Relaxation mechanisms for ^{63,65}Cu nuclear quadrupole resonance in Zn-doped $YBa_2Cu_3O_7$

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We have prepared Zn-doped $YBa_2Cu_{3-x}Zn_xO_7$, $x=0\sim0.09$ and performed ^{63,65}Cu nuclear quadrupole resonance measurements for the plane sites at 300 and 100 K as a function of Zn concentration. Both spin-lattice and spin-spin relaxation rates are reduced for high Zn concentration. The reduction of spin-lattice relaxation rate due to Zn doping is more significant at the lower temperature. The ratio of ^{63,65}Cu spin-lattice relaxation rates indicates that the magnetic contribution to the spin-lattice relaxation rate for the plane copper is reduced whereas the quadrupolar contribution is increased at the lower temperature. This confirms clearly that the antiferromagnetic spin fluctuation of the plane copper moments is suppressed significantly by Zn substitution. [S0163-1829(99)00717-1]

I. INTRODUCTION

Extensive research results up to date have shown that the antiferromagnetic spin correlation between the plane copper $3d$ moments dominates the dynamic susceptibility in the normal states of cuprate superconductors.[1] The antiferromagnetic correlation has been investigated mainly by controlling the oxygen stoichiometry in these oxide superconductors in order to unveil the underlying origin and mechanism for this unusual superconductivity. On the other hand, the magnetic interaction between the copper local moments has been studied through the substitution of copper by magnetic and nonmagnetic ions such as Ni and Zn.[2–6] Contrary to the conventional wisdom[7] as for the BCS-type superconductors, the superconducting transition temperature significantly decreases for the nonmagnetic Zn substitution into the plane copper sites whereas the magnetic Ni substituent weakly reduces the transition temperature.[8] This result is often quoted as evidence supporting that the origin of the pairing mechanism may be the antiferromagnetic spin fluctuation between the plane copper moments mediated by the plane oxygen orbitals. It is commonly agreed that the Ni substituent has a local moment. However, it is controversial whether or not the Zn substituent carries a local moment.[6,9–11] Furthermore, it is not decisively known on the microscopic ground where the Zn ion goes.

The absence of local moments at the Zn substituents is based mainly on macroscopic measurements such as magnetic susceptibility data. However, the microscopic measurements such as nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) measurements exhibit a discrepancy about this matter. For example, ^{63,65}Cu NQR and magnetic susceptibility data[6,9] support that the Zn substituent forms no local moment. On the other hand, ^{89}Y NMR (Refs. 10,11) exhibits an extra peak as a result of Zn substitution, which comes from the yttrium sites near the Zn substituents. In addition, the linewidth follows the Curie behavior. This indicates that Zn carries a local moment. It is suggested that Zn forms a moment possibly in a resonant state of the host copper bands.[10] Thus the size of the moment may be negligible for macroscopic measurements but Zn is more effective for the suppression of the antiferromagnetic fluctuation between the copper spins.

For ^{63,65}Cu$(I=3/2)$ NQR, the energy levels are degenerate for $I_z=\pm1/2$ and $I_z=\pm3/2$. Thus the spin-lattice relaxation occurs via two channels; the magnetic dipole relaxation $(\Delta I_z=1)$ via fluctuation of hyperfine fields and the electric quadrupole relaxation $(\Delta I_z=2)$ via fluctuation of electric-field gradients. The magnetic relaxation is proportional to the square of gyromagnetic ratio γ^2, whereas the quadrupole relaxation is proportional to the square of electric quadrupole moment Q^2. Since $^{63}\gamma<^{65}\gamma$ whereas $^{63}Q>^{65}Q$, the ratio of the spin-lattice relaxation rate for ^{63}Cu and ^{65}Cu, $^{65}(1/T_1)/^{63}(1/T_1)=(^{65}\gamma/^{63}\gamma)^2=1.15$ for a purely magnetic relaxation channel and $^{65}(1/T_1)/^{63}(1/T_1)=(^{65}Q/^{63}Q)^2=0.85$ for a purely quadrupole relaxation channel. In general, the total relaxation rate consists of both contributions. Thus, the ratio of the spin-lattice-relaxation rate for ^{63}Cu and ^{65}Cu can tell us what the dominant relaxation mechanism is.

