$^{63/65}$Cu/$^{203/205}$Tl NMR study on the antiferromagnetic phase of the Tl-based high-T_c oxide $TlBa_2YCu_2O_7$

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The end member of the Tl-based high-T_c cuprate $TlBa_2YCu_2O_7$ (Tl1212) with the zero nominal hole number has been synthesized and studied by Cu/Tl NMR. The existence of the antiferromagnetic ordering was demonstrated by the Zeeman-splitted zero-field Cu spectra. Static parameters at the Cu site such as the hyperfine field H_{Cu}=8.62 T and the quadrupolar frequency $^{63}\nu_Q$=20.44 MHz were found to be comparable to other high-T_c related antiferromagnets La_2CuO_4 and $YBa_2Cu_3O_6$. The relaxation rate T_1^{-1} of the Cu site of Tl1212 showed a significant deviation from the magnon theory, and was much smaller than La_2CuO_4 and $YBa_2Cu_3O_6$. The scaling between the temperature dependence of Tl T_1^{-1} and Cu T_1^{-1}, the ratio of which was consistently explained with the hyperfine coupling constants determined by the analysis of spectra, showed that the relaxation is dominated by the 3d spin fluctuation. A possible relation between the spin fluctuation in the antiferromagnetic phase and the superconductivity in the high-T_c phase is also stated. [S0163-1829(96)06429-6]

I. INTRODUCTION

From a number of works accumulated on the superconducting high-T_c cuprates in a past decade, it has been suggested that most of their physical properties are universally scaled by a single parameter, the carrier concentration. With doping the carrier, most high-T_c cuprates undergo the three regions: (1) nondoped oxides are antiferromagnets with the Néel point comparable to the room temperature, which are well described as the two-dimensional Heisenberg model, (2) with a small number of carriers doped, they show the high-T_c and many anomalous properties in the normal state such as the non-Korringa behavior of NMR T_1, or as the temperature-dependent Hall coefficient, and (3) further doping of excess carriers reduces T_c to zero, the region of which is called as the overdoped region, where the observed physical properties suggest that the conduction carrier in this region is Fermi-liquid-like.

Contrary to this universality, T_c itself does differ for different materials, and varies from 10 to 150 K. So far, there have been trials to find out a key parameter that possibly makes such a difference in T_c. A leading work of this category is μSR experiments by Uemura *et al.*[1] They report that the concentration of superconducting quasiparticles in $YBa_2Cu_3O_7$ is much higher than in $La_{1.85}Sr_{0.15}CuO_4$, though the nominal hole concentration of both the two systems is believed to be such that it gives the highest T_c in each group. Uemura also suggests that the concentration of superconducting quasiparticles is nearly proportional to T_c when the hole concentration is not too high. Kitaoka *et al.* investigated the Cu 3d spin fluctuation in high-T_c cuprates by NMR (Ref. 2) to reach a similar conclusion that the spectral weight of the spin fluctuation at the low-energy limit in $La_{1.85}Sr_{0.15}CuO_4$ is much larger than that in $YBa_2Cu_3O_7$. The viewpoint of these two works is based on the possibility that physical properties of $La_{1.85}Sr_{0.15}CuO_4$ and of $YBa_2Cu_3O_7$ differ in a certain aspect which may be involved in the determination of T_c.

Here we expect another possibility that the nondoped antiferromagnets also have a hidden key parameter which determines T_c. The motivation of our work on the antiferromagnetic phase of Tl-based cuprate $TlBa_2$ (Ca,Y)Cu_2O_7 (Tl1212) is based mainly on this point. The subject of this paper is to study the magnetic character in the antiferromagnetic phase to reveal different points between Tl-based system and other systems such as La_2CuO_4 and $YBa_2Cu_3O_6$. So far, the antiferromagnetic phase of high-T_c cuprates has been left to be considered simply as a two-dimensional Heisenberg antiferromagnet with the Néel temperature comparable with the room temperature. There have been only few investigations on their magnetic character,[6] though some early works on La_2CuO_4 and $YBa_2Cu_3O_6$ report the existence of the antiferromagnetic order.[3–5] Especially for Tl-based systems, the interest had so far been concentrated on the overdoped region.

We believe that the investigation on the magnetism for the end member is by itself important in the field of high-T_c cuprates, because the magnetism or the Cu 3d spin fluctuation is one of the candidates for the origin of the paring interaction. In addition, by the study of the antiferromagnetic phase, we expect to obtain directly the hyperfine coupling constant of Tl-based systems. There has been much difficulty in obtaining the hyperfine coupling constant in Tl-based systems, because the Knight shift is temperature independent, which disables one to carry out the K-χ plot, the conventional method for the determination of hyperfine coupling constants.

We emphasize here that it is not self-evident that the synthesis of the antiferromagnetic phase for Tl1212 is possible. In fact, for the superconducting phase, the effective carrier concentration does not change against the small amount of substitution of Y^{3+} for Ca^{2+}, which must act as hole filling.[7] For the end member compound $TlBa_2YCu_2O_7$, though the disappearance of the superconductivity is confirmed, there have been few reports on magnetic properties until now.[8]

In this paper, after commenting briefly on the synthesis and the characterization of samples of $TlBa_2YCu_2O_7$, we demonstrate the existence of the static antiferromagnetic order at 4.2 K by $^{63/65}$Cu NMR spectra at zero field. By the analysis of the spectrum, static parameters of the Cu site, that is, the internal field, the electric-field-gradient (EFG) tensor and the hyperfine coupling constant are extracted. The hyperfine coupling constant of the Tl site is obtained by the comparison between the resonance width of Tl NMR and Cu NMR. Next, the dynamic character of the Cu $3d$ spin is discussed through the temperature dependence of the nuclear spin-lattice-relaxation rate for Cu and Tl sites. Observed relaxation rates are well explained by hyperfine coupling constants, which are independently determined by the analysis of spectra. Finally, the spin dynamics is discussed and compared with the result on the superconducting phase of Tl1212. The discussion is extended to the possible relation between T_c and the spin fluctuation in the antiferromagnetic phase.

