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NMR study of spin dynamics at planar oxygen and copper sites in $YBa_2Cu_4O_8$

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The planar-oxygen Knight shift ^{17}K and nuclear spin-lattice relaxation rate $(^{17}T_1)^{-1}$ have been determined in the superconductor $YBa_2Cu_4O_8$. The present oxygen results have been analyzed in connection with the planar-copper relaxation rate $(^{63}T_1)^{-1}$ data. In the normal state, both ^{17}K and $(^{17}T_1T)^{-1}$ decrease as the temperature is lowered towards $T_c=81$ K, while $(^{63}T_1T)^{-1}$ shows a maximum around 160 K. Comparison with $YBa_2Cu_3O_{6+x}$ data strongly suggests that both the q and the temperature dependences of the magnetic fluctuations in $YBa_2Cu_4O_8$ present a similarity to those for the 60-K phase of $YBa_2Cu_3O_{6+x}$ in the normal state above 110 K. In the superconducting state, $(^{63}T_1T)^{-1}$ decreases significantly with decreasing temperature, while the slope for $(^{17}T_1T)^{-1}$ shows a slight change near T_c. The considerable decrease in $^{17}T_1/^{63}T_1$ below T_c suggests that the loss of antiferromagnetic fluctuations is dominant in the superconducting state.

I. INTRODUCTION

Nuclear-magnetic-resonance (NMR) and nuclear-quadrupole-resonance (NQR) studies have focused on $YBa_2Cu_3O_{6+x}$ (Y-1:2:3) in order to investigate the relationship between superconductivity and antiferromagnetic fluctuations in the CuO_2 plane of high-T_c materials.[1] The distinct temperature dependence of the spin-lattice relaxation rates at planar Cu and O sites has established a picture that the dynamical spin susceptibility in the normal state of Y-1:2:3 is enhanced around the $q=(\pi,\pi)$ position.[2] The T_c value for Y-1:2:3 is sensitive to the oxygen population at the CuO chain site. Both NMR and NQR studies have revealed that the oxygen content in superconducting Y-1:2:3 considerably changes both the temperature and the q dependences of the spin susceptibility in the CuO_2 plane.[3,4] Rossat-Mignod and coworkers[5] observed a loss of low-energy spin excitations in oxygen-deficient Y-1:2:3 at temperatures higher than T_c using the neutron inelastic-scattering technique. This observation seems to correspond to a spin-gap behavior proposed from a peak of $(^{63}T_1T)^{-1}$ at the planar Cu site as a function of temperature.[6]

The 81-K superconductor $YBa_2Cu_4O_8$ (Y-1:2:4) also belongs to the Y-Ba-Cu-O family. A high-quality Y-1:2:4 material has been synthesized under a high-oxygen-pressure atmosphere.[7] Y-1:2:4 has a crystal structure parallel to Y-1:2:3 with the exception of double CuO chain sites.[8] Both crystals have CuO_2 square planes and an apical oxygen related with the square in common. A characteristic feature of Y-1:2:4 is that the removal of oxygen in the double CuO chains is prevented in the range up to 800 °C. The oxygen content is fixed for high-pressure synthesized Y-1:2:4. This stability has raised the hope that we can derive the intrinsic nature of the CuO_2 plane in high-T_c superconductors from NMR and NQR studies on the stoichiometric compound Y-1:2:4. The oxygen spin-lattice relaxation rates $(^{17}T_1)^{-1}$ for Y-1:2:4 with $T_c=74$ K have been reported by Zheng *et al.*[9] For Y-1:2:4 $(^{17}T_1T)^{-1}$ are found to be considerably lower than those for the 60 K phase of Y-1:2:3 above 120 K, although the similarity of $(^{17}T_1T)^{-1}$ between these materials are noticeable at lower temperatures. Thus their $(^{17}T_1)^{-1}$ data suggest that the spin fluctuations in Y-1:2:4 fill a unique position in the Y-Ba-Cu-O family. They also found that the planar-oxygen Knight-shift in the normal state of Y-1:2:4 is higher than that for the 60-K phase of Y-1:2:3. On the other hand, Mangelschots *et al.*[10] showed that the planar-oxygen Knight shift for Y-1:2:4 is similar in behavior to that for oxygen-deficient Y-1:2:3. The point in controversy should be settled by further NMR experiments on Y-1:2:4 with $T_c=81$ K.

Previously Machi *et al.*[11] reported the Cu spin-lattice relaxation rates $(^{63}T_1)^{-1}$ up to 680 K in this material using the NQR technique. They showed that $(^{63}T_1)^{-1}$ in the normal state are divided into $q=(0,0)$ and $q=(\pi,\pi)$ contributions. Their data were consistent with those for Zimmermann *et al.*[12] except for the range above 500 K. The present NMR measurements extend to the planar-oxygen Knight-shift and spin-lattice relaxation rate in Y-1:2:4 with $T_c=81$ K. Comparison with Y-1:2:3 NMR data[3] reveals that the normal-state spin fluctuations at planar Cu and O sites for Y-1:2:4 are similar in behavior to those for the 60-K phase of Y-1:2:3 at temperatures above 110 K. Below T_c the ratio $^{17}T_1/^{63}T_1$ for Y-1:2:4 suggests the suppression of antiferromagnetic fluctuations with decreasing temperature. Magnetic fluctuations observed at both sites in Y-1:2:4 are discussed in conjunction with neutron and NMR experiments on the Y-1:2:3 system.

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II. EXPERIMENTAL PROCEDURE

The Y-1:2:4 materials were synthesized by a high-oxygen-pressure technique. Appropriate mixtures of Y_3O_3, $BaCO_3$, and CuO were fired at 920 °C in flowing O_2 at one atmosphere for a week. The powders were pressed into pellets and fired at 940 °C for two weeks with intermediate grinding. These ceramics were then reacted in a mixed gas of O_2 (20%) and Ar (80%) at 100 MPa and 1060 °C for 12 h using a hot isostatic press apparatus. Powder x-ray diffraction for the present samples indicated a single phase of Y-1:2:4. An exchange for ^{17}O was made by annealing the powdered sample at 500 °C for 80 h in a ^{17}O-enriched gas. A mixture of Y-1:2:4 powder with epoxy (Stycast 1266) was fixed in an 8-T magnetic field at room temperature to obtain a *c*-axis aligned sample.

