Ni-substituted sites and the effect on Cu electron spin dynamics of YBa$_2$Cu$_{3-x}$Ni$_x$O$_{7-\delta}$

Y. Itoh$^{1,2}$, S. Adachi$^1$, T. Machi$^1$, Y. Ohashi$^3$, and N. Koshizuka$^1$

$^1$Superconductivity Research Laboratory, International Superconductivity Technology Center, 1-10-13 Shinonome, Koto-ku Tokyo 135-0062, Japan
$^2$Japan Science and Technology Corporation, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan
$^3$Institute of Physics, University of Tsukuba, Ibaraki 305-8571, Japan

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We report Cu nuclear quadrupole resonance experiment on magnetic impurity Ni-substituted YBa$_2$Cu$_{3-x}$Ni$_x$O$_{7-\delta}$. The distribution of Ni-substituted sites and its effect on the Cu electron spin dynamics are investigated. Two samples with the same Ni concentration $x=0.10$ and nearly the same oxygen content but different $T_c$'s were prepared: One is an as-synthesized sample ($7-\delta=6.93$) in air ($T_c\approx 80K$), and the other is a quenched one ($7-\delta=6.92$) in a reduced oxygen atmosphere ($T_c\approx 70K$). The plane-site $^{63}$Cu(2) nuclear spin-lattice relaxation for the quenched sample was faster than that for the as-synthesized sample, in contrast to the $^{63}$Cu(1) relaxation that was faster for the as-synthesized sample. This indicates that the density of plane-site Ni(2) is higher in the quenched sample, contrary to the $^{63}$Cu(1) relaxation, which was faster for the as-synthesized sample. From the analysis in terms of the Ni-induced nuclear spin-lattice relaxation, we suggest that the primary origin of suppression of $T_c$ is associated with nonmagnetic depairing effect of the plane-site Ni(2).

Magnetic impurity causes depairing in both $s$-wave and $d$-wave superconductivity. Complete suppression of the superconducting transition temperature $T_c$ is observed for Ni-doped La$_{2-x}$Sr$_x$CuO$_4$ and YBa$_2$Cu$_3$O$_6$, somewhat more weakly than for Zn-doped ones. Ni impurity in the high-$T_c$ cuprate superconductor carries a localized moment, because the uniform spin susceptibility with Curie or Curie-Weiss law is observed. The depairing effect of potential scatterer Zn on the $d$-wave superconductivity is a natural consequence from breakdown of Anderson’s theorem. For YBa$_2$Cu$_3$O$_{7-\delta}$ with the optimized $T_c=92K$ however, the decrease of $T_c$ per Ni concentration is smaller than that per Zn concentration. Figure 1(a) shows the impurity doping dependence of $T_c$ for various high-$T_c$ superconductors with Ni or Zn. The decrease of $T_c$ by Ni doping for YBa$_2$Cu$_3$O$_{7-\delta}$ is smallest among these compounds with Ni in Fig. 1(a). This small decrease of $T_c$ by Ni doping for YBa$_2$Cu$_3$O$_{7-\delta}$ was attributed to a weak scattering of conducting carriers by Ni impurities (Born scatterer) or to a softening of pairing frequency itself. Nevertheless, it has been suspected that only a part of the doped Ni impurities is substituted for the plane Cu(2) site and that the remaining part is for the chain Cu(1) site (see the references in Ref. [18]). The bulk $T_c$ is considered to be determined by the amount of the in-plane Ni(2) impurity. One should note that YBa$_2$Cu$_3$O$_{7-\delta}$ has two crystallographic Cu sites, i.e. the chain Cu(1) and the plane Cu(2) sites. The recent observation of an in-plane anisotropy of optical conductivity for detwinned single crystal YBa$_2$Cu$_{3-x}$Ni$_x$O$_{7-\delta}$ indicates the existence of the chain-site Ni(1) [19]. A microscopic study on the selective substitution of Ni impurity is therefore of interest.

