

# Tl, Cu-NMR study on high $T_c$ cuprate $\text{TlBa}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_2\text{O}_7$

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## Abstract

Tl, Cu-NMR study has been performed on the high- $T_c$  cuprate,  $\text{TlBa}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_2\text{O}_7$  with wide range hole concentration from the antiferromagnetic ( $\text{Ca} = 0$ ) to the slightly overdoped ( $\text{Ca} = 1.0$ ). For superconducting samples ( $\text{Ca} = 0.6 \sim 1.0$ ) the local spin susceptibility ( $K_S$ ) at Cu-site stayed constant around room temperature, and starts slight a decrease from 160K, which is higher than  $T_c$ . This  $T$ -dependence is what has been reported in other high- $T_c$  cuprates in overdoped region.  $(T_1 T)^{-1}$  at Tl-site for every superconducting sample, which obeys Curie-Weiss law at high temperature, showed a significant reduction from  $T_{SG} (> T_c)$ , suggesting the existence of spin-gap even in slightly-overdoped region.

*Key words:* high- $T_c$  cuprate; NMR ; spin-gap ;

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## 1. Introduction

Recently electronic phase diagram of theoretical models, based on the spinon and the holon for the family of high- $T_c$  cuprates, have attracted much interest [1][2]. In underdoped region, for spinon condensates at  $T_{SG}$  higher than holon, there emerges a temperature region where the low-energy part of spin fluctuation is strongly suppressed. This is so-called spin-gap. The models predict a disappearance of the spin-gap in overdoped region, where  $T_{SG}$  coincides with  $T_c$ . We believe that the test of this model on many cuprates leads the full understanding of the phase diagram of cuprates.  $\text{TlBa}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_2\text{O}_7$  (Tl1212) system is one of the high- $T_c$  superconducting oxide with bilayer-type CuO plane, the structure of which is similar to YBCO and Bi2212. The electronic phase diagram of this system is unusual compared with other cuprates. The insulator of  $\text{Ca} = 0$  is doped hole by substitution of  $\text{Ca}^{2+}$  for  $\text{Y}^{3+}$ . With increasing hole-concentration, the superconducting phase appears suddenly at  $\text{Ca} = 0.6$  with  $T_c \simeq 100\text{K}$ , and with still further doping  $T_c$  decreases

only slightly to  $\simeq 80\text{K}$  for  $\text{Ca} = 1.0$ . So far, we have shown by Tl-NMR, where Tl nuclei is located at the block layer and can probe the electronic state of CuO plane through a large hyperfine coupling to Cu-3d spins [3], that the spin-gap exists even in slightly overdoped region [4]. We report in this paper the electronic state of CuO plane of Tl1212 probed by Cu-NMR.

## 2. Experiment

Polycrystalline samples of  $\text{TlBa}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_2\text{O}_7$  ( $x = 0 \sim 1.0$  step 0.1) were prepared by the conventional solid-state reaction method. The detailed process is published in elsewhere [5][6]. The powder samples mixed with epoxy resin were magnetically aligned along the crystalline  $c$ -axis for NMR measurements. Cu-NMR spectra were obtained by integrating spin echo amplitude by boxcar integrator with sweeping magnetic field around 10T. The  $^{63}\text{Cu}$  Knight shift, a measure for the uniform spin susceptibility, were obtained by measuring spectrum of the central transition ( $-1/2 \sim +1/2$ ) for several different resonance frequencies between 105 to 130 MHz. Tl nuclear spin-lattice relaxation rate,  $T_1^{-1}$ , is measured by the saturation-

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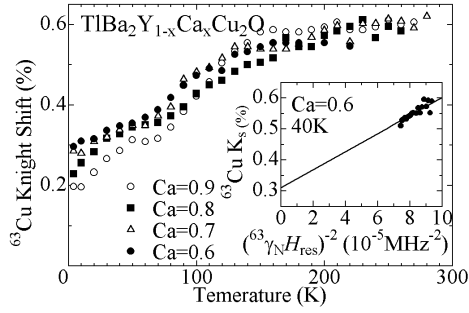


Fig. 1. Temperature-dependence of Cu-Knight shift. The inset indicates Knight shift vs  $\gamma_N H_{res}^{-2}$  plot for  $\text{Ca} = 0.6$  at 40K. The  $\nu_Q$  of Cu which may reflect the small distortion in CuO plane is estimated  $\simeq 13$  MHz at 40K. This value is much smaller than other cuprates (Bi,La-system 20  $\sim$  40 MHz).

recovery method with pulse train.

