.9%), the intensity of the Cu(1) NMR central transition line decreases when the
temperature decreases from 300 K to 200 K, which is opposite to the result of the
Zn (1.8%). It suggests that the additional field shifts the resonance frequency of
the Cu(1) nuclei out of the observed spectral range in the vicinity of the impurities.
And the large distortion of the Cu(2)$_{ab}$ NMR line compared with Zn (1.8%) and
Co (0.75%) at 100 K indicates that the lines are distorted by the polarized local
moments. These results imply that Fe substitutes on both sites even at low concen­
tration, 0.9%, and the amount of Fe in the Cu(2) sites should be larger than that of
Co.

As seen in Figure 5.2, the I.I. ratio of both Cu(1) and Cu(2) in Co doped
samples are substantially suppressed. The line widths and integrated intensities are
almost constant as the Co impurity increases from 0.75 to 1.5%. There may be two
contributions to this effect. First, some of the additional Co may have precipitated
out during the synthetic process. Second, Co has a strong effect on the EFG of
the surrounding Cu nuclei. If the added Co enter the area affected by another
Co, the clustering of the Co cause a concentration independence of intensity and
linewidth for both the Cu(1) and Cu(2) sites. The spin-lattice relaxation time of the
Co(0.75%) is different than that of Co(1.5%). The former is $4.0 \pm 0.2$ msec and the
latter is $3.5 \pm 0.1$ msec at 77 K. Also the frequency dependence of Cu(2) $T_1$ shows that the more Co in the YBCO124, the greater is the distribution of relaxation rate against the frequency. The spin dynamics of Cu(1) and Cu(2) are disturbed by the additional Co impurity, which rules out the first reason and suggests that the additional Co substitutes near the another Co within a minimum range at about $4a$.

Our studies of the site substitution are consistent with the results of most groups. The Zn preferentially substitutes for the Cu(2) sites. The Fe occupies both the Cu(1) and Cu(2) sites even at a small concentration of about $x = 0.9\%$. In the case of Co dopants, our studies show that Co strongly affects both sites while has been believed that it occupied mainly Cu(1) sites. As known from NQR and NMR, the local structure of Cu(2) sites is very sensitive to the distortion of the Cu(1) chain layer. The Co could mainly occupy Cu(1) sites with a small portion entering the Cu(2) sites. In addition, I found that the Co and Fe have a stronger effect on the surrounding local structure than Zn. The amount of Co entering the Cu(2) sites should be less than that of Fe in the YBCO124. Co has a tendency to cluster at the concentrations above 1.5%.

5.2. Local Moment in YBCO124:M

For Fe and Co doped YBCO, the local magnetic moments are introduced by the magnetic ion Fe$^{+3}$ and Co$^{+3}$. It is well known that the local moments couple to the conduction electrons by an exchange interaction (RKKY interaction) [60]. This interaction broadens the NMR line and the linewidth varies as the inverse of the temperature. In the case of Zn doping, the Curie-like broadening of Cu(2) and $^{89}Y$ NMR lines suggests that Zn introduces local moments in the system.

The Cu(2) NMR lines in metal doped YBCO124 show strong temperature dependences. The substantial change of the Cu(2) line in Fe doped samples at low temperature is strong evidence of the local moment introduced on the Cu(2) sites. In
order to avoid the temperature dependence of second order quadrupole broadening of the Cu(2) line, presumably affecting the low frequency side of the lines, the half width at half maximum (half FWHM) on the high frequency side of the lines are plotted as a function of inverse temperature in Figure 5.3. For Co doped samples, the data exhibit linear behavior, which shows the typical $T^{-1}$ temperature dependence of RKKY broadening caused by the local-moment-induced spin-density oscillation. The width of Zn doped samples shows a steep jump in the temperature range 225 - 150 K and a broadening greater than that of Co. If the line-broadening in the Co doped sample is caused by the local moments, the steep jump of the width suggests that a substantial amount of the spin-density-oscillation amplitude grows at that temperature range in Zn doped sample. In the case of Fe (0.9%), the width shows the same temperature dependence as the Co doped sample around 300 K. As the

FIGURE 5.3. Half linewidth of Cu(2) central ($\frac{1}{2} \leftrightarrow -\frac{1}{2}$) transitions vs. inverse temperature in YBCO124: Zn(1.8%), Fe(0.9%), Co(0.75%). The solid line shown is a linear regression on the Co(0.75%) data. The dotted lines are drawn to guide the eye.
temperature decreases, the width shows a steep increase, especially in the range of 225 – 150 K.

