NMR study of the spin dynamics in $Tl_2Ba_2CuO_y$ ($T_c = 85$ K)

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(Received 16 June 1992)

In order to understand the spin dynamics in the over-doped region of the high-T_c oxides, the temperature (T) dependence of the Knight shift and the spin-lattice relaxation time (T_1) at the Cu and the O sites of the CuO_2 plane were measured in the normal state of $Tl_2Ba_2CuO_y$ with maximum T_c ($T_c = 85$ K). The T dependence of the Knight shift at the O site is almost isotropic. In addition, the transferred hyperfine coupling constant is estimated to be fairly large at the Cu site. These facts indicate that the hybridization between the Cu $3d$ and the O $2p$ is strong in $Tl_2Ba_2CuO_y$ and the doped holes do not have strong O $2p$ character. The T dependence of the Knight shift at the O site is the same as that of the Cu site, suggesting that the single-spin-component model is likely in this over-doped system. Based on a comparison between the T_1 of the Cu and the O sites, the antiferromagnetic correlation is considered to be very weak in this system, and the antiferromagnetic correlation length (ξ/a) is estimated to be 1.2 at 120 K. Although the reason is unclear, the so-called psuedo-spin-gap behavior is observed below 120 K at the Cu site, and the relation $T_1TK = \text{const}$ was found to be more likely at the O site than the Korringa-type relation. In addition, the ratio of the T_1 at the Cu and the O sites becomes T independent in the vicinity of the T_c. These phenomena are also observed in the lightly doped system; thus they may be considered as universal features of the high-T_c oxides.

I. INTRODUCTION

It is well known that high-T_c superconductivity may occur when carriers are doped into the parent antiferromagnetic (AF) compound in the so-called lightly doped systems, i.e., $Ba_2YCu_3O_y$ ($BYCO_y$) and $La_{2-x}Sr_xCuO_4$ (LSCO). From various experiments performed on these systems, it is revealed that the metallic properties of the normal state are very unusual due to the strongly correlated nature of conduction electrons, and an understanding of the properties of the normal state will be necessary to elucidate the mechanism leading to the high T_c.[1] In this context, many models of a unique coupling between the spin degree of freedom and the charge degree of freedom were proposed to explain these unusual normal-state properties.[2]

Since NMR is a powerful technique used in the investigation of low-energy static and dynamic properties of the spin moment in solids, many experiments of this kind have been performed on high-T_c systems to date. The important facts and conjectures on the normal state of high-T_c materials derived from those measurements may be summarized as follows:

(1) The dynamic susceptibility $\chi''(q,\omega_n)$ ($\omega_n \sim 0$) has an enhancement around the zone boundary, i.e., $q = Q$.[3] Although the magnitude of this AF enhancement is different for each compound, the temperature (T) dependence seems to have a similar behavior for all such compounds. Namely, the enhancement increases with decreasing temperature to a characteristic temperature (T_s), then decreases with decreasing temperature to T_c.

(2) The existence of a pseudo-spin-gap is proposed to interpret the decrease of the $1/T_1T$ below T_s.[4,5]

(3) A possible correlation between T_c and the strength of AF correlations is proposed[6,7] because T_c increases when the strength of the AF correlation is weakened for the BYCO and the LSCO systems.

(4) The single-spin-component model is suggested, based on nearly the same observed temperature dependence of the Knight shift at the O and the Cu sites.[8]

(5) The relationship $T_1TK = \text{const}$ is established at the O site in the BYCO system, deviating from the expected Korringa relation.[8]

(6) The ratio of the ^{63}Cu and the ^{17}O relaxation rates becomes T independent around T_c.[9] It means that a coherent change in $\chi''(Q,\omega_n)$ and $\chi''(0,\omega_n)$ occurs around T_c.

These physical quantities contain important information on the spin dynamics but they are discussed so far mainly in the reference to BYCO system. Thus, in order to test the universality of these behaviors, an investigation of the spin dynamics in another system is of particular importance.

The $Tl_2Ba_2CuO_y$ (Tl 2:2:0:1) system is well known as a so-called over-doped system, of which the T_c ranges between 85 and 0 K, depending on the oxygen concentration.[10] In contrast to the BYCO system, the Tl 2:2:0:1 system does not have a parent AF insulating phase, but only a metallic phase. The reason for the lack of the AF phase is still unclear, but we nevertheless expect to find unique electronic characteristic of the over-doped region in the Tl 2:2:0:1 system. The AF correlation in the metallic state of the lightly doped high-T_c materials is believed to cause this metallic phase to be located near the AF phase, thus the estimation of the AF correlations in the Tl 2:2:0:1 system are crucial for an elucidation of the relation between the high-T_c and the AF correlations in all such systems. Furthermore, we could obtain Tl

2:2:0:1 samples that are homogeneous enough for the NMR measurements.

In order to investigate the detail spin dynamics in a typical over-doped phase, we have measured the T dependence of the Knight shift and the spin-lattice relaxation time (T_1) at the O and the Cu sites in the normal state of the Tl 2:2:0:1 sample with the maximum $T_c = 85$ K (Tl 2:2:0:1 No. 1) in this study. We could regard this sample as an over-doped phase because the electronic conductivity in the normal state is fairly large compared to the lightly doped systems.[11] We will discuss the unique spin dynamics as compared with the BYCO system on the basis of the physical parameters mentioned above.

II. EXPERIMENT

The ^{17}O enriched sample was prepared by a standard solid-state reaction method. From the x-ray-diffraction measurement, the crystal structure of the sample is *orthorhombic* ($a = 5.470$ Å, $b = 5.505$ Å, $c = 23.283$ Å). From the magnetic dc susceptibility measured by SQUID, the T_c is found to be 85 K and the superconducting volume fraction was estimated as 50% in the field-cooling process under magnetic field of 1.6 Oe and almost 100% in the zero-field-cooling process. We also measured the magnetic static susceptibility in the normal state under 1 T. Unfortunately, the Curie term due to an impurity was observed, thus we could not decide experimentally the T dependence of the intrinsic susceptibility. The polycrystalline sample was aligned in the magnetic field of 12 T for the NMR measurements. The NMR measurements were performed by the conventional pulse method using a superconducting magnet of 12 T.

III. KNIGHT SHIFT AND ELECTRIC FIELD GRADIENT

A. Oxygen sites

Figure 1 shows the field spectra of the ^{17}O NMR with the magnetic field parallel or perpendicular to the c axis. Three different O sites were observed (A, B, and C), in agreement with the results of the neutron-diffraction study.[12] Although the existence of a few interstitial oxygen atoms was suggested by the neutron-diffraction study, we could not detect any signal associated with those sites.

