$^{63/65}$Cu-NQR Study of Impurity-Induced Magnetic Order in $YBa_2(Cu_{1-x}M_x)_3O_7$ (M = Fe, Co)*

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We have studied $^{63/65}$Cu NQR at the Cu(1)-chain and Cu(2)-plane site of $YBa_2(Cu_{1-x}M_x)_3O_7$ (M = Fe, Co). The spin-lattice relaxation rate, T_1^{-1}, is enhanced at low temperatures and has in the Fe-system a peak at 2 and 4 K for $x = 0.005$ and 0.015, respectively. Below the peak temperatures the intensity of the Cu-NQR signal decreases rapidly. The results suggest that magnetic ordering of either Fe or Cu moments occurs without destroying the superconductivity below T_c on substituting Cu by magnetic ions.

Key words: NQR, Magnetic order, High-T_c superconductor, $YBa_2(Cu_{1-x}Fe_x)_3O_7$.

1. Introduction

Since the discovery of high T_c superconductivity [1], many investigations have been performed to elucidate its mechanism. As $YBa_2Cu_3O_7$ has two crystallographically different Cu-sites: one in the $(CuO)_n$ chain (hereafter denoted as Cu(1)) and the other in the $(CuO_2)_n$ plane (Cu(2)) [2], the substitution of Cu by 3 d transition elements poses interesting questions. Although a structural transformation from orthorhombic to tetragonal is induced by Fe and Co substitution, T_c decreases smoothly with increasing atom fraction x of the substituent [3, 4]. As the magnetic susceptibility follows the Curie-Weiss relation with a paramagnetic contribution in the Fe(Co) substitution system [4], the localized magnetic Fe(Co) moments seem to enhance the exchange interactions between Cu moments and to induce magnetic ordering, which is confirmed by measurements of the Mössbauer effect [5, 6], magnetic susceptibility [7], neutron diffraction [8, 9] and NQR [10, 11]. However, it is still unclear whether superconductivity and magnetic order coexist microscopically at the same sites.

In this paper we present results of $^{63/65}$Cu-NQR in $YBa_2(Cu_{1-x}Fe_x)_3O_7$ at zero external magnetic field and compare them briefly with results on Co substitution. Part of the results has been reported in [11, 12].

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2. Experimental

Samples of $YBa_2(Cu_{1-x}M_x)_3O_7$ with M = Fe and Co were prepared by solid-state reaction of appropriate amounts of high-purity Y_2O_3, $BaCO_3$, CuO, Fe_2O_3, and Co_2O_3. The powders were thoroughly mixed, pressed into pellets and heated at 900 °C for 12 h in air. The pellets were then pulverized, reformed into pellets, heated again at 900 °C for 30 h in air and slowly cooled to room temperature during 24 h. Details about the specimens were given by Maeno et al. [3, 13]. The pellets were crushed into a powder of 350 mesh for the NQR measurements. A conventional phase-coherent pulse NMR apparatus was used for the measurements of spectra and nuclear spin relaxation times, T_1 and T_2.

3. Results

3.1. Cu-NQR for Fe Substitution

Figure 1 shows the spin echo spectra of $^{63/65}$Cu-NQR in $YBa_2(Cu_{0.995}Fe_{0.005})_3O_7$ under zero external magnetic field below 10 K. Two pairs of NQR signals were obtained around 19–23 MHz and 29–32 MHz. They are similar to those in non-doped $YBa_2Cu_3O_7$. The pairs are due to the two Cu isotopes 63 and 65. The site assignment of the signals of non-doped $YBa_2Cu_3O_7$ having been established [14], the present NQR signals are safely ascribed as follows: the signals around 19–23 MHz are from the Cu(1) site (the $(CuO)_n$ chain between two Ba-layers) and the signals around 29–32 MHz are from the Cu(2) site (the

