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^{63,65}Cu nuclear quadrupole resonance study of Ni-doped $YBa_2Cu_3O_7$

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Abstract

We have prepared pure YBCO ($YBa_2Cu_3O_{7-\delta}$) and Ni-doped YBCO ($YBa_{2-x}La_xCu_{3-x}Ni_xO_{7-\delta}$, $x = 0.1$) samples and performed ^{63,65}Cu nuclear quadrupole resonance (NQR) measurements. La substitution introduced for charge compensation, as well as Ni doping, severely distorts the electric field gradient at the copper sites inducing extra ^{63,65}Cu NQR peaks other than the main peaks, for both the plane and the chain sites. ^{63,65}Cu NQR linewidths for the plane site increased significantly whereas those for the chain site remained similar. Furthermore, both the spin–lattice and the spin–spin relaxation times for the plane copper decreased whereas those for the chain copper increased. The Ni substitutional effects on linewidths and relaxation times confirm that Ni carrying a local moment substitutes for the plane copper.

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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 the 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 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 substitution of magnetic Ni 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 hole.

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It is commonly agreed that the Ni dopant has a local moment [10]. Although various workers are not unanimous on the point [4,9], a number of results indicate that Ni substitutes for the plane copper [5,9,11]. However, the Ni substitutional sites are not decisively known from microscopic measurements such as NMR and NQR. Despite a few NMR reports on Ni-doped YBCO [12–14], crucial evidence regarding the Ni sites is lacking. In this paper, we address this point utilizing ^{63,65}Cu NQR of the plane and the chain sites for Ni-doped YBCO. We have substituted Ni ions for the coppers and measured substitutional effects on ^{63,65}Cu NQR frequencies, linewidths and relaxation times as well as antiferromagnetic interaction. Substitution of Ni into the copper sites in various compositions may lead to significant changes in electronic structure and magnetic character at the neighboring copper sites.

2. Experiment

Sample of composition $YBa_{2-x}La_xCu_{3-x}Ni_xO_{7-\delta}$ with $x = 0.1$ was prepared using solid state reaction techniques. We tried to replace the d^8 Cu^{+3} ion by the isoelectronic d^8 Ni^{+2} ion. Lanthanum was substituted in equimolar amounts with nickel to provide necessary charge compensation, namely, substitution of lanthanum/nickel for Ba^{+2}/Cu^{+3} [15]. The sample preparation procedures for $x = 0.1$–1.0 were published by Thiel et al. [15]. They also reported X-ray diffraction and magnetic susceptibility measurements. There was almost no change in lattice parameters for $x = 0.1$, on which NQR measurements have been performed at room temperature. The superconducting transition temperature T_c, determined from zero resistivity and the diamagnetic transition, decreased by ~ 7 K for $x = 0.1$ [15]. For the larger x, T_c was reduced down to 29 K for $x = 0.5$.

We noticed that the high content of Ni dopant segregated the superconducting phase leading to a multiphase. Thus, we took only the $x = 0.1$ sample of $YBa_{2-x}La_xCu_{3-x}Ni_xO_{7-\delta}$ for ^{63,65}Cu NQR measurements. About 2 g of finely ground particles (~ 5 μm) was sealed in a nylon sample holder. 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 [16]. The spin–spin relaxation time, T_2, was measured by the spin–echo pulse sequence ($\pi/2$–τ–π–τ–echo). The length of the $\pi/2$ pulse was adjusted to maximize the echo height. To get rid of a spurious pulse ring-down prevalent for the short τ, the averaging sequence of alternating echo-addition followed by inverted-echo-subtraction [17] was employed.

3. Results and discussion

Fig. 1(a) is ^{63,65}Cu NQR spectrum for undoped YBCO. Two isotopes of copper, ^{63}Cu and ^{65}Cu, exist in nature with respective abundances of 69% and 31%. Since the quadrupole moments for ^{63}Cu and ^{65}Cu are similar ($^{63}Q/^{65}Q = 0.211/0.195 = 1.082$), the NQR spectrum always shows two peaks with ^{63}Cu NQR on the high frequency side. In a formula unit of $YBa_2Cu_3O_7$, there are two different sites for three coppers; two plane sites, Cu(2), in the superconducting CuO_2 plane and one chain site, Cu(1), in the CuO chain. Thus, ^{63,65}Cu NQR spectrum for undoped YBCO shows four resonance peaks, namely, ^{63,65}Cu(2) NQR at 31.2 and 28.85 MHz, respectively, whereas ^{63,65}Cu(1) NQR at 22.2 and 20.55 MHz, respectively, in agreement with other results [12,18–20]. We found out that the NQR signal intensity as well as the spectral width are very much dependent on sample quality, possibly on the oxygen stoichiom-