For $YBa_2Cu_3O_7$, the dominant spin-lattice relaxation mechanism is determined from the ratio of the spin-lattice relaxation rate for ^{63,65}Cu NQR.[12] This is found to be a magnetic hyperfine interaction of copper nuclear spins with antiferromagnetically fluctuating Cu $3d$ electronic spins at high temperature. Then the dominant mechanism crosses over to a quadrupolar interaction due to the electric-field gradient fluctuation at low temperature.[12] The crossover temperature is reported to be 30–50 K for $YBa_2Cu_3O_7$ (YBCO).[12,13]

In this paper we report a measurement of the ratio of ^{63,65}Cu NQR spin-lattice relaxation rates as a function of Zn concentration. From the Zn concentration dependence of this ratio, we can see how the dominant relaxation mechanism varies as the antiferromagnetic correlation between the copper moments are influenced. The core finding from our measurements is that the magnetic contribution to the spin-lattice relaxation rate for the plane copper is reduced whereas the

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quadrupolar contribution is increased at low temperature. This confirms that Zn develops no local moment and consequently the Zn substitution suppresses the antiferromagnetic spin correlation between copper moments in the superconducting plane.

II. EXPERIMENT

Zn-substituted YBCO samples were prepared by the solid-state reaction technique after mixing raw materials of high purity Y_2O_3, $BaCO_3$, CuO, and ZnO at the stoichiometric ratio. We noticed that the high contents of Zn might segregate the superconducting phase leading to a multiphase. So we prepared samples only up to $x=0.09$ of $YBa_2Cu_{3-x}Zn_xO_7$. The samples were ground into fine powders for the ac susceptibility and NQR measurements. The superconducting transition temperatures were measured by a homemade ac susceptometer operating at 1 kHz. The amplitude of magnetic field was estimated to be 0.3 Oe.

The pulse ^{63,65}Cu NQR measurements were carried out for the plane coppers at 100 and 300 K. The phase-alternating pulse sequences were employed to reduce the electromechanical vibration (ring-down) after pulses.[14] The broad spectra were scanned by the point-by-point method at different spectrometer frequencies. Meantime the pulse width was maintained long enough to slice a narrow frequency window. The spin-lattice relaxation time T_1 was measured by the saturation recovery pulse sequence.[14] The spin-spin relaxation time T_2 was measured by the solid-echo pulse sequence. The cryogenic measurements were performed in Oxford continuous flow cryostat (CF1200N).

III. RESULTS AND DISCUSSION

Figure 1 shows temperature dependence of the ac susceptibility for the Zn-doped YBCO, $YBa_2Cu_{3-x}Zn_xO_7$. The superconducting transition temperature decreases rapidly for higher Zn concentration. The derivatives of the susceptibility data are taken to measure the midpoint of the transition and the transition width. The transition width increases for high Zn contents. This is due to inhomogeneity after the Zn substitution. The superconducting onset temperatures are plotted in an inset. The slope of decrease in the transition temperature is found to be -2.84 K/%, which is roughly consistent with the published data, -3.3 ± 0.66 K/%.[8]

^{63,65}Cu NQR spectra of the plane copper in the Zn-doped YBCO at 100 K are shown in Fig. 2. The peak frequency at 100 K decreases slightly as the Zn concentration increases. The NQR line becomes progressively broader for higher Zn substitution. Since the NQR frequency is determined by the product of the nuclear quadrupole moment, which is constant for the ground state of a given nucleus, and the electric-field gradient at the resonating nucleus, the linewidth reflects the inhomogeneity of the electric-field gradient at the copper sites. Thus the broad linewidth indicates that the spatial charge distribution is severely distorted locally at the plane copper sites by the Zn substitution.

