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<td>Fujiwara, Kenji</td>
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NMR Study of High Tc Superconductor

\[ Tl_{2}Ba_{2}CuO_{y} \]

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TOTONAKA OSAKA
Thesis

NMR Study of High Tc Superconductor

: Tl$_2$Ba$_2$CuO$_{6+y}$

Kenji Fujiwara

Faculty of Engineering Science, Osaka University

February 1991
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ABSTRACT

$\text{Tl}_2\text{Ba}_2\text{CuO}_6+y(\text{Tl2201})$ is a typical material belonging to "heavy-doped" superconductor, and has many doping-holes in the CuO$_2$ plane. This compound shows a gradual transition from a 85 K superconductor to a nonsuperconducting normal metal, as excess oxygen content, $y$, is increased from 0 to 0.1. Three compounds ($T_c$=72, 40 and 0 K) were prepared. To study about static and dynamical properties of Cu-d spin in CuO$_2$ plane, Knight shift and nuclear relaxation rate, $1/T_1$ for $^{63}\text{Cu}$, were measured, and $1/T_1$ for $^{205}\text{Tl}$ was measured to obtain the information about Cu site indirectly.

In the normal state, $1/T_1$'s of $^{63}\text{Cu}$ for all compounds obey $T_1T=\text{const.}$ law in a wide temperature range. This is the first observation of the $T_1T=\text{const.}$ law of Cu in the CuO$_2$ plane. Applying the high magnetic field (= 11 T) along c-axis in superconducting compounds, $T_c$'s decrease from 72 K and 40 K to 55 K and 20 K, respectively. Then $1/T_1$'s also obey $T_1T=\text{const.}$ law above 55K and 20K, supporting that $T_1T=\text{const.}$ law is an intrinsic feature in Tl2201 compounds. As the $T_1T=\text{const.}$ law means that the energy spectrum of Cu spin excitation is continuous, Fermi liquid picture is applicable to Tl2201 compounds. All $1/T_1$'s are enhanced much as that of Cu in the CuO$_2$ plane for YBa$_2$Cu$_3$O$_7$. The magnitude of $1/T_1$ does not change with hole concentration, in contrast to the result that $1/T_1$ of Cu for the "light-doped" La-Sr-Cu-O superconductor decreases considerably with increasing holes. This difference may be attributed to the difference of
strength of Cu-d spin antiferromagnetic correlation between "heavy-doped" and "light-doped" superconductors.

In the superconducting states, temperature dependence of the spin susceptibility, $\chi_s$ estimated from spin contribution ($K_s$) to the Knight shift is explained by BCS model with a larger gap of $2\Delta = 4.4k_BT_C$ than the BCS value of $2\Delta = 3.5k_BT_C$. The behavior is similar to that for the CuO$_2$ plane in YBa$_2$Cu$_3$O$_7$. However, $1/T_1$ for $^{63}$Cu decreases rapidly without the enhancement just below $T_C$ predicted by the BCS model. The unconventional behavior is also observed for other several high $T_C$ oxides, and all the $1/T_1$'s normalized by the value at $T=T_C$ plotted against $T/T_C$ fall on a single curve, suggesting that the same mechanism is responsible for the relaxation process.
Chapter 1. Introduction

Since the discovery of high $T_c$ superconductor by Bednorz and Müller in 1986, several kinds of high $T_c$ materials (La$_2$Sr$_2$Cu$_2$O$_x$, Y$_2$Ba$_2$Cu$_3$O$_x$, Bi$_2$Sr$_2$Ca$_2$Cu$_2$O$_x$, Tl$_2$Ba$_2$Ca$_2$Cu$_2$O$_x$, Nd$_2$Ce$_2$Cu$_2$O$_x$, ...) have been found out. A number of studies have been carried out in the world to elucidate the mechanism for "high $T_c$" superconductor. They have layered perovskite structure and planer CuO$_2$ layers. There is a general consensus that the presence of the CuO$_2$ layers and carriers doping are essential for the occurrence of the superconductivity. Well known phase diagram for the high $T_c$ superconductors is shown in Fig. 1. Non-doped sample is an insulator and antiferromagnet caused by a super exchange interaction between Cu spins. With hole doping, the antiferromagnetic state is destroyed rapidly. With more hole doping, the superconducting state appears and then transforms to the metallic state.
Fig. 1. Schematic phase diagram for the high Tc superconductor.
The nuclear magnetic resonance (NMR) has brought much significant information for the superconductivity. The NMR is a powerful technique which provides information about the microscopic electronic state at each atomic site. For example, NMR contributes to determine phase diagrams of La-Sr-Cu-O system and Y-Ba-Cu-O system as seen in Fig. 1, which indicates that the antiferromagnetic phase is in contact with the superconducting phase. In these superconductors, the results of the nuclear spin relaxation time, $T_1$ of Cu for CuO$_2$ layers suggest that antiferromagnetic correlation of Cu d-spins is significant to superconductivity. And, it is important that $1/T_1$ has no enhancement just below $T_c$, which was observed in conventional BCS superconductors. However, until now, most studies are concerning to the left side region of superconducting phase diagram, what we call "light-doping" region, where the number of holes is small. In the "light-doping" region, it may be considered that the antiferromagnetic correlation is dominant yet.