II. EXPERIMENT

A polycrystalline sample of $TlBa_2YCu_2O_7$ was obtained by the conventional solid-state reaction of Tl_2O_3, Y_2O_3, BaO_2, and CuO with the purity of four nines. We also prepared the compound of $TlBa_2(Ca_{0.05}Y_{0.95})Cu_2O_7$, for which the small number of hole carriers is doped explicitly. The method of syntheses in detail is described elsewhere.[7] The powder x-ray diffraction, typical patterns of which are given in Ref. 7, showed that samples are of phase pure, and that the crystal structure is tetragonal. In order to avoid the rf skin effect in measurements of NMR, obtained samples of approximately 500 mg were ground into powder, and embedded in epoxy resin Stycast 1266. The crystallographic axis of each powder grains was aligned by curing the epoxy in a high magnetic field of 12 T.

Zero-field spectrum of $^{63/65}$Cu NMR was obtained at 4.2 K by plotting the integrated amplitude of the spin-echo signal against the frequency between 80 and 120 MHz with a step of 10 kHz. The frequency dependence of the observed spin-echo amplitude was compensated by the factor ω_0^{-2}. Width of the excitation and the refocusing pulses were set approximately 2 and 4 μs, the spectral width of which was narrow enough compared with the structure of the spectrum. The spin-lattice-relaxation rate T_1^{-1} of the ^{63}Cu nuclei was measured for both the central transition line and the satellite line at zero field by the conventional saturation-recovery method with a pulse train.

Field-swept spectra of the T1 site were obtained by recording the amplitude of the spin-echo signal with a box-car integrator with sweeping the applied field in the temperature range between 4.2 and 300 K. We measured spectra at several fixed frequencies between 100 and 200 MHz. The spin-lattice-relaxation rate of the T1 site was measured under the magnetic field approximately 6 T in temperatures between 4.2 and 50 K.

In order to avoid a ring down noise associated with the rf pulses and a drift in the base line, we employed the phase alternation technique with the coherent detection, which enabled us to measure spectra and relaxation rates with a high precision.

III. RESULTS

A. Cu NMR spectra

Figure 1 shows the zero-field spectrum of $^{63/65}$Cu NMR, where one can see the six resonance lines, some of which are overlapped.[9] These six lines were successfully assigned to the quadrupolar-split Zeeman signals from the single copper site with the two isotopes of ^{65}Cu and ^{63}Cu. The parameters of H_0, the internal field, ν_Q, the quadrupolar frequency, and θ, the angle between H_0 and the principal axis of the electric-field-gradient tensor were deduced by the numerical diagonalization of the nuclear-spin Hamiltonian for $I=3/2$. We assumed the axial symmetry in the electric-field gradient, which is a reasonable assumption because of the symmetry of the crystal structure $I4/mmm$. Obtained parameters are shown in Table I, where the results for La_2CuO_4 and $YBa_2Cu_3O_6$ are also given for comparison.[4,5] If we assume that the principal axis of the electric-field-gradient tensor is along the c axis, which is also reasonable for the symmetry of the crystal structure, the direction of the $3d$ spin is found to be slightly canted out of the CuO plane.

With these parameters obtained, and with the assumption of the Lorentzian form for each resonance line, we reproduced the profile of the spectrum, which is given as the solid curve in Fig. 1, showing an excellent agreement with the ob-

TABLE I. The static parameters of the Cu site in antiferromagnetically ordered state. The results on other antiferromagnetic phase of high-T_c oxides La_2CuO_4 and $YBa_2Cu_3O_6$ are also shown in comparison. The hyperfine coupling constant $|A_{ab}^{\mathrm{Cu}}-4B^{\mathrm{Cu}}|$ is obtained by employing the effective magnetic moment as theoretical estimation $\mu_{3d}\cong 0.6\mu_B$.

	$TlBa_2YCu_2O_7$	La_2CuO_4 (Ref. 4)	$YBa_2Cu_3O_6$ (Ref. 5)
H_{Cu} (T)	8.62	7.878	7.665
$^{63}\nu_Q$ (MHz)	20.44($\pm$1.3)	31.9	22.87
θ (deg)	81($\pm$9)	79	90($\pm$10)
$\lvert A_{ab}^{\mathrm{Cu}}-4B^{\mathrm{Cu}}\rvert$ (kOe/μ_B)	144	131.3	127.8

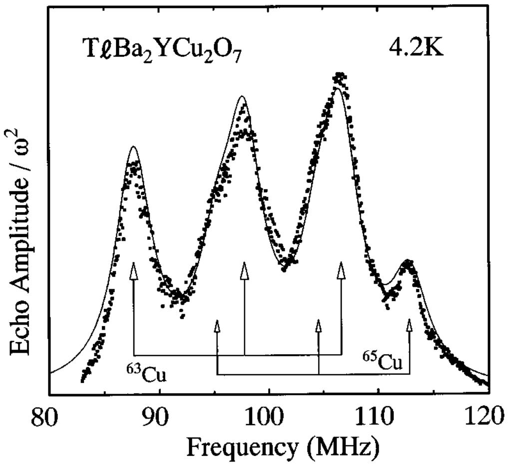

FIG. 1. Frequency spectrum of $^{63/65}$Cu NMR at 4.2 K, zero field. The solid curve is calculated from the obtained parameters H_{Cu}, $^{63}\nu_Q$, and θ, assuming that each transition line has the Lorentzian form.