Synthesis of oxides under reduced oxygen partial pressure is frequently effective in controlling cation solid solution, e.g. to synthesize the superconducting La$_{1+y}$Ba$_2$Cu$_{3-y}$O$_{7-\delta}$ [20], or to optimize the superconducting critical current density or the irreversible magnetic field of Nd$_{1+y}$Ba$_2$Cu$_3$O$_{7-\delta}$ with optimal oxygen content [5]. They synthesized two series of YBa$_2$Cu$_{3-z}$Ni$_z$O$_{7-\delta}$ samples having the different $T_c$’s per Ni concentration. Figure 1(b) shows the Ni doping dependence of $T_c$ of their samples. Here, we focus on two samples with the same Ni concentration $x=0.10$ ($z=0.033$ in Fig. 1(b)) and nearly the same oxygen content but different $T_c$. For convenience, let us call one sample with $T_c\approx 80K$ ($7-\delta=6.93$) as an as-synthesized one, because it was synthesized in flowing oxygen gas without quenching treatment, and the other sample with $T_c\approx 70K$ ($7-\delta=6.92$) a quenched one, because it was the as-synthesized sample once again fired and quenched in a reduced oxygen atmosphere at 800 °C. The details are given in Ref. [18]. Ni prefers the higher coordination of oxygen atoms [23,24]. The plane-site Cu(2) is located in the pyramid with five oxygen ions, whereas the chain-site Cu(1) is coordinated with two, three, or four nearest neighbor oxygen ions. The two series of samples with different $T_c$ suggest that the distribution of Ni-substituted sites over Cu(1) and Cu(2) sites is changed through synthesis under the reduced oxygen atmosphere.

In this paper, we report the measurements of Cu(1) and Cu(2) nuclear quadrupole resonance (NQR) spectra and nuclear spin-lattice relaxation curves, to study microscopically the distribution of Ni-substituted sites for the above mentioned two samples (as-synthesized and quenched ones). The observed difference in the $^{63}$Cu nuclear spin-lattice relaxation at Cu(1) and Cu(2) in the...
two samples must be a Ni doping effect. From the Cu NQR measurements, we give proof that the heat treatment in reduced oxygen atmosphere results in a redistribution of the Ni atoms in YBa$_2$Cu$_{3-x}$Ni$_x$O$_{7-δ}$.

Two samples with precisely the same mole number could not be prepared, because some parts of the samples have already been used for the characterization [15]. Hence, quantitative comparison of the relative intensity of Cu NQR spectra could not be made to estimate the relative number of the observed nuclei. The nuclear spin-lattice relaxation is independent of the sample volume and is relatively more sensitive to the impurity than the intensity of NQR spectrum. The powder samples were coated in paraffin oil. A coherent-type pulsed spectrometer was utilized for the zero-field Cu NQR measurements.

The Cu NQR frequency spectra with quadrature detection were measured by integration of the spin-echoes as a function of rf frequency. The Cu nuclear spin-lattice relaxation curves were measured by an inversion recovery function of rf frequency. The Cu nuclear spin-echo amplitude $M(t)$ was recorded as a function of time interval $t$ after an inversion $π$ pulse, in a $π - t - π/2 - π$-echo sequence, and $M(∞)$ was also recorded in a $π/2 - π$-echo sequence (no inversion pulse) as usual [11,12,24,25].

Figure 2 shows the Cu NQR spectra at $T=4.2$ K. The amount of the as-synthesized sample is more than that of the quenched one, nevertheless the intensity of Cu(1) NQR spectra for the as-synthesized sample was weaker than that for the quenched one. But, we could not find qualitative difference in the line profiles of Cu NQR spectra between two samples.

Figure 3 shows the $^{63}$Cu nuclear spin-echo recovery curves (spin-lattice relaxation curves) $p(t) ≡ 1 - M(t)/M(∞)$ for Ni-doped samples at $T=4.2$ K. Inset figures show the recovery curves for pure (impurity-free) YBa$_2$Cu$_3$O$_{6.98}$ ($T_c=92$ K). Solid curves are the least-squares fitting results using the theoretical function described below. First, from comparison with inset figures, all the recovery curves for both Ni-doped samples recover more quickly than those for pure YBa$_2$Cu$_3$O$_{6.98}$. Thus, Ni impurities distribute over both sites of Cu(1) and Cu(2). Second, the Cu(2) nuclear spin-echo signal recovers faster in the quenched sample than in the as-synthesized one, whereas the Cu(1) nuclear spin-echo signal recovers slower in the former than in the latter. The Cu(2) nuclear spin-echo signal is affected in the quenched sample more than in the as-synthesized one, whereas the Cu(1) is vice versa. Thus, it is natural to conclude that the amount of Ni(2) in the quenched sample is more than that in the as-synthesized one and that of Ni(1) is vice versa.

