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ABSTRACT

We report Nuclear Magnetic Resonance (NMR) measurements of the planar oxygen O(2,3) and yttrium Knight shift and spin lattice relaxation in the normal state of the superconductor YBa$_2$Cu$_3$O$_y$. The measurements were performed on an unaligned powder sample of YBa$_2$Cu$_3$O$_{7.5}$ with near (but slightly less than) optimal doping. $^{17}$O and $^{89}$Y NMR Knight shift (K) and spin lattice relaxation rate ($1/T_1$) are reported for temperatures ranging from $T_c$ up to 700 Kelvin. We find that the $^{17}$O ($T_1T$)$^{-1}$ exhibits a drop of a 14 ± 2% between 300 and 700 K, and the static susceptibility (which has the temperature dependence of the Knight shift) displays a 13 ± 2% drop over the same temperature range. In contrast, the $^{89}$Y behavior is quite surprising, displaying $^{89}(T_1T)^{-1} = constant$ behavior (within experimental precision of ± 4%) over the full temperature range. The contrasting behaviors of $^{17}$O, $^{89}$Y, and $^{63}$Cu (which has been reported elsewhere) are compared with theoretical predictions based on the "single
component" description of electronic structure. While the $^{17}\text{O}$ relaxation behavior is well explained within a one-component model, the $^{89}\text{Y}$ temperature independent behavior cannot be reconciled with a one-component model. We have not found any model, single component or otherwise, which is consistent with this set of experimental observations.
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CHAPTER 1

INTRODUCTION

Since H. Kamerlingh Onnes discovered superconductivity in 1911 [1] by noting that the electrical resistance of mercury completely vanished below a critical temperature (T$_c$), many scientists have studied superconductivity in an attempt to describe the microscopic properties of superconductors, including a complete description of the normal state or the mechanism responsible for superconductivity. Researchers have also attempted to bring about potential applications. One severe difficulty with applications, while the highest T$_c$ on record was 23 K in Nb$_3$Ge [2] for many years, was that costly refrigerants, such as LHe, were required to keep the material in a superconducting state. However, a boost to potential applications came about in 1986, when Bednorz and Müller discovered that La$_{1.85}$Ba$_{0.15}$CuO$_4$ is superconducting up to 35 K [3]. Soon
after, several related superconductors were discovered, among them La-
Sr-Cu-O ($T_c$ 40 K), Y-Ba-Cu-O ($T_c$ 93K), Bi-Sr-Ca-Cu-O ($T_c$ 110 K), and Tl-
Ba-Ca-Cu-O ($T_c$ 130 K). The excitement about these compounds, known
as “high $T_c$” superconductors, is that most have a transition temperature
above 77 K, the boiling point of liquid nitrogen and thus can be cooled
with relatively inexpensive LN$_2$.

Although the BCS theory, developed by Bardeen, Cooper, and
Schrieffer [4], successfully explains the properties of “conventional”
superconductors, it is not clear whether the BCS theory, even with
substantial modifications, will be able to explain the high $T_c$ materials
which have unusual properties such as long penetration depths ($\lambda_c \sim
1,000 \text{ Å}$) and short coherence lengths ($\zeta_{ab} \sim 10 \text{ Å}$), making them
“extreme Type II” superconductors with a $\kappa$ of $\sim$100; a large energy gap
$\Delta$ ($2\Delta \sim 4 - 8 k_BT_c$); and properties, including the gap, which are strongly
anisotropic. Structurally, the high $T_c$ compounds are all layered
compounds with at least one CuO$_2$ plane which is believed to dominate
the superconductivity. The planar copper are Cu$^{2+}$ in a 3d$^9$ configuration,
with quasi-permanent electron moments [5, 6]. These moments are
observed to be antiferromagnetically correlated [7-10], with a correlation length of several lattice constants [11].

For the work described in this thesis, we use the Nuclear Magnetic Resonance technique (NMR) to examine a specific high $T_c$ material, YBa$_2$Cu$_3$O$_7$. NMR is a useful technique since it allows one to observe properties at specific lattice sites in a material, allowing comparisons of properties between sites and yielding more information than just the bulk average of the material.

It has been observed that the nuclear spin lattice relaxation rates $(T_1)^{-1}$ of the planar copper Cu(2) and oxygen O(2,3) have different temperature dependencies [12]. The contrasting behavior of $^{63}$Cu and $^{17}$O NMR has been a source of great controversy in investigations of the high $T_c$ cuprates (for a helpful review see Ref. [13]). While $^{17}$O located in the CuO$_2$ planes follows the usual Korringa temperature dependence $(T_1T)^{-1} = \text{const.}$ associated with simple metals, $^{63}(T_1T)^{-1}$ follows an unusual non-monotonic "Curie-Weiss" temperature dependence $^{63}T_1T = a + bT$ [14]. This early observation suggested that a complete electronic structure description of the CuO$_2$ planes would require both Cu$^{2+}$ quasi-permanent moments and relatively independent oxygen hole carriers, with the former
acting as a relaxation agent on $^{63}\text{Cu}$ and the latter on $^{17}\text{O}$. This picture was severely challenged, however, when Takigawa et al. [15] observed that the NMR Knight shifts $K$ of $^{63}\text{Cu}$ and $^{17}\text{O}$ in oxygen reduced $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ($\delta \approx 0.3$, $T_c \approx 60K$) were strongly temperature dependent in the normal state, dropping steeply with decreasing temperature (behavior which has become known as “spin gap” behavior), and that their behaviors tracked one another, $^{17}K \propto ^{63}K$, within experimental precision.

Following Takigawa's observation the prevailing view has been that only a single spin degree of freedom is necessary to describe the CuO$_2$ planes. The contrasting $^{17}\text{O}$ and $^{63}\text{Cu}$ $T_1$ behaviors have been addressed using the idea of hyperfine “form factor” effects. It is believed that antiferromagnetic fluctuations play an important role for the cuprates, dominating the $^{63}\text{Cu}$ relaxation behavior, but that the $^{17}\text{O}$, located halfway between neighboring Cu$^{2+}$ moments, is insensitive to these fluctuations and has a relaxation rate dominated by longer wavelength ($q \approx 0$) fluctuations. This model, developed by Millis, Monien, and Pines (“MMP”) [16], has been thoroughly and quantitatively elaborated, and generalized by Zha, Barzykin, and Pines (“ZBP”) [11] to address incommensurate spin fluctuations and more general hyperfine coupling possibilities.
In order to probe further the applicability of the MMP, ZBP, and related "one component" models to NMR behavior we have performed, and report here, $^{89}\text{Y}$ and $^{17}\text{O}$ NMR measurements which extend to higher temperatures (up to ~700K) than have been reported previously. The physical motivation of our work is clear—if the contrasting NMR behaviors of $^{63}\text{Cu}$ and $^{17}\text{O}$ (or $^{89}\text{Y}$) result from antiferromagnetic correlations, then in the limit of high temperatures, where the correlations are diminished, the $^{63}\text{Cu}$, $^{89}\text{Y}$, and $^{17}\text{O}$ behaviors should converge. Both $^{17}(T_1T)^{-1}$ and $^{89}(T_1T)^{-1}$ should display a decrease, of predictable magnitude, with increasing temperature, accompanying the more steep fall-off of $^{63}(T_1T)^{-1}$. (See Figure 1.1). The behaviors of $^{17}(T_1T)^{-1}$ and $^{89}(T_1T)^{-1}$, both reflecting hyperfine coupling to long wavelength fluctuations, should have quite similar (though not identical) temperature dependencies.

Measurements to date of these quantities up to room temperature for the $T_c=90\text{K}$ superconductor have not resolved this decline. Our measurements, which extend from ~100 K to ~700 K, cover a larger temperature range as well as extending to higher temperatures.

We find (as reported in reference [17]), however, several important departures from theory. While the $^{17}\text{O}$ behavior is as predicted, the $^{89}\text{Y}$ is
Figure 1.1. Predictions for $(T_1 T)^{-1}$ of $^{89}$Y, $^{17}$O, and $^{63}$Cu based upon the theory of Zha et al [11] for the case of $\chi_o$ independent of temperature. Vertical scale is arbitrary.
quite surprising, with $^{89}(T_1T)^{-1}$ = constant (within experimental precision of ± 4%) over the full range, despite a 13 ± 2% drop (from 300K to 700K) in the static susceptibility and a 14 ± 2% drop in $^{17}(T_1T)^{-1}$. We have not found any simple model, single component or otherwise, which is consistent with this set of observations.

In this thesis, we will give background on superconductivity in Chapter 2. Chapter 3 will cover experimental techniques, including a discussion of Nuclear Magnetic Resonance and a characterization of the samples used in this work. Chapter 4 will present the experimental results of the yttrium and planar oxygen relaxation rate ($1/T_1$) and Knight shift (K). We will compare our results with theory in Chapter 5. Chapter 6 will be the conclusion.
CHAPTER 2

PROPERTIES OF SUPERCONDUCTORS

In this chapter we will discuss the properties of superconductors. Characteristics of conventional superconductors will be covered in section 2.1. The unique and unusual properties of the “high $T_c$” materials will be mentioned in section 2.2, along with a description of the hyperfine hamiltonians for the copper, oxygen, and yttrium nuclei in YBCO and a presentation of a theory for the electronic susceptibility in YBCO which has been successful in explaining many NMR results.

2.1. Conventional Superconductivity

2.1.1. Experimental Characteristics of Superconductivity

Superconductivity was discovered in 1911 [1] when H. Kamerlingh Onnes observed that the electrical resistance of various metals such as
mercury, lead, and tin completely vanished below a critical temperature \( (T_c) \), characteristic of the material. The vanishing of electrical resistance requires the material to have perfect conductivity. Nuclear Magnetic Resonance (NMR) has been used to measure the decay time of the current in a superconductor to be at least 100,000 years \([18]\).

Later, in 1933, superconductors were found to display perfect diamagnetism, in which any magnetic field within a bulk sample is expelled as the sample is cooled below its critical temperature \([19]\). This expulsion of magnetic fields is referred to as the “Meissner effect”.

A phase diagram is shown in Figure 2.1. For a “Type I” superconductor such as we have been describing, there is a critical magnetic field \( H_c(T) \) above which the superconductivity is destroyed.

### 2.1.2. Theoretical Description of Superconductivity

There have been several stages in the theoretical understanding of superconductivity. In 1935 the London equations \([20]\) were introduced to describe the electrodynamic properties of superconductors, specifically, the perfect conductivity and the exponential screening (with
a penetration depth $\lambda$ of magnetic fields from the interior of a sample. $\lambda$ is typically 100 - 300 Å for conventional superconductors.

A more complete (although still phenomenological) description of superconductivity did not appear until 1950 when Ginzburg and Landau (GL) [21] described the thermodynamics of superconductors by introducing a complex wavefunction $\psi$ as an order parameter in terms of which the free energy of the superconductor could be expanded. $\psi$ describes the superconducting electrons and is related to the superconducting electron density $n_s$ by $n_s = |\psi|^2$. GL theory was later shown [22] to be a limiting form, valid near $T_c$, of the microscopic BCS theory introduced later.

An important parameter in GL theory is $\kappa$, the ratio of the penetration depth $\lambda$ to the coherence length $\zeta$, which characterizes the distance over which the wavefunction can vary ($\zeta \approx 500 - 1,000$ Å in a conventional superconductor). In “Type I” superconductors, which are defined by having a small $\kappa$ ($\kappa < \frac{1}{\sqrt{2}}$), macroscopic domains of superconducting and normal material will form in the presence of a sufficiently large magnetic field.
Figure 2.1. Phase diagrams for (a) Type I and (b) type II superconductors.
In contrast, Abrikosov [23] showed that if \( \kappa > \frac{1}{\sqrt{2}} \), then for some temperatures and external field strengths, the domain walls would possess a negative surface energy, making it favorable to increase the surface area of domain walls and leading to penetration of magnetic flux in "vortices" which each contain one flux quantum \( \Phi_p = \frac{hc}{2e} \); this condition is known as the vortex state. (See Figure 2.1b). Materials with a \( \kappa > \frac{1}{\sqrt{2}} \) are known as "Type II" superconductors and include transition metals, many alloys, and all high \( T_c \) materials. These materials have two critical fields – \( H_{c1} \) is the field above which vortices enter the sample, and \( H_{c2} \) is the field above which superconductivity is destroyed.

In 1957 Bardeen, Cooper, and Schrieffer (BCS) introduced a microscopic theory of superconductivity [4], which describes the formation of bound pairs of electrons with opposite momentum and spin, known as "Cooper pairs." BCS showed that the fermi sea is unstable against the formation of bound pairs when an attractive interactions exists, no matter how weak the interaction. It is believed that the attractive interaction responsible for pairing in the classic BCS
superconductors is mediated by phonons; different interactions may be responsible for pairing in other systems.

One of the key results of BCS theory is that there is a minimum energy required to break a pair of electrons, and a corresponding gap $\Delta(T)$ in the electronic density of states. The magnitude of the gap varies between 0 at $T_c$ and $1.76 \, k_B T_c$ at $T=0$ for the classic or conventional superconductors. These superconductors (which have only weak electron-phonon coupling), are found to have an isotropic gap, i.e., $\Delta_k(T)$ is independent of wavevector $\mathbf{k}$; for other superconductors the gap is observed to be anisotropic.

The effect of the gap can be observed in measurements of the specific heat [24], electron tunneling [25], ultrasonic attenuation [26], far-infrared absorption [27], and nuclear relaxation [28] below $T_c$. Further information on the conventional superconductors can be found in references [29] and [30].

2.1.3. NMR Properties of Superconductors

The coherent pairing of electrons and the gap in the electronic density of states will affect both the spin lattice relaxation ($1/T_1$) and
Knight shift (K) measured in NMR experiments. We will consider here only the results in a superconductor with spin singlet pairing and an isotropic gap. For more details, see a review article such as references [13] and [31].

Let us first discuss the NMR Knight shift. The Knight shift is a shift of the nuclear resonance frequency from the Larmor frequency $\nu_o = \frac{\gamma_s H_o}{2\pi}$ (discussed further in Chapter 3). The Knight shift is due to an interaction between nuclear and electronic spin magnetic moments that occurs when the electronic spin magnetic moments are polarized by an external magnetic field, and the shift is proportional to the Pauli spin susceptibility of the electrons ($\chi_s$) [32]. $\chi_s$ is proportional to the electronic density of states at the fermi energy, $\rho(E_F)$.

In the superconducting state, the pairing of electrons in a spin singlet state results in the vanishing of the Pauli spin susceptibility, and thus a decrease of the Knight shift. The exponential decrease of K to zero has been calculated by Yosida [33] and observed experimentally in aluminum [34].

Now let us consider the relaxation of nuclei. Conservation of energy requires that nuclei can only undergo transitions which result in
relaxation (and which change the energy of the nuclei) when coupled to their surroundings. Nuclear spin lattice relaxation is typically dominated by coupling of the nuclear magnetic moments to the spin magnetic moments of conduction electrons [14], with nuclear relaxation occurring as the electrons scatter. The relaxation rate (1/T₁) of nuclei can be expressed as [14]

\[
\frac{1}{T_1} \propto \int |V|^2 \rho^2(E) f(E)(1-f(E))dE,
\]

(2.1)

where V is the scattering matrix element of the electrons, f is the fermi-dirac distribution function, and \(\rho(E)\) is the electronic density of states. \(f(E)\) and \((1-f(E))\) strongly overlap only within kT of the Fermi energy. Whenever \(\rho(E)\) is slowly varying near the fermi energy (as occurs in the normal state) Equation 2.1 can be re-expressed as

\[
\frac{1}{T_1} \propto T |V|^2 \rho^2(E_F).
\]

(2.2)

From Equation 2.2 and the fact that \(K \propto \rho(E_F)\) in the normal state, we see that \(T_1 TK^2\) is constant above \(T_c\). This is known as the “Korringa relation” [35]. Since \(\rho(E_F)\) is generally independent of temperature in metals (and the normal state of a superconductor is generally a poor
metal), we predict \( \frac{1}{T} \propto T \). This behavior has been observed in the normal state of aluminum [36-38]. (See Figure 2.2).

Just below \( T_c \) an enhancement of the relaxation rate is observed [28], with the peak in \( 1/T \) vs \( T \) known as the "coherence peak" or the "Hebel-Slichter peak". Two effects contribute to this enhancement: first, there is a coherence factor resulting from the coherent nature of the pairing states which enters into the matrix elements \( V \). Second, the gap formation results in a piling up of the density of states which appears in the integral of Equation 2.1.

One of the triumphs of the BCS theory was the simultaneous explanation of two phenomenon – the coherence peak in the nuclear spin lattice relaxation rate and the decrease in the ultrasonic attenuation over the same temperature region [26]; simpler models would incorrectly predict similar behavior for the relaxation rate and the attenuation [30]. BCS theory explains that the differing behaviors are due to different coherence factors resulting from opposite time reversal properties of the two processes.

Far below \( T_c \), the relaxation rate decreases relative to its normal state value. As the gap opens, the electrons pair, and the scattering of
Figure 2.2. Aluminum relaxation versus temperature in the normal state. Filled circles are data of Spokas and Slichter [38], open circles are from Anderson and Redfield [36], and open triangles are from Hebel and Slichter [37]. Figure taken from reference [38].
Figure 2.3. Aluminum relaxation rate vs temperature, illustrating the coherence peak just below $T_c$ and the decrease to zero at low temperature. Data from Masuda and Redfield [39].
electrons required for relaxation of the nuclei vanishes. The decrease of the relaxation rate at low temperatures, as well as the coherence peak near \( T_c \) is illustrated for aluminum in Figure 2.3 [39].

2.2. High \( T_c \) Superconductors

In 1986, Bednorz and Müller discovered that \( \text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4 \) is superconducting below 35 K [3], breaking the 13 year record of a 23 K \( T_c \) in \( \text{Nb}_3\text{Ge} \) [2]. Soon after, several related superconductors were discovered, among them \( \text{La-Sr-Cu-O} \) (\( T_c \) 40 K), \( \text{Y-Ba-Cu-O} \) (\( T_c \) 93K), \( \text{Bi-Sr-Ca-Cu-O} \) (\( T_c \) 110 K), and \( \text{Tl-Ba-Ca-Cu-O} \) (\( T_c \) 130 K). The excitement about these compounds is that most have a transition temperature above 77 K, the boiling point of liquid nitrogen. Thus, they can be cooled with relatively inexpensive \( \text{N}_2 \) rather than the more costly liquid helium, paving the way for future commercial applications.

2.2.1. Non-NMR Results

The high \( T_c \) superconductors behave as conventional Type II superconductors in many ways. Their magnetic properties are described by BCS and GL theory, exhibiting a Meissner effect and screening fields
from the interior of samples. Cooper pairs of two electrons form below $T_c$ [40-42]. The vortex structure is observed below $T_c$ [43].

However, the high $T_c$ superconductors also exhibit many unusual properties. They are all layered compounds with strong anisotropy. They have long penetration depths ($\lambda_c \sim 1,000 \text{ Å}$) and short coherence lengths ($\xi_{ab} \sim 10 \text{ Å}$), making them "extreme Type II" superconductors with a $\kappa$ of $\sim 100$. They have high values of $T_c$, a large energy gap $\Delta$ ($2\Delta \sim 4 - 8 k_B T_c$), and large critical fields ($H_{c2} \sim 100$ Tesla).

The high values of $T_c$ and $2\Delta/k_B T_c$ are hard to explain within a BCS theory which assumes "weak coupling" due to an electron-phonon interaction, although the gap width could be explained by a "strong coupling" version of BCS [44]. The lack of an "isotope effect" in some high $T_c$ materials [45] (in which $\Delta$ or $H_c$ scales as $M^{-1/2}$, where $M$ is the isotope mass) suggests that the attractive interaction is not due to phonons, whose characteristic frequency scales as $M^{-1/2}$.

The Knight shift approaches zero at low temperatures, implying that there is spin singlet pairing (as observed in conventional superconductors) rather than spin triplet pairing of the electrons. However, in contrast to conventional superconductors, there are states in
the superconducting gap, i.e. a finite density of electronic states at all energies, as evidenced by a lack of a coherence peak in the nuclear relaxation and a relaxation rate which does not exponentially approach zero [13]; a penetration depth with a different temperature dependence than predicted from BCS with a s-wave gap [46, 47]; and an electronic specific heat which does not exponentially decrease to zero at low temperatures [48].

The symmetry of the gap also differs from that of classic superconductors, and it is generally agreed that the gap has d-wave symmetry. It should not be surprising that the gap is anisotropic, as the underlying crystal structure is also anisotropic. Experiments of the trapped flux in a SQUID ring suggest that the phase of the gap depends on the wavevector [49]; angle resolved photoemission spectroscopy in BSCCO finds a gap along some directions in $\vec{k}$ space, but not along other directions [50]; and some NMR experiments support d-wave symmetry [51, 52]. The pairing and gap symmetry are important, as they place limits on theories attempting to explain the origin of the attractive interaction responsible for superconductivity in these materials.
The normal state, which is a poor metal, also exhibits unusual properties that are not characteristic of a metal. The Hall coefficient, which is positive indicating that the carriers are holes, has an unusual temperature dependence, \( R_H \propto \frac{1}{T} \) [53]. The resistivity is linear with temperature, with no \( \rho \propto T^3 \) term characteristic of scattering due to phonons [54]. The optical conductivity has an unusual mid-IR contribution [55].

Each high \( T_c \) material is related to an antiferromagnetic insulator; for example, \( \text{La}_{1.88}\text{Sr}_{0.12}\text{CuO}_4 \) is a superconductor and \( \text{La}_2\text{CuO}_4 \) is an antiferromagnet. The antiferromagnetism persists as dynamic antiferromagnetic correlations (with no true long range order) in the metallic phase, with a correlation length of perhaps several lattice constants. Inelastic neutron scattering experiments observe antiferromagnetic fluctuations in the superconductors, both in the normal and superconducting states [56, 8, 57]. These correlations diminish at higher temperatures.

Structurally, all the high \( T_c \) superconductors contain copper oxide (\( \text{CuO}_2 \)) planes (illustrated in Figure 2.4), although the number of planes per unit cell varies with the compound. (These materials are also known
as "cuprate superconductors" since each contains copper). The copper oxide planes are believed to dominate the superconductivity; for this reason many NMR experiments have been focused on the planar copper and oxygen. These materials are discussed further in references [58], [30], and [29].

2.2.2. Structure of YBa$_2$Cu$_3$O$_y$

YBa$_2$Cu$_3$O$_y$, discovered in 1987 [59-61] and known as "123" material, is one of the most studied high $T_c$ compounds and is the material studied in this thesis. Its unit cell is shown in Figure 2.5. Note that each unit cell contains two CuO$_2$ planes with a yttrium atom between the planes. YBa$_2$Cu$_3$O$_{y-δ}$ also contains Cu-O chains which exist in some, but not all, high temperature superconductors. Barium atoms lie in the center of the cell between the planes and the chains. There are two inequivalent copper positions: Cu(1) lies in the chains and Cu(2) in the chains. There are four inequivalent oxygen positions: O(1) is in the chains; O(2) and O(3), known collectively as O(2,3) are in the planes, and O(4) lies between the planes and chains.
Figure 2.4. The copper-oxygen plane common to all high-$T_c$ superconductors. The dashed box indicates the two dimensional unit cell.
Figure 2.5. Structure of YBa$_2$Cu$_3$O$_{7-\delta}$. Figure from reference [104].
Figure 2.6. Phase diagram of the YBa$_2$Cu$_3$O$_{6+x}$ system for x between 0 and 1. The Neel temperature is shown for the antiferromagnetic material with x<0.4 and the critical temperature is given for the superconducting material with x>0.4. Figure from reference [7].
Samples of YBCO can be prepared with the oxygen content varying continuously between $O_6$ and $O_7$ ($\delta$ between 1 and 0). As the oxygen content is increased, the properties of the material changes drastically. A phase diagram for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is shown in Figure 2.6. For $\delta=1$, the system is an antiferromagnetic insulator. $\delta>0.5$ corresponds to a metallic, non-magnetic system. A material with $\delta-1/3$ is a superconductor with a $T_c$ near 60 K, and a compound with $\delta$ near 0 is a superconductor with $\sim 90$ K transition.

2.2.3. Electronic Description of $\text{YBa}_2\text{Cu}_3\text{O}_7$

The valence of the atoms in $\text{YBa}_2\text{Cu}_3\text{O}_7$ is $\text{O}^{2-}$, $\text{Ba}^{2+}$, $\text{Y}^{3+}$, and $\text{Cu}^{2+}$, which results in full shells for the Y and Ba. The copper has a $3d^9$ configuration; for planar copper a single hole is in the $d_{x^2-y^2}$ orbital [6]. This hole is localized at the copper site [5, 6], acting as a localized magnetic moment. It is this unpaired electron spin which is antiferromagnetically aligned in the antiferromagnetic insulator $\text{YBa}_2\text{Cu}_3\text{O}_6$ [62] and which continues to be antiferromagnetically correlated in the superconducting material.
In addition to an unpaired spin at the copper sites, there are also holes at the O(2,3) sites. As the oxygen content increases from O₆, the oxygen enters the O(1) sites in the chains, and holes are doped into the p-orbitals of the planar oxygen where they are in σ bonding orbitals [63, 64].

An important question in the study of high temperature superconductors is the proper description for the holes at the copper and oxygen sites. In particular, one wants to know whether to treat the holes at the copper and oxygen sites independently (a 2 component model) or to view the copper and oxygen holes as being hybridized together and thus having a single degree of freedom per unit cell (a 1 component model). This issue will be discussed further in the section 2.2.5 on NMR properties of high T_c superconductors.

2.2.4. Neutron Scattering Results

Inelastic neutron scattering has been used to study the magnetic structure of the cuprate superconductors. Here we will consider only those results which impact our understanding and analysis of the NMR data. In particular, neutron scattering experiments suggest the form of
the imaginary electronic susceptibility, \( \chi'(\vec{q}) \) assumed in our analysis (see Equations 2.9 and 2.10).

The observed intensity in a neutron scattering experiment is

\[
I_{\text{Neutron Scattering}} \propto \frac{f(\vec{q})\chi'(\vec{q})}{1 - \exp(-\hbar \omega / k_B T)} \tag{2.3}
\]

where \( f(\vec{q}) \) is a known form factor [56] and the denominator is simply the Bose population. Thus \( \chi'(\vec{q}) \) can be extracted from a measurement of \( I(\vec{q}) \).

Neutron scattering experiments, which extend between 1 meV [65] and 120 meV [66] in the cuprates, study the dynamical behavior of the Cu\(^{2+} \) spins; in contrast, NMR experiments (typically \( \hbar \omega = 2 \times 10^{-4} \) meV) probe the low frequency limit (compare to \( k_B T = 25 \) meV).

The undoped materials \( \text{La}_{2.0}\text{CuO}_4 \) and \( \text{YBa}_2\text{Cu}_3\text{O}_{6.0} \) are antiferromagnetic insulators. They exhibit three dimensional antiferromagnetic long range order, with the spins lying in the copper oxide planes [67].

The superconductor \( \text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4 \) (LSCO) exhibits four "incommensurate" magnetic peaks which are located at \( \vec{q} = (\pi(1 \pm \delta), \pi) \) and \( (\pi, \pi(1 \pm \delta)) \) with \( \delta = 0.24 \) [65]. Both the correlation length \( (\xi) \) of these fluctuations [65, 57], which is inversely related to the width
of the peaks, and the magnitude of the peak [57] are temperature
dependent. $\xi/a$ varies from 5 at low temperature down to 2 at 100 K [65].