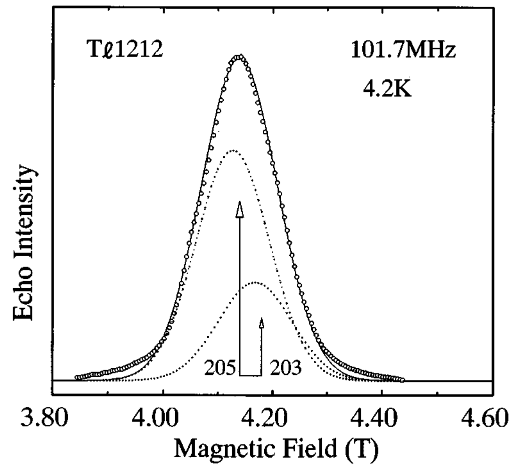

FIG. 2. A typical profile of the field-swept Tl NMR spectrum at 101.7 MHz. The dashed curves are deconvoluted two Gaussian forms corresponding to the two isotopes of ^{203}Tl and ^{205}Tl.

served spectrum. The coefficient of the resonance line width for Lorentzian was approximately 1.7 kOe [3.9 MHz for full width at half maximum FWHM in the unit of the frequency], almost the same for both the central transition line and the satellites. This proves that the width is mainly contributed by the inhomogeneity in the magnetic field rather than that in the electric-field gradient. That is, if it were the contribution from the latter, the width of the center peak would be much smaller than that of the satellites. Note that the Lorentzian form of the observed spectra is simply due to the distribution form of the internal field rather than to the homogeneous broadening. This is because the latter was found small enough to be neglected from the measurement of the spin-spin relaxation rate, $T_2^{-1} \simeq 50$ μs at 4.2 K.

We compared the observed resonance line width of 3.9 MHz with reported results[4,5] on La_2CuO_4 (1.5 MHz) and $YBa_2Cu_3O_6$ (3.5 MHz) to find that the inhomogeneity in the ordered magnetic field for our sample is comparable to other antiferromagnets. In addition, the x-ray powder-diffraction pattern does not show any impurity phases. These observations lead us to consider that the sample quality of Tl1212 is as good as other antiferromagnets of La_2CuO_4 and $YBa_2Cu_3O_6$. We mention that the finite and not negligible linewidth observed here can be caused by the small number of the hole carriers due to the oxygen nonstoichiometry, which had been demonstrated by NMR (Ref. 12) in $La_{2-x}M_xCuO_4$ (M=Ba,Sr) at the early stage of the high-T_c cuprates. Our speculation can be confirmed straightforwardly by experiments changing the oxygen content by Ar-annealing treatment, which is now under progress.

For the compound of $TlBa_2(Y_{0.95}Ca_{0.05})Cu_2O_7$, where a small amount of holes are explicitly introduced, no signal was observed in the frequency range 70–120 MHz within a signal-to-noise ratio at 4.2 K. This may also be due to the large inhomogeneity in the ordered field, which wiped out the entire spectrum.

B. Tl NMR spectra

Field-swept spectra of $^{203/205}$Tl nuclei were observed at the position of nearly zero internal field; the shift at 4.2 K was $K_s \simeq 0.3\%$. A typical spectrum is shown in Fig. 2. One can see an extremely broad peak, which was successfully deconvoluted to the two Gaussians, corresponding to signals from the isotopes of ^{203}Tl and ^{205}Tl. The profile of the spectrum was independent of the angle between the applied field and the aligned axis of the sample. In measurements under various magnetic fields between 3 and 8 T, the separation between the two Gaussians was proportional to the resonance field, reflecting the difference in the gyromagnetic ratios of the two isotopes $^{203}\gamma = 24.33$ and $^{205}\gamma = 24.567$. On the other hand, the width of each Gaussian, approximately 0.95 kOe, was independent of the resonance field.

Profiles of the spectra at several temperatures between 4.2 and 300 K are shown in Fig. 3, where one can see a significant decrease in the resonance linewidth at higher temperatures. At 300 K, the two resonance lines were observed sepa-

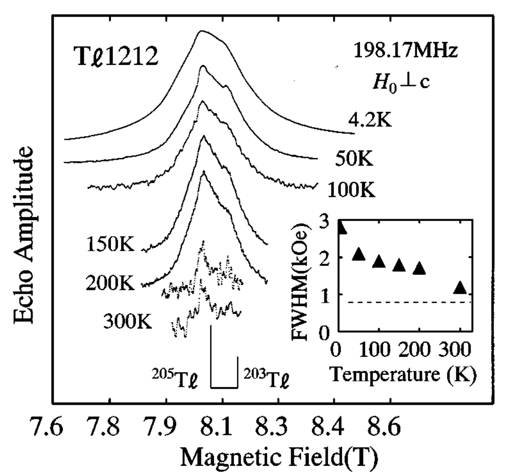

FIG. 3. Temperature dependence of the field-swept spectra. At 300 K, the two lines are completely separated, indicating that the system is paramagnetic. Temperature dependence of the resonance line width of Tl spectra is shown in the inset. The width is tentatively defined as the FWHM of the whole spectrum. The horizontal dashed line shows the separation between the resonance position of the two isotopes.

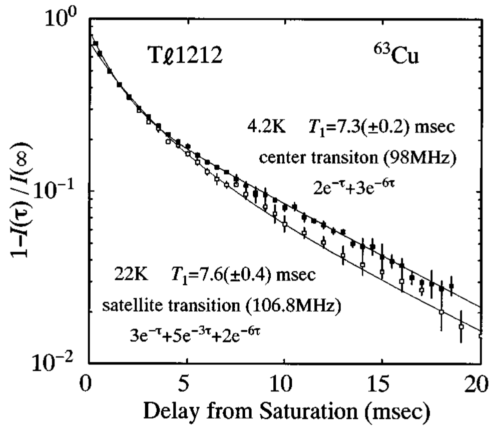

FIG. 4. The typical relaxation recovery of the Cu NMR at the central transition and the satellite. The theoretical relaxation curves are also shown.

