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Zn and Ni Doping Effects on Antiferromagnetic Spin Fluctuation in $YBa_2Cu_3O_7$

Zn와 Ni의 치환이 $YBa_2Cu_3O_7$의 반강자성적 스핀요동에 주는 효과

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We have performed $^{63,\,65}$Cu nuclear quadrupole resonance (NQR) measurements on Zn and Ni doped $YBa_2Cu_3O_7$ ($YBa_2Cu_{3-x}M_xO_7$, M=Zn or Ni, x = 0.00 ~ 0.09). Doping effects are markedly different in relaxation rates as well as in superconducting transition temperatures. Both the spin-lattice and the spin-spin relaxation rates decrease for Zn doped YBCO. However, those increase for Ni doped YBCO. This contrast in local electronic dynamics provides a clear microscopic evidence that Zn forms no local moment, while Ni develops a local moment. Consequently, the antiferromagnetic spin fluctuation is suppressed by Zn doping whereas it is preserved by Ni doping.

1. Introduction

Nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) have clearly shown that the antiferromagnetic spin fluctuation between the plane copper 3d moments plays a crucial role in development of high temperature superconductivity [1, 2]. 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 [3]. On the other hand, the magnetic interactions between the copper local moments can also be controlled and studied through substitution of copper by magnetic and nonmagnetic ions such as Ni and Zn [4-7]. In contrast to the magnetic impurity effects [8] on BCS type superconductors, the superconducting transition temperature rather slightly decreases after the magnetic Ni substitution into the plane copper sites whereas the nonmagnetic Zn substituent substantially suppresses the transition temperature [9]. This result is often quoted as an evidence supporting that the origin of pairing mechanism might 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 [10-13]. For example, $^{63,\ 65}$Cu NQR and magnetic susceptibility data [10, 11] support that the Zn substituent forms no local moment. On the other hand, ^{89}Y nuclear magnetic resonance (NMR) [12, 13] shows an extra peak after the Zn substitution, which originates from the yttrium sites near the Zn substituent. Then, the linewidth of the extra peak follows a Curie-Weiss increase supporting that Zn carries a local moment. It is suggested [12] that Zn forms a moment possibly in a resonant state of the host copper bands and consequently the size of the moment may be negligible for macroscopic measurements.

In this paper, we address this controversy utilizing $^{63,\ 65}$Cu NQR measurements for Zn and Ni doped YBCO superconductors. Depending on presence and absence of local moments at the substituted sites, the antiferromagnetic spin fluctuation between neighboring copper spins will be locally influenced significantly. This disturbance is going to generate marked difference in local spin dynamics, which can be probed by the spin-lattice and the spin-spin relaxation rates of $^{63,\ 65}$Cu NQR for the plane coppers in YBCO.

2. Experiment

Zn and Ni-substituted YBCO ($YBa_2Cu_{3-x}M_xO_7$, M=Zn or Ni, x=0.0~0.09) samples were prepared by the solid state reaction techniques after mixing raw materials of high purity Y_2O_3, $BaCO_3$, CuO, ZnO and NiO at the stoichiometric ratio. We noted that the high contents of Zn and Ni might segregate the superconducting phase leading to a multiphase. Thus we prepared samples only up to x=0.09 of $YBa_2Cu_{3-x}M_xO_7$ with M=Zn or Ni. The samples were ground into fine powders (~5 μm) and sealed in a nylon sample holder for NQR measurements. The pulse $^{63,\ 65}$Cu NQR measurements were carried out only 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. The broad spectra were scanned by the point-by-point method changing the spectrometer frequency. 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).

3. Results and Discussion

Figure 1 shows the spin-lattice relaxation recovery of ^{63}Cu NQR for plane coppers in Zn doped YBCO at 100 K. The recovery shows non-single exponential decay of NQR signal. For inhomogeneous systems as for these impurity doped YBCOs, the spin-lattice relaxation rate is distributed [14] depending on the local electronic structures and dynamics and consequently shows non-single exponential relaxation of nuclear magnetization. In undoped YBCO, it is known that the spin-lattice relaxation is single exponential and the dominant relaxation process is the antiferromagnetic spin fluctuation between copper 3d moments [1]. Is is also known that Zn substitutes for the plane coppers and

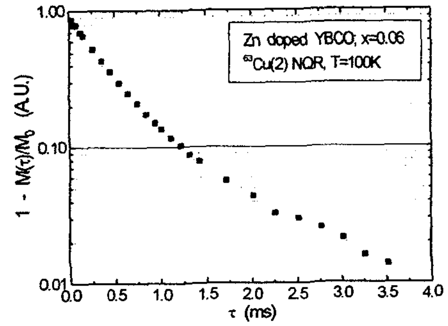

Fig. 1 The spin-lattice relaxation of ^{63}Cu NQR for the plane sites in Zn doped YBCO.

