Cu(1) NQR in $Y_{1-x}Pr_xBa_2Cu_3O_7$ *

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Cu(1) NQR spectra of the CuO chain site in $Y_{1-x}Pr_xBa_2Cu_3O_7$ ($x = 0.1$ and 0.2), and the ^{63}Cu(1) NQR spin-lattice relaxation rates $1/T_1$ in $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ have been measured. The half widths are about three times wider than those of the pure $YBa_2Cu_3O_7$. The peak frequencies are lowered by the Pr doping. This seems to indicate a decrease of on-site holes at the Cu(1) site. The relaxation rate $1/T_1$ is found to obey the same temperature dependence, $1/T_1 = aT + bT^3$ as reported for pure $YBa_2Cu_3O_7$.

Key words: $Y_{1-x}Pr_xBa_2Cu_3O_7$, CuO chain site, NQR, spectrum, spin-lattice relaxation rate.

Introduction

$Y_{1-x}Pr_xBa_2Cu_3O_7$ is an exceptional high-T_C superconductor since among the rare earth ions especially Pr damages the superconductivity of the Y123 compounds. It is very interesting and important to make clear the origin of this property of Pr. The coexistence of superconductivity and magnetism observed for $0.4 \leqq x \leqq 0.6$ is another interesting point.

We have investigated the NQR spectra and spin-lattice relaxation rates of the Cu(2) nuclei of the CuO_2 plane site in $Y_{1-x}Pr_xBa_2Cu_3O_7$. In [1] the Cu(2) NQR spectra of $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_7$ and the nuclear spin-lattice relaxation rate $1/T_1$ of $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ were reported. The spectra are broadened on the high-frequency side, and the spectral features are quite different from those of the oxygen-depleted $YBa_2Cu_3O_{7-\delta}$, in spite of a similar decrease of T_C. The $1/T_1T$ data observed at high temperatures were fitted to the equation $1/T_1T = a + C/(T + \theta)$, where the a-term is due to the Korringa mechanism (mostly due to the $q = 0$ components of the spin excitations), and the second term is due to the antiferromagnetically enhanced relaxation process. It was concluded that Pr doping enhances the 2D AF spin fluctuations due to the decrease of the Weiss temperature.

In [2] a fit of the ^{63}Cu(2) NQR $1/T_1$ data of the CuO_2 plane site in $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_7$ was made for high temperatures. The Weiss temperature θ, 67 K is smaller than that (= 92 K) of $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$. This shows that the AF spin-fluctuations are enhanced with increasing Pr doping. The pseudo spin-gap behavior observed in $Y_{1-x}Pr_xBa_2Cu_3O_7$ ($x = 0.1$ and 0.2) was discussed in detail. The Arrhenius plots of the reduced relaxation rates $(1/T_1T)_{obs}/(1/T_1T)_{CW}$ were given, where $(1/T_1T)_{CW}$ is the expected relaxation rate due to the AF spin fluctuations which obey the Curie-Weiss law. Fairly good activation type fits

$$(1/T_1T)_{obs}/(1/T_1T)_{CW} = A\exp(-\Delta/k_BT) \quad (1)$$

were obtained, and the pseudo spin-gap energies were estimated to be 157 K and 86.2 K for $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ and $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_7$, respectively. These results indicate the existence of an energy gap Δ in the spectrum of the AF spin fluctuations which contribute to the spin-lattice relaxation.

While Cu(2) NMR/NQR has extensively been studied because the CuO_2 plane plays the main role in the high-T_C superconductivity, Cu(1) NMR/NQR studies are also important to elucidate as a whole the mechanism of the high-T_C superconductivity in Y123 compounds.

In this paper, Cu(1) NQR spectra of the CuO chain site in $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ and $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_7$ are reported. In $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ also the ^{63}Cu(1) nuclear spin-lattice relaxation rate $1/T_1$ has been measured.

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1. Experimental

The samples of $Y_{1-x}Pr_xBa_2Cu_3O_7$ ($x = 0.1$ and 0.2) were prepared by the conventional solid-state reaction technique. They were annealed for 12 hours at 950 °C and for 12 hours at 500 °C with pure O_2 gas flowing in the final stage. X-ray diffraction measurements assured that they have no impurity phase. The electrical resistances of these samples are plotted against temperature in Figure 1. The transition temperatures are 86 K and 73 K for $x = 0.1$ and 0.2, respectively.