The purpose of this study are mainly to investigate Cu spin dynamics in Tl$_2$Ba$_2$CuO$_6+y$ belonging to "heavy-doping" region, and to search a mechanism of high $T_c$ superconductivity. In the "heavy-doping" region, indeed, the antiferromagnetic correlation is considerably weak. Therefore the study of Cu spin dynamics under such condition is significant itself. It is expected that this study gives some information whether the antiferromagnetic correlation is essential to superconductivity, or not.
Chapter-2. Superconductivity of Tl$_2$Ba$_2$CuO$_{6+y}$

It is noteworthy that Tl$_2$Ba$_2$CuO$_{6+y}$ (2201 compound) is a typical high $T_c$ superconductor in "Heavy-doping" region, and that this compound shows a gradual transition from a 85 K superconductor to a nonsuperconducting normal metal, as excess oxygen content, $y$ is increased from 0 to 0.1. (see Fig.2) The excess oxygens were controlled by the annealing temperature.\(^3\)

Recently, good quality samples have been made by Shimakawa et.al. and the features of 2201-compounds as below are revealed by their works.\(^3\)-\(^6\)

![Graph](image-url)

**Fig. 2.** $T_c$ values and c-axis lengths plotted against the relative change in the oxygen content in Tl$_2$Ba$_2$CuO$_6$. 

2-1. Structure

As seen in Fig. 3, the 2201 compounds have single CuO$_2$ plane, where Cu is surrounded by octahedral oxygens like the LaSrCuO system. Both Cu and Tl atoms have single site crystallographically. For 2201 compounds, two structures, namely, tetragonal and orthorhombic, were reported. However, there is no difference in physical properties between these structures. Our samples have tetragonal structure and perfect single phase.

Figure 2 shows that the lattice parameter along c axis becomes longer for the higher $T_C$ sample. It is found that the distance between Cu and apical oxygen becomes shorter as $T_C$ is higher. Very recently, Y. Shimakawa, et. al. have carried out a neutron diffraction measurement on the 2201 compounds with various $T_C$ values, and found that excess oxygen atoms are incorporated and released at an interstitial site between the double TIO layers.
Fig. 3. Crystal structure of $\text{Tl}_2\text{Ba}_2\text{CuO}_6+y$. 
2-2. Transport Properties

Electric Resistivity

Figure 4 shows $T$ dependence of electric resistivity. For the highest $T_c$ compound, the temperature dependence of the resistivity above $T_c$ is similar to the linear one observed in YBa$_2$Cu$_3$O$_7$, Bi$_2$Sr$_2$CuO$_6$, etc. For metallic sample ($T_c=0$ K), $T^2$ like temperature dependence is observed, which is characteristic of metal. These gradual change of temperature dependence may be one of the features of "heavy-doped" system.

![Graph showing temperature dependence of resistivity](image)

Fig. 4. The temperature dependence of the resistivity for Tl$_2$Ba$_2$CuO$_6+\delta$ with various $T_c$'s. ($T_c$'s of sample A-E are 81, 82, 47, 16 and 0 K, respectively.)
Hall Effect 5)

Figure 5 shows T dependence of the hole number. As Hall coefficient is positive and decreases with increasing excess oxygen content, y, in Ti$_2$Ba$_2$CuO$_{6+y}$, origin of hole doping is attributed to the excess oxygen. The hole number increases gradually with decreasing from $T_c = 85$ K to 0 K.

Fig. 5. The temperature dependence of the Hall number for Ti$_2$Ba$_2$CuO$_{6+y}$ with various $T_c$'s.
In Fig. 6, $T_c$ is plotted against the hole number per Cu for Tl$_2$Ba$_2$CuO$_{6+y}$ and (La$_{1-x}$Sr$_x$)$_2$CuO$_4$. It is convincing that 2201 compounds belong to "heavy-doping" region. However, the change of the hole number between the highest $T_c$ and metallic samples is about 0.5. On the other hand, the change of the excess oxygens between both samples is about 0.1. As excess oxygen creates two holes per Cu, the expected change of the hole number change is 0.2. This discrepancy is also observed in La-Sr-Cu-O system.

![Fig. 6. Relationship between $T_c$ and the hole number per Cu for Tl$_2$Ba$_2$CuO$_{6+y}$ and (La$_{1-x}$Sr$_x$)$_2$CuO$_4$.](image-url)
2-3. Magnetic Susceptibility

As seen in Fig. 7, the magnetic susceptibility shows Curie-like temperature dependence, and the Curie term becomes small with increasing Tc. Shimakawa et al. speculate that the Curie term does not result from impurity of extra phases, but Cu$^{2+}$ ions substituted for the Tl site. Actually, their Rietveld analysis of X-ray diffraction suggests that 3-5% of Tl sites are replaced by Cu atoms. They also consider that Cu atoms in Tl sites prefer to exist as Cu$^{1+}$ ion with no magnetic moment, and that, with hole doping, these Cu valence changes to Cu$^{2+}$ ion. By assuming that, in the highest Tc sample and metallic one, all Cu in Tl sites are Cu$^{1+}$ and Cu$^{2+}$ ions, respectively, an expected change of the hole number between both samples is at most 0.1. It may be considered that both the excess oxygens and substitution of Cu atoms for Tl sites are the origin of the hole doping.

It is important that the magnitude of magnetic susceptibility is smaller as Tc is higher (hole doping is smaller), which relates to the result of Knight shift.
Fig. 7. The temperature dependence of the total measured magnetic susceptibility for $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+y}$ with various $T_c$'s.
Chapter-3. NMR Theory

In this chapter, the temperature dependence of the Knight shift and nuclear relaxation rate, $1/T_1$, in a conventional BCS superconductor are reviewed.

