Oxygen Content Dependence of ^{63}Cu(1) NQR and Proton NMR in Hydrogen-Doped Antiferromagnetic $YBa_2Cu_3O_{6+x}H_y$*

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The oxygen content dependence of ^{63}Cu NQR at the Cu(1) site and proton NMR have been measured in the antiferromagnetic phase of powdered samples of hydrogen-doped $YBa_2Cu_3O_{6+x}H_y$ ($0.07 \leq x \leq 0.17$ and $y \approx 1$) from 4.2 to 90 K. The spectrum of ^{1}H NMR is a single line and the line width increases below 15 K due to magnetic interactions. The enhancements of T_1^{-1} and T_2^{-1} of ^{63}Cu(1) NQR occur around 35 and 15 K, respectively. These enhancements increase with increasing oxygen concentration. The maximum values of T_1^{-1} and T_2^{-1} for the sample with $x = 0.17$ reach 200 sec^{-1} and more than 7 msec^{-1}, respectively. The predominant source for the relaxation mechanism of ^{63}Cu(1) NQR and the line broadening of ^{1}H NMR are found to be the fluctuating magnetic field due to the staggered Cu^{2+} moments.

Key words: Antiferromagnetic materials, High-T_c superconductor, Spin-lattice Relaxation Time, Cu NQR, Proton NMR.

1. Introduction

The antiferromagnetism of the tetragonal $YBa_2Cu_3O_{6+x}$ (YBCO) was confirmed by neutron diffraction [1, 2], nuclear magnetic resonance (NMR) [3–5], and muon spin resonance (μSR) [6, 7] experiments. The magnetic moments of the Cu(2) atoms couple antiferromagnetically with the moments in the same plane, and also with the moments in the neighboring Cu(2) O_2 planes, while the copper ions on the Cu(1) sites in the oxygen-deficient layers have been considered to have no magnetic moment [1–4].

However, a neutron diffraction investigation on a single crystal of $YBa_2Cu_3O_{6.35}$ reported by Kadowaki et al. [8] has shown that a secondary magnetic transition occurs at 40 K, well below the Néel temperature $T_N = 410$ K. They concluded that this transition is associated with an ordering of the $Cu(1)^{2+}$ moments in the oxygen-deficient layer, and that part of the Cu(1) atoms in these layers have a small magnetic moment. Tranquada et al. [9] carried out a neutron diffraction experiment on a single crystal with $x = 0.3$ and found an extra diffuse intensity at temperatures below 30 K and a decrease of normal Bragg peak intensities. They explained those results in terms of an incoherent ordering of $Cu(1)^{2+}$ magnetic moments in the oxygen-deficient layers at low temperatures. These two neutron diffraction experiments [8, 9] also reported that the Cu(1) moment in the oxygen-deficient layer brings about the ferromagnetic spin alignment of the Cu(2) layers adjacent to the Cu(1) layer along the c axis. This ferromagnetic spin alignment is caused by the frustration due to the competition of the antiferro- and ferromagnetic interaction between Cu(2) layers mediated primarily by the Cu(1) layer. The difference between the two reports is that the $Cu(1)^{2+}$ magnetic moments appear either in the ordered or in the disordered state in the oxygen-deficient layers.

As hydrogen is well absorbed into YBCO, it can be used as a convenient probe to investigate the properties of a sample. Moreover, since the nuclear spin of ^{1}H is 1/2, one can apply the proton NMR method without suffering from any complexity owning to the quadrupolar

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effect. From measurement of ^{1}H NMR in the hydrogen-doped superconductor YBCO, Groß and Mehring [10] found a phase separation into an antiferromagnetic phase with a high ^{1}H-concentration and a superconducting phase with a low ^{1}H-concentration. They suggested that the reason for this phase separation is the formation of proton-rich antiferromagnetic clusters. Goren et al. [11] reported that the ^{1}H resonance yields a narrow line at low concentration of hydrogen, but a very wide line at high concentration due to the electromagnetic moments. In both reports it is suggested that the superconduor YBCO with the high concentration of hydrogen includes a non-superconducting part. Therefore, the amount of doped hydrogen in $YBa_2Cu_3O_{6+x}H_y$ in our present work should be small in order not to affect the properties of the original sample. To understand the results of neutron diffraction experiments, we measured the oxygen concentration dependence of ^{63}Cu NQR at the Cu(1) site and proton NMR in the antiferromagnetic state of $YBa_2Cu_3O_{6+x}H_y$.