Temperature dependence of the ac susceptibility has been measured with a commercial ac susceptometer (Lake Shore Cryotronics, model 7000), and typical data in an applied field of 1 Oe are shown in Figs. 2a and b for $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ and $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_7$, respectively. T_C's are determined to be 88 K and 71 K, respectively in reasonable agreement with the resistivity data. Both samples show nearly complete diamagnetism, and no sign of contamination by a second phase etc. was observed.

The spin-echo signals were measured with a conventional phase-coherent type NQR spectrometer. The NQR spectrum was obtained by recording the integrated spin-echo intensity step by step at 1.4 K. The spin-lattice relaxation rate $1/T_1$ was measured by recording the recovery of the nuclear magnetization against the delayed time t after the inversion π pulse of the $\pi/2 - \pi$ pulses.

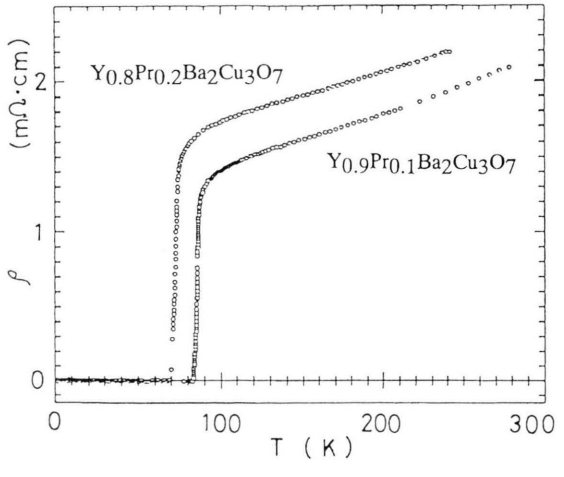

Fig. 1. Temperature dependences of the electrical resistivities of $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ and $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_7$.

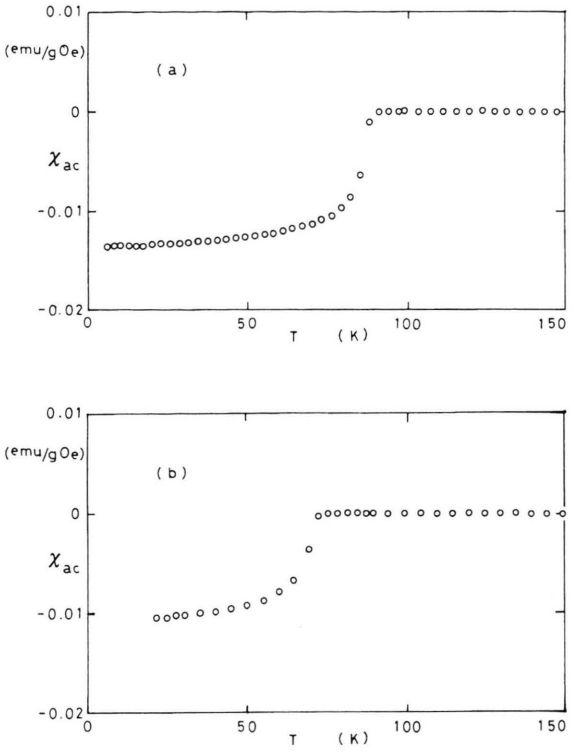

Fig. 2. ac susceptibilities of $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ (a) and $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_7$ (b).

2. Results and Discussion

2.1 NQR Spectrum

The Cu(1) NQR spectra of the CuO chain site at 1.4 K are shown in Figure 3. Figure 3a shows the spectrum of Cu(1) in the pure $YBa_2Cu_3O_7$, cited from [3]. Figures 3b and c show the spectra obtained for $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ and $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_7$, respectively.

The lines of $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ and $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_7$ are much broader than those of $YBa_2Cu_3O_7$. Their half widths are almost equal, about 790 kHz, and more than three times larger than those, 245 kHz, of the pure compound.

The peak NQR frequencies decrease with increasing Pr doping: they are 22.05 MHz, 21.90 MHz and 21.62 MHz for $YBa_2Cu_3O_7$, $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ and $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_7$, respectively.