3-1 Knight Shift

In non-transition metal like aluminum, the hyperfine field mainly attributed to Fermi contact interaction with conduction electrons. Then the Knight shift is proportional to the Pauli spin susceptibility, $\chi_n$. Under the external static field, $H_0$, the spin magnetization, $M_s$, is expressed by the formula,

$$M_s = \mu_B (n\uparrow - n\downarrow)$$

$$= \mu_B \sum_k \{ f(\epsilon_k - \mu_B H_0) - f(\epsilon_k + \mu_B H_0) \}$$

$$\sim -2\mu_B^2 H_0 \sum_k df/d\epsilon_k. \quad (3-1)$$

where $f(\epsilon_k)$ is the Fermi-Dirac distribution function for a electron of energy $\epsilon_k$, and $\mu_B$ is the Bohr magneton. Thus,

$$\chi_n = M_s/H_0 = -2\mu_B^2 \sum_k df/d\epsilon_k \quad (3-2)$$

In superconducting state, Cooper pairs formed by up and down-spins do not contribute to the spin susceptibility, $\chi_s$. Since only excited quasi-particles contribute to $\chi_s$, the expression of $\chi_s$ is
\[\chi_s = -2\mu B^2 \sum_k \frac{df/dE_k}{E_k}, \quad (3-3)\]

where \( E_k \) is the energy of excited states. In BCS scheme, the energy density of excited states, \( N_S \) is given by

\[N_S(E) = N_0 \cdot \frac{1}{E_1/(E^2 - \Delta^2)^{1/2}}, \quad (3-4)\]

where \( N_0 \) and \( \Delta \) are the density of states (in the normal state) at the Fermi level and the T-dependent energy gap parameter, respectively. The sum in eq. (3-3) is replaced by an integral.

\[\chi_s = -4\mu B^2 \int_{E_1}^{E_2} N_S(E)(df/dE)dE. \quad (3-5)\]

This result was calculated by Yosida \(^8\), and consistent with that of Knight shift for aluminum \(^9\), as seen in Fig. 8.

\[\text{Fig. 8. Spin susceptibility in superconducting aluminum}\]
3-2 Nuclear Relaxation Rate

**Normal State**

The expression of $1/T_1$, associated with the Fermi contact interaction, is given by

$$1/T_1 \propto \int N^2(E)f(E)(1-f(E))dE, \quad (3-6)$$

where $N(E)$ is the density of states of the conduction electrons. Since $f(E)(1-f(E))$ is nearly equal to $k_B T \delta(E-E_F)$, the eq. (3-6) yields

$$1/T_1 \propto k_B T N^2(E_F). \quad (3-7)$$

where $E_F$ is the Fermi energy. Then,

$$1/(T_1T) \propto N^2(E_F) = \text{const.} \quad (3-8)$$

This relation is called "Korringa law".

**Superconducting State**

In the superconducting state, $1/T_1$ is given by

$$1/T_1 \propto \int \left( N_s^2(E) + M_s^2(E) \right)f(E)(1-f(E))dE, \quad (3-9)$$

where $N_s(E)$ is given by the eq. (3-4), and what is called the "anomalous" density of states, $M_s(E)$, is given by
\[ M_s(E) = N_0 \Delta / (E^2 - \Delta^2)^{1/2}. \] (3-10)

Ms relate to "coherence effect". Since both \( M_s \) and \( N_s \) diverge at \( E = \Delta \), as seen in Fig. 9, \( 1/T_1 \) is enhanced just below \( T_C \). At low temperature (\( T < T_C \)), \( f(E) \) is nearly exponential and therefore \( 1/T_1 \) also decreases exponentially with the \( T \)-decrease. The behavior of \( 1/T_1 \) for \( ^{27}\text{Al} \) in the superconducting aluminum \(^9, 10\) is consistent with that calculated with using above eq. (3-9), as seen in Fig. 10.

![Fig. 9. BCS density of states](image)

![Fig. 10. Dependence of \( ^{27}\text{Al} \) relaxation time on \( T_C/T \) in superconducting aluminum. The solid line is calculated with the eq. (3-9).](image)
Chapter 4. Experimental Procedure

4-1. Sample Preparation

Single phase polycrystalline samples of Tl$_2$Ba$_2$CuO$_6+y$ were prepared by solid state reactions. Mixtures of Tl$_2$O$_3$, BaO and CuO powders were pressed into pellets. The pellets were wrapped in Au foil, and sintered at 860 °C for 5-10 hours in oxygen atomosphere. After grinding, they were sintered again at 880-890 °C for 5-10 hours in oxygen atomosphere.

Samples sintered in oxygen atomosphere were metallic and showed no superconductivity down to 10 K. They were then annealed in argon atomosphere at various temperatures ranging 300-590 °C for 5 hours, resulting in appearance of superconductivity with various T$_c$'s depending on the annealing temperature. In this way, three samples (T$_c$ = 0, 40, 72 K) were obtained. X-ray diffraction did not show any impurity phases for all samples. T$_c$, which is defined as temperature where the diamagnetic signal appears, was determined by the ac susceptibility measurement. All samples were powdered for NMR measurement.
4-2. Cryostat

63Cu and 205Tl NMR measurement were performed in the high field (H = 10-11 T) between T=4.2 K and 300 K. For 63Cu, NQR measurement in the zero field was performed.

**High Field Cryostat**

High field NMR of 63Cu and 205Tl were performed in a cryostat shown in Fig. 11. The cryostat enables us to control temperature between 1.3-400 K and apply field up to 12 tesla. The sample was set at the center of the superconducting magnet. The temperature was monitored by Pt thin film thermometer and carbon glass thermometer. Inhomogeneity of magnetic field at the center of the magnet is less than 10^-5 Thus, the precise measurement of the Knight shift is practicable.

**NQR Cryostat**

As seen in Fig. 12, NQR cryostat has a simple structure, since 63Cu NQR measurement was carried out in zero field and does not need the magnet. Sample's temperature is controlled by two heaters. The upper heater is used to warm the sample and the lower heater is used to cool down by evaporating 4He liquid. The temperature is monitored by the thermocouple thermometer.
Fig. 11. Cryostat for the high field NMR.
Fig. 12. Cryostat for Cu NQR.
4-3. NMR and NQR Measurement

NMR and NQR were performed by spin echo method using a conventional type NMR spectrometer. NMR spectra were obtained by the Box Car Integrator averaging spin echo intensity with sweeping magnetic field. NQR spin echo spectra were plotted as a function of frequency.

