Cu NQR Study on Transverse Relaxation Rate below T_c in $YBa_2Cu_3O_7$ *

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The transverse relaxation rate T_2^{-1} was measured in $YBa_2Cu_3O_7$ from 4.2 to 100 K in zero magnetic field. It showed a sudden drop just below T_c down to 1/3 of that above T_c. A cusp-shaped sharp peak of T_2^{-1} was found at 35 K for Cu(2) (plane) site, but not for Cu(1) (chain) site. Except the peak, all the behavior can be interpreted by the model of Pennington et al. that the origin of T_2^{-1} at 100 K is mainly the local field fluctuation by the Cu d-electron and secondly the indirect nuclear spin-spin coupling via superexchange interaction between Cu-ions. Below T_c the former is suppressed.

Key words: Nuclear quadrupole resonance, High T_c superconductor, Transverse relaxation rate, Super-exchange interaction, Electron spin fluctuation.

Introduction

Many theoretical approaches have been proposed to clarify the origin of the high-T_c superconductivity. Among them, much attention has been paid to the role of Cu d-electron spin fluctuations. Recently Pennington et al. [1] did show by an NMR experiment that the spin fluctuations are caused by the superexchange interaction between Cu-ions. In $YBa_2Cu_3O_{7-y}$ single crystals with $T_c \sim 90$ K they measured transverse relaxation rates T_2^{-1} at 100 K. By subtracting a calculated contribution due to the local field fluctuation caused by the Cu d-electrons, which also contributes to the longitudinal relaxation rate, they showed the presence of another small contribution to the transverse relaxation rate. They have concluded that it is caused by the indirect superexchange interactions between Cu-ions, based on the Cu isotope effects and the SEDOR experiment.

In this report we present an NQR experiment at temperatures below the superconducting transition temperature T_c. We measured the temperature dependence of the transverse relaxation rate T_2^{-1} and found a sudden drop just below T_c, which is a clearer demonstration than the ^{63}Cu T_2 data reported by Mali et al. [2], and a cusp-shaped sharp peak at 35 K. We ascribed the sudden drop to the local field fluctuation produced by the Cu d-electrons due to the transition to superconduction. Below T_c, T_2^{-1} was essentially constant except the sharp peak which is consistent with Pennington's et al. interpretation above T_c. The sharp peak is not yet explained, although it seems magnetic in origin.

Experimental

1) Sample Preparation

The $YBa_2Cu_3O_{7-y}$ samples were mostly prepared by the gel method [3]. y was determined as ~ 0.1 by I_2-metry. The spray-dry method and the conventional

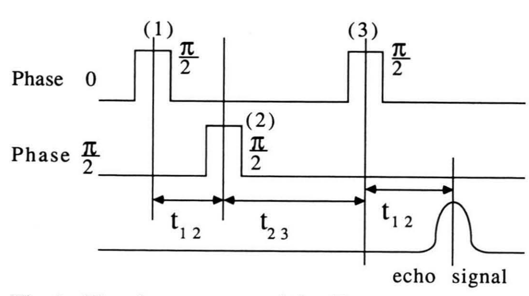

Fig. 1. JB pulse sequence of the T_2 measurement.

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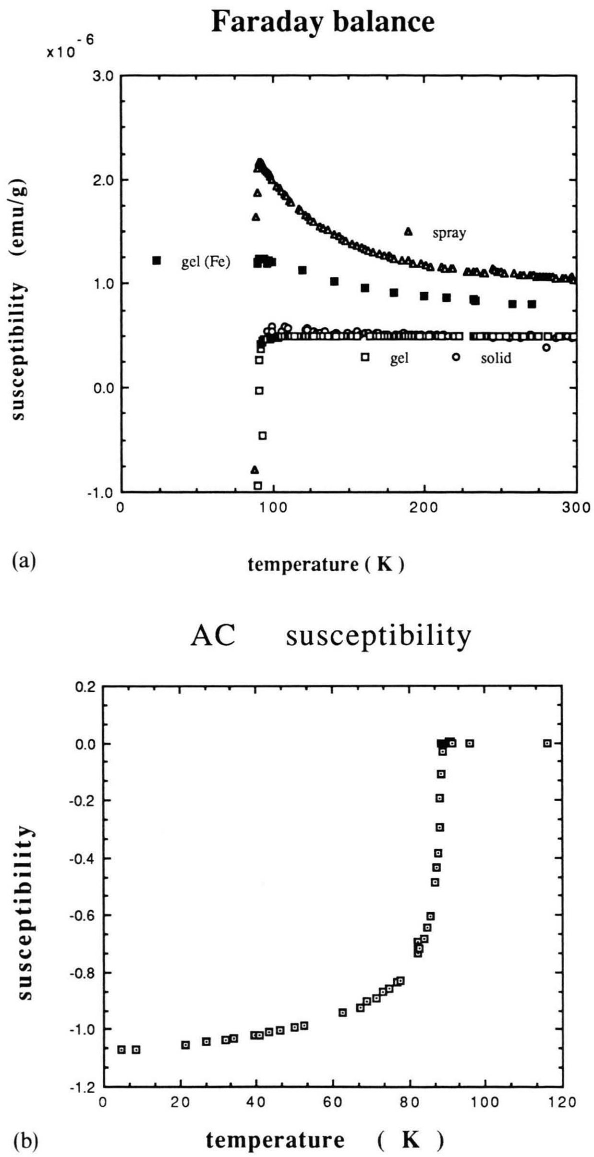

Fig. 2. (a) Magnetic susceptibility at $T > T_c$ measured by the Faraday balance. (b) AC susceptibility for a sample prepared by the gel technique.

