NMR Study of the Pseudogap in Pb$_2$Sr$_2$(Y,Ca)Cu$_3$O$_{8+\delta}$ Crystals

by

Ya-Wei Hsueh

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Dedicated to the memory of my father
ABSTRACT

In this thesis, we report Cu NMR/NQR studies of the high temperature superconductor Pb$_2$Sr$_2$(Y,Ca)Cu$_3$O$_8$ ($T_c = 80$ K) using slightly underdoped crystals. The structure of Pb$_2$Sr$_2$(Y,Ca)Cu$_3$O$_8$ contains two different Cu sites: Cu(2) in the CuO$_2$ plane and an oxygen-free Cu(1) layer.

The quadrupolar frequencies, 31.957 MHz and 29.88 MHz for $^{63}$Cu(1) and $^{65}$Cu(2) sites, respectively, have been obtained from the NQR spectrum. The Cu(1) line is narrow with a linewidth of 0.44 MHz, whereas the Cu(2) line is broad with a linewidth of 1.81 MHz, due to the inhomogeneity of electric field gradients (EFG) from the Ca$^{+2}$/Y$^{+3}$ layers.

We have obtained Cu(1) and Cu(2) NMR spectra. From the analysis of the field-dependent measurements, we found that the tilting of the EFG principal axis with respect to c-axis at the Cu(1) site is more than that at the Cu(2) site. The EFGs from the two nearest oxygen ions above and below Cu(1) are responsible for this extra tilting. The spin-lattice relaxation time obtained at $T = 85$ K for Cu(1) and Cu(2) are 15.5 sec and 520 $\mu$s respectively. The much longer relaxation time in Cu(1) is consistent with band structure calculations indicating that Cu(1) makes an extremely small contribution to the density of states at the Fermi surface.

The temperature dependence of the Knight shift and the spin-lattice relaxation rate for both Cu(1) and Cu(2) sites has been measured. Our analysis shows that the relaxation for Cu(1) is due to a quadrupolar-phonon coupling mechanism. We have observed a pseudogap in the Cu(2) Knight shift and spin-lattice relaxation rate. In contrast to other underdoped compounds, the pseudogap observed in the Knight shift is weak and occurs at a significantly lower temperature. On the other hand, the effect that the pseudogap has on spin-lattice relaxation is quite similar to the observed behaviour in other compounds. The manifestation of the pseudogap at $q=0$ is different than that at $q=Q$. The evidence and some qualitative theories of the pseudogap are reviewed and discussed in terms of experimental data, with emphasis on our NMR data.

The spin-lattice relaxation rate anisotropy measurements at Cu(2) sites reveal that
the hyperfine coupling constants are temperature independent and the hybridization between Cu(3d)-O(2p)-Cu(4s) orbits in PSYCCO are stronger than in Y-compounds.
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Chapter 1

Introduction

1.1 Overview

In 1986, Bednorz and Müller [1] discovered the high-$T_c$ superconductor La$_{2-x}$Ba$_x$CuO$_4$ with $T_c$ of 30 K. Subsequently many high-$T_c$ cuprates with $T_c$ above the boiling temperature of liquid nitrogen (77 K) were synthesized, such as Y-Ba-Cu-O ($T_c = 93$ K, 1987), Bi-Sr-Ca-Cu-O ($T_c = 110$ K, 1988), Tl-Ba-Ca-Cu-O ($T_c = 125$ K) and Hg-Ba-Ca-Cu-O with the highest $T_c$ of 135 K. The properties of high-$T_c$ cuprates are very different from conventional superconductors. The phonon-mediated electron pairing interaction, which successfully describes conventional superconductors, is not appropriate for the cuprates. While researchers have made progress in determining the symmetry of the superconducting order parameter (evidence for d-wave symmetry has gradually accumulated and is gaining acceptance), the mechanism of high-$T_c$ superconductivity is still not understood.

The common feature of high-$T_c$ compounds is that they are copper oxides and all contain CuO$_2$ planes. The undoped compound has antiferromagnetically (AF) ordered spins localized at Cu sites in the CuO$_2$ plane. Doping CuO$_2$ planes with charge carriers by varying the composition can turn the AF insulator into a superconductor. For example, one adds holes to YBa$_2$Cu$_3$O$_6$ (AF insulator) by increasing the oxygen content to obtain a superconductor (YBa$_2$Cu$_3$O$_{7-5}$). Fig. 1.1 shows the generic doping phase diagram. The doping destroys the long-range AF order and
results in short-range AF fluctuations. The doping phase diagram of high-$T_c$ superconductors can be split into three regions. An underdoped region where $T_c$ increases with increased hole doping. An optimally doped point where $T_c$ reaches its maximum. An overdoped region where $T_c$ decreases with increased hole doping, although the material becomes more metallic (increasing conductivity).

The behaviour of the normal state of high-$T_c$ superconductors is unusual. Unlike conventional superconductors, the normal state of high-$T_c$ superconductors does not behave like an ordinary metal. For example, the planar Cu spin-lattice relaxation rate $1/(T_1 T)$, which is proportional to the low-frequency spin susceptibility at $q = Q = (\pi/a, \pi/a)$, has an anomalous temperature dependence instead of being constant as in conventional metals. Presumably this is due to the strong antiferromagnetic fluctuations, which increase as the temperature decreases. The fluctuations also increase as the doping decreases. The underdoped high-$T_c$ compounds are even more unusual. As $T$ decreases, $1/(T_1 T)$ stops increasing at a temperature well above $T_c$ and then decreases as $T$ decreases, with no sharp transition near $T_c$ (see Fig. 1.2(a)). In the optimally-doped or overdoped case, $1/(T_1 T)$ starts decreasing slightly above $T_c$. The decrease in $1/(T_1 T)$ well above $T_c$ suggests a suppression of the density of states,
Figure 1.2: (a) Temperature dependences of NMR $1/(T_1 T)$ at the Cu(2) site of YBa$_2$Cu$_3$O$_{6.63}$ (underdoped) [6] and YBa$_2$Cu$_3$O$_7$ (optimally-doped) [72]. (b) Temperature dependences of the Cu(2) Knight shift of YBa$_2$Cu$_3$O$_{6.63}$ [6] and YBa$_2$Cu$_3$O$_7$ [70].

implying that an energy gap opens up in the normal state. The NMR Knight shift, which measures the low-frequency spin susceptibility at $q = (0, 0)$, also decreases with decreasing temperature in the normal state with no sharp transition at $T_c$. This is in contrast with the temperature independent Knight shift of the optimally-doped compounds which shows a sharp transition at $T_c$ (see Fig. 1.2(b)). The decrease in the spin susceptibility suggests the reduction in density of states, also implying the opening of a gap in the normal state. Originally, this gap is referred to as “spin gap”, “pseudogap” or “normal state gap”, depending on the experiments. Most people now refer to it as “pseudogap”; what they really mean is a suppression of the unknown origin of the excitations.

It is generally believed that the mechanism of superconductivity in the high-$T_c$ cuprates has its origin in their unusual properties in the normal state, particularly in the underdoped regime [2]. Discovering the origin of the pseudogap for underdoped compounds thus may be the key to understanding the mechanism giving rise to high-$T_c$ superconductivity.
The first observation of the pseudogap came from NMR measurements [3, 4, 5] in 1988, where $1/(T_1 T)$ was suppressed in the normal state. Underdoped compounds, such as $YBa_2Cu_3O_{6.63}$ [5, 6, 7], $YBa_2Cu_4O_8$ [8] and $Pb_2Sr_2(Y,Ca)Cu_3O_{8+\delta}$ [9], display a pseudogap in NMR measurements. Overdoped compounds, on the other hand, do not display a pseudogap. The pseudogap has been observed in the spin channel not only in NMR experiments but also in inelastic neutron scattering (INS) experiments and in the bulk susceptibility. The evolution of the energy dependence of dynamical susceptibility $\chi''(q,\omega)$ with temperature in underdoped $YBa_2Cu_3O_{6.69}$ shows that the low-energy excitations are suppressed above $T_c$, suggesting a gap in the normal state [10, 11]. The suppression of bulk susceptibility of $YBa_2Cu_3O_{6+x}$ in the normal state also indicates a gap opening up above $T_c$ [12].

The pseudogap appears also in the transport properties. Optical measurements on the underdoped systems revealed evidence for a gap formation above $T_c$. As shown
1.1 Pseudogap

Figure 1.4: Temperature dependence of in-plane resistivity of twinned YBa$_2$Cu$_3$O$_{7-y}$ crystals [18]. Inset: Temperature dependence of $\rho_a$ and $\rho_b$ for detwinned crystals of $T_c = 90$ and 60 K.

In Fig. 1.3, the scattering rate $1/\tau_{ab}(\omega, T)$, which is extracted from the ab-plane optical conductivity, deviates from near linearity in $\omega$ at low frequencies and is depressed rapidly, forming a pseudogap structure in the normal state. There is a large suppression in $1/\tau_{ab}(\omega, T)$ occurring in the normal state and a relatively small suppression occurring in the superconducting state. Such gaplike depressions in $1/\tau_{ab}(\omega, T)$ have been observed on the underdoped YBa$_2$Cu$_3$O$_{6+x}$ [13], YBa$_2$Cu$_4$O$_8$ [13] and Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ [14] systems, but not in the overdoped compounds. Moreover, the c-axis optical conductivity $\sigma_c(\omega)$ also shows a depression at low frequencies above $T_c$, suggesting the formation of a gap [15, 16]. However, identifying this feature with the pseudogap is quite controversial at the moment. It has been suggested that the physics underlying the appearance of a gap in the c-axis properties is of a different origin than that of the pseudogap [17].

Ito et al. [18] report that in underdoped YBa$_2$Cu$_3$O$_{7-y}$, the in-plane resistivity $\rho_{ab}$, as shown in Fig. 1.4, deviates from the $T$-linear behaviour below a certain temperature well above $T_c$. In contrast, in the optimally-doped compound the tem-
Figure 1.5: (a): $S(T)/T$ vs $T$ for $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [24]. (b): $\chi(T)$ of $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ [12].

Temperature dependence of $\rho_{ab}$ is linear. The deviation was found to correspond to the pseudogap formation in the spin excitation spectrum suggested by NMR and INS studies. The onset temperature of the deviation from $T$-linearity marks the opening of the pseudogap and increases with decreased doping. An intimate relationship between in-plane charge transport and spin fluctuations has been found through the comparison of $\rho_{ab}$ and NMR $1/(T_1 T)$. When the pseudogap opens, the suppressed spin fluctuations would reduce the in-plane scattering, leading to a decrease in the in-plane resistivity. The presence of a pseudogap in the underdoped region has also been suggested for other systems, $\text{YBa}_2\text{Cu}_4\text{O}_8$ [19, 20, 21] and $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ [22], where the deviation from $T$-linear dependence of $\rho_{ab}$ has also been observed.

When electronic spin and charge excitations are probed in electronic specific heat measurements, one also observes a suppression of density of states (the excitation spectrum) in the underdoped region [23, 24], which is attributed to the development
Figure 1.6: ARPES spectra of normal state (N) and superconducting state (SC) comparison for underdoped (U) and overdoped (O) samples[27].

of a pseudogap. A close relationship between the electronic entropy $S(T)$ and the bulk susceptibility $\chi(T)$ has been established by finding the similarity between the plot of $S/T$ and the plot of $\chi$ in the normal state, as shown in Fig. 1.5. This indicates, together with the experiments discussed in previous paragraphs, the development of a pseudogap in the entire excitation spectrum, involving both the spin and charge channels.

Perhaps the most direct evidence for the pseudogap is from angle-resolved photoemission (ARPES) studies. The photoemission spectrum for an ideal metal at zero temperature should be constant as a function of energy up to the Fermi energy, where it would drop sharply to zero. Both Ding’s group [25] and Shen’s group [26, 27] have observed an energy gap in the normal state through the studies of ARPES on Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$. Figure 1.6 shows the photoemission spectra near the Fermi energy $E_F$ (the vertical dashed line) for both an overdoped sample and an underdoped
Figure 1.7: The onset temperature of the pseudogap $T^*$ obtained from the in-plane resistivity measurements in single crystal samples of YBa$_2$Cu$_3$O$_y$ [30]. $T^*$ represents the departure from the high-temperature $T$-linear behaviour.

sample. For the overdoped sample, the leading edge is close to $E_F$ in the normal state (N-O) but is pulled back in the superconducting state (SC-O), signalling the superconducting energy gap. In the underdoped sample, the leading edges have receded from $E_F$ in both the normal (N-U) and superconducting states (SC-U), indicating that an energy gap has already developed above $T_c$. There is some indication that the gap either goes away at temperatures around 200–300 K or become much weaker there.

There is no doubt that a pseudogap appears in the normal state, though the nature of the pseudogap is far from clear. Considering the symmetry of the pseudogap, ARPES experiments reveal that the gap is anisotropic. The momentum dependence and the magnitude of the gap are very similar to those of the $d_{x^2-y^2}$ gap observed in the superconducting state [28, 25]. Williams et al. [29] analyzed and deduced the pseudogap energies from the NMR data of several underdoped high-$T_c$ compounds. The deduced pseudogap energies agree well with the gap determined from ARPES experiments and suggest a d-wave-like symmetry which is consistent with the ARPES
1.1 Pseudogap

There is evidence to show that the onset of the pseudogap depends strongly on doping. Uemura et al. [30] plots the onset of the pseudogap $T^*$ from the resistivity measurements versus doping for $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ (see Fig. 1.7). $T^*$ is the temperature where $\rho_{ab}$ deviates from the $T$-linear behaviour. As seen in Fig. 1.7, $T^*$ is low for optimally doped region and increases with decreasing doping and decreasing $T_c$ in the underdoped region. An analysis based on the electronic specific heat data of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ shows that the size of the pseudogap is proportional to $\delta$ [12]. Williams et al. [31] analyzed the NMR data of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and $\text{La}_{2-x}\text{Sr}_x\text{CaCu}_2\text{O}_6$ and found that the size of the pseudogap increases with decreasing hole concentration, which is consistent with the electronic specific heat data. Moreover they found the size of the pseudogap scales with the crossover temperature $T^*$.

What is the origin of the pseudogap? One possible explanation involves the evolution of local electronic structure with temperature, as suggested by Emery and Kivelson [32]. As shown by the phase diagram in Fig. 1.8, there are two crossovers $T^*_1$ and $T^*_2$ above $T_c$. At temperatures below the upper crossover $T^*_1$, a local charge inhomogeneity forms and results in a stripe structure. Pairing may exist in such a
1.1 Pseudogap

structure. The evolution of such a structure leads to the superconducting pairing at lower crossover $T_2^*$, at which the magnitude of the superconducting order parameter becomes well defined. The pseudogap is well established there. However, phase fluctuations are important in the underdoped region, where the pair formation and phase coherence do not occur at the same temperature \([33]\). The phase coherence sets in at a lower temperature $T_c$. They predict $T_2^*$ is relatively insensitive to doping until it is cut off by $T_1^*$ at large doping. However, as seen in Fig. 1.7, the onset temperature of the pseudogap $T^*$, which corresponds to $T_2^*$ in this model, depends strongly on doping even at low doping, which does not seem to agree with the theoretical prediction of Emery and Kivelson.