In Tl2Ba2CuO6+y, Cu (I=3/2) and Tl (I=1/2) nucleus were observable for NMR measurement. By the sample orientation in the high field, Knight Shift and 1/T1 measurement in the field parallel (H∥c) and perpendicular (H⊥c) to the c-axis have been made. The method of sample orientation was as follows,

1) perpendicular orientation (H⊥c)

Below Tc, there is a tendency for the powder to be aligned with the c-axis perpendicular to the magnetic field owing to the anisotropy of the diamagnetism. Actually, by the vibration of sample in the field (=11T), perpendicular orientation was achieved.

2) parallel orientation (H∥c)

Powdered sample and polymer (melting point=60K) were mixed at the ratio of 4:1 in the sample case. Sample case was put in the field (=11T) at 80°C for 20 minutes and was quenched. The powders were aligned with the c-axis parallel to the field. This orientation results from the effect of anisotropy of Cu spin susceptibility.

For both methods of orientation, the orientation was not perfect. This is due to the fact that the each powder particle was not a
single crystal. However, both orientations were enough to perform the precise measurements of Knight shift and $T_1$.

In order to determine the quadrupolar and Knight shifts for Cu separately, series of spectra were taken at several frequencies in the range of 110-130 MHz.

Saturation method was used for measurement of $T_1$. A $\pi/2$ pulse was applied to saturate nuclear magnetization. After the time, $t$, $\pi/2-\pi$ pulse series were applied to observe spin echo. Since intensity of spin echo is in proportion to the magnetization recovered after $t$, decay of magnetization is obtained by changing $t$. $T_1$ measurement of Cu was performed in the central peak of the quadrupolar split line. Then, the magnetization; $M(t)$ at $t$ obeys the following equation,

$$M(t) = M_0\left(1 - 0.9\exp\left(-\frac{6t}{T_1}\right) - 0.1\exp\left(-\frac{t}{T_1}\right)\right)$$

(4-1)

where $M_0$ is a thermal equilibrium magnetization. As seen in Fig.17, $T_1$ was obtained by a least square fitting to above equation in the recovery of magnetization observed.

As Cu nucleus has $I=3/2$ and quadrupole moment, NQR was observable. NQR measurement in the zero field has great advantage on studying about superconductivity. NQR spectra and $T_1$ for each sample were measured.
Chapter 5. Experimental Results

In Tl2Ba2CuO6+y belonging to "heavy-doped" system, Knight shift and $T_1$ for $^{63}$Cu and $^{205}$Tl were measured to investigate normal and superconducting properties. Results of Knight shift and $1/T_1$ of $^{63}$Cu were described in Sec.1 and Sec.2-3, respectively. Results of $1/T_1$ of $^{205}$Tl were described in Sec.4.

5-1. Knight shift of $^{63}$Cu

In order to study the intrinsic properties in the normal and the superconducting states in series of Tl2Ba2CuO6+y which have a simple structure like La2-xSrxCuO4, we have carried out a $^{63}$Cu high-field Knight shift measurement up to 11.5 T for three compounds with $T_C=72$ K, $T_C=40$ K and $T_C=0$. Here $T_C$ in the magnetic field of 11.5 T was determined as the temperature where the Knight shift starts to decrease. The polycrystalline samples were prepared by a conventional powder method described elsewhere. The Cu NMR spectrum was obtained by sweeping the magnetic field in a frequency range of 110 MHz - 130 MHz from 4.2 K to 150 K.

Fig. 13 (a) and (b) show the $^{63}$Cu NMR spectrum in the partially oriented powder, with the c-axis parallel and perpendicular to the magnetic field, respectively, at 4.2 K and 125.02 MHz for the compound with $T_C=72$ K. The spectrum comes from the $(1/2)-(-1/2)$ transition affected by the second order quadrupole effect. Although the orientation is not perfect, enhancement of NMR intensity by orientation is enough to determine the Knight shift precisely.
Fig. 13. $^{63}\text{Cu}$ NMR spectra of $\text{Tl}_2\text{Ba}_2\text{CuO}_6+y$ with $T_c=72$ K obtained by sweeping the magnetic field at 125.02 MHz. (a) and (b) correspond to the spectra for the powder samples with partially oriented in parallel and perpendicular to the external field, respectively.
In order to determine the quadrupolar and the Knight shift separately, the series of spectra were taken at several different frequencies between 110 and 130 MHz. Following the same procedure as in $YBa_2Cu_3O_7$\textsuperscript{12}), where the value of $(\omega_0 - 63\gamma N h_{\text{res}}(\theta))/63\gamma N h_{\text{res}}(\theta)$ are plotted against $(63\gamma N h_{\text{res}}(\theta))^2$, a nice linear relation was obtained, as seen in Fig. 14 (a)-(c). Here $\omega_0$ is the resonance frequency, $h_{\text{res}}(\theta)$ is the field corresponding to the peak of NMR intensity in Fig. 13 (a) and (b), and $63\gamma N$ the nuclear gyromagnetic ratio. In $Tl_2Ba_2CuO_6+y$, each sample has axial symmetry and its principal axis of the electric field gradient is c-axis. In this case, the shift along c-axis has no quadrupolar shift, and therefore has constant value independent of the frequency. Then the Knight shift $K$ and the second order quadrupole shift have been evaluated from the intercept and the slope of these lines, respectively. In these analyses, we neglect the higher order quadrupolar shift, $\Delta \nu$ which is estimated as $\Delta \nu/63\gamma N h_{\text{res}} < 0.7 \times 10^{-4}$, because there is an experimental error of +0.01 % for the determination of the shift. Thus obtained $K_\perp$ and $K_\parallel$ for the compounds with $T_c = 72$ K, 40 K and 0 K are shown as closed and open circles in Fig. 15 (a)-(c), respectively.
Fig. 14. The value of \((\omega_0 - 63\gamma N_{H_{res}}(\theta))/63\gamma N_{H_{res}}(\theta)\) is plotted against \((63\gamma N_{H_{res}}(\theta))^2\) for (a): \(T_c=72K\), (b): \(T_c=40K\) and (c): \(T_c=0\) K. Here \(\omega_0\) is the resonance frequency, \(H_{res}(\theta)\) is the field corresponding to the peak of NMR intensity in Fig. 15 (a) and (b). \(\theta\) is the angle between the direction of external field and c-axis. Open circles and solid triangles are correspond to \(K(\phi=90^\circ)\) and \(K_{\parallel}(\theta=0^\circ)\), respectively.
Fig. 15. $K_\perp$ and $K_\parallel$ for the compounds with $T_c=72K$, 40K and 0 K are shown as closed and open circles in Fig. 17 (a)-(c), respectively.
The spin part of $K_\perp$ and $K_\parallel$ are exclusively coupled to $\chi_s(T)$ by the formula\(^{13,14}\)