The $^{63}$Cu nuclear spin-echo recovery curves for Ni-doped samples in Fig. 3 are nonexponential functions. For quantitative discussion, we analyzed the experimental recovery curve $p(t)$ by the exponential function times a stretched exponential function $p(t) = p(0)\exp[-wt/(T_1)_{HOST} - \sqrt{wt/τ_1}]$ ($p(0)$, $(T_1)_{HOST}$ and $τ_1$ are the fit parameters, and $w=3$ at Cu(2) and $w=1$ at Cu(1)), after the dilute magnetic alloy YBa$_2$Cu$_3$O$_{6.98}$ with Ni impurities [24]. The multiplicative numerical factor $w$ is introduced to conform to the conventional expression of $T_1$ [27], and it is not essential in the below discussion. Here, $w = 3$ is defined for the Cu(2) NQR $T_1$ under a uniaxial electric field gradient. The Cu(1) site is under an asymmetric electric field gradient [28,29], so that all the $x$-, $y$-, and $z$-components of the fluctuating local field contribute to the Cu(1) NQR $T_1$. Then, we use a simple $w=1$. $(T_1)_{HOST}$ is the Cu nuclear spin-lattice relaxation time due to the host Cu electron spin fluctuation via a hyperfine coupling. $τ_1$ is the impurity-induced nuclear spin-lattice relaxation time via a longitudinal direct dipole coupling or a two-dimensional Ruderman-Kittel-Kasuya-Yosida interaction [30].

We have confirmed no significant contribution from nuclear spin diffusion by measuring $^{63}$Cu isotope dependence and pulse-strength $H_c$ dependence of the recovery curves [31]. Although for the heavily impurity-doped system [12] or spin glass system [32] where it is hard to assign separately the host and the guest contributions, a single stretched exponential function $p(t) = p(0)\exp[-(t/τ_1)^α]$ with a variable exponent $α$ might be appropriate, we believe that the present model with two time constants, $(T_1)_{HOST}$ and $τ_1$, is minimal and appropriate for the $x=0.10$ samples.

Figure 4 shows the temperature dependence of the estimated $(1/T_1)_{HOST}$ (a) [(c)] and of $1/τ_1$ (b) [(d)] at $^{63}$Cu(2) [$^{63}$Cu(1)]. Below $T_c$, the Ni-induced relaxation component (stretched exponential part) is predominant both at Cu(1) and Cu(2). In Figs. 4(b) and 4(d), the Ni-induced relaxation rate $1/τ_1$ of Cu(2) for the quenched sample is more enhanced than that for the as-synthesized one, whereas that of Cu(1) is vice versa. In Fig. 4(b), the upturn of $1/τ_1$ of Cu(2) below 10 K for the as-synthesized sample is consistent with the upturn of an initial relaxation rate $1/T_{1a}$ reported in Ref. [24]. In Fig. 4(d), the difference in $1/τ_1$ of Cu(1) between the two samples with Ni is larger at lower temperatures than about 30 K. It is hard to estimate precisely the small $1/τ_1$ and its difference above about 30 K, where the signal-to-noise ratio of Cu(1) NQR is poor in the Ni-doped samples.