Another possible explanation involves antiferromagnetic (AF) spin fluctuations and the evolution of the Fermi surface on temperature and doping, as suggested by Chubukov, Pines and Stojkovic \([2]\). The strong AF correlations between planar quasiparticles lead to unusual behaviour in the normal state. In this model, there are two classes of quasiparticles on the Fermi surface: hot and cold quasiparticles \([34]\). The hot quasiparticles, which locate at $(0, \pm \pi)$ and $(\pm \pi, 0)$, behave like a non-Fermi

Figure 1.9: The qualitative phase diagram of the high-$T_c$ cuprates as proposed by Pines et al.\([2]\).
liquid and are responsible for the creation of a pseudogap. On the other hand, the cold quasiparticles, located in the remaining parts of the Fermi surface, behave like a Fermi liquid and are responsible for the superconductivity. In the phase diagram shown in Fig. 1.9, the crossovers at $T_m$ and $T_*$ mainly reflect the behaviour of the hot quasiparticles. The strong AF correlations between hot quasiparticles result in the evolution of the Fermi surface with temperature taking place at $T_m$ and ending at $T_*$ and eventually give rise to an effective pairing interaction between hot quasiparticles at $T_*$. They claim that at $T_m$, the Fermi surface develops a minimum at hot spots and at $T_*$, the system begins to lose pieces of the Fermi surface. Recently, temperature dependent ARPES experiments have shown that the Fermi surface evolution takes place at $T \lesssim 200K$ in the underdoped BSCCO, but not in the overdoped BSCCO [35].

The AF correlations between hot quasiparticles also cause the evolution of the Fermi surface with doping. At near optimal doping, the Fermi surface is large and centered around $(\pi, \pi)$. As doping decreases, the Fermi surface splits into pockets centered at $(\pm \pi/2, \pm \pi/2)$, and eventually the large Fermi surface disappears and only four small pockets are left [36]. Marshall et al. [26] determine the Fermi surfaces
of slightly overdoped and underdoped Bi2212 by measuring the mid-point of the leading edge of the spectrum relative to the Fermi energy. As seen in Fig. 1.10(a), the slightly overdoped sample has a large Fermi surface centered at \((\pi, \pi)\), whereas in the underdoped sample a portion of the large Fermi surface disappears near \((\pi, 0)\) and that small pockets were found centered at \((\pm \pi/2, \pm \pi/2)\), suggesting the gap has a maximum near \((\pi, 0)\). However, using different analysis, Ding et al. [37] claim that a large Fermi surface is found even in the underdoped Bi2Sr2CaCu2O8+δ, with no evidence of a pocket around \((\pi/2, \pi/2)\) (see Fig. 1.10(b)). It is difficult to say which interpretation of the data is correct without a theory for the line shape.

### 1.3 NMR and Pb2Sr2Y1-xCaxCu3O8+δ

Nuclear magnetic resonance (NMR) has proven to be a powerful technique to probe electronic properties of high-\(T_c\) superconductors [38]. It provides valuable information of both the superconducting and normal states. The Knight shift \(K_s(T)\) is proportional to the spin susceptibility \(\chi'(q = 0, \omega \approx 0)\). The spin-lattice relaxation rate \(T_1^{-1}\) involves an average over all \(q\) of \(\chi''(q, \omega)\). As \(\chi''(q, \omega)\) is strongly peaked at the AF wavevector \(Q = (\pi/a, \pi/a)\), \(T_1^{-1}\) of the planar Cu nuclei predominantly probes \(\chi''(Q, \omega \approx 0)\). One of the advantages of using NMR is that it allows one to probe specific nuclear sites. Therefore NMR can probe the electronic properties of different planes, which is useful for samples with layered structures like high-\(T_c\) compounds. NMR has been useful in studies of high-\(T_c\) superconductors. NMR data exhibit the presence of the antiferromagnetic spin fluctuations [7, 39]. NMR data is also consistent with the symmetry of the order parameter. While more direct evidence for d-wave pairing in the superconducting state was observed in the tunneling experiments [40, 41], the NMR data has also provided evidence for d-wave pairing [42]. NMR data give justification of the one-component spin susceptibility in CuO2 plane: the Cu-3d spins and O-2p holes in CuO2 planes are described by the same susceptibility [6]. NMR data have been frequently used to provide evidence for and information on the pseudogap.
In this thesis, we focus on Cu-NMR studies of slightly underdoped Pb$_2$Sr$_2$Y$_{1-x}$Ca$_x$Cu$_3$O$_{6+\delta}$ (PSYCCO) crystals ($x \leq 0.5$). The smaller $T_c$ (80 K) and larger resistivity [16, 43] than optimally-doped PSYCCO indicate that these crystals are slightly underdoped. The deviation of temperature dependence of resistivity from linear-$T$ behaviour around 150 K [16] is another indication of underdoping.

The PSYCCO system was first discovered by Cava et al. [44] in 1988. The parent compound Pb$_2$Sr$_2$YCu$_3$O$_{6+\delta}$ ($\delta = 0$) is AF insulator. Superconductivity is induced in the parent compound either by partial substitution Ca$^{2+}$ on the Y$^{3+}$, or possibly by accommodation of excess oxygen ($\delta > 0$), or a combination of both. PSYCCO forms a layered structure similar to YBa$_2$Cu$_3$O$_7$ and contains the CuO$_2$ layer (Cu(2) site) and oxygen free Cu layer (Cu(1) site). The structure of PSYCCO is shown in Fig. 3.1 in Chapter 3. Jørgensen and Andersen have calculated the bond valency sum from the bond lengths data [45]. The Cu(2) bond valencies are $+2.24$ for Cu(2), $+2.05$ for Pb, $+1.20$ for Cu(1) in Pb$_2$Sr$_2$YCu$_3$O$_8$. In Pb$_2$Sr$_2$Y$_{0.5}$Ca$_{0.5}$Cu$_3$O$_8$, the bond valencies are $+2.285$ for Cu(2), $+2.10$ for Pb, $+1.20$ for Cu(1). The Cu(2) bond valency increases as increasing doping for $x = 0.0 - 0.5$, while the Pb bond valency increases up to $x = 0.4$ and is then saturated. The Cu(1) bond valency does not vary with increasing doping.

Reedyk et al. [46] observed the ab-plane properties on PSYCCO and obtained a high resistivity and large magnetic penetration depth, compared to YBa$_2$Cu$_3$O$_{7-\delta}$. This suggests that the in-plane carrier concentration is unusually small in this material, given the relatively high value of $T_c$. The penetration depth $\lambda_{ab}$ is 2575 Å for optimally-doped PSYCCO and 1200-1500 Å for YBa$_2$Cu$_3$O$_{7-\delta}$ [46]. Using $\lambda$, we can estimate that the carrier concentration in optimally-doped PSYCCO is only $\sim 25\%$ of that in YBa$_2$Cu$_3$O$_{7-\delta}$. Since our crystals are slightly underdoped, the carrier concentration should be less than 25% of that in YBa$_2$Cu$_3$O$_{7-\delta}$.

Uemura et al. [47] reported on the possible existence of a universal linear relation between $T_c$ and the muon-spin-relaxation rate $\sigma$ ($T \to 0$) of those high-$T_c$s which have less than optimally doped concentration, as seen in Fig. 1.11. With further hole doping, $\sigma$ ($T \to 0$) continues to increase while $T_c$ shows saturation and then suppression. PSYCCO, on the other hand, does not fall on this universal straight
1.1 NMR and $\text{Pb}_2\text{Sr}_7\text{Y}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_{8+\delta}$

![Graph showing transition temperature $T_c$ plotted vs the low-temperature muon-spin-relaxation rate $\sigma(T \to 0)$, measured in different high-$T_c$ superconductors.](image)

Figure 1.11: The superconducting transition temperature $T_c$ plotted vs the low-temperature muon-spin-relaxation rate $\sigma(T \to 0)$, measured in different high-$T_c$ superconductors [47].

The line $\sigma(T \to 0)$ is proportional to $\frac{1}{\lambda^2}$ ($\lambda$ is the magnetic penetration depth). The larger penetration depth [46] and relatively high $T_c$ put PSYCCO on the left side of the line. This peculiar property makes PSYCCO interesting to study.

There have been very few reports of magnetic resonance studies on PSYCCO. So far studies have been restricted to optimally doped powder samples with $x = 0.5$. Spin-lattice relaxation measurements [48, 49] of Cu spins in the CuO$_2$ planes are similar to those observed in $\text{YBa}_2\text{Cu}_3\text{O}_7$. The Pb NMR Knight shift [48] in PSYCCO is temperature independent in the normal state. Both of these temperature dependences are consistent with optimally doped samples, with no hint of a pseudogap.

We have performed NMR measurements of the $^{63}\text{Cu}(1)$ and $^{63}\text{Cu}(2)$ Knight shifts and the nuclear spin–lattice relaxation rates $T_1^{-1}$. The suppression of the $^{63}\text{Cu}(2)$ Knight shifts and $1/(T_1T)$ in the normal state suggest the opening of a pseudogap. The very different Knight shift in temperature scale between PSYCCO and the other pseudogap materials and the similar $1/(T_1T)$ in temperature scale suggest of a man-
manifestation of the pseudogap at $q = 0$ which is quite different than at $q = Q$.

This thesis is organized as follows. In Chapter 2 we will briefly review the NMR and NQR theory needed to analyze our experimental data. In Chapter 3, we will discuss the experimental technique used in this thesis. Experiment data and results will be presented in Chapter 4. Chapter 5 contains a discussion on the pseudogap seen in PSYCCO and the other underdoped compounds. Several theoretical models of the pseudogap will be reviewed in this chapter as well, and we will discuss them in terms of our NMR data. Finally, conclusions are given in Chapter 6.
Chapter 2

Nuclear Magnetic Resonance

NMR/NQR is the experimental technique used in this thesis. We have done measurements of the Knight shift, the spin-lattice relaxation rate, and the quadrupole frequency. In this chapter, we briefly review some of the basic concepts of NMR. A nuclear spin interacts with its electronic environment through electric and magnetic hyperfine couplings. As we discuss in Section 2.1, the magnetic coupling between the nuclear spin and its electronic environment gives rise to a NMR line shift, i.e., the Knight shift. We will discuss the spin-lattice relaxation rate in Section 2.2. In Section 2.3, we will consider the effect of electric interactions which also shifts NMR lines, due to the electric coupling of the nuclear quadrupole moment to the electric field gradient (EFG) tensor which is generated by the surrounding charge distribution.

2.1 Knight Shift

We first consider a bare nuclear spin $I$ in the presence of an applied magnetic field $H_0 = H_0 \hat{z}$. The Hamiltonian can be written as

$$\mathcal{H}_{\text{zeeman}} = -\gamma_n \hbar H_0 I_z .$$  \hspace{1cm} (2.1)

Therefore the allowed energies are
Fig. 2.1 shows the Zeeman levels for a Cu nuclear spin with \( I = \frac{3}{2} \). NMR can be used to detect such energy levels by inducing transitions between levels. The allowed transitions are between adjacent levels, and the separation between them is \( \gamma_n \hbar H_0 \).

Magnetic resonance occurs when the energy (provided by an r.f. field with frequency \( \omega \)) absorbed by the nuclear spin system is \( \hbar \omega = \gamma_n \hbar H_0 \). If we redefine \( \gamma_n \rightarrow \gamma_n/2\pi \) and use \( \nu \equiv \omega/2\pi \), this resonance condition becomes

\[
\nu = \gamma_n H_0 .
\]

Now we consider a system of a nuclear spin and electrons coupled together by the magnetic hyperfine interaction. In the presence of an applied magnetic field \( H_0 \), the total Hamiltonian of the nuclear spin \( I \) can be written as

\[
\mathcal{H} = \mathcal{H}_{\text{zeeman}} + \mathcal{H}_{\text{hyperfine}} ,
\]

where \( \mathcal{H}_{\text{hyperfine}} = -\gamma_n \hbar \Delta H I_z \). This latter term can be viewed as the interaction of a nuclear spin with a local magnetic hyperfine field generated by the electron spins and their orbital motions. For example, \( \mathcal{H}_{\text{hyperfine}} = A \mathbf{I} \cdot \mathbf{S} \) describes the magnetic coupling of a nuclear spin to the electron spin. The local field at the nucleus generated
by the electron spins is $\Delta H = -(\gamma_n \hbar)^{-1} A < S_z >$, which yields the NMR line shift.

The Knight shift is defined as $K \equiv \frac{\Delta H}{H_0}$. The resonance equation then becomes

$$\nu = \gamma_n H_0 (1 + K).$$

(2.5)

Therefore, the magnetic coupling between nuclear spin and electrons results in a NMR line shift from the bare nuclear resonance frequency $\gamma_n H_0$. In general, the Knight shift is separated into two parts $K^\alpha(T) = K^\alpha_{orb} + K^\alpha_s(T)$, with $K^\alpha_{orb}$ the temperature-independent orbital part and $K^\alpha_s(T)$ the temperature-dependent spin part. We shall discuss the orbital and spin parts of the Knight shift in the following sections.

### 2.1.1 Orbital Knight Shift

The magnetic coupling of the nuclear spin to the electron orbital gives rise to the orbital Knight shift. For the Cu $3d_{x^2-y^2}$ electron, its wave function can be written as equal combinations of $m_l = +2$ and $m_l = -2$, giving zero net current circulation and therefore quenching the orbital angular momentum. However, in the presence of a magnetic field in the $z$ direction, there exists an unquenched orbital angular momentum. The wave function will readjust so that the $m_l = -2$ state will be favored, giving a small circulating current. The nucleus then exerts an extra magnetic field due to the unquenched orbital angular momentum $L$, the Hamiltonian being given by

$$\mathcal{H}_L = \frac{\gamma_e \gamma_n \hbar^2 L \cdot I}{r^3}.$$  

(2.6)

The orbital Knight shift can be expressed as

$$K^\alpha_{orb} = \frac{A_{orb}}{\gamma_e \gamma_n \hbar^2} \chi^\alpha_{orb},$$

(2.7)

where $A_{orb}$ is the orbital hyperfine coupling constant and $\chi^\alpha_{orb}$ is the Van Vleck paramagnetic susceptibility. $\chi^\alpha_{orb}$ is not related to the density of states at the Fermi surface, so it is expected to be temperature-independent and unaffected by the transition to the superconducting state.
2.1.2 Spin Knight Shift

The magnetic coupling of the nuclear spin to the electron spin gives rise to the spin Knight shift. The Hamiltonian for the magnetic interaction between nuclear spin $I$ and the electron spin $S$ at the same site is given by

$$\mathcal{H}_s = \sum_\alpha I_\alpha A_\alpha S_\alpha ,$$

(2.8)

where $A_\alpha$ is the on-site hyperfine coupling constant in the $\alpha$-direction. With this Hamiltonian the spin Knight shift $K_s$ is given by

$$K_s^\alpha = \frac{A_\alpha}{\gamma_e \gamma_n \hbar^2} \chi_s ,$$

(2.9)

where $\chi_s \equiv \chi'(q = 0, \omega \simeq 0)$ is the uniform spin susceptibility and is assumed to be isotropic. The frequencies of interest for NMR experiments are of order MHz. therefore $\omega$ is very small and can be set to zero.