In contrast to LSCO, early reports on underdoped YBCO [7, 9]
showed a peak at the commensurate position $\vec{Q} = (\pi, \pi)$. However, more
recent results show incommensurability, with four peaks appearing at
$\vec{q} = (\pi(1 \pm \delta), \pi(1 \pm \delta))$ with $\delta=0.1$, below $\sim 200$K in both YBa$_2$Cu$_3$O$_{6.7}$ [68]
and YBa$_2$Cu$_3$O$_{6.6}$ [69]. (See Figure 2.7). A significant difference from
LSCO is that the correlation length in YBCO is observed to be
temperature independent for a wide range of doping ($0<\delta<0.55$) [70].

Optimally doped YBCO exhibits only a single peak with $\xi/a \sim 1$ [71];
however, incommensurability is suggested (although not clearly
observed) in this material near 100 K [68] and in a "resonant" peak
which is observed only in the superconducting state [72]. It has been
proposed [11] that the broad observed peak is actually the result of four
incommensurate peaks (each with $\xi/a \sim 2$) at positions
$(\pi(1 \pm 0.1), \pi(1 \pm 0.1))$ which are not completely resolved.
Figure 2.7. Inelastic neutron scattering results on the underdoped YBa$_2$Cu$_3$O$_{6.7}$ showing the $\bar{q}$ dependence of $\chi''(\bar{q})$ along the path $(q_x,q_y)$ = $\frac{2\pi}{a}(0.3,0.3)$ to $\frac{2\pi}{a}(0.8,0.8)$ at 10 K and 100 K. Figure from reference [68].
In YBCO, where there are two copper-oxide planes, both an "acoustic" branch, which is odd under exchange of the planes, and an "optical" branch, even under exchange of the planes, should exist. Although early measurements observed only the acoustical branch, more recent measurements have observed the optical branch in both YBa$_2$Cu$_3$O$_{6.5}$ [66] and YBa$_2$Cu$_3$O$_{6.7}$ [73]. The observation of two branches implies the existence of bilayer coupling.

2.2.5 NMR Results of YBa$_2$Cu$_3$O$_7$

Nuclear Magnetic Resonance (NMR) is a useful tool for examining the high $T_c$ materials since NMR probes the behavior of atoms at specific sites in the lattice, and allows a determination of the spatial variation of parameters such as the electronic susceptibility. For example, as will be explained in more depth later, a comparison of the behavior of the resonance frequency and the spin lattice relaxation times between different nuclear sites in the lattice has been crucial to the issue of whether the holes in the Cu d orbitals and the oxygen p orbitals are best treated as independent systems.
There have been review articles (such as references [74] and [13]) which discuss the results of NMR experiments on the high \( T_c \) superconductors, including YBa\(_2\)Cu\(_3\)O\(_7\). NMR has been used to determine the electronic structure [63, 5, 6, 64], to examine the pairing state and gap symmetry in the superconducting state [75-78, 51, 52], and to explore the "pseudogap" which appears as the opening of an effective gap in the low frequency density of states above the transition temperature [79, 80], among other issues.

However, here we will focus on work relating to the proper description of the electronic system and whether it is better described in a one-component or a two-component model. In a two component model, one thinks of a conduction band due to holes on the oxygen p-orbitals acting independently from antiferromagnetically correlated moments localized at the copper sites; in a one component model, one thinks of the oxygen holes hybridized to the Cu\(^{2+}\) moments so that there is only one independent spin degree of freedom per unit cell. In a single component model, the hybridized oxygen 2p holes and the nearby Cu\(^{2+}\) spins can form a spin singlet [81].
The two component model received support from the investigation of the nuclear spin lattice relaxation, which is the relaxation of nuclear spins toward their equilibrium polarization along an external magnetic field, driven by interaction of nuclear spins with the "lattice" or surrounding environment. Hammel et al [12] observed that the spin lattice relaxation of the planar oxygen and copper have different temperature dependencies above $T_c$. (See Figure 2.8). This suggests that different mechanisms are responsible for relaxation of the oxygen and copper – spins at the copper sites might relax the copper nuclei, while a conduction band on the oxygen p-orbitals might relax the oxygen nuclei. Yttrium relaxation behavior is similar to that of the oxygen [82]. Differing relaxation of the copper and oxygen nuclei has been observed at the planar sites in several high $T_c$ superconductors such as $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$ [15, 83], $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [84, 85], and $\text{YBa}_2\text{Cu}_4\text{O}_8$ [86], with more of a contrast in the more underdoped materials. The contrast between the copper and oxygen (or yttrium) relaxation rates is a well established characteristic of all high-$T_c$ superconductors, and any theory which attempts to describe cuprate superconductors must explain this observed difference in relaxation rates.
Figure 2.8. Oxygen and copper relaxation rates ($1/T_1$) vs temperature in YBa$_2$Cu$_3$O$_y$. Data from Hammel et al [12].
Figure 2.9. Temperature dependence of oxygen and copper Knight shifts in YBa$_2$Cu$_3$O$_{6.8}$ and the temperature independent values of shifts in YBa$_2$Cu$_3$O$_7$. Figure from Takigawa et al [15].
In contrast to the difference seen between the oxygen (or yttrium) and copper relaxation rates, the Knight shifts of all nuclei have very similar temperature dependencies. The Knight shift is a shift of the resonance frequency from the Larmor frequency due to the simultaneous polarization of electrons in an applied magnetic field and the interaction of the electron magnetic moments with nuclear spins, and thus is proportional to the electronic susceptibility. In the fully oxygenated material, YBa$_2$Cu$_3$O$_7$, the Knight shifts [63, 87], as well as the static susceptibility [15], have very little temperature dependence between $T_c$ and room temperature, making the fully oxygenated material of little use in comparing the temperature dependence of the relevant shifts. However, in the oxygen reduced material YBa$_2$Cu$_{4.6}$O$_{6.6}$ the same quantities have substantial temperature dependence. (It is this decrease of the shift above $T_c$, more pronounced in the more underdoped materials, which has become known as the “spin gap” or “pseudogap”). Surprisingly, Takigawa [15] found that the shifts of the various components of oxygen ($^{17}K_c$, $^{17}K_{ax} \propto (^{17}K_x - ^{17}K_y)$, and $^{17}K_{iso} \propto (^{17}K_x + ^{17}K_y + ^{17}K_z)$) as well as the copper shift ($^{63}K_{ab}$) track each other above $T_c$, as illustrated in Figure 2.9. (The temperature dependence of $^{63}K_c$ is not given as the magnitude of this
shift is essentially zero due to an accidental cancellation of the hyperfine constants which contribute to the shift [88]). Similarly, for the case of the fully oxygenated material Alloul et al [63] found that the \(^{89}\)Y shift is proportional to the macroscopic susceptibility. The fact that the shifts all have the same temperature dependence suggests that there is only a single degree of freedom; if the magnetic moments at the Cu sites and the oxygen holes were independent, the electronic susceptibility at the two sites in the lattice would be expected to have two different temperature dependencies, resulting in Knight shifts that have different temperature dependencies.

One way to reconcile the similar behavior seen in the NMR shifts with the contrasts observed in the NMR relaxation rates is to think of a one component picture [89, 81, 12, 90, 16] in which the spin lattice relaxation is due to antiferromagnetic fluctuations from electron spins located at the copper sites as well as to a \(\vec{q}\)-independent background. The fluctuating spins would dominate the copper relaxation; in contrast, due to their position in the lattice, the oxygen and yttrium would be screened from these fluctuations and would relax by the smaller background contribution. Since the relaxation due to the fluctuating
spins at the copper sites and to the background could have different
temperature dependencies, the differing relaxation of the oxygen (or
yttrium) and the copper would be explained. This model will be more fully
developed in the next section on the one component model.

2.2.6. One Component Model

Following Takigawa’s observation that the Knight shifts “track”
each other, the prevailing view has been that only a single spin degree of
freedom is necessary to describe the CuO$_2$ planes. In the case of the
cuprates it is believed that antiferromagnetic fluctuations play an
important role, dominating the $^{63}$Cu relaxation behavior, but that the $^{17}$O,
located halfway between neighboring Cu$^{2+}$ moments, is insensitive to
these fluctuations and has a relaxation rate dominated by longer
wavelength (\( \vec{q} \approx 0 \)) fluctuations. In the single component model the
differing behaviors of $^{17}(T_1T)^{-1}$ and $^{63}(T_1T)^{-1}$ arise from an interplay
between temperature dependent antiferromagnetic fluctuations of the
Cu$^{2+}$ moments and the contrasting hyperfine form factors of $^{17}$O and $^{63}$Cu.
2.2.6.1. Hyperfine Hamiltonians

The hamiltonian which we will use to describe the coupling between nuclear spins and Cu$^{2+}$ electron spins is a modified form of the Mila-Rice Hamiltonian [91]. The hyperfine Hamiltonian terms which we will employ to describe $^{63}$Cu is $^{63}\mathcal{H}_{nf}$:

$$^{63}\mathcal{H}_{nf} = \sum_{\beta}^{63} I_{\beta}\left[ A_{\beta} S_{\beta, on-site} + B \sum_{n=NN} S_{\beta,n} \right].$$

(2.4)

$^{63}I_{\beta}$ is the intrinsic spin of a copper nucleus and $S_{\beta}$ is the electron spin. The expression “n=NN” which appears denotes a summation over the four Cu atoms which are nearest neighbors to the nucleus under consideration. The A term is a coupling to the on-site electron, while the B term, the “transferred” coupling first proposed by Mila and Rice [91], is coupling to each of the four nearest neighbors.

For the coupling of $^{17}$O we expect a coupling to the two nearest neighbor Cu$^{2+}$ moments, first proposed by Shastry [90], but in addition we include a coupling $C'$ to the four next nearest neighbors (NNN) proposed by ZBP [11] in order to provide a more complete screening at the oxygen sites of the antiferromagnetic fluctuations:

$$^{17}\mathcal{H}_{nf} = \sum_{\beta}^{17} I_{\beta}\left[ C_{\beta} \sum_{n=NN} S_{\beta,n} + C'_{\beta} \sum_{n'=NNN} S_{\beta,n'} \right].$$

(2.5)
For $^{89}$Y we adopt the simple Mila-Rice form [92]:

$$ ^{89} \mathcal{H}_f = \sum_\beta ^{89} I_\beta \left[ D \sum_{n=NN} S_{\beta,n} \right] $$

with summation taken over eight nearest neighbors.

The NMR Knight shifts can be determined by writing the hyperfine hamiltonians in the form $\mathcal{H}_f = -\gamma_n \hbar H_{\text{eff}} = -\gamma_n \hbar K H_o$ where $H_{\text{eff}}$ is the effective magnetic field due to the electrons, yielding for $^{63}$Cu $^{63} K = \frac{(A + 4B) \langle S_\beta \rangle}{\gamma_n \hbar H_o}$. 

$\langle S_\beta \rangle$, the average value of the electron spin, is proportional to the static field and to the uniform ($\vec{q} = 0$), static spin susceptibility $\chi_0$,

$$ -\gamma_e \hbar \langle S_\beta \rangle = \chi_0 H_o. $$

We find the Knight shifts are

$$ ^{63} K_\beta = \frac{(A_\beta + 4B) \chi_0}{\gamma_e^{63} \gamma \hbar^2}, \quad ^{17} K_\beta = \frac{2(C_\beta + 2C') \chi_0}{\gamma_e^{17} \gamma \hbar^2}, \quad ^{89} K = \frac{8D \chi_0}{\gamma_e^{89} \gamma \hbar^2} $$

where $\beta$ denotes the axis of the applied field.

While the shift is related to $\chi_0$, the NMR spin lattice relaxation rate $1/T_1$ is related to the imaginary part $\chi''(\vec{q}, \omega)$ of the dynamical spin susceptibility according to the following relation

$$ ^{\alpha} T_{1,\beta}^{-1} = \frac{k_B T}{2 \mu_0^2 \hbar^2 \omega} \sum_{\vec{q}} ^{\alpha} F_\beta(\vec{q}) \chi''(\vec{q}, \omega \rightarrow 0), $$

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where \( \beta \) is the nuclear species and \( \alpha \) is the field direction. Equation 2.9 and the "form factors" \( F_{\beta} \) are derived in Appendix C. The form factors reflect that fluctuating magnetic fields at certain wavevectors are more effective in relaxing the nuclei than are magnetic fields at other wavevectors. The relative importance of the different wavevectors depends upon the symmetry of the locations of the electron spins to which the nuclei are coupled.

The interplay between the form factors and the temperature dependent \( \chi''(q, \omega) \) appearing in Equation 2.9 result in the very substantial differences in the temperature dependencies of the \( ^{63}\text{Cu}, ^{89}\text{Y}, \) and \( ^{17}\text{O} \) \( T_1 \)'s. For the applied field along the \( c \) crystal axis, the form factors are given by:

\[
\begin{align*}
^{63}F_c &= \left[ A_{ab} + 2B(\cos(q_x a) + \cos(q_y a)) \right]^2 \\
^{17}F_c &= 2 \left[ (C_1 + 2C' \cos(q_y a))^2 \cos^2(q_x a / 2) + (C_{11} + 2C' \cos(q_y a))^2 \cos^2(q_x a / 2) \right] \\
^{89}F_c &= 32D^2 \cos^2(q_x a / 2) \cos^2(q_y a / 2)
\end{align*}
\]

The \( q \) dependence of these form factors are shown in Figures 2.10, 2.11, and 2.12. (Figure 2.11 shows the oxygen form factor both with and without the next nearest neighbor (C') coupling). Among the important features of Equation 2.10, we note that \( ^{17}F \) and \( ^{89}F \) vanish at
\( \vec{q} = (\pi, \pi) \), the antiferromagnetic wavevector; however, this is the position at which \(^{63}\text{F}\) is broadly peaked. Since \(^{17}\text{F}\) and \(^{89}\text{F}\) vanish at \( \vec{q} = (\pi, \pi) \), they will not be relaxed by fluctuations occurring at that wavevector; in contrast, the relaxation of \(^{63}\text{Cu}\), whose form factor \(^{63}\text{F}\) is large at \( \vec{q} = (\pi, \pi) \), is dominated by fluctuations at that wavevector.

Figure 2.13 illustrates a simple picture in which the copper nucleus is relaxed by the on-site electron in the Cu 3d orbital. The oxygen, in contrast, is midway between two copper sites and thus between two oppositely oriented electrons. The magnetic field fluctuations due to those electrons will cancel at the oxygen site and thus not contribute to the relaxation of the oxygen nuclei. This simple picture overlooks that the oxygen is still sensitive to wavevectors near (but not exactly at) the antiferromagnetic wavevector which are associated with the antiferromagnetic fluctuations of the \( \text{Cu}^{2+} \) spins; thus, the oxygen experiences some relaxation due to those fluctuations. \(^{89}\text{Y}\), which is surrounded by eight \( \text{Cu}^{2+} \) spins, experiences more complete screening from the \( \text{Cu}^{2+} \) spins.
Figure 2.10. The copper form factor for the external field along the crystal c-axis, $^6\text{F}_c$. Vertical scale is arbitrary.
Figure 2.11. The oxygen form factor for the external field along the crystal c-axis, $^{17}F_c$. The solid line, which includes next nearest neighbor coupling, exhibits more complete screening near $(\pi,\pi)$ than does the dashed line, which only includes nearest neighbor coupling. Vertical scale is arbitrary.
Figure 2.12. The yttrium form factor, $^{89}$F. Vertical scale is arbitrary.
Figure 2.13. (a) $^{63}$Cu nuclei will be relaxed by the on-site electron spin, which is represented as a long arrow. (b) $^{17}$O nuclei, midway between two oppositely oriented electrons, will experience no net magnetic field from those electrons and will not experience significant relaxation.
2.2.6.2. Susceptibility

A phenomenological mean-field expression for the imaginary dynamical susceptibility, proposed by Millis Monien and Pines (MMP) [16], takes into account a large contribution from antiferromagnetic fluctuations as well as a smaller $\bar{q}$-independent background contribution,

$$\chi'(\bar{q}, \omega \to 0) = \frac{\pi \chi_0 \omega}{\Gamma} \left( 1 + \beta \frac{(\xi/a)^4}{(1 + (\xi/a)^2 ((q - Q_{AF}) a)^2)^2} \right). \quad (2.11)$$

$\chi_0$ is the static susceptibility, $\Gamma$ is a characteristic spin fluctuation frequency, and $\xi$ is the correlation length of the fluctuations ($\xi^{-1}$ is the HWHM of the Lorentzian $\chi$; this is equivalent to 1.6 HWHM of the squared Lorentzian $\chi''$).

$\beta$ controls the ratio of the susceptibility arising from the antiferromagnetic fluctuations, which we will call $\chi_{AF}$, to the background term appropriate for a fermi liquid (the first term in Equation 2.11 which we will refer to as $\chi_{FL}$) since the form of $\chi_{AF}$ may not be valid for $\bar{q}$ far from the peaks. The fermi liquid susceptibility is $\bar{q}$-independent, while the antiferromagnetic contribution is strongly peaked at the antiferromagnetic wavevector $\bar{Q}_{AF} = (\pi/a, \pi/a)$. One should recognize that while there are two contributions to the susceptibility, this is one component model since the same susceptibility relaxes all nuclei. (It is
the form factors which are different for each nucleus, leading to the different temperature behaviors.)

In the original presentation, the only parameters in Equation 2.11 which had any temperature dependence were the correlation length ξ and, in the underdoped materials [93, 94], the static susceptibility χ_0. For various choices of the parameters, MMP were able to reasonably fit the available data on ^63Cu(2), ^17O(2,3) and ^89Y relaxation rates in the cuprate superconductors, while satisfying the constraints imposed on the hyperfine constants by the experimentally determined Knight shifts.

However, there were several slight problems with the MMP formalism: it was later [95, 96] determined that ξ/a was better fit by a different temperature dependence than originally given by MMP; the temperature dependent anisotropy of the oxygen relaxation rate [97] could not be understood without including a next nearest neighbor coupling for the oxygen [11], although this coupling cannot be included without modifying the susceptibility; inelastic neutron scattering experiments observed only a broad peak in YBCO, [7-10], indicating a much shorter correlation length than required to explain NMR experiments.
Figure 2.14. ZBP imaginary susceptibility shown for \((q_x, q_y)\) along the path \((0,0)\) to \((2\pi,2\pi)\). Vertical scale is arbitrary.
Figure 2.15. ZBP imaginary susceptibility shown for \((q_x, q_y)\) along the path \((\pi,0)\) to \((\pi,2\pi)\). Vertical scale is arbitrary.
<table>
<thead>
<tr>
<th>CONSTANT</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_c$</td>
<td>-1.6 $10^{-6}$ ev</td>
</tr>
<tr>
<td>$A_{ab}$</td>
<td>0.29 $10^{-6}$ ev</td>
</tr>
<tr>
<td>$B$</td>
<td>0.4 $10^{-6}$ ev</td>
</tr>
<tr>
<td>$C_c$</td>
<td>1.56 $10^{-7}$ ev</td>
</tr>
<tr>
<td>$C_{par}$</td>
<td>2.5 $10^{-7}$ ev</td>
</tr>
<tr>
<td>$C_{perp}$</td>
<td>1.3 $10^{-7}$ ev</td>
</tr>
<tr>
<td>$C'$</td>
<td>0.38 $10^{-7}$ ev</td>
</tr>
<tr>
<td>$D$</td>
<td>4.8 $10^{-9}$ ev</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>14.8 ev$^{-1}$</td>
</tr>
<tr>
<td>$\hbar\Gamma$</td>
<td>0.308 ev</td>
</tr>
<tr>
<td>$c'$</td>
<td>0.035 ev</td>
</tr>
<tr>
<td>$\chi_e(290$K)$/\mu_B^2$</td>
<td>2.49 ev$^{-1}$</td>
</tr>
</tbody>
</table>

Table 2.1. Temperature independent constants appearing in the formula for the nuclear relaxation rates. Values have been taken from references [16], [96], and [11].
Table 2.2. Temperature dependent parameters appearing in the formula for the nuclear relaxation rates. Formulas are from references [96] and [11].

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\xi/a$</td>
<td>$(0.11808 + 0.00075225 , T , (K))^{-1/2}$</td>
</tr>
<tr>
<td>$\omega_{sf}$</td>
<td>$2c'/\xi^2$</td>
</tr>
</tbody>
</table>

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Subsequently, Zha et al (ZBP) [11] proposed the following phenomenological expression for the dynamical susceptibility, which can be seen as a refinement of the MMP susceptibility:

\[ \chi(\bar{Q}, \omega) = \chi_{AF} + \chi_{FL} = \frac{1}{4} \sum \frac{\alpha \xi^2 \mu^2}{1 + (\bar{q} - \bar{Q})^2 \xi^2 - i \omega / \omega_{SF}} + \frac{\chi_o}{1 - i \pi \omega / \Gamma} \]  

(2.12)

where \( \omega_{SF} \) is a typical spin fluctuation frequency.

Several features of the ZBP susceptibility are important. The first term \( \chi_{AF} \) yields peaks at the four incommensurate wavevectors \( \bar{Q} = \left( \frac{\pi(1 \pm 0.1)}{a}, \frac{\pi(1 \pm 0.1)}{a} \right) \), which are close to the antiferromagnetic wave vector \( \bar{Q} = \left( \frac{\pi}{a}, \frac{\pi}{a} \right) \). ZBP differs in an important way from the earlier model of MMP in that these peaks are incommensurate. For typical ZBP parameters, however, the four peaks are heavily overlapping, with widths characterized by correlation lengths \( \xi \) of ~2 lattice constants, and thereby sum to yield a susceptibility which by design mimics the single broad feature centered at \( \bar{Q} = \left( \frac{\pi}{a}, \frac{\pi}{a} \right) \) which is observed in neutron scattering experiments. (See Figure 2.14 and 2.15).

The second term in Equation 2.12, \( \chi_{FL} \) ("FL"="Fermi liquid") is added to provide a "background" for the antiferromagnetic fluctuations,
similar to the background term in Equation 2.11. A temperature independent scaling factor $\alpha$ is included to adjust the ratio of $\chi_{AF}$ and $\chi_{FL}$.

The imaginary part of $\chi(\vec{q}, \omega)$ is then

$$
\chi''(\vec{q}, \omega \rightarrow 0) = \chi''_{AF}(\vec{q}, \omega \rightarrow 0) + \chi''_{FL}(\vec{q}, \omega \rightarrow 0)
$$

$$
= \frac{1}{4} \sum_i \frac{\alpha \gamma^2 \mu \omega}{(1 + (\vec{q} - \vec{Q}_i)^2 \xi^2)^2} + \frac{\chi_0 \pi \omega}{\Gamma},
$$

We will include these modifications in our presentation here, but we stress that the conclusions which we derive are not particularly sensitive to the absence or presence of the ZBP generalizations.

2.2.6.3. ZBP Parameters

Quantitative predictions can be made for the temperature dependent relaxation rates of the copper, oxygen, and yttrium nuclei in a one component theory using the ZBP susceptibility. The constants and temperature independent formulas for the parameters appearing in the ZBP susceptibility are given in Tables 2.1 and 2.2. Most are from references [96] and [11]; the $^{89}$Y hyperfine constant is from reference [16] after being appropriately adjusted to reflect the different value of $\chi_0(290 \text{ K})$ used in references [16] and [11]. The temperature dependence of the correlation length is extrapolated from the
temperature dependence given up to 300 K, in accordance with the theoretically expected form [96].

The temperature dependence of the static susceptibility was taken from our experimental measurements of the Knight shift between 300 and 700 K in both oxygen and yttrium. For the oxygen calculations, we used \( \frac{\chi_o(T)}{\mu_B^2} = 2.717(1 - 2.89 \cdot 10^{-4} T(K)) eV^{-1} \), which has the temperature dependence of \(^{17}\text{K}\) and has the room temperature value shown in Table 2.1; for the yttrium calculations we used \( \frac{\chi_y(T)}{\mu_B^2} = 2.705(1 - 2.75 \cdot 10^{-4} T(K)) eV^{-1} \), based upon the \(^{89}\text{Y}\) shift measurements of sample A over the entire temperature range.

To make quantitative predictions, we converted the sum over \( \vec{q} \) appearing in Equation 2.9 into an integral over the first Brillouin zone. We then numerically integrated Equation 2.9 without any approximations.

### 2.2.6.4. Predictions for Relaxation Rates

Specific predictions can be made for the temperature dependent relaxation rates of the copper, oxygen, and yttrium when one assumes a specific expression, such as given by ZBP in Equation 2.13, for the
imaginary part of the susceptibility. Recalling Equation 2.9 for the relaxation, one can thus write expressions for $1/T_1$ in terms of two distinct contributions:

$$ (T_1T)^{-1} = (T_1T)^{-1}_\text{AF} + (T_1T)^{-1}_\text{FL} , $$

with:

$$ (aT_\beta T)^{-1}_\text{AF} = \frac{k_B}{2\mu_B^2\hbar^2} \sum_q \alpha F_\beta(q) \left[ \frac{1}{4} \sum_i \frac{\alpha \xi^2 \mu_B^2 / \omega_{\text{AF}}}{(1 + (q - Q)^2 \xi^{-2})^2} \right] $$

and

$$ (aT_\beta T)^{-1}_\text{FL} = \frac{k_B}{2\mu_B^2\hbar^2} \sum_q \alpha F_\beta(q) \left[ \frac{\chi_0 \pi}{\Gamma} \right] . $$

Using ZBP parameter values, $^{63}$Cu, with a form factor peaked near $\bar{Q} = \left( \frac{\pi}{a}, \frac{\pi}{a} \right)$, has a spin lattice relaxation rate which is dominated by the “AF” term; at 300 K, 74% of the $^{63}(T_1T)^{-1}$ is from AF. In contrast, the oxygen and yttrium form factors are zero near $\bar{Q} = \left( \frac{\pi}{a}, \frac{\pi}{a} \right)$, screening the AF contribution to $\chi''$. Thus, $^{89}(T_1T)^{-1}$ and $^{17}(T_1T)^{-1}$ are dominated by $(T_1T)^{-1}_\text{FL}$; only 13% and 20% of the respective $(1/T_1T)$'s are due to the AF term. $(1/T_1T)_\text{AF}$ and $(1/T_1T)_\text{FL}$ have drastically different temperature
dependencies, as can be see by examining the temperature dependencies of $\chi''_{FL}$ and $\chi''_{AF}(\pi,\pi)$ illustrated in Figure 2.16.