In Fig. 4(a), the host relaxation rate $(1/T_1)_{HOST}$ of Cu(2) in the as-synthesized and the quenched samples decreases more steeply than that in pure YBa$_2$Cu$_3$O$_{6.98}$, as the temperature is decreased below $T=18$–20 K and below $T=25$–30 K, respectively. The dashed lines are $T^3$ functions characteristic of $d$-wave superconductivity. The steep decrease of $(1/T_1)_{HOST}$ and the upturn of $1/τ_1$ is also observed for YBa$_2$Cu$_{4-x}$Ni$_x$O$_6$ with $x=0.12$ ($T_c=15$ K) [24]. It is theoretically suggested that the spin-orbit coupling between an itinerant electron and a Ni local moment induces a local superconducting state with a different order parameter ($d_{xy}$-wave symmetry) around Ni in
the \(d_{x^2-y^2}\)-wave superconducting state \(\bar{\omega}\). The steep decrease of \((1/T_1)_{\text{HOST}}\) far below \(T_c\) may indicate a Ni-induced impurity band associated with the different order parameter, more gapped on the Fermi surface than a pure \(d_{x^2-y^2}\)-wave gap.

Figure 5 shows the temperature dependence of \((1/T_1)_{\text{HOST}}\) (a) and \(1/\tau_1\) (b) at Cu(2) in linear scale to show up the above \(T_c\) data. The host \((1/T_1)_{\text{HOST}}\) of Cu(2) above \(T_c\) is nearly independent of Ni doping, whereas \(1/\tau_1\) increases with decreasing \(T_c\). In general, \(1/\tau_1\) is an increasing function of the impurity concentration \(N_f\). Thus, the observed increase of \(1/\tau_1\) indicates the systematic increase of the in-plane Ni(2) concentration \(x_{\text{plane}}\).

In the theoretical model of superconducting pairing mediated by antiferromagnetic spin fluctuations, the external deparing effect on \(T_c\) is written by \(T_c = T_{c0} - \Delta T_c\) with \(T_{c0} \sim \Gamma_0(Q)/\Gamma_0(Q)\) is the host antiferromagnetic spin-fluctuation frequency, and \(\chi_0(Q)\) is the static staggered spin susceptibility) \[33\,37\] and with \(\Delta T_c \propto x_{\text{plane}}\). In the spin-fluctuation theory \[39\], one can obtain \((1/T_1)_{\text{HOST}} \propto TC/(T + \Theta)\) \((C \propto \chi_0(Q)/\Gamma_0(Q)\) and \(\Theta \propto \Gamma_0(Q)\) \[14\]) in the leading order. The actual fit result by this function is the dotted curve in Fig. 5(a). Thus, the quantitative temperature dependence of \((1/T_1)_{\text{HOST}}\) tells us the characteristic spin-fluctuation parameters, \(\chi_0(Q)\) and \(\Gamma_0(Q)\), which describe the pairing interactions. The nearly Ni-independent \((1/T_1)_{\text{HOST}}\) in Fig. 5 indicates that the host spin-fluctuation spectrum is nearly invariant under Ni doping. In Ref. \[3\], the host \((1/T_1)_{\text{HOST}}\) was estimated to be systematically enhanced by Ni doping, which was regarded as evidence for softening of the spin-fluctuation frequency \(\Gamma_0(Q)\) and for the central origin to reduce \(T_c\). However, our analysis indicates that the Ni-enhanced Cu(2) nuclear spin-lattice relaxation comes from the extra relaxation in the stretched exponential part. The central origin to reduce \(T_c\) is the external pair braking effect due to the increase of the in-plane Ni(2) concentration \(x_{\text{plane}}\) in \(\Delta T_c\). This is consistent with the original result for YBa\(_2\)Cu\(_4-x\)Ni\(_2\)O\(_8\). However, it is still hard to estimate the quantitative value of \(x_{\text{plane}}\).

Here, we analyze the temperature dependence of \(1/\tau_1\) and discuss the pair breaking mechanism of Ni. If an impurity spin-spin relaxation process dominates the impurity spin correlation, \(1/\tau_1\) may not change with temperature \[28\]. The widely known expression of \(1/T_1\) or \(1/\tau_1 \propto (A/h)^2 S(S+1)/\omega_e A\) is the coupling constant of the nuclear moment to an electron, \(S\) is the electron spin, \(\omega_e\) is the exchange frequency of mutual spin interaction) is derived from exchange narrowing limit \[27\,11\]. However, the estimated \(1/\tau_1\) changes with temperature as in Figs. 4(b) and 4(d). This indicates a significant contribution from an impurity spin-lattice relaxation process.