### 3. Results and Discussion

Figure 1 shows the  $T$ -dependence of the Knight shift at Cu-site from 4.2 to 280 K. The Knight shift is  $T$ -independent above 200 K, and shows a slight decrease from 160 K, which is much higher than  $T_c$ . This  $T$ -dependence is seen in overdoped region of other cuprates [7]. Note the difference from the typical spin-gap behavior reported in Knight shift of underdoped region where the significant reduction starts from room temperature. Tl-Knight shift for every superconducting sample is  $T$ -independent in the normal state [4], which is explained by relatively weak hyperfine coupling of Tl-site compared with on-site Cu ( $A_{Tl} \simeq 1/4 A_{Cu}$ ). These results indicate that underdoped region does not exist or is confined in a very narrow region ( $\text{Ca} = 0.5 \sim 0.6$ ) in this system.

The averaged value of Cu-Knight shift in high temperature region is nearly constant for  $\text{Ca} = 0.6 \sim 0.9$ . On the other hand Tl-Knight shift increases with hole-doping as seen in Fig.2. This difference means that in the overdoped region some carrier is bound in the Tl-O layer and does not contribute to the density of states of CuO plane.

Figure 3 shows Tl nuclear spin-lattice relaxation rate.  $(T_1 T)^{-1}$  for all samples follows the Curie-Weiss law in the normal state, indicating that the two-dimensional antiferromagnetic spin fluctuation remains even in the slightly overdoped region. With decreasing temperature,  $(T_1 T)^{-1}$  deviates from the Curie-Weiss law at  $T_{SG}$  higher than  $T_c$ .  $T_{SG}$  decreases with hole doping, and is still higher than  $T_c$  even in the overdoped region. The existence of spin-gap in overdoped region, which has also been reported in other cuprates of La,Bi-system [8][7], indicates either that another mechanism, different from the one in underdoped region, causes the spin-gap, or that  $T_c$  is anomalously suppressed in the region  $\text{Ca} = 0.8 \sim 1.0$ .

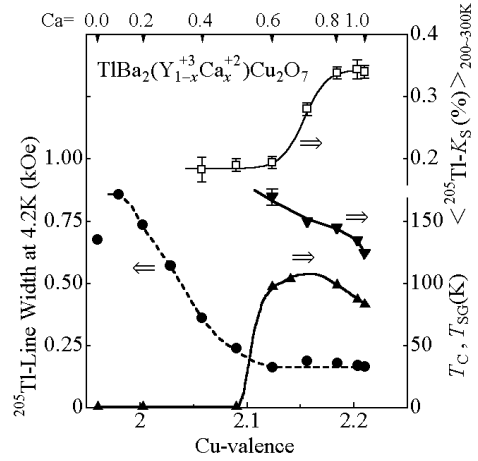


Fig. 2. Nominal Cu-valence vs  $T_c$ ,  $T_{SG}$ , the average value of  $^{205}\text{Tl}$ -Knight shift at 200  $\sim$  300K, and the width of Tl-NMR resonance peak [4]. Nominal Cu-valence is obtained as to be  $2 + (x/2) - \delta$ , where  $\delta$  is the oxygen defect [9].

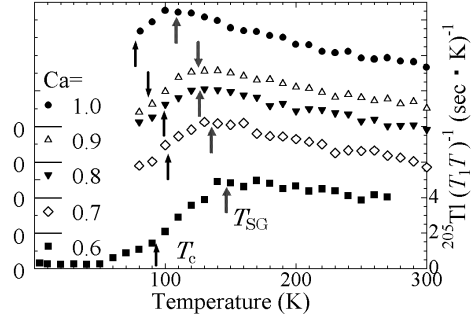


Fig. 3. Temperature-dependence of  $(T_1 T)^{-1}$  at Tl-site for  $\text{Ca} = 0.6 \sim 1.0$ . The arrows indicate  $T_c$  and  $T_{SG}$ , where  $(T_1 T)^{-1}$  deviates from Curie-Weiss law.

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