Hydrogen-doped Antiferromagnetic $YBa_2Cu_3O_{7-\delta}H_x$ 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 $YBa_2Cu_3O_{6.1}H_{0.14}$ between 5 and 300 K. The line width, $\Delta\omega$, of ^1H 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 $\Delta\omega$ 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 $YBa_2Cu_3O_{7-\delta}$ (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 μ_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 Néel temperature, T_N (ca. 410 K). In the investiga-

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tions using a single crystal of $YBa_2Cu_3O_{6.35}$, Kadowaki 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 ^1H 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 $YBa_2Cu_3O_{6.94}H_x$ ($x=0.2$, 0.53) we measured the temperature dependence of the line width of ^1H 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 $x \leqq 0.2$. 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 μ^+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 ^1H NMR spectra and line widths of a powdered sample of $YBa_2Cu_3O_{6.1}H_{0.14}$ 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_2O_3 (99.9%, Nippon Yttrium), 2 moles of $Ba(OH)_2 \cdot 8H_2O$ (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 $YBa_2Cu_3O_x$ thus obtained, hyrdogen 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 $YBa_2Cu_3O_{6.1}H_{0.14}$ 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 ^1H by the continuous wave (CW) method [9]. A phase-coherent pulsed spectrometer was employed to measure the ^1H 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_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 ($90°-t-180°$ 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 ^1H and other nuclei [9]. This shows that the line width of ^1H 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 sandwiched by $Cu(2)O_2$ planes and Cu(1) sites in the oxygen-deficient layer.

Ohno et al. measured the NMR line width of ^{89}Y in $YBa_2Cu_3O_6$ [14]. They reported that the NMR 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-

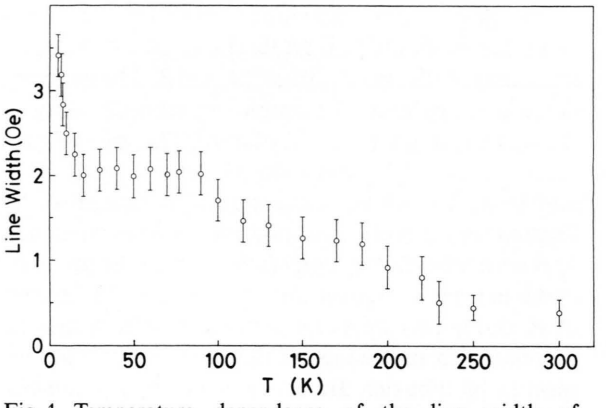

Fig. 1. Temperature dependence of the line width of ^1H NMR in $YBa_2Cu_3O_{6.1}H_{0.14}$.

uted 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 $YBa_2Cu_3O_{6.94}H_x$ ($x=0.2$ 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 ^1H 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 ± 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 $YBa_2Cu_3O_{6.94}H_x$ ($x=0.2$ 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 $YBa_2Cu_3O_{6.1}H_{0.14}$. Further investigations are necessary to clarify this origin.

In order to study the reason of the broadening of the ^1H 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

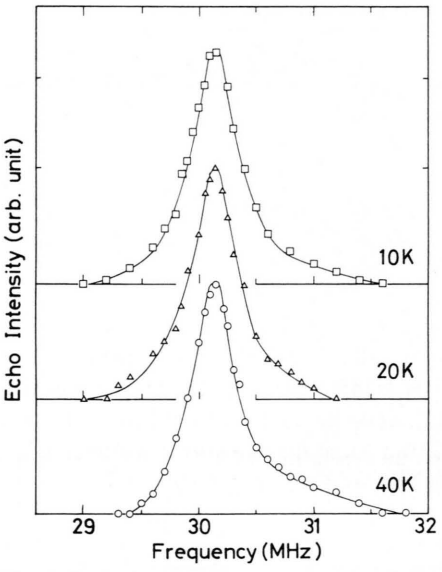

Fig. 2. Resonance spectra at several temperature of ^{63}Cu NQR for Cu(1) atoms in $YBa_2Cu_3O_{6.1}H_{0.14}$.

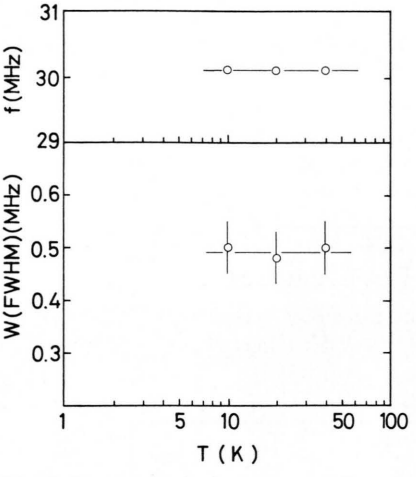

Fig. 3. Temperature dependence of central resonance frequency, f, and line width, W, of ^{63}Cu NQR spectra for Cu(1) atoms in $YBa_2Cu_3O_{6.1}H_{0.14}$.

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.