The temperature dependences of \(1/\tau_1\) far below \(T_c\) in Figs. 4(b) and 4(d) are different between two Ni-doped samples. Both the impurity spin-lattice relaxation rate \(\Gamma_{\text{SS}}\) and the impurity spin-spin relaxation rate \(\Gamma_{\text{SS}}\) contribute to the actual total impurity relaxation rate \(\Gamma_{\text{L}}\), e.g. \(\Gamma_{\text{L}} = \Gamma_{\text{SL}} + \Gamma_{\text{SS}}\). As temperature is decreased, \(\Gamma_{\text{SL}}\) decreases moderately but rapidly below \(T_c\) \[12\,13\], and then \(\Gamma_{\text{SS}}\) can play an important role in \(\Gamma_{\text{L}}\). In general, \(\Gamma_{\text{SS}}\) is proportional to the number density of impurity \(x_{\text{imp}}\) but \(\Gamma_{\text{SL}}\) is independent of \(x_{\text{imp}}\), and \(1/\tau_1\) is proportional to \(x_{\text{imp}}^2 S(\omega_N/\Gamma_L)\) \((S(\omega_N/\Gamma_L)\) is the impurity magnetic spectral function at the nuclear resonance frequency \(\omega_N/2\pi\)) \[26\,27\]. Thus, the difference in \(1/\tau_1\) may result from the different weight of \(\Gamma_{\text{SS}}\) with \(x_{\text{imp}}\).

In the below analysis, however, we neglect \(\Gamma_{\text{SS}}\) and then the difference in the temperature dependence of \(1/\tau_1\) for simplicity.

For an isolated local moment system in a conventional metal, the dynamical spin susceptibility as a function of frequency \(\omega/2\pi\) is expressed by \(\chi(q,\omega) = \chi_L/(1-i\omega/\Gamma_L)\), where \(\chi_L \propto S(S+1)/T\) is the static spin susceptibility and \(\Gamma_L = \alpha T = 4\pi(J_N F)^2 k_B T/\hbar J\) \((J\) is the coupling constant of the localized moments to the band, and \(J_N F\) is the density of states at the Fermi level per spin) is the impurity fluctuation frequency due to Korringa relaxation \[14\]. Then, one obtains \(1/T_1 \propto \Gamma_L/\omega_N\) \((\omega_N = \omega_N(x_{\text{imp}})\) \(\propto x_{\text{imp}}\). Since \(1/\tau_1 \propto \omega_N/\alpha\) at high temperatures \((T \gg \omega_N/\alpha)\) and \(1/\tau_1 \propto \omega_N^2/\alpha\) at low temperatures \((T \ll \omega_N/\alpha)\), then \(1/\tau_1\) takes a maximum value at \(T = \omega_N/\alpha\) \((\Gamma_L = \omega_N)\).