Although intrinsic antiferromagnetic spin correlations could contribute to broadening in Co doped YBCO, the steep increase of the width in the case of the Zn and Fe doped samples indicates the existence of local moments and, presumably, enhancement of the spin-density-oscillation.

5.3. \( T_c \) Suppression of YBCO124:M

The following is a discussion of the reasons for the \( T_c \) suppression in metallic doped YBCO124. The possible reasons discussed are distortion of Cu (2) local structure, decrease of the carrier concentration, and change of the spin dynamics. Actually, for a complex structure like YBCO, those reasons may correlate with each other. Nevertheless, the different effects of Co and Zn dopants on \( T_c \) in our samples help us to reduce this complexity.

5.3.1. Static Distortion of Cu(2) Local Structure

Since superconductivity originates from the CuO\(_2\) plane, one might think that the metal substituted for Cu(2) should have a large effect on \( T_c \). According to the above discussion, the Zn and Fe impurities substitute for Cu(2) sites and produce a lower \( T_c \). However, Co distorts the atomic structure of the Cu(2) planes substantially more than Zn does and the Co dopant has a smaller effect on the superconductivity. The static distortion of the lattice by the impurity is not the main reason why Zn has a dramatic effect in suppressing \( T_c \).

5.3.2. Decrease of Carrier Concentration

Experimental results for Fe and Co doped YBCO123 indicate that impurities occupy the Cu(1) sites causing a transition of the crystal structure from orthorhomb-
bic to tetragonal and a decrease of charge carriers on the CuO$_2$ plane [12]. But Co and Fe have a smaller effect on T$_c$ than Zn does. In YBCO124, the Fe and Co also substitute for Cu(1), which was shown by their strong effect on the Cu(1) NQR and NMR spectra. The structural transition with a large concentration of Fe and Co dopant has been observed by XRD [17]. However, the same temperature dependence of $^{89}$Y Knight shift for Zn (1.8%), Fe (1.8%), Co (1.5%), and pure YBCO124 suggests that the spin density of states is not changed by the impurity [19]. Also, Carretta et al. [61] showed that the $^{89}$Y Knight shift is insensitive to changes of oxygen content in YBCO124. The Cu(2) spin lattice relaxation rate increases with Co and Fe dopants, similar to the results observed in oxygen-deficient YBCO123, which suggests that the lower charge carrier density results in localization of the Cu spin. The same behavior has been seen in Sr doped La$_{1-x}$Sr$_x$CuO$_4$ by Borsa et al. [62], in which the Cu(2) relaxation rate in the normal state increases by reducing the hole content on decreasing the Sr concentration. The rate enhancement by antiferromagnetic spin correlations is increased by removing the doping holes. Decrease of the carrier concentration may be the reason why Co in the YBCO123 and YBCO124 have T$_c$ suppression rate of about 3 – 5 K/at.\% and 8 K/at.\%, respectively. But this effect is not enough to account for the large T$_c$ suppression, 23 K/at.\%, by Fe in the YBCO124.

5.3.3. Change of the Cu(2) Spin Dynamics

Investigating the Cu spin dynamics (1/T$_1T$) at 77 K, I find that a larger enhancement of relaxation rate correlates with increasing impurity concentration and decreasing T$_c$. The constant Cu relaxation rate across the broad Cu(2) NQR line suggests that the impurities affect the spin fluctuation system uniformly away from the impurities. The temperature dependence of the relaxation rate shows that the so called “spin-gap” or “spin pseudogap” behavior (reduction of the spin excitation
spectrum at the nuclear resonance frequencies range is removed by the impurities, which means that the maximum value of $1/T_1T$ moves to lower temperatures than observed in pure YBCO124 ($T^* = 150$ K). The pseudogap energy $\Delta_\pi$ can be determined by fitting the analytical expression equation (2.30). The progressive increase of $1/T_1T$ with decrease in temperature suggests a rapid development of the antiferromagnetic spin-spin correlation by doping impurity. The plot of $1/T_1T$ and $\Delta_\pi$ versus transition temperature $T_c$ is shown in Figure 5.4. The graph shows a strong correlation of the suppression of the pseudogap for $q = (\pi, \pi)$ and the suppression of $T_c$ by the impurities. For Zn and Fe, they have the same transition temperature at 0.9% and 1.8% and different value of relaxation rate, i.e. at 77 K the rate of Fe is about 3.5 times higher than that of the pure samples, and Zn is about 2.5 times. But they show the same fitted value $\Delta_\pi$ and $\alpha$ with equation (2.30) within the error bar. Up to now there is no physical meaning of the pseudogap energy. The same values of pseudogap energy suggest that the relaxation rates of Zn- and Fe doped samples have the same temperature dependence. That may be related to the reason why they have the same effect on superconductivity.