Magnetization measurements were carried out using a superconducting quantum interference device magnetometer. The susceptibility χ for the powder sample used for this work was taken under field-cooled (FC) and zero-field-cooled (ZFC) conditions at 10 Oe. As shown in Fig. 1, the present Y-1:2:4 sample indicates a sharp superconducting transition at $T_c = 81$ K and the 60% Meissner volume at 5 K without any demagnetization correction. Figure 2 shows the normal-state susceptibility at 1 T. The bulk susceptibility χ in the normal state decreases gradually with decreasing temperature. This is similar in behavior to χ for the oxygen-deficient Y-1:2:3 with $T_c = 60$ K.[13]

In this paper we use the following notation for each copper and oxygen site. The double Cu(1)-O(1) chains are parallel with the *b* axis. The Cu(2)-O(2)-Cu(2) bond axis in the CuO_2 plane is parallel with the *b* axis, and the other Cu(2)-O(3)-Cu(2) bond axis is along the *a* axis. The apical oxygen O(4) connects Cu(1) and Cu(2) along the *c* axis.

The NMR spectra were taken with a standard pulsed NMR apparatus. The spin-echo intensity vs the magnetic field was obtained using a boxcar integrator. Knight shifts were determined by using a set of first and second satellite lines at 65.1 MHz. The spin-lattice relaxation rates $^{17}T_1^{-1}$ for O(2) at 33 MHz in a 5.71-T field parallel to the *c* axis were determined by measuring the spin echo from the first higher-field satellite ($\frac{3}{2} \leftrightarrow \frac{1}{2}$) transition. Furthermore, we measured the planar Cu(2) NQR relaxation rate on the same sample up to 300 K and found that the present data are in good agreement with the results reported previously.[11]

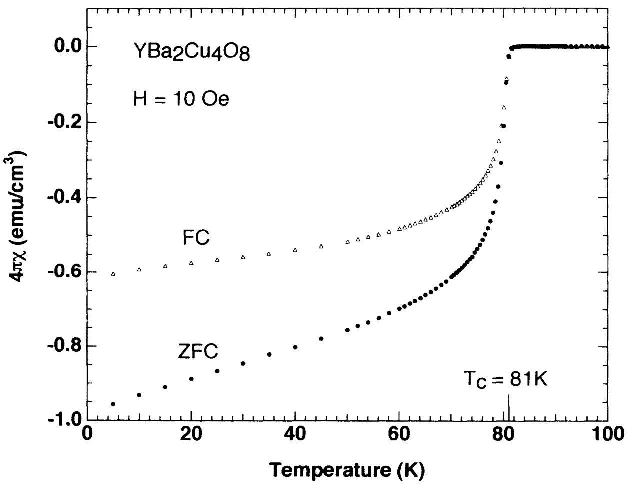

FIG. 1. Temperature dependence of zero-field-cooled (ZFC) and field-cooled (FC) susceptibilities for $YBa_2Cu_4O_8$ used for the present study. The data were taken at a 10-Oe field.

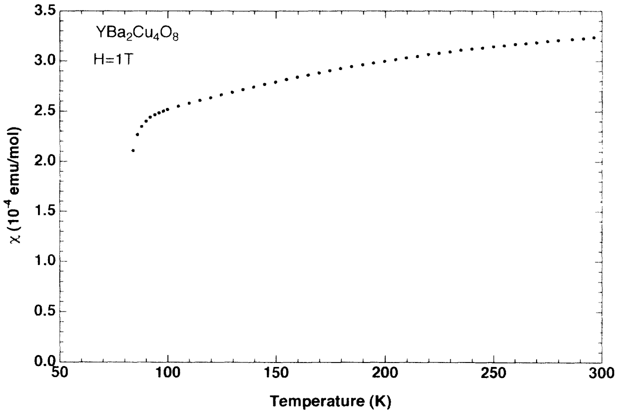

FIG. 2. Normal-state susceptibility for $YBa_2Cu_4O_8$ sample measured at 1 T.

III. OXYGEN NMR SPECTRA AND ELECTRIC-FIELD GRADIENT

Figure 3 shows the ^{17}O NMR spectrum of Y-1:2:4 at 100 K and 65.1 MHz for the applied field along the *c* axis ($H \parallel c$). The quadrupole interaction with the nuclear spin $I = \frac{5}{2}$ should give a set of five resonance lines for each oxygen site. In Fig. 3, four pairs of slightly split satellite lines from O(2,3) indicate a little difference in the electric-field gradient (EFG) between the O(2) and O(3) sites. A similar situation has been found for the planar oxygen in Y-1:2:3 (Ref. 14). We assumed that the absolute value of quadrupole frequency ν_c for the O(2) site is larger than for the O(3) site, in view of the Y-1:2:3 re-

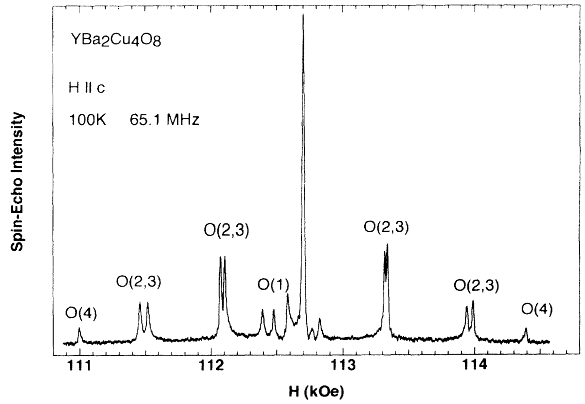

FIG. 3. ^{17}O NMR spectrum taken at 65.1 MHz and 100 K of aligned $YBa_2Cu_4O_8$ sample with *c* axis parallel to applied field.