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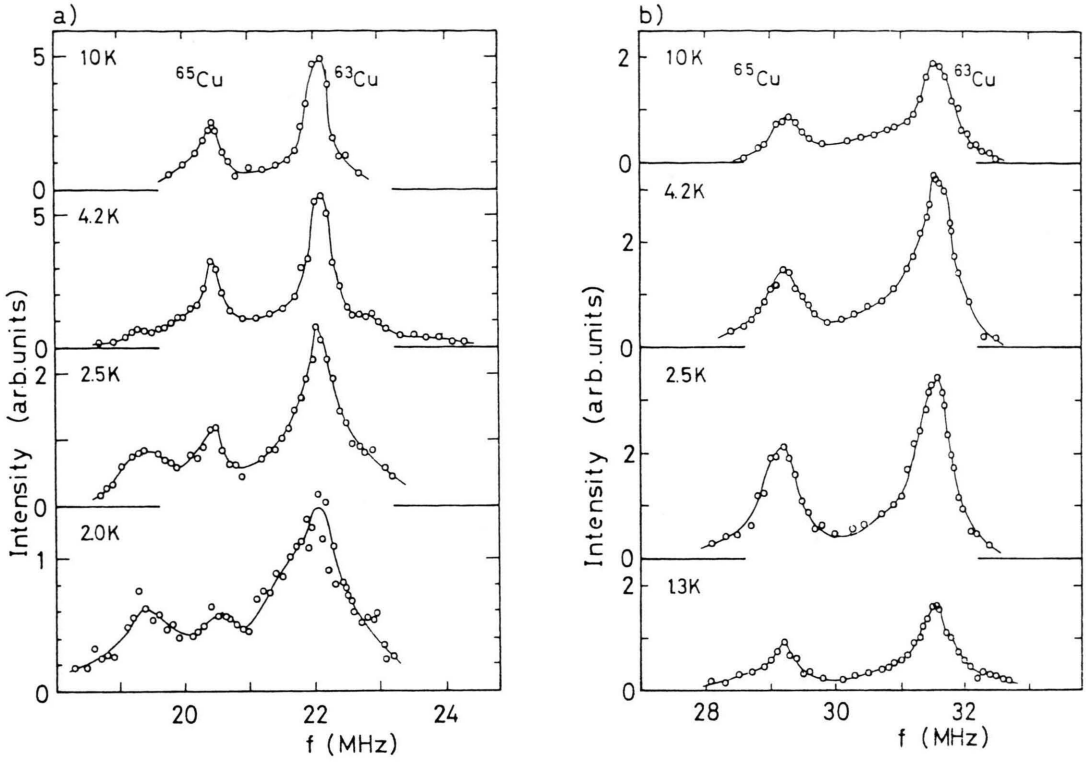

Fig. 1. Cu-NQR spectra of $YBa_2(Cu_{0.995}Fe_{0.005})_3O_7$ at various temperature below 10 K. a) Cu(1)-chain site, b) Cu(2)-plane site.

$(CuO_2)_n$ planes between Y- and Ba-layers). No appreciable shifts of the resonance frequency to both Cu sites were observed with decreasing temperature. The resonance frequencies were also independent of the Fe concentration at least in the dilutely-doped region. However, an additional signal from Cu(1) was observed around 19.4 MHz at low temperatures. The resonance frequency of this signal did not shift with Fe concentration below 4.2 K and might be attributed Cu(1) nuclei near oxygen vacancies.

We measured T_1 of Cu in both Cu sites. Figure 2 shows the typical recovery curves of the ^{63}Cu nuclear magnetization in Cu(2) for $x=0.005$. Above about 40 K, the recovery curves follow the relation

$$M_z(t) = M_0[1-\exp(-t/T_1)]\,. \tag{1}$$

The recovery curves for Cu(1) also follow (1) below T_c (ca. 90 K). However, they do not follow (1) at temperatures below ca. 30 K, but are then characterized by the equation

$$M_z(t) = M_0\{1-\exp[-(t/T_1)^{1/2}]\}\,. \tag{2}$$

Quite similar results have been obtained in the independent study of Kohori et al. [10].