The Knight shift (K) and the electric field gradient (EFG) at each oxygen site are tabulated in Table I. As is reported by Takigawa *et al.*,[13] we use the peak or the edge positions of the first and second satellites to determine K and the EFG considering the second-order effect. In this paper, we define the oxygen of the CuO_2 plane as O(1), of the BaO plane as O(2), of the TlO layer as O(3). The site assignment for the observed spectrum was performed as follows. The site of the largest K and the shortest T_1 (site A) is assigned to O(1). Since the EFG component of O(1) in the CuO_2 plane is considered to be largest along the bonding axis (a axis), we could distinguish $^{17}K_a(\mathbf{H}\|a$ axis) from $^{17}K_b(\mathbf{H}\|b$ axis). Although the reason is unclear, it is worth noting that the uniaxiality of the ^{17}K along the bonding axis is not observed in Tl

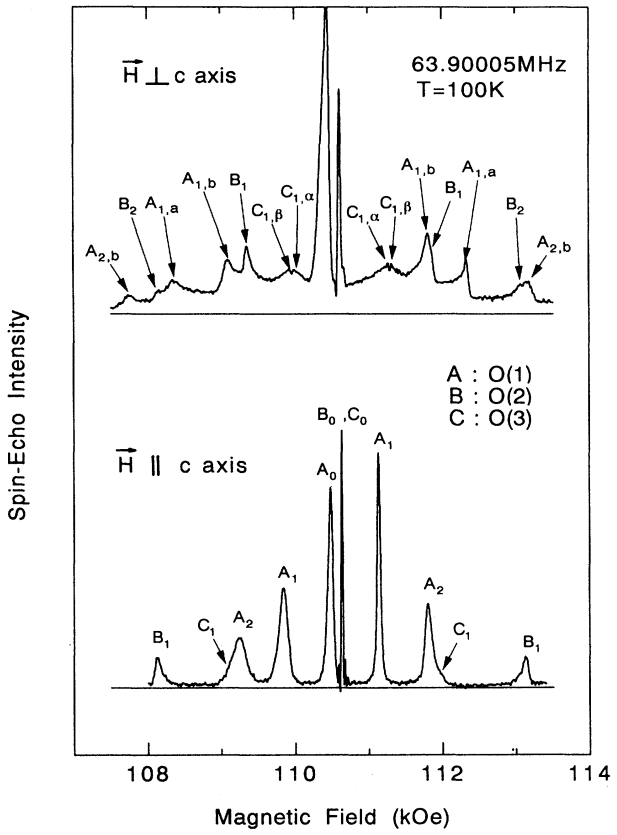

FIG. 1. Field spectra of ^{17}O NMR. Subscripts 0, 1, and 2 correspond to the central, first satellite, second satellite transitions of each site. The straight solid lines correspond to the base lines. Subscripts a and b correspond to the a axis and b axis. Subscripts α and β correspond to the principal axes of the EFG perpendicular to the c axis in the O(3) site, although we could not decide the relationship between the principal axes and the lattice axes at the O(3) site.

2:2:0:1 No. 1. The site with $\eta = 0$ along the c axis (site B) is assigned to O(2). From the structural consideration, the disappearance of η at the O(2) site is quite reasonable. The site which has rather broadened spectra and a finite η (site C) is assigned to O(3). This is consistent with the random displacement of oxygen at the TlO layer observed by neutron diffraction.[12] Furthermore, finite η is suggested from the point charge model.

Generally, the Knight shift is composed of spin (K_s) and orbital (K_{orb}) parts,

$$K = K_s + K_{\text{orb}} , \tag{1}$$

K_{orb} is considered to be independent of temperature and regarded as K in the fully superconducting state (i.e., at 4.2 K) for the oxide superconductors approximately. Unfortunately, we could not separate the $^{17}K_s$ from $^{17}K_{\text{orb}}$ for each component independently because of the large ambiguity of the orbital part due to the broadening of the spectra in the superconducting state. Nevertheless, we have succeeded in estimating the isotropic part of $^{17}K_{\text{orb}}$

TABLE I. EFG(ν), asymmetric parameter η, and Knight shift tensors of oxygens in $Tl_2Ba_2CuO_y$ (T_c=85 K) at 100 K. [α and β correspond to the principal axes perpendicular to the c axis at the O(3) site (see Fig. 1).]

			EFG(ν) (MHz)	η	^{17}K (%)	$^{17}K_{iso}$	$^{17}K_{ani}$
O(1):	CuO_2 plane	$\|a$	1.154		$^{17}K_a$=0.332±0.002		
		$\|b$	−0.790	0.36	$^{17}K_b$=0.233±0.002	0.256	0.038
		$\|c$	−0.369		$^{17}K_c$=0.203±0.002		
O(2):	BaO plane	$\perp c$	−0.73	0	0.079±0.005	0.07	0.003
		$\|c$	1.45		0.060±0.005		
O(3):	TlO plane	$\perp c$	−0.41		$^{17}K_\beta$=0.072±0.01		
		$\perp c$	−0.35	0.05	$^{17}K_\alpha$=0.095±0.01	0.10	−0.004
		$\|c$	0.76		0.143±0.01		

at the O(1) site (see Sec. III C). The Knight shift at the O(3) site is fairly large, and this fact is suggestive of clarifying the electronic nature of the TlO layer. We will discuss this subject with the NMR results of the Tl site elsewhere.

Figure 2 shows the T dependence of the Knight shift at O(1) [$^{17}K_\alpha$ ($\alpha=a,b,c$ axis)] in the normal state. It should be noted, because of the strong magnetic field, the sample is in the normal state at 85 K ($=T_c$ of zero field). For each component, $^{17}K_\alpha$ decreases very slightly with decreasing temperature. In what follows we confine ourselves to discuss only the O(1) site and define it simply as the O site.

Figure 3 shows the T dependence of the isotropic Knight shift [$:^{17}K_{iso}\equiv(^{17}K_a+^{17}K_b+^{17}K_c)/3$] and the anisotropic Knight shift [$:^{17}K_{ani}\equiv\{^{17}K_a-(^{17}K_b+^{17}K_c)/2\}/3$] in the normal state. For comparison, the results of $BYCO_{6.96}$ (heavily doped) and $BYCO_{6.6}$ (lightly doped) are also presented.[14] We focus on only the T dependence of $^{17}K_{iso}$ and $^{17}K_{ani}$ in this paper because the absolute value of the spin part in the $^{17}K_{ani}$ could not be estimated as mentioned above. The T dependence of $^{17}K_{iso}$ of $BYCO_{6.96}$ in the normal state is weak compared to that of the $BYCO_{6.6}$ system because of the weak T dependence in the static susceptibility. The weak T dependence of $^{17}K_{iso}$ in Tl 2:2:0:1 No. 1 may also arise for the same reason. On the other hand, almost no T dependence of the $^{17}K_{ani}$ is observed within an experimental error both in Tl 2:2:0:1 No. 1 and $BYCO_{6.96}$ in contrast to $BYCO_{6.6}$. More precisely, if we define $\epsilon\equiv\{^{17}K_{ani}(T_c)-^{17}K_{ani}(200\ K)\}/\{^{17}K_{iso}(T_c)-^{17}K_{iso}(200\ K)\}$, the value of ϵ in $BYCO_{6.6}$ is appreciably larger than those of $BYCO_{6.96}$ and Tl 2:2:0:1 No. 1.