2. Experimental

Sample preparation procedures were described in [12]. Three powdered samples with different amounts x of oxygen (x = 0.07, 0.11, and 0.17) were used. The experimental result for a sample with $x = 0.1$ ($YBa_2Cu_3O_{6.1}H_{0.14}$ denoted as YBC06.1H [12, 13]) is compared with these new ones. The samples were doped by hydrogen under a pressure of about 8 torr at 200 °C for about 1 day. From the decrease of the hydrogen pressure, the amount of hydrogen in all samples was estimated to be about 0.1 per formula unit in YBCO.

The measurements of nuclear spin-lattice relaxation time (T_1) and nuclear spin-spin relaxation time (T_2) of the ^{63}Cu NQR were carried out by a phase-coherent pulsed spectrometer. T_1 was measured by a 90°-t-90°-t'-180° pulse sequence ($t' \ll t$). The nuclear magnetization $M(t)$ at a time interval t after the first 90° pulse was obtained from the height of the spin-echo signals. T_1 was determined from $\log(1 - M(t)/M_0)$ vs. t plots, where M_0 is the nuclear magnetization in thermal equilibrium. T_2 was measured by a spin-echo method. A phase-coherent pulsed spectrometer was employed to measure the ^{1}H NMR spectra using the Fourier Transform (FT) technique. A single phase detection method was applied for the FT NMR.

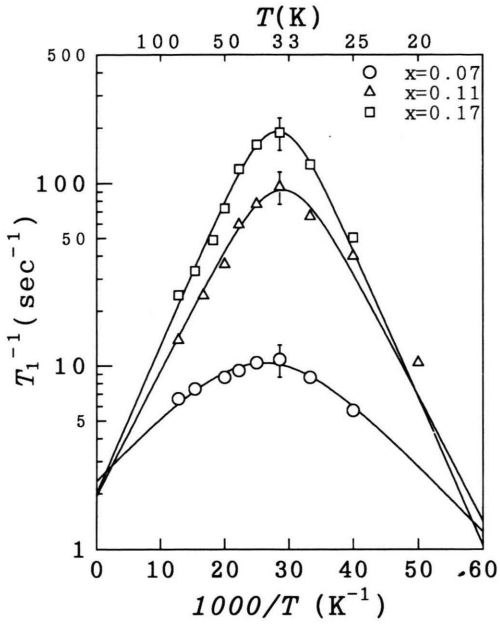

Fig. 1. Temperature dependence of T_1^{-1} of ^{63}Cu NQR at the Cu(1) site for the three samples with different oxygen contents x in $YBa_2Cu_3O_{6+x}H_y$ (x = 0.07, 0.11, and 0.17). The curves shown by solid lines are calculated by (1).

3. Results

3.1. T_1 of the ^{63}Cu NQR at Cu(1) Site

T_1 of ^{63}Cu NQR at Cu(1) sites was measured to investigate antiferromagnetic state of YBCO at temperatures from 20 to 78 K. The logarithmic nuclear magnetization recovery LMR(t) is defined as $\mathrm{LMR}(t) = \log[1 - M(t)/M_0]$. In this temperature range, LMR(t) is proportional to $t^{1/2}$, which is caused by a distribution of T_1's without spin diffusion [14, 15]. In this case, T_1 is commonly evaluated from the time t satisfying the condition $[1 - M(t)/M_0] = e^{-1}$ in the LMR(t) vs. $t^{1/2}$ curve [14]. The temperature dependence of T_1^{-1} of ^{63}Cu is shown in Figure 1. T_1^{-1} shows an enhancement around 35 K. These enhancements increase with increasing the oxygen concentration. The maximum value of T_1^{-1} for the sample with $x = 0.17$ reaches about 200 s^{-1}.

3.2. T_2 of the ^{63}Cu NQR at Cu(1) Site

The temperature dependences of T_2^{-1} of ^{63}Cu NQR at Cu(1) sites were measured in the temperature range from 4.2 to 90 K. The results are shown in Figure 2. The re-