Figure 3 shows the temperature dependence of T_1^{-1} of ^{63}Cu for both Cu sites. The open-symbols show the values derived with (1) and the closed-symbols the ones derived with (2). The recovery curves are not well described by (1) or (2) in the cross-over region, where estimated values are given by broken lines. T_1^{-1} decreases rapidly with decreasing temperature below T_c, this behavior being the same as that of $YBa_2Cu_3O_7$ [15, 16]. With further decreasing temperaure, T_1^{-1} increases in both Cu sites. Though the enhancement of T_1^{-1} in Cu(2) is more pronounced than that in Cu(1), the maximum occurs at the same temperature T_m. T_m equals 2.5 and 4 K for $x=0.005$ and 0.015, respectively.

Figure 4 shows the temperature dependence of the intensity of the ^{63}Cu-NQR signals for $x=0.005$ and $x=0.015$. The intensity is reduced due to the spin-spin relaxation time, T_2. Generally, the NQR intensity, S, is proportional to $1/T$, so that the decrease of ST is caused either by the existence of unobservable compo-

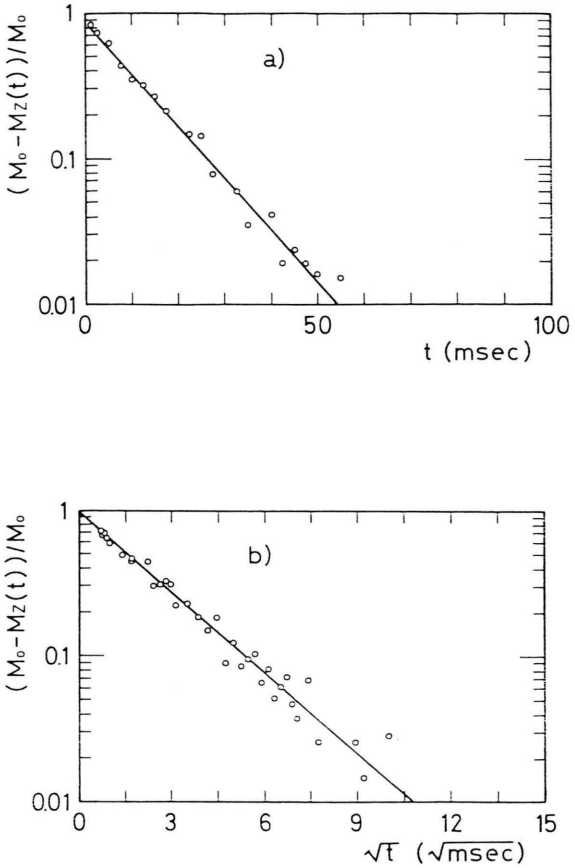

Fig. 2. Recovery curves of nuclear magnetization of ^{63}Cu in Cu(2) of $YBa_2(Cu_{0.995}Fe_{0.005})_3O_7$, a) vs. t at 50 K, b) vs. $\sqrt{t}$ at 4.2 K.