In Figs. 4(b) and 4(d), \(1/\tau_1\) of \(63\text{Cu}(2)\) and of \(63\text{Cu}(1)\) takes a maximum at about 60 K and 10–20 K, respectively, which can be associated with the maximum at \(T = \omega_N/\alpha\). Assuming the Korringa relaxation \(\Gamma_L = 4\pi(J_N F)^2 k_B T/\hbar\) and putting \(\Gamma_L = \omega_N = 22\) MHz for Cu(1) at \(T = 10\) K and \(\Gamma_L = 31.5\) MHz for Cu(2) at \(T = 60\) K, one obtains \(J_N F = 0.5 = \bar{\omega}/\Delta_{\text{max}} = 0.003\) for Cu(1) and \(= 0.0014\) for Cu(2). From a typical value of \(N_F = 1.5\) states/eV-spin direction, \(|J| = 1.9\) meV for Cu(1) and 0.94 meV for Cu(2). The actual maximum of \(1/\tau_1\) takes place in the superconducting state. Thus, replacing the Korringa term \(k_B T\) by a \(d\)-wave gapped term \(k_B T/(\Delta_{\text{max}}^2) = 2(\Delta_{\text{max}} = 8k_B Tc)^{1/4}\) one estimates \(|J_N F| = 0.009\) and then \(|J| = 5.8\) meV for Cu(2) (if taking into account the effect of the antiferromagnetic spin correlation, one gets a smaller \(|J|\)). The estimated magnitude of \(|J|\) is smaller than the in-plane exchange interaction \(J_{x_{\text{Ni}}-x_{\text{Ni}}} = 11-31\) meV of \(\text{La}_2\text{NiO}_{4+\delta}\) \[43\,48\], \(|J_{\text{Cu}-Cu}| = 150\) meV of \(\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}\) \[41\], or a typical 4s-3d exchange interaction \(|J_{\text{ad}}| \sim 0.1\) eV. Since \(|\pi J_N F S| = 0.03 < L_0\) the decrease of \(T_c\) due to the magnetic scattering can be calculated within the lowest order Born approximation \[48\]. From \(\Delta T_c = 0.25\pi^2 x_{\text{plane}} N_F J^2 S(S+1)/k_B\) with \(S=1\) in a \(d_{x^2-y^2}\)-wave superconductor \[4\], the sole occupation at Cu(2) \((x_{\text{plane}}=x/2=0.05)\) in the quenched sample yields \(\Delta T_c = 0.08\) K at most. This value is smaller than the observed \(\Delta T_c \sim 20\) K in the quenched sample by a factor.
$\sim$250, suggesting that magnetic pair breaking is not the mechanism of suppression of $T_c$ in YBa$_2$Cu$_{3-x}$Ni$_x$O$_{7-\delta}$ (similar estimation for Zn doping is seen in Ref. [51]).

Here, one may doubt the assumption of $\Gamma_L=\omega_N$ at the temperature of maximum $1/\tau_1$. Instead of $\Gamma_L=\omega_N$, one may associate the maximum of $1/\tau_1$ with a minimum behavior of $\Gamma_L(\gg \omega_N)$ as a crossover from the high temperature $\Gamma_{SL}$ to the low temperature $\Gamma_{SS}$. As mentioned above, $\Gamma_{SS}$ is proportional to $x_{\text{plane}}$, so that the crossover temperature must increase with increasing $x_{\text{plane}}$. However, the temperature of maximum $1/\tau_1$ is nearly the same in two samples. Thus, this scenario is unlikely. In passing, if the Ni spin freezing temperature $T_M \sim 1.5$ K ($x \sim 0.09$) in Ref. [52] is assigned to the maximum temperature $T = \omega_N/\alpha$, one obtains $|JN_F|=1.9$ and then $|J|=1.3$ eV. This magnitude of $|J|$ is too large, although it can easily reproduce the observed $\Delta T_c$. In addition, the Ni spin fluctuation frequency $\Gamma_L$ increases up to $\sim 20$ meV at $T_c$ due to the large $|J|$, so that the neutron scattering technique must probe the increase of magnetic response around 20 meV due to Ni spin. But, the existing data do not support the observation of Ni spin fluctuation [52]. Thus, $T_M \sim \omega_N/\alpha$ is also unlikely.

From $\Delta T_c = 0.25\pi^2 x_{\text{plane}}|N_F|^2 S(S+1)/k_B$ with $0 < x_{\text{plane}} < 0.05$ in a $d_{x^2-y^2}$-wave superconductor [53], $|J| > 68$ meV ($S=1$) or $|J| > 111$ meV ($S=1/2$) is required to account for $\Delta T_c \sim 20$ K in the quenched sample (similar estimation for Zn doping is seen in Refs. [53,55]). Then, $|\pi N_FJS| > 0.3$ indicates moderately strong scattering. The expression of $\Delta T_c$ should be extended to include both potential scattering and strong scattering.