In the general case the nuclear relaxation rate is proportional to the effective number of spins coupled to the nuclei. This is related to the $\chi_S'(0,0)$. So it is important to look at the impurity effects on the Knight shift which probes the static and uniform susceptibility, $\chi_S'(0,0)$, and also shows the spin pseudogap behavior in YBCO124. The $^{63}$Cu(2)$_{ab}$ Knight shift is unaffected by Co and Zn in the normal state. In the case of Fe doping, the Cu(2) line is distorted by second order quadrupole broadening towards the low frequency side and by the polarized Fe local moment which imposes an additional field on the Cu(2) sites especially at low temperature. Thus the Knight shift can not be precisely determined by choosing the peak in such a broad line. Under the assumption of the one-component picture, the $^{89}$Y Knight shift measurement also gives information on the spin density on the CuO$_2$ plane.
Because $^{89}\text{Y}$ has no quadrupole moment, its NMR line will not be affected by the EFG on the Y sites. The $^{89}\text{Y}$ Knight shift of the Zn(1.8%), Co(1.5%), and Fe(1.8%) materials have the same values and temperature dependence from 300 to 100 K [19]. The same results have also been seen in various YBCO systems showing spin pseudogap behavior, i.e. YBa$_2$Cu$_4$O$_{8-\delta}$ and Zn doped YBa$_2$Cu$_3$O$_{7-\delta}$ [61], which have different transition temperatures. These indicate that the pseudogap behavior probed by Knight shift measurements is insensitive to the effect of impurities and to the change of the superconductivity in the underdoped YBCO. Thus the large changes of the Cu(2) spin dynamics ($1/T_1T$) observed in metallic doped YBCO124 are caused by modification of the electronic spin dynamic susceptibility at wave vector $q \neq 0$.

Enhancement of the relaxation rate in Co doped samples can be caused by its substitution on Cu(1) sites or by the introduction of local moments. The former results in a decrease of hole carriers in the plane. That pushes the spin-fluid back toward localization and increases antiferromagnetic correlations in the case of the Co doped YBCO123, it has less effect on superconductivity (Ref. Section 5.3.2). The reduction of carriers does not show a sizeable modification in the $^{63}\text{Cu}(2)$ $K_{ab}^S$ and $^{89}\text{Y}$ Knight shift. It could be masked by the large modification of the spin pseudogap effect seen in the Knight shift measurement.

There are generally three mechanisms for the local moment coupling to nearby nuclei. The first is the direct dipole-dipole coupling. The fluctuating local moment generates a time-varying electromagnetic field which relaxes nearby nuclei through magnetic coupling. The hyperfine interaction is expressed as

$$H_{hf}(r, t) = \sum_i \frac{\hbar^2 \gamma e\gamma_n}{r_i^3} \left[ \vec{S}_{dt}(t) \cdot \vec{I}_{Cu} - 3 \left( \vec{S}_{dt}(t) \cdot \vec{r}_i \right) \left( \vec{I}_{Cu} \cdot \vec{r}_i \right) \right]$$

where $S_{dt}(t)$ represents the fluctuating local moment spin, the index $i$ sums to the number of the local moments, and $r_i$ is the distance between the nuclei and the $i$th local moment. The local hyperfine field is a superposition of contributions from all
FIGURE 5.4. Spin pseudogap energy $\Delta(\pi, \pi)$ and $^{63}\text{Cu}(2) (T_1 T)^{-1}$ at 77 K versus $T_c$ in YBCO124:M
the local moments and depends only on the distance to the moment, i.e. is the same for impurities substituted for Cu(1) or Cu(2). It increases the relaxation rate. The second is the scalar spin-spin coupling which only exists when the electron wave function of the local moment has a non-vanishing value at the nuclei site. This interaction exists at the first few neighbors of the local moment and determines on the occupied site of the local moment. It is expressed as

\[ H_{hf}(r,t) = I_{cu} \cdot A(r) \cdot S_d(t), \]

where \( A(r) \) is the interaction strength which has an complex form but with a property of fast decay as \( r \) extends to next nearest neighbors of the local moment.