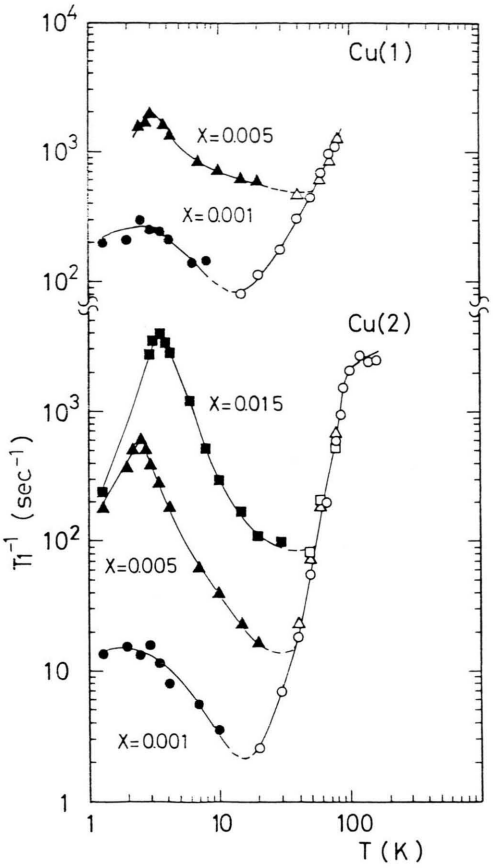

Fig. 3. Temperature dependence of T_1^{-1} of ^{63}Cu for Cu(1) and Cu(2) in $YBa_2(Cu_{1-x}Fe_x)_3O_7$.

nents (due to the limitation of apparatus) of extremely short T_2 or by the wipe out from the observed NQR frequency range for the both Cu sites. For the higher Fe concentration of $x > 0.15$, the nuclear magnetic resonance signals are observed around 70–100 MHz under zero external field [17].

3.2. Cu-NQR for Co Substitution

Cu-NQR signals from both Cu sites of the Co-system are observed in the same frequency range to those for the Fe-system. The recovery curve also follows (1) below T_c (ca. 90 K), and (2) at low temperatures. Figure 5 shows the temperature dependence of T_1 of ^{63}Cu for both Cu-sites. T_1^{-1} decreases rapidly below T_c. The enhancement of T_1^{-1} of Cu(2) at lower temperatures is very small compared to that of the Fe-system, and a maximum is missing. The behavior of T_1^{-1} of Cu(1) is very similar to that of the Fe-system. The ^{63}Cu-NQR intensities for $x = 0.005$ are shown as functions of temperature in Figure 6. The NQR intensity from both Cu sites decreases gradually with decreasing temperature, a behavior which is qualitatively different from that of the Fe-system (see Figure 4). This qualitative difference may be caused by a different preferential occupation of the two Cu sites by the Fe and Co ions [18, 19].

4. Discussion

In our systems, the nuclear relaxation involves the additional relaxation induced by the magnetic impurities. The observed value of T_1^{-1} is considered to be the sum of the host contribution, $(1/T_1)_{\text{host}}$, and the

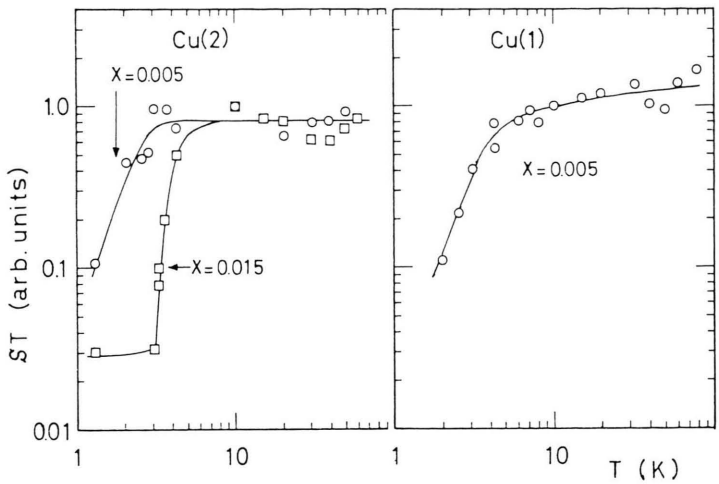

Fig. 4. Temperature dependences of intensity times temperature, ST, of ^{63}Cu-NQR for $YBa_2(Cu_{1-x}Fe_x)_3O_7$. The intensities are normalized by the respective values at 10 K.

