Hydrogen-doped Antiferromagnetic YBa$_2$Cu$_3$O$_{7-\delta}$H$_x$ as Studied by Proton NMR and Cu NQR *

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Proton NMR and Cu NQR of the Cu(1) site have been measured on the antiferromagnetic phase of a powdered sample of hydrogen-doped tetragonal YBa$_2$Cu$_3$O$_{7-\delta}$H$_x$ between 5 and 300 K. The line width, $\Delta a$, of $^1$H NMR increases abruptly below 20 K. The enhancement of $T_2^{-1}$ and that of $T_1^{-1}$ of $^{63}$Cu (1) NQR occurs around 20 K and 40 K, respectively. The nuclear magnetization does not recover in a simple exponential manner below 80 K. The predominant mechanism governing $T_1$ below 80 K was found to be the fluctuating magnetic field which originates from the staggered Cu$^{2+}$ moments in either the Cu(1) oxygen-deficient layer or the Cu(2)O$_2$ plane induced by the hole doping effect. These enhancements and the abrupt increase in $\Delta a$ are attributed to this fluctuating magnetic field.

Key words: Antiferromagnetic materials, High-$T_c$ superconductor, Spin-lattice relaxation time, Spin-spin relaxation time, Proton NMR.

Introduction

Since the discovery of the oxide high-$T_c$ superconductors, many experimental and theoretical studies have been carried out to elucidate the mechanism of superconductivity of these materials. It has been found that a superconducting state of YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) with an orthorhombic structure can be transformed to an antiferromagnetic one with a tetragonal structure by varying the concentration of oxygen atoms from $\delta = 0$ to 1 [1-6].

The copper ions in the Cu(2) sites on the Cu(2)O$_2$ plane in the antiferromagnetic state of YBCO have a magnetic moment of about 0.6 $\mu_B$. The magnetic moments at the Cu(2) atoms couple antiferromagnetically not only with those in the same plane, but also with those in the neighboring Cu(2)O$_2$ planes. The direction of the aligned moments is perpendicular to the $c$-axis [1, 2, 5, 6]. Contrary to the Cu(2) moments, the copper ions on the Cu(1) sites in the oxygen-deficient layers have no magnetic moment.

Neutron diffraction [7] and Cu NQR [8] experiments have shown that the secondary magnetic transition might occur at a temperature sufficiently below the Neel temperature, $T_N$ (ca. 410 K). In the investiga-

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tions using a single crystal of YBa$_2$Cu$_3$O$_{6.35}$, Kad-owaki et al. [7] reported that this transition is associated with the ordering of the Cu$^{2+}$ moments on the oxygen-deficient layer.

As hydrogen atoms are well absorbed into YBCO, they can be used as a convenient probe to investigate the properties of the 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 effect. Previously, for the superconducting state of YBa$_2$Cu$_3$O$_{6.94}$H$_x$ ($x = 0.2, 0.53$) we measured the temperature dependence of the line width of $^1$H NMR [9, 10], the shape of the NMR spectra [11, 12], and the spin-lattice relaxation time, $T_1$, [10, 13]. From these investigations we have confirmed that hydrogen atoms are trapped in the vicinity of Cu(1) atoms in the oxygen-deficient layer, and that they do not destroy the superconductivity if $x \leq 0.2$. The penetration depth of the magnetic field in the superconducting state was determined to be 2500 Å [9], which is comparable to that obtained by the $\mu^+\text{SR}$ method.

In this paper, in order to investigate the sites occupied by the absorbed hydrogen atoms and to obtain a detailed knowledge on the secondary magnetic transition in the antiferromagnetic state of YBCO, we measured $^1$H NMR spectra and line widths of a powdered sample of YBa$_2$Cu$_3$O$_{6.1}$H$_{0.14}$ between 5.2 and 300 K. In addition to the proton NMR, we also applied the $^{63}$Cu NQR method: line width, $T_1$, spin-spin relaxation time, $T_2$, and the shape of the spectra of the $^{63}$Cu NQR were measured for Cu(1) atoms located in the oxygen-deficient layers in the same sample.