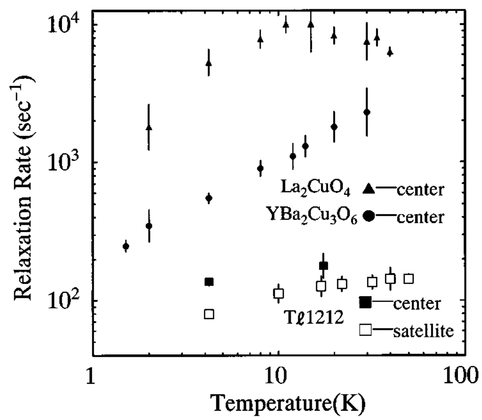

FIG. 5. The temperature dependence of Cu T_1^{-1}. Results on $YBa_2Cu_3O_6$ and La_2CuO_4 by Tsuda (Ref. 4) are also shown for comparison.

rately. We tentatively extracted the temperature dependence of the width determined as a FWHM of the whole spectrum, which is given in the inset of Fig. 3.

C. Cu NMR relaxation rate T_1^{-1}

The nuclear-spin-relaxation rate T_1^{-1} was obtained from the recovery curve of the nuclear magnetization after the saturation by a pulse train. Since the nuclear spin of ^{63}Cu and ^{65}Cu are 3/2, the recovery of the magnetization to its thermal equilibrium follows the so-called multiexponential function $1-Ae^{-t/T_1}-Be^{-3t/T_1}-Ce^{-6t/T_1}$, where A, B, and C are constants, which depends on the initial condition, or in other words, the occupation number of the nuclear-spin energy levels right after the saturation.[10,11]

If the populations on levels except for the saturated transition are completely unchanged, (A,B,C) is proportional to (1,0,9) for the central transition between $I=\pm 1/2$, and to (1,5,4) for the satellite transitions between $+1/2\leftrightarrow+3/2$ or $-1/2\leftrightarrow-3/2$. Next, if the populations on the levels other than the saturated are set to be the thermal equilibrium with the neighboring saturated levels, (A,B,C) is proportional to (2,0,3) for the central transition, and to (3,5,2) for the satellites. Observed relaxation curves for both the center line and the satellites in Fig. 4 followed what is expected for the latter case. This indicates that there does exist a rapid relaxation process which modifies the population of the neighboring levels immediately after the saturation. Note that this relaxation process should be considered anomalously fast, because the Cu spectrum spreads over the frequency range as wide as tens of megahertz. The existence of this rapid relaxation has been reported[6] also for La_2CuO^4 and $YBa_2Cu_3O_6$, and is characteristic to the antiferromagnetic phase, because the relaxation curve for the superconducting phase is well described by the former case.[2,10] In reports on La_2CuO_4 and $YBa_2Cu_3O_6$ by Tsuda,[6] the possibility of the spectral diffusion is pointed out, but the detailed origin of the relaxation is still not clear.

The temperature dependence of the relaxation rate T_1^{-1} for the central transition line and the satellites is plotted in Fig. 5, where the results on La_2CuO_4 and $YBa_2Cu_3O_6$ reported by Tsuda, Ohono, and Yasuoka[6] are also shown. The relaxation rate for Tl1212 was smaller than that of the other two antiferromagnets by one or two orders of magnitude. The temperature dependence of the relaxation rate was also weak compared with the other two.

D. Tl NMR relaxation rate T_1^{-1}

The relaxation curve of the Tl nuclei was described by the multiexponential function $1-I_Le^{-t/T_{1L}}-I_Se^{-t/T_{1S}}$, where T_{1S}^{-1} is the short component, and T_{1L}^{-1}, the long. Typical relaxation curves are shown in Fig. 6. The observed two components in relaxation curves indicate that there exist two Tl sites belonging to the different environments, though there is only one crystallographic Tl site. This is because Tl nuclei have spins of 1/2, for which the single exponential recovery is expected in homogeneous systems.

The ratio of the two relaxation times T_{1L}/T_{1S}, and of the two amplitudes I_L/I_S had almost no temperature dependence between 4.2 and 50 K. In order to keep the number of free parameters minimum, we kept T_{1L}/T_{1S} and I_L/I_S as fixed values 6.3 and 0.43 in the determination of the relaxation rate by the least-squares method. We show in Fig. 7 the

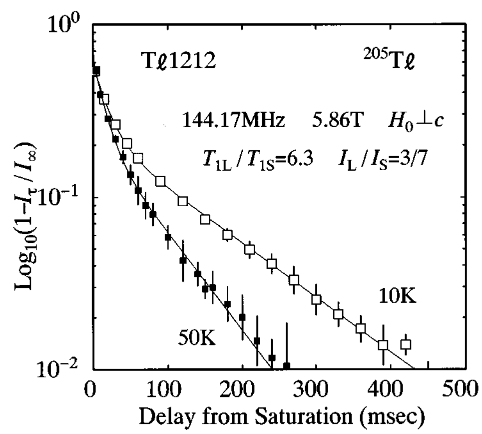

FIG. 6. The typical relaxation recovery of the Tl NMR. The relaxation curves were obtained by the least-squares method on the assumption that the relaxation rates have the two components of the short and the long term.