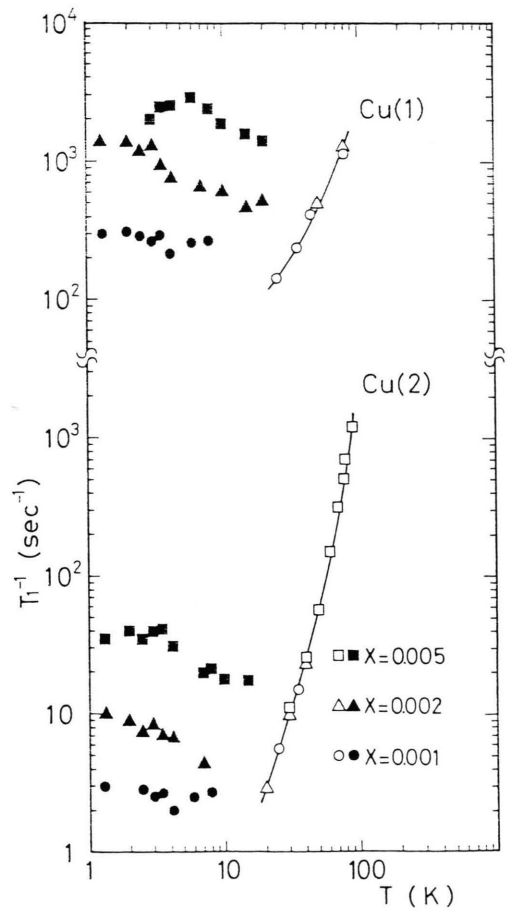

Fig. 5. Temperature dependence of T_1^{-1} of ^{63}Cu for Cu(1) and Cu(2) in $YBa_2(Cu_{1-x}Co_x)_3O_7$.

contribution from magnetic impurities, $(1/T_1)_{imp}$, i.e.

$$(1/T_1)_{obs} = (1/T_1)_{host} + (1/T_1)_{imp} . \quad (3)$$

When the host relaxation dominates over the impurity effect, the recovery curve is characterized by (1). On the other hand, when the impurity effects dominate at low temperature, the recovery curve follows (2), which describes the relaxation process without spin diffusion for mutual nuclear spins. The following factors are characteristic for the systems. Close proximity of nuclei to impurities minimizes the spin diffusion effect. The relaxation arises from fluctuations of the magnetic field at the nuclear site, and the recovery curve results from recoveries with various T_1, dependent on the distances of the nuclei from magnetic impurities [20].

T_1^{-1} of the Fe-system is almost comparable to the host relaxation rate of $YBa_2Cu_3O_7$ above 50 K. However, the T_1^{-1} of Cu in the two Cu sites are much larger than those of $YBa_2Cu_3O_7$ at temperatures below about 30 K, where the impurity relaxation process is dominant. If there are many oxygen vacancies induced by Fe substitution, T_1^{-1} might be enhanced by isolated Cu^{2+} moments adjacent to oxygen vacancies [21]. However, the absence of a distribution and shift of the resonance frequency of the NQR signals in the Fe(Co)-doped samples suggests that the effect of oxygen vacancies is not important because the NQR frequency in the Y-system is known to depend largely on oxygen concentration [22]. As the peak tempera-

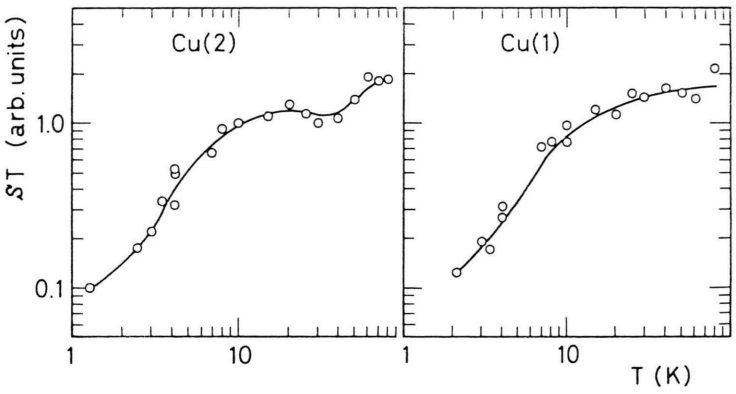

Fig. 6. Temperature dependence of intensity times temperature of ^{63}Cu-NQR for the Cu sites in $YBa_2(Cu_{0.995}Co_{0.005})_3O_7$.