A possible origin of the hyperfine field at the O site is due to the O 2p hole and/or the transferred hyperfine field from the Cu 3d hole, thus, if we stand on the ionic model,[15] the spin part of $^{17}K_{iso}$ ($:^{17}K_{iso,s}$) and is $^{17}K_{ani}$ ($:^{17}K_{ani,s}$) could generally be expressed as

$$^{17}K_{iso,s}=^{17}A^{Cu}_{iso}\chi^{Cu}_s+^{17}A^{h}_{iso}\chi^{h}_s\ ,$$
$$^{17}K_{ani,s}=^{17}A^{Cu}_{ani}\chi^{Cu}_s+^{17}A^{h}_{ani}\chi^{h}_s\ , \quad (2)$$

where χ^{Cu}_s and χ^{h}_s are the isotropic spin susceptibilities associated with the Cu 3d hole and the O 2p hole, respectively. $^{17}A^{Cu,h}_{iso}$ and $^{17}A^{Cu,h}_{ani}$ are the isotropic and the anisotropic hyperfine coupling constants, respectively. In this paper we assume the isotropic spin susceptibility for both the Cu and the O site holes. In addition, we define $\Delta\,^{17}K(T)_{iso,s}$, $\Delta\,^{17}K(T)_{ani,s}$, and $\Delta\chi^{Cu,h}_s$ as follows:

$$[\Delta\,^{17}K(T)]_{iso,s}=[^{17}K(T)]_{iso}-[^{17}K(T_0)]_{iso}\ ,$$
$$[\Delta\,^{17}K(T)]_{ani,s}=[^{17}K(T)]_{ani}-[^{17}K(T_0)]_{ani}\ , \quad (3)$$
$$[\Delta\chi(T)]^{Cu,h}_s=[\chi(T)]^{Cu,h}_s-[\chi(T_0)]^{Cu,h}_s\ ,$$

where T_0 is a certain fixed temperature. In the cases of Tl 2:2:0:1 No. 1 and $BYCO_{6.96}$,

$$[\Delta\,^{17}K(T)]_{ani,s}=^{17}A^{Cu}_{ani}[\Delta\chi(T)]^{Cu}_s+^{17}A^{h}_{ani}[\Delta\chi(T)]^{h}_s\sim 0\ . \quad (4)$$

In the case of $BYCO_{6.6}$, as Takigawa *et al.* reported,[8]

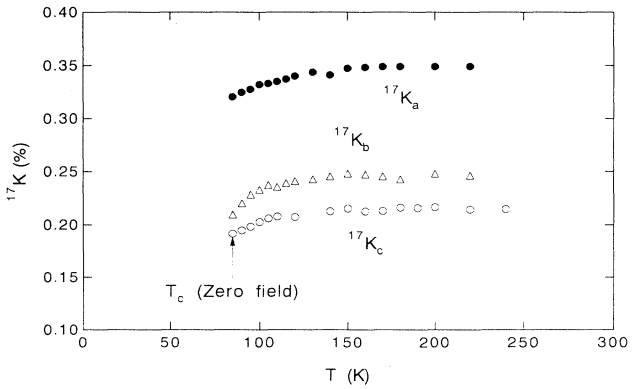

FIG. 2. Temperature dependence of the Knight shift at the O(1) site of the CuO_2 plane in Tl 2:2:0:1 No. 1 for the magnetic field parallel to the a, b, and c axes.

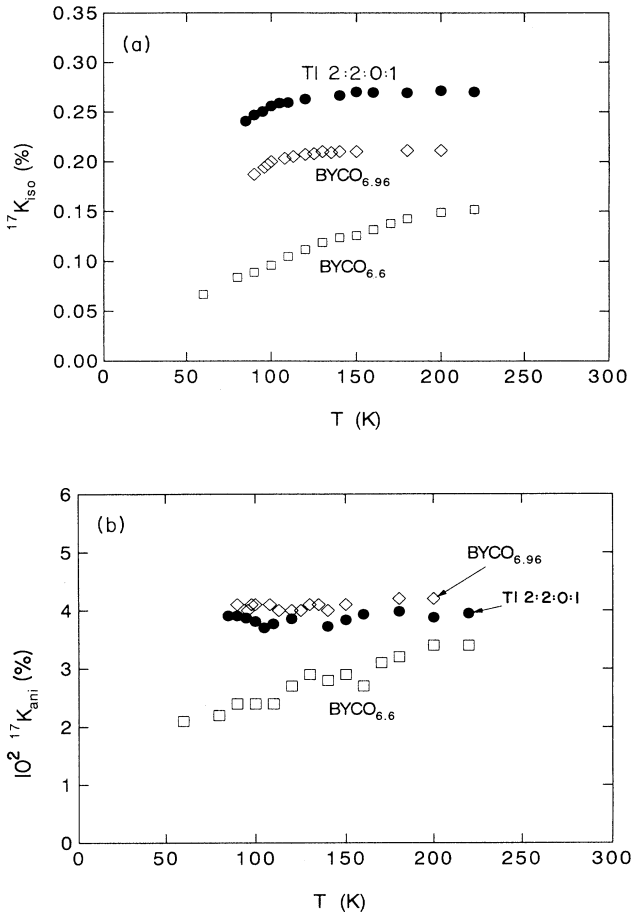

FIG. 3. Temperature dependence of (a) $^{17}K_{\rm iso} \equiv (^{17}K_a + {}^{17}K_b + {}^{17}K_c)/3$ and (b) $^{17}K_{\rm ani} \equiv \{ {}^{17}K_a - (^{17}K_b + {}^{17}K_c)/2\}/3$ in the normal state of Tl 2:2:0:1 No. 1, $BYCO_{6.96}$, and the $BYCO_{6.6}$ (Ref. 14).

$$\Delta [{}^{17}K(T)]_{{\rm ani},s} = {}^{17}A^{\rm Cu}_{\rm ani} [\Delta\chi(T)]^{\rm Cu}_s + {}^{17}A^{h}_{\rm ani} [\Delta\chi(T)]^{h}_s \propto [\Delta\chi(T)]^{\rm Cu}_s \ . \quad (5)$$

$[\Delta\, {}^{17}K(T)]_{{\rm iso},s}$ shows the same T dependence of the Knight shift at the Cu site in each specimen (see Sec. III C and Ref. 8),

$$[\Delta\, {}^{17}K(T)]_{{\rm iso},s} = {}^{17}A^{\rm Cu}_{\rm iso} [\Delta\chi(T)]^{\rm Cu}_s + {}^{17}A^{h}_{\rm iso} [\Delta\chi(T)]^{h}_s \propto [\Delta\chi(T)]^{\rm Cu}_s \ , \quad (6)$$

indicating the existence of the transferred hyperfine field at the O site. Since the hyperfine field from the O $2p$ state is expected to be fully anisotropic (i.e., $^{17}A^{h}_{\rm iso}=0$, $^{17}A^{h}_{\rm ani}\neq 0$), for Tl 2:2:0:1 No. 1 and $BYCO_{6.96}$,

$$[\Delta\chi(T)]^{h}_s \sim -{}^{17}A^{\rm Cu}_{\rm ani}/{}^{17}A^{h}_{\rm ani} [\Delta\chi(T)]^{\rm Cu}_s \ , \quad (7)$$

for $BYCO_{6.6}$,

$$[\Delta\chi(T)]^{h}_s \propto [\Delta\chi(T)]^{\rm Cu}_s \ . \quad (8)$$

For both cases, the linear relationship between $\Delta\chi^{\rm Cu}_s$ and $\Delta\chi^{h}_s$ should be established, indicating the single-spin-component model is likely in each specimen. In the cases of Tl 2:2:0:1 No. 1 and $BYCO_{6.96}$, however, the ratio of $\Delta\chi^{\rm Cu}_s$ and $\Delta\chi^{h}_s$ should be equal to $-{}^{17}A^{\rm Cu}_{\rm ani}/{}^{17}A^{h}_{\rm ani}$ in order to cancel out the T dependence of $\Delta\, {}^{17}K(T)_{{\rm ani},s}$.