\[ K_\perp(T) = A_\perp \chi_s(T) + K_\perp \text{orb.}, \quad (1) \]
\[ K_\parallel(T) = A_\parallel \chi_s(T) + K_\parallel \text{orb.}, \quad (2) \]

where $K_{\text{orb}}$ is the orbital shift and generally $T$-independent. The results in YBa$_2$Cu$_3$O$_7$ were analyzed by assuming $K_{\text{spin}}(T)=0$ at $T=0$ and $K_{\text{orb}}=0.28\chi$.\(^{14,15}\) In the superconducting vortex state, the screening diamagnetic current produces an additional local field at all nuclear sites. This diamagnetic correction to the shift at 11.5 T is estimated to be less than $-0.01\chi$ by assuming the same value as in YBa$_2$Cu$_3$O$_7$ obtained at lowest temperature and 7.5T.\(^{14,15}\) With these assumptions, $K_{\perp \text{orb}}$ for Tl$_2$Ba$_2$CuO$_{6+y}$ with $T_C=72$ K and 40 K are evaluated to be $0.24\chi$ and $0.26\chi$, respectively. The $T$-dependence of $K_\perp$ is similar to that of YBa$_2$Cu$_3$O$_7$ reported previously.\(^{14,15}\) Namely, above $T_C$, $K_\perp$ is almost $T$-independent, while below $T_C$, decreases rapidly. $K_\perp$ for the non-superconducting compound is $T$-independent with a larger value of $K_\perp=0.95\chi$. Different from the Curie like behavior of the bulk susceptibility\(^6\), $\chi_s(T)$ is $T$-independent in the normal state for Tl$_2$Ba$_2$CuO$_{6+y}$. If $K_{\perp \text{orb}}$ for the non-superconducting material is assumed to be almost the same as in the superconducting compounds, the magnitude of the spin susceptibility, $\chi_s(T)$ appears to increase with decreasing $T_C$, in other word, increasing hole concentration.
On the other hand, for the superconducting samples with $T_c=72$ K and 40 K, both $T_c$'s estimated from the results of $K_\parallel$ drop sharply down to 55 K and 20 K, respectively, by the magnetic field. This is consistent with the fact that the magnetic field along the c-axis has a great effect on $T_c$ in the high $T_c$ superconductor. Apparently, it is found that $K_\parallel$ also contains spin contributions, which is quite different to the result ($K_\parallel$ spin=0) in YBa$_2$Cu$_3$O$_7$.[14],[15] Since the value of $K_\parallel$ orb (=1.27%) for 72 K compound is almost same as that (=1.28%) in YBa$_2$Cu$_3$O$_7$[14],[15], $K_\parallel$ orb is assumed as constant independent of $T_c$. Then rough estimations of spin susceptibility for respective samples are made by using the same analysis as above. Table 1 shows the spin and orbital contribution to $K$ in each sample.

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<tr>
<th>Sample</th>
<th>$K_{\perp}$ (%)</th>
<th>$K_{\perp}$ orb (%)</th>
<th>$K_{\parallel}$ (%)</th>
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<td>$T_c=72$ K</td>
<td>0.45</td>
<td>0.24</td>
<td>0.25</td>
<td>1.27</td>
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<tr>
<td>$T_c=40$ K</td>
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<td>0.26</td>
<td>0.30</td>
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<tr>
<td>$T_c=0$ K</td>
<td>0.69</td>
<td>0.26</td>
<td>0.49</td>
<td>1.28</td>
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<tr>
<td>YBa$_2$Cu$_3$O$_7$</td>
<td>0.30</td>
<td>0.28</td>
<td>~0</td>
<td>1.28</td>
</tr>
</tbody>
</table>
To argue the spin susceptibility below $T_c$, the normalized spin susceptibility $\chi_s/\chi_n=(K_1-K_{1 orb})_s/(K_1-K_{1 orb})_n$ deduced from eq. (1) is indicated in Fig. 16 for the compounds with $T_c=72$ K (solid circles) and 40 K (open circles). As seen in the figure, both appear to show the almost same T-dependence. It should be noted that this T-dependence is quite similar to that for the CuO$_2$ plane of YBa$_2$Cu$_3$O$_{7-\delta}$.

When the data of Fig. 18 are tentatively fitted to a calculation based on an isotropic gap model (s-wave) with a larger energy gap of $2\Delta=4.4k_BT_c$ than the BCS value of $3.5k_BT_c$, which is indicated by solid line in Fig. 18, the experiment and the calculation are in good agreement to each other.