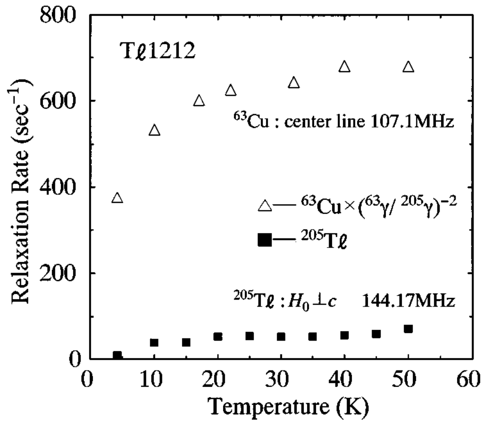

FIG. 7. The temperature dependence of the short component of Tl T_{1S}^{-1}. The relaxation rate for Cu scaled by the gyromagnetic ratio is also shown.

temperature dependence of T_{1S}^{-1}, with the result of Cu T_1^{-1} scaled by gyromagnetic ratios. The relaxation rate of the TL site T_{1S}^{-1} and hence T_{1L}^{1} was much smaller than the scaled relaxation rate of the Cu site $T_1^{-1}(^{63}\gamma/^{205}\gamma)^{-2}$.

IV. DISCUSSION

A. Spectra

The observed spectrum of Cu NMR at zero-field, which is explained in terms of Zeeman-splitting with a quadrupole interaction, clearly demonstrates the existence of the antiferromagnetic ordering in $TlBa_2YCu_2O_7$ at low temperatures. The observation of Tl spectra at nearly zero shift assures that the magnetic ordering is antiferromagnetic along the c axis, and hence the three dimensional. The averaged value of the internal field produced by the ordered $3d$ spins is canceled to be zero at the Tl site due to the geometrical symmetry. This static cancellation along c axis makes a clear contrast to the superconducting phase of Tl1212, where $3d$ spins belonging to the two adjacent CuO plane facing across the TlO layer fluctuate incoherently rather than antiferromagnetically. We briefly describe this result in the Appendix.[13–15]

From the observed internal field $H_{\mathrm{Cu}} \simeq 86.2$ kOe, we estimated the hyperfine coupling constant of the Cu site to be $|A_{ab}^{\mathrm{Cu}} - 4B^{\mathrm{Cu}}| = H_{\mathrm{Cu}}/\mu_{3d} \simeq 144$ kOe/μ_B, where A_{ab}^{Cu} and B^{Cu} denote the on-site hyperfine coupling constant[16] within the CuO plane and the transferred hyperfine coupling constant from the neighboring $3d$ spin, and value of the theoretical prediction $\mu_{3d} \simeq 0.6\mu_B$ was adopted for the magnetic moment of the $3d$ spin.[17]

All the obtained parameters for the Cu site except for the quadrupolar frequency are comparable to the antiferromagnetic phase of other high-T_c cuprates, as shown in Table I. Here we reach the first conclusion that the existence of the three-dimensional antiferromagnetism was confirmed in the Tl-based cuprate, and that the static parameters within CuO planes are universal for the antiferromagnetic phase of most high-T_c oxides. This is a reasonable consequence of the fact that the static character of the ordered state is rooted in the nature of Cu $3d$ spins.

It is noticeable that only the quadrupolar frequency $^{63}\nu_Q$ shows a significant difference for the three systems. For $^{63}\nu_Q$ sensitively depends on the number of oxygen coordination, a direct comparison of those observed values seems to be difficult. However, as a qualitative argument, we can see that $^{63}\nu_Q$ is smaller for the system with a smaller tolerance factor between the CuO plane and the block layer.[18]

The transferred hyperfine coupling constant at the Tl site can be obtained from the observed width of resonance lines by the following procedure. While the mean value of the ordered field produced by $3d$ spins is canceled at the Tl site as stated above, its inhomogeneity δH_{Cu} is expected to reside and contribute to the inhomogeneous width of Tl NMR. This is confirmed by the fact that the observed profile of the Tl spectra was independent of the angle between the sample axis and the applied field, indicating that the internal field at the Tl site is random. Since there are two contributions from the $3d$ spins above and below the Tl site to the width, the inhomogeneity in the hyperfine field at Tl site is given as

$$\delta H_{\mathrm{Tl}} \simeq \sqrt{2} A^{\mathrm{Tl}} \delta H_{\mathrm{Cu}} / |A_{ab}^{\mathrm{Cu}} - 4B^{\mathrm{Cu}}|, \quad (1)$$

where A^{Tl} is the transferred hyperfine coupling constant for the Tl site. The factor $\sqrt{2}$ in this formula is due to the fact that δH_{Tl} is the sum of two random variables. Substituting the observed values of δH_{Tl} and δH_{Cu} to Eq. (1), we obtained $A^{\mathrm{Tl}} \simeq 56$ kOe/μ_B, which is too large to be explained in terms of the classical dipole-dipole interaction, and hence suggests the existence of the supertransferred hyperfine interaction from Cu to Tl site via the apical oxygen.

So far, there has been reported much experimental evidence that suggest little spin transfer from Cu to the adjacent noncopper layers in La-based and Y-based cuprates. For example, an extremely small hyperfine field of 1 kOe at the La site in La_2CuO_4 was reported by Nishihara[3] and explained[19] in terms of the antibonding between $2p_{\sigma z}$ of apical oxygen and $3d_{x^2-y^2}$, which is believed to be the ground state of the Cu hole. Takahashi, Nishio, and Kanamori[19] have shown by the cluster-model calculation that the supertransferred hyperfine interaction to the La site through the apical oxygen does not exist, if one assumes the $6s$ band in the La atom. Also for the superconducting phase of $YBa_2Cu_3O_7$, a very small relaxation rate and Knight shift of the apical oxygen have been reported,[20] suggesting the unlikeliness of the superexchange interaction between the plane site Cu and the block layer.