Although this accidental cancellation could not be excluded from the present results, another possible explanation for the observed difference is as follows. In $BYCO_{6.96}$ and Tl 2:2:0:1 No. 1, because of the strong metallic nature, in other words, the strong hybridization between the Cu $3d$ and the O $2p$ states, the doped holes lose the strong O $2p$ character, it seems to be rather meaningless to consider $\chi^{\rm Cu}_s$ and χ^{h}_s independently, namely the ionic model presented above is not appropriate in the heavily and over-doped regions. If we assume the isotropic single spin component χ_s in $BYCO_{6.96}$ and Tl 2:2:0:1 No. 1, the observed result is expressed simply as

$$[\Delta\, {}^{17}K(T)]_{{\rm ani},s} = {}^{17}A_{\rm ani}\, \Delta\chi_s \ , \quad {}^{17}A_{\rm ani} \sim 0 \ . \quad (9)$$

In this formula, the reason for the T-independent $[\Delta\, {}^{17}K(T)]_{\rm ani}$ is the disappearance of $^{17}A_{\rm ani}$ instead of the accidental cancellation between the contribution of $\Delta\chi^{\rm Cu}_s$ and $\Delta\chi^{h}_s$. In addition, $^{17}K_{\rm ani}$ should be equal to $^{17}K_{\rm ani,orb}$ in $BYCO_{6.96}$ and Tl 2:2:0:1 No. 1. Reliable estimations of $^{17}K_{\rm ani,orb}$ for $BYCO_y$ and Tl 2:2:0:1 systems are awaited.

In $BYCO_{6.6}$, to the contrary, the presented ionic model may be rather appropriate, the doped holes may be introduced in the state which has strong O $2p$ character because of its ionic nature. Thus, the finite change of $^{17}K_{\rm ani}$ with T may be due to the O $2p$-hole spin, although that spin strongly coupled with the Cu $3d$ spin (i.e., $\Delta\chi^{h}_s \propto \Delta\chi^{\rm Cu}_s$).

The nature of hyperfine coupling at the O site depends on the hole doping concentration, in the case of the lightly doped system the O $2p$-hole spin nature may remain, and the T dependence of $^{17}K_{\rm ani}$ is observed. On the other hand, in the heavily and over-doped systems hyperfine coupling may become isotropic because of the strong hybridization between the Cu $3d$ and the O $2p$ states.

B. Copper site

Figure 4 shows spectra for the central transition $(-\frac{1}{2}\leftrightarrow\frac{1}{2})$ of ^{63}Cu NMR. From the NQR measurements, the orthorhombic Tl 2:2:0:1 system has two different Cu sites with slightly different EFG's.[16] However, the Knight shift of these sites was found to be the same and the difference in the second-order effect of the EFG to the central transition is negligible. In the same manner as reported by Takigawa *et al.*,[8] we have measured the frequency dependence of the peak position of these spectra in order to determine the Knight shift values. Figure 5 shows the T dependence of ^{63}K along the c axis ($:{}^{63}K_c$) and perpendicular to the c axis ($:{}^{63}K_{ab} \equiv {}^{63}K_a = {}^{63}K_b$) in the normal state. The EFG of the Cu site in the Tl

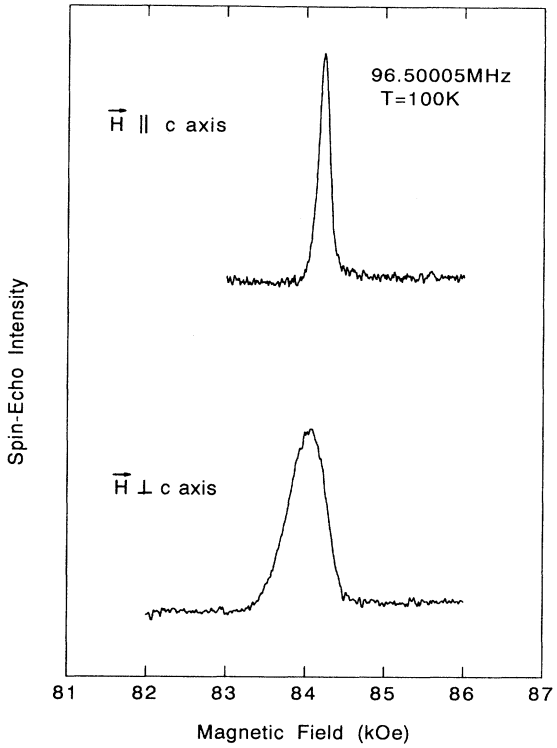

FIG. 4. Field spectra of ^{63}Cu NMR (central transition) in Tl 2:2:0:1 for the magnetic field parallel and perpendicular to the c axis.

2:2:0:1 system is more distributed than the BYCO system as reported before.[16] It should be noted, however, that the T dependence of the Knight shift determined from the center of the gravity in the spectra has the same behavior, indicating that we probe the real change in the Knight shift. Although the static susceptibility has the Curie term because of the paramagnetic impurity as mentioned above, the intrinsic static susceptibility is considered to have the same T dependence as ^{63}K. The origin of the T dependence is still unknown, but it is remarkable that the behavior of the static susceptibility in the Tl 2:2:0:1 system with the maximum T_c is similar to that of BYCO ($T_c \sim 90$ K). It should be noted here that Fujiwara *et al.* have observed no T dependence of ^{63}K in the normal state of the Tl 2:2:0:1 system (T_c=72–0 K).[17] The discrepancy with the present result may arise from the difference of T_c.