**Experimental**

Polycrystalline samples of the tetragonal YBCO were prepared from a mixture in the ratios 0.5 moles of Y$_2$O$_3$ (99.9%, Nippon Yttrium), 2 moles of Ba(OH)$_2$•8H$_2$O (analytical grade, Wako Chemicals) and 3 moles of CuO (99.9%, Furuuchi Chemicals). After mixing in an agate mortar, the mixture was heated at a rate of 2°C/min till 600°C and calcined at 600°C for 2 h in air. The calcined product was ground in the agate mortar, molded using a cold isostatic press, and then fired at 950°C in air. After 20 h, the fired specimen was allowed to cool to room temperature in air. The fired product was reground and then molded into pellets 18 mm in diameter and 2 mm in thickness by a uniaxial press. The pellet was heated at 800°C for 5 h in vacuum. Into the tetragonal YBa$_2$Cu$_3$O$_x$ thus obtained, hydogen atoms were absorbed by a gas charging method using an apparatus of Sieverts type [9, 13]. The concentration of hydrogen atoms in the powdered sample of YBa$_2$Cu$_3$O$_{6.1}$H$_{0.14}$ obtained was low enough to prevent an influence of the H atoms on the physical properties of YBCO.

The NMR measurements were performed at 33 MHz (ca. 7700 Oe). A bridge spectrometer was used for measurements of the line width of $^1$H by the continuous wave (CW) method [9]. A phase-coherent pulsed spectrometer was employed to measure the $^1$H spectra by Fourier Transform (FT), and the $^{63}$Cu NQR spectra, $T_1$ and $T_2$ of the NQR. $T_1$ was measured by a 90°–t–90°–t’–180° sequence ($t' \ll t$). The nuclear magnetization $M(t)$ at t after the first 90° pulse was determined from the height of the spin-echo signals. $T_2$ was measured by a spin-echo method (90°–t–180° pulse sequences). A single phase detection method was applied for FT NMR. Free decay signals used for FT NMR were obtained from induction tails of the proton NMR following the 90° pulse or the echo signals.

**Results and Discussion**

Figure 1 shows the temperature dependence of the width of the proton NMR line in the range 5.2 to 300 K. The width was determined from the peak-to-peak separation of the absorption derivative for the CW and FT NMR methods. The line is narrow above 230 K because of the movement of hydrogen atoms, it broadens below 230 K and keeps an almost constant value of about 2 Oe below about 90 K. This line width is caused by nuclear dipolar interactions between $^1$H and other nuclei [9]. This shows that the line width of $^1$H NMR is not influenced by the distributed internal fields originating from the magnetic moments of the Cu(2)O$_2$ plane. The structural symmetry of YBCO suggests that the internal magnetic fields produced from Cu(2) moments are cancelled at Y sites and other nuclei [9]. They reported that the line width of $^{89}$Y, with a nuclear spin of 1/2, is determined by the nuclear dipolar interaction above $T_N$, but that the line is broadened drastically because of the distrib-
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Fig. 1. Temperature dependence of the line width of $^1$H NMR in YBa$_2$Cu$_3$O$_{6.1}$H$_{0.14}$.

culated internal magnetic fields originating from the ordered magnetic moments produced in the Cu(2)O$_2$ plane below $T_N$. On the other hand, 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 completely cancelled [1, 2, 5, 6]. This clarifies that the hydrogen atoms are trapped in some site near Cu(1) atoms, which is similar to the site occupied by hydrogen in YBa$_2$Cu$_3$O$_{6.94}$H$_x$ ($x=0.2$ and 0.53) [9, 10].

However, the line width increases abruptly below 20 K, reaching about $3.5$ Oe at 5.2 K, as shown in Figure 1. Since $^1$H has a half spin and no quadrupole moment, and since the hydrogen atoms are trapped, the increase in the line width below 20 K must be caused by magnetic interactions. The peak-shift of the resonance line is within $\pm 10$ ppm from the resonance peak of water used as a reference sample in the temperature range investigated.

As shown in Fig. 1, the line broadening is extending over the wide temperature range from 230 K to 90 K. As reported in previous papers [9, 10], the broadening of proton NMR occurs in a narrow temperature region in YBa$_2$Cu$_3$O$_{6.94}$H$_x$ ($x=0.2$ and 0.53): it occurs from 170 K to 150 K for $x=0.2$ and from 190 K to 130 K for $x=0.53$. The existence of many vacant oxygen sites in the oxygen-deficient layer and the antiferromagnetic state may influence the line broadening of proton NMR in YBa$_2$Cu$_3$O$_{6.1}$H$_{0.14}$. Further investigations are necessary to clarify this origin.