On the other hand, in Tl-based systems of Tl1212 and Tl2201 ($Tl_2Ba_2CuO_{6-\delta}$), the existence of the supertransferred hyperfine interaction has been suggested in the early stage of the study to explain the observed large relaxation rate of the Tl site.[21,22] Brom, Reefman, and Jol[22] suggest the existence of the small atomic distortion so as to avoid the problem of the antibonding between $p_{\sigma z}$ and $3d_{x^2-y^2}$. According to them, it is possible to explain the large relaxation rate at the Tl site, if the apical oxygen is moved only 0.17 Å from the plumb line passing the Cu site. However, this idea does not seem to be likely, because the structural distortion is more significant in La-based systems, where the existence of the large tilting of CuO_6 octahedra is reported.[23] Another idea, which seeks the origin of the large hyperfine coupling constant in the atomic character of Tl is also unlikely, because it contradicts the theoretical calculation by Takahashi, Nishio, and Kanamori,[19] which proposes that the hyperfine interaction is small, assuming a $6s$ band. So far, the experimental evidence for the large hyperfine coupling between the block layer and the Cu site has been reported only for Tl-based systems. Since this issue is closely related to the ground-state symmetry of the Cu $3d$ band, a theoretical re-investigation seems to be necessary.

Finally in this section, we give a detailed account for the observed spin canting of approximately 8° in the Tl1212 system. The existence of the spin canting had been reported also for La_2CuO_4 by NMR (Ref. 4) and neutron[24] experiments, and is interpreted in terms of the Dzyaloshinsky-Moriya interaction between $3d$ spins. Generally, the Dzyaloshinsky-Moriya interaction, the form of which is $\mathbf{D}\cdot\mathbf{S}_i\times\mathbf{S}_j$, is induced by the spin-orbit interaction between the two spins, when the middle point of the two is *not* the inversion center. Since the interaction constant $\mathbf{D}$ can be determined to some extent by the symmetry, we try to examine the case of Tl1212. First, the CuO planes in Tl1212 are of the bilayer type, so that there is no inversion centers at the middle point of the two nearest-neighboring $3d$ spins. By the consideration of the symmetry,[25,26] one can easily find $\mathbf{D}$ to be proportional to $(0,0,d_x)$, where d_x is constant. Therefore, the interaction form $\mathbf{D}\cdot\mathbf{S}_i\times\mathbf{S}_j$ contains the spin component of S_z, which is consistent with the experimental observation of the canting out of the CuO plane.

In the case of La_2CuO_4, on the other hand, the inversion center at the middle point of the two nearest-neighboring spins is lost, only when the large buckling in CuO planes is brought by the structural phase transformation[23] around 500 K from the tetragonal phase ($I4/mmm$) to the orthorhombic phase ($Cmca$). It has been argued that this orthorhombic distortion[23] plays a crucial role for the occurrence of the Dzyaloshinsky-Moriya interaction, and hence of the spin canting. Noting that the spin canting in Tl1212 is driven by the intrinsic crystal symmetry rather than by the structural instability, one can see that the mechanism of the spin canting is quite different for Tl1212 and La_2CuO_4, though they show similar experimental results.

B. Relaxation rate

The mechanism of the nuclear-spin relaxation by the magnon processes in antiferromagnets had been studied extensively by Beeman and Pincus[27] in 1968. As for the antiferromagnetic phase of high-T_c cuprates, Chakravarty[28] investigated theoretically the two- or three-magnon process by taking the two dimensionality into account to report the strong temperature dependence of T^2 or T^3 for the nuclear-spin-relaxation rate. However, according to the report by Tsuda, Ohono, and Yasuoka,[6] the temperature dependence of T_1^{-1} for both $YBa_2Cu_3O_6$ and La_2CuO_4 is much weaker compared with the theoretical prediction. And as is clear for Tl1212, the observed temperature dependence of T_1^{-1} is not explained in terms of the conventional magnon theory. Therefore, we would like to represent mainly qualitative arguments here.

First, we show that the dominant relaxation mechanism for both the Cu and the Tl site is the spin fluctuation of Cu $3d$ spins, and that other mechanisms such as paramagnetic centers or the electric quadrupolar interaction are not the main contribution. The nuclear relaxation rate is generally described by Kubo's formula as

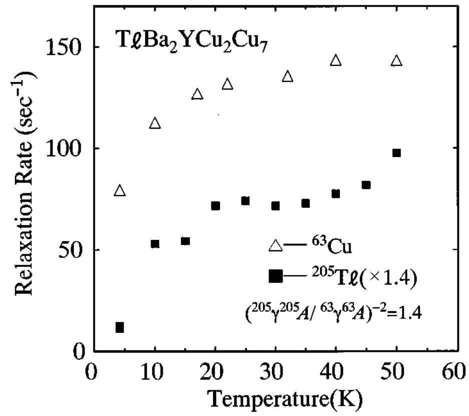

FIG. 8. The comparison of the relaxation rate for Cu and Tl sites, which are scaled by the factor of $\gamma_n^{-2}|A|^{-2}$.

$$T_1^{-1}\propto T\gamma_n^2\sum_q |A_q|^2\chi''(\mathbf{q},\omega_0)/\omega_0, \tag{2}$$

where γ_n is the gyromagnetic ratio, A_q is the hyperfine coupling constant, $\chi''(q,\omega)$ is the dynamical susceptibility, and ω_0 is the Larmor frequency of the nuclear spin. If the nuclear-spin relaxation at both the Cu and Tl sites is driven by a single spin degree of freedom, one expects that the scaled relaxation rate $T_1^{-1}\gamma_n^{-2}|A|^{-2}$ for Cu and Tl must be equal. The hyperfine coupling constants for the two sites have been already obtained by the analysis of the spectra in Sec. IV A.[29] In Fig. 8, we present the scaled relaxation rates ^{63}Cu T_1^{-1} and ^{205}Tl T_{1S}^{-1} to indicate that both the magnitude and the temperature dependence of the two sites are nearly scaled, considering the ambiguity in the determination of hyperfine coupling constants. Therefore, we can conclude that the relaxation at both the Cu and Tl sites is driven by the single relaxation mechanism, and that this relaxation mechanism is magnetic, because the Tl nuclear spin is free from the electric quadrupole disturbance. The possibility of the paramagnetic center as a relaxation mechanism is also denied, because the measurement of the Tl site is under the magnetic field of approximately 6 T, which is usually high enough to suppress the spin fluctuation of paramagnetic centers.