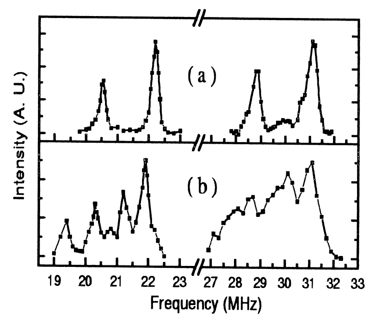

Fig. 1. ^{63,65}Cu NQR spectra of undoped ($YBa_2Cu_3O_{7-\delta}$) (a), and Ni-doped YBCO ($YBa_{2-x}La_xCu_{3-x}Ni_xO_{7-\delta}$, $x = 0.1$) (b) at room temperature.

etry. For the best sample of our $YBa_2Cu_3O_{7-\delta}$, the full-width-at-half-maximum (FWHM) was 250 kHz for ^{63,65}Cu(2) NQR and 150 kHz for ^{63,65}Cu(1) NQR. This indicates good quality of the samples used in comparison with other measurements [12,18–20]. However, the NQR peak frequencies hardly vary from sample to sample.

^{63,65}Cu NQR spectrum for Ni-substituted YBCO ($YBa_{2-x}La_xCu_{3-x}Ni_xO_{7-\delta}$, $x = 0.1$) was significantly changed, as shown in Fig. 1(b). The NQR intensity was very weak and broad. Extra NQR peaks, other than the main peaks close to those for undoped YBCO, showed up for both plane and chain sites as a result of Ni substitution. The main peaks were at 31.1 and 28.7 MHz, respectively, for ^{63,65}Cu(2) and at 21.9 and 20.3 MHz for ^{63,65}Cu(1), respectively. Thus, compared with the undoped YBCO, the peak frequencies for ^{63,65}Cu(2) decreased by 0.1 MHz whereas those frequencies for ^{63,65}Cu(1) decreased by 0.3 MHz. It is obvious that these NQR came from the copper nuclei, which were far away and weakly influenced by the Ni substitution. On the other hand, the extra peaks showed up at much lower resonance frequencies. The extra peaks were at 30.1 and 27.8 MHz, respectively, for ^{63,65}Cu(2) and at 21.2 and 19.5 MHz for ^{63,65}Cu(1), respectively. Apparently, these peaks originated from the copper near the substituted Ni.

As for the site information of Ni substituents, if Ni substitutes for either the plane copper site or the chain copper site, then it is expected, based on a simple picture, that the extra peak appears only for the substituted site. Since the extra peaks are observed for both the plane and the chain sites, it seems that Ni unpreferentially substitutes for the chain and the plane sites. However, we note that not only Ni but also La, introduced for the charge balance, may influence copper NQR. In fact, since La sits in an intervening BaO layer between plane and chain coppers, it is most likely that La perturbs both the plane and the chain sites. Thus, the appearance of extra peaks does not reflect site information of Ni substituents. The larger decrease of the main peak frequencies for the chain sites is likely related to the La substitution.

It is known from magnetic susceptibility measurements that Ni substituents in YBCO carry local moments [10]. Thus, the Ni substituents are expected to significantly smear out the NQR peaks of neighboring coppers due to the dipolar field of local moments. Usually even small magnetic fields, for example, dipolar field from nearby magnetic mo-

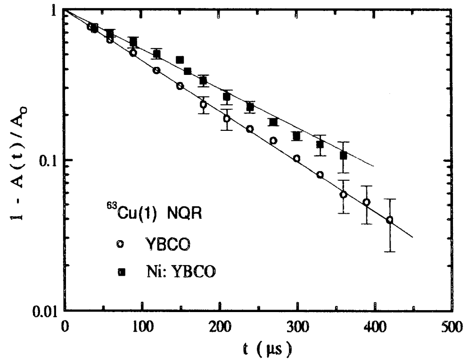

Fig. 3. The spin–lattice relaxation of ^{63}Cu NQR for the chain site in undoped and Ni-doped YBCO.