Considering Cu(2) spins in the CuO$_2$ plane, the Knight shift can be expressed within a single spin fluid model as [50]

$$K_s^\alpha = \frac{(A_\alpha + 4B)}{\gamma_e \gamma_n \hbar^2} \chi_s ,$$

(2.10)

where $A_\alpha$ is the coupling of a Cu nuclear spin to the Cu 3d$_{x^2-y^2}$ spin at the same site. $A_\alpha$ is anisotropic due to d$_{x^2-y^2}$ anisotropy. $B$ is the transferred hyperfine coupling constant. It expresses the coupling between a Cu nuclear spin and the Cu-3d spin at a neighboring Cu site. $B$ is isotropic because the coupling to the nuclear spin is through the Fermi contact interaction. The hybridization of the Cu-4s orbitals with the Cu-3d orbitals of neighboring sites through the O-2p orbitals allows the neighboring Cu-3d spin to interact with its neighboring Cu nuclear spin. $A$ is considered to be nearly invariant in most of high-$T_c$ compounds [51], while $B$ can be quite different from compound to compound.
2.2 Spin-Lattice Relaxation Rate

The spin-lattice relaxation rate $T_1^{-1}$ is the rate at which nuclear spins, disturbed from thermal equilibrium, relax back to thermal equilibrium through interaction with the lattice. The spin-lattice relaxation rate can be expressed quite generally in terms of the low-frequency dynamical spin susceptibility [52]

$$\left(\frac{1}{T_1}\right)_\alpha = \frac{k_B T}{4\mu_B^2 h^2} \lim_{\omega \to 0} \sum_{\alpha \neq \alpha} |F_\alpha(q)|^2 \frac{\chi''(q, \omega)}{\omega}. \tag{2.11}$$

where $\alpha$ denotes the direction of quantization (i.e., the direction of $V_{zz}$ in NQR and of $H_0$ in NMR experiments), $\alpha$ are the directions perpendicular to $\alpha$, and $F(q)$ is the form factor

$$F(q) = \sum_i A_i \exp(iq \cdot r_i). \tag{2.12}$$

$A_i$ is the on-site ($r_i = 0$) and the transferred ($r_i \neq 0$) hyperfine coupling between the nuclear spin and the electron spin at site $r_i$. In Eq. (2.11), $\omega$ is in the MHz range, which is very small and can be set to zero. For a Fermi-liquid without strong magnetic correlations, which is the case for conventional metals, $\sum_q \frac{\chi''(q, \omega)}{\omega}$ in Eq. (2.11) is proportional to $N^2(E_F)$. Thus $1/T_1 \propto T$, since $N(E_F)$ is temperature independent.

The form factor at the Cu site in the CuO$_2$ plane is given by [53] $^{63}F_{\perp\perp}(q) = A_{\perp\perp} + 2B(\cos(q_x a) + \cos(q_y a))$, which peaks at $q = (\pi/a, \pi/a)$. Moreover, $\chi''(q, \omega)$ is strongly peaked at the antiferromagnetic wave vector $Q = (\pi/a, \pi/a)$. Therefore the major contribution to the $T_1^{-1}$ in Eq. (2.11) is at $q = Q$, i.e.,

$$\frac{1}{T_1 T} \propto \frac{\chi''(Q, \omega)}{\omega}. \tag{2.13}$$

Thus $T_1^{-1}$ of the planar Cu predominantly probes $\chi''(Q, \omega \approx 0)$. 
2.3 Quadrupolar Interaction

2.3.1 Quadrupole Frequency

In this section, we shall consider the electric coupling between a nuclear spin and its electronic environment. A nuclear spin possessing an electrical quadrupole moment can interact with an electric field gradient (EFG) generated by the surrounding electric charges at that site. By choosing the principle axes of the EFG tensor as the coordinates axes, the Hamiltonian of a nuclear spin $I$, having a quadrupole moment $eQ$, can be written as

$$\mathcal{H}_Q = \frac{e^2qQ}{4I(2I-1)} \left(3I_z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 + I_-^2)\right). \quad (2.14)$$

Here the field gradient $eq$ and the asymmetry parameter $\eta$ are defined as

$$eq = V_{zz},$$

$$\eta = \frac{(V_{xx} - V_{yy})}{V_{zz}}, \quad 0 \leq \eta \leq 1 \quad (2.15)$$

where $V_{\alpha \alpha} = \frac{\partial^2 V}{\partial \alpha \partial \alpha}$ ($\alpha = x, y, z$), denotes the principle components of the EFG tensor $V$, with the axes labelled according to the convention $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. Assuming the EFG has cylindrical symmetry so that $\eta$ vanishes, Eq. (2.14) becomes

$$\mathcal{H}_Q = \frac{e^2qQ}{4I(2I-1)} \left(3I_z^2 - I(I+1)\right). \quad (2.16)$$

The allowed energies are

$$E_m = \frac{e^2qQ}{4I(2I-1)} \left(3m_z^2 - I(I+1)\right). \quad (2.17)$$

Fig. 2.2 shows the energy levels for $I = 3/2$ which is the case for Cu nuclei. There are two doubly degenerate $\pm \frac{1}{2}$ and $\pm \frac{3}{2}$ energy levels. A transition between these levels yields a single NQR signal at frequency...
2.3.2 Quadrupolar Shift

We shall now discuss the quadrupole interaction in the presence of a large magnetic field. The Hamiltonian can be written as

$$ \mathcal{H} = \mathcal{H}_{\text{Zeeman}} + \mathcal{H}_Q , $$

(2.20)

where $\mathcal{H}_Q$ is expressed in Eq. (2.16). Since the Zeeman coupling is large in comparison with the quadrupole coupling, $\mathcal{H}_Q$ can be treated as a perturbation. As a result, the quadrupole coupling shifts the Zeeman levels and causes a splitting of the Cu NMR signal into a central line arising from the central transition $-\frac{1}{2} \leftrightarrow \frac{1}{2}$, and two satellite

$$ m = \pm \frac{3}{2}, \quad \pm \frac{1}{2} $$

Figure 2.2: Energy levels for $I = 3/2$.

$$ \nu_Q = \frac{e^2 q Q}{2h} . $$

(2.18)

The EFG tensor is a ground state property of a crystal depending on the charge distribution in the material. The EFG at a nuclear site consists of three contributions.

$$ V_{\alpha\alpha} = (1 - \gamma_\infty) V_{\alpha\alpha}^{\text{latt}} + (1 - R_Q) V_{\alpha\alpha}^{\text{val}} . $$

(2.19)

The first contribution $V_{\alpha\alpha}^{\text{latt}}$ arises from the surrounding ions. The second is the valence contribution $V_{\alpha\alpha}^{\text{val}}$ arising from nonfilled shells of the subject ion. The third contribution, which is expressed in terms of Sternheimer antishielding factor $\gamma_\infty$ and $R_Q$, arises from the distortion of the close shells under the influence of the nonspherical potential associated with $V_{\alpha\alpha}^{\text{latt}}$ and $V_{\alpha\alpha}^{\text{val}}$ respectively.
2.3.2 Quadrupolar Shift

lines due to the $\pm \frac{1}{2} \leftrightarrow \pm \frac{3}{2}$ transitions. Instead of a single resonance frequency, there are now three frequencies. The frequency of the central transition is unaffected by the quadrupole coupling to first order because $-\frac{1}{2}$ and $\frac{1}{2}$ are shifted down by the same amount. However, it is shifted to 2nd order by

$$\Delta \nu = \frac{\nu_L^2}{\nu_L} h(\theta). \quad (2.21)$$

where $\nu_L$ is the Larmor frequency, $\theta$ is the angle between the $z$-axis of the EFG principal axis and the magnetic field, and $h(\theta) = -\frac{3}{2} \sin^2 \theta \cos^2 \theta + \frac{9}{16} \sin^4 \theta$.

In summary, we have reviewed some of the basic concepts of NMR and NQR theory. The observed Knight shift can be separated into two parts: the temperature independent orbital Knight shift and the temperature dependent spin Knight shift. The coupling of the nuclear spin to the electron orbital in the presence of the magnetic field gives rise to the orbital Knight shift. In the CuO$_2$ plane, the Cu nuclear spin would couple to the orbital angular momentum of an electron in Cu-3d$_{x^2-y^2}$ orbital. The coupling of the nuclear spin to the electron spin gives rise to the spin Knight shift and spin-lattice relaxation of the nuclear spins. Within a single Fermi fluid model, the Cu spin Knight shift in the CuO$_2$ plane can be expressed in terms of the on-site and transferred hyperfine coupling contants $A_\omega$ and $B_\omega$ and electron spin susceptibility $\chi$, $(\chi_\omega = \chi(q=0, \omega \approx 0))$. The spin Knight shift is proportional to $\chi(q=0, \omega \approx 0)$. $A_\omega$ arises from the coupling of a Cu nuclear spin to the Cu-3d$_{x^2-y^2}$ spin at the same site. $B_\omega$ arises from the coupling of a Cu nuclear spin to the Cu-3d$_{x^2-y^2}$ spin at the neighboring Cu site via the Cu-4s orbital. The spin-lattice relaxation rate involves a $q$-average over the imaginary part of the spin susceptibility $\chi''(q, \omega)$. As $\chi''(q, \omega)$ peaks at $q=Q$ in the CuO$_2$ plane, $T^{-1}$ of Cu predominately probes $\chi''(Q, \omega \approx 0)$.

We have also discussed the quadrupolar interaction which is the electric coupling between a nuclear spin and its electronic environment. In the absence of a magnetic field, the quadrupolar interaction yields a single NQR signal ($\pm \frac{1}{2} \leftrightarrow \pm \frac{3}{2}$ transition) for Cu nuclei. In the presence of a magnetic field, the quadrupolar interaction yields three NMR signals ($-\frac{3}{2} \leftrightarrow -\frac{1}{2}$, $-\frac{1}{2} \leftrightarrow \frac{1}{2}$ and $\frac{1}{2} \leftrightarrow \frac{3}{2}$ transitions) for Cu nuclei and to
the second order the central line $(-\frac{1}{2} \leftrightarrow \frac{1}{2})$ is shifted. We will use the results of this chapter when we analyze our NMR and NQR data in the following chapters.
Chapter 3

Experimental Techniques

In this chapter we will discuss the experimental techniques we used to study PSY-CCO. We will briefly describe in Section 3.1 the NMR Apparatus. In Section 3.2 we will describe the single crystals of Pb$_2$Sr$_2$(Y,Ca)Cu$_3$O$_{8+\delta}$ and the crystal alignment. Finally, in Section 3.3, we will define the pulse sequences used in this work.

3.1 Standard NMR Apparatus

The magnet used in the NMR measurements is a niobium titanium superconducting magnet in the form of a solenoid with a critical field of 9 Tesla at 4.2 K. The magnet power supply is controlled by a home-made power supply controller which can be remote controlled by the user with a PC. I have written a program which interfaces with the user and with the power supply controller to ramp the magnetic field automatically. Adding this to the data collecting software is particularly useful when doing field sweeps with small signals. Automatic field ramping also enables us to do overnight runs efficiently.

The NMR probe consists of the resonant circuit, antenna, thermometer, heater, sample chamber and liquid nitrogen chamber. The NMR coil is connected in parallel to a tuning capacitor and in series to a coupling capacitor to form the resonant circuit. We have used Cu wire to make the coil. The sample is placed within the coil. The coil is not only used to apply RF pulses to the spins, but also to detect their
precession in the static magnetic field. The sample can shields the coil to prevent any RF from outside the probe from interfering with the small NMR signal. The antenna is placed near the coil to monitor the change in the power absorbed in the coil. The thermometer and heater are in contact with the sample can and connected electrically to a Lakeshore temperature controller to regulate the temperature of the sample. The probe is put into a variable temperature insert which isolates the sample chamber and the helium bath of the cryostat.

A standard NMR spectrometer with quadrature detection was built by B. W. Statt. We have used a pulse programmer to implement the pulse sequences. The Pulse Sequence Generator, with four phase outputs, is controlled by the pulse program. It executes the commands in the pulse program to generate the pulse and then turn the RF input into a RF pulse with specific phase and duration. The signal is detected with the quadrature detection system which measures orthogonal phases (0° and 90° phases) simultaneously.

3.2 Sample

3.2.1 Single Crystal Sample

The samples used for NMR measurements in this thesis are single crystals of Pb2Sr2(Y,Ca)Cu3O8+. The crystals were prepared by Xue. Reedyk. Lin. Stager and Greedan at McMaster University. The preparation of the crystals is described in Xue et al. [43].

Typical dimensions of the crystals are ~ 0.5mm × 0.5mm × 0.3mm. The crystals are flat with the c-axis perpendicular to the flat plane. They are considerably thicker along the c-direction than typical crystals of YBa2Cu3O7−δ. The crystals exhibit an orthorhombic structure with lattice parameters $a = 5.383\text{Å}$, $b = 5.423\text{Å}$ and $c = 15.765\text{Å}$ [43]. Fig. 3.1 shows the structure of Pb2Sr2(Y,Ca)Cu3O8+. It can be derived from that of YBa2Cu3O6 by substituting the Cu layer with blocks of PbO-Cu-PbO. The structure contains two different types of Cu atoms: Cu(2) in the CuO2
Figure 3.1: The structure of $\text{Pb}_2\text{Sr}_2(\text{Y,Ca})\text{Cu}_3\text{O}_{8+\delta}$
3.2.1 Single Crystal Sample

Figure 3.2: Coil resonant frequency shift $\Delta \nu_{\text{res}}$ as a function of temperature in zero field. $\nu_{\text{res}} = 92.76$ MHz.

plane, common to all presently known high-$T_c$ copper oxides, and an oxygen-free Cu(1) layer. The four in-plane oxygens and one apical oxygen complete a square pyramidal coordination for Cu(2). Cu(1) is inserted between two PbO layers and has a two-fold coordination with two oxygens lying above and below it along the c-axis. The very different local electronic environments of Cu(1) and Cu(2) suggest the physical properties of these two sites should be very different.

In our preliminary measurements on single crystals of Pb$_2$Sr$_2$(Y.Ca)Cu$_3$O$_{8+\delta}$ we have used a multicrystal sample, consisting of 27 single crystals. In subsequent reported work and in most measurements reported here, we use another multicrystal sample, consisting of approximately 300 single crystals, from the same batch as the previous 27. The total mass of the $\sim$300 crystals is 145 mg.

The presence of superconductivity in these crystals was established by magnetic susceptibility measurements through the coil resonant frequency shift and magnetic flux exclusion. In Fig. 3.2 we show the coil resonant frequency shift $\Delta \nu_{\text{res}}$ as a
**3.2.1 Single Crystal Sample**

![Graph](image)

Figure 3.3: The temperature dependence of the magnetic flux exclusion of PSYCCO. The magnetic field used was 5 Gauss.

function of temperature in zero field. At $T \sim 84$ K, $\Delta \nu_{res}$ undergoes a transition due to the onset of the superconductivity of the sample. The resonant frequency is inversely proportional to the square root of the coil inductance which is affected by the transition of the superconducting sample inside the coil. The change of the inductance of the coil from $L_0$ without the sample to $L_0(1 + \chi(T))$ with the sample shifts the coil resonant frequency. There is a kink near 77 K, but the reason for this is not clear. The temperature dependence of the magnetic flux exclusion on the other hand, as shown in Fig. 3.3, does not show this kink. The magnetic flux exclusion, performed using a Quantum Design SQUID magnetometer, provides a better measurement of susceptibility. The onset of diamagnetic behaviour is seen to occur at $T_c = 80$ K.
3.2.2 Crystal Alignment

In this section I will describe how we put these 300 crystals together and maintained good alignment. The idea is to make several slabs, which are made from Duco cement, each with aligned crystals in it. We stack these slabs face to face and use teflon tape to hold them together to form a block which is then inserted into the NMR coil.

How do we make such a cement slab? We have tried several methods. One method is to put a drop of diluted Duco cement on the aligned crystals to form a slab. We found this method to be poor, as the crystals move with the application of the cement. We observed that the viscosity of the Duco cement tends to drag the crystals around. Eventually we found a better method, so that when Duco cement was added the crystals did not move.

First we put one drop of Duco cement on a smooth teflon surface, and spread it evenly with a plastic ruler to make a thin cement layer. The thickness should be less than half of the thickness of a crystal. After it dries, we put one layer of crystals near the central area of the cement layer with each c-axis normal to the surface. Crystals are arranged as close packed as possible to attain a good filling factor. Then we applied one small drop of acetone to the system of crystals + cement layer, after which one could see the cement layer dissolving. (Acetone, which is less viscous, will not make crystals move if one applies it gently.) In the meantime, we pressed the crystals into the cement layer with a plastic ruler, making sure that each ab-plane of the crystal touched the teflon surface. This procedure is crucial in order to get good crystal alignment. As drying proceeds, the bottom of the crystals now stick onto the cement layer, whereas the ruler doesn’t because there is no cement on the upper surfaces of the crystals. Duco cement is then put on top of the crystals and spread evenly to form a cement slab. During this process, the viscosity of the cement does not make the crystals move because they are held by the thin cement layer at the bottom. When everything dries, we carefully remove the cement slab (which has the crystals embedded in it) from the teflon surface using a razor blade. The edges of the cement slab are cut with scissors to form a rectangle.
3.2.3 Sample Deterioration

The 27-multicrystal sample had been in the air for a certain period of time during preparation. The crystals had absorbed enough oxygen from the air to have deteriorated somewhat. This was shown in the temperature dependence of the resonant frequency shift, showing that the superconducting transition was not as sharp as before. We annealed our sample to remove the extra oxygen.