In order to study the reason of the broadening of the $^1$H NMR line below 20 K, the temperature dependences of the line width, $T_2$, and $T_1$ of the $^{63}$Cu NQR of Cu(1) atoms were measured. Figure 2 shows the resonance spectra at three temperatures. In Fig. 3, the resonance frequency (top) and the line width (bottom) of the $^{63}$Cu NQR of the Cu(1) atoms are shown (the line width is the full width at half maximum). As shown in Figs. 2 and 3, the line width stays practically constant below 40 K. As the line of the $^{63}$Cu NQR is very wide (ca. 500 kHz), the weak magnetic interaction, which increases the proton NMR line width up to only $3.5$ Oe, does not influence the $^{63}$Cu NQR line width.
Interestingly, the behaviour of the temperature dependence of $T_2$ of $^{63}$Cu NQR shown in Fig. 4 differs from that of the line width of $^1$H NMR. The recovery curve of $T_2$ exhibits the simple exponential decay in the temperature region investigated. The spin-spin relaxation rate, $T_2^{-1}$, has enhancements around 20 K and 80 K. The former enhancement is related to the fluctuating magnetic field and the latter corresponds approximately to the temperature where the predominant mechanism governing $T_1$ changes. At around 80 K, though the appearance of the $T_2^{-1}$ peak may be correlated to the change of the predominant mechanism for $T_1$, the relation between the two phenomena is not clear at present.

$T_1$ of $^{63}$Cu NQR was measured between 5 and 120 K. The logarithmic nuclear magnetization recovery, LMR $(t)$, is defined as

$$\text{LMR}(t) = \log \left( \frac{1 - M(t)}{M_0} \right),$$

where $t$ is the time interval between the first and the second pulse and $M_0$ the nuclear magnetization in thermal equilibrium.

Above ca. 80 K, LMR $(t)$ depends linearly on $t$ as shown in Figure 5. Below about 80 K, however, because of the distribution of $T_1$'s the nuclear magnetization does not recover in a simple exponential manner and LMR $(t)$ depends linearly on $t^{1/2}$, as shown in Figure 6. This means that the main contribution to the relaxation mechanism changes around 80 K.

When the contribution of the magnetic impurities dominates the $T_1$ relaxation mechanisms without spin diffusion, LMR $(t)$ depends linearly on $t^{1/2}$ [15]. Recently, Nakamichi et al. [16] reported that LMR $(t)$ of $T_1$ of Cu NQR in impurity-induced magnetic ordered YBa$_2$(Cu$_{1-x}$M)$_3$O$_7$ (M = Fe, Co) depends linearly on $t^{1/2}$ as the results of the effect of magnetic impurities at low temperatures. In their report, they evaluated $T_1$ at the time $t$ satisfying the condition $(1 - M(t)/M_0) = e^{-1}$ in the LMR $(t)$ vs. $t^{1/2}$ curve. We have adopted the same method for the determination of $T_1$ below 80 K.

Figure 7 summarizes the temperature dependence of the spin-lattice relaxation rate $T_1^{-1}$ of $^{63}$Cu. The full circles show the values derived from LMR $(t)$ vs. $t^{1/2}$ curves and the open circles the ones derived from LMR $(t)$ vs. $t$ curves. $T_1^{-1}$ also shows a maximum around 40 K and a shoulder around 20 K. The temperatures at which the enhancements of $T_1^{-1}$ and $T_2^{-1}$
occur agree well with those obtained by Matsumura et al. [8].

The enhancements of $T_1^{-1}$ and $T_2^{-1}$ of the $^{63}$Cu NQR and the abrupt increase of the line width of the proton NMR suggest the existence of an additional magnetic field fluctuating with a correlation time $\tau_c$, which increases with decreasing temperature. $T_1^{-1}$ at 40 K is expected to be enhanced if $\tau_c$ equals the reciprocal of the resonance frequency $\omega_0^{-1}$ [17]. $T_2^{-1}$ has an enhancement around 20 K if $\tau_c$ equals the reciprocal of the line width. At temperatures lower than 20 K, the fluctuation of the magnetic field is frozen.

A neutron diffraction study suggested the possibility of a secondary magnetic transition occurring at a temperature (below ca. 40 K) sufficiently below the Néel temperature $T_N$ [7]. Using a single crystal of YBa$_2$Cu$_3$O$_{6.5}$, the neutron diffraction experiment showed that this transition is associated with an ordering of the Cu$^{2+}$ moments of the oxygen-deficient layer, and that a part of Cu(1) atoms in the oxygen-deficient layer have a small magnetic moment because of the effect of the hole-doping in this layer. The Cu(1) moment in the oxygen-deficient layer brings about the ferromagnetic spin alignment along the c axis between the Cu(2) layers adjacent to the Cu(1) layer. The Cu(1) moments frustrate the antiferromagnetic ordering of the Cu(2) moments. The staggered Cu(1) and Cu(2) moments produced by the hole-doping effect are responsible for the fluctuating magnetic field mentioned above.