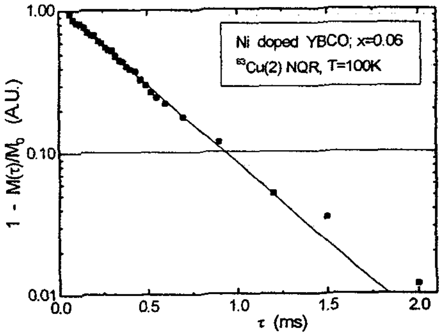

Fig. 2 The spin-lattice relaxation of ^{63}Cu NQR for the plane sites in Ni doped YBCO.

forms no local moment. Then the antiferromagnetic spin correlation between plane copper spins is disrupted and the relaxation rates are different between coppers near and far away from the Zn site resulting non-single exponential decay. Thus the non-single exponential decay for Zn-doped YBCO confirms that Zn forms no local moments. This feature is prominent at low temperature since the antiferromagnetic correlation length between copper moments increases. In contrast, the spin-lattice relaxation for Ni doped YBCO shows a nearly single exponential decay even at low temperature, as shown in Fig. 2. The single exponential decay suggests that the antiferromagnteic correlation between coppers is still preserved after Ni doping since the Ni dopant forms a local moment at the substituted site. The marked difference in the relaxation profiles confirms that Zn and Ni dopants develop significant distintion in local electronic structures including the formation of local moments.

This contrast in formation of local moments for Zn and Ni dopants is also confirmed by the spin-lattice relaxation rate as a function of dopant concentration. Figure 3 and Figure 4 show the spin-lattice relaxation rate of ^{63,} ^{65}Cu NQR for Zn and Ni doped YBCO, respectively. The spin-lattice relaxation rate $1/T_1$ decreases as Zn concentration increases. The reason is that the antiferromagnetic spin fluctuation as a dominant relaxation mechanism is suppressed [15] since the antiferromagnetic correlation between plane coppers is disturbed by the absence of local moments at the zinc sites. For Ni doped YBCO, however, $1/T_1$ increases for higher Ni concentration. This increase is due to the local moment at the Ni site. Generally speaking, a local moment near probing nuclei increases $1/T_1$. Therefore, the clear difference in

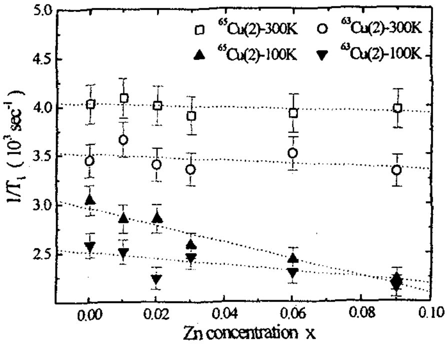

Fig. 3 Zn concentration dependence of the spin-lattice relaxation rate of ^{63,} ^{65}Cu NQR for Zn doped YBCO.

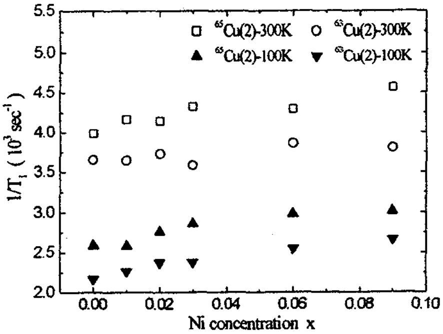

Fig. 4 Ni concentration dependence of the spin-lattice relaxation rate of $^{63,\ 65}$Cu NQR for Ni doped YBCO.

the concentration dependence of $1/T_1$ for Zn and Ni doped YBCO clearly proves that Zn forms no local moment whereas Ni develops a local moment.

The spin-spin relaxation rate $1/T_2$ also shows the same concentration dependence for Zn and Ni doped YBCO. This behavior of $1/T_2$ is also consistent with that of $1/T_1$ since both relaxations are dominated by the antiferromagnetic spin fluctuation [16].

4. Conclusion

We have performed $^{63,\ 65}$Cu nuclear quadrupole resonance (NQR) measurements on Zn and Ni doped $YBa_2Cu_3O_7$ ($YBa_2Cu_{3-x}M_xO_7$, M=Zn or Ni, x = 0.00 ~ 0.09). As the dopant concentration increases, both the spin-lattice and the spin-spin relaxation rates of $^{63,\ 65}$Cu NQR for the plane coppers decrease for Zn-doped YBCO. However, those increase for Ni-doped YBCO. This contrast in local electronic dynamics provides a clear evidence that Zn forms no local moment, while Ni develops a local moment. Due to this difference, the antiferromagnetic spin fluctuation is suppressed by Zn doping whereas it is fairly preserved by Ni doping.

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