The third is the indirect coupling mediated by the electron carriers. The local moment interacts with the conduction electrons which induce an electronic magnetization varying in space. Thus an indirect interaction appears between the Cu nuclei and the local moment. In a two-dimensional electron gas, as described by Kittel [63] the local moment induces a spatial spin oscillation with the expression

\[ H_{hf}(r,t) = \frac{B}{r^2} S_d(t) \cos(2K_Fr + \phi) \cdot I_{Cu}. \]

This coupling depends especially on the exchange interaction of the local moment and carrier. It varies from Cu(2) site to site and is of long range. In a system of strong antiferromagnetic correlations, the effect of this coupling on the relaxation rate is not known.

The relaxation rate was measured at the hot zone of the NQR spectra, which probes the rate of the Cu nuclei outside the wipe-out radius about 4a from the Co and Fe impurities. If the local moments play a role in the enhancement of the rate in Co doped samples, the mechanism should be long range and the Cu(2) site should be dependent via the indirect RKKY interaction. The progressive enhancement of the Cu(2) relaxation rate in Fe doped samples with respect to the Co doped and the pure YBCO124 should result from the indirect RKKY interaction. Since the studies
of NQR and NMR spectra indicate that the amount of Fe ion substituting for Cu(2) sites is larger than that of Co, the large relaxation rate results from the local magnetic moments Fe$^{+3}$ on the Cu(2) sites interacting with nearby Cu nuclei through indirect coupling. That causes the antiferromagnetic-like increase of relaxation rate. The enhancement of the rate competes with pseudogap effect resulting in the retreat of the maximum point of $1/T_1 T$ and presumably suppression of superconductivity. This concept is further supported by the increase of the Cu(2) indirect spin-spin coupling rate $1/T_{2G}$, from 26 - 30 msec$^{-1}$, with adding the Fe from 0.9% to 1.8%. Also their $1/T_{2G}$ is higher than the Co, which is 24 msec$^{-1}$.

For Zn doped YBCO124, the relaxation rate has a complex temperature dependence in the normal state. The rate has a large reduction relative to the pure compound at room temperature. As the temperature decreases the reduction become smaller and a crossover happens around the temperature where the pseudogap starts to affect the relaxation rate of pure YBCO124. In a YBCO123:Zn(7%) study, Warren et al. [64] found that the magnetization recovery curve was not single exponential. This indicates a distribution of the relaxation rate caused by nonmagnetic Zn which disrupts the local antiferromagnetic correlation leading to more rapid local field fluctuations at intermediate distances from the impurity. The NQR frequency dependence of the relaxation rate in YBCO124:Zn(3%) shows a relative suppression of the rate as the frequency increases and decrease from that of the peak position at 300 K. It suggests that the Cu near the Zn impurity experiences large EFGs and a suppression of its relaxation rate. This behavior disappears at 77 K. It could be case that the measurement is not sensitive enough to distinguish the tiny differences of average relaxation rate. The average rate shows a small decrease with increase Zn concentration from 0.9% to 3% at $T > 150$ K, which indicates that the more Zn, the faster electron spin fluctuation and smaller spin-spin correlation time on the Cu nuclei. As $T < 150$ K, the rate increases steeply on lowering the temperature.
The increasing rate in Zn(3%) is stronger than than of Zn (1.8%) and Zn(0.9%). A new mechanism is needed to provide such a fast relaxation path. The Cu(2) NMR line in Zn (1.8%) shows a steep line-broadening at the temperature range 225 - 150 K caused by formation of the local moment. The existence of local moments is suggested by the argument that the line is broader than the YBCO124:Co(0.75%), and the Fe doped sample shows the steep line-broadening at the same temperature range.