On the other hand, if a d-wave model is assumed with a gap zeros of line ($\Delta=\Delta_0 \cos \theta$) on the Fermi surface and a large energy gap of $2\Delta_0=10.5k_BT_c$, which explain the Cu relaxation result just below $T_c$, there is a distinct discrepancy in low temperature as indicated by a dashed line in Fig. 18. Furthermore, the T-dependence of $\chi_s(T)$ extracted from 170 Knight shift for CuO$_2$ plane in YBa$_2$Cu$_3$O$_7$ has also been shown to be well fitted by a s-wave model with $2\Delta=4.9k_BT_c$. Thus the Knight shift results in the CuO$_2$ plane are consistently interpreted by the s-wave model with a larger energy gap than the BCS value.
Fig. 16. Temperature dependence of the normalized spin susceptibility $\chi_s/\chi_n$ below $T_C$ deduced from $K_{ab}$ of $^{63}$Cu (see text) for Tl$_2$Ba$_2$CuO$_{6+y}$ with $T_C=72$ K (solid circles) and $T_C=40$ K (open circles). Solid line corresponds to a calculation based on the s-wave model with a larger energy gap of $2\Delta = 4.4 k_B T_C$ than the BCS value of $2\Delta = 3.5 k_B T_C$. Dashed line indicates a calculation based on a d-wave model with a larger energy gap of $2\Delta_0 = 10.5 k_B T_C$ and gap zeros of line on the Fermi surface ($\Delta = \Delta_0 \cos \theta$).
5-2. $1/T_1$ of $^{63}$Cu in the High Field NMR

$1/T_1$ of $^{63}$Cu in fields perpendicular and parallel to the c-axis were measured by observing ($1/2 - -1/2$) transition in the NMR spectrum split by electric quadrupole interaction.

(1) Temperature Dependence of $1/T_1$(⊥)

$1/T_1$(⊥) for each sample was measured between 4.2 K and 210 K under a high magnetic field (about 11T) at 125.02MHz. For all samples, the recovery curves are quite well fitted to eq.(1) in chapter 4, as seen in Fig. 17.

![Fig. 17. The recovery curve of the nuclear magnetization with the fit to the eq.(4.1) for compounds with $T_c=72K$ at 12K and 74K.](image-url)
Fig. 18 and 19 show the temperature dependence of $1/T_1(\perp)$ and $(T_1T)^{-1}$, respectively. Remarkably, $1/T_1(\perp)$ for the superconducting samples obey the $T_1 \cdot T = \text{const.}$ law, in the wide temperature range above $T_c$, which is in contrast to the results in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$-18), $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ ($x=0.075$)-19), etc. This is the first observation of the Korriga like law of Cu in CuO$_2$ plane. However, at higher temperature, $1/T_1(\perp)$ deviates gradually from the Korriga like law. $1/T_1(\perp)$ for the nonsuperconducting compound also obeys the Korriga law over all temperature range measured (between 4.2 K and 130 K). The magnitude of $1/T_1(\perp)$ in the normal state is almost same for all compounds. It should be noted that $1/T_1$ is enhanced as in the case of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$-18), manifesting to be also affected by Cu-d spin fluctuation in Tl compounds.

In the superconducting state, $1/T_1(\perp)$ decreases rapidly without the enhancement just below $T_c$. This is a common feature for all high $T_c$ superconductors and cannot be interpreted by the conventional s-wave model.
Fig. 13. The temperature dependence of $1/T_1$ for $^{63}$Cu in Tl$_2$Ba$_2$CuO$_{6+y}$. Open circles, solid squares and open triangles indicate the data for compounds with $T_C$=72K, 40K and 0K, respectively.
Fig. 19. The temperature dependence of $1/(T_1T)$ for $^{63}$Cu in Tl$_2$Ba$_2$CuO$_{6+y}$. Open circles, solid circles and cross marks indicate the data for compounds with $T_c$=72K, 40K and 0 K, respectively.
(2) Temperature Dependence of $1/T_1(\parallel)$

It was hard to measure $1/T_1(\parallel)$ precisely at high temperature, since the orientation was not perfect and NMR spin echo signal was weak. However, it was found that the temperature dependence of $1/T_1(\parallel)$ was largely affected by the magnetic field. By applying the field, $1/T_1(\parallel)$ for both samples with $T_c=72$ K and 40 K decrease to 55 K and 20 K, respectively, as seen in Fig. 20 and 21, which is consistent with the results of $K_\parallel$. 
Fig. 20. The temperature dependence of $1/T_1$ for $^{63}\text{Cu}$ in the compound with $T_c=72\text{K}$. Open and solid circles indicate the data measured by the high field NMR and the zero field NQR, respectively.
Fig. 21. The temperature dependence of $1/T_1$ for $^{63}$Cu in the compound with $T_c=40K$. Open and solid squares indicate the data measured by the high field NMR and the zero field NQR, respectively.
5-3. $1/T_1$ of $^{63}$Cu by NQR

Cu NQR spectrum for each compound has been measured by sweeping frequency in the zero external field. Figure 22 shows the spectrum at 4.2 K. As seen in the Fig. 22, $^{63}$Cu and $^{65}$Cu line overlap each other because of the broad line width. There is a tendency that NQR line width for the compound with lower $T_c$ is more broader. This tendency may be due to some inhomogeneity owing to the introduced excess oxygens. The peak frequency of $^{63}$Cu line for the compounds with $T_c=72$ K, 40 K, and 0 K were roughly estimated as 22.2MHz, 23.8MHz, and 26.2MHz, respectively. These values are nearly equal to those estimated from the quadrupolar shift, namely, 21.5MHz, 23.8MHz and 26.9MHz.