We briefly discuss the contribution of $(1/T_1T)_{AF}$ for $^{63}$Cu, $^{89}$Y, $^{17}$O. The temperature dependence of $(1/T_1T)_{AF}$ results from the interplay between the form factors (Equation 2.10) and $\chi''_{AF}$ (Equation 2.13). In the regime over which $\omega_{sf}$ scales as $\xi^{-2}$ (which is appropriate for the measurements discussed in this paper) [96], the AF part of $(1/T_1T)$ can be written as:

$$
(\alpha T \beta T)_{AF}^{-1} \propto \xi^2 \sum_q \alpha F_\beta(q) \left[ \sum_i \frac{\xi^2}{(1 + (q - Q_i)^2 \xi^2)^{\beta} \xi^2} \right].
$$

(2.16)

The antiferromagnetic fluctuations lessen at higher temperatures. As the correlation length is decreased with increasing temperature, the peak in $\chi''$ will broaden as the magnitude is reduced. (See Figure 2.17). If we were to assume a $\bar{q}$-independent form factor, then we find that integration of the bracketed term yields a result independent of $\xi$, and thus one would expect $(T_1T)^{-1}_{AF} \propto \xi^2$. (Restricting integration to the first Brillouin zone results in an expectation of $(T_1T)^{-1}_{AF} \propto \xi^{2-0.08}$). The $\bar{q}$ dependence of the form factor may either enhance or diminish the strength of the $\xi$ dependence. We find that $^{17}(1/T_1T)_{AF}$ scales
approximately with $\zeta^{0.9}, 89(1/T_1T)_{AF}$ with $\zeta^{0.5}$ and $63(1/T_1T)_{AF}$ with $\zeta^{2.5}$. (See Figure 2.18).

In contrast to the copper, most of the oxygen and yttrium magnitude and temperature dependence of $(1/T_1T)$ is due to $(1/T_1T)_{FL}$; the temperature dependence is that of $\chi''_{FL}$, which has the temperature dependence of the static susceptibility. To a large extent, then, we expect the oxygen and yttrium $(1/T_1T)$ to scale with the Knight shift.

In order to probe the applicability of the MMP, ZBP, and related “one component” models to NMR behavior we have performed $^{89}Y$ and $^{17}O$ NMR measurements which extend to higher temperatures (up to $\sim 700K$) than have been reported previously. The physical motivation of our work is clear—if the contrasting behaviors of $^{63}Cu$ and $^{17}O$ (or $^{89}Y$) NMR result from antiferromagnetic correlations, then in the limit of high temperatures, where the correlations are diminished, the $^{63}Cu$, $^{89}Y$, and $^{17}O$ behaviors should converge. To express this more concretely we recall Figure 1.1. Shown are theoretical predictions, based on the model and parameters of ZBP, of $(T_1T)^{-1}$ for $^{63}Cu$, $^{17}O$, and $^{89}Y$, each normalized to one at 300K. (The uniform static susceptibility is taken here to be temperature independent.) At low temperatures the $T$ dependence of
$^{63}(T_1T)^{-1}$ is much stronger than that of $^{17,89}(T_1T)^{-1}$. Within the MMP and ZBP models this contrast results from strong temperature dependent antiferromagnetic fluctuations. At higher temperatures, however, the $(T_1T)^{-1}$ behaviors of all three nuclei converge, i.e. the slope of $^{63}(T_1T)^{-1}$ is approaching that of $^{17}(T_1T)^{-1}$ and $^{89}(T_1T)^{-1}$.

Regrettably, the highest temperatures of Figure 1.1 and thus the crudest overall features are not experimentally accessible. Nevertheless over the available temperature range up to ~700K there are robust features which can be tested. Both $^{17}(T_1T)^{-1}$ and $^{89}(T_1T)^{-1}$ should display a decrease, of predictable magnitude, with increasing temperature, accompanying the more steep fall-off of $^{63}(T_1T)^{-1}$. Measurements to date of these quantities up to room temperature for the $T_c=90K$ superconductor have not resolved this decline. The behaviors of $^{17}(T_1T)^{-1}$ and $^{89}(T_1T)^{-1}$, both reflecting hyperfine coupling to long wavelength fluctuations, should have quite similar temperature dependencies. To a large extent, we expect the oxygen and yttrium $(1/T_1T)$ to scale with the Knight shift.
Figure 2.16. The temperature dependencies of $\chi_{FL}$ and $\chi_{AF}(\pi, \pi)$, both normalized to 1 at 300 K.
Figure 2.17. AF (Antiferromagnetic Fluctuation) contribution to the imaginary susceptibility $\chi''(q,\omega)$ for two values of the correlation length, $\xi/a=2$ (solid line) and $\xi/a=1$ (dashed line). Vertical scale is arbitrary.
Figure 2.18. $(1/T_1T)_A$ for $^{17}$O, $^{89}$Y, and $^{63}$Cu as a function of the correlation length. The relaxation rates per unit temperature scale as $\xi^{0.9}$, $\xi^{0.5}$, and $\xi^{2.5}$ respectively.
2.2.6.5. Challenges to a one component model

Recently, several observations have emerged which have challenged this single component picture. First, Walstedt et al have shown that a comparison of inelastic neutron scattering results and NMR leads to the conclusion that the $^{17}$O hyperfine coupling to the Cu$^{2+}$ moments is much weaker than required [98, 99]. Second, measurements of the $^{17}$O $T_1$ anisotropy (dependence upon magnetic field orientation) [100, 97] have revealed a temperature dependence which is unexpected in the simplest one component formulation, but which has been addressed by ZBP by postulating that $^{17}$O is coupled not only to nearest neighbor Cu moments but also to next nearest neighbors. Third, measurements of Gorny et al [101] of indirect nuclear spin-spin coupling suggest that antiferromagnetic correlations in optimally doped YBa$_2$Cu$_3$O$_7$ are characterized by a correlation length $\xi$ less than one lattice constant, much less than the 2-3 lattice constants required in MMP-type models. Finally, Suter et al have observed that the ratio of the $^{17}$O spin lattice relaxation rate to the $^{89}$Y rate in YBa$_2$Cu$_4$O$_8$ has more complicated temperature dependence than is predicted by the ZBP theory [102] and that the ZBP model cannot explain the temperature dependence of the
ratio of characteristic time scale of a Cu SEDOR experiment to the Cu $T_{2G}$ [103].

Additionally, there is the question of how to interpret the inelastic neutron scattering results. The broad peaks observed in the YBCO materials might correspond to four narrow incommensurate peaks (giving $\xi \sim 2$-3 lattice constants) as suggested by ZBP, or they might indicate that a substantially shorter correlation length exists.
3.1. **Nuclear Magnetic Resonance**

In Nuclear Magnetic Resonance (NMR), one examines the nuclear spins, $\vec{I}$, that are subject to an external static magnetic field, while interacting with electrons and other nuclear spins in the material under consideration. The relaxation and resonance frequencies of nuclei at specific lattice sites are observed.

The motivation behind examining the resonance properties of nuclei is that the nuclei are coupled to the conduction electrons. By measuring the spin susceptibility of nuclei, we learn about the spin susceptibility of the electrons; by measuring the relaxation rates for nuclei, we learn about the magnetic fields produced by the electrons to which the nuclei are coupled. In this way, we hope to build up an understanding of the unusual electronic properties of the high temperature superconductor.
NMR is a useful technique since it allows one to observe properties at specific lattice sites in a material; this yields more information than does an average over the bulk material. In the work described in this thesis, we have looked at the superconducting material YBa$_2$Cu$_3$O$_y$, and have performed NMR on oxygen in the copper-oxygen planes and yttrium nuclei between adjacent CuO$_2$ planes.

3.1.1. Spins in Static Magnetic Fields

In Nuclear Magnetic Resonance, one observes the magnetic moments associated with nuclear spins. Any nucleus which has a non-zero intrinsic nuclear spin $\vec{I}$ will have a non-zero spin angular momentum $\vec{J} = h\vec{I}$ as well as a magnetic moment $\vec{\mu} = \gamma_n h \vec{I}$ due to the spin angular momentum [105, 32]. The gyromagnetic ratio, $\gamma_n$, which is the proportionality constant between $\vec{\mu}$ and $\vec{J}$, is unique for each nuclear species. The gyromagnetic ratios for the nuclei examined in this thesis are $2\pi \times 5.772$ MHz/Tesla for $^{17}$O and $2\pi \times 2.086$ MHz/Tesla for $^{89}$Y.

The magnetic moment of the nucleus can interact with an external magnetic field $\vec{H}$ through the Zeeman interaction [106, 32]; the Zeeman Hamiltonian is
\[ \mathcal{H} = -\mu \cdot \vec{H}. \] (3.1)

For a static constant field \( \vec{H} = H_o \hat{z} \), this hamiltonian leads to energy levels
\[ E = -m\gamma_n \hbar H_o, \]
where \( m \) is the eigenvalue of \( I_Z \). The equilibrium population of each energy level will be given by the Boltzmann distribution,
\[ p_m \propto \exp(m\gamma_n \hbar H_o / k_B T). \] (3.2)

For typical NMR parameters \( \gamma_n \hbar H_o / k_B T \) is on the order of \( 10^{-4} \). It is thus often appropriate to use the high temperature approximation in which Equation 3.2 reduces to
\[ p_m \propto 1 + m\hbar \omega_o / k_B T, \]
where \( \omega_o = \gamma_n H_o \). This distribution is illustrated for a spin 5/2 nucleus (such as \(^{17}\text{O}\)) in Figure 3.1.

From Equation 3.2 we see that there will be more spins in the lower energy states (states with larger values of \( m \)) than in the higher energy states. Since the magnetization due to an individual spin is proportional to \( m \), there will be a net magnetization of the spins along the applied field \( H_o \). The net magnetization will have a magnitude of
\[ M = N \gamma_n \hbar \sum_m e^{m \gamma_n H_o / k_B T} / \sum e^{m \gamma_n H_o / k_B T}, \] (3.3)
where \( N \) is the total number of nuclei and the sum is over the allowed \( m \) values.
Figure 3.1. The probability of energy vs energy for the allowed energies of a spin 5/2 nuclei such as $^{17}\text{O}$. 

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Figure 3.2. The magnetic moment $\vec{\mu}$ associated with a nuclear spin precesses about an applied magnetic field $H_o\hat{z}$. 
If a spin system is disturbed from its equilibrium distribution, the spins will return to their equilibrium population distribution with a characteristic time constant known as “$T_1$,” or the “nuclear spin lattice relaxation time” [32] (“lattice” refers to the fact that the spins must interact with the lattice in order to allow the total energy of the spin system to change as the moments align with the static field). In a spin 1/2 system, where there are only two allowed energy levels, the relaxation to the equilibrium distribution is single exponential, i.e. $M_0 - M(t) \propto \exp(-t/T_1)$, where $M_0$ is the equilibrium value of the magnetization. For spins greater than 1/2, the relaxation from an arbitrary initial state will be multiexponential since relaxation will generally involve multiple transitions (m$\leftrightarrow$m-1) and the transition rate between energy levels depends upon the levels involved; however, all of the exponentials are known in terms of a single constant $T_1$. The relaxation of a spin 5/2 nucleus is discussed in Appendix A.

An applied magnetic field will also cause the spins to precess about the field. This can be discussed in terms of classical mechanics since the equations of motion for the classical magnetic moment $\bar{\mu}$ are the same as for the quantum mechanical expectation value $\langle \mu \rangle$ [32].
magnetic moment will experience a torque due to the applied field \([107, 32]\),

\[
\vec{\tau} = \vec{\mu} \times \vec{H}. \tag{3.4}
\]

Equating the torque with the time rate of change of the angular momentum, \(\frac{d\vec{L}}{dt} = \vec{\tau}\), and recalling that \(\vec{\mu} = \gamma \vec{L}\) leads to an equation of motion for the magnetic moment

\[
\frac{d\vec{\mu}}{dt} = \gamma \vec{\mu} \times \vec{H}. \tag{3.5}
\]

Equation 3.5 shows that the magnetic moments are precessing around \(H_o\) with a precession frequency of \(\omega_o = \gamma \omega H\), as illustrated in Figure 3.2. This frequency is known as the Larmor frequency. The precession frequencies, \(\nu_o\), of oxygen and yttrium in a 9 Tesla field are 52.0 and 18.8 MHz, respectively.

3.1.2. Spins in Alternating Magnetic Fields

Now that we understand the effect of a static field upon spins, we wish to examine the effect of an alternating magnetic field. We will see that an alternating field can be used to rotate the magnetization away from the z-axis, allowing us to observe the magnetization.
An oscillating magnetic field can be applied to spins which are already in a static field. An alternating field of \( \vec{H} = 2H_{L} \cos(\omega t) \) is easily produced by applying an alternating voltage to a solenoid (coil) wrapped around the sample \([107, 32]\). As is typical for resonance phenomena, the oscillating frequency \( \omega \) must be near the Larmor frequency \( \omega_{0} \) in order for the oscillating field to effectively excite a transition \([32]\). Since \( \gamma_{n} \) is unique for each nuclear species, each nuclear species will have a different resonance frequency; thus, an oscillating field will only rotate spins of one nuclear species. For NMR in a static field of 10 Tesla, the frequency \( \omega \) is typically between 10 and 400 MHz, which is in the radio frequency (rf) range.

In order to analyze the effect of this alternating field, it is convenient to switch to a rotating reference frame \([108, 32]\). We choose to work in a (non-inertial) reference frame rotating at a frequency \( -\omega \) with respect to the lab frame. The effective field in the rotating frame is \( \vec{H}_{\text{eff}} = \vec{H}_{\text{applied}} - \frac{\omega}{\gamma_{n}} \). Including both static and alternating magnetic fields leads to \( \vec{H}_{\text{eff}} = (H_{o} - \frac{\omega}{\gamma_{n}})\vec{x} + H_{L}\vec{x} + H_{L}(\cos(2\omega t)\vec{x} + \sin(2\omega t)\vec{y}) \), where the primed unit vectors refer to the rotating reference frame. The final term which is at twice the resonant frequency can be neglected.
Choosing $\omega$ to be the Larmor frequency, we have a field in the rotating frame of $H_{1r}\mathbb{R}$, independent of time. As discussed in section 3.1.1, the spins will precess about the field, which will rotate them around the $x'$ axis. In a time $t_p$, they will rotate an angle $\theta = \gamma \hbar H_{1r} t_p$. If the rf field is left on for a time $t_p$ such that the angle precessed is $\pi$, then the pulse is referred to as a $\pi$ pulse. Similarly, for a $\pi/2$ pulse, the spins precess through an angle of $\pi/2$. The pulse can also be labeled by the axis about which the spins precess (the $x'$ axis in this example).

3.1.2.1. Free Induction Decay

After a $\pi/2$ pulse has been applied, we can monitor the net transverse (in the $xy$-plane) magnetization of the spins with the same coil which was initially used to apply the rf field. There will be an induced voltage (emf) in the coil due to the magnetic flux through the coil [107]. The flux through the coil (which is fixed in space) will oscillate as the net magnetization rotates about the static field.

The signal after a $\pi/2$ pulse, in which the magnetization decays in a region free of an alternating rf field (although the static field is still present), is known as a free induction decay (FID) [108, 32]. The net
magnetization in the lab frame will be in the xy-plane after the $\pi/2$ pulse, and will be precessing around the static field.

However, the transverse magnetization will eventually decay due to the range of resonance frequencies experienced by individual spins. The actual resonance frequency of an individual spin is determined by the local magnetic field ($H_{\text{loc}} = H_o + \delta H$) at that position in the sample. $\delta H$ can be due to inhomogeneities in the applied static field (which is not intrinsic to the sample under study) [108], to the fields associated with the magnetic moments of neighboring nuclei through either a direct dipolar [32] or an indirect interaction [109-111], the anisotropic fields arising from the orbital and spin angular momentum of electrons (anisotropy occurs in a powder sample in which the crystallites are oriented in random directions), or impurities in the sample [106, 108]. The physical origin of some contributions to $\delta H$ will be discussed further in Section 3.1.3. Additionally, $T_1$ relaxation can contribute to the decay of the transverse magnetization [106, 108, 32]; however, this is a secondary effect in most solids.

$\delta H$ will cause some spins to precess slightly faster than the resonance frequency while other spins precess slightly slower. Thus, the
orientation of individual spins will spread out in the x-y plane. The net transverse magnetization, which is the vector sum of the magnetization of individual spins, will decrease as the spins dephase. The decay of the transverse magnetization following a $\pi/2$ pulse is illustrated in Figure 3.3. The characteristic time for the transverse magnetization to decay is known as the spin-spin relaxation time, $T_2$ (or $T_2^*$ which includes effects due to magnet inhomogeneity).

3.1.2.2. Spin Echoes

An FID can be used to observe the magnetization of a sample. However, in some systems (especially solids) it can be difficult to detect a FID. The beginning of the FID will be obscured by ringdown in the electronics (from the large $H_1$ pulse) and thus is not observable, while $T_2^*$ decay limits the length of time over which the signal can be seen. An alternate method for observing the magnetization is the spin echo [112, 108, 32], which will be described in this section.

After a $\pi/2$ pulse is applied, the spins will precess according to their local fields and the spins will dephase. After a time $\tau$, each spin will be at a different angle $\theta$ with respect to the y-axis. A $\pi$ pulse can be applied
along the x-axis, rotating all the spins by 180 degrees around the x-axis; this will cause a spin which was previously at an angle $+\theta$, with respect to the $+y$ axis to now be at an angle $-\theta$, with respect to the $-y$-axis. (See Figure 3.4). After the $\pi$ pulse, each spin will precess about the z-axis with the same direction and speed as before ($\omega$ is unchanged since the local fields of individual spins are largely unaffected by the $\pi$ pulse) and begin to rephase. After a second period of time $\tau$ has occurred, each spin will have precessed through the same angle that it precessed during the first period $\tau$. All spins, regardless of their local field, will be along the $-y$ axis. Thus, the net magnetization will again be a maximum. It is said that the spins have been refocused. This refocusing process is known as a spin echo, i.e. an "echo" of the original magnetization.

A spin echo is simply two FIDs back to back -- in the first half of the echo, the individual spins are precessing towards each other, and in the second half (just as in the FID) the spins are precessing away from each other. Thus an FID and an echo yield the same information about the system.
Figure 3.3. Free Induction Decay. Before $t=0$, the net magnetization is along the $z$-axis, and $M_{xy}=0$. At $t=0$, a $\pi/2$ pulse is applied, rotating the magnetization into the $xy$-plane. The spins then dephase as they precess according to their individual resonance frequencies. For $t-T_2^*$, $M_{xy}$ is greatly decreased. Eventually, for $t-T_1$, the equilibrium magnetization returns.
Figure 3.4. Spin Echo. At $t=0$, a $\pi/2$ pulse is used to rotate magnetization into the xy-plane. The spins start to dephase. At $t=\tau$, a $\pi$ pulse rotates all spins by $\pi$; the spins start to rephase. At $t=2\tau$, all spins lie along the -y-axis and the spin echo is formed.
3.1.3 Detailed Nuclear Hamiltonian

So far we have considered a spin which interacts with an applied magnetic field through the Zeeman interaction. However, the actual hamiltonian for a nuclear spin includes many terms. There are two contributions to the hamiltonian, in addition to the Zeeman term, which we will consider in this thesis -- the hyperfine and quadrupole hamiltonians,

\[ \mathcal{H} = \mathcal{H}_{Zeeman} + \mathcal{H}_{hf} + \mathcal{H}_{quad} \]  

(3.6)

The hyperfine hamiltonian, \( \mathcal{H}_{hf} \), is associated with the extra magnetic fields due to the angular momentum of electrons. The quadrupole term, \( \mathcal{H}_{quad} \), is the interaction of the electric quadrupole moment of the nucleus with the Electric Field Gradients (EFG) at the site of the nucleus.

3.1.3.1. Zeeman Hamiltonian

The Zeeman hamiltonian, as given in Equation 3.1, is

\[ \mathcal{H}_{Zeeman} = -\mathbf{\mu} \cdot \overline{\mathbf{H}}_{applied} = -\gamma_n \hbar \mathbf{I} \cdot \overline{\mathbf{H}}_{applied} \].

This is just the interaction of a magnetic moment in an externally applied field. Quantum mechanically, the energy levels in an applied field of \( \mathbf{H}_a \hat{z} \) are \( E = -\gamma_n \hbar \mathbf{H}_a \), the difference between adjacent energy levels is \( \gamma_n \hbar \mathbf{H}_a \), and so transitions between different
energy levels will occur at a frequency \( \omega = (\Delta m)\gamma_n H_o \). In NMR, transitions are excited with an alternating magnetic field, which has non-zero matrix elements only between adjacent energy levels; thus there is only a single transition frequency of \( \omega_o = \gamma_n H_o \) or \( \nu_o = \gamma_n H_o / 2\pi \).

For the work described in this thesis, the applied field is approximately 9 Tesla. In such a field, the Zeeman energy is much larger than either of the other energies. This allows us to consider the other terms as perturbations to the Zeeman Hamiltonian.

### 3.1.3.2. Hyperfine Hamiltonian

A nuclear spin magnetic moment can interact with the magnetic moment of electrons. In an external magnetic field, electrons will be partially polarized by an external magnetic field; their interaction with nuclear spin moments will take the form of an additional magnetic field, proportional to \( H_o \), experienced by the nuclei. The hyperfine Hamiltonian, which represents the interaction of a nuclear spin magnetic moment with an extra magnetic field due to nearby electrons, can be written as \([32]\)

\[
\mathcal{H}_{\text{hf}} = -\gamma_n \hbar \mathbf{I} \cdot \mathbf{K} \cdot \mathbf{H}_o. \tag{3.7}
\]
Figure 3.5. The energy levels for a spin 5/2 system. The levels are shown for Zeeman interaction only; Zeeman and hyperfine; and Zeeman, hyperfine, and quadrupole. For Zeeman or Zeeman and hyperfine, the energy splitting between adjacent levels is independent of the transition. However, when the quadrupole interaction is added, the energy splitting depends upon the transition. The splittings are not to scale.
K is referred to as the magnetic shift tensor and the product $KH_0$ represents the additional field that a nuclear spin experiences. The hyperfine interaction shifts all energy levels by an amount proportional to $m$ and shifts the resonance frequency by $\delta \omega = \gamma_n \hbar KH_0$; since $\delta \omega$ is independent of $m$, there is only a single resonance frequency. (See Figure 3.5).

The magnetic shift tensor is composed of three terms,

$$K = \sigma + K'^L + K'^S. \quad (3.8)$$

Each term in the shift tensor results from, and is proportional to, a different electronic susceptibility.

$\sigma$ and $K'^L$ are both due to the orbital motion of electrons [106, 32]. Together, these terms are known as the “orbital” or “chemical” shift. $\sigma$ is the diamagnetic shift (opposing the applied field) resulting from the orbital motion of electrons in a closed core; it is proportional to the diamagnetic susceptibility of the electrons. We typically measure resonance frequencies relative to a reference compound which also has a closed core, and thus do not measure this shift. $K'^L$ is due to the orbital motion of valence electrons, and is proportional to the Van Vleck
susceptibility of those electrons. Both $\sigma$ and $K^L$ are independent of temperature.

The Knight shift, $K^n$, is due to the spin angular momentum of the conduction electrons [106, 32]. It is proportional to the Pauli spin susceptibility [113] of those electrons. Since the Knight shift is associated with the electronic spin susceptibility, measurement of the Knight shift will yield information about the electronic spin system and is important to the work described in this thesis. The Knight shift, as well as the orbital shifts, depend upon the orientation of the sample with respect to the applied field. Unlike the orbital shift, the Knight shift is temperature dependent.

Yttrium, which is spin $1/2$ and is thus described by only the Zeeman and hyperfine hamiltonians, has a resonance frequency given by

$$\nu_{\text{res}} = \nu_o (1 + K).$$  \hspace{1cm} (3.9)

### 3.1.3.3. Quadrupole Hamiltonian

The third term in the nuclear Hamiltonian (Equation 3.6) is the electric quadrupole term [106, 32], $\mathcal{H}_{\text{quad}}$. This term is non-zero for all nuclei which have spin greater than $1/2$. For these nuclei, the nucleus has an
electric quadrupole moment, $Q$, that depends on the charge distribution within the nucleus. The electric quadrupole will interact with the local electric field gradients (EFGs) at the site of the nucleus. These gradients can be due to the lattice, as well as to the average position of electrons around that nucleus. In general, these gradients are anisotropic.

Using the Wigner-Eckart Theorem, the interaction between the quadrupole moment $Q$ and the EFGs can be written in terms of the spin operator $\mathbf{l}$ [32]. This yields

$$\mathcal{H}_Q = \frac{eQ}{4I(2I-1)} [V_{zz}(3l_z^2 - l^2) + (V_{xx} - V_{yy})(l_x^2 - l_y^2)] ,$$

(3.10)

where $V_{zz}$ is the second derivative of the electric potential $V$ at the site of the nucleus. Second order perturbation theory must be used to find the energy levels in the presence of the quadrupole interactions if the EFGs are not axially symmetric. This problem is solved for a spin-5/2 nuclei (such as $^{17}\text{O}$) in Appendix B.

When the quadrupole interaction is included in the total Hamiltonian of a system, the energy splitting between adjacent energy levels depends upon the specific transition ($m\leftrightarrow m-1$). This causes the resonance line to be split into $2m$ different lines (resonant frequencies). The $m=+1/2\leftrightarrow m=-1/2$ transition is referred to as the central line, while the other
transitions are known as satellites. Half the satellites have a higher frequency than the central line, while half have a lower frequency. This splitting is illustrated in Figure 3.5. For a spin 5/2 nucleus in a general EFG, the resonance frequencies are given by (see Appendix B)

\[ v_{\text{res}} = v_o + v_\sigma K_z + \frac{2}{9} \left( v_s - v_y \right)^2 v_o \]

\[ v_{\text{res}} = v_o + v_\sigma K_z \mp v_z + \frac{5}{36} \left( v_s - v_y \right)^2 v_o \]

\[ v_{\text{res}} = v_o + v_\sigma K_z \mp 2v_z - \frac{1}{9} \left( v_s - v_y \right)^2 v_o \]  

(3.11)

where \( v_\sigma = \frac{3}{20} |eQ| \nu_{\alpha \alpha} \).

For the O(2,3) sites in YBCO, the central transition in a 9 Tesla field is at 52.0 MHz and the first high frequency satellite transition is at 52.7 MHz; these are the two oxygen transitions which we observed.

### 3.1.4. Advanced Pulse Sequences

While a spin echo sequence can be used to observe the resonance frequency of a nucleus, there are other pulse sequences which can be more advantageous. A double resonance experiment, in which two transitions are excited, can isolate the spins at a particular lattice site or
of a particular orientation. Additionally, since a spin-echo does not give information about the spin lattice relaxation, other sequences such as an inversion recovery or saturation recovery are needed to measure $T_1$. Phase cycling can be used to increase the signal-to-noise (S/N). The different pulse sequences used in the work described in this thesis are described below.

3.1.4.1. Double Resonance Experiment to Determine the Oxygen Shift

A spin echo sequence can be used to observe the lineshape and to determine the resonance frequency and hence the shift of a nucleus. Unfortunately, there are limitations to the spin echo. A spin echo measurement cannot isolate the contribution to the lineshape from specific spins. This is a problem in YBCO, in which there are four lattice sites at which oxygen reside, with different shifts and EFGs [64]. We are interested only in the oxygen at the O(2) and the O(3) sites – known collectively as the O(2,3) sites, since these are the oxygen which are located in the copper oxygen planes crucial to superconductivity. Furthermore, for reasons to be discussed in section 3.2.2, we are working
with an unaligned powder sample; yet, we are only interested in the oxygen shift for those crystallites whose crystal c-axis is parallel to the applied magnetic field, $^{17}K_c$.

Unfortunately, the central transition for oxygen spins with all orientations and at all sites heavily overlap. One cannot distinguish the contribution of the $O(2,3)$ spins parallel to c to the central transition from the contributions of all other spins. Thus, we could not measure the $O(2,3) \quad ^{17}K_c$ by observing just the central transition.