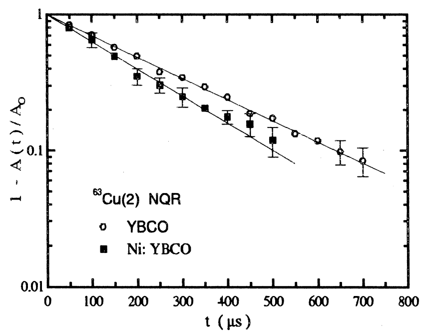

Fig. 2. The spin–lattice relaxation of ^{63}Cu NQR for the plane site in undoped and Ni-doped YBCO.

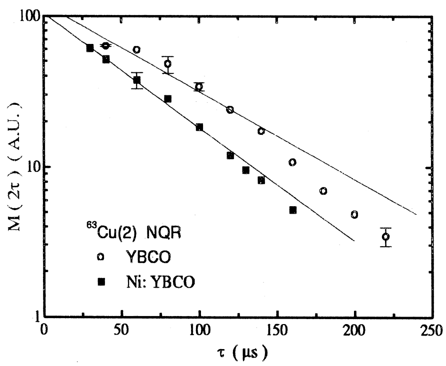

Fig. 4. The spin–spin relaxation of ^{63}Cu NQR for the plane site in undoped and Ni-doped YBCO.

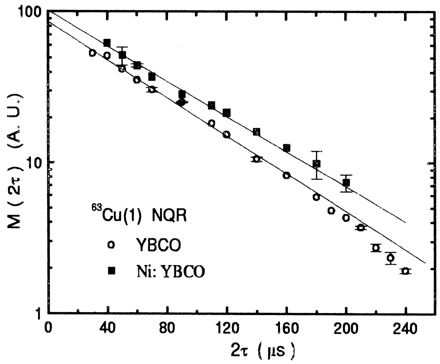

Fig. 5. The spin–spin relaxation of ^{63}Cu NQR for the chain site in undoped and Ni-doped YBCO.

ments of substituents, can tremendously broaden NQR lines [16]. We noticed that the linewidths of ^{63,65}Cu(2) NQR significantly increased for Ni-doped YBCO whereas those of ^{63,65}Cu(1) NQR remained similar. This contrast in linewidth is dramatic. Consequently, the linewidths strongly confirmed that Ni preferentially substitutes for the plane copper.

The NQR spin–lattice relaxation time, T_1, provides information about dynamics of electron system and so we can possibly relate effects on relaxation time to changes in local electronic structure. In YBCO, it is widely accepted that the antiferromagnetic spin fluctuation between Cu 3d spins in the CuO_2 superconducting plane dominates the spin–lattice relaxation of both ^{63,65}Cu(2) and ^{63,65}Cu(1) NQR [1]. Fig. 2 shows the spin–lattice relaxation of ^{63}Cu(2) NQR for undoped YBCO and Ni-doped YBCO. The spin–lattice relaxations were measured for the main peaks of ^{63}Cu(2) NQR, namely, at 31.2 MHz for undoped YBCO and at 31.1 MHz for Ni-doped YBCO. The spin–lattice relaxation recoveries for undoped and Ni-doped YBCOs are a single exponential over a decade of amplitude decay. Fig. 2 clearly exhibits the Ni substitutional effect on the spin–lattice relaxation for the main peaks of ^{63}Cu(2) NQR. Ni substitution decreases T_1.

Fig. 3 shows Ni substitutional effect on the spin–lattice relaxation of ^{63}Cu(1) NQR. The spin–lattice relaxations were measured for the main peaks of ^{63}Cu(1) NQR, namely, at 22.2 MHz for undoped YBCO and at 22.0 MHz for Ni-doped YBCO. Fig. 3 clearly shows that T_1 of ^{63}Cu(1) NQR increases due to the Ni substitution. Thus, T_1 of ^{63}Cu(2) NQR decreases whereas T_1 of ^{63}Cu(1) NQR increases after Ni substitution. It is well known that the local moments make T_1 short by the local field fluctuation due to the thermal excitation of moments [16]. In addition, it is established from the isotopic ratio of T_1, namely $^{63}T_1/^{65}T_1$, that in undoped YBCO the plane copper nuclei relax through the magnetic channel due to the antiferromagnetic spin fluctuation whereas the chain coppers relax through the quadrupolar channel due to the fluctuation of electric field gradient [21]. Thus, the contrast in T_1 for Ni-doped YBCO, namely, decrease of T_1 for ^{63}Cu(2) vs. increase of T_1 for ^{63}Cu(1), confirms that Ni carrying local moments preferentially substitutes not for the chain copper but for the plane copper. This result is consistent with the interpretation based on the linewidth.