C. Linear scaling relation between $^{63}K_{ab}$, $^{63}K_c$, and $^{17}K_{iso}$

Figure 6 shows the plots of $^{63}K_{ab}$ vs $^{63}K_c$, and $^{17}K_{iso}$. As clearly seen, a good linearity with following relations have been obtained (K in units of %),

$$^{17}K_{iso} = 0.302\,^{63}K_{ab} + 0.0288\ ,$$
$$^{63}K_c = 0.531\,^{63}K_{ab} + 1.124\ . \tag{10}$$

The observed change in the Knight shifts at each site is due to the spin part of the Knight shift (K_s) (i.e., spin susceptibility), thus if we assume that the observed value of $^{63}K_{ab}$ at 4.2 K (=0.25%) as $^{63}K_{ab,orb}$ and the above relations are established below T_c, we obtain $^{63}K_{c,orb}$=1.26%. The fact that these values are similar to those of the BYCO system indicates that the crystal field splitting of the Cu $3d^9$ orbital in the Tl 2:2:0:1 system is the same as that in the BYCO system.[17] Also $^{17}K_{iso,orb}$ is estimated as 0.10%, which is rather large compared to that of $BYCO_{6.6}$.[8]

The linear relation between $^{17}K_{iso}$ and $^{63}K_{ab}$ indicates that the dominance of the transferred hyperfine field at the O site and the single-spin-component model is appropriate in Tl 2:2:0:1 No. 1, as mentioned above.

As proposed by Mila and Rice,[18–20] K_s is expressed as follows, if the isotropic single-spin component is assumed:

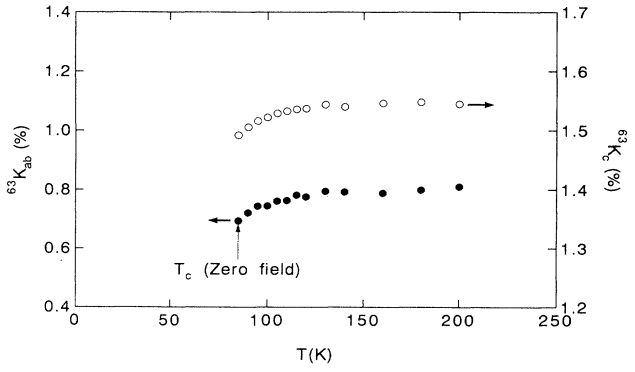

FIG. 5. Temperature dependence of the Knight shift at the Cu site in Tl 2:2:0:1 for the magnetic field perpendicular to the c axis, $^{63}K_{ab}$, and parallel to the c axis, $^{63}K_c$.

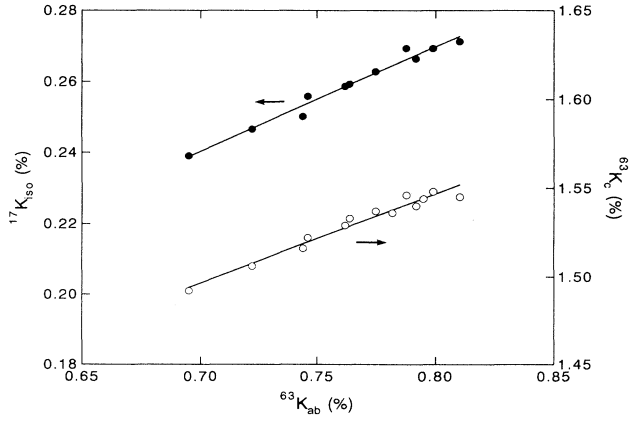

FIG. 6. $^{63}K_c$ and $^{17}K_{iso}$ are plotted against $^{63}K_{ab}$ with T as an implicit parameter. The solid lines are obtained from the least-squares fitting.

$$^{63}K_{s,\alpha}=(A_\alpha+4B)\chi_s \quad (\alpha=ab,c)\ ,$$
$$^{17}K_{s,\mathrm{iso}}=2C\chi_s\ , \tag{11}$$

where A_α and B are the on-site and the (super-) transferred hyperfine coupling constants of the Cu site, respectively, $2C$ is the isotropic hyperfine coupling constant of the O site, χ_s is the isotropic single-spin susceptibility. Based on these formulas, the observed linear relationships correspond to following relations because the slope of the plots represents the ratio among the coupling constants:

$$2C/(A_{ab}+4B)=0.302\pm0.02\ ,$$
$$(A_c+4B)/(A_{ab}+4B)=0.531\pm0.03\ . \tag{12}$$

In the case of $BYCO_{\sim 7}$, the values of $2C/(A_{ab}+4B)$ and (A_c+4B) are ~ 0.7 and ~ 0, respectively.[6] These relations will be used for an estimate of each coupling constant and an analysis of T_1 later.

IV. SPIN-LATTICE RELAXATION TIMES

Figure 7 shows the temperature dependence of $(^{63}T_1T)^{-1}$ (96.5-MHz central transition) and $(^{17}T_1T)^{-1}$ (63.9 MHz first satellite at a higher magnetic field) of $\mathbf{H}\|c$ axis in the normal state. $(^{63}T_1T)^{-1}$ (96.5-MHz central transition) of $\mathbf{H}\|ab$ plane was also measured (see Fig. 10). The behaviors are different because of the different q dependence of the hyperfine form factor, i.e., the Cu site probes the $q=Q$ component but the O site does not.

$(^{63}T_1T)^{-1}$ is maximum around 120 K. The Korringa-type relation was not observed in the measured temperature range. Although the temperature dependence is weaker than that of the BYCO system, $(^{63}T_1T)^{-1}$ increases with decreasing temperature due to the enhancement of $\chi''(q,\omega_n)$ at $q\sim Q$ $[:\chi''(Q,\omega_n)]$, and decreases suddenly below 120 K to T_c. This behavior of the Cu sites is considered to be the universal nature of the oxide superconductors. Thurston *et al.* pointed out that the pseudogap behavior was observed only at $q=Q$, but not at $q=Q+\delta$ in LSCO, which has an incommensurate peak of $\chi''(q,\omega_n)$ at $q=Q+\delta$.[21] However, $(^{63}T_1T)^{-1}$ is supposed to probe the change in both $q=Q+\delta$ and $q=Q$ because of the broadened q dependence of the hyperfine form factor around $q=Q$.

$(^{17}T_1T)^{-1}$ slightly decreases with temperature, and shows a sudden decrease below 100 K. We could not observe the sudden decrease of $(^{17}T_1T)^{-1}$ at 120 K. Two possible explanations for this difference between the O and Cu sites could be considered. One is that the transfer of the spectral weight of $\chi''(Q,\omega_n)$ to another q space or the decrease of $\chi''(Q,\omega_n)$ below 120 K. The transfer of the spectral weight may be unlikely because the increase of $(^{17}T_1T)^{-1}$ below 120 K is not observed. However, the decrease of $\chi''(Q,\omega_n)$ is also unlikely because it is against the moment sum rule proposed by Millis and Monien.[22] The other possibility is that the behavior of the pseudo-spin-gap is different between $q\sim 0$ and $q\sim Q$. The essence of the pseudo-spin-gap may be regarded as the transfer of the spectral weight of $\chi''(q,\omega_n)$ to a high-energy region (the moment sum rule could be established in this case). Thus, the observed difference may be attributed to the fact that the T dependence of the transfer is different between $q\sim 0$ and $q\sim Q$. Unfortunately, since the NMR proves only the q summation of $\chi''(q,\omega_n)$, clarification of the detailed structure of $\chi''(q,\omega_n)$ must await a more detailed neutron-scattering study.