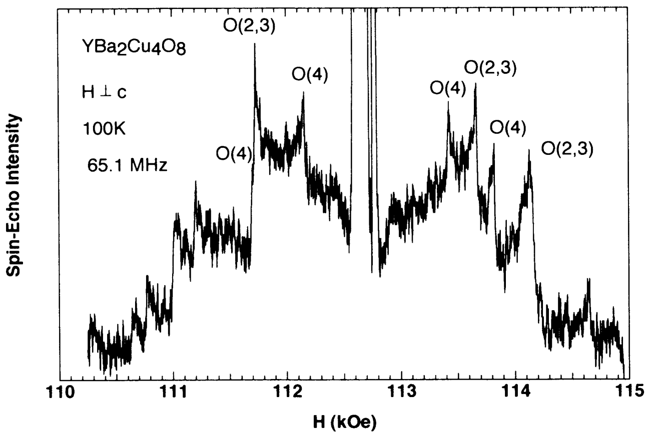

FIG. 4. ^{17}O NMR spectrum taken at 65.1 MHz and 100 K of aligned $YBa_2Cu_4O_8$ sample with c axis perpendicular to applied field.

sult.[14] Figure 4 shows the ^{17}O spectrum of Y-1:2:4 at 100 K and 65.1 MHz with the field perpendicular to the c axis ($H \perp c$). A two-dimensional powder spectrum should exhibit two sets of five singularities for each oxygen site, corresponding to the condition that the external field H is parallel or perpendicular to the Cu-O-Cu bond axis. In Fig. 4, the O(2) resonance lines for $H \| b$ overlap with the O(1) lines for $H \| b$, indicating that the quadrupole frequency ν_b for the O(2) site is nearly equal to that for the O(1) site. A detail analysis of this spectrum will be published elsewhere.[15]

We derive the quadrupole frequencies ν_α from the first ($\frac{1}{2} \leftrightarrow \frac{3}{2}$) and the second ($\frac{3}{2} \leftrightarrow \frac{5}{2}$) satellite lines. Here ν_α is expressed as $\nu_\alpha = \frac{3}{20} |eQ| V_{\alpha\alpha}$, where Q is the nuclear electric quadrupole moment, and $V_{\alpha\alpha}$ is the EFG with respect to the α direction. The ν_α values in Table I are obtained using the relation $\nu_a + \nu_b + \nu_c = 0$. The present data in Table I are in good agreement with the results of Mangelschots *et al.*[10] The ν_c values at the O(2,3) and the O(4) sites for Y-1:2:4 are comparable to those for Y-1:2:3 (Refs. 4 and 14). The structural difference at the chain site has a slight influence on EFG at the other oxygen positions.

The present ν_α data for Y-1:2:4 are consistent with the EFG calculation made by Ambrosch-Draxl, Blaha, and Schwarz.[16] The EFG at the O site of high-T_c materials is mainly dominated by an asymmetric internal charge distribution around the nucleus. The EFG calculation shows that the axis for the maximum EFG component at each O site is parallel to the Cu-O dp-σ bonding axis.[16,17]

TABLE I. Quadrupole frequency components (in MHz) at oxygen sites for $YBa_2Cu_4O_8$ and $YBa_2Cu_3O_7$. The $YBa_2Cu_3O_7$ data were taken from Takigawa *et al.* (Ref. 14).

	$YBa_2Cu_4O_8$			$YBa_2Cu_3O_7$		
Position	ν_a	ν_b	ν_c	ν_a	ν_b	ν_c
O(1)	0.845	0.905	−0.0641	−0.484	1.629	−1.145
O(2,3)	0.909	−0.558	−0.349	0.986	−0.598	−0.387
			−0.365	0.966		−0.369
O(4)	−0.366	−0.612	0.978	−0.375	−0.721	1.096

IV. OXYGEN KNIGHT SHIFT

Figure 5 shows the temperature dependence of the oxygen Knight shifts for $H \| c$, $^{17}K_{i,c}$, where i denotes the oxygen site. Here we derived the $^{17}K_{i,c}$ value from a set of resonance lines except for the central line. In the normal state, $^{17}K_{2,c}$ for the planar O(2) site decreases gradually with decreasing temperature. Note that $^{17}K_{2,c}$ is slightly higher than $^{17}K_{3,c}$ below 175 K. The existence of double CuO chains along the b axis appears to induce the Knight-shift difference between the two planar-oxygen sites. The $^{17}K_{2,c}$ value at 100 K is in agreement with the value reported by Mangelschots *et al.*[10] The present data, however, are different from those reported by Zheng *et al.*[9] in a wide temperature range. This discrepancy may be related to the fact that their Y-1:2:4 sample has a lower superconducting temperature ($T_c = 74$ K).

The O(2,3) hyperfine interaction between the ^{17}O nuclear spin I and the Cu electron spin S is expressed as

$$H_{\mathrm{O}} = \sum_{\alpha,j} C_\alpha I_\alpha S_{\alpha,j} , \tag{1}$$

where C_α is the transferred hyperfine coupling. The Knight shift $^{17}K_{2,c}$ consists of the spin and orbital parts,

$$^{17}K_{2,c} = {}^{17}K_{2,c}^{\mathrm{spin}} + {}^{17}K_{2,c}^{\mathrm{orb}} , \tag{2}$$

where $^{17}K_{2,c}^{\mathrm{orb}}$ is temperature independent. The spin part is related to the spin susceptibility χ^{spin} by

$$^{17}K_{2,c}^{\mathrm{spin}} = C_c \chi^{\mathrm{spin}} / \mu_B N , \tag{3}$$

where μ_B is the Bohr magneton, and N is the Avogadro's number. The Knight shift $^{17}K_{2,c}$ is plotted in Fig. 6 as a function of bulk susceptibility χ. The temperature-

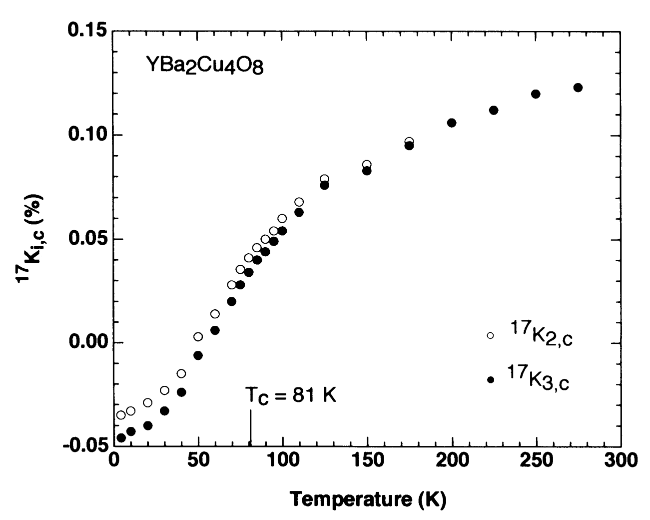

FIG. 5. Temperature dependence of $^{17}K_{i,c}$ for O(i) site in $YBa_2Cu_4O_8$. The superconducting-state data are plotted without any diamagnetic field correction.