The crystal annealing is as follows. Following the advice of M. Reedyk (Department of Physics, Brock University), we used a platinum boat to hold our crystals while annealing. The platinum boat with crystals in it was put into an Al$_2$O$_3$ boat, which was placed in a furnace. We annealed the crystals in flowing nitrogen at 600°C for 40 hours. Before annealing, we used methanol to clean the crystals. platinum boat and Al$_2$O$_3$ boat, and preheated the platinum boat and Al$_2$O$_3$ boat at 600°C for one hour to make sure they are clean enough. After the annealing procedure, the transition of the sample was much sharper. We also used the same method to anneal the sample of 300 crystals before doing crystal alignment.

3.3 Pulse Sequences

3.3.1 Spin Echo

The spin echo sequence we use in our experiment is given by

$$90^\circ_x - \tau - 90^\circ_x - \tau - \text{echo}$$

where $90^\circ_x$ denotes a $90^\circ$ pulse, which rotates the magnetization by $90^\circ$, about the x-axis in the rotating frame. The first $90^\circ$ pulse rotates the z-magnetization onto the x-y plane. During the period $\tau$, the magnetization dephases. The second $90^\circ$ pulse refocuses the magnetization and after a time $\tau$ the echo appears and is measured.

To eliminate the ringdown arising from the second $90^\circ$ pulse, we used an add-subtract spin echo sequence

$$90^\circ_x - \tau - 90^\circ_x - \tau - \text{echo} \quad \text{ADD}$$
Table 3.1: Cyclops, with the phases for each echo sequence in the first two columns and the signals observed from both channels in the last two columns. d denotes dispersion-like and a denotes absorption-like signals.

\[
\begin{array}{cccc}
90^\circ & 90^\circ & A & B \\
1 & x & x & +d & -a \\
2 & y & x & -a & -d \\
3 & -x & x & -d & +a \\
4 & -y & x & +a & +d \\
5 & -x & y & +d & -a \\
6 & -y & y & -a & -d \\
7 & x & y & -d & +a \\
8 & y & y & +a & +d \\
\end{array}
\]

By alternating the first pulse between $90^\circ_x$ and $90^\circ_{-x}$, one alternates the sign of the echo. Adding the first echo and subtracting the second gives constructive addition. The sign of the ringdown, on the other hand, is unchanged since the phase of the second pulse is not alternated. After the add-subtract procedure, the ringdown adds destructively and cancels.

3.3.2 Cyclops

The Cyclops sequence, given by Table 3.1, is designed to effectively eliminate the background signals arising from various sources, such as the imperfection of the pulses, the FID and the ringdowns after pulses. The dispersion and absorption like signals, d and a respectively, are in channel A and B. We swap channels and then add up with appropriate signs to obtain constructive addition of these echo signals.

3.3.3 Saturation Recovery

Saturation recovery is used to measure the NMR/NQR spin-lattice relaxation rate. The sequence is given by:
The first pulse destroys the z-magnetization. Following a time \( t \), the magnetization rebuilds in the z-direction. The following pulses are just the spin-echo sequence which makes the rebuilt z-magnetization observable. Magnetization recovery is then obtained by measuring this rebuilt z-magnetization as a function of \( t \).

By alternating the phase of the second pulse and using the add-subtract procedure as we did in spin-echo sequence, one cancels the ringdown from the third pulse. A more effective way to eliminate the background signals is to apply Cyclops in saturation recovery sequence by adding a 90° pulse before each sequence of Cyclops in Table 3.1. With Cyclops in saturation recovery, one not only eliminates the background signals but also cancels out the stimulated echoes due to the presence of the third pulse.

### 3.3.4 Lecho

Lecho is used to distinguish a signal with a much longer relaxation time from that with a short relaxation time when they overlap each other in the NMR spectrum. We have discovered (see Sec. 4.2) that the NMR spectrum of PSYCCO consists of two overlapping lines: Cu(1) and Cu(2). The relaxation time of Cu(1) is four orders of magnitude larger than Cu(2). To obtain the Cu(1) signal, we have to use a longer repetition time \( T_{rep} \) to obtain saturation. Since \( T_{rep} \) is long enough for the Cu(2) magnetization to fully recover, we pick up the Cu(2) signal at the same time. To separate Cu(1) from Cu(2), we designed a special pulse sequence “Lecho”. Lecho enables us to obtain Cu(1) signal without the contamination of Cu(2).

As shown in Table 3.2, Lecho contains four spin-echo pulse sequences and four consecutive saturation pulses. The first two spin-echo sequences collect both Cu(1) and Cu(2) signals with a long \( T_{rep} \). The last two spin-echo sequences collect only Cu(2) since \( T_{rep} \) is short enough to saturate Cu(1). After the add-subtract procedure, the four Cu(2) echoes cancel out and we obtain only the Cu(1) signal. The four consecutive saturation pulses after the first two sequences completely destroy the Cu(1) z-magnetization to ensure only Cu(2) is observed in the following two sequences.
### Table 3.2: Lecho

Ideally, one can obtain the Cu(1) spectrum by taking the difference of two spectra: one with a longer \( T_{rep} \) containing Cu(2)+Cu(1) lines, and another with a short \( T_{rep} \) containing Cu(2) line. This takes longer than obtaining the Cu(1) spectrum directly using Lecho. Additionally, in order to ensure that the subtraction is meaningful, one has to keep all the conditions the same for the two spectra. It is hard to do so with two very different \( T_{reps} \). For example, amplifier drift is one of the problems. Using Lecho, we do not have to be concerned about long time drifts.
Chapter 4

Experimental Results

We now present NMR and NQR data obtained on our PSYCCO compound. We report Cu-NQR lineshapes and quadrupole frequencies in Section 4.1. In Section 4.2, we present the Cu-NMR spectra and confirm the site assignments. In Section 4.3, the \(^{63}\text{Cu}\) Knight shifts for the planar Cu(2) sites and oxygen-free Cu(1) sites in both the superconducting and normal state of PSYCCO are given. In Section 4.4, we report the measurements of the NMR spin–lattice relaxation rate \(T_1^{-1}\) for Cu(1) and Cu(2) sites in the normal state. The anisotropy in \(T_1^{-1}\) is discussed in Section 4.4.

4.1 Cu(1) and Cu(2) NQR Lineshapes

We have performed pulsed nuclear resonance experiments without applying an external magnetic field to obtain the Cu(1) and Cu(2) NQR lineshapes at \(T = 86\) K. We have searched for signals in the frequency range between 25 MHz and 33 MHz. Each signal was collected at a fixed frequency using the CYCLOPS pulse sequence with pulse widths 4 \(\mu\)s, the echo delay of \(\tau = 25\mu\)s and a repetition time of \(T_{\text{rep}} = 25\) ms. Taking into account the effect of the frequency sweep, the signal is normalized by dividing by the voltage observed from the antenna \(V_{\text{antenna}}\) near the sample coil and the synthesizer frequency \(\omega_0\). The precessing of the magnetization \(M\) in the coil generates a voltage (signal), hence the signal is proportion to \(\omega_0 M\). Dividing by \(V_{\text{antenna}}\) eliminates the effect of \(\omega_0\) in the signal as well as the different power ab-
4.1 Cu(1) and Cu(2) NQR Lineshapes

Figure 4.1: NQR spectrum at $T = 36$ K.

sorption due to any power amplifier gain variations. The magnetization itself is also proportional to $\omega_0$ since, in thermal equilibrium, the population of a state is proportional to the Boltzmann factor and, as we know, the magnetization depends on the difference in populations between states. Dividing by $\omega_0$ eliminates the effect of $\frac{h\nu_0}{k_B T}$ in the magnetization. In Fig. 4.1, we show the NQR spectrum.

We fit the spectrum with four gaussians making use of the ratio of the quadrupolar moments and the natural abundance of the two Cu isotopes. According to Eq. (2.18), for the same site, the ratio of the quadrupolar frequencies of isotope $^{63}\text{Cu}$ and $^{65}\text{Cu}$ depends on the ratio of the nuclear quadrupole moments, namely $\frac{^{63}\nu_Q/^{65}\nu_Q}{^{63}Q/^{65}Q} = 1.081$. The ratio of the intensities of $^{63}\text{Cu}$ and $^{65}\text{Cu}$ depends on the ratio of the natural abundances ($^{63}A/^{65}A = 2.235$).

The spectrum was then decomposed into two sets of lines: a pair of narrow peaks and a pair of broad lines. Each set of lines correspond to $^{63}\text{Cu}/^{65}\text{Cu}$ NQR lines. The narrow and broad lines are considered to be associated with the two different
4.1 Cu(1) and Cu(2) NQR Lineshapes

crystallographic Cu sites. The sharp peak with \( \nu_Q(1) = 31.957 \pm 0.008 \) MHz and FWHM = 0.44±0.02 MHz is assigned to the \(^{63}\)Cu(1) site. The broad line with \( \nu_Q(2) = 29.88 \pm 0.01 \) MHz and FWHM = 1.81 ± 0.02 MHz is assigned to the \(^{63}\)Cu(2) site. These values are similar to those obtained previously [48, 49]. The broad linewidth of the quadrupole frequency distribution for \( \nu_Q(2) \) can be attributed to the fact that the Cu(2) site is adjacent to the Ca/Y site as seen in Fig. 3.1. The randomly distributed Y\(^{3+}\) and Ca\(^{2+}\) ions producing the inhomogeneity of EFGs at the Cu(2) site, leads to a broad distribution of quadrupole frequencies.

We measured the NQR-\( T_1 \) for Cu(2) and Cu(1) at \( T = 86 \) K, just above \( T_c \). The magnetization (i.e., spin-echo intensity) recovery \( M(t) \) is obtained using the saturation recovery pulse sequence with a monitoring CYCLOPS pulse sequence. The NQR-\( T_1 \) is extracted by fitting \( M(t) \) to the single exponential

\[
M(t) = M_0(1 - me^{-2W_\parallel t}) ,
\]

which is appropriated for a spin \( 3/2 \) nucleus in zero field. \( W_\parallel \) is the probability per second of transitions between states \( \pm 3/2 \) and \( \pm 1/2 \) and is related to the spin-lattice relaxation rate \( (1/T_1)_NQR = 2W_\parallel \). In Eq. (4.1), \( M_0 \) is the equilibrium signal amplitude and \( m \) is a parameter depending on the saturation pulse. For saturation with a \( \pi/2 \) pulse, \( m = 1 \). Note that the quadrupole interaction yields two doubly degenerate \( \pm \frac{1}{2} \) and \( \pm \frac{3}{2} \) energy levels. Since the NQR line is quite broad, resulting in a poor signal to noise ratio, extra signal averaging is required. We decided to take as few points as possible in order to improve the signal to noise and cut down the run time. With these preliminary measurements, we obtain the order of magnitude of \( T_1 \) for Cu(1) and Cu(2). Fitting \( M(t) \) to Eq. (4.1) yields \( T_1 \sim 600 \pm 100 \)\( \mu \)s at 30.2 MHz and \( T_1 \sim 20 \pm 0.4 \) sec at 31.9 MHz respectively. The \( T_1 \) of Cu(1) is about four orders of magnitude larger than that of Cu(2). This information is useful when making the Cu(2) and Cu(1) site assignments in NMR/NQR spectra. \( T_1 \) of Cu(2) has the same order of magnitude as those in the other high-\( T_c \) copper oxides. The much longer \( T_1 \) at the Cu(1) site is consistent with the band structure calculations. which show that
4.2 NMR Spectra

We have performed $^{63}$Cu pulsed nuclear magnetic resonance experiments with spin echo techniques to obtain the Cu(1) and Cu(2) NMR spectra from the central transition. By fixing the frequency, we collect the spin echo signal at each field. The signal is tuned with a $\pi/2$ pulse of width 8 $\mu$s. The time separation between the exciting and refocusing pulses $\tau = 25\mu$s. We sweep through certain field regions and obtain the NMR line shape.

With $\mathbf{c} \perp \mathbf{H}_0$ we observed two lines as shown in Fig. 4.2, a broad line and a very narrow line, using a repetition time $T_{rep} = 25$ ms at $T = 85$ K. We also found another

Figure 4.2: NMR spectrum with $\mathbf{c} \perp \mathbf{H}_0$ at 90.60 MHz and $T = 85$ K.

Cu(1) makes almost no contribution to the density of states at the Fermi surface [54]. The $T_1$ measurements performed using NMR, which gives better signal to noise, will be described later.
broad line and very narrow line at the lower field with smaller intensity relative to the ones at higher field. The ratio of the intensities is close to that of the natural abundance. These signals are identified to be two sets of $^{63}$Cu/$^{65}$Cu signals. The ones at lower field are $^{65}$Cu signals and the ones at higher field are $^{63}$Cu signals. The intensity of the broad line decreases as $T$ decreases below $T_c$ indicating the broad line comes from the superconducting sample. There are fewer spins polarized in the superconducting state than that in the normal state because the magnetic field can only penetrate a few thousands Angstroms (London penetration depth) near the surface of the crystal in the superconducting state. Therefore the intensity of the signal drops going into the superconducting state. Nevertheless, the broad line has $T_1 = 520 \pm 20 \mu s$ at $T = 85$ K which is similar to that obtained from the NQR–Cu(2) line. We identify the broad line as the NMR–Cu(2) line.

On the other hand, the intensity of the very narrow line increases as $T$ decreases below $T_c$, which is not expected for a superconductor, but is for a normal metal since the signal rises due to the Boltzmann factor. Its $T_1$ of 87 ms is an order of magnitude smaller than that of the NQR–Cu(1) $T_1$. Therefore it is unlikely to be the Cu(1) in PSYCCO. Assuming there is no quadrupolar shift, which is the case for Cu metal, we calculated the Knight shift of the very sharp line to be 0.23% which is just the Knight shift of Cu metal. The very sharp line is probably Cu metal from the Cu coil.

By comparing the spectra obtained using different repetition rates, $T_{rep} = 25$ ms and $T_{rep} = 500$ ms, we found the shape of the broad line changed as seen in Fig. 4.3. We further analyzed the data by subtracting one from the other and we get a weak narrow peak whose $T_1 = 15.5 \pm 0.6$ sec has a similar order of magnitude as that of NQR–Cu(1) $T_1$. Therefore we conclude the Cu(2) and Cu(1) spectra lie on top of each other. For $T_{rep} = 25$ ms, the Cu(1) signal is saturated due to its long relaxation time (of order one second) i.e., Cu(1) spins still lie along the xy-plane whereas Cu(2) spins (which recover in several hundred $\mu$s) have already relaxed back to the z-axis, hence we mainly detect the Cu(2) signal. For $T_{rep} = 500$ ms, the repetition time is long enough so that the Cu(1) magnetization has partially recovered, hence it contributes to the spectrum. Therefore, making use of their very different spin-lattice relaxation
Figure 4.3: The NMR spectra obtained using $T_{\text{rep}} = 500$ ms and $T_{\text{rep}} = 25$ ms with $c \perp H_0$ at 90.60 MHz and $T = 85$ K. The $^{63}\text{Cu}(1)$ signal was found after taking the difference of the two spectra.