Recent band calculations by Schwarz et al. [4] show that the NQR frequency at the Cu site ν_Q(Cu) may be explained by contributions from the fractional

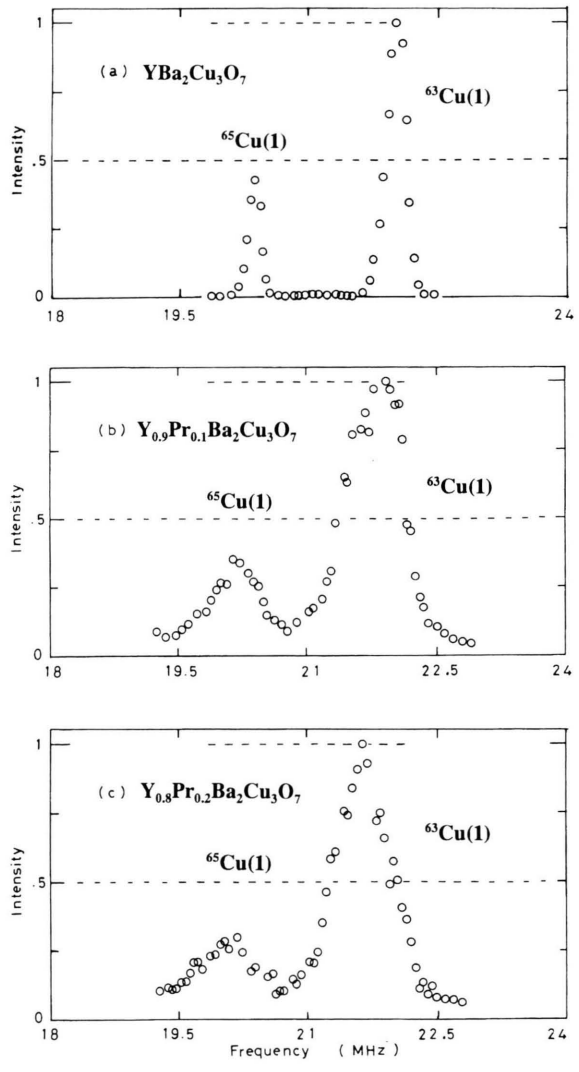

Fig. 3. Cu(1) NQR spectra of the CuO chain site of the pure $YBa_2Cu_3O_7$ (a), $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ (b) and $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_7$ (c) measured at 1.4 K. Figure 3a is cited from [3] published by Yasuoka et al.

occupation of both the $3d$ holes and $4p$ electrons of Cu ion:

$$\nu_Q(\mathrm{Cu}) = n_{3d}\,\nu_Q^{3d} + n_{4p}\,\nu_Q^{4p}\,, \tag{2}$$

where n_i and ν_Q^i are the number of $3d$ holes and $4p$ electrons and the NQR frequency per unit hole and electron, respectively. As for the CuO_2 plane, the cluster calculation of Ohta et al. [5] shows that the $4p$ contribution to $\nu_Q(\mathrm{Cu})$ does not depend on the compound and is about -65 MHz, that corresponds to a $4p$ fraction of about 0.1 for all compounds. The $3d$ hole contribution ν_Q^{3d} was calculated to be 117 MHz per one hole. The observed NQR frequencies, therefore, correspond to changes of the hole number in the Cu $3d$ orbital. Some authors [6, 7] have analyzed their NQR frequency data observed in Cu oxide superconductors by (2). If it is assumed that (2) can approximately be applied to the Cu(1) sites, it is deduced that the 10% Pr doping decreases the on-site holes at the Cu(1) site by about 0.001, and 20% Pr doping by about 0.003 comparing with those of $YBa_2Cu_3O_7$, respectively. This gives an important hint to understand the suppression of the superconductivity by the Pr doping.

2.2 $^{63}Cu(1)$ NQR Spin-lattice Relaxation Rate

As for the Cu(2) nuclear spin-lattice relaxation rate, the following consensus has been obtained; (i) in the normal state, the relaxation rate $1/T_1$ is very much enhanced by the antiferromagnetic Cu spin fluctuations $\chi(Q_{AF}, \omega)$, (ii) in the superconducting state, the coherence enhancement peak has not been observed just below T_C, and the relaxation rate $1/T_1$ is proportional to T^3 well below T_C, which is very different from the observations in the conventional BCS superconductors [8].

The $^{63}Cu(1)$ nuclear spin-lattice relaxation rate $1/T_1$ has been measured in the normal state of $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$. The signal to noise ratio of the $^{63}Cu(1)$ NQR spin-echo signals is much worse than that of the $^{63}Cu(2)$ NQR signals, and we had to accumulate and average the signals for a long time. An example of the recovery of the $^{63}Cu(1)$ nuclear magnetization observed at 100 K is shown in Fig. 4, which is considered to be single-exponential. The estimated $1/T_1$ is plotted against temperature in Figure 5. It should be noted that the present NQR relaxation rate equals to $6W$ and three times of the NMR relaxation rate $2W$, where W is the transition probability between the adjacent nuclear spin levels split by the quadrupolar interaction.