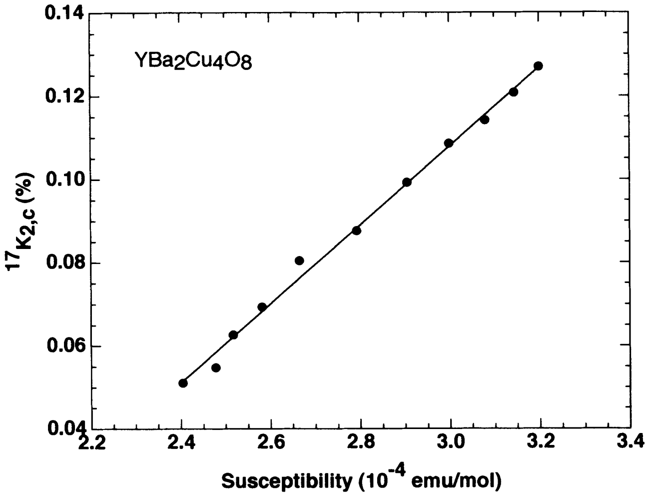

FIG. 6. Knight shift $^{17}K_{2,c}$ vs bulk susceptibility χ in $YBa_2Cu_4O_8$. The line is a linear fit.

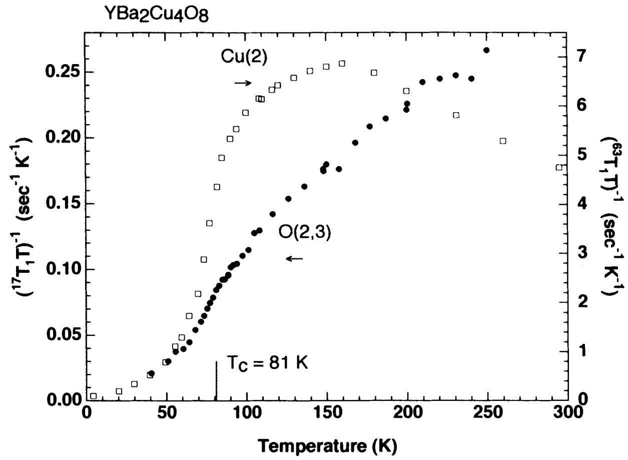

FIG. 7. Temperature dependence of $(^{17}T_1T)^{-1}$ for O(2) sites and $(^{63}T_1T)^{-1}$ for Cu(2) sites in $YBa_2Cu_4O_8$.

dependent part of the bulk susceptibility χ originates from the spin susceptibility $\chi_{\rm spin}$. In Y-1:2:4 the spin susceptibility is given by $\chi^{\rm spin}=2\chi_1^{\rm spin}+2\chi_2^{\rm spin}$, where $\chi_i^{\rm spin}$ stands for the Cu(*i*) site spin susceptibility. In the normal state $^{63}K_{1,c}$ has a slight decrease with decreasing temperature, while $^{63}K_{2,ab}$ shows a marked decrease.[18] Room-temperature value for $^{63}K_{1,c}$ is two-thirds of that for $^{63}K_{2,ab}$. We evaluate $C_c=140$ kOe/μ_B from the slope $dK_{2,c}/d\chi$ in Fig. 6, on the following assumptions. (1) The orbital Knight-shift components are the same as in Y-1:2:3 (Ref. 19). (2) In the normal state $\chi_1^{\rm spin}$ is proportional to $\chi_2^{\rm spin}$ and the ratio $\chi_1^{\rm spin}/\chi_2^{\rm spin}$ is equal to $^{63}K_{1,c}^{\rm spin}/^{63}K_{2,ab}^{\rm spin}$. Here we estimate $^{63}K_{1,c}^{\rm spin}=0.10\%$ and $^{63}K_{2,ab}^{\rm spin}=0.24\%$ at room temperature from the Y-1:2:4 data.[18] On the other hand, Yoshinari *et al.*[4] obtained that the C_c value for Y-1:2:3 is of the order of 100 kOe/μ_B. They made two assumptions; (1) $\chi_1^{\rm spin}$ at the fourfold Cu(1) site is equal to $\chi_2^{\rm spin}$ and (2) $\chi_1^{\rm spin}$ at the two- or threefold Cu(1) site is zero. Although all the Cu(1) sites in Y-1:2:4 are surrounded by four neighbor O(1) sites, the assumption that $\chi_1^{\rm spin}$ is equal to $\chi_2^{\rm spin}$ is not applicable to the case of Y-1:2:4. The role of the Cu(1) spin should be clarified to compare the C_c value for Y-1:2:4 with that for the 60-K phase of Y-1:2:3.

V. RELAXATION RATES AT THE PLANAR-OXYGEN AND COPPER SITES

A. Relaxation rates above T_c

Figure 7 shows the temperature dependence of $(^{17}T_1T)^{-1}$ for the O(2) sites and $(^{63}T_1T)^{-1}$ for the Cu(2) sites in Y-1:2:4. For O(2), $(^{17}T_1T)^{-1}$ decreases with decreasing temperature, changes the slope at temperatures just below T_c, and then decreases gradually below 50 K. Our $(^{17}T_1T)^{-1}$ data above 160 K are considerably higher than the values measured by Zheng *et al.*[9]