In the satellite transitions, however, the resonance frequencies of oxygen at the different sites and crystal orientations are spread out such that there is a broad range of frequencies for which some spin is resonant [64]; this is known as a "powder pattern." [106, 32] It turns out that in YBCO the edge of the first high frequency satellite of the powder pattern is an extrema due to $O(2,3)$ spins along c. Thus, we can isolate the desired spins at the edge of the powder pattern. Unfortunately, the edge is not a sharp feature; it is too broad of a feature (~70kHz HHFW) from which to obtain a precise measurement of the shift. The central transition and high frequency satellite edge are shown in Figure 3.6.
We were able to measure the shift due to O(2,3) spins parallel to c by performing a double resonance experiment which utilized both the relative narrowness of the central transition and the isolation of the desired spins at the satellite edge.

In the double resonance experiment, we first carry out a spin echo on the central transition. This gives us information about the resonance frequencies for spins of all orientations and at all sites.

Next, we apply a "soft pulse" to the edge of the powder pattern associated with O(2,3) along c. The "soft pulse" means that we use a small H₁ field so that only a narrow bandwidth of spins are affected, allowing us to be selective as to which spins are influenced (we used a T₁₀ of 15 µsec, which corresponds to a Δν of 16 kHz). As illustrated in Figure 3.7, this pulse partially inverts the population distribution for the first high frequency satellite, which corresponds to the m=-1/2 to m=-3/2 transition. It is important to realize that the population distribution is altered only for O(2,3) spins along c; the population distribution remains the same for all other spins. This can be though of in terms of transferring the intensity from the satellite singularity down to the central transition, as illustrated in Figure 3.6.
Figure 3.6. The oxygen central transition and satellite edge. The intensity from the shaded area of the satellite was flipped down to the central transition.
### Energy Levels for Oxygen

<table>
<thead>
<tr>
<th>Energy Level</th>
<th>Excess Population in equilibrium</th>
<th>Excess Population after satellite flip</th>
</tr>
</thead>
<tbody>
<tr>
<td>m = -5/2</td>
<td>-5σ</td>
<td>-5σ</td>
</tr>
<tr>
<td>m = -3/2</td>
<td>-3σ</td>
<td>-1σ</td>
</tr>
<tr>
<td>m = -1/2</td>
<td>-1σ ↕</td>
<td>-3σ ↕</td>
</tr>
<tr>
<td>m = 1/2</td>
<td>+1σ ↘</td>
<td>+1σ ↘</td>
</tr>
<tr>
<td>m = 3/2</td>
<td>+3σ</td>
<td>+3σ</td>
</tr>
<tr>
<td>m = 5/2</td>
<td>+5σ</td>
<td>+5σ</td>
</tr>
</tbody>
</table>

Figure 3.7. Energy levels and excess population of oxygen. In equilibrium, there is a difference of 2σ between m=1/2, -1/2 levels, which can be measured by a spin echo on the central transition. After a flip of the satellite, there is a population difference of 4σ (although this affects only sites, orientations which have been flipped). Thus a spin echo on the central transition will have a greater intensity after the satellite is flipped.
After applying the soft pulse to the satellite edge, we immediately perform a second spin echo on the central transition. The contribution to the spin echo from most of the spins remains the same. However, the contribution to the echo due to \( O(2,3) \) spins along \( c \) is larger than it was the previous time. This is because \( O(2,3) \) spins along \( c \) now have an increased population difference between the \( m=+1/2 \) and \( m=-1/2 \) levels.

By subtracting the first echo from the second echo, the contribution of \( O(2,3) \) spins along \( c \) can be identified, and the resonance frequency can be determined from the resulting (relatively narrow) lineshape. The resonance frequency obtained from this analysis was used (through Equation 3.11) to calculate the \(^{17}\text{O}\) shift at various temperatures.

The \(^{17}\text{O}\) NQR frequencies of \( v_{\alpha}=(.954,-.584,-.362) \) MHz at 270 K are known from the work of Yoshinari [114]. We assumed the \(^{17}\text{O}\) NQR frequency would have the same temperature dependence as does the \(^{63}\text{Cu}\) NQR frequency; extrapolating the temperature dependence seen in copper gives a 2.1% decrease of the NQR frequencies between 290 and 710 K. This results in approximately a 4.2% change in the second order quadrupolar shift, which itself is quite small (11% of the Knight shift).
Thus, it is quite simple to correct for the second order quadrupole shift. The shift associated with the (slightly magnetic) high temperature probe has been corrected for as described in section 3.3.1.

Subsequent to our use of this method to measure the $^{17}$O shift we learned of work by Haase et al [115] which provides a general framework, with specific examples, for a family of double resonance techniques designed to isolate and make measurements, including shifts, $T_1$'s, and $T_2$'s, on desired subsets of NMR spins. The method which we employ here is one specific realization of Haase's ideas, illustrating their great utility.

3.1.4.2. Inversion Recovery Sequence for Oxygen $T_1$ Measurement

$T_1$ is the characteristic time constant for the net magnetization to recover its equilibrium value parallel to the static field, following a change in the magnetization caused by a rf pulse. For a spin $5/2$ nucleus such as $^{17}$O (actually, for any spin other than 1/2), the relaxation of the magnetization towards its equilibrium value is most often multiexponential. Multiple exponentials appear since transitions occur between various sets of energy levels. There are different transition
rates corresponding to the different sets of levels [32], although all the rates can be calculated in terms of the constant $T_1$. In order to understand the relaxation from a given initial state, one must solve a normal modes problem. In general, the relaxation for $^{17}$O will involve a sum of five exponentials. For the case of relaxation following an inversion of the first satellite transition (see Appendix A),

$$M(t) = M_\infty \{2 - \alpha \left(\frac{1}{35}\exp(-t / T_1) + \frac{3}{56}\exp(-3t / T_1) + \frac{1}{40}\exp(-6t / T_1) + \frac{25}{56}\exp(-10t / T_1) + \frac{25}{56}\exp(-15t / T_1)\right)\}$$

where $\alpha=2$ for a complete inversion.

The sequence used to measure the recovery of the magnetization following the inversion of the oxygen central transition is known as an inversion recovery sequence [108]. A $\pi$ pulse is used to invert the satellite transition; immediately following the pulse $M = -M_\perp$. Next, the magnetization is allowed to relax toward equilibrium for a period of time $\tau'$. At time $\tau'$ a spin echo is performed to observe how much of the magnetization has recovered. The amplitude of the spin echo (as discussed later in this section, we actually recorded the intensity at a particular frequency) is proportional to $M(\tau')$. Finally, the magnetization is allowed to almost fully return to its equilibrium value during the last delay.
LD is typically 8 times as long as the expected $T_1$; this allows the magnetization to return to 99.99% of its equilibrium value.

One difficulty with the oxygen measurement is that we were working with a powder sample, in which the individual crystallites were unaligned and thus were randomly oriented with respect to the applied field. We wanted to know the relaxation rate of the $O(2,3)$ spins whose crystal c-axis was aligned with the static field. In order to measure the relaxation of only the desired spins, we worked on the edge of the powder pattern where there is a peak which corresponds to the desired spins. However, at the peak frequency there still was a background of spins with other positions or orientations. To correct for the background signal, we used the technique pioneered by Martindale et. al. [97], in which we recorded $M(\tau')$ both at the peak of the powder pattern edge and near the base of the powder pattern edge. (See Figure 3.8). The magnetization at the peak was due mostly $O(2,3)$ along c, but also to the background from other spins; the magnetization at the baseline is due to the background from other spins. We could obtain the contribution just from $O(2,3)$ spins along c by subtracting $M(\tau')$ at the baseline from $M(\tau')$ at the peak.
Figure 3.8. High frequency satellite of oxygen used in the oxygen $T_1$ measurement. The two labeled lines indicate the peak and baseline positions at which $M(t)$ was obtained, as explained in the text. Data from 350 K.
Figure 3.9. Oxygen magnetization (echo size) vs time since the inversion pulse, for an inversion recovery experiment at 320 K. Diamonds are experimental points, and the solid line is a fit.
Figure 3.10. Deviation from equilibrium magnetization, $M_0 - M(t)$, for an inversion recovery experiment on $^{17}$O at 320 K. Diamonds are experimental points, and the solid curve is a fit.
M(τ') was measured for 10 different values of τ'. We deemed that 10 values of τ' be enough to accurately determine $T_1$; there were a total of 3 fitting constants ($M_0$, $α$, and $T_1$) to be determined from the 10 experimental values of $M(τ')$. The values of $τ'$ ranged from 1 $\mu$s (the shortest time we could use) up to approximately 1.5 $T_1$. The data were fit with the commercial program KaleidaGraph (Synergy Software) which uses [116] the Levenberg-Marquardt algorithm, a non-linear least squares routine [117, 118]. The curve-fit is illustrated for a typical measurement in Figures 3.9 and 3.10.

3.1.4.3. Carr-Purcell-Meiboom-Gill Sequence

We have already seen that the magnetization from a decaying FID can be refocused in a spin echo sequence. We will now examine how the initial spin echo itself can be refocused many times. By refocusing the echo multiple times, we will increase the total observable signal and thus enhance the signal-to-noise. This is a great advantage, particularly for nuclei such as $^{89}$Y which have a small signal and long $T_1$. 

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Figure 3.11. A Carr-Purcell-Meiboom-Gill sequence. The top line shows the rf pulses used in this sequence. The second line illustrates the transverse magnetization; the gray line represents the real part. The third line shows the times during which data is acquired; data is acquired only during one precession period (relative to the oscillator) for each echo.
Figure 3.12. Echo train from Carr-Purcell-Meiboom-Gill sequence in $^{89}$Y in YBCO at 320 K. This is from a $T_1$ experiment; $\tau'$ is 45 seconds (3.5 $T_1$). The first 65 echoes (25 msec) of the 256 total echoes (98 msec) are shown. This data has not yet been weighted by an exponential.
Figure 3.13. Carr-Purcell-Meiboom-Gill echo train. (a) The first 5 msec (13 echoes). (b) Echoes from milliseconds 15 – 20 (echoes 39 – 52). This is the same data as is shown in Figure 3.12.
Figure 3.14. When a single spin echo is Fourier Transformed (FT), the result is a smooth lineshape. When an echo train is Fourier Transformed, the result is a series of spikes, spaced at frequency $1/T_{\text{rep}}$, whose magnitude follows the "envelope" of the lineshape.
The sequence for an echo train (multiple refocuses of the echo) is to apply a $\pi/2$ pulse to rotate the magnetization into the xy-plane, wait a time $\tau$, apply a $\pi$ pulse, wait $\tau$, observe the echo, wait $\tau$, apply a second $\pi$ pulse, and observe a second echo after a time $\tau$. This is illustrated as

$$(\pi/2)_x \rightarrow \tau \rightarrow (\pi)_y \rightarrow \tau \rightarrow \text{echo} \rightarrow \tau \rightarrow (\pi)_y \rightarrow \tau \rightarrow \text{echo} \rightarrow \ldots$$

The last four steps can be repeated many times as desired. This sequence was first used by Carr and Purcell [119], and was then improved by Meiboom and Gill [119]; it is referred to as a CPMG sequence.

Due to both $T_1$ relaxation and $T_2$ decay which is not completely refocused, the magnetization at the peak of the each echo will be smaller than that of the previous echo. This limits the number of echoes which are observable. We used such an echo train when measuring the yttrium $T_1$'s. We acquired 256 echoes; the 50th echo had an amplitude that was roughly 15% that of the initial echo. Depending on the parameters used, the first 50 - 100 of the echoes were significantly larger than the noise. The rational for acquiring so many echos is explained in section 3.1.4.4.

We analyzed the echo train by acquiring data only near the peak of the spin echo, as illustrated in Figure 3.11. We choose the oscillator
frequency such that the offset (between the resonance and the oscillator frequencies) was the inverse of the acquisition time (the length of time we acquired data during one echo – 384 μs for our yttrium experiment), $\omega_{\text{offset}} = 1/T_{\text{acq}}$. This meant that there was one precession period, relative to the oscillator frequency, during each acquisition of an echo, and that the precession periods from adjacent acquisition windows matched up smoothly. Typical time domain data is shown in Figures 3.12 and 3.13.

Once the data were acquired, we analyzed the echo train by multiplying the time domain data by a decaying exponential (typically 5 – 10 Hz). This is an important step. It ensures that the earlier echoes, which had a larger (S/N) were weighted more heavily in the Fourier transform than were the later echoes, which had a much smaller (S/N).

The Fourier transform of a repeated function which is also decaying (such as our echo train) is a series of spikes at the repetition frequency ($1/T_{\text{acq}}$). As illustrated in Figure 3.14, these spikes follow the envelope which would result from Fourier transforming a single part.

We had chosen $T_{\text{acq}}$ such that $1/T_{\text{acq}}$ was greater than the yttrium linewidth of 2.4 kHz. In this way, our signal intensity consisted of a single spike which represented contributions from the entire lineshape. That is,
the single spike was essentially a powder average over the different orientations of crystallites in the powder we were using.

As far as we know, Fourier transforming the entire echo train, rather than adding the echos together to obtain a single large echo in the time domain before Fourier transforming, is a unique approach to analyzing a CPMG echo train. It was the simpler approach to use with the particular software we use to control our analog-to-digital converter and to analyze the data. However, our result is identical to the traditional approach when one considers the contributions of all spins to the powder average.

3.1.4.4. Saturation Recovery for Yttrium $T_1$ Measurement

$T_1$ is the characteristic time needed for the net magnetization to return to its equilibrium value, aligned along the static field. For a spin 1/2 nuclei, such as $^{89}$Y, the relaxation of the net magnetization of the spin system towards its equilibrium value follows a single exponential, i.e.,

$$M_m - M(\tau) \propto \exp(-\tau / T_1).$$

To measure the $^{89}$Y spin lattice relaxation rate, we saturated the magnetization, such that the orientation of individual spins are oriented
randomly in the xy-plane and there is no net magnetization (M=0). We then wait a time τ' before using the CPMG echo train (discussed in section 3.1.4.4.) to observe the magnetization M(τ'). Saturating the magnetization and then waiting a time τ' to observe how much of the magnetization has recovered is known as a saturation recovery experiment [108].

It turned out, conveniently, that the same pulses which are used to observe the echo train also serve to saturate the magnetization. This is why more echoes were used in the CPMG sequence than were needed to observe the signal. Using the same pulses for both saturation and the echo train saved time in the sequence, yielding a higher (S/N) value for a given total measurement time.

This sequence was repeated for 10 values of τ'. The values of τ' ranged from one second (which corresponds to 6% of the equilibrium magnetization at room temperature) up to three times T₁, at which point the magnetization had recovered to 95% of its equilibrium value. The resulting data were fit to

\[ M(\tau') = M_0(1 - \alpha \exp(-\tau' / T_1)). \]  \hspace{1cm} (3.13)
Figure 3.15. Yttrium magnetization $M(t)$ vs time for a saturation recovery experiment at 320 K. The diamonds are experimental data; the solid curve is a single exponential fit.
Figure 3.16. Deviation from equilibrium magnetization, $M_0 - M(t)$, for a saturation recovery $T_1$ experiment on $^{89}$Y at 320 K. Diamonds are experimental points, and the solid curve is a fit. This is the same data as is plotted in Figure 3.15.
$M_\infty$, $\alpha$, and $T_1$ were all fitting parameters; $\alpha$ was close to 1. The data was fit with the commercial program KaleidaGraph (Synergy Software). A typical fit is illustrated in Figures 3.15 and 3.16.

3.1.4.5 Phase Cycling

In any NMR measurement, whether it is a measurement of the resonance frequency of a nucleus or the $T_1$ relaxation time, one wants a large signal-to-noise ratio (S/N). This allows a more precise measurement with smaller experimental uncertainties. The signal-to-noise ratio can be enhanced either by increasing the signal in a single scan (using a larger sample, for example), increasing the number of scans ($\langle S/N \rangle$ for a large number of scans is proportional to the square root of the number of scans), or else by decreasing the noise.

Phase cycling is one method for increasing $\langle S/N \rangle$ by canceling the ringdown -- the repeatable (not random) transient signal from the electronics in the receiver after a power pulse is used to produce an rf magnetic field. This transient signal can partially obscure spin echoes, as well as FIDs. In phase cycling, the angles along which $\pi$ and $\pi/2$ pulses of a spin echo are performed are cycled. This will allow one to cancel the
ringdown from the pulses while adding the signal from the echo [120]. Unwanted stimulated echoes will also be cancelled [121, 122].

An initial spin echo can be collected by applying a $\pi/2$ pulse along the $x'$ axis, waiting a time $\tau$, applying a $\pi$ pulse along the $x'$ axis, and then observing the echo which will form along the $-y'$ axis. This is the sequence which was discussed in section 3.1.2.2 on spin echoes, and is schematically illustrated as

$$(\pi/2)_x -- \tau -- (\pi)_x -- \tau -- \text{observe echo along } -y$$

A second spin echo can be collected as

$$(\pi/2)_x -- \tau -- (\pi)_y -- \tau -- \text{echo along } +y.$$  

If these two signals are subtracted from each other, any ringdown from the $\pi/2$ pulse will be subtracted. However, the signal which forms along $-y$ in the first echo and along $+y$ for the second echo will be added together.

The ringdown from the $\pi$ pulses can be cancelled by using

$$(\pi/2)_x -- \tau -- (\pi)_x -- \tau -- \text{echo along } +y \text{ (subtract)}$$

$$(\pi/2)_x -- \tau -- (\pi)_y -- \tau -- \text{echo along } -y \text{ (add)}$$

Phase cycling can also be used to eliminate a problem known as a quadrature ghost. In our experiments we use quadrature detection [32]
to observe both the real and imaginary parts of the spin echo (i.e., two independent components of the complex signal that have a relative phase shift of $\pi/2$) at the same time. We split the signal into two channels, which are mixed with an rf frequency (with a relative phase shift of $\pi/2$ between the two channels) to produce the real and imaginary low frequency (beat) signals which are sent to an analog-to-digital converter. (This is discussed further in section 3.3.2.) However, the amplifiers and ADCs might have slightly different gains, causing one channel to (falsely) appear larger than the other. When such data is Fourier transformed, a "ghost" shows up at the negative of the true frequency.

The quadrature ghost can be eliminated by a phase cycle in which all of the pulse lines are rotated by $\pi/2$ to switch the channel through which the real and imaginary signals travel. The final signal must be multiplied by $\pm i$ (rather than simply adding or subtracting) so that the desired signal adds correctly. Over 8 echoes, the real and imaginary signals will have experienced the same gain. The additional sequence of 4 lines are shown below.

$$(\pi/2)_y - \tau - (\pi)_y - \tau - \text{echo along } -x \text{ (mult by } +i)$$

$$(\pi/2)_y - \tau - (\pi)_x - \tau - \text{echo along } +x. \text{ (mult by } -i)$$
\[ (\pi/2)_y - \tau -- (\pi)_y -- \tau -- \text{echo along } +x \text{ (mult by } -i) \]

\[ (\pi/2)_y - \tau -- (\pi)_x -- \tau -- \text{echo along } -x \text{ (mult by } +i) \]

Such an 8 cycle phase cycling routine was used with all spin echo measurements. In the yttrium T₁ measurements which utilized a CPMG sequence, a four line phase cycling was used to eliminate ringdown from the π pulses and to eliminate any quadrature ghost.

3.2. Samples

The samples used in the experiments described in this thesis are powder samples of YBa₂Cu₃O₇-δ; that is, each sample contains a large number of small (typically less than 40 microns in diameter) crystallites. The preparation and characterization of the powder is discussed in section 3.2.1. The rationale for using an unaligned sample is discussed in section 3.2.2. The oxygen content of our samples is discussed in section 3.2.3.

3.2.1. Sample Preparation and Properties

The samples we used were all from a single batch of YBa₂Cu₃O₇-δ powder. The powder was made by Hults and Smith, using standard
<table>
<thead>
<tr>
<th>MEASUREMENT</th>
<th>TEMPERATURE RANGE (K)</th>
<th>SAMPLE</th>
<th>DATES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yttrium T₁</td>
<td>290 - 710</td>
<td>A</td>
<td>10/96 - 2/97</td>
</tr>
<tr>
<td>SQUID (Tₛ)</td>
<td>10 - 110</td>
<td>B</td>
<td>2/97</td>
</tr>
<tr>
<td>Oxygen T₁</td>
<td>290 - 710</td>
<td>B</td>
<td>5/97 - 6/97</td>
</tr>
<tr>
<td>Oxygen shift (mag. probe)</td>
<td>290 - 710</td>
<td>B</td>
<td>7/97</td>
</tr>
<tr>
<td>Yttrium T₁</td>
<td>290 - 590</td>
<td>B</td>
<td>8/97 - 9/97</td>
</tr>
<tr>
<td>Yttrium shift (mag. probe)</td>
<td>290 - 710</td>
<td>B</td>
<td>9/97</td>
</tr>
<tr>
<td>SQUID (Tₛ)</td>
<td>10 - 110</td>
<td>A2</td>
<td>11/97</td>
</tr>
<tr>
<td>Yttrium shift</td>
<td>290 - 430</td>
<td>A1, B</td>
<td>11/97</td>
</tr>
<tr>
<td>Oxygen shift, T₁</td>
<td>100 - 290</td>
<td>B</td>
<td>5/98</td>
</tr>
<tr>
<td>Yttrium shift, T₁</td>
<td>100 - 290</td>
<td>A1</td>
<td>5/98 - 6/98</td>
</tr>
<tr>
<td>Yttrium shift</td>
<td>300 - 523</td>
<td>A2</td>
<td>2/99</td>
</tr>
<tr>
<td>Yttrium shift</td>
<td>290</td>
<td>A1, A2, B</td>
<td>2/99</td>
</tr>
</tbody>
</table>

Table 3.1. List of experimental measurements and the sample(s) upon which they were performed. The shift measurements performed in a magnetic probe are indicated.
techniques as described in reference [123]. After the powder was prepared, it was separated into portions to be used as separate samples. Sample A, 3.56 grams, was used as prepared. Sample B, 1.36 grams, was enriched with oxygen-17, as described below. After some of the measurements were completed, sample A was split into two smaller samples, A1 (2.25 grams) and A2 (1.31 grams); this facilitated using the same coil for measurements on sample A1 as was used for measurements on sample B. Table 3.1 lists the different samples and the experiments for which they were used.

We enriched sample B with oxygen-17 to increase the oxygen NMR signal and allow measurements at the oxygen sites; natural abundance oxygen is composed of 99.96% oxygen-16, which has intrinsic spin zero and thus is not observable with NMR, and only 0.04% oxygen-17 (spin 5/2) which is observable with NMR. The sample was enriched with oxygen-17 in an oxygen transfer procedure: in the presence of oxygen-17 enriched O₂ gas, the sample is heated to 1200 K at which temperature oxygen will continuously leave and re-enter the sample; during this process some of the oxygen-16 is replaced by oxygen-17. Sample B was enriched with oxygen in such a procedure, described in more detail in
reference [124], by Dr. Joseph Martindale. Since oxygen leaves the sample and is replaced during this process, the oxygen content of the sample can be changed slightly during the oxygen enrichment; it is possible that samples A and B might have slightly different oxygen contents.

The T$_c$'s of samples A and B were determined from SQUID magnetometer measurements of the magnetization versus temperature. (The samples were zero field cooled before a magnetic field of 20 Gauss was introduced). Sample B has an onset transition temperature of 92 K, with 50% of maximum shielding occurring at 88 K. Sample A also has a T$_c$ near 92 K and a similarly narrow transition (65% of maximum shielding at 89 K). The magnetization curves are shown in Figure 3.17.

3.2.2. Unaligned Powder

YBCO is anisotropic, i.e., its properties are different along the different crystal axes. For this reason, we often want to measure a property (such as T$_1$ or Knight shift) along a single crystal axis rather than measuring an average over all the axes. However, our sample is a
Figure 3.17. Zero-field cooled SQUID susceptibility. The magnetic moment (normalized to -1 at 10 K) is shown for both oxygen enriched and non-enriched samples. The vertical line at 92 K is to guide the eye.
powder consisting of a large number of crystallites, which are all randomly oriented; this makes measurements along a single axis difficult.

One common method for dealing with a powder sample is to partially align the sample by utilizing the orientational dependence of the energy of a crystallite in a magnetic field (due to the anisotropy of the magnetic susceptibility). In YBCO, the crystallite will have the lowest energy if it is oriented with the crystal c-axis along the static field. Using the technique of Farrell et al [125], the YBCO powder can be mixed in epoxy and placed in a strong magnetic field. The crystallites will experience a torque due to the magnetic field and align with the field; as the epoxy hardens, the orientation of the crystallites will be permanently fixed. Unfortunately, typical epoxies cannot be used above about 500 K [126]. Thus, we could not use a sample aligned in epoxy for our high temperature measurements up to 700 K.

We attempted to align the sample in some other materials. We tried mixing a small amount of YBCO powder in a molten salt -- a mixture of 52% CaCl₂ and 48% NaCl that will melt when brought to 770 K and will form a eutonic mixture upon cooling. Unfortunately, the YBCO powder clumped together such that the crystallites were not separated from each
other and would interfere with the rotation of neighboring crystallites, which would hinder proper alignment [120].

We also tried aligning YBCO powder in a cement powder (Sauereisen Electrotemp Ceramic cement). The YBCO powder mixed nicely in the cement powder and did not show visible signs of clumping. However, when we tried aligning YBCO powder in the cement, we found that the central transition for the planar copper along c had a width of 140 kHz, corresponding to an essentially unaligned sample (a completely unaligned sample prepared in epoxy had a linewidth of 160 kHz whereas a well aligned sample has a width of about 20 kHz [120]). We had similar results with the Sauereisen cement ground to a finer powder and with a second type of cement. Thus, neither the molten salt nor the ceramic powder were appropriate materials in which we could align YBCO powder.

Thus, we had no alternative to performing our experiments on an unaligned sample. While this makes the experiments more difficult, they are still possible. We have to deal with the "powder pattern" which results from spins at different orientations relative to the applied field experiencing different chemical and Knight shifts (and different quadrupolar interactions for oxygen) and thus having a range of
resonance frequencies (recall Equations 3.9 and 3.11). The range of resonance frequencies is indicated schematically in the powder pattern shown in Figure 3.18, although oxygen, a spin $\frac{5}{2}$ nucleus has a more complicated powder pattern due to the quadrupolar satellites. The oxygen picture is further complicated by spins at inequivalent lattice sites which have strongly overlapping powder patterns. For the oxygen measurements, we were able to use the methods described in section 3.1.4 to isolate the spins which had the desired orientation. For yttrium, the properties are close enough to isotropic that we decided to measure a "powder average" (i.e. an average over the different orientations which are possible in the powder sample) of the properties.

3.2.3. Oxygen Concentration

An important property of $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$ is the oxygen content of a particular sample. The oxygen content can vary smoothly between $O_{6.0}$, which is an antiferromagnetic insulator and not a superconductor; to $O_{6.5}$, around which doping level superconductivity starts, and which has a $T_c$ near 60 K; to $O_{6.95}$ which is referred to as "optimal doping" since it produces the highest $T_c$'s of 93 K; up to $O_{7.0}$ which is slightly overdoped.
Figure 3.18. A powder pattern for a non-axially symmetric spin 1/2 nucleus. The range of frequencies over which there is NMR intensity is schematically illustrated.
Any material which has an oxygen content near $O_{6.9}$ or $O_{7}$ will have many similar properties, including a critical temperature of approximately 90 K, and is often grouped together with similar samples referred to as “90 K” or $O_{7}$ material. However, there are slight, but important, distinctions between samples all on the 90 K “plateau” \cite{127}.