Figure 3 shows the spin-lattice relaxation rate $1/T_1$ of ^{63,65}Cu NQR for the plane copper of the Zn-substituted YBCO ($YBa_2Cu_{3-x}Zn_xO_7$) at 300 and 100 K. We note that $1/T_1$ for ^{63}Cu at 100 and 300 K are consistent with the published data.[15] Up to $x=0.09$, the recovery is measured to be single exponential within a high accuracy of data. We note that a nonsingle exponential recovery has been reported by Ishida *et al.*[9] The nonsingle exponential recovery makes the interpretation model dependent and the results may not have a strong footing. Since we thought this was due to the impure phases for a high concentration of Zn, we tried to avoid this problem by sticking to a low concentration of Zn and consequently measured the single exponential recovery.

Ishida *et al.*[9] have reported and analyzed the nonexponential recovery into a double exponential recovery, assuming a

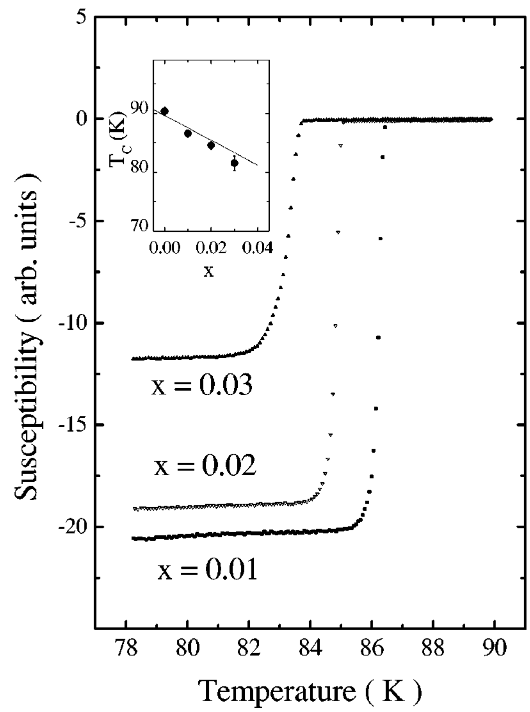

FIG. 1. The ac susceptibility of Zn-doped YBCO ($YBa_2Cu_{3-x}Zn_xO_7$). The inset; T_c versus x.

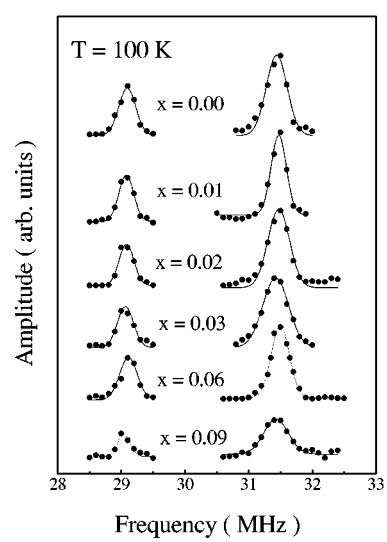

FIG. 2. ^{63,65}Cu NQR spectra of the plane copper in Zn-doped YBCO ($YBa_2Cu_{3-x}Zn_xO_7$) at 100 K. The solid lines are fits to Gaussian line shapes.

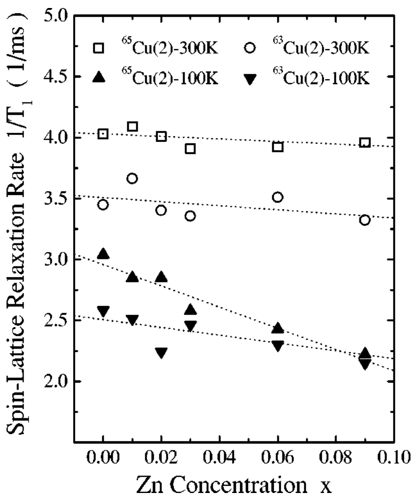

FIG. 3. The spin-lattice relaxation rate $1/T_1$ of ^{63,65}Cu NQR for the plane copper in Zn-doped YBCO ($YBa_2Cu_{3-x}Zn_xO_7$) at 300 and 100 K. The dashed lines are guides for the eye.