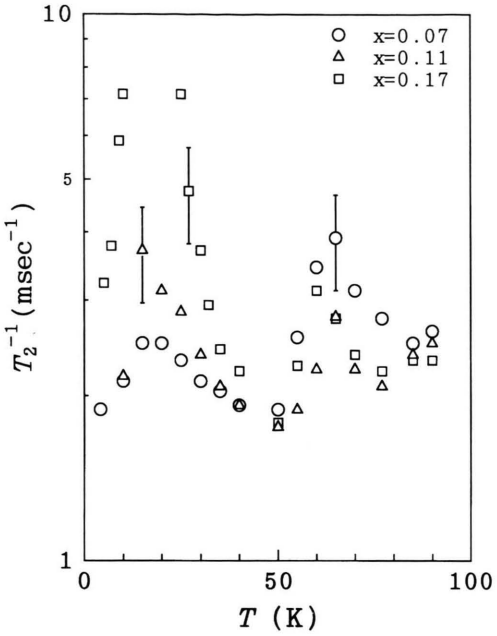

Fig. 2. Temperature dependence of T_2^{-1} of ^{63}Cu NQR at the Cu(1) site for the three samples with different oxygen contents x in $YBa_2Cu_3O_{6+x}H_y$ (x = 0.07, 0.11, and 0.17).

covery curve of T_2 exhibits a simple exponential decay. T_2^{-1} is enhanced around 15 and 65 K. The enhancements around 15 K increase with increasing oxygen concentration. The maximum of T_2^{-1} for the sample with $x = 0.17$ reaches more than 7 msec^{-1}. However, the concentration dependence can not be observed for the enhancement around 65 K: the sample with $x = 0.07$ shows a maximum value of about 3.9 msec^{-1}. The temperature dependence of T_2^{-1} for the sample of YBCO6.1H, which was measured previously [12, 13], shows the same tendency as the new samples, except for the magnitude of T_2 depending on the sample preparation.

3.3. Proton NMR

Proton NMR measurements were performed at 33 MHz (ca. 7700 Oe). The ^{1}H NMR spectra in each sample show a single peak in the observed temperature range as presented in Figure 3. At room temperature the full width at half maximum (FWHM) of ^{1}H NMR in each sample is less than about 0.3 Oe because of motional narrowing due to hydrogen movements. The line width in YBCO6.1 was less than about 0.3 Oe down to 230 K due to the hydrogen movements, it became wid-

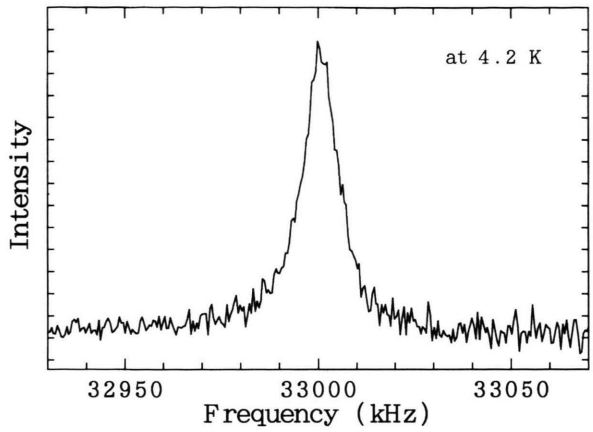

Fig. 3. Proton NMR spectrum of $YBa_2Cu_3O_{6.11}H_y$ at 4.2 K.

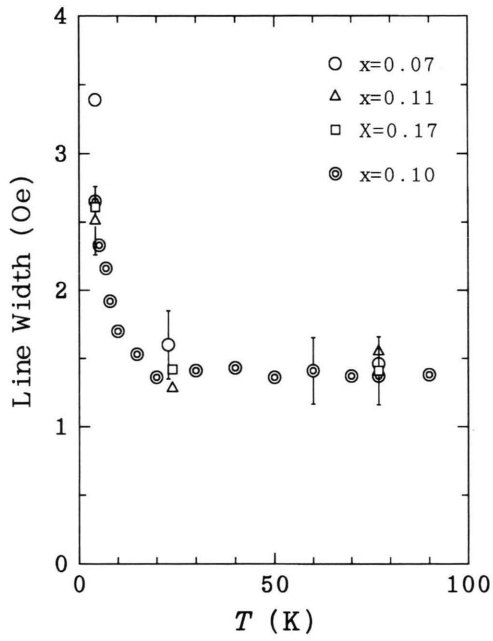

Fig. 4. Temperature dependence of the line width of ^{1}H NMR for the four samples with different oxygen contents x in $YBa_2Cu_3O_{6+x}H_y$ (x = 0.07, 0.11, and 0.17 and YBCO6.1H) (the x of YBCO6.1H is 0.10).

er from 230 to 90 K, and became constant below 90 K, as described in [12]. Figure 4 shows the temperature dependence of the width (FWHM) of proton NMR line in the temperature range from 4.2 to 90 K. The line width, which is caused by nuclear dipolar interactions between ^{1}H and other nuclei [16], is almost constant (about 1.5 Oe) between 15 and 90 K. In the previous experiment of proton NMR in YBCO6.1H [12], in the tem-

perature independent region the line width broadened up to about 2.0 Oe because of an inhomogeneity caused by the magnet. Therefore, we measured it again in an improved system and confirmed it to be 1.5 Oe (Figure 4). However, the line width for the sample of YBCO6.1H broadens abruptly below 15 K. The value exceeds 2.6 Oe at 4.2 K. The line width of the other samples shows similar behaviour, recording a value of about 3.4 Oe at 4.2 K for oxygen concentration $x = 0.07$.