$1/T_1$'s of $^{63}$Cu for all compounds have been measured at each peak frequency. As the principal axis of the electric field gradient is the c-axis, $1/T_1$ measured by NQR gives information along c-axis. The signal-to-noise ratio at 4.2 K is about 3. Figure 23 shows the temperature dependence of $1/T_1$. The behavior of $1/T_1$ is similar to that of $1/T_1(\perp)$. But the magnitude of $1/T_1$ above $T_c$ for superconducting compounds is different from that of $1/T_1(\perp)$, and this difference results from anisotropy of $T_1$. For nonsuperconducting compound, the magnitude of $1/T_1$ is equal to that of $1/T_1(\perp)$, as seen in Fig. 24.
Fig. 22. $^{63}\text{Cu}, ^{65}\text{Cu}$ NQR spectrum in $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+y}$ at 4.2 K in the zero field.
Fig. 23. The temperature dependence of $1/T_1$ for $\text{Cu}^{63}$ measured by the zero field NQR in $\text{Tl}_2\text{Ba}_2\text{CuO}_6-y$. Solid and open circles and solid squares indicate the data for compounds with $T_c=72K$, 40K and 0 K, respectively.
Fig. 24. The temperature dependence of $1/T_{1\parallel}$ and $1/T_1$ for $^{63}$Cu in the compound with $T_C=0$ K. Open squares and triangles indicate the data of $1/T_1$ measured by the high field ($H \parallel c$) NMR and the zero field NQR, respectively. Solid circles indicate the data of $1/T_1$ measured by the high field ($H \perp c$) NMR.
5-4. $1/T_1$ of $^{205}$Tl in the High Field NMR

The $T_1$ has been measured along the direction perpendicular to the c-axis between 4.2 K and 293 K at 240 MHz. Since $^{205}$Tl has no quadrupole moment, $T_1$ is measured precisely. Actually, above $T_c$, the recovery curve of the nuclear magnetization was fitted to a single exponential function, as seen in Fig. 25. As NMR spectrum is very sharp, the signal-to-noise ratio is enough to measure $T_1$ precisely up to nearly 300 K. Figure 26 shows the temperature dependence of $(T_1 T)^{-1}$. The behavior of $T_1$ of $^{205}$Tl is similar to that of $T_1$ of $^{63}$Cu. The temperature, $T^*$, which begin to deviate from Korriga law, was estimated for each sample with $T_c=72$ K, 40 K, and 0 K, to be about 150 K, 160 K, and 200 K, respectively.

It is confirmed that $1/T_1$ of $^{205}$Tl and $^{63}$Cu for the compound with $T_c=72$ K scale to each other above $T_c$. Figure 27 shows $1/T_1$ of $^{63}$Cu plotted against $1/T_1$ of $^{205}$Tl between 80 K and 203 K with temperature as an implicit parameter. The ratio of $^{205}(T_1)/^{63}(T_1)$ is constant above $T_c$, suggesting that the origin of the relaxation is the same in both Cu and Tl sites. Therefore the relaxation behavior of Cu site is obtained indirectly from that of Tl site.
Fig. 25. The recovery curve of the nuclear magnetization with the fit to a single exponential function for the compound with $T_c=72$ K at 284 K.
Fig. 26. The temperature dependence of $1/(T_1 T)$ for $^{205}$Tl in
$\text{Tl}_2\text{Ba}_2\text{CuO}_{6+y}$. Open and solid circles and solid
triangles indicate the data for compounds with $T_c = 72$ K,
40 K and 0 K, respectively.
Fig. 27. $\frac{1}{T_1}$ of $^{63}$Cu are plotted against $\frac{1}{T_1}$ of $^{205}$Tl between 80 K and 203 K with temperature as an implicit parameter.
Chapter 6. Discussion

6-1. Normal State

(1) Evidence for Fermi liquid excitation

$1/T_1$'s of $^{63}$Cu and $^{205}$Tl for all compounds obey $T_1T=\text{const.}$ law in a wide temperature range. Applying the high magnetic field along c-axis in superconducting compounds ($T_C=72$ and 40 K), $T_C$'s decrease from 72 and 40 K to 55 and 20 K, respectively. Then $1/T_1$'s of $^{63}$Cu also obey $T_1T=\text{const.}$ law above 55 and 20 K. The results support that $T_1T=\text{const.}$ law is an intrinsic feature in Tl2201 compound. As the $T_1T=\text{const.}$ law means that the energy spectrum of Cu spin excitation is continuous, it is considered that Fermi liquid picture is applicable to Tl2201 compound.

Judging from the fact that this series of compounds possess a sufficiently high temperature superconducting transition ($=85$ K), the a Fermi liquid picture may be a suitable approach to describe the normal state property in high $T_C$ superconductor in general.

$1/T_1$'s of $^{63}$Cu and $^{205}$Tl for all compounds deviate from $T_1T=\text{const.}$ law at higher temperature above $T^*$. This origin seems to be due to the Cu spin fluctuation. The tendency that $T^*$ increases with hole doping was found.

(2) Comparison with YBCO and LSCO systems

In YBCO and LSCO systems, $1/T_1$ of Cu in CuO$_2$ plane does not obey $T_1T=\text{const.}$ law above $T_C$, and is enhanced by about one order of the magnitude than the band calculation, reflecting the strong Cu spin correlation.\(^{18)}-19\) $1/T_1$ is generally given by
\[ 1/T_1 \approx k_B T \chi(q), \]  

where \( \chi(q) \) is a dynamical spin susceptibility. The behavior of \( 1/T_1 \) for Cu is qualitatively explained by assuming that \( \chi(q) \) has a sharp peak around \( q=Q \) as seen in Fig. 30 because of the antiferromagnetic correlation between Cu spins, and that \( \chi(Q) \) decreases with \( T \)-increase. A phenomenological treatment for \( 1/T_1 \) taking account of the Cu-d spin AF correlation has been carried out in YBCO system by several groups. Recently, Moriya et al. have extended the self-consistent renormalization theory (SCR theory) of a weakly or nearly AF metal to the two-dimensional system, and predicted that \( 1/(T_1 T) \sim \chi_Q(T) \) and \( \chi_Q(T) \) is proportional to \( 1/(T+\Theta) \).
6-2. Superconducting State