With $c \parallel H_0$, we also observed two lines as shown in Fig. 4.4. The broad line is Cu(2) and the very sharp line is the Cu metal which we have seen in the NMR spectrum for $c \perp H_0$ at the same frequency. Using the same analysis described in the previous paragraph, we don’t see the Cu(1) signal hiding underneath Cu(2). We also searched for the Cu(1) signal in other parts of the spectrum in Fig. 4.4 with $T_{\text{rep}} = 500$ ms, subtracting it from the spectrum with $T_{\text{rep}} = 25$ ms. We found no sign of a Cu(1) signal, although we did not use the special pulse sequence “lecho” (described in Sec. 3.3.4.).
Figure 4.4: NMR spectrum with $c \parallel H_0$ at 90.53 MHz and $T = 85$ K.

4.3 Knight Shift Measurements

In this section, we discuss the Knight shift data for Cu(1) and Cu(2). To second order, the resonance frequency $\nu_{\text{res}}$ is given by

$$\nu_{\text{res}} = \nu_L + \frac{\nu_Q^2}{\nu_L} h(\theta) ,$$

where $\nu_L = \gamma H_0 (1 + K)$. $h(\theta) = 3/16$ for $c \perp H_0$ and $h(\theta) = 0$ for $c \parallel H_0$. For $c \parallel H_0$, the NMR line is not affected by the second-order quadrupole shift. For $c \perp H_0$, the Knight shift was obtained from the peak of the line position $H_0$ after subtracting the second-order quadrupolar shift. Solving Eq. (4.2), $K$ can then be expressed as

$$K = \frac{\nu_{\text{res}} + \sqrt{\nu_{\text{res}}^2 - 4\nu_Q^2 h(\theta)}}{2\gamma H_0} .$$

(4.3)
4.3.1 Field Dependent Measurements

Since we don’t know how good the crystal alignment is, i.e., how close \( h(\theta) \) is to \( \frac{3}{16} \), we took field dependent measurements which gives a more reliable value for \( \nu_Q^2 h(\theta) \) (described in the next Section).

4.3.1 Field Dependent Measurements

As mentioned in Sec. 4.3, the field dependent measurements give a reliable value for \( \nu_Q^2 h(\theta) \). The measurements are performed at \( c \perp H_0 \). We measured the line positions \( H_0 \) at different resonance frequencies \( \nu_{\text{res}} \). Defining \( K_{\text{eff}} \equiv \frac{\nu_{\text{res}}}{c} - 1 \), we can rewrite Eq. (4.2) as

\[
K_{\text{eff}} = \frac{\nu_Q^2 h(\theta)}{1 + K} \left( 1 + \frac{K_{\text{eff}}}{\nu_{\text{res}}} \right)^2 + K .
\]

Therefore, plotting \( K_{\text{eff}} \) vs. \( \left( \frac{1 + K_{\text{eff}}}{\nu_{\text{res}}} \right)^2 \) should yield a straight line with y-intercept \( K \) and slope \( \frac{\nu_Q^2 h(\theta)}{1 + K} \). As shown in Fig. 4.5, our result for Cu(2) show a straight line at \( T = 85 \) K. This indicates Eq. (4.2) is good enough to describe the resonance in this system. From the y-intercepts and the slopes of the lines, \( \nu_Q^2 h(\theta) \) is worked out to be \( 160.9 \pm 0.5 \) MHz\(^2\) and \( 161.6 \pm 0.4 \) MHz\(^2\) for \( T = 85 \) K and \( T = 143 \) K, respectively. These two values are equivalent within experimental error, indicating that \( \nu_Q \) does not vary significantly with temperature. Cu(1) measurements also give a straight line with \( \nu_Q^2 h(\theta) = 173.6 \pm 0.6 \) MHz\(^2\) at \( T = 89.4 \) K.

\( \nu_Q(2) \) is calculated to be \( 29.30 \pm 0.05 \) MHz, assuming \( h(\theta) = 0.1875 \). The discrepancy between this value and \( \nu_Q(2) = 29.88 \pm 0.01 \) MHz from the NQR spectrum can be attributed to the crystal alignment and the direction of EFG principal axis with respect to the c-axis. Using \( \nu_Q(2) = 29.88 \) MHz, we calculated \( h(\theta) = 0.180 \pm 0.005 \) which yields an angle \( \theta \sim 86.5^\circ \). This indicates the alignment is \( 3.5^\circ \) off, if the EFG principal axis lies along c-axis at Cu(2) site as expected crystallographically. \( \nu_Q(1) \) is calculated to be \( 30.41 \pm 0.05 \) MHz, assuming \( h(\theta) = 0.1875 \). The larger discrepancy between this value and \( \nu_Q(1) = 31.957 \pm 0.008 \) MHz from the NQR spectrum can be attributed to the crystal alignment and the larger tilt angle of the EFG principal axis at the Cu(1) site. Using \( \nu_Q(1) = 31.957 \) MHz, we calculated \( h(\theta) = 0.170 \pm 0.003 \) which yields an angle \( \theta \sim 84.5^\circ \). The \( 5.5^\circ \) offset is larger than that in Cu(2) site.
4.3.1 Field Dependent Measurements

Figure 4.5: $K_{\text{eff}}$ vs. $(\frac{1 + K_{\text{eff}}}{\nu_{\text{res}}})^2$ at $T=85$ K

to the tilting of EFG principal axis at Cu(1) site. The EFG from the two nearest O ions above and below Cu(1) is the major effect that leads the principal axis at the Cu(1) site to tilt by a larger angle with respect to the c-axis. Our observation suggests that the two O ions are not directly above and below Cu(1). If the two O ions locate directly above and below the Cu(1), the sequence O-Cu(1)-O should lie along the c-axis, hence the EFG principal axis should be along the c-axis. The results of neutron scattering experiments [55], where all the positions of the ions are given, is consistent with our observation. It shows that the two O ions are not located right above and below the Cu(1), as a result, the sequence O-Cu(1)-O makes an angle with respect to the c-axis, hence tilting the EFG principal axis.
4.3.2 Cu(2) Knight Shift

We now present the measurements of the $^{63}\text{Cu}$ Knight shifts for the planar Cu(2) sites of PSYCCO in the superconducting and normal state. As discussed in Sec. 4.2, using $T_{\text{rep}} = 25$ ms, we saturate the Cu(1) signal to obtain the Cu(2) NMR spectrum. The pulse sequence used in this measurement is a simple alternating phase echo sequence. We measured the $^{63}\text{Cu}(2)$ Knight shift for both $c \perp \mathbf{H}_0$ and $c \parallel \mathbf{H}_0$. In Fig. 4.6, we show the $^{63}\text{Cu}(2)$ lineshape for $c \perp \mathbf{H}_0$. The $^{63}\text{Cu}(2)$ line has an asymmetric lineshape as well as a large linewidth. The large linewidth is due to the distribution of EFGs from the Ca$^{2+}$/Y$^{3+}$ layer between the Cu(2)O$_2$ bilayer as well as the distribution of c-axes of our multicrystal sample. The distribution of EFGs results in a distribution of $\nu_Q$s. The spread of angles from the distribution of c-axes in the sample leads to the distribution of the EFG principal axes, i.e., a distribution of $h(\theta)$. Since the Cu(2)-NQR lineshape appears symmetric (i.e., the distribution of $\nu_Q$ is symmetric).
the asymmetry does not come from the EFG distribution.

The asymmetric lineshape is probably due to the distribution of EFG principal axes, as well as the angular spread among the crystal mosaic c-axes. These two contributions lead to the spread of angle \( \theta \) in Eq. (2.21), which is the angle between EFG principal axis and the static magnetic field. The distribution of EFG principal axes can be estimated by a point charge model with Monte Carlo method. In a point charge model, the actual charge distribution is replaced by ions with point charges. It is assumed that the Cu(1) and Cu(2) ions are Cu\(^{1+}\) and Cu\(^{2+}\) respectively and that the other ions are Pb\(^{2+}\), Sr\(^{2+}\), Y\(^{3+}\), Ca\(^{2+}\) and O\(^{2-}\). The EFG at a nuclear site can be obtained numerically by summing the EFG over all the lattice points. The Monte Carlo method is used to obtain the quadrupole frequency distribution, as well as the EFG principal axis distribution through the lattice. The EFG principal axis distribution is estimated to be 2–3°.

We could estimate the spread of \( \theta \) in our data by producing this asymmetric lineshape. Assuming a Gaussian lineshape for Cu(2), with peak position and width given by the quadrupolar frequency \( \nu_Q \) and width obtained from measured NQR spectrum, we first generate the Cu(2) NQR spectrum. The spread of \( \theta \) is assumed to be uniformly distributed up to a cutoff angle. For fixed \( \nu_{res} \), we take each \( \nu_Q \) from the generated Cu(2) NQR spectrum and each \( \theta \) from the uniform distribution, and substitute into Eq. 4.2 to solve for the field \( H_0 \). The lineshape is then generated by forming a histogram of calculated \( H_0 \)s and then compared to our Cu(2) NMR spectrum. Different cutoff angles are tried until the generated lineshape is similar to the Cu(2) NMR spectrum. The spread of \( \theta \) is estimated to be 6–8°. In this 6–8° angular spread, 2–3° comes from the EFG principal distribution and the rest comes from the spread of mosaic c-axes.

Since the lineshape of Cu(2) is asymmetric, it is difficult to obtain a good fit with a symmetric gaussian function. The \(^{63}\)Cu(2) line is then fitted with two gaussian functions: a narrow component with large intensity and a broad component with small intensity. The uncertainty of line position of the narrow component is partly dependent on the large uncertainty of line position of the broad component due to
its weaker intensity. In order to reduce this error and cut down the run time, we decided to trace only the top of the narrow peak. We collect five points at the top of the narrow component i.e., the top of the line where the broad component has least effect. The line position was then determined by fitting these five points of the line with one gaussian function. If the asymmetric lineshape is temperature independent, no systematic error will be introduced. We have shown in the field dependent measurements that \( \nu^2_{\theta}(2) \) does not vary with temperature, suggesting the asymmetric lineshape is temperature independent.

According to Eq. (4.3), we calculated the Knight shifts with \( c \perp \mathbf{H}_0 \) using \( \nu^2_{\theta}(2) h(\theta) = 160.9 \pm 0.5 \) MHz\(^2\) obtained from the field dependent measurements. There is no apparent temperature dependence of \( \nu^2_{\theta}(2) \) which was checked out at two temperatures \( T = 85 \) K and \( T = 143 \) K using the field dependent measurements described earlier. The \(^{63}\text{Cu}(2)\) Knight shift data are shown in the lower part of the graph.
of Fig. 4.7. $^{63}K_{ab}(2)$ (Cu(2) Knight shift with $c \perp H_0$) is temperature independent over the range from 260 K to 180 K, then slowly decreases linearly as temperature decreases. Starting at $T \approx 100$ K the Knight shift gradually decreases faster until at $T_c$ it enters the superconducting state. Below $T_c$, $^{63}K_{ab}(2)$ decreases more rapidly. The decrease of $K$ with decreasing temperature in the normal state implies a pseudogap develops around 180 K. In YBa$_2$Cu$_3$O$_6.63$[6, 5, 7], YBa$_2$Cu$_4$O$_8$[8] and La$_{2-x}$Sr$_x$CuO$_4$[56], the reduction of Knight shift with decreasing temperature starts at much higher temperatures (above room temperature) than that in PSYCCO. This unusual break at such low temperature indicates that the nature of the pseudogap in PSYCCO is weaker. A comparison between PSYCCO and other underdoped compounds, especially YBa$_2$Cu$_4$O$_8$ which shows strong pseudogap behavior, will be made in Chapter 5.

In the upper part of Fig. 4.7, we show that $^{63}K_c(2)$ (the $^{63}$Cu(2) Knight shift with $c \parallel H_0$) is temperature independent over the range from 40 K to 250 K. as in other high-$T_c$ materials. This indicates that there is no contribution from the temperature dependent spin Knight shift $K_s$, only the orbital Knight shift, which is temperature independent. According to Eq. (2.10), the vanishing of $K_s$ in the CuO$_2$ plane implies $A_{||} = -4B$ i.e., the cancellation between on-site and transferred hyperfine fields at the Cu(2) site.

### 4.3.3 Cu(1) Knight Shift

We next present the $^{63}$Cu Knight shift measurements for the Cu(1) sites in the normal state with $c \perp H_0$. A special pulse sequence "lecho" (described in Sec. 3.3.4) was used for collecting the Cu(1) signal with long $T_{rep} = 1$ s and short $T_{rep} = 25$ ms so that the Cu(2) signal is cancelled out. In Fig. 4.8 we show the lineshape of $^{63}$Cu(1). Since Cu(1) is far away from the Ca$^{2+}$/Y$^{3+}$ layer, the substitution of Ca for Y has less influence on the EFGs at the Cu(1) sites. Thus the linewidth is narrower than that of $^{63}$Cu(2). Like $^{63}$Cu(2), the effect of the angular spread among the crystal mosaic $c$-axes also reflects on the asymmetric lineshape of $^{63}$Cu(1).

We collect five points at the top of the line and fit them with one gaussian to
4.4 NMR Spin-Lattice Relaxation Measurements

In this section, we describe NMR spin-lattice relaxation measurements for the Cu(2) site with both \( c \perp \mathbf{H}_0 \) and \( c \parallel \mathbf{H}_0 \) and Cu(1) site with \( c \perp \mathbf{H}_0 \). The measurements were performed on the central transition \((+\frac{1}{2} \leftrightarrow \frac{1}{2})\). We have used a saturation recovery pulse sequence to obtain the magnetization recovery curve. The relaxation

Figure 4.8: \(^{63}\text{Cu}(1)\) lineshape with \( c \perp \mathbf{H}_0 \) at \( \nu_s = 90.50 \) MHz and \( T = 85 \) K.

determine the line position as we did with Cu(2). The Knight shift was then obtained after subtracting the second-order quadrupolar shift using \( \nu^2 h(\theta) = 173.6 \pm 0.6 \) MHz\(^2\), obtained from the field dependent measurements. As shown in Fig. 4.9, \(^{63}\mathbf{K}_{ab}(1)\) (Cu(1) Knight shift \( c \perp \mathbf{H}_0 \)) is temperature independent. We would have liked to compare our Cu(1) Knight shift data to that in \( \text{YBa}_2\text{Cu}_3\text{O}_6 \), whose O-depleted "chain" site is analogous to the Cu(1) site in PSYCCO. Unfortunately, the Knight shift for the chain Cu of \( \text{YBa}_2\text{Cu}_3\text{O}_6 \) does not seem to be available.
4.4.1 Cu(2) Spin-Lattice Relaxation Rate

Figure 4.9: $^{63}$Cu(1) Knight shift with $c \perp H_0$.

time $T_1$ is obtained by fitting the recovery curve $M(t)$ to the double exponential

$$M(t) = M_0 \left(1 - m(9e^{-4Wt} + e^{-\frac{3}{3}Wt})\right).$$

which is appropriate for the central transition of a spin 3/2 nucleus. $W$ is the probability per second of transitions between states $\pm 3/2$ and $\pm 1/2$ and is related to the spin lattice relaxation rate $(\frac{1}{T_1})_{NMR} = \frac{2}{3}W$. In Eq. (4.5). $M_0$ is the equilibrium signal amplitude and $m$ is a parameter depending on the saturation pulse. For saturation with an exact $\pi/2$ pulse $m = 0.1$.