The reason that the oxygen content of a sample is so important is that it is related to the hole content in the CuO$_2$ planes. In general, as the oxygen content increases, so do the number of holes in the planes. The hole concentration appears to determine many properties of the material. However, this is complicated since there is not necessarily an exact correspondence between the oxygen concentration and the concentration of holes in the planes.

We were obviously interested in determining the oxygen concentration of our samples. We used two methods for determining the oxygen concentration. First, we performed a SQUID measurement of magnetization versus temperature on sample B (and later, after completion of high temperature measurements, on sample A2). From this plot, we could determine the temperature (onset $T_c$) at which screening first occurred and superconductivity appears. We observed an onset $T_c$
near 91 K, in both samples, as reported in section 3.2.1. A $T_c$ near 90 K tells us that we have a "90 K" material rather than a "60 K" material but cannot give us more specific information.

A more precise way to check the oxygen content is to observe the Knight shifts of both oxygen and yttrium. There is a well known "spin gap" effect in which the underdoped materials show an effective gap in the density of states and consequently the Knight shift of these materials drops above $T_c$, as has been discussed more fully in section 2.2.5. The more underdoped a material is, the higher the temperature at which the Knight shift starts to decrease. Thus, a measurement of the Knight shift, and the temperature at which the "spin gap" appears, can be used to determine the oxygen concentration.

After we had completed nearly all of the high temperature measurements on samples A2 and B, we measured the Knight shift of yttrium in sample A2 and the Knight shift of Oxygen in sample B between $T_c$ and room temperature. We compare our yttrium shifts to the data of Alloul et al [63], in which the shift was measured for various known oxygen contents. (See Figure 3.19). Comparing the extent of our measured "spin gap" effect with that observed by Alloul et al, we
conclude that our non-enriched sample had an oxygen content close to that of O$_7$. In our oxygen-17 enriched sample, we compared the extent of the “spin gap” effect measured on the $^{17}$O nucleus with that observed by Yoshinari et al. [114] and find that the oxygen content is close to or greater than O$_{6.9}$. (See Figure 3.20). The oxygen enriched sample shows more of a spin gap and thus has a slightly lower oxygen concentration than the non-enriched sample. However, after completion of the high temperature measurements, both samples have an oxygen content greater than O$_{6.9}$.

One problem with the above measurements is that they do not directly probe the oxygen concentration while the sample is at high temperature. Since oxygen can leave the samples at high temperatures, there is a concern that the oxygen content might be different at our highest experimental temperatures.

To minimize this effect, we utilized the fact that a partial pressure of oxygen will inhibit oxygen from leaving the sample [128]. Thus, as oxygen leaves the sample in any appreciable quantity it sharply increases the PO$_2$ in the surrounding environment, thereby increasing the
Figure 3.19. Yttrium shift vs temperature. Filled circles are sample A; open circles are Alloul's data [63] for various known oxygen concentrations, as indicated in the key.
Figure 3.20. Oxygen Knight shift vs temperature. Filled circles are sample B; open symbols are Yoishinari's samples [114] of known oxygen concentration, as indicated in the key.
Figure 3.21. Shape of a typical sample container. Not to scale.
equilibrium concentration of oxygen in the sample at that temperature and preventing further oxygen from escaping.

For this reason, we sealed each sample (except sample A1 which was never used for high temperature measurements) in a small quartz container that was designed to have as little excess space (space not taken up by the high T_c material) as possible. The sample containers we used are illustrated schematically in Figure 3.21. Our containers were created and sealed by the scientific glassblower employed by the Ohio State University. We attempted to make the body of the container the same volume as the powder. The inverted “ice cream cone” at the top was used to pour the powder into the container and was the final part sealed. The samples were sealed under a partial vacuum to ensure that the pressure (which increases as temperature increases according to Boyle’s law) does not become excessive enough to cause the container to explode. During the sealing process, the body of the container was submerged in liquid nitrogen to keep the sample cool.

Knowing the molecular weight of YBa_2Cu_3O_y is 666.2 grams/mol and the lattice constants [129] of a unit cell of YBa_2Cu_3O_7 are 3.82 Å, 3.88 Å, and 11.67 Å, we calculate that YBa_2Cu_3O_7 has a density of 6.40
grams/cm³ (although any powder sample will have a packing fraction less than unity and thus have a lesser density). From the density of the material, the weight of powder in each sample, and the estimated volume (including the "ice cream cone" area) of the sample container, we estimate that each sample occupied 50% ± 10% of the container volume.

Consulting equilibrium concentration measurements of Gallagher et al [128] we find that a partial oxygen pressure of 2 atmospheres at 700 K is sufficient to keep the oxygen concentration in the superconducting sample greater than O_{6.9}; however we calculate that a sample volume that occupies 50% of the container will result in an oxygen partial pressure of 5 atmospheres for a very modest loss of 2% of the oxygen at one oxygen site (i.e., O_7 to O_{6.98}). Thus we can be assured that even at the highest temperatures the oxygen concentration should exceed O_{6.9}.

3.3. Apparatus

The experiments described here were performed in a superconducting magnet from Oxford which is run in persistent current mode. Most of the measurements were taken at an applied field of 9.05 Tesla, giving resonance frequencies of 52.250280 MHz for the ^{17}O
resonance of H₂O and 18.886874 MHz for the $^{89}\text{Y}$ in YCl₃. Depending on the temperature range of the measurement, either a high temperature probe (described in section 3.3.1) or a standard non-magnetic brass probe was used. The room temperature yttrium shift of the different samples (A1, A2, and B) was later taken at a field of 9.00 Tesla, giving a resonance frequency of 18.791444 MHz for the $^{89}\text{Y}$ in YCl₃. The yttrium shift of sample A1, however, was measured between 290K and 530K in a standard non-magnetic probe in a 400 MHz Bruker solid state NMR facility in a field of 9.4 Tesla with a yttrium resonance frequency of 19.608122 MHz.

### 3.3.1. High Temperature Probe

In order to make measurements up to 700 K, we needed a special probe. Standard probes cannot be used at high temperatures since they lack a method of heating the sample and since they contain no insulation to protect the magnet or keep heat from solder or Teflon probe parts (such as capacitors) which can melt.
Figure 3.22. Schematic diagram of the high temperature probe.
Figure 3.23. Shift in $^{39}$K resonance frequency, as a function of temperature, measured in the high temperature probe.
A previous student in the lab, Chris Hahm, designed and built the high temperature probe which we used for many of the measurements described in this thesis. It is illustrated in Figure 3.22. The basic design is that the sample chamber is housed at the end of an insert; the insert also houses a capacitor chamber which is insulated from the sample chamber. A heater tape (High temperature Thermolyne 468 Watt tape) winds around a metal annulus that surrounds the sample region of the insert, and a K-type (Ni-Cr and Ni-Al leads) thermocouple is attached to the annulus near the end of the heater tape. (Unfortunately with this arrangement, the thermocouple is closer to the heater tape than to the sample. We typically waited at least one hour after reaching the desired temperature before taking any measurements to ensure that the sample had equilibrated to the desired temperature). Surrounding the heater was a vacuum region to provide for thermal insulation, which was further surrounded by a water jacket to cool the outside of the probe.

The placement of the heater proved to be a difficulty with the probe – whenever the heater tape broke, it was necessary to disassemble the entire probe to repair or change the heater tape. We had significant problems with the heater tape burning, although we were operating at the
rated voltage. We solved the problem by using a variable transformer to decrease the voltage going to the heater, using the smallest voltage which would keep the probe at the desired temperature (typically between 30% of the rated voltage at 350 K and 75% at 700 K). It is possible that this problem was caused or exacerbated by poor thermal contact between the metal annulus and the heating tape.

This probe included parts made of stainless steel, due to its strength and desirable thermal properties relative to the usual material of choice for a probe, which is brass. The inclusion of stainless steel, which we found to be slightly magnetic, had the undesirable effect of contributing a shift, relative to a brass probe. Matt Buoni and Karen Nippert measured the shift at room temperature to be −170 ppm. Observing the $^{89}\text{K}$ resonance of KCl, we measured the resonance frequency in the probe as a function of temperature. (The resonance frequency of $^{39}\text{K}$ in KCl has been measured by Ron Groves to be temperature independent between 200 K and 400 K within the experimental error of less than 1 ppm.) The shift associated with the probe changed by approximately 100 ppm as the temperature increased from room temperature to 710 K, as illustrated in Figure 3.23. (An
earlier measurement by Chris Hahm on $^{87}$Rb in RbCl showed a change of shift associated with the probe of only ~60 ppm over a similar temperature range.) The added shift from the probe behaved hysteretically with temperature cycling, with variations of some 10 – 20 ppm from one run to the next.

This shift is small (but not negligible) compared to an oxygen shift of ~0.16%. We used the data shown in Figure 3.23 to calibrate the probe and correct for the shift due to the probe during measurements of the oxygen shift. Any deviation from our calibration due to hysteresis of the probe was considered too small to be consequential.

However, the yttrium shift is only ~100 ppm, and so, for the most precise yttrium shift measurements, it was not adequate to calibrate the probe in advance. Therefore, during all $^{89}$Y shift measurements made in the high temperature probe we placed a separately sealed sample of KCl directly into the NMR coil along with the YBa$_2$Cu$_3$O$_7$ sample. At each temperature, we measured both the yttrium frequency and the reference frequency of $^{39}$K.
3.3.2. Spectrometer

The spectrometer used for our NMR measurements was a homebuilt spectrometer which utilized an ARIES Signal Averager (from Tecmag) as a pulse programmer and analog-to-digital converter (ADC); it was controlled with the MacNMR software from Tecmag. Figure 3.24 shows the design of the spectrometer.

The pulse programmer had 24 control lines which could be used for producing TTL signals from 1 μs up to 99 μs in duration, with 0.1 μs increments. We typically used one TTL line to control the rf gate to produce the rf pulses, a second line to gate the amplifier and a third line as a trigger for our oscilloscope. Four TTL lines went to our oscillator, a PTS 310, to control the phase of the rf pulse; this was required for phase cycling. The PTS 310 oscillator can produce output frequencies between 0.1 and 309.999999 MHz with a resolution of 1 Hz.

To run an experiment, one would use the MacNMR software to set the desired pulse lengths, separations, and phases as well as the parameters to control the ADCs. The ARIES would send appropriate TTL signals to the rf gate, which is used to produce pulses from the continuous wave output of the oscillator which are then amplified with
the power amp. The peak-to-peak voltage (typically between 100 and 500 V) of these amplified pulses is set by appropriately attenuating the oscillator signal to the rf gate. The rf pulses are then sent to the probe, after passing through a series of crossed diodes to block noise.

In the probe was a resonance circuit which contained a coil, of inductance L, into which the sample was inserted. The coil was used both to provide a rf magnetic field (as describe in Section 3.1.2) and to monitor the signal resulting from the emf induced in the coil by the spins precessing about the static field (also discussed in section 3.1.2).

The resonance circuit included two variable capacitors as shown in Figure 3.25. The capacitors have capacitance $C_m$ and $C_t$, and are known, respectively, as the “matching” and “tuning” capacitors. The variable capacitors are used to tune the circuit so that at frequency $\omega_0$ the complex circuit impedance matches the impedance used in most rf devices, which is 50 Ohms real and zero ohms imaginary ($Z_0 = 50 \text{ Ohms} + 0 \text{ i}$); matching the impedance is necessary to transfer the maximum power between the coil and the rest of the spectrometer [130, 131]. In the limit of a large quality factor ($Q = \frac{\omega L}{R}$), the capacitance...
needs to be adjusted such that \( \omega = \frac{1}{\sqrt{L(C_m + C_r)}} \) and \( C_m^2 = \frac{1}{QZ_0\omega L} \), where

\( Z_0 \) is 50 Ohms.

The induced voltage in the coil was sent through a quarter wavelength (\( \lambda/4 \)) cable to the preamplifiers where it was amplified by typically 50 – 70 dB. The \( \lambda/4 \) cable which ends with a diode (actually contained in the first preamplifier) allows the low voltage signal from the probe to reach the preamplifiers, while blocking the high voltage pulses (typically 200 – 400 volts peak-to-peak) [131, 132].

The amplified signal was split into two channels and then mixed down to near dc frequency. One channel was mixed with a rf signal with a phase of 0° relative to the oscillator, and the second channel was mixed with rf at 90° relative to the oscillator. In this way we could monitor both the “real” (0°) and “imaginary” (90°) signal at the same time. It is necessary to observe both the real and imaginary signals to determine the sign (positive or negative) of the NMR signal with respect to the oscillator frequency. Signal from both channels was filtered and digitized. The signal averager was a 12-bit digitizer which could digitize at a rate of 1 \( \mu \)s per point (with the real and imaginary channels sampled simultaneously) with a 256k 32-bit word memory.
For the oxygen double resonance experiment, two separate oscillators were used to generate two rf pulse "output channels" (each carried in a separate BNC cable) at the oxygen central transition and satellite edge frequencies. The pulse "channels" were combined with a splitter into a single "channel" carried in a single cable before amplification by the power amplifier. The coil was damped to provide a low enough quality factor of $Q \approx 25 \left( Q = \frac{\omega}{\Delta \omega} \right)$ so that the circuit could be simultaneously tuned at both frequencies. Only a single coil, with the standard single resonance tuning circuit shown in Figure 2.25, was needed to perform the double resonance experiment.
Figure 3.24. Diagram of spectrometer.
Figure 3.25. Resonance circuit.
This chapter will present the experimental results of the magnitude and the temperature dependence of high temperature measurements of both the nuclear spin lattice relaxation rates \(1/T_1\) and Knight shift \(K\) for the planar oxygen and yttrium nuclei in the normal state of superconducting YBa\(_2\)Cu\(_3\)O\(_7\) powder. Many of these results have been reported in reference [17].

The spin lattice relaxation of nuclei is due to interactions of nuclei with fluctuating magnetic fields due to the magnetic moments of electrons. Below room temperature, the oxygen and yttrium relaxation exhibit similar behavior of decreasing rate with increasing temperature; however, the behavior of the copper relaxation is strikingly different [83]. We decided to measure the high temperature behavior of oxygen and
yttrium, extending previous measurements which only probed the behavior up to room temperature [133, 134]. This will allow us to test a significant prediction of a one component model in which the electron susceptibility arises from Cu\(^{2+}\) spins hybridized with O 2p\(\sigma\) holes.

As a step in understanding the temperature dependence of spin lattice relaxation it is necessary to extract from experiment the temperature dependence of the uniform, static electronic spin susceptibility, \(\chi_0\). Since \(\chi_0\) is proportional to the Knight shift, we have also measured the Knight shifts of both oxygen and yttrium over the same temperature range.

We find that the static susceptibility, as measured by both the oxygen and the yttrium Knight shifts, drops by 13\% \(\pm\) 2\% between room temperature and \(\sim 700\) K. The oxygen relaxation rate per unit temperature exhibits similar behavior, with a drop of 14\% \(\pm\) 2\% over the same temperature range. This strongly contrasts with the yttrium relaxation rate, which displays \(\frac{8\gamma(T,T)^{-1}}{T} = \text{constant behavior within the experimental precision of} \pm 4\% \text{ over the full range.}\)

The experimental details have already been fully described in section 3.1.4; only the significant aspects are repeated here. The
experiments were all performed with standard pulse NMR techniques in an applied magnetic field of 9 Tesla.

4.1. Oxygen Spin Lattice Relaxation

The oxygen spin lattice relaxation is due to interactions of the oxygen nuclei with fluctuating magnetic fields from the electronic spins, as described in Equation 2.7. Thus, the temperature dependence of this relaxation can offer clues to the electronic susceptibility, and set limits on possible forms (such as Equation 2.11) of the imaginary susceptibility.

We measured the oxygen spin lattice relaxation of O(2,3) spins with the static field aligned along the crystal c-axis. We made the measurement on Sample B which had been enriched with oxygen-17.

Since we were working with a powder sample, the individual crystallites were unaligned and thus were randomly oriented with respect to the applied field. In order to measure the relaxation of only the desired spins, we used the technique pioneered by Martindale et al[97], in which we recorded the magnetization both at the peak of the powder pattern edge corresponding to the desired spins and near the base of the powder pattern edge. We obtain the contribution just from O(2,3) spins the
static field along the crystal c-axis by subtracting the magnetization at the baseline from the magnetization at the peak.

We used an inversion recovery experiment to measure the relaxation time ($T_1$) to be 10.05 ± 0.12 msec at room temperature (~290 K), in agreement with previously reported results [114, 83]. The relaxation time decreased as the temperature increased, down to a value of 4.79 ± 0.09 msec at 710 K. Results for the relaxation rate, $1/T_1$, vs temperature between 290 K and 710 K are plotted in Figure 4.1, and the relaxation rate per unit temperature, $1/T_1T$ is shown in Figure 4.2. The important result is a drop of 14% ± 2% in $(T_1T)^{-1}$ over this temperature range. The drop is monotonic and approximately linear with temperature.

We have also measured the relaxation time between room temperature and $T_c$. We observe a spin gap opening above $T_c$, suggesting that our sample is slightly underdoped; this is consistent with the Knight shift measurements described in section 3.2.3 on the oxygen concentration.
Figure 4.1. Oxygen spin lattice relaxation rate vs temperature.
Figure 4.2. Oxygen \((1/T_1T)\) vs temperature.
4.2. Oxygen Shift

As a first step in understanding the temperature dependence of spin lattice relaxation it is necessary to extract from experiment the temperature dependence of the uniform, static electronic spin susceptibility, $\chi_o$, which enters into the calculation of the spin lattice relaxation rate through Equation 2.7.

The magnetic shift tensor is composed of three terms, $K = \sigma + K^L + K^S$. Each term in the shift tensor results from, and is proportional to, a different electronic susceptibility. $\sigma$ and $K^L$, both due to the orbital motion of electrons [106, 32] and together known as the "orbital" or "chemical" shift, are independent of temperature. The Knight shift, $K^S$, which is due to the spin angular momentum of the conduction electrons [106, 32], is proportional to the Pauli spin susceptibility [113] of those electrons. Since the Knight shift is proportional to the uniform, static electronic spin susceptibility, $\chi_o$, measurement of the Knight shift determines the temperature dependence of $\chi_o$.

Since our measurements are made on an unaligned powder we receive signals from crystallites having all possible orientations. For the $^{17}O$ NMR central transition the various crystallite orientations yield central
transition resonance frequencies which heavily overlap. In contrast, the transition \((-3/2, -1/2)\) occurs at a resonance frequency which is strongly dependent on crystallite orientation; the orientation with field parallel to the crystal c-axis gives a frequency which is an extrema, and intensity at this identifiable singularity comes from crystallites having the proper orientation. It is not, however, easy to extract the Knight shift from the position of this singularity because it is broadened. Our procedure, then, was to use a soft pulse to "flip" the intensity in this satellite singularity down to the central transition. Knowing that the "extra" central transition intensity is from spins with the field parallel to c, we can easily measure the shift for that field orientation.

The oxygen resonance frequency as a function of temperature measured using this procedure is used to determine the oxygen shift through Equation 3.11. The temperature dependence of the oxygen shift is shown in Figure 4.3. We used an orbital shift of \(-0.008\%\) \([114]\), and \(^{17}\text{O} NQR frequencies of } v_a=(.954,-.584,-.362)\text{ MHz which are known at 270 K }[114],\text{ assuming the }^{17}\text{O NQR frequency would have the same temperature dependence as does the }^{63}\text{Cu NQR frequency (a 2.1\% decrease between 290 and 710K).}
We found a room temperature shift of 0.166%, which is in agreement with previously reported results [64, 114]. The shift is observed to decrease with increasing temperature, decreasing by 13% (i.e., from 0.166% to 0.145%) over this temperature range.

The magnitude of this decrease is not surprising as it continues the decrease observed below room temperature; the spin susceptibility (inferred from Knight shift data) for YBa$_2$Cu$_3$O$_y$ between 200 and 300 K shows a drop of $0.031 \pm 0.003$ % per Kelvin [96], while our oxygen Knight shift exhibits a drop of $0.028 \pm 0.001$ % per Kelvin when fit to a straight line between 300 K and 700 K.

We observe that the oxygen $1/T_1 T$ and the oxygen Knight shift approximately track each other over the entire temperature range, both decreasing with increasing temperature. (See Figure 4.4). The $(T, T)^{-1}$ shows only slightly more temperature dependence than does $^{17}$K; in Chapter 5 we will see that the relaxation rate predicted by the ZBP model [11] based on the temperature dependence of $\chi_0$, fits the experimental $^{17}(T, T)^{-1}$ data extremely well.
Figure 4.3. Oxygen Knight shift vs temperature.
Figure 4.4. $^{17}(T_{1}TK)^{-1}$ vs temperature. $^{89}K$ was interpolated at two temperatures.
4.3. Yttrium Spin Lattice Relaxation

We measured the yttrium spin lattice relaxation rate with a saturation recovery experiment, utilizing a CPMG echo train [119, 135] to increase the signal to noise. The same pulses which are used to observe the echo train also serve as the “saturation comb”.

Measurements on the non-enriched sample (Sample A) give a room temperature relaxation time of 14.72 ± 0.08 seconds. This agrees well with published results [134]. We also performed measurements on the smaller, ¹⁷O enriched Sample B, and found agreement within the somewhat greater experimental error. The measurements on Sample B, along with the Sample A relaxation rate data down to Tᵯ are shown in Figure 4.5.

The relaxation rate is seen to obey 1/Tᵯ = constant, within experimental precision of ±4%, above room temperature. (See Figure 4.6.) The yttrium relaxation rate per unit temperature has the value of 2.38 ± 0.05 10⁻⁴ sec⁻¹ K⁻¹, independent of temperature.

The temperature independence of ⁸⁹(1/Tᵯ) is remarkable; the ⁸⁹(1/Tᵯ) temperature behavior contrasts strongly with that of ¹⁷(1/Tᵯ). To allow comparison of the temperature dependence of the two
Figure 4.5. Yttrium relaxation rate ($1/T_1$) for both sample A and sample B.
Figure 4.6. Yttrium $(1/T_1 T)$ vs temperature.
Figure 4.7. Ratio of $^{17}(1/T_1T)$ to $^{89}(1/T_1T)$ vs temperature.
relaxation rates, we have also plotted the ratio of $^{17}(1/T_1T)$ to $^{89}(1/T_1T)$ in Figure 4.7, as suggested by refs [134] and [136]. It is obvious from inspection of Figure 4.7 that $^{89}\text{Y}$ and $^{17}\text{O}$ have substantially different temperature dependencies. This different temperature dependencies of oxygen and yttrium relaxation have been noted by Takigawa et al. [134] in both underdoped and overdoped YBa$_2$Cu$_3$O$_{7-\delta}$ below room temperature.

Suter et al. [102] find the ratio $^{89}T_1/^{17}T_1$ in Y$_2$Ba$_4$Cu$_7$O$_{15}$ is constant between $\sim$180 K and room temperature; however, with their error bars, their data would also be consistent with a temperature dependence of the magnitude that we observe.

It will be a challenge, as will be discussed in Chapter 5, to explain the temperature independence of $^{89}(1/T_1T)$ as compared to a temperature dependence of $^{17}(1/T_1T)$ which tracks that of $\chi_o$.

4.4. Yttrium Knight Shift

While we had, in principle, already measured the temperature dependence of the uniform, static electronic spin susceptibility, $\chi_o$, with a measurement of the oxygen Knight shift, we decided to check it by measuring the yttrium Knight shift. Since both of these quantities are
expected to be proportional to $\chi_\alpha$, we expect the oxygen and yttrium Knight shifts to track.

For $^{89}\text{Y}$ we measure simply the powder average shift, appropriate since the shift is relatively isotropic. The shift is measured with a spin echo experiment. To quantify the shift of the resonance frequency with increasing temperature, we use the $^{89}\text{Y}$ lineshape measured at one temperature as a fitting function for the lineshapes at all other temperatures (the line position was the only fitting parameter, appropriate since the width was relatively constant, decreasing only from 1.7 kHz at 290 K to 1.4 kHz at 710 K), or for the measurements on sample B, perform a Gaussian fit. To determine the shift relative to YCl at room temperature we define the resonance frequency of the $^{89}\text{Y}$ in YBCO using a Gaussian fit. We take the $^{89}\text{Y}$ chemical shift in YBCO to be 155 ppm relative to YCl [134].

One difficulty we encountered is that the total shift (chemical plus Knight shift) of the yttrium in a powder sample is observed to depend upon how tightly the powder is packed. When sample A2 was "loosely packed" we observed a shift of 107 ppm relative to YCl$_3$; however, when the same sample was "tightly packed" we detected a shift of only 84
The dependence of the shift upon the packing conditions was observed several times, although the shift values were not reproducible (not surprising since it is difficult to duplicate the packing conditions). We do not have an understanding of why the shift depends upon the packing conditions.

The yttrium room temperature Knight shifts are $-242$ and $-235$ ppm for samples A1 and B, respectively. We estimate an uncertainty of 3 ppm. These values are in reasonable agreement with the shifts reported by other groups [63, 134]. The small difference in shift between samples A and B might indicate that the oxygen-17 enriched sample (sample B) has a slightly lesser oxygen content than does the non-enriched sample. (Recall Figure 3.19 which shows that the magnitude of the shift increases with increased oxygen content).

The yttrium shift in the oxygen enriched sample was measured in the high temperature probe. It varied by 29 ppm, relative to solid KCl, between 290 and 710K, corresponding to a decrease in the $^{89}$Y Knight of 12%. The yttrium shift in sample A2 was measured in a non-magnetic probe between room temperature and 523 K; the non-enriched sample exhibited a change in shift of approximately 20 ppm over this
temperature range. (See Figure 4.8). The temperature dependencies of
the shifts in the two samples are quite similar. The yttrium shift in
sample A1 had earlier been measured in a non-magnetic probe, over the
smaller temperature range of 290 K to 430 K; over this temperature
range the shift was found to vary by 10 ppm.

In Figure 4.9 we plot $^{89}(T_1TK)^{-1}$ vs T (analogous to Figure 4.4 for
oxygen). We note that this quantity increases with increasing
temperature, indicating that $(1/T_1T)$ and the Knight shift do not scale for
yttrium. This phenomenon has also been observed in $\text{YBa}_2\text{Cu}_4\text{O}_8$ measured up to 250 K [137], as well as in both optimally (up to 500 K)
and underdoped (up to 350 K) $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by Alloul [133] and up to
room temperature by Takigawa [134].