The data points are fitted to

$$1/T_1 = a\,T + b\,T^3 \tag{3}$$

with the parameters $a = 9.34\ \mathrm{s}^{-1}\,\mathrm{K}^{-1}$ and $b = 2.12 \times 10^{-4}\ \mathrm{s}^{-1}\,\mathrm{K}^{-3}$. The best fitted curve is shown in Figure 5. Pennington et al. [9] measured the $^{63}Cu(1)$ relaxation rate in pure $YBa_2Cu_3O_7$ up to 500 K and got a temperature dependence with $a = 55.2\ \mathrm{s}^{-1}\,\mathrm{K}^{-1}$

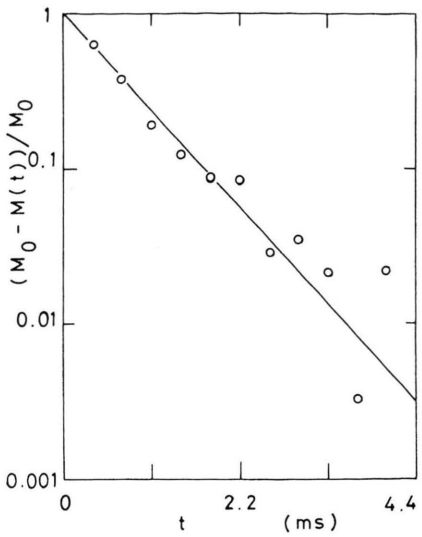

Fig. 4. An example of the recovery of ^{63}Cu(1) nuclear magnetization of the CuO chain site in $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$.

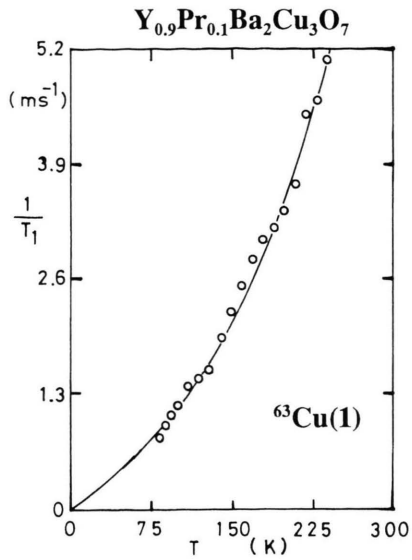

Fig. 5. ^{63}Cu(1) nuclear spin-lattice relaxation rates $1/T_1$ measured for $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ are plotted against temperature. The solid curve shows the best fitted temperature dependence $1/T_1 = 9.34\,T + 2.12 \times 10^{-4}\,T^3\,(s^{-1})$.

and $b = 3.90 \times 10^{-4}\,s^{-1}\,K^{-3}$. The relaxation mechanism of ^{63}Cu(1) is not yet understood. The a term of $1/T_1T$, $9.34\,s^{-1}\,K^{-1}$ observed in $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ is about one-sixth of $55.2\,s^{-1}\,K^{-1}$ observed in $YBa_2Cu_3O_7$. If the a term is considered to be due to the Korringa mechanism, this result reflects the decrease of the on-site holes at the Cu(1) site, that is, the decrease of the density of states because of the Pr doping. This fact is consistent with the decrease of the ^{63}Cu(1) NQR frequency as described in 2.1.

3. Conclusion

NQR spectra of Cu(1) of the CuO chain site in $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ and $Y_{0.8}Pr_{0.2}Ba_2Cu_3O_7$, and the ^{63}Cu(1) NQR spin-lattice relaxation rates $1/T_1$ in $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$ have been measured. The half widths are enhanced by about a factor three compared to that of the $YBa_2Cu_3O_7$. The peak frequencies are lowered by the Pr doping. The present NQR spectra seem to indicate that the number of the on-site holes at the Cu(1) site is decreased by the Pr doping, this giving an important hint to understand the origin of the suppression of the superconductivity by the Pr doping. The ^{63}Cu(1) nuclear spin-lattice relaxation rate $1/T_1$ obeys the same temperature dependence $1/T_1 = aT + bT^3$ as reported for pure $YBa_2Cu_3O_7$. The a term of $1/T_1T$, $9.34\,s^{-1}\,K^{-1}$, observed in $Y_{0.9}Pr_{0.1}Ba_2Cu_3O_7$, which is considered to be due to the Korringa mechanism, is about one-sixth of $55.2\,s^{-1}\,K^{-1}$ observed in $YBa_2Cu_3O_7$. This reflects the decrease of the on-site holes at Cu(1) site due to Pr doping, which is consistent with the decrease of the ^{63}Cu(1) NQR frequency.

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