In considering the magnetic impurity effect in $s$-wave superconductors, one can neglect nonmagnetic potential scattering which should accompany each magnetic impurity, because of Anderson’s theorem, unless the localization effect takes place. However, the situation is completely different in the $d$-wave state. The potential scattering also affects $d$-wave superconductivity as well as the magnetic impurity scattering; thus one has to take into account both effects (see also [56]). Let us treat magnetic impurities as classical spins ($S_z = \pm S$) and assume that they also have nonmagnetic potential scatterings described by $u$. Taking into account the impurity scatterings within a $t$-matrix approximation, Ohashi derived the theoretical expression of $T_c$ ($x_{\text{plane}} \ll 1$) in a $d_{x^2-y^2}$-wave superconductor [57],

$$\Delta T_c = \frac{x_{\text{plane}}}{4k_B N_F} \left[ 1 - \frac{1}{2\pi} + \frac{1}{1 + (\gamma_n - \gamma_m)^2} + \frac{1}{1 + (\gamma_n + \gamma_m)^2} \right].$$  \hspace{1cm} (1)

Here, $\gamma_n$ and $\gamma_m$, respectively, describe the deparing effects originating from nonmagnetic and magnetic parts of the magnetic impurities:

$$\left\{ \begin{array}{l}
\gamma_n = \pi N_F u, \\
\gamma_m = \pi N_F J S.
\end{array} \right.$$  \hspace{1cm} (2)

Putting $\gamma_m = 0$ in eq. (1), we obtain $\Delta T_c$ in the case of nonmagnetic impurity Zn, being in agreement with the expression in Refs. [52,55,56]. On the other hand, $\gamma_n = 0$ gives $\Delta T_c$ in the case of magnetic impurity without nonmagnetic potential scattering part. In the limit of $\gamma_m \to 0$ and $\gamma_n \to 0$, eq. (1) leads to the expression of $\Delta T_c$ in the lowest order Born approximation, being in agreement with the expression in Ref. [51]. In addition, $\gamma_n \to \infty$ or $\gamma_m \to \infty$ corresponds to the unitarity limit $\Delta T_c = x_{\text{plane}}/8k_B N_F \approx (1.9 \times 10^3 \text{K}) x_{\text{plane}}$. If cancellation of $\gamma_n - \gamma_m = 0$ in the unitarity limit takes place for Ni, one obtains $\Delta T_c = x_{\text{plane}}/(8k_B N_F)$, which is two times smaller than that due to pure nonmagnetic scattering. For YBa$_2$Cu$_{3-x}$Ni$_x$O$_{7-\delta}$, however, one should assume $\gamma_n \gg \gamma_m$. In the moderately strong scattering (a finite $u$), since $\Delta T_c \propto x_{\text{plane}} N_F$ at $N_F \ll 1/\pi u$ ($\gamma_n < 1$) and $\Delta T_c \propto x_{\text{plane}} N_F$ at $N_F \gg 1/\pi u$ ($\gamma_m > 1$), then $\Delta T_c$ takes a maximum of 0.125$x_{\text{plane}}/k_B N_F$ at the optimal $N_F = 1/\pi u$ ($\gamma_n = 1$). If $N_F$ of YBa$_2$Cu$_{3-x}$Ni$_x$O$_{7-\delta}$ is optimal, that is $u = 1/|\pi N_F| = 212$ meV ($\gamma_n = 1$), using $\Delta T_c = (9.5 \times 10^2 \text{K}) x_{\text{plane}}$, we estimate $x_{\text{plane}} = 0.01$ (as-synthesized) and 0.02 (quenched). In the unitarity limit, eq. (1) does not explicitly depend on $u$ nor $J$. Then, using $\Delta T_c = (1.9 \times 10^3 \text{K}) x_{\text{plane}}$, we estimate the minimum values of $x_{\text{plane}} = 0.005$ (as-synthesized) and 0.01 (quenched). These values are so reasonable as to satisfy $0 < x_{\text{plane}} < 0.05$. Thus, we suggest that the moderately strong, nonmagnetic scattering of Ni is a promising origin of $T_c$ suppression. This is qualitatively consistent with a report on a large $|u|$ (> $|JS|$) of Ni in Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ [53].