4.4.1 Cu(2) Spin-Lattice Relaxation Rate

The $^{63}$Cu(2) spin-lattice relaxation rate $T_1^{-1}$ measurements have been carried out for $c \perp H_0$ over the temperature range from 70 K to 260 K at 90.50 MHz. The data were obtained by measuring the magnetization (i.e., spin-echo intensity) recovery
Figure 4.10: $^{63}\text{Cu}(2)$ Magnetization recovery with $\mathbf{c} \perp \mathbf{H}_0$ at 90.50 MHz. $H_0 = 7.833 \text{T}$, and $T = 85 \text{ K}$.

using the saturation recovery pulse sequence with $\tau = 25 \mu\text{s}$. $T_{\text{rep}} = 25 \text{ ms}$ and pulse width 8 $\mu\text{s}$. Fig. 4.10 shows the recovery of magnetization at $T = 85 \text{ K}$. The signals are collected at $H_0 = 7.833 \text{ T}$, which is slightly lower than the $^{63}\text{Cu}(2)$ line position to avoid picking up signal from Cu(1) at the higher field. By plotting $\ln(1 - \frac{M(t)}{M_0})$ vs. time, we show in Fig. 4.11 the data does not fall on a single line, which is the case for single exponential recovery. $T_1$ is obtained by fitting the magnetization recovery data with the double exponential curve given by Eq. (4.5). The fit gives $T_1 = 520 \pm 20 \mu\text{s}$ at $T = 85 \text{ K}$.

We have measured $T_1$ for several temperature points. For all temperatures, $T_1$ has been measured at the field slightly lower than the peak position of the $^{63}\text{Cu}(2)$ central transition. Fig. 4.12 shows the temperature dependence of $(T_1 T)^{-1}$ for $^{63}\text{Cu}(2)$ with $\mathbf{c} \perp \mathbf{H}_0$. As mentioned in Sec.2.2, in the presence of the strong AF correlations, $(T_1 T)^{-1}$ in the CuO$_2$ layer predominately probes spin fluctuations near $q=(\pi/a, \pi/a)$. The AF spin fluctuations get stronger as temperature decreases, therefore $(T_1 T)^{-1}$
increases as the temperature decreases. It stops increasing at $T = 140$ K, then turns over and starts decreasing. The suppression of $(T_1 T)^{-1}$ at a temperature well above $T_c$ in PSYCCO is a signature of the pseudogap, which has been observed in the other underdoped compounds such as YBa$_2$Cu$_3$O$_{6.63}$ [6, 5, 7] and YBa$_2$Cu$_4$O$_8$ [8]. Unlike the Knight shift, the behavior of $(T_1 T)^{-1}$ in PSYCCO is similar to that in the other underdoped compounds. A further comparison of the onset temperature of the pseudogap in $K_{ab}(2)$ and $(T_1 T)^{-1}$ between PSYCCO and the other underdoped systems will be given in Chapter 5.

### 4.4.2 Spin-Lattice Relaxation Rate Anisotropy

The spin-lattice relaxation rate anisotropy measurements at Cu(2) have been made on the 29 crystal mosaic. We have measured Cu(2)-$T_1^{-1}$ with $c \perp H_0$ and $c \parallel H_0$ and obtained the anisotropy in the spin-lattice relaxation rate $\frac{W_\perp}{W_\parallel} \left( (\frac{1}{T_1})_{NMR} = \frac{2}{3} W' \right)$. Us-
4.4.2 Spin-Lattice Relaxation Rate Anisotropy

Figure 4.12: Temperature dependence of $(T_1 T)^{-1}$ at $^{63}\text{Cu}(2)$ site with $c \perp \mathbf{H}_0$.

Using the expression in Eq. (2.11) and taking into account that $\chi''$ may not be isotropic, $W^\perp/W^\parallel$ of Cu in the CuO$_2$ plane in the normal state can be expressed in terms of the hyperfine coupling constants $A$ and $B$, and the uniform spin susceptibility $\chi_s$.

$$
\frac{W^\perp}{W^\parallel} \sim \frac{(A_\perp - 4B)^2 \chi_s^\perp + (A^\parallel - 4B)^2 \chi_s^\parallel}{2(A_\perp - 4B)^2 \chi_s^\perp} = \frac{1}{2} + \frac{1}{2} \left( \frac{A^\parallel - 4B}{A_\perp - 4B} \right)^2 \frac{\chi_s^\parallel}{\chi_s^\perp},
$$

(4.6)

where we have taken the form for $\chi''(Q)$ from Ref. [52]. Therefore, the anisotropy in the spin-lattice relaxation rate is related to the ratio of hyperfine coupling constants and the anisotropy of $\chi_s$. The anisotropy of $\chi_s$ is originated from the anisotropy of $g$ factor. According to the spin Hamiltonian model of the Cu$^{2+}$ ground state in this lattice, $\chi_s \propto g^2$.

To estimate the anisotropy of $g$ factor, we take the following form from the ionic
4.4.2 Spin-Lattice Relaxation Rate Anisotropy

Figure 4.13: Temperature dependence of spin-lattice relaxation rate anisotropy $\frac{W_\perp}{W_\parallel}$ at $^{63}\text{Cu(2)}$ site.

Model [57],

\[
g_\perp = 2 - \frac{\lambda}{\Delta_1} \quad \text{and} \quad g_\parallel = 2 - \frac{\lambda}{\Delta_0}.
\]  

(4.7)

where $\lambda$ is the spin-orbit coupling constant for $\text{Cu}^{2+}$ and we adopt $\lambda \approx -0.088$ eV from $\text{Cu}^{2+}$ impurity studies [58]; $\Delta_0$ and $\Delta_1$ are the crystal field splitting between the $d_{x^2-y^2}$ orbital and the $d_{xy}$ and $d_{(xz,yz)}$ respectively. Since the orbital Knight shift $K_{\text{orb}} = A_{\text{orb}} \chi_{\text{orb}}$ and $A_{\text{orb}} = 2\gamma_e \gamma_n \hbar^2 < r^{-3} >$, $\Delta_0$ and $\Delta_1$ can be obtained from orbital Knight shift data using ionic model expressions for $\chi_{\text{orb}}^\alpha$, namely, $\chi_{\text{orb}}^\parallel = 0.81 * 2\mu_B^2 \frac{1}{\Delta_0}$ and $\chi_{\text{orb}}^\perp = 0.81 * 2\mu_B^2 \frac{1}{\Delta_1}$ [58]. Using our Knight shift data, $K_{\text{orb}}^\parallel = 0.218 \pm 0.009$ and $K_{\text{orb}}^\perp = 1.179 \pm 0.002$ for PSYCCO, and taking $< r^{-3} > = 5.57$ a.u. [59], we obtained $\Delta_0$ and $\Delta_1$, which are then put into Eq. (4.7) to obtain $g_\parallel$ and $g_\perp$. $\frac{g_\parallel}{g_\perp}$ in PSYCCO...
4.4.2 Spin-Lattice Relaxation Rate Anisotropy

$\frac{W_\perp}{W_\parallel}$

YBCO(60K)  YBCO(90K)  LSCO  Y124
Bi2212    Tl2201(72K)  Tl2201(42K)  Tl2201(0K)

Figure 4.14: $\frac{W_\perp}{W_\parallel}$ for various underdoped to overdoped compounds.

is estimated to be $1.126\pm0.007$, which is quite similar to that in YBCO$_7$ [59] (1.13), YBCO$_{6+x}$ [60] (1.10±0.02) and in LSCO [61] (1.11±0.05).

As shown in Fig. 4.13, $\frac{W_\perp}{W_\parallel}$ in PSYCCO seems independent of temperature over the range 80 K to 270 K. This suggests the hyperfine coupling constants are temperature independent as expected. The anisotropy of $\chi_s$ is temperature independent as well. $\frac{W_\perp}{W_\parallel} \simeq 2.6$ which is smaller than 4 in YBCO$_7$ and 4.2 in YBCO$_{6.6}$ [62]. Since $\frac{\delta s}{\delta L}$ in PSYCCO is similar to that in YBCO, the anisotropies in $\chi_s$ are similar in these two compounds. The on-site hyperfine coupling constants $A_\perp$ and $A_\parallel$ are considered to be nearly invariant in most high-$T_c$ materials as argued previously [51]. Therefore $\frac{W_\perp}{W_\parallel}$ is largely determined by $B$. $\frac{W_\perp}{W_\parallel}$ is small if $B$ is large. Therefore the transferred hyperfine coupling constant $B$ in PSYCCO is larger than those in YBCO compounds. Since $B$ arises from the coupling of a Cu nuclear spin to the neighboring Cu-3d spins through Cu(3d$_{x^2-y^2}$)-O(2p)-Cu(4s), the larger $B$ indicates stronger hybridization between Cu(3d)-O(2p)-Cu(4s) orbitals.

Ishida et al. [62] have collected the anisotropy ratios for various underdoped to
4.4.3 \textit{Cu(1) Spin-Lattice Relaxation Rate}

The spin-lattice relaxation rate $T_1^{-1}$ measurements at the $^{63}$Cu(1) site have been performed for $\mathbf{c} \perp \mathbf{H}_0$, over a temperature range from 70 K to 260 K at 90.50 MHz. We have used a saturation recovery pulse sequence to obtain the magnetization curve. In the saturation recovery pulse sequence, we use $\tau = 25 \mu s$, $T_{rep} = 25$ ms and $8 \mu s$ for the pulse width. Note Cu(1) and Cu(2) sit on top of each other and the time we wait for measuring the Cu(1) magnetization after destroying its z-magnetization is chosen to be in the range from 10 ms to 15 sec at which Cu(2), with a short $T_1$ (520\mu s),

Figure 4.15: $^{63}$Cu(1) Magnetization recovery with $\mathbf{c} \perp \mathbf{H}_0$ at 90.50 MHz, $H_0 = 7.838$ T and $T = 85$ K.

overdoped compounds as shown in Fig. 4.14. The anisotropies of the underdoped or optimally doped compounds ($\frac{W_{\perp}}{W_{\parallel}} \sim 3.5$) are notably larger than that of the overdoped compounds ($\frac{W_{\perp}}{W_{\parallel}} \sim 1.5$). We find that PSYCCO falls midway between these two groupings.
4.4.3 $\text{Cu(1) Spin-Lattice Relaxation Rate}$

![Graph showing $1/(T_1T)$ vs. Temperature (K)]

Figure 4.16: $(T_1T)^{-1}$ as a function of temperature for $^{63}\text{Cu}(1)$ with $c \perp H_0$.

has fully recovered. It is unavoidable to pick up the full Cu(2) magnetization when measuring the Cu(1) magnetization recovery. However, we can remove the full Cu(2) magnetization from each data point in the Cu(1) recovery curve by subtracting the magnetization measured at 10 ms, which is the fully recovered Cu(2) magnetization. In Fig. 4.15, we show the recovery of magnetization at $T = 85$ K. The signals are collected at $H_0 = 7.338$T which is about the peak of the $^{63}\text{Cu}(1)$ line. A $ln(1 - \frac{M(t)}{M_0})$ vs. $t$ plot does not show a straight line, indicating that the recovery is not a single exponential. $T_1$ is obtained by fitting the magnetization recovery data with the double exponential given by Eq. (4.5). The fit gives $T_1 = 15.5 \pm 0.6$ sec which is much longer than that of Cu(2) at the same temperature ($T_1$ of Cu(2) is 520 $\mu$s). The extremely long $T_1$ for Cu(1) sites suggests that Cu(1) is in the nonmagnetic $d^{10}$ state and the valence is almost +1. Therefore Cu(1) is essentially electrically inert. This is consistent with the results of Yoshikawa et al. [49] and T. Oashi et al. [63].

We have measured $T_1$ at several temperatures. For all temperatures, $T_1$ has been
4.4.3 \( \text{Cu(1) Spin-Lattice Relaxation Rate} \)

Figure 4.17: \( T_1^{-1} \) as a function of \( T^2 \) for \( ^{63}\text{Cu(1)} \) with \( c \perp H_0 \).

measured at the peak line position of the \( ^{63}\text{Cu(1)} \) central transition. As shown in Fig. 4.16, \( (T/T)_{-1} \) of \( ^{63}\text{Cu(1)} \) increases linearly with \( T \), i.e., \( T_1^{-1} \propto T^2 \). The temperature dependent behaviour and magnitude of \( (T/T)_{-1} \) of \( \text{Cu(1)} \) is quite different from that of \( \text{Cu(2)} \), indicating that \( \text{Cu(1)} \) and \( \text{Cu(2)} \) have different relaxation mechanisms and that there is no coupling between them. Fig. 4.17 illustrates that \( T_1^{-1} \) is proportional to \( T^2 \).

We have measured \( T_1^{-1} \) of isotopes \( ^{63}\text{Cu(2)} \) and \( ^{65}\text{Cu(2)} \) at \( T = 122 \text{ K} \) and the ratio \( ^{63}T_1^{-1}/^{65}T_1^{-1} \) is \( 1.3 \pm 0.2 \), indicating that the relaxation for \( \text{Cu(1)} \) is not of magnetic origin. For magnetic relaxation by spin-spin coupling or spin-phonon coupling, \( T_1^{-1} \) contains the gyromagnetic ratio \( \gamma \), as a result \( ^{63}T_1^{-1}/^{65}T_1^{-1} = (^{63}\gamma/^{65}\gamma)^2 = 0.8714 \). Our result of \( 1.3 \pm 0.2 \) shows that magnetic relaxation is not responsible for \( \text{Cu(1)} \) relaxation, although the Raman process of the magnetic spin-phonon coupling does yield the proportionality of \( T_1^{-1} \) to \( T^2 \) [64]. It is more likely that the relaxation is of quadrupole origin. For relaxation of quadrupole origin, \( T_1^{-1} \) contains the nuclear
quadrupole moment, therefore \( T_1^{-1}/T_2^{-1} = (Q/Q)^2 = 1.17 \), which is consistent with our result of \( 1.3 \pm 0.2 \) within the experimental error. The possible candidates that the nuclear quadrupole moment can couple to are phonons (lattice vibrations) and the electronic excitations [65]. In many crystals, the electric coupling of the lattice vibrations with the nuclear quadrupole moments is much more important and is known to be responsible for nuclear relaxation [66]. It is unlikely that the relaxation is due to the coupling of the quadrupole moment to the electronic excitations, although we cannot rule out this possibility.

A. Abragam [67] has calculated \( T_1^{-1} \) for the direct and Raman process by considering the quadrupole moment-phonon coupling. The Raman process yields the proportionality of \( T_1^{-1} \) to \( T^2 \) in the high temperature limit. The nuclei couple with the lattice vibrations through the interaction of the nuclear quadrupole moment to the electric field gradient, therefore \( T_1^{-1}/T_2^{-1} = (Q/Q)^2 = 1.17 \). The temperature dependence of \( T_1^{-1} \) and the ratio of \( T_1^{-1}/T_2^{-1} \) of our Cu(1) data suggest that the relaxation is due to quadrupole moment-phonon coupling. We have estimated that \( T_1^{-1} \propto T^2 \) is valid when \( T \geq 0.25 \Theta \), where \( \Theta \) is the Debye temperature. By making \( 0.25 \Theta \) agree with the observed low temperature limit \( (\sim 70 \text{ K}) \) of our data, we obtain \( \Theta \sim 280 \text{ K} \) which yields a cut-off frequency \( \nu_D = K_B \Theta / h \approx 5.8 \text{ THz} \) or \( 200 \text{ cm}^{-1} \). Raman process involves phonons with frequencies from 0 to \( \nu_D \). Therefore any phonon mode associated with Cu(1) with frequency smaller than \( \nu_D \) could relax Cu(1). The Raman data obtained by Thomsen et al. [68] shows that the modes observed at either 99 and 96 cm\(^{-1} \) or at 119 and 114 cm\(^{-1} \) are associated with Cu(1) in-plane vibrations. The phonons from one of these pairs might contribute to the relaxation of Cu(1). The typical frequency of the acoustic vibrations for high-\( T_c \) cuprates is several THz \( (\sim 3 \text{ THz} \text{ for } \text{YBa}_2\text{Cu}_3\text{O}_6 \text{ and } \sim 2.7 \text{ THz} \text{ for } \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \text{ [69]}) \), which is the same order as \( \nu_D \). Therefore, the acoustic phonons might also contribute to the relaxation of Cu(1).
Chapter 5

Pseudogap

An unusual feature of the normal-state properties of some high-$T_c$ superconductors, in particular the underdoped ones, is the pseudogap. This manifests itself, for example, in spin susceptibility which decreases with decreasing temperature. Knight shift measurements of YBa$_2$Cu$_3$O$_{6.63}$ [6, 5, 7] and YBa$_2$Cu$_4$O$_8$ [8], display the pseudogap. Overdoped compounds, on the other hand, do not display the pseudogap. We will described in Sec. 5.1 the manifestation of the pseudogap in both spin and charge properties of the underdoped compounds. In Sec. 5.2, we will compare the pseudogap in PSYCCO with that in other underdoped compounds. Furthermore, we will try to correlate the pseudogap observed in NMR measurements to that observed in other experiments to get a better understanding of the origin of the pseudogap. In Sec.5.3, we discuss several theoretical models of the pseudogap which are currently being considered.