In the case of the BYCO system, $(^{17}T_1T)^{-1}$ has the same temperature dependence as $^{17}K_{\mathrm{iso},s}$ (i.e., $^{17}T_1T\,^{17}K_{\mathrm{iso},s}=\mathrm{const}$). We could obtain the T dependence of $^{17}K_{\mathrm{iso},s}$ $(=^{17}K_{\mathrm{iso}}-^{17}K_{\mathrm{iso,orb}})$, based on the estimated value of $^{17}K_{\mathrm{iso,orb}}=0.10\%$, although this estimation may have a large ambiguity. Figure 8 shows $^{17}T_1T\,^{17}K_{\mathrm{iso},s}$ and $^{17}T_1T\,^{17}K^2_{\mathrm{iso},s}$ vs T plots. As clearly seen, the relationship of $^{17}T_1T\,^{17}K_{\mathrm{iso},s}=\mathrm{const}$ is more likely in Tl 2:2:0:1 No. 1 although some deviations are found. If we assume the narrow and Lorentzian distribution of $\chi''(q,\omega_n)$ around ω_n, then $\chi''(q,\omega_n)$ may be given as

$$\chi''(q,\omega_n)/\omega_n=\pi\chi'(q,\omega_n)/\Gamma_q\ , \tag{13}$$

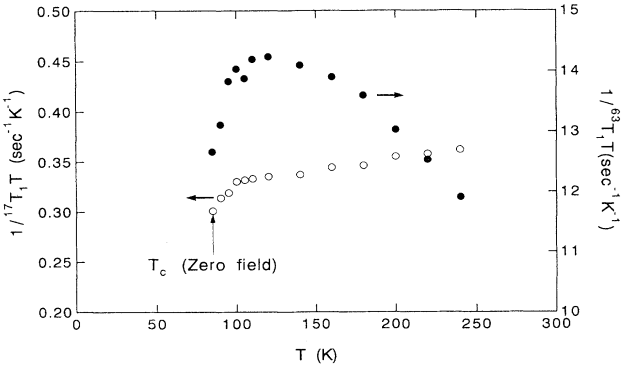

FIG. 7. Temperature dependence of the spin-lattice relaxation rate at the Cu site, $(^{63}T_1T)^{-1}$ of $H\|c$ axis $(=^{63}W_c)$, and the O site of the CuO_2 plane, $(^{17}T_1T)^{-1}$ of $\mathbf{H}\|c$ axis $(=^{17}W_c)$.

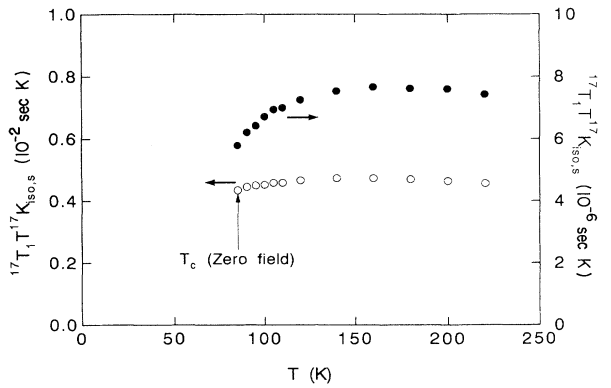

FIG. 8. Temperature dependence of $^{17}T_1T\,^{17}K_{\mathrm{iso},s}$ and $^{17}T_1T\,^{17}K^2_{\mathrm{iso},s}$ (Korringa type).

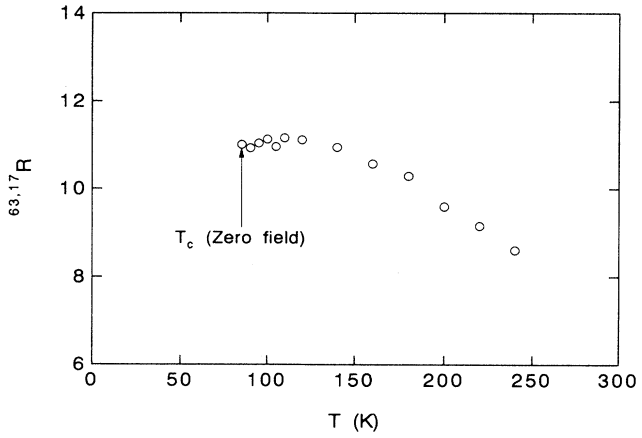

FIG. 9. Temperature dependence of the ratio of the spin-lattice relaxation rate between ^{63}Cu and ^{17}O (H$\|c$ axis): $^{63,17}R \equiv (^{63}W_c\ ^{17}\gamma_n^2)/(^{17}W_c\ ^{63}\gamma_n^2)$.

where $\chi'(q,\omega_n)$ is the real part of the generalized susceptibility and Γ_q is the characteristic spin fluctuation energy. The observed relation corresponds to the following relations:

$$(^{17}T_1T)^{-1} \propto \sum_{q\sim 0} \chi'(q,\omega_n)/\Gamma_q \ ,$$
$$\sum_{q\sim 0} \chi'(q,\omega_n)/\Gamma_q \propto \chi'(0,0)=\chi_s \propto K_s \ . \tag{14}$$

From the present study, we could not conclude which term of $\sum_{q\sim 0}\chi'(q,\omega_n)/\Gamma_q$ has a dominant contribution to the decrease of $(^{17}T_1T)^{-1}$ below 100 K. Contributions from rather wide q space may be considered because of the fairly wide q dependence of the hyperfine form factor at the O site. It is remarkable that the second relation is established in both lightly doped and over-doped oxide superconductors.

Figure 9 shows the T dependence of $^{63,17}R\ [\equiv (^{17}T_1\ ^{17}\gamma_n^2)/(^{63}T_1\ ^{63}\gamma_n^2)]$, where $^{17}\gamma_n$, $^{63}\gamma_n$ are the nuclear gyromagnetic ratios of ^{17}O and ^{63}Cu, respectively. $^{63,17}R$ becomes T independent below 120 K to T_c, although a weak maximum is observed at 120 K. Since similar behavior is also observed in the BYCO system, this behavior seems to be universal in high-T_c superconductors, although the microscopic reason is still unclear.

The increase of $^{63,17}R$ with decreasing temperature in the high-temperature region ($120<T<240$ K) corresponds to the enhancement of $\chi''(Q,\omega_n)$ against $\chi''(0,\omega_n)$ in Tl 2:2:0:1 No. 1. We will discuss the nature of this enhancement accompanied by the estimated hyperfine coupling constants later.

V. ESTIMATE OF THE HYPERFINE COUPLING CONSTANTS

We could not obtain the absolute values of the hyperfine coupling constants without an adequate assumption because of the lack of the real static susceptibility data. Nevertheless, we could estimate the ratio between each coupling constant based on the present Knight shift and T_1 data.