4. Discussion

4.1. The Behavior of the Doping Hydrogen

At temperatures below 90 K, the NMR line width, which is caused by the nuclear dipolar interactions between ^1H and other nuclei [16], is almost constant (about 1.5 Oe) because hydrogen is trapped in some sites near Cu(1) atoms. As Cu(1) atoms in the oxygen-deficient layer have no magnetic moment and the internal fields in this layer arising from the moments in the Cu(2) O_2 plane are cancelled [1–4], hydrogen atoms in the present compound are expected to be trapped in some sites near Cu(1) atoms, that is similar to the hydrogen site in $YBa_2Cu_3O_{6.94}H_y$ ($y = 0.2$ and 0.53) [16, 17]. Moreover, it is confirmed that the hydrogen in $YBa_2Cu_3O_{6.94}H_y$ ($y = 0.2$ and 0.53) exists inside the crystal since the temperature dependence of T_1 of ^1H NMR reflects the superconducting state in the sample [17, 18]. Therefore, hydrogen does not exist on the surface but inside the crystal in the case of the new three samples ($x = 0.07$, 0.11, and 0.17) and YBCO6.1H. As double peaks such as the Pake doublet are not observed, it is concluded that there is no water or H_2 inside of the crystal. The line broadening below 15 K is caused by a magnetic interaction since ^1H has a half spin and no quadrupole moment, and since the hydrogen is trapped.

4.2. T_1 and T_2 of the ^{63}Cu NQR at Cu(1) Site

The enhancements of T_1 around 35 K and T_2 around 15 K stem from the same relaxation mechanism due to a magnetic or quadrupole interaction, since these enhancements increase with increasing oxygen concentration. In the case of the quadrupole interaction, the predominant relaxation mechanism is expected to originate from the fluctuating field due to a hopping or moving of oxygen ions or holes in the crystal, taking into account that the magnitude of the field increases with increasing oxygen. The NMR study by Mendels at al. [19] revealed that the induced holes stay in the oxygen deficient layer at least up to the oxygen content 6.2 in YBCO. As the oxygen contents in our samples are less than 6.2, holes stay in the oxygen deficient layer. Therefore, it seems reasonable to suggest that the oxygen ions or holes hop or move in the oxygen deficient layer.

However, the magnetic interaction rather than the quadrupole one should be responsible for the relaxation mechanism of T_1 and T_2 for the following reasons: 1) The enhancements of T_1^{-1} around 35 K and T_2^{-1} around 15 K of the $^{63}Cu(1)$ NQR, and the increase of the line width of the proton NMR below 15 K can be explained by the fluctuating magnetic field. 2) The enhancement of T_1^{-1} at 35 K is expected when τ_c equals the reciprocal of the resonance frequency ω_0^{-1} [20, 21]. 3) The enhancement of T_2^{-1} seems to occur around 15 K if τ_c equals the reciprocal of the line width. 4) At temperatures lower than 15 K, the fluctuation of the magnetic field is suggested to be frozen. Since ^1H has a half spin and no quadrupole moment, and since the hydrogen atoms are trapped, the increase in the line width below 15 K must be caused by magnetic interactions. 5) Therefore, the origin of the fluctuating field should be magnetic.

As the logarithmic nuclear magnetization recovery LMR(t) is proportional to $t^{1/2}$, the T_1's at Cu(1) sites are distributed. However, if the distribution of T_1's is weak in the crystal, the equation

$$\frac{1}{T_1} = \gamma_n^2 \overline{H_\perp^2} \frac{\tau_c}{1+\omega_0^2 \tau_c^2} \tag{1}$$

can be used [20, 21], where γ_n and ω_0 are the nuclear gyromagnetic ratio and the resonance frequency of ^{63}Cu. $\left(\overline{H_\perp^2}\right)^{1/2}$ (denoted as $H_{L\perp}$) and τ_c are the effective transverse component and correlation time of the fluctuating magnetic field, respectively. In this case, we adopt the equation

$$\tau_c = \tau_\infty e^{E/kT} \tag{2}$$

for the correlation time [20, 21]. The activation energy E is the potential barrier of the field fluctuating with the period τ_c.