As mentioned in Section 2.4.3, the $^63\text{Cu}$ nuclear spin-lattice relaxation rate is proportional to the mean-square-fluctuation of the hyperfine coupling between the Cu $d$-electrons and $^63\text{Cu}$ nuclei, to the number of the electron spins coupling to the nuclei, and to the correlation time $\tau_c$ characterizing the rate of fluctuation of the local hyperfine field. The RKKY perturbation is unlikely to reduce the mean-square hyperfine field fluctuation. From the relaxation rate of Fe and Co doped samples, we can infer that the local moment on the Cu(2) sites cooperates with the antiferromagnetic fluctuation of the CuO$_2$ plane and slows down the fluctuation ($\tau_c$ is longer). Introducing Zn, nonmagnetic ion, in the planar Cu sites produces a spin hole in the plane lattice which breaks the translational symmetry thus it may decrease the mean-square fluctuation field or decrease the $\tau_c$ on nearby sites. Our results suggest that there are two opposite effects of Zn impurities on the antiferromagnetic fluctuation spin system. The first is breaking the translational spin symmetry which reduces the average relaxation rate and dominate at high temperature about $T > 150$ K. The second is the formation of local moments which enhance the relaxation rate and dominate at $T < 150$ K behaving paramagnetically in the plane site. The origin and spatial distribution of the local moment is not clear.

In summary, there is a strong correlation between the suppression of $T_c$ and the behavior of Cu(2) spin dynamics in YBCO124:M. The large suppression of $T_c$ could be related to the large enhancement of the relaxation rates, which shows the
removal of spin pseudogap behavior in the imaginary part of the spin susceptibility at the wave vector \( q \neq 0 \). The rate enhancement is caused by the presence of local moments which behave paramagnetically in CuO\(_2\) plane, thus it removes the spin pseudogap behavior. The local moments result in continuously-developing antiferromagnetic spin correlations as in the case of Zn and Fe doped YBCO124. The static, uniform magnetic susceptibility is not affected by the doped impurity. The removal of the gap-like behavior is also observed with the temperature dependence of \( \chi''(\omega) \) at wave vector \( q(\pi, \pi) \) measured by low energy inelastic neutron diffraction in Zn doped oxygen-deficiency Yba\(_2\)(Cu\(_{1-x}\)Znx)\(_3\)O\(_{7-\delta}\) [65], [66].

5.4. Zn in YBCO123 and YBCO124

Zn has a strong effect on suppression of superconductivity in both YBCO123 and YBCO124. I found that there are the following similar effects of Zn substitution. The temperature behavior of \(^{63}\text{Cu}(2)_{ab}\) Knight shift is not affected by Zn, which indicate that the spin density state does not change. The Zn has little effect on the Cu(2) local atomic structure with increase concentration especially at low temperature. So the disorder induced by Zn in the CuO\(_2\) plane is not enough to account for the suppression of \( T_c \). The Cu(2) relaxation rate shows little dependence on NQR frequency, which can not resolve the distribution of the relaxation rate of the Cu with respect to the distance of impurity Zn. However, in the case of YBCO124:Zn at room temperature, the relaxation rate was observed to be systematically lower as the frequency was either increased or decreased relative to the pure YBCO value. This confirms that sites near the Zn experience lower nuclear relaxation rates and more rapidly fluctuating local fields.

The temperature dependence of the Cu(2) relaxation rates are substantially affected by Zn in both YBCO123 and YBCO124, but the effects are different. In YBCO123, Zn substantially suppresses the Cu(2) relaxation rate, but does not
change the general character of the temperature dependence of $T_1$. As one increases the Zn concentration, it result in more depression of the rate. This is interpreted as the local collapse of the antiferromagnetic correlation by Zn (spin doping, $S = 0$) on the CuO$_2$ plane. In Zn doped YBCO124, the rate was suppressed at room temperature and as the temperature was decreased, it showed an antiferromagnetic-type enhancement and a steep increase after the rate crossed that of pure compound. The enhancement is caused by the formation of local moments in the plane.

The local collapse of the antiferromagnetic spin correlations near the Zn impurity in YBCO123, provides a signature that the superconductivity prefers the presence of the antiferromagnetic spin correlation. However, in a system with spin pseudogap behavior, such as YBCO124, the antiferromagnetic correlation substantially increases with increasing Zn impurity and that results in dramatic effect in suppressing superconductivity. This effect is even stronger than that of Zn in YBCO123. This conflict provides a challenging test about the statement: spin-fluctuation-induced superconductivity in HTSC.
6. CONCLUSION

Examination of the Cu(1) and Cu(2) resonance spectra in metallic doped YBCO124 shows that Co and Fe have significant effects in destroying the local atomic structure on both Cu sites and Zn mainly affects the Cu(2) spectra. This is not in conflict with the site substitution addressed from most of the groups. However, it indicates that the static distortion of the Cu(2) local structure is not the main reason why Zn has a dramatic effect in suppressing T_c, and why Co does not in our samples.