5.1 Manifestation of a Pseudogap

How does the pseudogap manifest itself in NMR measurements? The NMR Knight shift is proportional to the spin susceptibility $\chi'(q = 0, \omega \approx 0)$. For an ordinary metal, the Knight shift is temperature-independent since the Pauli susceptibility is temperature-independent. In optimally-doped (carrier density that gives the highest $T_c$) or overdoped (carrier density is more than that at optimally-doped) high-$T_c$
5.1 Manifestation of a Pseudogap

Figure 5.1: Cu(2) Knight shift for YBa$_2$Cu$_3$O$_{6.63}$ (solid dots) [6] and YBa$_2$Cu$_3$O$_7$ (solid line) [70] with c $\perp$ H$_0$.

compounds, for example YBa$_2$Cu$_3$O$_7$ [70], the Knight shift in the normal state is temperature-independent\(^1\) (see Fig. 5.1), indicating the normal state is metallic like. It drops drastically upon entering the superconducting state due to spin singlet cooper pair formation. The spin susceptibility is proportional to the difference between the number of electrons aligned with an applied magnetic field and those opposed. Electrons pair up in the singlet state ($S=0$) below $T_c$, resulting in a suppression of the spin susceptibility. The underdoped compounds (carrier density lower than that of optimally-doped), on the other hand, seem to behave differently from the optimally or overdoped compounds in many aspects. In the underdoped compounds, such

\(^1\)Subsequent and more precise measurements show that the Knight shift in the normal state is not temperature-independent, but slightly temperature-dependent [71]. The Knight shift gradually increases with decreasing temperature down to 125 K. Below 125 K, the Knight shift decreases as $T$ decreases and display a small pseudogap.
5.1 Manifestation of a Pseudogap

Figure 5.2: Spin-lattice relaxation rate for $YBa_2Cu_3O_{6.63}$ (solid dots) [6] and $YBa_2Cu_3O_7$ (open circles) [72] with $c \parallel H_0$.

as $YBa_2Cu_3O_{6.63}$ [6], the drop in the Knight shift starts from the normal state (see Fig. 5.1). There is no drastic change near $T_c$. The reduction of the Knight shift in the normal state suggests that a gap may be opening up well above $T_c$. As seen in Fig. 5.1, $K_s$ in $YBa_2Cu_3O_{6.63}$ drops mostly in the normal state; in other words the drop in $K_s$ in the superconducting state is quite small compared to that in $YBa_2Cu_3O_7$.

A pseudogap also appears in the spin-lattice relaxation rate. In the $CuO_2$ planes, $^{63}T_1^{-1}$ predominantly probes $\chi''(Q)$, i.e., antiferromagnetic spin fluctuations. As $T$ decreases, ($T_1T$)$^{-1}$ increases due to stronger spin fluctuations. In optimally-doped or overdoped compounds, such as $YBa_2Cu_3O_7$ [72], ($T_1T$)$^{-1}$ stops increasing just a few degrees above $T_c$, then drops (see Fig. 5.2). The sudden drop is due to spins condensing out, leading to a loss of both carriers and spin fluctuations. On the other hand, in the underdoped compound, $YBa_2Cu_3O_{6.63}$ [6], ($T_1T$)$^{-1}$ stops increasing at a temperature well above $T_c$, indicating the absence of spin excitations to which the
nucleus can couple. This suppression of spin excitations suggests the opening of a gap above $T_c$.

A pseudogap appears not only in spin properties, but also in charge transport. The ab-plane scattering rate $1/\tau_{ab}(\omega, T)$ which is extracted from the ab-plane optical conductivity reveals that a pseudogap develops above $T_c$. Puchkov et al. \cite{14, 73} have systematically analyzed the evolution of $1/\tau_{ab}(\omega, T)$ in infrared reflectivity in a series of compounds from underdoped to overdoped. In the underdoped region they see a gap-like depression (pseudogap) in $1/\tau_{ab}(\omega, T)$ opening up below $T \approx 140-160$ K, while in the overdoped region they do not observe a gap. DC resistivity measurements also display signs of a pseudogap. The resistivity for YBa$_2$Cu$_3$O$_7$ follows a linear temperature dependence over a very wide temperature range above $T_c$. On the other hand the resistivity of YBa$_2$Cu$_4$O$_8$ deviates from linearity at a temperature well above $T_c$ \cite{20}, consistent with the pseudogap observed in other measurements.

The c-axis optical conductivity $\sigma_c(\omega)$ of several underdoped materials, YBa$_2$Cu$_3$O$_{6.63}$ and YBa$_2$Cu$_4$O$_8$, also show a gap-like feature in the normal state \cite{74} below about 300-400 cm$^{-1}$. Identifying this feature with the pseudogap is quite controversial at the moment. It has been suggested that the physics underlying the appearence of a gap in the c-axis properties is of a different origin than that of the pseudogap \cite{17, 75}. There are several pieces of evidence in support of this view. An analysis based on the NMR data \cite{29} shows that the magnitude of the ab-plane pseudogap is strongly dependent on doping. In contrast, the c-axis optical conductivity measured by Homes et al. \cite{76} on YBa$_2$Cu$_3$O$_{6+\delta}$ at different doping indicates that the size of the c-axis gap is almost independent on doping. Moreover, NMR data \cite{29} suggests that the pseudogap is anisotropic and is d-wave like, which is consistent with the ARPES results. However, the depression of $\sigma_c(\omega)$ within the gap is flat, suggesting that the c-axis gap is s-wave like \cite{76}. These argument seems to suggest that the pseudogap is not related to the c-axis gap and the origin of these two gaps is quite different.
5.2 Weak Pseudogap

The Knight shift of PSYCCO displays a weak pseudogap. This is in contrast to the strong pseudogap of YBa$_2$Cu$_4$O$_8$ (Y124) [8]. As shown in Fig. 5.3, the two crossover temperatures in PSYCCO, $T^* \simeq 100K$ and $T^0 \simeq 180K$, are much lower than that in Y124 ($T^* \simeq 240K$ and $T^0 \simeq 500K$), indicating the pseudogap in PSYCCO is weaker. In Y124, the total excursion in $K_s$ is 0.26% from high temperature to $T = 0$, with 80% of that occurring in the normal state (i.e., most of the Knight shift drops in the normal state). A similarly strong pseudogap is observed in YBa$_2$Cu$_3$O$_6.63$ [6, 5, 7]. However in PSYCCO, $K_s$ at $T_c$ has only dropped to 50% of the total excursion in $K_s$ (0.14%). The degree of suppression of $K_s$ in PSYCCO is not as significant as that in Y124. In this sense, one might say that the pseudogap observed in PSYCCO is not as fully developed as the strong pseudogap seen in the two yttrium compounds.

Shown in Fig. 5.4(a) and Fig. 5.4(b) are $^{63}T_1T$ for PSYCCO and Y124 for c $\perp$ H$_0$. 

Figure 5.3: Knight shift for PSYCCO (open circles) and Y124 (solid dots) [8] with c $\perp$ H$_0$. $T^*$ and $T^0$ are described in the text.
Figure 5.4: (a) Temperature dependence of $T_1T$ for PSYCCO. $T^D$ is described in the text. (b) Temperature dependence of $T_1T$ for Y124 [8].
5.2 Weak Pseudogap

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<tr>
<td>PSYCCO</td>
<td>100</td>
<td>180</td>
<td>140</td>
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<td>YBa(_2)Cu(_4)O(_8)</td>
<td>240</td>
<td>500</td>
<td>200</td>
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Table 5.1: \( T^* \), \( T^0 \) and \( T^D \) for PSYCCO and Y124.

For typical of high-\( T_c \) compounds, \( (T_1 T)^{-1} \) is increasing with decreasing temperature at high temperature, due to increasing AF spin fluctuations. In optimally-doped compounds this continues to just above \( T_c \). Underdoped compounds, on the other hand, start to deviate from the linear temperature dependence well above \( T_c \). In PSYCCO, this occurs at \( T^D \approx 140 \) K whereas in Y124 \( T^D \approx 200 \) K. As seen in Table 5.1, \( T^* \) and \( T^0 \) in Y124 are \( \sim 2.5 \) times higher than those in PSYCCO whereas \( T^D \) in Y124 is only \( 1.4 \) times larger than that in PSYCCO. Although the crossover in the Knight shift occurs over a temperature region which is quite different in strong and weak pseudogap materials, the spin-lattice relaxation rate crossovers are not that different.

The most striking feature of our work is that the Knight shift of weak and strong pseudogap materials are quite different, while their spin-lattice relaxation rates are similar. In order to elucidate this situation, we consider the resistivity measurements on PSYCCO and Y124. In both cases, the linear \( T \) resistivity observed at high temperatures changes at \( T \approx 160 \) K to a more rapidly decreasing resistivity with temperature. This is quite similar to the behaviour of \( 1/T_1 T \) at \( T^D \). Both the spin-lattice relaxation and resistivity predominately probe properties at \( q=0 \), i.e., AF spin fluctuations [77]. Thus it is not surprising that the pseudogap at \( q=0 \) manifests itself at a similar temperature for both spin-lattice relaxation and resistivity. The Knight shift though is a measure of the long wavelength spin susceptibility \( \chi'(q = 0) \), which may be affected by the pseudogap in a different manner. In contrast to \( 1/T_1 T \) and resistivity measurements, the onset temperatures for the weak and strong pseudogap materials are quite different, suggesting that the effect of the pseudogap at \( q=0 \) is
5.2 Weak Pseudogap

strongly dependent on the pseudogap strength. In both cases though, $T^*$ is greater than $T_D$. But in PSYCCO $T^*$ is less than $T_D$ and in Y124 $T^*$ is greater than $T_D$ (see Table 5.1). This suggests the effect of the pseudogap at $q=Q$ is not strongly dependent on pseudogap strength. Thus the manifestation of the pseudogap at $q=0$ is quite different than at $q=Q$.

In contrast to Y124, the pseudogap observed in the Knight shift in the very-nearly optimally doped Bi$_2$Sr$_2$CaCu$_2$O$_8$ [71] is similar to that in PSYCCO. In the very-nearly optimally doped Bi$_2$Sr$_2$CaCu$_2$O$_8$ ($T_c = 90$ K), the two crossover temperatures in the Knight shift, $T^* \simeq 170K$ and $T^* \simeq 110K$, are similar to those of PSYCCO. In addition, the Knight shift drops 50% in the normal state in Bi$_2$Sr$_2$CaCu$_2$O$_8$, which is also similar to that of PSYCCO. Hence, the 90 K Bi$_2$Sr$_2$CaCu$_2$O$_8$ displays a weak pseudogap as does PSYCCO. The crossover temperature in the spin lattice relaxation rate $T_D'$ ($\simeq 200$ K), on the other hand, is not close to that of PSYCCO (weak pseudogap), but close to that of Y124 (strong pseudogap). This suggests that $T_D'$ in Bi$_2$Sr$_2$CaCu$_2$O$_8$ does not strongly depend on the pseudogap strength, a further evidence that the manifestation of the pseudogap at $q=0$ is different than at $q=Q$.

Another interesting correlation between the weak and strong pseudogap materials is that the weak pseudogap develops at a much lower temperature and the change in magnitude of the Knight shift down to $T_c$ is much less than that for the strong pseudogap. Thus it seems that the weak pseudogap is not as developed as the strong pseudogap at $T_c$. Perhaps this is due to the fact that $T^*$ is much closer to $T_c$ in the weak pseudogap material and that had $T_c$ been proportionally reduced, the Knight shift would have been more heavily suppressed at $T_c$. Among the various underdoped compounds, PSYCCO is unique in this respect.

One would expect $T^*$ and $T^*$ to be correlated with the energy at which the pseudogap opens up in the optical spectrum if the pseudogap was indeed due to a gap in the excitation spectrum. Homes et al. [15] and Basov et al. [78] have found the gap develops in the c-axis optical conductivity $\sigma_c(\omega)$ at about 300–400 cm$^{-1}$ in YBa$_2$Cu$_3$O$_6.63$ and Y124. These compounds both have $T^* \geq 500$ K. On the other hand PSYCCO has a much lower $T^*$ of 180 K with the gap in $\sigma_c$ still well developed [16] at 700 cm$^{-1}$. 
Thus it seems that the gap's onset temperature $T^o$ is either negatively correlated to the onset frequency or perhaps not at all. This provides support to the conjecture of Wu et al. [17, 75] that the physical origin of the gap-like features in the c-axis properties are unrelated to the pseudogap observed in the ab-plane properties.

5.3 Theoretical Models

To date there is no consensus on the origin of the pseudogap. Emery and Kivelson [32] suggest that the evolution of local electronic structure is responsible for the formation of the pseudogap. High temperature superconductors are doped AF insulators. Adding holes to the AF insulator tends to expel the doped holes. For neutral holes this leads to a phase separation [79], but for charged holes, the competition between phase separation and the long-range Coulomb interaction generates a dynamical local charge inhomogeneity in the sample. At high temperature the holes are more or less uniformly distributed and randomly disrupt AF correlations. As the temperature goes below the upper crossover $T_1^*$, a dynamical local charge inhomogeneity occurs so as to form hole rich and hole free regions in the sample. In the hole rich region, the mobile holes are typically confined in charged "stripes". In the hole free region, it allows a mixture of local AF correlation and spin singlets to develop. There is much evidence to show that some of the low-energy spin degrees of freedom acquire an energy gap in such a structure, which results in the smooth drop of the Knight shift at $T_1^*$. They also relate $T_1^*$ to the temperature at which the gap-like feature shows up in the c-axis optical conductivity $\sigma_c(\omega)$. The evolution of such a stripe structure with decreasing temperature eventually leads to superconducting pairing at the lower crossover $T_2^*$, at which the amplitude of order parameter is well established. Therefore the pseudogap is well defined at this temperature, where we see the strong drop of the Knight shift and $(T_1 T)^{-1}$, and the depression of ab-plane scattering rate. The phase coherence does not set in at $T_2^*$, but at $T_c < T_2^*$. The lower carrier density in the underdoped region depresses the phase coherence scale and results in pair formation without phase coherence at $T_2^*$ [33].
Based on this model, the two crossover temperatures $T^\circ$ and $T^*$ seen in the Knight shift measurements for PSYCCO and Y124 correspond to $T_1^*$ and $T_2^*$. The lower $T^\circ$ in PSYCCO, which is slightly underdoped than that in Y124, is consistent with this theory. According to this model, $T^D$ seen in $(T_1T)^{-1}$ should also correspond to $T_2^*$ as well as corresponding to $T^*$ seen in the Knight shift. However in PSYCCO and Y124, $T^*$ from the Knight shift does not exactly match $T^D$ from $(T_1T)^{-1}$ (see Table 5.1).

As have discussed previously, $T^\circ$ is not correlated to the energy at which pseudogap opens up in $\sigma_c(\omega)$. Therefore $T^\circ$ is not correlated to the onset temperature of c-axis gap, if the energy scales with the onset temperature. In this model, they correlate the upper crossover $T_1^*$ to the onset temperature of the c-axis gap, which is not consistent with our analysis.