To summarize the Knight shift results, we find that between 290 K
and 710 K the oxygen shift decreases by 13%, while the magnitude of
the yttrium shift decreases by 12%. As expected, we find similar
temperature dependencies for the oxygen and yttrium Knight shifts. For
comparison, both the oxygen and yttrium shifts above room temperature
are shown in Figure 4.10. Within our experimental error these declines
are monotonic and approximately linear with temperature above the spin
gap temperature. Thus the $^{17}$O and $^{89}$Y shifts behave in a manner which is not unusual. The quantitative measurements of these shifts will assist us in analysis of the spin-lattice relaxation rates.
Figure 4.8. Yttrium Knight shift vs temperature.
Figure 4.9. $89(T_{1}TK)^{-1}$ vs temperature. $89\text{K}$ is interpolated for the temperatures at which it was not measured.
Figure 4.10. Knight shifts of both oxygen and yttrium.
An important question in the study of high temperature superconductors is the proper description of the holes at the copper and oxygen sites. The planar copper is a Cu$^{2-}$ in a 3d$^9$ configuration, with a single hole localized in the 3d$_{x^2-y^2}$ orbital, acting as a quasi-permanent magnetic moment [6]. This unpaired electron spin is antiferromagnetically aligned in the related antiferromagnetic insulator YBa$_2$Cu$_3$O$_6$ [62] and is antiferromagnetically correlated in the superconducting material with a correlation length of perhaps 2 lattice constants [11] at 300 K.

In addition to unpaired spin at the copper sites, there are also holes at the O(2,3) sites. The holes at the oxygen sites are in the 2p-orbitals of the planar oxygen where they are in $\sigma$ bonds, which overlap...
with the nearby copper orbitals [91]. One wants to know whether to
treat the holes at the copper and oxygen sites independently (a 2
component model) or to view the copper and oxygen holes as being
hybridized, resulting in a single degree of freedom per unit cell (a 1
component model).

The spin lattice relaxation of copper, oxygen and yttrium is driven
by interaction of the nuclear spins with fluctuating magnetic fields from
nearby electrons. Thus, the nuclear spin lattice relaxation probes the
behavior of the electrons. Below room temperature, the copper and
oxygen (or yttrium) relaxation have drastically different temperature
dependencies [12]. We have measured the high temperature behavior of
the oxygen and yttrium spin lattice relaxation to see if the behavior is
quantitatively as predicted by a one-component model such as that of

This chapter will discuss possible theoretical interpretations of our
experimental results of the temperature dependence of both the nuclear
spin lattice relaxation rates (1/T₁) and Knight shift (K) for the oxygen
and yttrium nuclei in the normal state of superconducting YBa₂Cu₃O₇
powder. In section 5.1, we find that the one-component model of ZBP
does not explain the temperature independence of $^8\text{g}(T,T)^{-1}$. We try several simple "fixes" to the ZBP theory in sections 5.1.2 through 5.1.4, without any success. It is an important result that the commonly accepted theory cannot account for our experimental results of $^8\text{g}(T,T)^{-1}$, suggesting that it requires substantial modifications if it is to explain all available NMR data. This result is independent of the details of the theory, strongly suggesting that any similar one-component model will be incapable of explaining our experimental results. In section 5.2, we briefly discuss other theories, which unfortunately also fail to explain our results.

5.1. One Component Model

In a one-component model, the difference between the copper and oxygen relaxation is due to the interplay between the $\bar{q}$-dependent electronic susceptibility and the nuclear form factors. (See Chapter 2 for a more detailed discussion). The form factors, which are based upon the position of the nuclei in the lattice, determines the wavevector of fluctuating magnetic field to which the nucleus is most sensitive. $^{63}\text{F}$ is peaked near the antiferromagnetic wavevector $\bar{Q}_{\text{AF}} = \left(\frac{\pi}{a}, \frac{\pi}{a}\right)$, while $^{17}\text{F}$ and $^{89}\text{F}$ are maximum at longer wavelengths ($\bar{q} = \bar{0}$).
5.1.1. ZBP Model

The electronic susceptibility takes on a specific form in a given model such as ZBP [11] (Equation 2.12) or the earlier MMP [16] (Equation 2.11); however, general features of the electronic susceptibility are that it is peaked near the antiferromagnetic wavevector due to antiferromagnetic fluctuations of the Cu$^{2+}$ spins, and that far from the antiferromagnetic wavevectors the susceptibility is due to a background term which is proportional to the static susceptibility, appropriate for a fermi-liquid. We can write the contributions separately as $\chi(\vec{q}, \omega) = \chi_{AF} + \chi_{FL}$.

Both the oxygen (or yttrium) and copper nuclear relaxation are described by the same electronic susceptibility; however, due to their differing form factors, the copper is relaxed primarily by interaction with the antiferromagnetic fluctuations at the Cu$^{2+}$ sites ($\chi_{AF}$) while the oxygen and yttrium are relaxed primarily by the fermi liquid background term ($\chi_{FL}$). The oxygen and yttrium are predicted to have slightly different temperature dependencies as the yttrium is more completely screened from the antiferromagnetic fluctuations than is the oxygen.
In Figures 5.1 and 5.2, we show the predictions of the ZBP model along with experimental results for \( ^{17}(T_1T)^{-1} \) and \( ^{89}(T_1T)^{-1} \). We see that the oxygen data is well fit by the ZBP prediction; the experimental data drops by 14 $\pm$ 2% between 290 K and 710 K and the prediction drops by 15.5%, with $-1/3$ of this drop resulting from the T dependence of $\chi_{AF}$ and $-2/3$ from $\chi_{FL}$ and the temperature dependent Knight shift. However, the ZBP model predicts substantially more temperature dependence (13.3% drop, with $-1/5$ of this drop resulting from the T dependence of $\chi_{AF}$ and $-4/5$ from $\chi_{FL}$) than the experimentally observed temperature independence of \( ^{89}(T_1T)^{-1} \) within 4%.

For completeness, the predictions of the earlier MMP model, which has largely been replaced by ZBP, are shown in Figures 5.3 and 5.4. Although the static susceptibility was originally taken to be independent of temperature for the YBa$_2$Cu$_3$O$_7$ material, we have allowed the static susceptibility to have the measured temperature dependence of the Knight shifts. This is a reasonable generalization as the MMP model applied to underdoped materials included a temperature dependent static susceptibility [93, 94]. The MMP model predicts slightly more temperature dependence (20% drop) than is observed for the $^{17}$O.
relaxation rate, although the rates are quite similar. (Due to the lack of coupling with the next nearest neighbor spins, $^{17}$O is not as well shielded from the AF fluctuations in this model). Again, we find that for $^{89}$Y the model predicts substantially more temperature dependence (13.1% drop) than is measured experimentally. However, we will not consider the MMP model further as it is generally agreed that the refined ZBP model is needed to explain the temperature dependent oxygen $T_1$ anisotropy and conform with the latest neutron scattering results.

Let us comment upon the magnitude of the ZBP predictions. The magnitude of the yttrium prediction has been reduced by ~30% to approximately match the experimental magnitude. This is within the uncertainty of the yttrium hyperfine constant and is not a cause for concern. However, the predicted oxygen magnitude has been multiplied by ~2 in order to match the experimental magnitude. It is not understood why the predicted and experimental magnitudes of oxygen disagree, although this discrepancy has also been noted by others in terms of magnitude of the oxygen relaxation rate [138] and in terms of the ratio of the yttrium relaxation rate to the oxygen relaxation rate [134].
Figure 5.1. $^{17}(T,T)^{-1}$. Open diamonds are the experimental data; solid line is the prediction of ZBP.
Figure 5.2. $^{89}(T_1T)^{-1}$. Open diamonds are the experimental data; thick solid line is the prediction of ZBP; thin solid line is a constant value of $2.383 \times 10^{-4} \text{ K}^{-1} \text{ s}^{-1}$. 
Figure 5.3. $^{17}(T_1, T)^{-1}$. Open diamonds are the experimental data; solid line is the prediction of MMP.
Figure 5.4. $^{89}(T_1T)^{-1}$. Open diamonds are the experimental data; solid line is the prediction of MMP.
5.1.2. Dipolar Relaxation

In the one-component model, we have so far considered only relaxation of the nuclei due to hyperfine coupling with local electron spins. We have not included the effects of dipolar coupling between the electron magnetic moment and the nuclear spin magnetic moment. For the copper and the oxygen, the dipolar coupling is much smaller than the relevant hyperfine coupling. Takigawa et al [134] first noted that the dipolar coupling to the yttrium is non-negligible and calculated its effect upon the yttrium relaxation.

The dipolar coupling is the coupling between two magnetic dipoles; it depends on the relative orientation of the dipoles as well as the strength of the dipoles and the distance between them [139, 32]. The dipolar coupling is

\[ E_{\text{dipolar}} = \frac{\gamma_e \gamma_n \hbar^2}{r^3} \left( \vec{S} \cdot \vec{S} - \frac{3}{r^2} (\vec{I} \cdot \vec{r})(\vec{S} \cdot \vec{r}) \right) \]  (5.1)

where \( \vec{r} \) is the vector distance between the electron and the \(^{89}\text{Y}\) nuclei. The dipolar energy is of order \( E_{\text{dipolar}} = \frac{\gamma_e \gamma_n \hbar^2}{r^3} \). Using a distance of 3.20 Å and gyromagnetic ratios of \((2\pi)^*2.086\) MHz/T and \((2\pi)^*28024\) MHz/T for the yttrium and electron, respectively, and recalling the unit
conversion that \( \text{erg} = G^2 \text{cm}^3 \), we find \( E_{\text{dipolar}} \approx 4.9 \times 10^{-10} \text{ ev} \). This is only an order of magnitude smaller than the hyperfine constant \( D = 4.8 \times 10^{-9} \text{ ev} \).

We can incorporate the dipolar coupling into a one component model by recalculating the form factor to include the effects of both dipolar coupling and hyperfine coupling between the yttrium nuclei and the electronic spins at the Cu sites. Since it is the same spins which are coupled in both the dipolar and hyperfine coupling, it is appropriate to consider the two effects to be correlated. For this reason we must add the contributions to \( \vec{q} \)-space hyperfine constants \( ^{89} A(\vec{q}) \) from both effects before squaring the hyperfine constants.

Using the method discussed in Appendix C, we can calculate the hyperfine constants to be

\[
A_{xy} = A_{yx} = 12 \alpha^2 G \sin \left( \frac{q_x a}{2} \right) \sin \left( \frac{q_y a}{2} \right)
\]

\[
A_{zx} = A_{xz} = 12 \alpha \gamma G \cos \left( \frac{q_z}{2} \right) \sin \left( \frac{q_x}{2} \right) \sin \left( \frac{q_y}{2} \right) \tag{5.2}
\]

\[
A_{yz} = A_{zy} = 12 \beta \gamma G \cos \left( \frac{q_y}{2} \right) \sin \left( \frac{q_x}{2} \right)
\]

where \( G \) is the dipolar energy we calculated above and \( \alpha, \beta, \) and \( \gamma \) are the direction cosines between the \( ^{89}\text{Y} \) and electron spins. Since \( \vec{r} = (\pm 1.92 \text{Å}, \pm 1.92 \text{Å}, \pm 1.68 \text{Å}) \), we find \( \alpha = \beta = 0.60 \) and \( \gamma = 0.53 \).
Figure 5.5. $^{89}(T_1T)^{-1}$. Diamonds are experimental points. The thick line is the ZBP prediction including both hyperfine and dipolar coupling; the thick dotted line is the ZBP prediction for hyperfine coupling only.
Calculating the $^8\text{T}_1 T^{-1}$ averaged along the three crystal axes, we find

$$\frac{1}{T'T} \propto \left\{ \frac{32}{3} \left[ D + G(1 - 3\gamma^2)/2 \right]^2 + \frac{16}{3} \left[ D - G(1 - 3\gamma^2) \right]^2 + 96\alpha^2 G^2 - 192\alpha^2 \gamma^2 G^2 \right\}$$

$$\times \int \frac{K''}{\omega} (1 - \cos(q_x a))(1 - \cos(q_y a))dq$$

$$+ \left\{ 384\alpha^2 \gamma^2 G^2 - 384\alpha^4 G^2 \right\} \times \frac{4}{5} \int \frac{K''}{\omega} (1 - \frac{1}{2}(\cos(q_x a) + \cos(q_y a))^2 dq$$

$$+ \left\{ 384\alpha^4 G^2 \right\} \times \frac{4}{5} \int \frac{K''}{\omega} dq$$

where, if we had considered no dipolar coupling, we would have had only the terms which contain the hyperfine constant $D$.

The effect of including dipolar coupling in the calculation is shown in Figure 5.5. We have chosen the hyperfine constant $D$ to match the theoretical and experimental magnitudes; the other constants are known with greater precision and are not adjusted.

We see that including dipolar coupling introduces additional temperature dependence – the prediction now drops by 15% rather than 13% between 300 and 700 K. We can understand this temperature dependence if we note that introducing dipolar coupling adds in some contribution from wavevectors which experience the antiferromagnetic fluctuations; these antiferromagnetic fluctuations decay substantially at increased temperature. Mathematically, this arises as the second and
third integrals in Equation 5.3 drop by 36% and 18%, respectively, between 300 and 700 K while the first integral, which is the only contribution in the case of pure hyperfine coupling, drops by only 13% over the same temperature range.

We conclude that considering dipolar coupling results in a small, but perceptible, increase of the predicted temperature dependence of $^{88}(1/T,T)$. Unfortunately, the effect is in the wrong direction for explaining why $^{89}(1/T,T)$ is constant with temperature. We will not consider dipolar coupling any further within a one-component model.

5.1.3. Interlayer Correlations

In the YBCO system, there are two adjacent copper-oxide planes in each unit cell. This allows the possibility of interlayer correlations, between adjacent CuO$_2$ planes, in addition to the intralayer correlations, within a single plane, which we have discussed up to this point. We need to consider whether these interlayer correlations could be responsible for our observed independence of temperature of $^{89}(T,T)$. Takigawa [134] noted that their oxygen to yttrium relaxation rate $R = \frac{17(1/T,T)}{89(1/T,T)}$ in both optimally and underdoped YBa$_2$Cu$_4$O$_{7-8}$ increased
at lower temperatures, showing a behavior not predicted by the one-component MMP model and suggested interlayer (also known as bilayer) correlations as the mechanism responsible for this unexpected temperature dependence of R, although they did not perform any calculations to determine if interlayer correlations are a large enough effect to account for the significant temperature dependence they observed. Similarly, Kambe et al. [137] ascribe the difference between their observed and predicted R in the material YBa$_2$Cu$_4$O$_8$ to bilayer coupling, although they see a significant effect only below 120 K.

Millis and Monien [140] had earlier shown that $^{89}$Y nuclei are relaxed only by fluctuations which are symmetric with respect to interchange of the two copper-oxide planes; due to their position in the lattice, they are not relaxed by fluctuations which are odd with respect to the bilayers. They argued that the symmetric fluctuations are suppressed at lower temperature as singlets form between the two planes. Thus, as the temperature is lowered and more singlets form, there are less symmetric fluctuations, and the yttrium (1/T$_{1T}$) is decreased. Since these symmetric fluctuations do not affect the oxygen relaxation, the ratio R is enhanced as the temperature is lowered.
Figure 5.6. The susceptibilities $\chi_{11}$, $\chi_{12}$, and $\chi_0$ for $J_\perp = .15$ meV at 300 K where $\xi/a = 1.7$. 
Figure 5.7. The susceptibilities $\chi_{11}$, $\chi_{12}$, and $\chi_o$ for $J_\perp = .15$ meV at 1000 K where $\xi/a=1.1$. 
Figure 5.8. AF contribution to $^{89}Y (T_1T)^{-1}$ from in-plane fluctuations, $(T_1T)^{-1}_{11}$, and from bilayer correlations, $(T_1T)^{-1}_{12}$. 
Figure 5.9. AF contribution to $^{89}Y \langle T_1 T \rangle^{-1}$ both with and without bilayer correlations.
The magnetic coupling of adjacent planes has been demonstrated. Inelastic neutron scattering has observed that the fluctuations at $\bar{Q}=(\pi,\pi)$ are anticorrelated between adjacent planes in YBa$_2$Cu$_3$O$_{6.6}$ [56] and in YBa$_2$Cu$_3$O$_7$ [8]; even fluctuations, responsible for $^{89}$T$_1$, have been observed in the underdoped materials [66, 73]. Other convincing evidence for magnetic coupling of the bilayers comes from the study of Y$_2$Ba$_4$Cu$_7$O$_{15.5}$, which is composed of alternating layers of YBa$_2$Cu$_4$O$_7$ and YBa$_2$Cu$_4$O$_8$ and contains two inequivalent copper-oxygen planes. $^{63}$K and also $^{63}$T$_1$ have the same temperature dependence in both planes [141], and SEDOR experiments [78, 103] reveal a coupling between copper nuclei in adjacent inequivalent planes over the entire temperature range studied (up to 200 K).

We can quantitatively calculate the effects of interlayer coupling upon the yttrium relaxation rate per unit temperature, $^{89}(1/T_1T)$. Following Millis and Monien [142], we will consider two contributions to the susceptibility. $\chi^{11}$ is the susceptibility of a given plane; $\chi^{12}$ is proportional to the spin correlation function between spins in adjacent layers. Here we will consider only the antiferromagnetic (AF) contribution to the susceptibility, and not the $\bar{q}$ independent Fermi-liquid (FL)
“background” contribution. In the weak coupling approximation (which is both required for the random phase approximation to be appropriate and holds for the YBCO system where $J_{\perp} \sim 0.015$ ev and $1/\chi_{\text{max}} \sim 0.07$ ev) the susceptibilities are [142]

\[ \chi^{11}(\vec{q}, \omega) = \chi_o(\vec{q}, \omega) / \Delta_o(\vec{q}, \omega) \]  
\[ \chi^{12}(\vec{q}, \omega) = -J_{\perp}(\chi_o(\vec{q}, \omega))^2 / \Delta_o(\vec{q}, \omega), \]  

where

\[ \Delta_o(\vec{q}, \omega) = 1 - |J_{\perp}\chi_o(\vec{q}, \omega)|^2 \]  

and $\chi_o(\vec{q}, \omega)$ is the susceptibility of an isolated plane. In the limit of weak interplane coupling, $\chi^{11} \sim \chi_o$ and $\chi^{12} \sim -J_{\perp}\chi_o^2$, where $J_{\perp}$ is the intraplaner coupling constant.

The susceptibilities are plotted in $\vec{q}$ space in Figures 5.6 and 5.7; we see that $\chi^{11}$ is indeed similar to $\chi_o$ and that $\chi^{12}$ is negative. It is the sign of $\chi^{12}$ that will lead to a lesser temperature dependence in the predicted $^{89}(1/T_1T)$.

We can calculate the nuclear spin lattice relaxation rate by [143]

\[ \frac{1}{T_1T} \propto \sum_{\vec{q}} F^{\text{even}} \frac{\text{Im}[\chi^{11}(\vec{q}, \omega) + \chi^{12}(\vec{q}, \omega)]}{\omega} + \sum_{\vec{q}} F^{\text{odd}} \frac{\text{Im}[\chi^{11}(\vec{q}, \omega) - \chi^{12}(\vec{q}, \omega)]}{\omega}. \]  

(5.5)
This replaces the earlier Equation 2.9. The even and odd superscripts refer to the part of the form factor which couples to fluctuations which are even or odd, respectively, with respect to the two adjacent planes. In the case of yttrium, $F^{\text{odd}} = 0$ [144, 143] and $F^{\text{even}}$ is proportional to the yttrium form factor given earlier in Equation 2.10.

We numerically calculated the predicted relaxation for the yttrium. We used $J_\perp = 15$ meV [142], which is in reasonable agreement with earlier estimates of $J_\perp$ between 10 and 20 meV from band structure calculations [145] and of $J_\perp = 25$ meV from comparing the temperature dependence of $^{63}$K in the inequivalent planes of $Y_2Ba_4Cu_7O_{15}$ [141]. We also assumed that the AF fluctuations within a single plane were commensurate and peaked at ($\pi, \pi$).

The AF contributions of $\chi^{11}$ and $\chi^{12}$ to $(1/T_1T)$ (which we shall refer to as $(T_1T)^{-1}\chi^{11}$ and $(T_1T)^{-1}\chi^{12}$) are shown in Figure 5.8; the total AF contribution to $(1/T_1T)$ is given in Figure 5.9, both with and without including the interlayer correlations. We see that $(T_1T)^{-1}\chi^{12}$ is negative with a magnitude that decreases with increasing temperature (33% drop between 300 and 700 K); thus, this contribution does correspond to a relaxation rate per unit temperature which increases with increasing
temperature. However, at room temperature $(T_1T)^{-1}_{12}$ is only 12% of $(T_1T)^{-1}_{11}$; the temperature dependence of $(T_1T)^{-1}_{11}$, which decreases with increasing temperature, dominates the total AF relaxation rate. Including bilayer correlations, the AF contribution to $^{89}(T_1T)^{-1}$ drops by 11% between 300 and 700 K. This is not a significant change from the case with no bilayer correlations which shows a drop of 13% over the same temperature range. (Using $J_\perp$ of 60 meV, four times the suggested value, still results in a drop of 8.5%).

Recall, also, that so far we have only considered the AF contribution to $^{89}(T_1T)^{-1}$. The FL contribution, which we have seen dominates the yttrium relaxation (accounting for 87% of the relaxation at room temperature), also decreases with increasing temperature. We therefore predict that the total relaxation rate,

$$^{89}(T_1T)^{-1}_{\text{Tot}} = ^{89}(T_1T)^{-1}_{\text{AF}} + ^{89}(T_1T)^{-1}_{\text{FL}}$$

should exhibit a decrease with increasing temperature of about 13%, whether or not interlayer correlations are considered.

We conclude that while including bilayer correlations does decrease the predicted temperature dependence of $^{89}(T_1T)^{-1}$ and enhances $R$ at lower temperatures, it is not nearly a large enough effect to describe our
data and to explain the temperature independence of $^{89}(T_1T)^{-1}$ that we observe.

5.1.4. Temperature Independent Static Susceptibility

So far, we have assumed that the static susceptibility $\chi_o$ is temperature dependent, with the temperature dependence of the Knight shift. This assumption was following that used for the underdoped materials [93, 94]. However, we could attempt to understand $^{89}(T_1T)^{-1}$ with a temperature independent $\chi_o$. In this case, ZBP would predict a drop of $^{89}(T_1T)^{-1}$ of only 2.3% between 300 and 700 K, which would be consistent with our experimental measurements, within the experimental uncertainty.

However, we must simultaneously understand both $^{89}Y$ and $^{17}O$ relaxation – it is not adequate to explain the yttrium relaxation while neglecting the oxygen relaxation. In Figure 5.10, we show the $^{17}(T_1T)^{-1}$ vs temperature, with a fit from the ZBP model with a temperature independent $\chi_o$. We see that a temperature independent static susceptibility fails to explain the oxygen data. This implies that we
Figure 5.10. $^{17}(T,T)^{-1}$ vs temperature. The filled diamonds are the experimental values and the solid line is the ZBP prediction for the case of static susceptibility independent of temperature.
cannot fix the yttrium problem, while simultaneously explaining the oxygen rate, simply by assuming a temperature independent $\chi_o$.

5.1.5. General Comments

We find that not only is the $^{89}(T_1T)^{-1}$ behavior unusual, it is unusual in a very simple way – it is temperature independent. The temperature independence of $^{89}(T_1T)^{-1}$ is the most serious anomaly of our work.

The expected temperature dependence of $^{89}(T_1T)^{-1}$ of approximately the magnitude illustrated in Figure 5.2 must be regarded as a rather robust feature of ZBP. We would like to reiterate that in a one-component model, such as ZBP, one can write expressions for $1/T_1$ in terms of two distinct contributions, $(T_1T)^{-1} = (T_1T)^{-1}_{AF} + (T_1T)^{-1}_{FL}$. We expect that any model will include the key feature that the temperature dependence of $(T_1T)^{-1}_{FL}$ is proportional to that of $\chi_o$ and in turn to that of the Knight shift. As the yttrium is largely screened from the antiferromagnetic fluctuations due to the location of the yttrium nuclei in the lattice, most of the relaxation of the yttrium is due to the $(T_1T)_{FL}^{-1}$. We thus expect the temperature dependence of $^{89}(T_1T)^{-1}$ to be dominated...
by that of \( ^{89}(T, T)^{-1} \), and, to a large extent, we expect that the yttrium
\( (1/T, T) \) should scale with the Knight shift.

The relaxation rates of \(^{17}\text{O}\) and \(^{63}\text{Cu}\), and even \(^{89}\text{Y}\) at lower
temperatures, have all displayed behavior which correlates with the
temperature dependence of the Knight shift, suggesting rather strongly
that \(^{89}\text{Y}\), as well as \(^{17}\text{O}\), must be hyperfine coupled to the same
excitations involved in relaxing the \(^{63}\text{Cu}\) and \(^{17}\text{O}\). In almost any scenario,
either the temperature dependence of \( \chi_{AF} \) required to understand \(^{63}\text{Cu}\)
spin lattice relaxation behavior or the observed temperature dependence
of \( \chi_{O} \) (and hence \( \chi_{FL} \)) would result in some measurable temperature
dependence of \( ^{89}(T, T)^{-1} \).

5.2. Other Theories

We have briefly considered two other theories to explain our data,
analyzing the \(^{89}\text{Y}\) relaxation rate solely in terms of dipolar coupling to
spins at \( \text{Cu}^{2+} \) sites in section 5.2.1, and in terms of a two component
model in section 5.2.2. Unfortunately, neither model is capable of
describing our yttrium relaxation data.
5.2.1. Dipolar Coupling Only

We have attempted to understand the yttrium relaxation rate in terms of dipolar coupling to electron spins at the planar Cu sites. As we will see below, dipolar coupling only yields a relaxation rate which is an order of magnitude smaller than that observed experimentally, and which is temperature independent.

The dipolar coupling hamiltonian [32] between a \(^{89}\)Y nucleus and an electron spin is
\[
\mathcal{H} = \frac{\gamma_{^{89}\text{Y}} h_0^2}{r^3} \left[ (\vec{I} \cdot \vec{S}) - 3(\vec{I} \cdot \hat{r})(\vec{S} \cdot \hat{r}) \right].
\]
When \(\vec{S}\) lies along \(\hat{x}\) (we know it lies in the xy plane), we find that \(^{89}\)Y experiences an effective magnetic field
\[
\vec{h} = 564G \left\{ (0.5 - 1.5 r_2^2) \hat{x} - 1.5 r_x r_y \hat{y} - 1.5 r_x r_z \hat{z} \right\},
\]
where \(\hat{r} = (0.6, 0.6, 0.5)\) is the vector from \(^{89}\)Y to the electron spin. Considering the four nearest neighbor Cu spins in a single plane, we can show that the x and z components of \(\vec{h}\) will cancel, leaving \(\vec{h} = 1000G\hat{y}\).

We can calculate the relaxation rate from \(\frac{1}{\alpha_{T_1}} = ^{89}\gamma^2 \tau_o \sqrt{\frac{\alpha^2}{\alpha^2 + \alpha'^2}}\), where \(\alpha, \alpha', \text{ and } \alpha''\) are orthogonal directions [32]. Using \(\tau_o = 2.3 \times 10^{-15} \text{ s}\) [6], and calculating the powder average of \(T_1^{-1}\), we predict \(^{89}(1/T_1) = 0.005 \text{ s}^{-1}\). This is an order of magnitude smaller than the room temperature experimental value of 0.07 \text{ s}^{-1}, and is independent of temperature in...
contrast to the experimental behavior. Thus, we conclude that we cannot explain $^{89}(1/T_1)$ in terms of dipolar coupling only.