The spin–spin relaxation time T_2 also probes the local field fluctuation. In YBCO, the antiferromagnetic spin fluctuation also contributes to T_2 [22]. In addition to that, the indirect exchange interaction between Cu nuclear spins, mediated by intervening oxygen holes, play a role [22,23]. Combination of two relaxation processes generates non-single expo-

Table 1
^{63}Cu NQR data of undoped ($x = 0$) and Ni-doped YBCO $x = 0.1$) at room temperature

	Peak	Frequency (MHz)	T_1 (μs)	T_2 (μs)
^{63}Cu(1) NQR				
Undoped YBCO	single narrow	22.2	132 ± 10	63 ± 5
Ni-doped YBCO	double narrow	21.9	155 ± 10	78 ± 5
^{63}Cu(2) NQR				
Undoped YBCO	single narrow	31.2	290 ± 10	75 ± 5
Ni-doped YBCO	double broad	31.1	241 ± 10	57 ± 5

nential decay of spin–spin relaxation recovery of ^{63}Cu(2) NQR for undoped YBCO [22], as shown in Fig. 4. T_2 is measured only for the main peak of ^{63}Cu(2) NQR, as for T_1. For Ni-doped YBCO, T_2 of ^{63}Cu(2) NQR becomes shorter in Fig. 4. The shorter T_2 originates from the local field fluctuation of neighboring Ni moments and has the same origin as the shorter T_1 of ^{63}Cu(2) NQR. Therefore, the Ni substitutional effect on T_2 also suggests that Ni carrying moments substitutes mainly for the plane coppers. On the other hand, the Ni substitutional effect on T_2 is opposite for the chain site. As shown in Fig. 5, T_2 of ^{63}Cu(1) NQR increases for Ni-doped YBCO. Thus, this contrast in T_2, namely decrease of T_2 for ^{63}Cu(2) vs. increase of T_2 for ^{63}Cu(1), is the same as in T_1. In consequence, the contrast in T_2 also strongly confirms that Ni carrying moments substitute for the plane coppers. In total, linewidth, T_1 and T_2 consistently support that Ni preferentially replaces the plane copper. For the extra peaks of NQR, neither T_1 nor T_2 was measured because of their poor signal-to-noise ratio. The NQR data are summarized in Table 1.

4. Conclusions

We have prepared pure YBCO ($YBa_2Cu_3O_{7-\delta}$) and Ni-doped YBCO ($YBa_{2-x}La_xCu_{3-x}Ni_xO_{7-\delta}$, $x = 0.1$) and performed ^{63,65}Cu NQR measurements in order to search for microscopic evidences about the Ni substitutional site. The Ni doping effects were observed in resonant frequencies and linewidths of NQR spectra, and spin–lattice and spin–spin relaxation times. The main peaks similar to the peaks for pure YBCO were weakly disturbed by the Ni substitution. However, the extra peaks showed up as results of the Ni substitution. These extra peaks appeared not only for the plane sites but also for the chain sites. The appearance of these extra peaks is interpreted to have originated from the La substitution, which was introduced for charge balance. On the other hand, the linewidth after Ni substitution increased significantly for the plane sites whereas it remained unchanged for the chain sites. This contrast is dramatic. Since Ni is well known to carry a local moment in YBCO, this difference in the Ni substitutional effect on linewidth strongly confirms that Ni preferentially substitutes for the plane sites. Furthermore, the spin–lattice and the spin–spin relaxation times decreased for the plane sites whereas those times increased for the chain sites after Ni substitution.

These contrasts in T_1 and T_2 also support that Ni carrying local moments substitutes for the plane copper and decreases both T_1 and T_2.

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