For Cu(2), $(^{63}T_1T)^{-1}$ increases with decreasing tem-

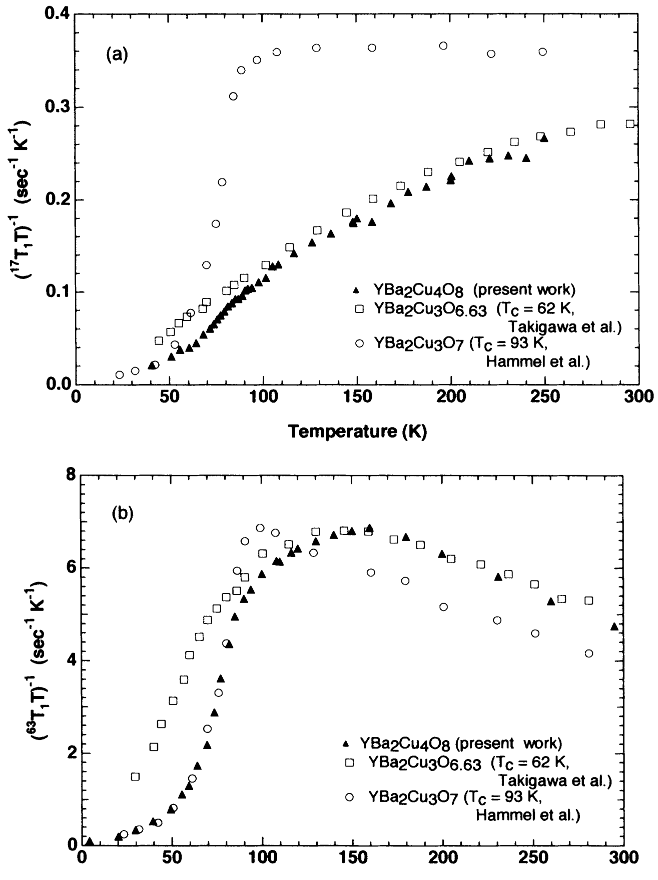

FIG. 8. Comparison of present $(^{\alpha}T_1T)^{-1}$ data for $YBa_2Cu_4O_8$ (triangles) with those for $YBa_2Cu_3O_{6+x}$. The data for the 90-K phase (circles) and the 60-K phase (squares) of $YBa_2Cu_3O_{6+x}$ were taken from Hammel *et al.* (Ref. 2) and Takigawa *et al.* (Ref. 3), respectively. (a) $(^{17}T_1T)^{-1}$ at the O(2,3) site. (b) $(^{63}T_1T)^{-1}$ at the Cu(2) site.

perature, exhibits a broad peak near 160 K and then decreases drastically in the vicinity of T_c. The present $({}^{\alpha}T_1T)^{-1}$ data for Y-1:2:4 are compared with the Y-1:2:3 data of Hammel *et al.*[2] and Takigawa *et al.*[3] in Fig. 8. Note that the normal state $({}^{17}T_1T)^{-1}$ for Y-1:2:4 is nearly equal to that for the oxygen-deficient Y-1:2:3 in a wide temperature range above 110 K. A similar situation is found for $({}^{63}T_1T)^{-1}$ in the same range between the two materials.

In general, $({}^{\alpha}T_1T)^{-1}$ for the nucleus α is expressed in terms of the imaginary part of the spin susceptibility $\mathrm{Im}\chi(q,\omega)$

$$({}^{\alpha}T_1T)^{-1}=\frac{{}^{\alpha}\gamma^2k_B}{2\mu_B^2}\sum_q|{}^{\alpha}A(q)|^2\frac{\mathrm{Im}\chi(q,\omega)}{\omega}\ . \tag{4}$$

Here, ω is the nuclear Larmor frequency and ${}^{\alpha}\gamma$ is the nuclear gyromagnetic ratio. The form factor ${}^{\alpha}A(q)$ represents the Fourier transform of the hyperfine coupling. Under the present experimental condition, these are given by

$${}^{17}A(q)=2C\cos(q_x/2)\ , \tag{5}$$

$${}^{63}A(q)=A_{ab}-2B(\cos q_x+\cos q_y)\ , \tag{6}$$

where A_{ab} is the direct hyperfine coupling of the ^{63}Cu nuclei, and B is the transferred hyperfine coupling to the nearest-neighbor Cu spins.[20] The O(2) nuclei have the form factor ${}^{17}A(q)$ that filters antiferromagnetic fluctuations in the neighboring Cu sites. Thus the O(2) relaxation rate is dominated by spin fluctuations in a broad q space around $q=(0,0)$. On the other hand, the form factor ${}^{63}A(q)$ has double peaks at $q=(0,0)$ and $q=(\pi,\pi)\equiv Q$.

First, we consider the Cu(2) relaxation behavior in the normal state. We have found that $({}^{63}T_1T)^{-1}$ above 250 K are well described by a Curie-Weiss form

$$({}^{63}T_1T)^{-1}=a+\frac{b}{(T+\theta)}\ , \tag{7}$$

where the first term is the contribution around $q=(0,0)$, and the second term is the contribution from antiferromagnetic spin fluctuations. The solid line in Fig. 9 is the fit to the data with $a=0.28(\mathrm{sec}^{-1}\,\mathrm{K}^{-1})$, $b=1454$ sec^{-1} and $\theta=29$ K. The agreement is quite good. This means that the normal-state Cu(2) relaxation rate is dominated by antiferromagnetic fluctuation near Q.

The normal-state $({}^{63}T_1T)^{-1}$ in Y-1:2:4 deviates from the Curie-Weiss law at lower temperatures, as shown in Fig. 9. The gradual decrease behavior of $({}^{63}T_1T)^{-1}$ is also recognized for oxygen-deficient Y-1:2:3 in a broader range between 160 K and $T_c=60$ K. This anomaly has been discussed in connection with the existence of a spin gap above T_c.[6] Here we argue that the spin gap opens at the temperature T^* where $({}^{63}T_1T)^{-1}$ reaches the maximum in the normal state. Rossat-Mignod *et al.*[5] pointed out that the $\mathrm{Im}\chi(q,\omega)$ vs ω relationship deduced from neutron scattering for the oxygen-deficient Y-1:2:3 is consistent with the temperature dependence of $({}^{63}T_1T)^{-1}$ determined from NMR experiments. The deviation from the Curie-Weiss law implies that the low-energy spectral weight in $\chi(Q,\omega)$ shifts to the high-energy part with decreasing temperature. For Y-1:2:4 with $T_c=81$ K and the 60-K phase of Y-1:2:3, $({}^{63}T_1T)^{-1}$ has a broad peak at $T^*\approx160$ K. On the other hand, $({}^{63}T_1T)^{-1}$ for the 90-K phase of Y-1:2:3 has not a clear peak above T_c. These results imply that T^* for the development of a spin gap has little correlation with T_c.