Now, it is well known that $\chi''(q,\omega_n)$ has enhancement at $q\sim Q$ in the normal state of the oxide superconductors, and because of the different q dependences of the hyperfine form factor, the Cu site probes $\chi''(Q,\omega_n)$ but the O site does not. Thus, we divide the spin-lattice relaxation rate $W\equiv 1/(T_1T)$ into two parts of $q\sim 0$ and $q\sim Q$ approximately,[6]

$$^{63}W_\alpha \sim {}^{63}W_{0,\alpha} + {}^{63}W_{Q,\alpha} \quad (\alpha = ab,c) \ ,$$
$$^{17}W_c \sim {}^{17}W_{0,c} \ . \tag{15}$$

Based on the Mila-Rice model, $^{63\text{ or }17}W_0$ and $^{63\text{ or }17}W_Q$ for each direction are expressed as follows:

$$^{63}W_{0,ab} \sim {}^{63}\gamma_n^2(A_{ab}^2 + A_c^2 + 8B^2)\sum\chi''(0) \ ,$$
$$^{63}W_{0,ab} \sim {}^{63}\gamma_n^2(2A_{ab}^2 + 8B^2)\sum\chi''(0) \ ,$$
$$^{63}W_{Q,ab} \sim {}^{63}\gamma_n^2\{(A_{ab}-4B)^2 + (A_c-4B)^2\}\sum\chi''(Q) \ ,$$
$$^{63}W_{Q,c} \sim 2\,{}^{63}\gamma_n^2(A_{ab}-4B)^2\sum\chi''(Q) \ ,$$
$$^{17}W_c \sim {}^{17}W_{0,c} \sim 4\,{}^{17}\gamma_n^2C^2\sum\chi''(0) \ , \tag{16}$$

where $\sum\chi''(0)$ and $\sum\chi''(Q)$ mean $\sum_{q\sim 0}\chi''(q,\omega_n)/\omega_n$ and $\sum_{q\sim Q}\chi''(q,\omega_n)/\omega_n$, respectively. In addition, we define parameters α, β, δ, and ζ as

$$\alpha \equiv 2C/(A_{ab}+4B) \ ,$$
$$\beta \equiv (A_c+4B)/(A_{ab}+4B) \ ,$$
$$\delta \equiv 4B/A_{ab} \ ,$$
$$\zeta \equiv A_c/A_{ab} \ . \tag{17}$$

From these formulas, the anisotropy of the relaxation rate at the Cu site ($^{ab,c}R \equiv {}^{63}W_{ab}/{}^{63}W_c$) could generally be expressed as a function of α, β, δ, ζ, and $^{63,17}R$. The values of α and β have already been determined experimentally ($\alpha=0.30$, $\beta=0.53$), thus only δ and ζ are unknown free parameters in the present case, then we have

$$^{ab,c}R = F_1(\delta,\zeta,{}^{63,17}R)$$
$$= \frac{1}{2}\left[1+\frac{(\zeta-\delta)^2}{(1-\delta)^2}\right] - \frac{1}{{}^{63,17}R\,\alpha^2(1+\delta)^2}\left[\frac{(\zeta-\delta)^2(1+\delta^2/4)}{(1-\delta)^2} - (\zeta^2+\delta^2/4)\right] \ ,$$
$$\beta = (\zeta+\delta)/(1+\delta) = 0.53 \ . \tag{18}$$

Because the temperature dependence of $^{ab,c}R$ and $^{63,17}R$ are observed, we could estimate δ and ζ from these two equations. Figure 10 shows the observed T dependence of $^{ab,c}R$ and the calculated F_1 curve based on the present results of $^{63,17}R$ and the optimized values of $\delta=11\pm3$ and $\zeta=-4.7\pm1$. This optimization was performed above 120 K, i.e., except the pseudo-spin-gap region. It should be noted that no assumption on A_{ab} and A_c was made in this estimation of δ and ζ. The optimized value of ζ is similar to that of $BYCO_{\sim7}$ (-5.1).[6] This provides the experimental suggestion that the on-site hyperfine coupling at the Cu sites is the same for both in Tl 2:2:0:1 No. 1 and $BYCO_{\sim7}$. In contrast to that, the value of δ is fairly large as compared to that of $BYCO_{\sim7}$ (4.2)[6]. (This has also been reported by Kitaoka *et al.*[23]) Since we succeeded in obtaining every ratio of the coupling constants, we could estimate the absolute values of each constant if only one coupling constant value is assumed. We assume that A_{ab} is the same as that of the $BYCO_{\sim7}$ system (37 kOe/μ_B),[6] which is supported by the result of ζ and $^{63}K_{\rm orb}$, then each constant is estimated as

$$A_c\sim-170\ \text{kOe}/\mu_B\ ,$$
$$B\sim100\ \text{kOe}/\mu_B\ , \tag{19}$$
$$C\sim70\ \text{kOe}/\mu_B\ .$$

Now, we discuss the unique nature of the hyperfine interaction in Tl 2:2:0:1 No. 1 based on these estimations. The B term is considered to arise from the supertransferred hyperfine interaction, thus the large B term is an evidence of the strong hybridization between Cu $3d,4s$ and the O $2p$ states. This is consistent with the disappearance of the O $2p$ nature suggested by the $^{17}K_{\rm ani}$ results. It is worth noting that the C term is about the same as that of $BYCO_{\sim7}$ (Ref. 24) in spite of the fact that the B term is appreciably larger. Although the reason is unclear, probably the O $2s$ spin polarization may have a dominant contribution to the C term in Tl 2:2:0:1 No. 1. Since the direct transfer or the overlap effect between the Cu $3d$ and O $2s$ states is considered to be insensitive to the Cu $3d-$O $2p$ hybridization and the crystal structure, a similar C term is expected in Tl 2:2:0:1 No. 1 and $BYCO_{\sim7}$.

VI. THE NATURE OF $\chi''(q,\omega_n)$ IN THE Tl 2:2:0:1 SYSTEM

In this section we focus on the strength and the T dependence of the AF correlation. We deal with only the temperature range where the Knight shift is almost T independent (above 120 K).

If the AF correlation completely vanishes, the value of $^{63,17}R$ becomes a simple ratio of the hyperfine coupling constant, i.e., $^{63,17}A\equiv(A_{ab}^2+4B^2)/2C^2$. Thus, the value of $(^{63,17}R)/(^{63,17}A)$ corresponds to the real magnitude of the AF correlation. Figure 11 shows the T dependence of $(^{63,17}R)/(^{63,17}A)$ in Tl 2:2:0:1 No. 1 and $BYCO_{6.96}$.[14] The value of $(^{63,17}R/(^{63,17}A)$ should be asymptotic to unity with the temperature increasing because the AF correlation is expected to vanish in the high-temperature limit. It is clearly seen that the AF correlation in Tl 2:2:0:1 No. 1 is weak and less temperature dependent as compared to $BYCO_{6.96}$.