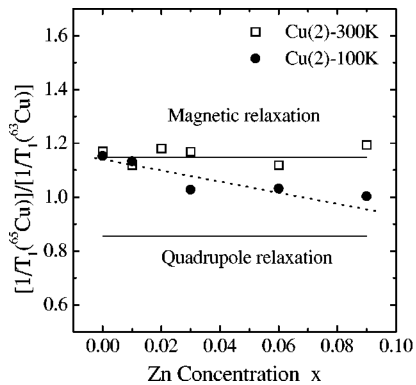

FIG. 4. The ratio of ^{63,65}Cu NQR spin-lattice relaxation rates for the plane copper in Zn-doped YBCO ($YBa_2Cu_{3-x}Zn_xO_7$) at 300 and 100 K. The solid lines are drawn for the purely magnetic and the purely quadrupole relaxations. The dashed line is a guide for the eye.

model where the copper nuclei near Zn relax slowly and the copper nuclei far away from Zn relax quickly. In their data, however, the deviation from a single exponential recovery is not prominent and almost single exponential. In short, two relaxation rates are very close to each other. We think this nonexponential recovery may be extrinsic and reflects the sample inhomogeneity due to the high Zn concentration in their samples.

The spin-lattice relaxation rate at 300 K decreases slowly for the higher Zn concentration. However, the spin-lattice relaxation rate at 100 K decreases very fast for higher Zn concentration. From the ratio of the spin-lattice relaxation times for ^{63}Cu and ^{65}Cu NQR in $YBa_2Cu_3O_7$, it is confirmed that above 50 K the dominant mechanism of the spin-lattice relaxation for the plane copper nuclei is not an electric-field fluctuation but a magnetic-field fluctuation.[12,13] It is also known that the spin-lattice relaxation rate for the plane copper is dominated by the antiferromagnetic spin fluctuation between the copper $3d$ spins.[1] This means that the copper nuclear spins dominantly relax via the magnetic hyperfine interaction with the copper $3d$ moments.

Therefore, the decrease of $1/T_1$ upon Zn doping strongly supports that the spin fluctuation is suppressed by the Zn substitution. This should be due to the absence of local moments at the Zn sites. Namely, the nonmagnetic Zn ion destroys the antiferromagnetic spin correlations between the copper moments. Since the spin-lattice relaxation rate is likely to be enhanced for higher Zn concentration if Zn develops local moments, the decrease of $1/T_1$ upon Zn doping suggests that Zn does not carry local moments.

In the normal state of YBCO, the spin-lattice relaxation rate for copper is given by[16]

$$\frac{1}{T_1} \propto A^2 + n(x) B^2,$$

where A is the hyperfine coupling of the copper nucleus to the on-site Cu $3d$ spin and B is the transfer hyperfine coupling between a nucleus on one Cu site and the electron spin on an adjacent Cu site, which is mediated by the intervening oxygen orbitals. Here $n(x)$ is the number of the neighboring Cu $3d$ moments. Since the antiferromagnetic fluctuation is locally collapsed by the absence of local moment at Zn, $1/T_1$ is reduced by the Zn substitution, as shown in Fig. 3.