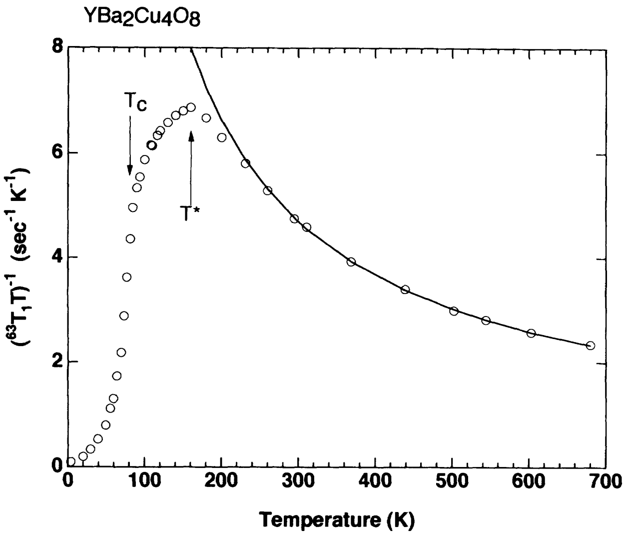

FIG. 9. Temperature dependence of $({}^{63}T_1T)^{-1}$ for Cu(2) sites in YBa$_2$Cu$_4$O$_8$ up to 680 K. The data above 250 K are taken from Machi *et al.* (Ref. 11). The line is a fit to the data above 250 K with Eq. (7).

Second, we discuss the $({}^{17}T_1T)^{-1}$ data in the normal state. For noninteracting conduction electrons, both ${}^{\alpha}K^{\mathrm{spin}}$ and $({}^{\alpha}T_1T)^{-1}$ obey the Korringa relation

$$[{}^{\alpha}T_1T({}^{\alpha}K^{\mathrm{spin}})^2]^{-1}=\frac{{}^{\alpha}\gamma^2 4\pi k_B}{\gamma_e^2\hbar}\equiv S\ , \tag{8}$$

where γ_e is the electronic gyromagnetic ratio. The Korringa value S is estimated to be 6.98×10^4 sec^{-1} K^{-1} for an oxygen nucleus. In Fig. 10 we plot $({}^{17}T_1T\,{}^{17}K_{2,c}^{\mathrm{spin}})^{-1}$ and $[{}^{17}T_1T\,{}^{17}(K_{2,c}^{\mathrm{spin}})^2]^{-1}$ for the O(2) site in Y-1:2:4 as a function of temperature. Here we use ${}^{17}K_{2,c}^{\mathrm{orb}}=-0.014\%$ for Y-1:2:4, assuming that ${}^{17}K_{2,c}^{\mathrm{orb}}$ is the same as in Y-1:2:3 (Ref. 3). The quantity $[{}^{17}T_1T\,{}^{17}(K_{2,c}^{\mathrm{spin}})^2]^{-1}$ is practically constant in the range above 150 K. However, deviation from the Korringa relation $T_1TK^2=$const is found in the vicinity of T_c. This is similar in behavior to the result for the 60-K phase of Y-1:2:3 (Ref. 3). A shown in Fig. 10, $[{}^{17}T_1T\,{}^{17}K_{2,c}^{\mathrm{spin}}]^{-1}$ is weakly temperature dependent near T_c. Comparison with the data for the oxygen-efficient Y-1:2:3 (Ref. 3) suggests that $({}^{17}T_1T)^{-1}$ is roughly proportional to ${}^{17}K_{2,c}^{\mathrm{spin}}$ in the vicinity of T_c in the two materials.

As shown in Fig. 8(a), the normal-state $({}^{17}T_1T)^{-1}$ values for Y-1:2:4 and the 60-K phase of Y-1:2:3 are considerably lower than for the 90 K phase of Y-1:2:3.

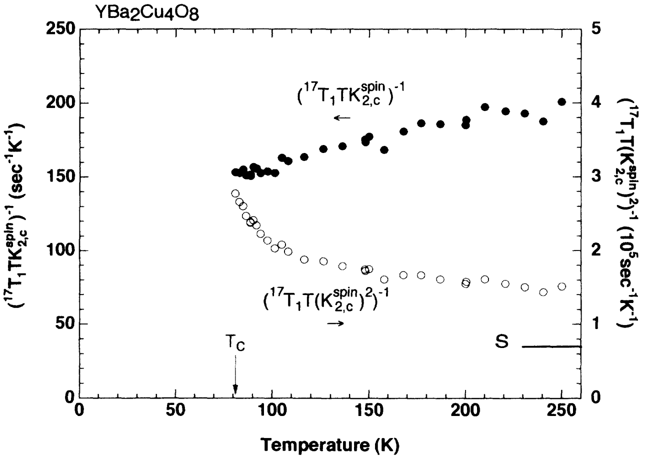

FIG. 10. Plots of $({}^{17}T_1 T {}^{17}K^{\text{spin}}_{2,c})^{-1}$ and $[{}^{17}T_1 T {}^{17}(K^{\text{spin}}_{2,c})^2]^{-1}$ for O(2,3) sites in $YBa_2Cu_4O_8$ as a function of temperature. The line indicates the Korringa value S for an oxygen nucleus.

Moreover, $({}^{17}T_1 T)^{-1}$ for Y-1:2:4 exhibits a steady decline as the temperature is lowered toward T_c. The temperature dependent $({}^{17}T_1 T)^{-1}$ remains an unsolved problem of cuprate superconductors. Based on Eq. (4), the $({}^{17}T_1 T)^{-1}$ data indicate the decrease in $\text{Im}\chi(q,\omega)$ around $q=(0,0)$ with decreasing temperature.