Takatsuka et al. [18] have carried out Cu NQR measurements in the antiferromagnetic state of YBa$_2$(Cu$_{1-x}$T$_x$)$_3$O$_6$ (T = Fe, Co and Ni). Fe and Co ions replace copper ions in Cu(1) sites, while Ni ions occupy Cu(2) sites. According to that study, the secondary magnetic transition is induced below 40 K by the substitution of Cu by transition elements, and the ferromagnetic spin alignment between the Cu(2) layers is brought about but Cu(1) moments in the oxygen-deficient layer are not produced [18]. This transition may be caused by the frustration due to the competition of the antiferro- and ferromagnetic interaction between Cu(2) layers mediated primarily by the Cu(1) layers. With respect to Cu(1) moments, their result is different from that of the neutron diffraction study by Kadowaki et al. [7] mentioned above. The substitution of Cu by transition elements corresponds to a change of the oxygen concentration of YBCO. If the same spin alignment as that caused by the substitution of Cu mentioned above occurs in YBa$_2$Cu$_3$O$_{6.1}$H$_{0.14}$, staggered Cu(2) moments in the Cu(2)O$_2$ plane can produce the fluctuating magnetic field.

In the case of YBa$_2$Cu$_3$O$_{6.1}$H$_{0.14}$, the dominant contribution determining $T_1$ below 80 K seems to be the fluctuating magnetic field, caused by either the staggered Cu(1) or Cu(2) moments induced by the hole doping effect. The concentration of the staggered Cu moments existing in YBa$_2$Cu$_3$O$_{6.1}$H$_{0.14}$ is considered to be low, and the interaction between $^1$H and the fluctuating magnetic fields is expected to be weak. Then, the increase in the line width of proton NMR below 20 K appears to be slight.

The $T_1^{-1}$ vs. $T$ relation in Fig. 7 shows a shoulder at around 20 K. According to the neutron diffraction study of Kadowaki et al. [7], the amount of staggered Cu$^{2+}$ moments in the oxygen-deficient layer and CuO$_2$ plane increases with decreasing temperature below 40 K, and a structural phase transition does not occur around 20 K. The increase in the amount of Cu$^{2+}$ moments may give rise not only to an increase of the magnitude of the fluctuating magnetic field, but also to a distribution of the correlation time of the fluctuating field because several kinds of fluctuating fields are produced, and each of them has a different correlation time. Then, the decrease of $T_1^{-1}$ may be depressed to result in the shoulder of $T_1^{-1}$ vs. $T$ curve at around 20 K. As mention above, the enhancement
of $T_2^{-1}$ around 20 K is produced by the fluctuating magnetic field giving the enhancement of $T_1^{-1}$ around 40 K. The fluctuating field causing the shoulder of $T_1^{-1}$ is expected to make a shoulder of $T_2^{-1}$ at a temperature lower than about 10 K, but the shoulder of $T_2^{-1}$ may be slight. At present, however, we can not propose a quantitative explanation for the behavior of $T_1$ around 20 K.

Above 80 K, however, the contribution of the fluctuating magnetic field to $T_1$ decreases rapidly because $\tau_\phi$ is much shorter than $\omega_0^{-1}$. Then, one can consider the ordered antiferromagnetic moments of Cu(2) atoms in the Cu(2)O$_2$ plane as a major contribution governing $T_1$ above 80 K. However, the transferred hyperfine or the dipolar field of Cu(2) moments in the Cu(2)O$_2$ plane is completely canceled at the Cu(1) sites [5]. Therefore, $T_1$ at ca. 80 K may be much longer than the observed value, because 80 K is sufficiently below the Néel temperature $T_N$. Now we must consider the contribution of the lattice vibrations to $T_1$ as a residual contribution to $T_1$. According to Jeffery and Armstrong [19], $T_1$ of $^{63}$Cu NQR in Cu$_2$O is 1.85 s at 77 K and 0.26 s at 195 K, and the predominant contribution determining $T_1$ is the lattice vibrations. Although these $T_1$ values are longer than those of YBa$_2$Cu$_3$O$_{6.14}$, $T_1$ of the present compound could be explained by the lattice vibrations. At present, however, we can not tell precisely which is the origin of the predominant contribution to $T_1$, the ordered antiferromagnetic Cu(2) moments in the Cu(2)O$_2$ plane or the lattice vibrations, because the temperature region above 80 K in our present measurement is very narrow.

To obtain detailed knowledge of the antiferromagnetic state of YBCO including this point, further NQR and NMR investigations, including the study of the effect of oxygen concentration, are required and are now in progress.

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