5.2.2. Two Component Theory

We illustrate in Figure 5.11 a comparison of the rates $^{63}(1/T_1)$, $^{17}(1/T_1)$, and $^{89}(1/T_1)$ vs $T$. We have multiplied the rates for each nucleus by a constant such that at high temperatures the slopes $d(1/T_1)/dT$ are equal to one unit per Kelvin. The striking feature of Figure 5.10 is that the rates for all three nuclei at high temperature approach the behavior $(1/T_1)=A+BT$. This kind of behavior was noted in lower temperature $^{63}$Cu measurements as a suggestion of a two component behavior, with the existence of a "Fermi liquid" relaxation contribution $BT$, and a $T$-independent contribution $A$ from localized spins. It appears that all three nuclei behave in this manner to a reasonable approximation at high temperature (with the $A$ term equal to zero for the case of $^{89}$Y), and then deviate at lower temperatures. We have attempted to understand this behavior of all three nuclei in terms of the “$A$” term arising from the interaction of nuclei with a fluctuating magnetic field due to the hyperfine coupling with electrons at the Cu sites and the “$B$” term arising from the
interaction of nuclei with an independent conduction band. In this scenario, the Knight shift would have a temperature independent contribution from a conduction band formed from oxygen p-holes as well as a temperature dependent contribution from fluctuating magnetic fields of electron spins at the Cu sites.

\[ \beta K^s = \beta K_{p-holes}^s + \frac{\beta N A}{\gamma_e \gamma h} \mathcal{X}_{d-holes}^s (T) \]  

(5.6)

where \( \beta \) is the nuclear species and \( \beta N \) is the number of Cu\(^{2+} \) spins to which the nucleus is coupled (\( ^{63}\text{N}=1, \ ^{17}\text{N}=2, \) and \( ^{89}\text{N}=8 \)).

From the temperature dependent portion of the Knight shift, we can determine the magnitude of the fluctuating field at that nuclear site,

\[ \frac{\beta h^2}{h^2} = 4 \left( \frac{A}{\beta h} \right)^2 \]  

(5.7)

Finally, we can determine the relaxation caused by the fluctuating field experienced by a nucleus [32],

\[ \left( \frac{1}{T_{1\alpha}} \right)^{\beta} = \frac{N \gamma^2}{A} \left( \frac{h^2}{h_{\alpha}} + \frac{h^2}{h_{\alpha}} \right) \tau_0 \]  

(5.8)

and predict \( A \). We use the values of \( \chi = 31.2 \ 10^{-29} \) emu/Cu and \( \tau_0 = 2.3 \ 10^{-15} \) s from reference [6]. In Table 5.1 we compare the predicted and experimental values of \( A \). We notice that for the yttrium, the predicted
and experimental values of A are an order of magnitude different; the oxygen prediction is wrong by a factor of 5. Thus, this model fails to explain the \( \frac{1}{T_1} = A + BT \) behavior; we have found no quantitative accounting for this observation.
Figure 5.11. $1/T_1$ for $^{63}$Cu (filled squares), $^{17}$O (open circles) and $^{89}$Y (filled circles). ($^{63}$Cu rate taken from Barrett et al [146]). Rates for each nucleus are multiplied by a constant selected so that at high temperatures the slopes $d(1/T_1)/dT$ are each equal to one unit per Kelvin.
Table 5.1. Predicted and experimental values of A for a model to explain the observed $(1/T_i)=A+BT$ behavior at high temperatures.

<table>
<thead>
<tr>
<th>Species</th>
<th>Predicted A (sec$^{-1}$)</th>
<th>Experimental A (sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{63}\text{Cu}$</td>
<td>804</td>
<td>804</td>
</tr>
<tr>
<td>$^{17}\text{O}$</td>
<td>135</td>
<td>27</td>
</tr>
<tr>
<td>$^{89}\text{Y}$</td>
<td>0.05</td>
<td>-0.0046</td>
</tr>
</tbody>
</table>
CHAPTER 6

CONCLUSIONS

We have utilized Nuclear Magnetic Resonance to examine a sample of near (but slightly less than) optimally doped YBa$_2$Cu$_3$O$_y$. We measured the nuclear spin lattice relaxation rate ($1/T_1$) and the Knight shift (K) at both the planar oxygen (O(2,3)) sites and at the yttrium sites located between the copper-oxide planes.

The contrasting behavior of $^{63}$Cu and $^{17}$O NMR has been a source of great controversy in investigations of the high $T_c$ cuprates. Following Takigawa's observation [15] that the NMR Knight shifts K of $^{63}$Cu and $^{17}$O in oxygen reduced YBa$_2$Cu$_3$O$_{7-\delta}$ tracked one another within experimental precision ($^{17}K \approx ^{63}K$), the prevailing view has been that only a single spin degree of freedom is necessary to describe the CuO$_2$ planes. The contrasting $^{17}$O and $^{63}$Cu $T_1$ behaviors [12] are addressed with hyperfine
“form factor” effects in which antiferromagnetic fluctuations dominate
the $^{63}$Cu relaxation behavior, but are screened from $^{17}$O whose relaxation
is dominated by longer wavelength ($\bar{q} \approx 0$) fluctuations.

In order to probe further the applicability of the MMP, ZBP, and
related “one component” models to NMR behavior we have performed
$^{89}$Y
and $^{17}$O NMR measurements which extend to higher temperatures (up to
~700K) than have been reported previously. Within ZBP's one
component model [11], both $^{17}(T_1T)^{-1}$ and $^{89}(T_1T)^{-1}$ should display a
decrease, of predictable magnitude, with increasing temperature,
accompanying the more steep fall-off of $^{63}(T_1T)^{-1}$. The behaviors of
$^{17}(T_1T)^{-1}$ and $^{89}(T_1T)^{-1}$, both reflecting hyperfine coupling to long
wavelength fluctuations, should have quite similar temperature
dependencies.

We find, however, an important departure from theory. While the
$^{17}$O behavior is as predicted, the $^{89}$Y is quite surprising, with $^{89}(T_1T)^{-1} =$
constant (within experimental precision of $\pm 4\%$) over the full range,
despite a $13 \pm 2\%$ drop (from 300 K to 700 K) in the static susceptibility
and a $14 \pm 2\%$ drop in $^{17}(T_1T)^{-1}$. Thus our expectation that $^{17}(T_1T)^{-1}$ and
$^{89}(T_1T)^{-1}$ should both reflect hyperfine coupling to long wavelength
fluctuations and consequently have the temperature dependence of the static susceptibility is found to be untrue. In particular, our data suggests that the widely accepted one-component model must be substantially modified if it is to explain all available NMR data. We have not found any simple model, single component or otherwise, which is consistent with this set of observations.
APPENDIX A

OXYGEN SPIN LATTICE RELAXATION

Oxygen-17 is a spin 5/2 nucleus and so has 6 possible energy levels in a static magnetic field. These energy levels, along with the transition rates between them, are shown in Figure A.1. Only transitions between adjacent energy levels are shown; when the nuclear spin-lattice relaxation is due primarily to the interaction with the spin magnetic moment of electrons [32], the other transitions have almost zero probability of occurring. This can be seen by writing the interaction as $V \propto I \cdot S$ where $I$ is the nuclear spin and $S$ is the electron spin. This interaction involves the nuclear spin operators $I_x, I_y, I_z$; the only nonzero matrix elements for transitions involve nuclear spin levels $m \rightarrow m \pm 1$, that is, adjacent levels. We can also see that for this interaction, the
Figure A.1. Oxygen energy levels and transition rates between adjacent levels. Transition rate will be identical for the transitions $m \rightarrow m-1$ and $-(m-1) \rightarrow -m$. 
transition rate will be identical for the transitions $m \rightarrow m-1$ and $-(m-1) \rightarrow -m$.

The rate equations for the number of spins in each of the six energy levels are

$$\begin{align*}
\frac{dN_{-5/2}}{dt} &= -W_{\downarrow,5/2}N_{-5/2} + W_{\uparrow,3/2}N_{-3/2} \\
\frac{dN_{-3/2}}{dt} &= +W_{\downarrow,5/2}N_{-5/2} - W_{\uparrow,3/2}N_{-3/2} - W_{\downarrow,1/2}N_{-1/2} + W_{\uparrow,1/2}N_{+1/2} \\
\frac{dN_{-1/2}}{dt} &= +W_{\downarrow,1/2}N_{-1/2} - W_{\uparrow,1/2}N_{+1/2} - W_{\downarrow,3/2}N_{+3/2} + W_{\uparrow,3/2}N_{+3/2} \\
\frac{dN_{1/2}}{dt} &= +W_{\downarrow,3/2}N_{+3/2} - W_{\uparrow,3/2}N_{+3/2} - W_{\downarrow,5/2}N_{+5/2} + W_{\uparrow,5/2}N_{+5/2} \\
\frac{dN_{3/2}}{dt} &= +W_{\downarrow,1/2}N_{+1/2} - W_{\uparrow,1/2}N_{+1/2}
\end{align*}$$

(A.1)

These equations can be simplified if we express the "down" rates ($W_{m\downarrow}$) in terms of the "up" rates ($W_{m\uparrow}$). We know that at thermal equilibrium

$$\frac{dN_m}{dt} = 0. \quad \text{(A.2)}$$

For the $-5/2$ level, this gives us

$$0 = -W_{\downarrow,5/2}N_{-5/2}^o + W_{\uparrow,3/2}N_{-3/2}^o. \quad \text{(A.3)}$$

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However, we also know that in thermal equilibrium, the populations will be given according to the Boltzmann distribution [147, 32]

\[ N_m \propto \exp\left(-\frac{E_m}{k_B T}\right) \propto \exp\left(+\frac{\gamma \hbar H_o}{k_B T}\right) \]  

(A.4)

Thus,

\[ \frac{N^{a}_{\sigma \downarrow}}{N^{a}_{\sigma \uparrow}} = \exp\left(-\frac{\gamma \hbar H_o}{k_B T}\right) \]  

(A.5)

Combining Equations A.3 and A.5, we find

\[ W_{\sigma \downarrow} = W_{\sigma \uparrow} \exp\left(-\frac{\gamma \hbar H_o}{k_B T}\right) \approx W_{\sigma \uparrow}(1 - \frac{\gamma \hbar H_o}{k_B T}) \]  

(A.6)

Typical values for an NMR experiment are \( \gamma = 2\pi \times 5.772 \text{ MHz/Tesla} \), \( T=300 \text{ K} \), and \( H_o=9 \text{ Tesla} \); this gives \( \frac{\gamma \hbar H_o}{k_B T} \approx 10^{-4} \). Thus we can make the "high temperature approximation" [32] and neglect \( \frac{\gamma \hbar H_o}{k_B T} \) in Equation A.6 to set \( W_{\sigma \uparrow} = W_{\sigma \downarrow} = W_{\downarrow} \). The same argument is true for all pairs of rates.

Defining \( n_m \) to be the deviation from equilibrium, \( n_m = N_m - N^{a}_m \), we can rewrite Equations A.1 as
\[
\frac{dn_{-5/2}}{dt} = -W_3n_{-5/2} + W_4n_{-3/2}
\]
\[
\frac{dn_{-3/2}}{dt} = +W_3n_{-5/2} - W_4n_{-3/2} - W_2n_{-3/2} + W_5n_{-1/2}
\]
\[
\frac{dn_{-1/2}}{dt} = +W_2n_{-3/2} - W_4n_{-1/2} - W_5n_{-1/2} + W_6n_{+1/2}
\]
\[
\frac{dn_{+1/2}}{dt} = +W_4n_{-1/2} - W_6n_{+1/2} - W_5n_{+1/2} + W_2n_{+3/2}
\]
\[
\frac{dn_{+3/2}}{dt} = +W_2n_{+1/2} - W_6n_{+3/2} - W_5n_{+3/2} + W_3n_{+5/2}
\]
\[
\frac{dn_{+5/2}}{dt} = +W_3n_{+3/2} - W_4n_{+5/2}
\]

We can further simplify Equations A.7 by using Fermi’s Golden Rule to write all of the relaxation rates in terms of a single rate \( W \). As discussed earlier in this section, the spin lattice relaxation is due to the interaction of the nuclear spin with an electron spin, and this interaction will be proportional to \( \tilde{I} \); the terms which induce transitions are \( I_− \) and \( I_+ \). From Fermi’s Golden Rule [32, 148], we know that each rate will be proportional to a matrix element squared of either \( I_− \) or \( I_+ \).

For a transition between the \(-5/2 \) and \(-3/2 \) levels,

\[
W_3 \propto \langle -5/2 | I_- | -3/2 \rangle^2 \quad (A.8)
\]

\[
\propto |I(I+1) - m(m-1)| \quad \text{where } I=5/2 \text{ and } m=-3/2
\]

\[
\propto 5
\]
Similarly, $W_2 = 8$ and $W_1 = 9$. We can express these rates as $W_1 = 9W$, $W_2 = 9W$, and $W_3 = 5W$, where $W$ is still unknown.

We can rewrite Equation A.7 using matrix notation as

$$
\begin{pmatrix}
    n_{-5/2} \\
    n_{-3/2} \\
    n_{-1/2} \\
    n_{+1/2} \\
    n_{+3/2} \\
    n_{+5/2}
\end{pmatrix}
= 
\begin{pmatrix}
    -5W & 5W & 0 & 0 & 0 & 0 \\
    5W & -13W & 8W & 0 & 0 & 0 \\
    0 & 8W & -17W & 9W & 0 & 0 \\
    0 & 0 & 9W & -17W & 8W & 0 \\
    0 & 0 & 0 & 8W & -13W & 5W \\
    0 & 0 & 0 & 0 & 5W & -5W
\end{pmatrix}
\begin{pmatrix}
    n_{-5/2} \\
    n_{-3/2} \\
    n_{-1/2} \\
    n_{+1/2} \\
    n_{+3/2} \\
    n_{+5/2}
\end{pmatrix}
$$

(A.9)

These equations can be solved with the help of a computer program such as Mathematica (Wolfram). The eigenvalues are $-30W$, $-20W$, $-12W$, $-6W$, $-2W$, and $0$. The eigenvalue of $0$ corresponds to thermal equilibrium, while the other eigenvalues correspond to relaxation towards equilibrium.

The corresponding eigenvectors are

$$
\begin{pmatrix}
    -1 \\
    5 \\
    10 \\
    10 \\
    -5 \\
    1
\end{pmatrix}
= 
\begin{pmatrix}
    1 \\
    -3 \\
    2 \\
    2 \\
    -3 \\
    1
\end{pmatrix}
= 
\begin{pmatrix}
    -5 \\
    7 \\
    4 \\
    -4 \\
    -7 \\
    5
\end{pmatrix}
= 
\begin{pmatrix}
    5 \\
    -1 \\
    -4 \\
    -4 \\
    -1 \\
    5
\end{pmatrix}
= 
\begin{pmatrix}
    -5 \\
    -3 \\
    1 \\
    1 \\
    3 \\
    5
\end{pmatrix}
$$

(A.10)
Thus, the population as a function of time can be written as

\[
\begin{pmatrix}
    n_{-3/2} \\
n_{-3/2} \\
n_{+1/2} \\
n_{+1/2} \\
n_{+3/2} \\
n_{+3/2}
\end{pmatrix} = C_1 \begin{pmatrix}
    -1 \\
    5 \\
   -10 \\
    10 \\
   -5 \\
    1
\end{pmatrix} \exp(-30Wt) + C_2 \begin{pmatrix}
    1 \\
   -3 \\
    2 \\
    2 \\
   -3 \\
    1
\end{pmatrix} \exp(-20Wt)
\]

\[+ C_3 \begin{pmatrix}
    -5 \\
    7 \\
    4 \\
   -4 \\
   -7 \\
    5
\end{pmatrix} \exp(-12Wt) + C_4 \begin{pmatrix}
    5 \\
   -1 \\
   -4 \\
   -4 \\
   -1 \\
    5
\end{pmatrix} \exp(-6Wt) + \begin{pmatrix}
    -5 \\
   -3 \\
   -1 \\
    1 \\
    3 \\
    5
\end{pmatrix} \exp(-2Wt) \tag{A.11}
\]

Consider now an inversion recovery experiment in which we invert the first high frequency satellite \(m=-3/2,-1/2\). At equilibrium, the populations are \(N^0\), and after the satellite is inverted, the populations are \(N(t=0)\), where,

\[
N^0 = \begin{pmatrix}
    1 - 5\sigma \\
    1 - 3\sigma \\
   1 - \sigma \\
   1 + \sigma \\
   1 + 3\sigma \\
   1 + 5\sigma
\end{pmatrix}, \text{ and } N(t = 0) = \begin{pmatrix}
    1 - 5\sigma \\
    1 - \sigma \\
   1 - 3\sigma \\
   1 + \sigma \\
   1 + 3\sigma \\
   1 + 5\sigma
\end{pmatrix} \tag{A.12}
\]
Subtracting, we find that

\[ n(t = 0) \propto \begin{pmatrix} 0 \\ 1/2 \\ -1/2 \\ 0 \\ 0 \\ 0 \end{pmatrix}. \]  \hspace{1cm} (A.13)

We can solve Equations A.13 and A.11 to obtain the constants \( C_1 = 5/84, \ C_2 = -5/28, \ C_3 = 1/60, \ C_4 = 1/28, \) and \( C_5 = -1/35. \)

Experimentally, we measure the difference between the two population levels, \( n_{1/2} - n_{3/2}. \) From Equation A.11 and the constants for which we have just solved, we see that

\[ M(t) - M_\infty \propto n_{1/2} - n_{3/2} \]

\[ \propto \frac{1}{35} \exp(-2Wt) + \frac{3}{56} \exp(-6Wt) + \frac{1}{40} \exp(-12Wt) \]

\[ + \frac{25}{56} \exp(-20Wt) + \frac{25}{56} \exp(-30Wt) \]  \hspace{1cm} (A.14)

We can write this equation in terms of the constant \( T_1 \) if we follow the convention that \( T_1 \) is the time constant for relaxation when all of the levels are inverted [32]. By examination, we see from Equation A.10 that all the levels are inverted for the mode with relaxation rate 2W. Hence, \( T_1 = 1/2W. \)
For relaxation following an inversion of the first satellite we finally obtain

\[
M(t) = M_\infty \left\{ 1 - 2\left( \frac{1}{35} \exp(-t / T_1) + \frac{3}{56} \exp(-3t / T_1) \right) + \frac{1}{40} \exp(-6t / T_1) + \frac{25}{56} \exp(-10t / T_1) + \frac{25}{56} \exp(-15t / T_1) \right\} \tag{A.15}
\]
APPENDIX B

OXYGEN RESONANCE FREQUENCIES

We have measured the Knight shift of oxygen because the Knight shift is proportional to the static electronic susceptibility, as discussed in Chapter 2. The temperature dependence of the static susceptibility is an important parameter in the ZBP [11] expression for the imaginary electronic susceptibility, which has been proposed to help explain the unusual electronic properties found in the cuprate superconductors.

In order to analyze our data to determine the shift of oxygen from an experimental measurement of the resonance frequency, we need to know how the resonance frequency depends on the shift. In order to calculate this, we will use second order perturbation theory on the nuclear hamiltonian to find the resonance frequencies.
The complete hamiltonian for oxygen nuclear spins is

\[ \mathcal{H} = -\gamma H_s (1 + K_z) I_z + \frac{e^2 q Q}{4I(2I-1)} \left[ 3I_z^2 - I_z^2 + \frac{\eta}{2} (I_z^2 + I_z^2) \right]. \]  

(E.1)

The first term of Equation E.1 combines the Zeeman hamiltonian (Equation 3.1) and the hyperfine hamiltonian (Equation 3.7) for the case that the static field \( H_o \) lies along a principle axis \( z \) so that the spins are quantized along the \( z \)-axis. In YBCO, the principle axes (x, y, and z) correspond to the crystal axes (a, b, and c).

The second term in Equation E.1 is the quadrupole hamiltonian (Equation 3.10) where we have made the definitions \( I_z = I_x \pm i I_y \),

\[ \eta = \frac{V_x - V_y}{V_z} \text{, and } e Q = V_z. \]

Although it is a common practice to assume that \( |V_z| \geq |V_y| \geq |V_x| \), nowhere in this derivation do we rely upon that definition.

Thus, our result for the resonance frequency along the \( z \)-axis can be applied to any principle axis by a cyclic permutation of all indices.

We will use second order perturbation theory [106, 148] to solve for the oxygen energy levels. For the large (9 Tesla) fields used in our experiments, the Zeeman hamiltonian is the largest contribution to the total hamiltonian, and both the hyperfine and quadrupole hamiltonians can
be treated as perturbations. The zero order energy states are the \( |m\rangle \) 
states, and the zero order energies are

\[
E^{(0)}_m = \langle m | - \gamma \hbar H_o I_z | m \rangle \\
= - \gamma \hbar H_o m 
\] (B.2)

We can define \( \omega_o = \gamma H_o \), or alternatively, \( v_o = \frac{\gamma}{2\pi} H_o \).

The first order energy shift is given by the diagonal elements of the 
perturbing Hamiltonian,

\[
E^{(1)}_m = \langle m | - \gamma \hbar H_o K_z I_z + \frac{e^2 Q}{4I(2I-1)} \left[ 3I_z^2 - I^2 + \frac{\eta}{2} (I_{z'}^2 + I_{z''}^2) \right] | m \rangle \\
= - \gamma \hbar H_o K_z m + \frac{e^2 Q}{4I(2I-1)} (3m^2 - I(I + 1)) 
\] (B.3)

The second order energy shift is calculated with the formula

\[
E^{(2)}_m = \sum_m \frac{|\langle m' | H_{\text{perturbation}} | m \rangle|^2}{E_m^{(0)} - E_m^{(0)}}. 
\] (B.4)

The first step in using Equation B.4 is to calculate the off diagonal matrix 
elements. The number of matrix elements which must be calculated is 
decreased by noting that \( I_z \) does not connect any off diagonal matrix 
elements, and \( I_{z'} \) only connects the state \( |m\rangle \) to \( |m\pm 2\rangle \).

Recalling the action of the raising and lowering operators, 
\( I_z |m\rangle = \sqrt{I(I+1) - m(m\pm 1)} |m\pm 1\rangle \), we find that the off diagonal matrix 
elements are

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\(\langle m \pm 2 | H_{\text{perturbation}} | m \rangle = \frac{e^2 q Q}{4I(2I-1)} \frac{\eta}{2} \sqrt{I(I+1) - m(m \pm 1)} \sqrt{I(I+1) - (m \pm 1)(m \pm 2)}. \) \hspace{1cm} (B.5)

Combining Equations B.4 and B.5 gives

\[ E_{m}^{(2)} = \left( \frac{e^2 q Q}{4I(2I-1)} \right)^2 \frac{\eta^2}{8\hbar \omega_o} 4m(1-2I(I+1) + 2m^2) \] \hspace{1cm} (B.6)

So, through second order,

\[ E_{m} = -\hbar \nu_o (1 + K_z) + \frac{e^2 q Q}{4I(2I-1)} (3m^2 - I(I+1)) \\
+ \left( \frac{e^2 q Q}{4I(2I-1)} \right)^2 \frac{\eta^2}{8\hbar \omega_o} 4m(1-2I(I+1) + 2m^2) \] \hspace{1cm} (B.7)

Once we know the energy levels, we can calculate the resonant frequencies according to

\[ \nu_{\text{res}} = \frac{E_{m+1} - E_m}{\hbar} \] \hspace{1cm} (B.8)

We find that

\[ \frac{E_{m+1} - E_m}{\hbar} = \nu_o (1 + K_z) + \frac{e Q}{4I(2I-1)} \nu (3 - 6m) \\
+ \left( \frac{e Q}{4I(2I-1)} \right)^2 \frac{1}{2\nu_o} (\nu_{\alpha} - \nu_{\beta})^2 (-6m^2 + 6m + 2I(I+1) - 3) \] \hspace{1cm} (B.9)

For oxygen, which has \( l=5/2 \), the central \( (m = 1/2 \leftrightarrow -1/2) \), first satellite \( (m = 1/2 \leftrightarrow 3/2 \text{ or } m = -1/2 \leftrightarrow -3/2) \), and the second satellite \( (m = 3/2 \leftrightarrow 5/2 \text{ or } m = -3/2 \leftrightarrow -5/2) \) transitions respectively, the
difference between the resonance and Larmor frequency, \( \delta \nu = \nu_{\text{res}} - \nu_o \), is given by

\[
\delta \nu = \nu_o K_z + \frac{2 (\nu_x - \nu_y)^2}{9 \nu_o}
\]

\[
\delta \nu = \nu_o K_z \mp \nu_z + \frac{5 (\nu_x - \nu_y)^2}{36 \nu_o}
\]  

(B.10)

\[
\delta \nu = \nu_o K_z \mp 2 \nu_z - \frac{1 (\nu_x - \nu_y)^2}{9 \nu_o}
\]

where \( \nu_o = \frac{3}{20} eQ | \nu_{\alpha\alpha} | \), and the upper sign refers to the \((3/2, 1/2)\) or \((5/2, 3/2)\) transition.
APPENDIX C

DERIVATION OF SPIN LATTICE RELAXATION RATE FORMULA

In the work described in this thesis, we measured the nuclear spin lattice relaxation rate of oxygen and yttrium nuclei. The spin lattice relaxation is a useful quantity to measure as it is related to the spin susceptibility of the electrons in the copper oxygen planes of the high temperature superconductors, which have unusual properties we hope to describe. The formula which gives the relation between the imaginary susceptibility and the spin lattice relaxation rate will be derived in this appendix. This formalism was originally derived by Moriya [149]; the derivation in this appendix follows that given in references [13] and [32].

We will consider a nuclear spin system which is described by a temperature $T$; this requires that the population of each energy level obeys the Boltzmann distribution, $p(E_n) = \exp(-E_n / k_B T) / Z$ for some
temperature $T$. We have used the notation that $Z = \sum_n \exp(-E_n \beta)$ and $
abla = 1/k_B T$. The temperature $T$ which describes the spin system might not be the same as the temperature of the lattice, $T_L$, which acts as a thermal reservoir; however, $T_L$ is the equilibrium temperature of the spin system. We will show that the temperature of the spin system obeys the differential equation $\frac{d\beta}{dt} = \frac{\beta - \beta_L}{T_1}$, and thus will exponentially approach its equilibrium value. Further, we will calculate the time constant $T_1$ of the nuclei, assuming that the relaxation is driven by interactions between nuclear and electron spins and that the electronic system can be described by a complex susceptibility $\chi(\omega)$.

To derive the differential equation which describes the temperature of the spin system we will consider two different ways to express the quantity $\frac{d\bar{E}}{dt}$, where $\bar{E}$ is the average energy of the spin system. First, we recall that $\bar{E} = \sum_n P_n(\beta) E_n$ (where the dependence of the probability $p(E_n)$ on temperature is made explicit in the expression $P_n(\beta)$), and write $\frac{d\bar{E}}{dt}$ as $\frac{d\bar{E}}{d\beta} \frac{d\beta}{dt}$.
We have made the high temperature approximation that \( \exp(-E_n\beta) = 1 \) and thus also that \( Z = \sum_n \exp(-E_n\beta) = \sum_n 1 = Z_w \).