One possibility is that the appearance of a spin gap at $q=Q$ disturbs the $\text{Im}\chi(q,\omega)$ spectrum around $q=(0,0)$. For Y-1:2:4 and the oxygen-deficient Y-1:2:3, the gap is created at $T^*=160$ K. Figure 7 illustrates that $({}^{17}T_1 T)^{-1}$ starts to decrease at a high-temperature region where the spin gap disappears. Tanamoto, Kuboki, and Fukuyama[21] calculated the dynamical spin susceptibility $\chi(q,\omega)$ based on the *t-J* model. According to this model, the maximum of $({}^{63}T_1 T)^{-1}$ is due to the spin gap near 0.1 J. The calculated $\chi(q,\omega)/\omega$ shows that the suppression of the peak at $q=Q$ gives rise to an anomaly along the diagonal line joining $q=(0,0)$ and $q=Q$. The temperature-independent $({}^{17}T_1 T)^{-1}$ is predicted in a highly doped region. Their calculation, however, shows that $({}^{17}T_1 T)^{-1}$ in a lightly doped region increases gradually with decreasing temperature, in contrast to the observed behavior. Subsequently Tanamoto, Kohno, and Fukuyama[22] proposed the concept that singlet resonating-valence-bond (RVB) pairing is responsible for the decrease in $\chi(q)$ at $q=0$ and $q=Q$ for the lightly doped region. Bucher *et al.*[23] found that the CuO_2 plane resistivity along the *a* axis in Y-1:2:4 exhibits a strong correlation with the spin dynamics. The normal-state resistivity deviates from the linear temperature dependence below T^*. Furthermore, the Hall coefficient R_H in Y-1:2:4 varies inversely as the temperature above T^* and increases considerably in the range between T_c and T^*.[23,24] Thus the opening of the spin gap appears to have an influence on these transport properties of Y-1:2:4. The transport behavior connected with the spin gap seems consistent with the theoretical prediction.[22] From the experimental point of view, it is still open to question whether an RVB state exists in high-T_c superconductors or not.

Millis and Monien[25] calculated $({}^{\alpha}T_1 T)^{-1}$ based on the spin Hamiltonian including a large exchange interaction within the CuO_2 planes, J_1, and a small exchange interaction between nearest-neighbor CuO_2 planes, J_2. According to their model, the decrease in $({}^{17}T_1 T)^{-1}$ is governed by J_2, and the $({}^{63}T_1 T)^{-1}$ peak is determined by the interplay between J_1 and J_2. For the 90-K phase of Y-1:2:3, $({}^{17}T_1 T)^{-1}$ is temperature independent. Above 110 K the $({}^{17}T_1 T)^{-1}$ data for Y-1:2:4 are nearly equal to those for the 60-K phase of Y-1:2:3. In view of these results, the model should satisfy the following two conditions. (1) J_2 is sensitive to the hole population in the CuO_2 plane, and (2) the hole population in the CuO_2 plane of Y-1:2:4 is comparable to that for the 60-K phase of Y-1:2:3.

The Hall coefficient R_H for Y-1:2:4 is about 15% of that for Y-1:2:3 at room temperature.[26,27] The large difference in R_H appears to be unfavorable for the picture that $\chi(q,\omega)$ for the Y-Ba-Cu-O family is determined by the average hole concentration. To be consistent with the picture we interpret that the excess holes in the double CuO chain of Y-1:2:4 contribute to R_H. The anisotropic resistivity data in the *ab* plane suggest that some part of the mobile holes is distributed at the CuO chain sites.[23,27]

Third, we consider the ratio of the relaxation rate at the Cu(2) site to that at the O(2,3) site, ${}^{17}T_1/{}^{63}T_1$, in the normal state. In Fig. 11, the present ${}^{17}T_1/{}^{63}T_1$ data for Y-1:2:4 are compared with those for the Y-1:2:3 system obtained by Yoshinari, Yasuoka, and Ueda.[28] For Y-1:2:4, ${}^{17}T_1/{}^{63}T_1$ increases with decreasing temperature, reaches a peak just above T_c. A similar behavior has been found for the 60-K phase of Y-1:2:3 in the range above 100 K. The maximum ${}^{17}T_1/{}^{63}T_1$ value for Y-1:2:4 is considerably higher than that for the 90-K phase of Y-1:2:3.

Based on the antiferromagnetic Fermi-liquid model proposed by Millis, Monien, and Pines (Ref. 29) ${}^{17}T_1/{}^{63}T_1$ is approximately proportional to $(1+\xi^2)$ where ξ is the antiferromagnetic correlation length. Thus the Y-1:2:4 data in Fig. 11 suggest that the normal-state ξ

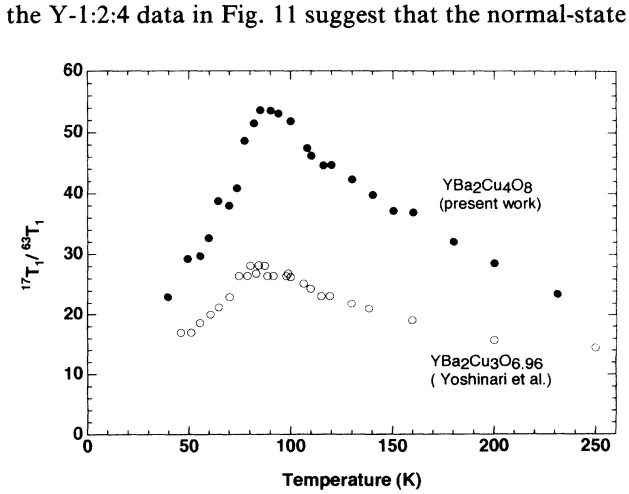

FIG. 11. Temperature dependence of ratio ${}^{17}T_1/{}^{63}T_1$ for $YBa_2Cu_4O_8$ and $YBa_2Cu_3O_{6.96}$. The $YBa_2Cu_3O_{6.96}$ data with $T_c=87$ K are taken from Yoshinari, Yasuoka, and Ueda (Ref. 28).

increases gradually with decreasing temperature. In addition, the opening of the spin gap near $T^*=160$ K appears to have no effect on the gradual increase in ξ. Neutron-scattering studies on the Y-1:2:3 system, however, have suggested that ξ derived from $\chi(q,\omega)$ is essentially independent of temperature in a wide temperature range.[5,30] Millis and Monien[31] pointed out the possibility that the half-width of the peak in $\mathrm{Im}\chi(q,\omega)$ is independent of ξ at high ω even if ξ is temperature dependent. Tranquada *et al.*[30] have shown that the q dependence of $\mathrm{Im}\chi(q,\omega)$ around Q is anisotropic in the *ab* plane of Y-1:2:3. Furthermore, the q width of the $\mathrm{Im}\chi(q,\omega)$ peak is ω dependent. This complicated situation presents difficulty in comparing ξ deduced from the ${}^{17}T_1/{}^{63}T_1$ data with ξ determined by neutron experiments.

Note that the normal-state ratio ${}^{17}T_1/{}^{63}T_1$ saturates in the vicinity of T_c where $({}^{63}T_1T)^{-1}$ decreases rapidly. A saturation behavior was also observed for the ratio for the 90-K phase of Y-1:2:3 (Ref. 3). The ${}^{17}T_1/{}^{63}T_1$ peak means that the temperature derivative $d\,\mathrm{Im}\chi(q,\omega)/dT$ is essentially q independent near T_c.