In conclusion, the Cu NQR experiment demonstrated that both Cu(1) and Cu(2) nuclear spin-lattice relaxations in YBa$_2$Cu$_{3-x}$Ni$_x$O$_{7-\delta}$ are affected by Ni doping, that is, the doped Ni impurities are substituted for both Cu(1) and Cu(2) sites. One of the reasons for the small decrease of $T_c$ by Ni doping in YBa$_2$Cu$_{3-x}$Ni$_x$O$_{7-\delta}$ is partial substitution of the Ni impurities for the chain site. In the light of the Ni-induced nuclear spin-lattice relaxation, the host Cu(2) spin fluctuation spectrum in YBa$_2$Cu$_{3-x}$Ni$_x$O$_{7-\delta}$ with optimal oxygen content is quite robust for Ni doping.

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The decrease of $T_c$ for Y124, and 0.62 for LS214. The decrease of $T_c$ for Y123 is smallest among these materials. (b) Ni doping for Y123 is smallest among these materials. 

FIG. 1. (a) Impurity doping dependence of $T_c$ as functions of the concentration $z$ for various high-$T_c$ superconductors with $M=\text{Ni}$ or $\text{Zn}$. The solid (open) symbols are the Ni(Zn) doping dependence of $T_c$. The data are adopted from [9] for YBa$_2$(Cu$_{1-z}$M$_z$)$_3$O$_7$ (Y123, upward triangles), [10] for Bi$_2$Sr$_2$Ca(Cu$_{1-z}$M$_z$)$_2$O$_y$ (Bi2212, squares), [11,12] for YBa$_2$(Cu$_{1-z}$M$_z$)$_4$O$_y$ (Y124, circles), and [1] for La$_{1.85}$Sr$_{0.15}$Cu$_{1-z}$M$_z$O$_4$ (LS214, downward triangles). The dashed and the solid lines are fit by $T_c=\frac{T_{c_{0}}-mMz}{m_{M=N1,23}M} \frac{1}{m_{M_{N1,23}}} \frac{1}{m_{M_{N1,23}}}$ (the fitting parameter) for the respective materials. The estimated ratio $m_{M_{N1,23}}$ is about 0.26 for Y123, 0.46 for Bi2212, 0.80 for Y124, and 0.62 for LS214. The decrease of $T_c$ by Ni doping for Y123 is smallest among these materials. (b) Ni doping dependence of $T_c$ for "as-synthesized" or "quenched" Y123, adopted from [18]. The solid curves are guide for the eyes. Note that the Ni concentration $z$ in the text is defined by $z=3z$ in YBa$_2$Cu$_{3-x}$M$_x$O$_{7-\delta}$ ($7-\delta=6.92-6.95$ [18]). The decrease of $T_c$ by Ni doping is larger in "quenched" Y123 than in "as-synthesized" one.

FIG. 2. Zero-field frequency spectra of the chain-site and the plane-site $^{63,65}$Cu NQR for YBa$_2$Cu$_{3-x}$Ni$_x$O$_{7-\delta}$ at $T=4.2$ K. The line shapes are scaled after $T_2$ corrections have been made.

FIG. 3. The Ni-doping effect on the $^{63}$Cu nuclear spin-echo recovery curves $p(t) \equiv 1-M(t)/M(\infty)$ at $T=4.2$ K. Inset figures show the recovery curves for the pure (Ni-free) sample at $T=4.2$ K. The solid curves are the least-squares fitting results using the theoretical function including a stretched exponential function (see the text).

FIG. 4. Log-log plots of $^{63}(1/T_1)_{\text{HOST}}$ (a) [(c)] and $^{63}(1/T_1)_{\text{Cu}}$ (b) [(d)] at $^{63}$Cu(2) [$^{63}$Cu(1)] as functions of temperature for the Ni-free and for the Ni-doped samples. The dashed lines are $T^x$ functions. The solid curves are guide for the eyes.
FIG. 5. The Ni-doping effect on the temperature dependence of $^{63}(1/T_1)_{\text{HOST}}$ (a) and $^{63}(1/\tau_1)$ (b) at $^{63}\text{Cu}(2)$ in linear scale. The thick bars indicate the respective $T_c$'s. The dotted curve is the least-squares fitting result by a function of $TC/(T + \Theta)$ ($C=1.7 \text{ ms}^{-1}$ and $\Theta=128 \text{ K}$) above $T_c$. 