Antiferromagnetic (AF) spin fluctuations and the evolution of the Fermi surface on doping may also be responsible for the creation of the pseudogap. Chubukov, Pines and Stojkovic study the temperature crossovers seen in the magnetic and transport properties of cuprates using a nearly antiferromagnetic Fermi liquid model (NAFLM) [2]. In the NAFLM, the magnetic interaction between planar quasiparticles is strong and peaks at the antiferromagnetic wave vector $\bf{Q}$. The unusual normal state behaviour with two crossover temperatures, $T_{cr}$ and $T_*$, observed in magnetic measurements of underdoped systems result from the strong antiferromagnetic correlations. In NAFLM there are two distinct groups of quasiparticles on the Fermi surface: hot and cold quasiparticles [80]. Hot quasiparticles, located in the vicinity of hot spots ((0, $\pm\pi$) and ($\pm\pi$,0)) on the Fermi surface which can be connected by $\bf{Q}$, interact strongly and display highly anomalous (non-Fermi liquid) behaviour. Cold quasiparticles are found in the remaining parts of the Fermi surface and their behaviour is closer to that of a strong coupled Fermi liquid. The crossovers at $T_{cr}$ and $T_*$ mainly reflect the behaviour of quasiparticles located in hot regions of the Fermi surface. Below $T_{cr}$, the behaviour of hot quasiparticles begins to be modified by the strong AF correlations and the Fermi surface can develop a substantial temperature dependence. The evolution of the Fermi surface with temperature takes place at $T_{cr}$ and ends at $T_*$. 

5.3 Theoretical Models
5.4 Concluding Remark

Recent angle resolved photoemission (ARPES) experiment on the BSCCO system show that a distinct evolution in the Fermi surface takes place at $T \leq 200$ K in the underdoped systems, while for overdoped BSCCO no such evolution is observed [35]. The formation of a precursor to a spin density wave below $T_c$, eventually gives rise to an effective pairing interaction between hot quasiparticles at $T_s$, hence the formation of a gap $\Delta_{hot}$. Therefore $\Delta_{hot}$ corresponds to the pseudogap and $T_s$ marks the onset of pseudogap behaviour. This gapping of the hot quasiparticles at $T_s$ is seen directly in the BSCCO ARPES experiments [35, 37]. The cold quasiparticles do not form into cooper pairs until at $T_c$. The superconductivity comes from d-wave pairing of cold quasiparticle with a gap $\Delta_{cold}$ which scales with $T_c$. $\Delta_{cold}$ denotes the superconducting gap. The hot quasiparticles do not participate in the superconducting transition since they have been gapped at $T_s > T_c$.

The two crossover temperatures $T^*$ and $T^0$ seen in the Knight shift for PSYCCO and Y124 correspond to the two crossovers $T_s$ and $T_c$ in this model. According to this model, the Knight shift and spin-lattice relaxation rate should have the same temperature crossovers. However, in PSYCCO and Y124, $T^*$ from the Knight shift does not exactly match $T^0$ from the spin-lattice relaxation rate (see Table 5.1).

5.4 Concluding Remarks

In summary, we have observed a weak pseudogap in underdoped PSYCCO crystals. The effect of the pseudogap on the Knight shift ($q = 0$) depends strongly on whether the pseudogap is strong or weak. In contrast, the effect of the pseudogap on the AF spin fluctuation spectrum ($q = Q$), as measured by spin-lattice relaxation and resistivity, is almost independent of the pseudogap strength. Thus the manifestation of the pseudogap at $q = 0$ is different than at $q = Q$.

We have found that neither of the crossover temperatures $T^*$ and $T^0$ obtained from $K_{ab}$ are correlated with the gap energy obtained from c-axis optical conductivity. This provides support to the conjecture of Wu et al. [17, 75] that the gap-like feature in the c-axis properties are unrelated to the pseudogap observed in the ab-plane properties.
Chapter 6

Conclusions

We have made a sample of Pb$_2$Sr$_2$(Y,Ca)Cu$_3$O$_{8+\delta}$ crystals with good alignment and performed Cu NMR and NQR experiments in this slightly underdoped sample. The NQR spectrum contains a pair of narrow peaks $^{63}$Cu(1)/$^{65}$Cu(1) and a pair of broad lines $^{63}$Cu(2)/$^{65}$Cu(2). The quadrupolar frequency of $^{63}$Cu(1) is 31.957 MHz, with linewidth 0.44 MHz (FWHM). The quadrupolar frequency of $^{63}$Cu(2) is 29.88 MHz with linewidth 1.81 MHz (FWHM). These values are similar to those obtained previously [48, 49]. The large linewidth of the Cu(2) line indicates a broad distribution of quadrupolar frequencies. This is due to the inhomogeneity of electric field gradients (EFG) from Ca$^{2+}$/Y$^{3+}$ layers between the Cu(2)O$_2$ bilayers. The inhomogeneity of EFGs results in a wide distribution of quadrupolar frequencies, which broaden the Cu(2) line.

We have obtained the Cu(2) NMR spectrum which displays an asymmetric lineshape and a large linewidth. The large linewidth comes from two sources of broadening: the distribution of EFGs from the Ca$^{2+}$/Y$^{3+}$ layers and the distribution of c-axes of our multicrystal sample. The asymmetric lineshape is due to the distribution of EFG principal axes, as well as the angular spread among the crystal mosaic c-axes. These two effects lead to the spread of angle between EFG principal axis and the static magnetic field. The spread of angle between EFG principal axis and the static magnetic field is estimated to be 6--8°, where we estimate that 2--3° is from the distribution of EFG principal axes and the rest is from the spread of mosaic c-axes.
The temperature dependence of Cu(2) Knight shifts are measured for both $c \perp \mathbf{H}_0$ and $c \parallel \mathbf{H}_0$. The ab-plane Knight shift ($c \perp \mathbf{H}_0$) displays temperature dependence in the normal state: it decreases with decreasing temperature. Such behaviour has been seen in the other underdoped high-$T_c$ compounds and is attributed to the opening of a normal state gap (pseudogap). The Knight shift measured in $c \parallel \mathbf{H}_0$ in both normal and superconducting states, on the other hand, is temperature independent as in other high-$T_c$ compounds. The cancelation between on-site hyperfine field $A_\parallel$ and transfer hyperfine fields $B$ from the four nearest neighbors results in the vanishing of the spin part of the Knight shift $K_s$. Therefore only the temperature independent orbital part contributes to the Knight shift.

The Cu(1) NMR spectrum displays a narrow linewidth and asymmetric lineshape. Like the Cu(2) line, the asymmetric lineshape comes from the angular spread among the crystal mosaic c-axes. The Cu(1) Knight shift measured with $c \perp \mathbf{H}_0$ in the normal state is temperature independent. From the results of field-dependent measurements, we found there is a larger tilt angle to the EFG principal axis with respect to c-axis at the Cu(1) site than that at the Cu(2) site. The EFGs from the two nearest oxygen ions above and below Cu(1) are responsible for this extra tilting of EFG principal axis. Our observation suggests that the two O ions are not directly above and below Cu(1). If the two O ions locate right above and below the Cu(1), the sequence O-Cu(1)-O should lie along the c-axis, hence the EFG principal axis should be along the c-axis. The results of the neutron scattering experiments [55] are consistent with our observation. They show that the two O ions are not located directly above and below the Cu(1), so that the sequence O-Cu(1)-O make an angle with respect to the c-axis, hence tilting the EFG principal axis.

The relaxation time $T_1$ at $T = 85$ K is 520 $\mu$s for Cu(2) and 15.5 sec for Cu(1). $T_1$ of Cu(2) has the same order of magnitude as in other high-$T_c$ copper oxides. The $T_1$ of Cu(1) on the other hand is much longer than that of Cu(2). The extremely long $T_1$ for Cu(1) sites shows that Cu(1) is in the nonmagnetic $d^{10}$ state and the valence is almost +1. Therefore Cu(1) is essentially electrically inert. This is consistent with the results of Yoshikawa et al. [49] and T. Oashi et al. [63].
The temperature dependence of the relaxation rate \((T_1T)^{-1}\) at Cu(2) site is similar to that in the other underdoped high-\(T_c\) compounds. It increases as temperature decreases at high temperature, due to stronger AF spin fluctuations. Below 140 K \((T_1T)^{-1}\) is suppressed and decreases with decreasing temperature, signalling the opening of a pseudogap in the normal state. The temperature dependence of \((T_1T)^{-1}\) at the Cu(1) site increases linearly with \(T\), i.e., \(T_1^{-1} \propto T^2\). The very different temperature dependences of the relaxation rate between Cu(1) and Cu(2) indicate that Cu(1) and Cu(2) have different relaxation mechanisms and that there is no coupling between them. Our analysis suggests that the relaxation for Cu(1) is due to quadrupolar-phonon coupling where the nuclei couple with the lattice vibrations through the interaction of the nuclear quadrupolar moment to the electric field gradient.

The spin-lattice relaxation rate anisotropy \(\frac{W_{\perp}}{W_{\parallel}}\) measurements at the Cu(2) site have been performed. \(\frac{W_{\perp}}{W_{\parallel}}\) (which is related to the ratio of hyperfine coupling constants \(A\) and \(B\), and the anisotropy of \(\chi_s\)) is temperature independent over the range 80 K to 270 K, suggesting \(A\), \(B\), and the anisotropy of \(\chi_s\) are temperature independent. \(\frac{W_{\perp}}{W_{\parallel}}\) for PSYCCO is about 2.6 which is smaller than those in YBCO compounds. The smaller \(\frac{W_{\perp}}{W_{\parallel}}\) in PSYCCO indicates that \(B\) is larger and hence the hybridization between Cu(3d)-O(2p)-Cu(4s) orbits in PSYCCO is stronger than that in YBCO compounds. A comparison of \(\frac{W_{\perp}}{W_{\parallel}}\) of PSYCCO with those of underdoped/optimally doped compounds (\(\sim 3.5\)) and overdoped compounds (\(\sim 1.5\)) shows PSYCCO falls midway between these two groupings.

Although the Cu(2) Knight shift of PSYCCO shows the same pseudogap behaviour as other underdoped compounds, the reduction of Knight shift with decreasing temperature starts at much lower temperature than in \(\text{YBa}_2\text{Cu}_3\text{O}_{6.63}\) and \(\text{YBa}_2\text{Cu}_4\text{O}_8\). We compared the Knight shifts of PSYCCO with \(\text{YBa}_2\text{Cu}_4\text{O}_8\) in temperature scale and the degree of reduction at \(T_c\) and the result suggests a weak pseudogap in PSYCCO. Moreover, our discussion of the weak pseudogap material (PSYCCO) and strong pseudogap material (\(\text{YBa}_2\text{Cu}_4\text{O}_8\)) in relation to their Knight shift (\(q=0\)) and spin-lattice relaxation rate \((T_1T)^{-1}\) (\(q=0\)) shows that the Knight shifts of weak and strong pseudogap materials are quite different in temperature scale while the spin-
lattice relaxation rates are similar. Therefore the manifestation of the pseudogap at q=0 is different than at q=Q. In addition, we also discuss two weak pseudogap materials (PSYCCO and 90 K Bi$_2$Sr$_2$CaCu$_2$O$_8$) in relation to their Knight shift (q=0) and spin-lattice relaxation rate (q=Q). While the Knight shifts of these two materials are similar in temperature scale, the spin-lattice relaxation rates are quite different, a further evidence that the manifestation of the pseudogap at q=0 is different than at q=Q.

We have also discussed the relation between the ab-plane pseudogap and the gap seen in the c-axis optical conductivity. By comparing PSYCCO, YBa$_2$Cu$_3$O$_{6.63}$ and YBa$_2$Cu$_4$O$_8$, we found that the onset temperature of the pseudogap obtained from the Knight shift does not correlate with the gap energy obtained from c-axis optical conductivity. Together with evidence from other experiments [17], we suggest that the gap-like features in c-axis properties are unrelated to the pseudogap seen in the ab-plane properties.

We have discussed the theory in which the two crossovers seen in the Knight shift is a consequence of the evolution of the local electronic structure, as proposed by Emery and Kivelson [32]. Based on this theory, the two crossover temperatures $T^\circ$ and $T^*$ seen in the Knight shift measurements for PSYCCO and Y124 correspond to $T^*_1$ and $T^*_2$. The doping dependence of $T^\circ$ is consistent with this. According to this model, $T^D$ seen in $(T_1T)^{-1}$ should correspond to $T^*$ seen in the Knight shift. However, in PSYCCO and Y124 $T^*$ from the Knight shift does not exactly match $T^D$ from $(T_1T)^{-1}$. In addition, they correlate the upper crossover $T^*_1$ to the onset temperature of the c-axis gap, which is not consistent with our analysis. Their prediction about the doping dependence of $T^*_2$ is also not consistent with the analysis done by Uemura et al. [30].

A theory based on the nearly antiferromagnetical Fermi liquid model proposed by Chubukov, Pines and Stojkovic [2], explains the two crossover temperatures $T^\circ$ and $T^*$ seen in the Knight shift. The temperature dependence of $(T_1T)^{-1}$ can be understood with this model as well. Within this model, the onsets of the pseudogap in both Knight shift and $(T_1T)^{-1}$ occur at $T^*$. However, the experimental data does
not seem to be consistent with this: the onset temperature of the pseudogap $T^*$ in the Knight shift is different from that $(T^D)$ in $(T_1T)^{-1}$. This inconsistency in crossover temperatures of the Knight shift and $(T_1T)^{-1}$ has also been observed in $Y_{1-x}Pr_xBa_2Cu_3O_7$, where $T^* \sim 110K$ while $T^D \sim 150K$ [81]. It seems that this model needs to be refined. Furthermore, there is controversy concerning the ARPES results of two groups [26, 37] on whether a pocket around $(\pi/2, \pi/2)$ is seen on the Fermi surface, another assumption of the model of Chubukov et al. [36].

Two crossover temperatures above $T_c$ are only observed in the Knight shift: at the upper crossover, the Knight shift drops slowly; at the lower crossover, it drops more quickly. In other experiments, such as spin-lattice relaxation rate, optical measurements and resistivity measurements, only one crossover temperature is observed. The temperature where the suppression of $(T_1T)^{-1}$ occurs does not exactly match with the lower crossover seen in the Knight shift; it is much closer to the lower crossover than the upper crossover. The deviation of the in-plane resistivity from linearity and the depression of ab-plane scattering rate occur at a temperature much closer to the lower crossover as well. All these facts suggest that the lower crossover seen in the Knight shift marks the onset of the pseudogap, whereas the upper crossover is probably associated with some other phenomena.

The pseudogap is observed in both the Cu(1) and Cu(2) Knight shifts in $YBa_2Cu_4O_8$ [82]. Although the degree of suppression is weaker in Cu(1) than in Cu(2), the temperature dependence is similar, indicating some kind of coupling between Cu(1) and Cu(2). The Knight shifts of Cu(1) and Cu(2) in $YBa_2Cu_3O_8$ also are similar. It would be interesting to do the Knight shift measurement on Pb in PSYCCO, which is metallic, and to discover if the same thing occurs in the Knight shift of Cu(2) and Pb as those of Cu(2) and Cu(1) in $YBa_2Cu_4O_8$ and $YBa_2Cu_3O_8$. If there is a coupling, one would like to estimate its size.

We have noticed the size of the pseudogap deduced indirectly from the NMR data scales with the onset temperature $T^*$. It would be nice to have some optical measurements on the ab-plane scattering rate, which would give a direct measurement of the size of the gap. One could then check if the size of the pseudogap from ab-
plane optical properties scales with $T^*$. There is not much work done in ARPES experiments on the studies of the evolution of Fermi surface with temperature, which would also provide useful information about the pseudogap.
References


References


References


References