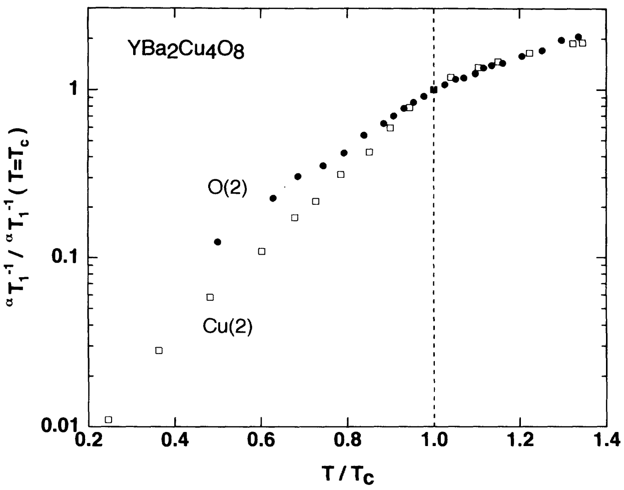

FIG. 12. $({}^{\alpha}T_1T)^{-1}$ normalized to the value at T_c as a function of reduced temperature T/T_c in $YBa_2Cu_4O_8$.

B. Relaxation rates below T_c

Here we discuss the Cu(2) and the O(2) relaxation behaviors in the superconducting state. Note in Fig. 8(b) that the superconducting-state $({}^{63}T_1T)^{-1}$ in Y-1:2:4 is almost the same as that for the 90-K phase of Y-1:2:3. The similarity below 80 K is in marked contrast to the distinct temperature dependences of the normal state $({}^{63}T_1T)^{-1}$. Therefore the appearance of superconductivity makes essentially no difference in magnetic fluctuations near $q=Q$ between Y-1:2:4 and the 90-K phase of Y-1:2:3. As shown in Fig. 8(a), there is a large difference in the superconducting state $({}^{17}T_1T)^{-1}$ between these materials. The slope of $({}^{17}T_1T)^{-1}$ just below T_c for Y-1:2:4 is smaller than that for the 90-K phase of Y-1:2:3. The decrease in $({}^{17}T_1T)^{-1}$ in the normal state of Y-1:2:4 appears to reduce the superconducting effect on magnetic fluctuations around $q=(0,0)$.

Figure 12 shows $({}^{\alpha}T_1)^{-1}$ normalized to the value at T_c as a function of reduced temperature T/T_c in Y-1:2:4. Both $({}^{63}T_1)^{-1}$ and $({}^{17}T_1)^{-1}$ change their slopes near T_c. In the superconducting phase, there is a difference in the slope between the Cu(2) and O(2) sites. Figure 11 indicates that the superconducting state ${}^{17}T_1/{}^{63}T_1$ shows a marked decrease with decreasing temperature. These results suggest that antiferromagnetic fluctuations are suppressed considerably compared with the spin fluctuations around $q=(0,0)$. The decrease in ${}^{17}T_1/{}^{63}T_1$ has also been observed for the 90-K phase of Y-1:2:3 reported by Yoshinari, Yasuoka, and Ueda[28] and Martindale *et al.*[32] On the other hand, Hammel *et al.*[2] found that the ratio ${}^{17}T_1/{}^{63}T_1$ is temperature independent in the superconducting state of Y-1:2:3. The reason for this discrepancy in the Y-1:2:3 materials is unexplained.

The pairing symmetry in cuprate superconductors is still in controversy. Bulut and Scalapino[33] pointed out that an *s*-wave pairing has a difficulty in explaining the absence of the Hebel-Slichter peak just below T_c. They interpreted the temperature-independent ${}^{17}T_1/{}^{63}T_1$ below T_c as the evidence for a *d*-wave pairing state. Thelen, Pines, and Lu[34] showed that a *d*-wave pairing state is in favor of the decrease in ${}^{17}T_1/{}^{63}T_1$ below T_c for the 90-K phase of Y-1:2:3. The pronounced decrease in ${}^{17}T_1/{}^{63}T_1$ is found for Y-1:2:4. In view of the similarity in $({}^{63}T_1T)^{-1}$ between Y-1:2:4 and Y-1:2:3, the difference in the slope of ${}^{17}T_1/{}^{63}T_1$ implies that the temperature dependence of magnetic fluctuations around $q=(0,0)$ is sensitive to the hole concentration even below T_c.

VI. CONCLUSION

The planar-oxygen Knight shift in Y-1:2:4 shows the decrease as the temperature is lowered toward T_c. In the normal state $({}^{17}T_1T)^{-1}$ at the O(2,3) site is roughly proportional to ${}^{17}K_{2,c}$ near T_c. On the other hand, $({}^{63}T_1T)^{-1}$ at the Cu(2) site shows a maximum around $T^*=160$ K. Comparison with the Y-1:2:3 data strongly suggests that both the q and the temperature dependences of magnetic fluctuations in Y-1:2:4 present an almost complete similarity to those for the 60-K phase of Y-1:2:3 in the normal state above 110 K. In the normal state, the ratio ${}^{17}T_1/{}^{63}T_1$ increases with decreasing temperature, and reaches a broad peak near T_c. The absence of anomaly in ${}^{17}T_1/{}^{63}T_1$ around 160 K suggests that the appearance of the spin gap has no influence on the antiferromagnetic correlation length.

In the superconducting state, $({}^{63}T_1T)^{-1}$ decreases dramatically with decreasing temperature. Below T_c there is a striking similarity in $({}^{63}T_1T)^{-1}$ between Y-1:2:4 and the 90-K phase of Y-1:2:3. The antiferromagnetic fluctuations in the superconducting phase of Y-1:2:4 appear to be unaffected by the development of the spin gap observed at temperatures up to $T^*=160$ K. The slope for $({}^{17}T_1T)^{-1}$ shows a slight change in the vicinity of T_c. Magnetic fluctuations around $q=(0,0)$ in the superconducting state of Y-1:2:4 are smaller than those for the

90-K phase of Y-1:2:3. The significant decrease in $^{17}T_1/^{63}T_1$ suggests that the loss of antiferromagnetic fluctuations are dominant in the superconducting state of Y-1:2:4.

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