Study of Cu(2) spin dynamics of YBCO124:M in the normal state indicates a strong correlation of the antiferromagnetic enhancement of the relaxation rate and the suppression of T_c. The rate enhancement results in the suppression of the spin gap energy \( \Delta(\pi, \pi) \) and the temperature T* of maximum \( 1/T_1 T \). It is different from the general picture of the spin pseudogap behavior, which states that the T* retreat or \( \Delta(\pi, \pi) \) decrease with adding hole concentration which result in increasing T_c [52], [50]. In the case of Co doped samples, the rate enhancement results from the decrease of the carrier concentration or/and a small amount of local moment exist in the CuO_2 plane. In the case of the Zn and Fe doped compound, the significant enhancement of the relaxation rate, starts to happen at the temperature range 150 \( \leq T \leq 225 \) K, result from the strong interaction of the local moment and conduction carriers. How a nonmagnetic ion Zn substitution results in the local moment behavior in a antiferromagnetic correlated CuO_2 system is not understood yet. However, my study suggests that the spin dynamics will play a significant role in the unveiling of the mechanism of destruction the superconductivity by metal dopant.

Metal substitution in YBCO has been intensely studied since the discovery of YBCO. From the observations I found and other have also found that a qualitative
picture of spin pseudogap behavior observed by nuclear resonance method in the high $T_c$ cuprates can be stated as follow. The Cu spin dynamics, $1/T_1T$, represents the competing effect of the spin pseudogap and the antiferromagnetic fluctuation at the low spectral energies weighted at high $q \neq 0$ point [35]. The former, the spin pseudogap effect, suppresses the dynamic susceptibility. The latter, the spin-spin antiferromagnetic fluctuations, increases with decreasing temperature up to the $T_c$ around the $q (\pi, \pi)$ point, as in the case of fully doped YBCO123. The $^{63}\text{Cu}(2)_{ab}$ Knight shifts probe the carriers' spin density state in the CuO$_2$ plane, which affects the number of carriers and is suppressed by spin gap effect. Metal substitution affects the spin dynamics through added or induced local moment in the CuO$_2$ plane, results in antiferromagnetic enhancement of the relaxation rate and suppression the superconductivity, but render little effect on the profiles of the Knight shift. This indicate that the superconductivity does not favor the antiferromagnetic spin correlation. Hole doping (Ca in YBCO124) or removing (YBa$_2$Cu$_4$O$_{8-\delta}$) show less effect on the static and dynamical correlations of Cu$^{+2}$ spins [61]. The effect of changing the hole carrier in the Cu plane on the magnetic property of Cu spin is mainly masked by the spin pseudogap behavior.

Comparing the effect of metal substitution in YBCO on Cu(2) spin dynamics, we conclude that the suppression of the relaxation rate in Zn doped compounds at the normal state is caused by destruction of short-range antiferromagnetic correlation with substitution of nonmagnetic ion Zn on Cu(2) sites.

In the future, the investigation of Cu(2) $1/T_1T$ of Zn doped oxygen-deficiency YBCO123 and Co doped YBCO124 samples which has low $T_c$, especially those samples synthesized by high oxygen pressure method, will provide more support for our qualitative picture of spin pseudogap behavior in HTSC and the statement - local moment on the CuO$_2$ planes has a strong effect on $T_c$. If the statement is right, an antiferromagnetic correlation enhancement of the relaxation rate should be observed...
in those samples. The former is caused by the local moment behavior induced by the impurity Zn. The latter is contributed to the local moment introduced by Co substitution on the Cu(2) sites. Our statement does not concur with the case of Ni doped YBCO. Ni, a magnetic ion, occupies the Cu(2) sites mainly and has a less effect in $T_c$ than Zn and Fe in YBCO124. Maybe there is less exchange interaction between the local moment on Ni ion and the mobile carriers in the CuO$_2$ plane. Therefore, Ni has less effect on the superconductivity. Study of the temperature dependence of Cu(2) NMR linewidth and Cu(2) relaxation rate in YBCO124:Ni will give us the answer.
BIBLIOGRAPHY