As a consequence of the above observation, we can draw out another conclusion that there is *little* antiferromagnetic spin correlation between the two $3d$ spins on the adjacent CuO planes facing each other across the TlO layer. In other words, most of the nearest-neighboring two Cu $3d$ spins above and below the Tl site fluctuate incoherently, so that both of them contribute to the relaxation at the Tl site. If, on the other hand, there is an antiferromagnetic spin correlation between bilayers, the magnetic field induced by the $3d$ spins will be canceled out at the Tl site due to the geometrical symmetry, and the relaxation rate at the Tl site must become much smaller than observed.

In this argument, we have been concentrating on the short component of the relaxation rate of the Tl site T_{1S}^{-1}. The long component in the Tl site relaxation T_{1L}^{-1} is explained consistently if there exists a small number of Tl sites where the geometrical cancellation partially holds. Those Tl sites are expected to contribute to the long component of the relaxation. Considering the magnetization fraction of the two relaxation components $I_S/I_L \simeq 3.7$, the geometrical cancellation holds only for a limited number of Tl sites, while it is broken for the other dominant Tl sites possibly due to the thermal disturbance or the inhomogeneity in the sample. This result on the spin correlation makes a significant contrast to that in the superconducting phase of Tl1212, where the antiferromagnetic spin correlation between bilayers is completely lost, as shown in the Appendix.[14,15]

Next, we examine whether or not the obtained hyperfine coupling constants in the antiferromagnetic phase are the same as those in the superconducting phase.[13] Following the procedure by Kitaoka *et al.*,[30] we first assume that $\chi''(q,\omega_0)$ of the superconducting phase is enhanced around the antiferromagnetic vector $q_{\rm AF} \simeq (\pi,\pi)$. Then the ratio of the relaxation rates of the Cu and Tl sites for the superconducting phase is expressed as

$$\frac{{}^{205}T_1^{-1}\cdot{}^{205}\gamma^{-2}}{{}^{63}T_1^{-1}\cdot{}^{63}\gamma^{-2}}=\frac{2(A^{\rm Tl})^2}{(A_{ab}^{\rm Cu}-4B^{\rm Cu})^2+(A_c^{\rm Cu}-4B^{\rm Cu})^2}, \quad (3)$$

where ${}^{205}\gamma$ and ${}^{63}\gamma$ are gyromagnetic ratio of Tl and Cu, and $A_c^{\rm Cu}$ is the Cu hyperfine coupling constant parallel to the c axis. We compare the experimentally obtained value for the left side with the right side calculated from hyperfine coupling constants. Making a further assumption[30] that the on-site hyperfine coupling constants $A_{ab}^{\rm Cu}$ and $A_c^{\rm Cu}$ are nearly the same for most high-T_c cuprates as $A_{ab}^{\rm Cu} \simeq 30$ kOe/μ_B and $A_c^{\rm Cu} \simeq 160$ kOe/μ_B, we can estimate the transferred hyperfine coupling constant $B^{\rm Cu}$ to be 43.4 kOe/μ_B. By inserting these constants into Eq. (3), the right side is calculated to be 0.047, which almost reproduces the observed value of $({}^{205}T_1^{-1}\cdot{}^{205}\gamma^{-2})/({}^{63}T_1^{-1}\cdot{}^{63}\gamma^{-2}) \simeq 0.077$ for the superconducting phase with $T_c = 78$ K, belonging to the slightly overdoped region.[13] This agreement indicates that hyperfine coupling constants for the Cu site of Tl1212 does not change much from the antiferromagnetic phase to the slightly overdoped region.

Finally, we compare the Cu T_1^{-1} of Tl1212 with other antiferromagnets $YBa_2Cu_3O_6$ and La_2CuO_4 to search the hidden key parameter related to T_c. As shown in Fig. 5, the significant difference in the magnitude of Cu T_1^{-1} among the three systems suggests the difference in the dynamic character of CuO planes for various systems. Since these three systems have the comparable hyperfine coupling constants of the Cu site, as was revealed in Sec. IV A, the difference in T_1^{-1} is directly related with that in $\chi''(q \simeq q_{\rm AF},\omega_0)$, which is a measure for the spectral weight of the spin fluctuation of $3d$ spins at the low energy at $E=\hbar\omega_0$. Therefore, the smaller T_1^{-1} suggests that the center-of-mass in the spin-excitation spectrum is shifted to the higher-energy region. Consequently, we can conclude that the characteristic spin-fluctuation energy, usually denoted[32] as Γ, of Tl1212 is higher than that of $YBa_2Cu_3O_6$ and La_2CuO_4.

Theoretical arguments on the importance of the spin fluctuation with a rather high characteristic energy have been repeatedly proposed. Monthaux and Pines[32] and Moriya and co-workers[33] reported independently that T_c for the spin-fluctuation-induced superconductivity is nearly proportional to Γ. This prediction was supported by Imai[16] and later by Kitaoka[2,31] with NMR for various high-T_c cuprates of the superconducting phase. Kitaoka extracted $\chi''(q \simeq q_{\rm AF},\omega_0)$ from T_1 data to show that Γ in $YBa_2Cu_3O_7$ ($T_c \cong 90$ K) is possibly higher than that in $La_{1.85}Sr_{0.15}CuO_4$ ($T_c \cong 35$ K). He attributed this difference in Γ to the different hole carrier concentration between $YBa_2Cu_3O_7$ and $La_{1.85}Sr_{0.15}CuO_4$. The direct measurement of the superconducting carrier concentration was performed by Uemura's μSR experiments,[1] which agreed qualitatively with Kitaoka's speculation. Combining their arguments, we note that the carrier concentration may determine the spin fluctuation, which may determine T_c. Now, let us turn to our NMR results on the antiferromagnetic phase, where the intensity of the spin fluctuation increases from Tl1212, $YBa_2Cu_3O_6$ to La_2CuO_4. This order coincides with that in the superconducting phase,[2] suggesting the possibility that we can predict the intensity of the spin fluctuation in the superconducting phase, and hence even T_c, by investigating the spin fluctuation in the antiferromagnetic phase.