Following the above equations, the calculated values for each concentration are consistent with the experimental values, as shown by the solid lines in Figure 1.

Table 1. The effective transverse component $H_{L\perp}$, activation energy E, and correlation time τ_∞ of the fluctuating magnetic field.

x	0.07	0.11	0.17
$H_{L\perp}$ (Oe)	8.8	26.3	38.0
E (K)	83	157	186
τ_∞ (sec)	6.03×10^{-10}	5.58×10^{-11}	2.76×10^{-11}

Table 1 shows $H_{L\perp}$, τ_∞ and E for each oxygen concentration. $H_{L\perp}$ becomes larger as the oxygen concentration is increased. $H_{L\perp}$, E and τ_∞ for YBCO6.1H were calculated also as 25.1 Oe, 177 K, 3.29×10^{-11} sec, respectively. These values are comparable to those of the sample with $x = 0.11$.

The relaxation mechanism enhancing the T_2^{-1} around 65 K can affect also T_1 at higher temperatures. This mechanism may originate from the fluctuating field due to the motion of the induced holes or hydrogen. Measurement of the oxygen content dependence of T_1 at temperatures higher than those reported in this paper (78 K) is required to be clarify this point.

4.3. The Origin of the Fluctuating Magnetic Field at Cu(1) Site

The two neutron experiments [8, 9] imply that the staggered Cu(1) or Cu(2) moment, which is produced in our sample in the low temperature region, is responsible for the fluctuating magnetic field contributing dominantly to T_1 at the Cu(1) site. The fluctuating local field at the Cu(1) site is generated by the dipolar or transferred hyperfine fields from these staggered moments. At present, however, we can not clarify which field mainly contributes to the local one. The logarithmic nuclear magnetization recovery LMR(t) is proportional to $t^{1/2}$. This means that each nucleus feels a different fluctuating field dynamically. Therefore it is concluded that the staggered Cu^{2+} moments should be distributed randomly in the crystal.

The density of the staggered Cu^{2+} moments increases with increasing oxygen content. Therefore, the magnitude of the fluctuating magnetic field at the Cu(1) site increases with increasing oxygen. In the case of small x of $YBa_2Cu_3O_{6+x}$, the staggered Cu^{2+} moments can easily move or hop in the crystal, but as x increases, it is getting hard to move since the potential barrier of the movement becomes higher (Table 1).

When oxygen ions or holes hop or move in the oxygen deficient layer as described in the case of the quadrupole relaxation mechanism, their movement may affect the spin arrangement on the CuO_2 plane and the cancellation of the internal magnetic field at the Cu(1) site may become incomplete. Then, the fluctuating magnetic field corresponding to the correlation time of the movement of oxygen or holes occurs at Cu(1) sites. In this case, it is possible to explain the relaxation mechanism of Cu(1) NQR and the broadening of the line width of ^{1}H NMR by means of the movement of oxygen or holes. However, the incomplete cancellation of the internal magnetic field at the Cu(1) site is just an assumption. On the other hand, the existence of staggered Cu^{2+} moments is a solid experimental fact. Therefore, in our opinion the consideration of the staggered Cu^{2+} moments as the origin of the fluctuating magnetic field is preferable.

5. Conclusion

The oxygen content dependence of ^{63}Cu NQR at Cu(1) site and proton NMR have been measured in the antiferromagnetic phase of hydrogen-doped $YBa_2Cu_3O_{6+x}H_y$ ($0.07 \leq x \leq 0.17$ and $y \approx 0.1$). The spectrum of ^{1}H NMR shows a single peak in the observed temperature range. Hydrogen atoms are expected to be trapped near the oxygen-deficient layer inside of the crystal.

The logarithmic nuclear magnetization recovery LMR(t) is proportional to $t^{1/2}$ in the temperature range from 20 to 78 K. The enhancements of T_1^{-1} and T_2^{-1} of ^{63}Cu(1) NQR occur around 35 and 15 K, respectively. These enhancements increase with increasing oxygen concentration. The line width of ^{1}H NMR increases below 15 K. The enhancements of T_1^{-1} and T_2^{-1} of ^{63}Cu(1) NQR and the abrupt increase of the line width of proton NMR are originated from fluctuating magnetic fields due to the staggered Cu^{2+} moments.

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