Millis, Monien, and Pines (MMP) analyzed the NMR data of the BYCO system based on $\chi''(q,\omega_n)$ as below,[25]

$$\chi''(q,\omega_n)=(\pi\omega_n\chi_s/\Gamma_0)\{1+\beta_1(\xi/a)^4/(1+\xi^2q^2)^2\}\ , \tag{20}$$

where ξ is the AF correlation length, Γ_0 is the characteristic spin fluctuation energy around $q=0$, β_1 represents the contribution of the AF fluctuation. Aside from the discussion of the validity of this model, we made a similar analysis in order to compare Tl 2:2:0:1 No. 1

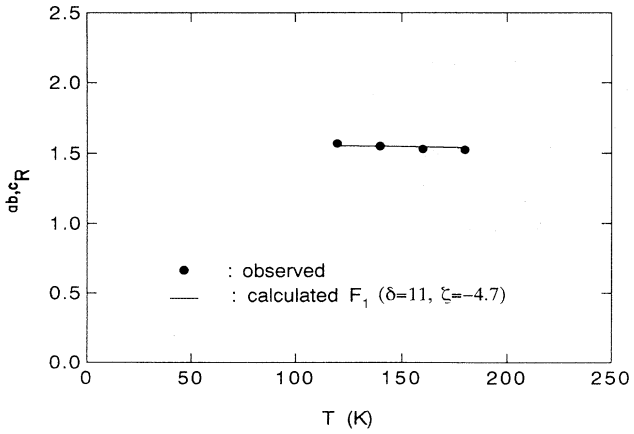

FIG. 10. Temperature dependence of the observed and the calculated anisotropies of the relaxation rate at the Cu site: $^{ab,c}R(\equiv{}^{63}W_{ab}/{}^{63}W_c)$.

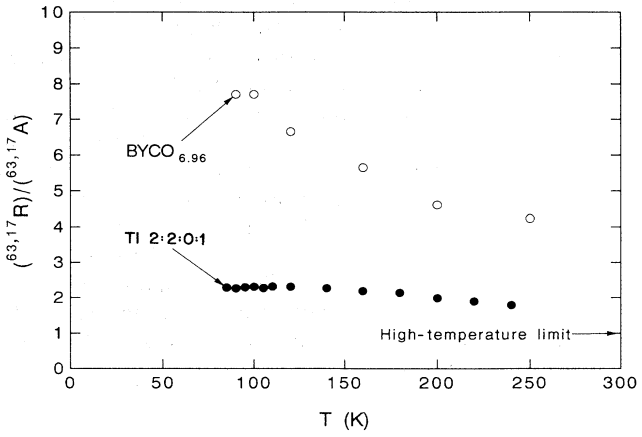

FIG. 11. Temperature dependence of the $(^{63,17}R)/(^{63,17}A)$ in Tl 2:2:0:1 No. 1 and $BYCO_{6.96}$. $[^{63,17}A\equiv(A_{ab}^2+4B^2)/2C^2]$. If the antiferromagnetic correlation vanishes in the high-temperature limit, $(^{63,17}R)/(^{63,17}A)$ should become the unity.

with the BYCO system. We have optimized the values of ξ/a and β_1 in a similar manner as MMP by fitting $^{ab,c}R$ and $^{63,17}R$. In that process we have adopted the approximate q integral of the hyperfine form factor and $\chi''(q,\omega_n)$ proposed by Millis and Monien,[22] and the estimated values of α, β, δ, ζ in the previous section. ξ/a is estimated as ~ 1.2 at 120 K and ~ 1.0 at 180 K. β_1 is also estimated as ~ 5. We assumed that β_1 is independent of temperature. These values are about half of those in $BYCO_{\sim 7}$ estimated by Monien ($\xi/a \sim 2.1$ at 120 K and ~ 1.9 at 180 K, $\beta_1 \sim 10$).[26] This tendency is consistent with the rough estimation of the AF correlation discussed above. We could also estimate Γ_0 as ~ 0.3 eV based on the $^{17}T_1T\,{}^{17}K_{\mathrm{iso},s}$ vs T plot with $C \sim 70$ kOe/μ_B. The correction of Γ_0 due to the contribution of $\chi''(q\neq 0,\omega_n)$ is small because $\xi/a \sim 1$. This value is similar to that of the BYCO system (~ 0.4 eV).[25] In contrast, the characteristic energy of the spin fluctuation around $q=Q$ [$:\Gamma_Q \equiv \Gamma_0\beta_1^{-0.5}(\xi/a)^{-2}$] is estimated as ~ 0.09 eV at 120 K, which is quite larger than 0.02 eV of $BYCO_7$.[25] It should be noted that the quality of the sample is homogeneous enough to compare the value of ξ/a with that of the BYCO system, thus ξ is intrinsically short in Tl 2:2:0:1 No. 1. Although the relationship between the strength of the AF correlation and T_c is unclear, experimentally Tl 2:2:0:1 No. 1 possesses the very weak antiferromagnetic correlation in spite of the fact that $T_c=85$ K. Kitaoka *et al.* suggested that the AF correlation is weakened with over-doping in the Tl 2:2:0:1 system,[23] but the present result indicates that the AF correlation is already weak in the specimen of the maximum T_c. The weak antiferromagnetic correlation in the over-doped region is predicted by the two-dimensional self-consistent renormalization (2D-SCR) theory[27] and the mean-field calculation of the t-J model[28] qualitatively. The random-phase approximation (RPA) of the 2D Hubbard model has not treated the over-doped region so far.[29]

VII. SUMMARY

We have measured the Knight shift and the spin-lattice relaxation time of ^{63}Cu and ^{17}O in the normal state of $Tl_2Ba_2CuO_y$ ($T_c=85$ K). From the Knight shift results, it is revealed that the doped holes do not have a strong O $2p$ nature and the single-spin-component model is likely in this system, indicating strong hybridization between the Cu $3d$ and O $2p$ states in the over-doped system. The supertransferred hyperfine coupling constant between the Cu sites is estimated as three times larger than that of the BYCO system in spite of the fact that the on-site coupling constants of the Cu site and the transferred hyperfine coupling constant of the O site are estimated as similar to those of the BYCO system. From the spin-lattice relaxation time results, the AF correlation is remarkably weak as compared to that of $BYCO_{6.96}$ in spite of the fact that these two specimens possess similar T_c. The characteristic spin fluctuation energy is similar at $q\sim 0$ and larger at $q\sim Q$ as compared to those of the BYCO system. Although the T dependence is small, the sudden decrease of $(T_1T)^{-1}$ above T_c is observed in the O site at 100 K and the Cu site at 120 K. In addition, the relationship of $^{17}T_1T\,{}^{17}K=$const is likely for the T range 90–240 K. A possible story is that the pseudo-spin gap of $q\sim Q$ may open at 120 K and the slight change of $\sum_{q\sim 0}\chi'(q,\omega_n)/\Gamma_q$ may cause a decrease of $(^{17}T_1T)^{-1}$ below 100 K.

ACKNOWLEDGMENTS

The authors thank Dr. Y. Yoshinari for useful suggestions and discussions on the NMR measurements. Y. Itoh is also thanked for fruitful discussions on the spin dynamics. This work has been partially supported by a Grant-in-Aid for Scientific Research on Priority Areas by the Ministry of Education, Science and Culture.

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