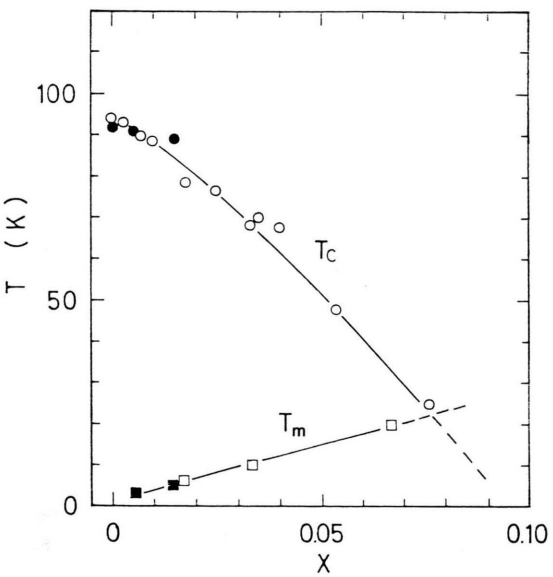

Fig. 7. Superconducting transition temperature, T_c, and magnetic transition temperature, T_m, as functions of x in $YBa_2(Cu_{1-x}Fe_x)_3O_7$. Open circles: T_c determined by Maeno et al. [3]. Open squares: T_m determined by Mössbauer experiment [5]. Closed circles and squares: T_c and T_m, respectively, obtained in this work. T_c is determined by magnetic susceptibility measurement.

ture of T_1^{-1} changes with Fe concentration, the enhancement of T_1^{-1} is not attributed to any precipitated magnets such as BaY_2CuO_5 [23]. As the hyperfine or dipolar coupling constant is essentially independent of temperature, the enhancement of T_1^{-1} at low temperatures is attributed to an increase of the spectrum density at the Larmor frequency due to the change of correlation times of the local field fluctuations induced by magnetic moments. Therefore the behavior of T_1^{-1} at low temperatures may arise from the critical slowing down of fluctuations of local fields associated with the magnetic ordering of either Fe or Cu magnetic moments in the Fe-system.

Furthermore, we observed decreases (and almost losses) of the NQR intensity both of Cu(1) and Cu(2) sites in the Fe(Co)-system. The decrease the NQR signals is caused either by extremely short T_2 or by the wipe out from the NQR frequency range below T_m due to magnetic order of Fe or Cu moments in the Cu(1) sites. The large enhancement of T_1^{-1} and the loss of signals below T_m indicate the existence of antiferromagnetic order for the dilutely-doped region. As far as concerning superconductivity, we obtain the characteristic relaxation behavior below T_c; T_1^{-1} decreases rapidly with decreasing temperature below T_c for both Cu sites, which is similar to those of non-doped $YBa_2Cu_3O_7$ [15, 16]. The fact indicates that T_1^{-1} is suppressed by the superconduction energy gap in the Fe substitution system.

Thus, the NQR signals, of which the relaxation behavior is clearly affected by superconductivity at high temperatures, show the characteristic temperature-dependence in both relaxation and intensity which is owing to magnetic order at low temperatures. Although we can not rule out the possibility that the coexistence of two ordered states is due to microscopic inhomogeneity of the Fe(Co)-distribution in the order of 10 A, the coherence length of superconductivity in the oxides, we suggest that magnetic order of Fe(Co) moments and also presumably of Cu moments exists without destroying superconductivity in the Fe(Co)-substitution system. Figure 7 shows T_c and T_m as a function of x for the Fe system. The results of T_m obtained by Mössbauer effect experiments [5] are given in Figure 7. T_c decreases gradually and T_m increases proportionally with increasing x. The region of the coexistence seems to extend to $x=0.08$.

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