Then the larger decrease in $1/T_1$ at 100 K suggests that the suppression of the spin fluctuation is enhanced at low temperature. This can be explained by the temperature dependence of correlation length between the copper $3d$ spins. From ^{63,65}Cu NMR for the plane copper, it is reported that the correlation length increases at low temperatures.[1] The correlation length at 300 K is shorter than the near-neighbor copper distance but that at 100 K is slightly longer than the distance.[1] Thus the Zn substitution suppressing the spin fluctuation affects more copper moments and reduces $1/T_1$ drastically at low temperature. In detail, assuming that all zincs of concentration x replace only the plane coppers, we notice that the average distance between neighboring zincs is 4.7 lattice constant for $x = 0.09$. Assuming that the correlation length between the copper $3d$ moments at 100 K is ~ 2.5 lattice constant,[1] we find that 36% of copper nuclei are influenced by the Zn substitution. Therefore, a large amount of copper nuclei relaxes slowly by the loss of antiferromagnetic spin fluctuation between neighboring copper $3d$ spins.

The spin-spin relaxation rate $1/T_2$ is also single exponential. In addition, the spin-spin relaxation rates are slightly reduced for the high Zn concentration. Since it is known that the spin-spin relaxation is also dominated by the fluctuating local field due to the antiferromagnetic spins,[17] this behavior is consistent with the spin-lattice relaxation rate. Thus both the spin-lattice and the spin-spin relaxation rates of the plane copper NQR are determined by the spin dynamics of antiferromagnetically fluctuating copper moments.

The ratio of the spin-lattice relaxation rate for ^{63,65}Cu NQR is shown in Fig. 4 as a function of Zn concentration. The relaxation mechanism at 300 K is almost purely magnetic due to the antiferromagnetic spin fluctuation. This is consistent with the published data, which reports that the magnetic relaxation dominates above 30 or 50 K.[12,13] Then as the Zn concentration increases, the ratio decreases toward the quadrupole relaxation. However, the relaxation mechanism is not purely quadrupole in origin yet at 100 K. The magnetic relaxation still contributes although it becomes weak. The relaxation mechanism may be purely quadrupole for higher Zn concentration and at lower temperature since the magnetic relaxation is frozen by the formation of cooper pairs. From Fig. 4, it is concluded that the magnetic contribution to the spin-lattice relaxation rate for the plane copper is reduced whereas the quadrupolar contribution is increased at the lower temperature. This is due to a reduction of the antiferromagnetic fluctuation by the Zn substitution and an enhanced contribution from the quadrupole relaxation. This is a consequence of the loss of the local moment by the Zn substitution.

IV. CONCLUSIONS

We have prepared Zn-doped $YBa_2Cu_{3-x}Zn_xO_7$, $x=0\sim0.09$ and performed ac magnetic susceptibility and $^{63,65}Cu$ NQR measurements to probe Zn substitutional effects on the copper $3d$ spin dynamics. The substitution effects are observed in resonant frequencies, linewidths of spectra, and the relaxation rates as well as in superconducting transition temperatures. For the Zn-doped YBCO, $^{63,65}Cu$ NQR frequency of plane copper weakly depends on the Zn concentration but the linewidth becomes much broader for the higher Zn concentration.

The spin-lattice relaxation rate at 300 K decreases slowly as the Zn concentration increases. However, the rate at 100 K drops very fast for higher Zn contents. This suggests that the Zn substituents carry no local moment and suppresses the antiferromagnetic spin fluctuation between the copper $3d$ moments. The larger reduction in the spin fluctuation at 100 K is explained by the increase of the correlation length between the copper $3d$ spins, which causes the more copper $3d$ spins to be influenced by the Zn substitution. The spin-spin relaxation rate also decreases for higher Zn concentration. This is also due to the suppression of the spin fluctuation by the Zn substitution. This decrease is consistent with that of the spin-lattice relaxation rate.

The ratio of $^{63,65}Cu$ spin-lattice relaxation rates indicates that the magnetic relaxation is reduced whereas the quadrupole relaxation is increased at the lower temperature. This strongly confirms that the antiferromagnetic spin fluctuation of the plane copper moments is suppressed significantly by Zn substitution.

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