The second way to calculate \( \frac{d\bar{E}}{dt} \) is to use the rate equations

\[
\frac{dp_n}{dt} = \sum_m (p_m W_{mn} - p_n W_{nm})
\]

which describe the changing population of an energy level,

\[
\frac{d\bar{E}}{dt} = \frac{d}{dt} \left[ \sum_n p_n E_n \right] = \sum_n \left[ E_n \frac{dp_n}{dt} \right] = \sum_n \left[ E_n \sum_m (p_m W_{mn} - p_n W_{nm}) \right] = \frac{1}{2} \sum_{n,m} \left[ (E_n - E_m)(p_m W_{mn} - p_n W_{nm}) \right]
\]
When the system is in thermal equilibrium with the lattice (so that the probabilities are given by their equilibrium values \( p_n^{(L)} \), \( \frac{dp_n^{(L)}}{dt} = 0 \) and \( p_n^{(L)} W_{mn} = p_m^{(L)} W_{mn} \). Recalling that \( p_n^{(L)} = p_m^{(L)} e^{(E_m - E_n) \beta_L} \), we find \( W_{mn} = W_{nm} e^{(E_n - E_m) \beta_L} \). Using the high temperature approximation introduced earlier, we can simplify Equation C.2

\[
\frac{dE}{dt} = \frac{1}{2} \sum_{n,m} W_{mn} \left[ 1 - \exp((E_m - E_n) \beta) \exp(-(E_m - E_n) \beta_L) \right] (E_n - E_m)
\]

\[
= \frac{1}{2} \sum_{n,m} W_{mn} \left[ 1 - (1 - (E_m - E_n)(\beta - \beta_L)) \right] (E_n - E_m)
\]

\[
= \frac{1}{2} \sum_{n,m} W_{mn} (E_n - E_m)^2 (\beta - \beta_L) \tag{C.3}
\]

Equating the two expressions (Equations C.1 and C.3) for \( \frac{dE}{dt} \), and rearranging, we find

\[
\frac{d\beta}{dt} = \frac{\frac{1}{2} \sum_{n,m} W_{mn} (E_m - E_n)^2 (\beta - \beta_L)}{\sum_n E_n^2}
\]

This differential equation can be written as

\[
\frac{d\beta}{dt} = \frac{(\beta - \beta_L)}{T_1}, \tag{C.4}
\]
where

\[
\frac{1}{T_1} = \frac{1}{2} \sum_{m,n} W_{mn} (E_m - E_n)^2 \sum_n E_n^2 .
\]  

(C.5)

This formula for $T_1$ is valid when, as we assumed in this derivation, the spin system can be described with a temperature. Physically, this corresponds to inverting (either completely or partially) all of the energy levels, rather than inverting just a single transition.

We can calculate the transition rates $W_{mn}$ which occur in Equation C.5. We will assume that the mechanism responsible for relaxation of the nuclei is a nuclear-electron interaction, $\nu \propto \vec{I} \cdot \vec{S}$, where $\vec{I}$ is the nuclear spin and $\vec{S}$ is the spin of the electron. Whenever a nuclear spin flips from state $|m\rangle$ to state $|n\rangle$, there must also be a transition of the electronic state from $|\alpha\rangle$ to $|\alpha'\rangle$ in order to conserve the total energy of the system.

Fermi’s Golden Rule can be used to evaluate the transition rates

\[
W_{mn} = \sum_{\alpha,\alpha'} P(E_\alpha) W_{m,\alpha,n,\alpha'}
\]  

(C.6)

where

\[
W_{m,\alpha;n,\alpha'} = \frac{2\pi}{\hbar} |\langle \alpha, m | V_{\text{en}} | \alpha', n \rangle|^2 \delta(E_\alpha + E_m - E_{\alpha'} - E_n)
\]  

(C.7)
and the nuclear-electron interaction is given as

\[ V_{en} = \sum_{\eta, \eta', r} A_{\eta \eta'}(r) S_\eta'(r) I_\eta \]

where the sum is over \( \eta, \eta' \), which are the principle axes \( x, y, \) and \( z \), and is also over all the electron sites \( \vec{r} \). \( A_{\eta \eta'}(\vec{r}) \) gives the magnitude of the hyperfine coupling between the nuclear spin and an electron spin at position \( \vec{r} \); this nuclear-electron interaction connects a single nucleus to many electrons. We can also express \( V \) in terms of its Fourier components,

\[ V_{en} = \sum_{\eta, \eta', \vec{q}} A_{\eta \eta'}(\vec{q}) I_\eta \sum_{\vec{r}} S_\eta'(\vec{r}) e^{i\vec{q} \cdot \vec{r}} \tag{C.8} \]

where

\[ A_{\eta \eta'}(\vec{q}) = \sum_{\vec{r}} A_{\eta \eta'}(\vec{r}) e^{-i\vec{q} \cdot \vec{r}}. \tag{C.9} \]

Combining, we find that

\[ W_{mn} = \frac{2\pi}{\hbar} \sum_{n, \eta, \eta', \vec{q}, \vec{q}', \alpha, \alpha', \vec{q}, \vec{q}'} P(E_\alpha)|A_{\eta \eta'}(\vec{q})| I_\eta \sum_{\vec{r}} S_{\eta'}(\vec{r}) \cos(\vec{q} \cdot \vec{r}) (\alpha', m) \]

\[ \times (\alpha', n)|A_{\eta \eta'}(\vec{q}')| I_{\eta'} \sum_{\vec{r}} S_{\eta''}(\vec{r}') \cos(\vec{q}' \cdot \vec{r}') (\alpha, m) \]

\[ \times \delta(E_\alpha + E_{\alpha'} - E_n - E_m) \tag{C.10} \]

We can simplify Equation C.10 in two ways. First, we can characterize each electronic state \( |\alpha\rangle \) and \( |\alpha'\rangle \) by a wavevector; for each pair of states, only one value of \( \vec{q}' \) will have non-vanishing matrix
elements. Second, we can suppose that the wavefunction is a product of nuclear and electronic systems, so that we can separate the two systems. We can then say that \( \langle \alpha, m | I_\eta S | \alpha', n \rangle = \langle m | I_\eta | n \rangle \langle \alpha | S | \alpha' \rangle \) for any electronic operator \( S \). This yields

\[
W_{mn} = \sum_{\eta, \eta', \eta''} \langle m | I_\eta | n \rangle \langle n | I_{\eta'} | m \rangle \alpha_{mn; \eta, \eta', \eta''}.
\] (C.11)

where

\[
\alpha_{mn; \eta, \eta', \eta''} = \frac{2\pi}{\hbar} \sum_{\eta, \eta', \eta''} A_{\eta \eta'}(\bar{q}) A_{\eta'' \eta'}(\bar{q}) \sum_{a, a'} P(E_a) \langle \alpha | \sum_{\tilde{r}} S_{\eta'}(\tilde{r}) \cos(\bar{q} \cdot \bar{r}) | \alpha' \rangle \\
\times \langle \alpha' | \sum_{\tilde{r}} S_{\eta''}(\tilde{r}) \cos(\bar{q} \cdot \bar{r}) | \alpha \rangle \delta(E_a + E_m - E_{\alpha'} - E_n).
\] (C.12)

It will be useful to notice that when \( \eta'' = \eta''' \),

\[
\alpha_{mn; \eta, \eta', \eta''} = \frac{2\pi}{\hbar} \sum_{\eta, \eta', \eta''} A_{\eta \eta'}(\bar{q}) A_{\eta'' \eta'}(\bar{q}) \sum_{a, a'} P(E_a) \left| \langle \alpha | \sum_{\tilde{r}} S_{\eta'}(\tilde{r}) \cos(\bar{q} \cdot \bar{r}) | \alpha' \rangle \right|^2 \\
\times \delta(E_a + E_m - E_{\alpha'} - E_n).
\] (C.13)

We can make a connection between the transition rates \( W_{mn} \) and the physical description of a sample, in particular its imaginary susceptibility \( \chi''(\omega) \), by considering the power dissipated in a NMR coil. Imagine a coil which has inductance \( L_o \) and resistance \( R_o \); it will have a complex impedance \( Z = R_o + iL_o\omega \). The power dissipated in the coil is \( P = i_0^2 R/2 \), where \( i_0 \) is the current flowing through the coil. If a material with complex susceptibility \( \chi(\omega) = \chi'(\omega) - i\chi''(\omega) \) is inserted into the coil,
the inductance of the coil will be modified to $L = L_0(1 + 4\pi\chi(\omega))$; the impedance will be $Z = [R_0 + 4\pi L_0 \omega \chi'\prime(\omega)] + i[L_0 \omega(1 + 4\pi\chi'(\omega))]$. There is an extra resistance, $\Delta R = 4\pi L_0 \omega \chi'\prime(\omega)$, due to the imaginary susceptibility $\chi'\prime(\omega)$. This extra resistance will produce power dissipation in the sample, where

$$\bar{P} = i^2 \Delta R / 2 = 2\pi i^2 L_0 \omega \chi'\prime(\omega).$$

Recall that the current flowing through the coil is related to the magnetic field in the coil by $\frac{L_0 i^2}{2} = \frac{H^2}{8\pi}$, where $V$ is the volume inside the coil. Substituting for $L_0$ in the above equation gives the average power (per unit volume, per unit field) as

$$\bar{P} = \omega \chi'\prime(\omega) / 2.$$

Another expression for the average power $\bar{P}$ can be found by considering the energy absorbed by electrons during transitions between electronic states (the energy absorbed by nuclei can be neglected in comparison). Denoting $W_{a\alpha}$ to be the transition rate from one electronic state $|\alpha\rangle$ to another $|\alpha'\rangle$ and $P(E_\alpha)$ to be the Boltzmann probability that an electron has energy $E_\alpha$, we can write the net rate of transitions from
\[ |\alpha\rangle \rightarrow |\alpha'\rangle \text{ as } W_{\alpha,a} P(E_a) - W_{\alpha',a} P(E_{a'}). \] Summing over all possible transitions, the power absorbed by the electrons is

\[ \bar{P} = \sum_{E_{\alpha'} > E_a} (E_{\alpha'} - E_a) [W_{\alpha,a} P(E_a) - W_{\alpha',a} P(E_{\alpha'})]. \]

In the high temperature approximation, \( W_{\alpha,a} = W_{\alpha',a} \), and the ratio of probabilities \( P(E_a) / P(E_{\alpha'}) \) is \( (E_{\alpha'} - E_a) / kT \). Thus the power absorbed simplifies to

\[ \bar{P} = \sum_{E_{\alpha'} > E_a} (E_{\alpha'} - E_a)^2 W_{\alpha,a} P(E_a) \beta. \] (C.15)

Comparing the two expressions (Equations C.14 and C.15) for power absorbed, we see that we can express the imaginary susceptibility, \( \chi''(\omega) \), in terms of the transition rates \( W_{\alpha,a} \). We find that

\[ \chi''(\omega) = \frac{2}{\omega} \sum_{E_{\alpha'} > E_a} (E_{\alpha'} - E_a)^2 W_{\alpha,a} P(E_a) \beta \]

\[ = \frac{1}{\omega} \sum_{\alpha,a} (E_{\alpha'} - E_a)^2 W_{\alpha,a} P(E_a) \beta \] (C.16)

If the transitions are due to an interaction between electron spins and a unit magnetic field \( h(r,t) \cos(\omega t) \cos(\vec{q} \cdot \vec{r}) \), the perturbing hamiltonian is

\[ \mathcal{H}_{\text{pert}} = -\gamma_e \hbar \sum_{\vec{r}} S(\vec{r}) h(r,t) = -\gamma_e \hbar \sum_{\vec{r}} S(\vec{r}) \cos(\vec{q} \cdot \vec{r}) \cos(\omega t). \]

Fermi's Golden Rule states that

\[ W_{\alpha,a} = \frac{2\pi}{\hbar} \left| \langle \alpha | - \gamma_e \hbar \sum_{\vec{r}} S(r) \cos(\vec{q} \cdot \vec{r}) | \alpha' \rangle \right|^2 \delta(E_{\alpha'} - E_a - \hbar \omega). \]
This allows us to rewrite \( \chi''(\omega) \) as

\[
\chi''(\omega) = \frac{(\gamma \hbar)^2 (\hbar \omega)^2}{k_B T \omega} \frac{2\pi}{\hbar} \sum_{\alpha,\alpha'} P(E_\alpha) \left| \sum_{\bar{r}} S_{\eta'}(\bar{r}) \cos(\bar{q} \cdot \bar{r}) \alpha' \right|^2 \delta(E_\alpha - E_{\alpha'} - \hbar \omega)
\]

where the subscript on \( \chi''(\omega) \) refers to the principle axis along which the susceptibility is given. Only one subscript needs to be given (compare to Equation C.12 for \( a_{mn,\eta,\eta',\eta'',\eta'''} \)) since by definition there are no off diagonal components to \( \chi''(\omega) \) when we are working in the principle axis system.

An interpretation of the imaginary susceptibility, based on Equation C.17, is that \( \chi''(\bar{q},\omega) \) relates the power absorbed by electrons in the presence of a fluctuation magnetic field associated with the nuclei. The electrons will absorb the excess energy that the nuclei must release in order to return to their equilibrium temperature, according to Equation C.4.

We can now rewrite \( W_{mn} \) (Equation C.11) in terms of \( \chi''(\omega) \),

\[
W_{mn} = \sum_{n,\eta,\eta'} \sum_{\bar{q}} \langle m|I_{\eta}|n|I_{\eta'}|m \rangle \frac{k_B T}{\hbar^2 (\gamma' \hbar)^2} \omega_{mn} \frac{A_{\eta''}(\bar{q}) A_{\eta,\eta'}(\bar{q}) \chi_{\eta''}(\bar{q})}{\omega_{mn}} \quad (C.18)
\]
Substituting Equation C.18 into the formula for $T_1$ (Equation C.5), we find

$$\frac{1}{T_1} = \frac{1}{2} \sum_{m,n} \frac{k_B T}{\hbar^2 (\gamma_e \hbar)^2 \omega_{mn}} (E_m - E_n)^2 \sum_{n', \eta'} \sum_{\tilde{q}} \langle m | I_{\eta} | n \rangle \langle n | I_{\eta'} | m \rangle A_{\eta \eta'} (\tilde{q}) A_{\eta \eta'} (\tilde{q}) \chi_{\eta \eta'} (\tilde{q}) \delta_{\eta \eta'} \delta_{\tilde{q} \tilde{q}} \sum_m E_m^2$$

Equation C.19 can be simplified considerably if we specialize to the case of a nuclear Hamiltonian which is dominated by the Zeeman energy. Take $H_0$ parallel to the z-axis. We can ignore terms with $\eta = z$, which are only joined if $|n\rangle$ is the same as $|m\rangle$, in which case $E_n - E_m = 0$ and term does not contribute to the sum. For all other pairs of states which are joined by $I_\eta$, $|E_n - E_m| = \hbar \omega_\eta$. The only remaining $m$ and $n$ dependence in Equation C.19 is in the $\langle m | I_{\eta} | n \rangle \langle n | I_{\eta'} | m \rangle$ factor. This can be written as

$$\sum_{m,n} \langle m | I_{\eta} | n \rangle \langle n | I_{\eta'} | m \rangle = \sum_m \langle m | I_{\eta} | I_{\eta'} | m \rangle = Tr(I_{\eta} I_{\eta'})$$

which vanishes unless $\eta = \eta'$. Noting that $Tr(I_{\eta}^2) = \sum_m (E_m / \hbar \omega)^2$, we find

$$\frac{1}{T_1} = \frac{k_B T}{2 \hbar^2 (\gamma_e \hbar)^2 \omega} \sum_\tilde{q} \left[ (A_{xx}^2 + A_{yy}^2) \chi''_{xx} + (A_{xy}^2 + A_{yx}^2) \chi''_{xy} + (A_{yz}^2 + A_{zy}^2) \chi''_{yz} \right].$$

If the susceptibility is isotropic, we finally obtain

$$\frac{1}{T_1} = \frac{k_B T}{2 \hbar^2 (\gamma_e \hbar)^2 \omega} \sum_\tilde{q} \left[ A_{xx}^2 + A_{yy}^2 + A_{zz}^2 + A_{xy}^2 + A_{yz}^2 + A_{zx}^2 \right] \chi''.$$ (C.20)
For most materials, including YBCO, the only nonzero form factors are $A_{xx}$ and $A_{yy}$, the diagonal elements.

We can calculate the hyperfine constants $A_{\eta\eta}(\vec{q})$ for YBCO once we determine to which electrons a nucleus is hyperfine coupled. We will use the nuclear spin hamiltonians

\begin{align}
\mathcal{H}^{63} &= A_{z}S_z(\vec{r} = 0) + \sum_{i=1}^{4} B_{z}S_z(\vec{r}_i) \quad (C.21a) \\
\mathcal{H}^{17} &= \sum_{i=1}^{2} C_{z}S_z(\vec{r}_i) + \sum_{i=1}^{4} C'_{z}S_z(\vec{r}_i) \quad (C.21b) \\
\mathcal{H}^{89} &= \sum_{i=1}^{8} D_{z}S_z(\vec{r}_i) \quad (C.21c)
\end{align}

for copper, oxygen, and yttrium respectively. For the copper, we have included a direct hyperfine coupling, $A$, to the on-site electron spin as well as a transferred hyperfine coupling, $B$, first suggested by Mila and Rice [91], to the electron spins at the four nearest neighbor copper sites. For oxygen, we have included transferred hyperfine couplings, $C$, to spins at the two nearest neighbor sites as first proposed by Shastry [90]. Also, following the proposal by Zha et al [11], we have included a transferred hyperfine coupling, $C'$, to spins at the four next-nearest neighbor sites. Yttrium is hyperfine coupled, with a hyperfine constant $D$, to electron spins at the eight nearest neighbor copper sites [92]. The hyperfine
Figure C.1. Hyperfine couplings within the copper-oxygen plane. The on-site hyperfine coupling $A$, and the transferred hyperfine couplings, $B$, to the four nearest neighbors are shown between a copper nucleus and the electron spins located at copper sites. For oxygen, the couplings $C$ to the two nearest neighbors and $C'$ to the four next-nearest neighbors are shown.
Table C.1. Hyperfine constants and positions of electrons spins, relative to the nuclei, for copper.

<table>
<thead>
<tr>
<th>Hyperfine constant</th>
<th>Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>(0,0)</td>
</tr>
<tr>
<td>B</td>
<td>(a,0)</td>
</tr>
<tr>
<td>B</td>
<td>(-a,0)</td>
</tr>
<tr>
<td>B</td>
<td>(0,a)</td>
</tr>
<tr>
<td>B</td>
<td>(0,-a)</td>
</tr>
<tr>
<td>Hyperfine constant</td>
<td>Position</td>
</tr>
<tr>
<td>--------------------</td>
<td>----------</td>
</tr>
<tr>
<td>C</td>
<td>(a/2,0)</td>
</tr>
<tr>
<td>C</td>
<td>(-a/2,0)</td>
</tr>
<tr>
<td>C'</td>
<td>(a/2,a)</td>
</tr>
<tr>
<td>C'</td>
<td>(a/2,-a)</td>
</tr>
<tr>
<td>C'</td>
<td>(-a/2,a)</td>
</tr>
<tr>
<td>C'</td>
<td>(-a/2,-a)</td>
</tr>
</tbody>
</table>

Table C.2. Hyperfine constants and positions of electrons spins, relative to the nuclei, for oxygen.
<table>
<thead>
<tr>
<th>Hyperfine constant</th>
<th>Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>((a/2, a/2, d/2))</td>
</tr>
<tr>
<td>D</td>
<td>((-a/2, a/2, d/2))</td>
</tr>
<tr>
<td>D</td>
<td>((a/2, -a/2, d/2))</td>
</tr>
<tr>
<td>D</td>
<td>((-a/2, -a/2, d/2))</td>
</tr>
<tr>
<td>D</td>
<td>((a/2, a/2, -d/2))</td>
</tr>
<tr>
<td>D</td>
<td>((-a/2, a/2, -d/2))</td>
</tr>
<tr>
<td>D</td>
<td>((a/2, -a/2, -d/2))</td>
</tr>
<tr>
<td>D</td>
<td>((-a/2, -a/2, -d/2))</td>
</tr>
</tbody>
</table>

Table C.3. Hyperfine constants and positions of electrons spins, relative to the nuclei, for yttrium. Since yttrium lies between the two copper-oxygen layers, \(\vec{r}\) is a three dimensional vector. The distance between the copper-oxygen layers is \(d\).
couplings for copper and oxygen are illustrated in Figure C.1. The hyperfine constants \((A_{\eta\eta}(\vec{r}))\) and positions of electron spins \((\vec{r})\) are given in Tables C.1, C.2, and C.3.

Using \(A_{\eta\eta}(\vec{q}) = \sum \vec{r} A_{\eta\eta}(\vec{r}) e^{-i\vec{q} \cdot \vec{r}}\) (Equation C.9) and the information in Table C.1, we find the hyperfine constant for copper is

\[
{}^{63}A(\vec{q}) = A + Be^{-iq_xa} + Be^{iq_xa} + Be^{-iq_ya} + Be^{iq_ya} \\
= A + 2B(\cos(q_xa) + \cos(q_ya))
\]  

(C.22a)

In writing this, we have neglected to indicate the direction along which the field lies. However, the direction is important to include as the hyperfine constant \(A\) is anisotropic.

Similarly, we can find \(\vec{q}\) space hyperfine constants for oxygen and yttrium. Writing them in a form which treats \(x\) and \(y\) symmetrically, we have

\[
{}^{17}A(\vec{q}) = (\cos(q_xa/2) + \cos(q_ya/2))(C + C'(\cos(q_xa) + \cos(q_ya))) \\
= 8D\cos(q_xa/2)\cos(q_ya/2)\cos(q_zd/2) \\
= 8D\cos(q_ya/2)\cos(q_ya/2)\cos(q_zd/2)
\]  

(C.22b)

Once \(A(\vec{q})\) is squared, the \(\cos(q_zd/2)\) factor in Equation C.22c will be integrated to yield a factor of 1/2, following established practice [16].

One often encounters the "form factors" \(F\) which are related to \(A_{\eta\eta}(\vec{q})\) by \(F_{\alpha\alpha} = A_{\alpha\alpha}^2 + A_{\alpha'\alpha'}^2\). The \(q\)-dependence of these form factors is
important in determining the relaxation behavior of the various nuclei. Since the form factor for copper has a maximum at \((\pi,\pi)\), whereas the form factors for oxygen and yttrium are zero at that same wavevector, only the copper can be relaxed by antiferromagnetic fluctuations (discussed in section 2.2.6) centered at \((\pi,\pi)\). In contrast, the oxygen and yttrium form factors “screen” these fluctuations, so that the antiferromagnetic fluctuations do not contribute significantly to the oxygen and yttrium relaxation.
APPENDIX D

MATHEMATICA PROGRAM FOR CALCULATING RELAXATION RATES

An essential step in the work described in the thesis was the calculation of the spin lattice relaxation rate, \(1/T_1\), for various nuclei. In this calculation, we used Moriya's formula [149] for \(1/T_1T\), which we have derived in Appendix C. We use the imaginary magnetic susceptibility given by Millis, Monien, and Pines [16], with modifications by Zha, Barzykin, and Pines [11].

We used the commercially available program Mathematica 2.2 from Wolfram Research in order to numerically calculate \(1/T_1T\) for yttrium and oxygen at various temperatures. The Mathematica program we used, along with comments in italics, is given below.
THIS MATHEMATICA PROGRAM CALCULATES 1/T1T FOR OXYGEN AND YTTRIUM, ACCORDING TO THE ZBP MODEL.

First, define some constants. These are given in Table 2.1.

delta = .1 * [Pi]

gamma = .308

alpha = 14.8

Cperp = .865 * 33

Cpar = 1.63 * 33

Cpr = .25 * 33

Dev = N[4.8 10^-9]

chi is the static susceptibility, xi is the correlation length, and wsf is the spin fluctuation frequency. We are using slightly different temperature dependencies of the static susceptibility for the 17O calculation and for the 89Y calculation – throughout the program, “17” refers specifically to the 17O calculation and “89” to the 89Y calculation. The formulas for wsf and chi are only valid above Tcr (~150K)

chi17[tp_] := 2.717 ( 1 - 2.89 10^-4 tp)

chi89[tp_] := 2.705 ( 1 - 2.75 10^-4 tp)
The imaginary part of the low frequency susceptibility, divided by frequency, is the sum of two parts: \( AF[x_, y_, tp_] \), which is a function of position in q-space, is due to the AF correlations; \( FLConst[tp_] \) is the normal fermi liquid contribution.

\[
FLConst17[tp_] := (3.14159/gamm)*chi17[tp]
\]

\[
FLConst89[tp_] := (3.14159/gamm)*chi89[tp]
\]

\[
AFConst[tp_] := alpha * (xi[tp])^2 / wsf[tp]
\]

\[
AF[x_, y_, tp_] := .25 * AFConst[tp] *
\]

\[
(((1+xi[tp]^2*((x-Pi-delta)^2+(y-Pi-delta)^2))^-2)
+ (1+xi[tp]^2*((x-Pi+delta)^2+(y-Pi-delta)^2))^-2)
+ (1+xi[tp]^2*((x-Pi-delta)^2+(y-Pi+delta)^2))^-2)
+ (1+xi[tp]^2*((x-Pi+delta)^2+(y-Pi+delta)^2))^-2)
\]

\( F17 \) is the form factor for Oxygen, and \( F89 \) the form factor for Yttrium. \( Fxxconst \) is the integral of \( Fxx \) over the first Brillouin zone – since this does not change with temperature, it only needs to be
integrated once. Axx contains numerical constants and $\gamma_n^2$ and sets the magnitude of the entire calculation.

\[
F_{17}[x_, y_] := \cos\left(\frac{x}{2}\right)^2 (C_{\text{perp}} + 2C_{\text{pr}} \cos y)^2 + \\
\cos\left(\frac{y}{2}\right)^2 (C_{\text{perp}} + 2C_{\text{pr}} \cos x)^2 + \\
\cos\left(\frac{x}{2}\right)^2 (C_{\text{par}} + 2C_{\text{pr}} \cos y)^2 + \\
\cos\left(\frac{y}{2}\right)^2 (C_{\text{par}} + 2C_{\text{pr}} \cos x)^2
\]

F_{17}\text{const} = \text{NIntegrate}[F_{17}[x,y],\{x,0,\pi\},\{y,0,\pi\}]

A_{17} = \text{N}[1.4919 \times 10^{-6} \times 4 \times (2\pi)^{-2}]

\[
F_{89}[x_, y_] := 32 \text{Dev}^2 \cos\left(\frac{x}{2}\right)^2 \cos\left(\frac{y}{2}\right)^2
\]

F_{89}\text{const} = \text{NIntegrate}[F_{89}[x,y],\{x,0,\pi\},\{y,0,\pi\}]

A_{89} = 6.62 \times 10^9

This loop performs the actual calculation. It gives the temperature at which the calculation was performed, the contribution to $1/T, T$ from the AF part of the susceptibility, and the contribution to $1/T, T$ from the FL part of the susceptibility.

\[
\text{Do[Print[\{tpr,A_{17}\times\text{NIntegrate}[AF[x,y,tpr]\times F_{17}[x,y],\{x,0,\pi\}, \\
\{y,0,\pi\}],A_{17}\times F_{17}\text{const}\},\{tpr,290,710,30\}]]}
\]
Do[Print[{tpr,A89*NIntegrate[AF[x,y,tpr]*F89[x,y],{x,0,Pi},
{y,0,Pi}],A89*FLConst89[tpr]*F89const}]],
{tpr,290,710,30}]

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BIBLIOGRAPHY


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[116] KaleidaGraph (Synergy Software).


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