In $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+y}$, the $^{63}\text{Cu}$ Knight shift results below $T_c$ can be well explained in terms of the isotropic gap ($s$-wave) model if a larger energy gap with $2\Delta = 4.4k_B T_c$ is assumed in contrast to the BCS value of $2\Delta = 3.5k_B T_c$. This behavior of the spin susceptibility below $T_c$ appears to be a rather unique feature when compared to the results of $^{63}\text{Cu}$ and $^{17}\text{O}$ in the CuO$_2$ plane in YBa$_2$Cu$_3$O$_7$.\(^{13)-15},25$) This point is different from the result of the penetration depth by $\mu$SR experiment supporting the BCS $s$-wave model ($2\Delta = 3.5k_B T_c$).\(^{26}$)

In contrast to the Knight shift result, the $T$-dependence of the nuclear relaxation rate, $1/T_1$ of $^{63}\text{Cu}$ is unconventional, that is, the $1/T_1$ decreases rapidly without an enhancement just below $T_c$ characteristic of a BCS superconductor. As seen in Fig. 29, the unconventional behavior is also observed for other several high $T_c$ oxides, and all the $1/T_1$'s normalized by the value at $T=T_c$ plotted against $T/T_c$ fall on a single curve in a wide temperature range below $T_c$. This result suggests that the same mechanism is responsible for the relaxation process. There may be an alternative explanation for $T_1$ within the framework of the $s$-wave model which involves a pair-breaking effect only near $T_c$. 
Fig. 23. The temperature dependence of \( \frac{1}{T_1T} \) of \( ^{63}\text{Cu} \) in the CuO\(_2\) plane sites for Tl\(_2\)Ba\(_2\)Cu\(_6\)\(\_y\) (\(T_c = 40\) K), \((\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4\), \((x = 0.073, 0.15)\), YBa\(_2\)Cu\(_3\)O\(_7\), respectively.
6-3. Anisotropies of Knight shift and \(1/T_1\)

Figure 30 shows \(K_s\) and \((T_1)^{-1}\) plotted against the hole number per Cu in the CuO\(_2\) plane in Tl\(_2\)Ba\(_2\)CuO\(_{6+y}\), YBa\(_2\)Cu\(_3\)O\(_7\) and La\(_{1.85}\)Sr\(_{0.15}\)CuO\(_4\). Here \(K_s\) is a spin contribution to the Knight shift. In Tl2201, as the hole number increases, both \(K_s\) and \((T_1)^{-1}\) increase and \((T_1)^{-1}\) approaches 1 gradually, that is, the anisotropies of \(K_s\) and \(T_1\) become small. It is well known that the origin of the anisotropy is due to the anisotropy of the hyperfine coupling constant. In the high \(T_c\) superconductors, \(K_s\) and \(K_s^{||}\) of Cu in the CuO\(_2\) plane are generally given by

\[
K_s^{\perp} = A_{\perp} \chi_s = (A_{ab} + 4B)\chi_s, \\
K_s^{||} = A_{||} \chi_s = (A_c + 4B)\chi_s.
\]

Here \(A_{ab}\) and \(A_c\) are components perpendicular and parallel to c-axis of an on-site hyperfine coupling constant. B is an isotropic term resulting from supertransferred hyperfine interaction between nearest neighbor Cu sites. Unfortunately, in Tl2201, since both \(K_s\) and \(\chi_s\) are independent of temperature above \(T_c\), it is impossible to estimate \(A_{\perp}\) and \(A_{||}\).

In YBa\(_2\)Cu\(_3\)O\(_7\), \(A_{ab}\), \(A_c\) and B are estimated at 30, -164 and 41kOe/\(\mu_B\), respectively. Taking account of the fact that \(A_{ab}\) and \(A_c\) are not affected by hole doping in YBCO system, we assume that \(A_{ab}\) and \(A_c\) in Tl2201 are nearly equal to those in YBa\(_2\)Cu\(_3\)O\(_7\). Then it is considered that both \(K_s^{\perp}\) and \(K_s^{||}\) are increased by increase of B term with hole-doping.
Fig. 30. The temperature dependence of $1/T_1$ of $^{63}$Cu in the CuO$_2$ plane sites for Tl$_2$Ba$_2$CuO$_{6-y}$ ($T_c=72K$), La$_{1.88}$Sr$_{0.15}$CuO$_4$, YBa$_2$Cu$_3$O$_7$, Bi$_2$Pb-Sr-Ca-Cu-O and Pb-Sr-(Y-Ca)-Cu-O.
Chapter-7. Summary

By studying about Ti2Ba2CuO6+y using NMR technique, "heavy-doped" superconductor was found to possess a characteristic feature. In the normal state, 1/T1's of 63Cu in the CuO2 plane for all compounds obey Korringa like (T1T=const.) law in a wide temperature range, suggesting that Fermi liquid picture is applicable to Tl2201 compound. The magnitude of 1/T1 does not change with hole concentration, in contrast to the result that 1/T1 of Cu for "light-doped" La-Sr-Cu-O superconductor decreases considerably with increasing holes. This difference may be attributed to the difference of strength of Cu-d spin antiferromagnetic correlation between "heavy-doped" and "light-doped" superconductors.

In superconducting state, the temperature dependence of the susceptibility is explained by BCS model with a larger gap of 2Δ = 4.4kBTc than the BCS value of 2Δ = 3.5kBTc. However 1/T1 of 63Cu is unconventional and decreases rapidly without the enhancement just below Tc predicted by the BCS model. The unconventional behavior is commonly observed in other several high Tc superconductors.
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