V. SUMMARY

The existence of antiferromagnetic ordering in the Tl1212 system with the zero nominal hole concentration was demonstrated by the zero-field Cu NMR spectra. The static parameters of the Cu site was obtained by the analysis of the spectra: the internal field $H_{\rm Cu} = 8.62$ T, the quadrupolar frequency ${}^{63}\nu_Q = 20.44$ MHz, and the angle between the principal axis of the EFG tensor and the internal field $\theta \cong 81°$, and the on-site hyperfine coupling constant $|A_{ab}^{\rm Cu} - 4B^{\rm Cu}| = 144$ kOe/μ_B, which are all comparable to those in $YBa_2Cu_3O_6$ and La_2CuO_4, suggesting that the static character at the Cu site was almost the same for most antiferromagnetic phases of high-T_c cuprates. On the contrary, the character of the block layer and the dynamic character of the CuO planes in Tl1212 were found to be quite different from those in $YBa_2Cu_3O_6$ and La_2CuO_4.

The hyperfine coupling constant of the Tl site $A^{\rm Tl} = 65$ kOe/μ_B was much larger than the La site in La_2CuO_4,

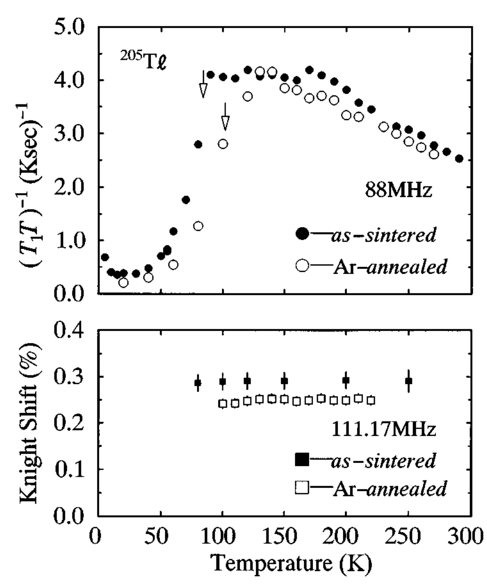

FIG. 9. Temperature dependence of Tl $(T_1T)^{-1}$ and Tl Knight shift for the superconducting phase of Tl1212. Open arrows indicate T_c.

$A^{La}=1.7$ kOe/μ_B. This large value indicates the existence of the supertransferred hyperfine interaction from the Cu site to the Tl site. The relaxation rate of the Cu site was much smaller than that of $YBa_2Cu_3O_6$ and La_2CuO_4, indicating the weak 3d spin fluctuation in Tl1212 system.

The scaling behavior of Cu T_1^{-1} and Tl T_1^{-1} showed that the nuclear-spin relaxation of both the Cu and Tl sites in this system is driven by the Cu 3d spin fluctuation. The scaling factor was consistent with what was expected from the hyperfine coupling constants, independently obtained by the spectra analysis, which assures the validity of our analysis. The temperature dependence of the relaxation rate was much weaker than is expected from the theory based on the two- or three-magnon process.

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APPENDIX: SPIN DYNAMICS IN THE SUPERCONDUCTING PHASE OF Tl1212

In this appendix, we briefly state on the antiferromagnetic spin correlation between bilayers for the superconducting phase of Tl1212. So far, the existence of the two-dimensional *intra*plane antiferromagnetic spin correlation has been confirmed by neutron and NMR experiments for most high-T_c cuprates. However, it is not self-evident whether or not there exists the spin correlation between bilayers, or in other words, the dynamic antiferromagnetic correlation between 3d spins on adjacent planes. For 90 K class Y-Ba-Cu-O, the interplane spin correlation is confined within a bilayer,[34] while for $La_{2-x}Sr_xCuO_4$ ($x=0.11$), a significant modulation along the c axis is observed in the low-energy inelastic neutron scattering, suggesting that this system is magnetically three dimensional.[35] We investigated the *inter*plane spin correlation in Tl1212 system with the following procedure.

First, we note the symmetrical location of the two copper atoms above and below the Tl site. If the two 3d spins of these copper atoms correlate antiferromagnetically, the fluctuating field produced by these spins must be canceled out at the Tl site. On the other hand, if the two spins fluctuate incoherently, the fluctuating field resides at the Tl site and is expected to contribute to the Tl nuclear relaxation. This issue is quite analogous to the case of the antiferromagnetic spin correlation within the CuO plane. The antiferromagnetic spin correlation does not affect the nuclear relaxation of the plane site oxygen because of the geometrical cancellation. The contribution of the antiferromagnetic spin correlation to the nuclear relaxation is easily detected, because $(T_1T)^{-1}$ shows the characteristic temperature dependence of Curie-Weiss type rather than of Korringa type.

The observed temperature dependence of the Tl nuclear relaxation is shown in Fig. 9 with the Knight shift.[13] A significant decrease in $(T_1T)^{-1}$ appears at the higher temperature region, while the Knight shift stays constant. This shows clear evidence for the contribution of the antiferromagnetic spin fluctuation to the Tl nuclear relaxation. Consequently, we can conclude that the antiferromagnetic spin correlation is confined within an each bilayer, and hence that there does not exist an antiferromagnetic correlation between two CuO planes facing across the TlO layer.

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