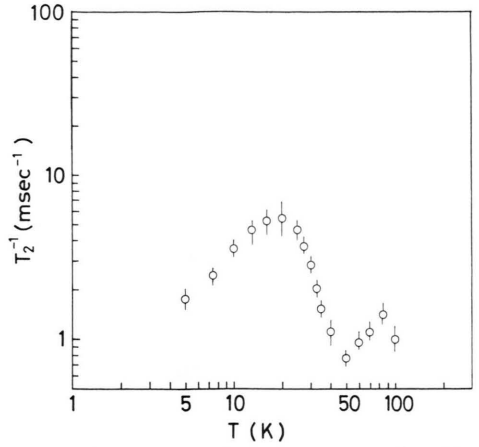

Fig. 4. Temperature dependence of T_2^{-1} of ^{63}Cu NQR for Cu(1) atoms in $YBa_2Cu_3O_{6.1}H_{0.14}$.

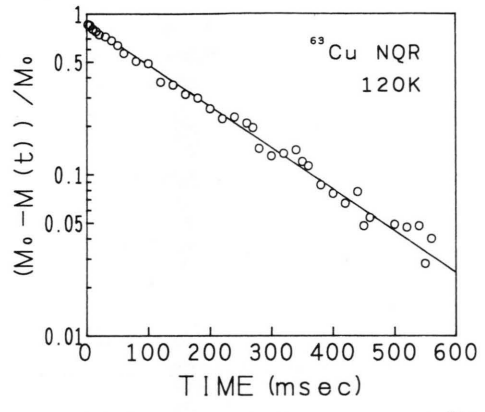

Fig. 5. Nuclear magnetization recovery of ^{63}Cu NQR for Cu(1) atoms in $YBa_2Cu_3O_{6.1}H_{0.14}$ at 120 K versus time.

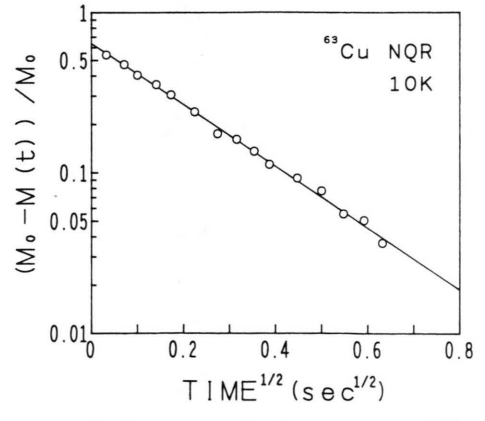

Fig. 6. Nuclear magnetization recovery of ^{63}Cu NQR for Cu(1) atoms in $YBa_2Cu_3O_{6.1}H_{0.14}$ at 10 K versus square root of time.

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

$$\mathrm{LMR}(t)=\log\left[1-\frac{M(t)}{M_0}\right], \tag{1}$$

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 $YBa_2(Cu_{1-x}M_x)_3O_7$ (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 as 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}

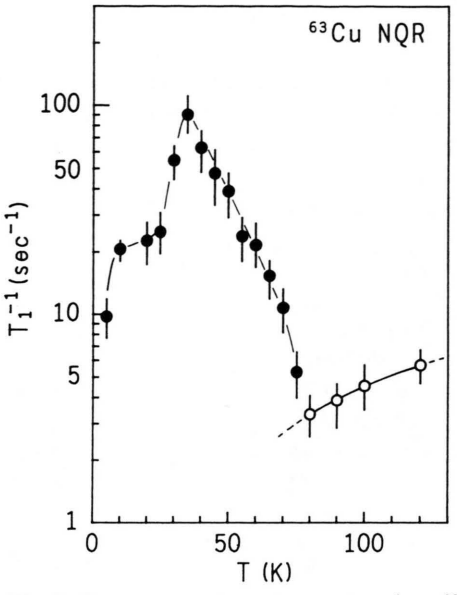

Fig. 7. Temperature dependence of T_1^{-1} of ^{63}Cu NQR for Cu(1) atoms in $YBa_2Cu_3O_{6.1}H_{0.14}$. Solid lines are guides to the eye.

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, τ_c, which increases with decreasing temperature. T_1^{-1} at 40 K is expected to be enhanced if τ_c equals the reciprocal of the resonance frequency, ω_0^{-1} [17]. T_2^{-1} has an enhancement around 20 K if τ_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 $YBa_2Cu_3O_{6.35}$, 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 layers 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 $YBa_2(Cu_{1-x}T_x)_3O_6$ (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 $YBa_2Cu_3O_{6.1}H_{0.14}$, staggered Cu(2) moments in the $Cu(2)O_2$ plane can produce the fluctuating magnetic field.

In the case of $YBa_2Cu_3O_{6.1}H_{0.14}$, 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 $YBa_2Cu_3O_{6.1}H_{0.14}$ 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 τ_c is much shorter than ω_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 Jefferey and Armstrong [19], T_1 of ^{63}Cu NQR in Cu_2O 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 $YBa_2Cu_3O_{6.1}H_{0.14}$, 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.

Acknowledgements

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