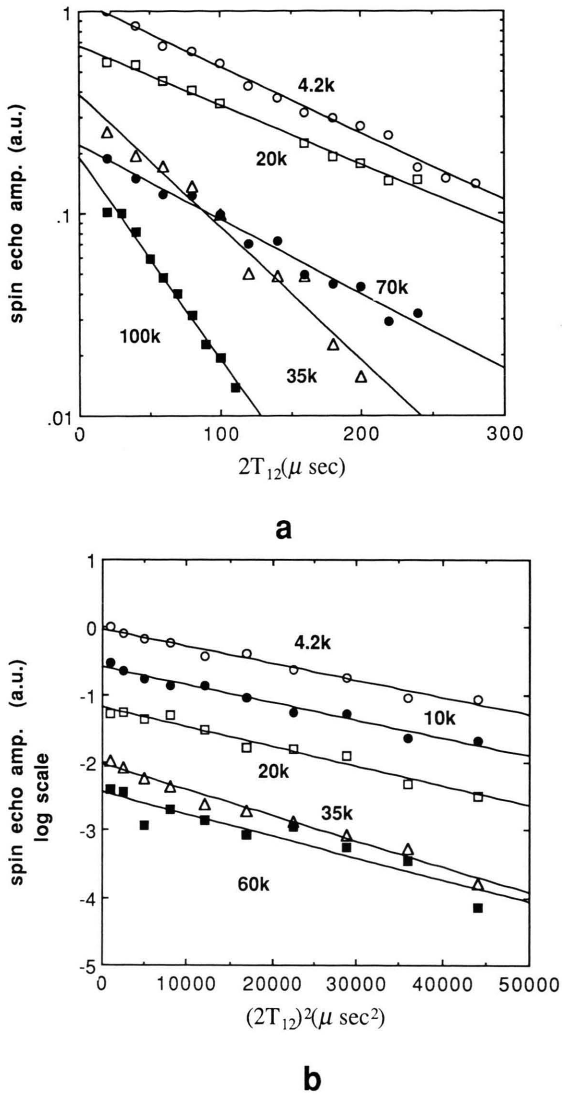

Fig. 3. Transverse magnetization decay for (a) Cu(2) plane site and (b) Cu(1) chain site. Notice that the abscissa displays time for (a) but square of time for (b).

solid-state reaction method were also applied. An iron-substituted sample was also prepared.

2) *Magnetic Susceptibility*

The magnetic susceptibilities were measured by a Faraday-balance above T_c and an AC method below T_c. The results of the magnetic susceptibility measurements are shown in Figure 2.

3) *Transverse Relaxation Rates* T_2^{-1}

The transverse relaxation rates T_2^{-1} were measured by a JB pulse sequence [4] (Figure 1). By subtracting two signals with different t_{12} we obtained clear echo signals without any spurious ringing. The dead time was about 2 microseconds. The transverse magnetization was found to decay exponentially for the Cu(2) plane site and more Gaussian like for the Cu(1) chain site, as shown in Figure 3.

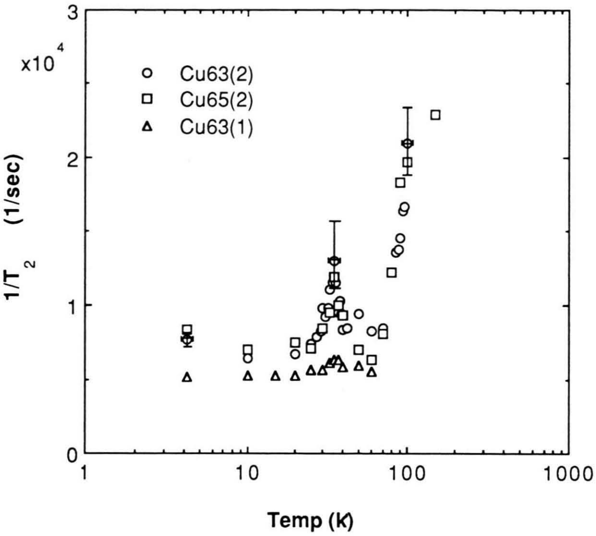

Fig. 4. Temperature dependence of the transverse relaxation rate T_2^{-1}. T_2^{-1} for $^{63}Cu(2)$ and $^{65}Cu(2)$ behave similarly but T_2^{-1} for $^{63}Cu(1)$ chain site has no peak.

Results

Figure 4 summarizes the temperature dependence of T_2^{-1} below T_c. Just below T_c, T_2^{-1} of the plane Cu(2) suddenly decreased down to 1/3 of those above T_c. T_2^{-1} is essentially constant down to 4.2 K, except an extraordinary cusp-shaped sharp peak at 35 K. The sharp peak is observed for the plane site Cu(2) but not for the chain site Cu(1). The sharp peak was observed in every sample, irrespective of having a Curie-component above T_c or not (Figure 2). No structural change was observed across the peak by an X-ray diffraction analysis.

Discussion

The transverse relaxation rate T_2^{-1} of NMR is expressed by a sum of two mechanisms;

$$1/T_2 = (1/T_2)_{\text{II}} + (1/T_2')_{\text{IS}} + (1/T_1')_{\text{IS}} \,. \tag{1}$$

The first, $(1/T_2)_{\text{II}}$, is due to a nuclear spin-spin coupling $H_{\text{II}} = \alpha \boldsymbol{I}_j \cdot \boldsymbol{I}_k$ via the superexchange indirect magnetic interaction $\sum J \boldsymbol{S}_j \cdot \boldsymbol{S}_k$ between Cu-ions. The coefficient α is given by $\alpha = A^2/J_{\text{eff}}$, where A is a hyperfine coupling constant. The second, $(1/T_2')_{\text{IS}} + (1/T_1')_{\text{IS}}$, is due to a fluctuating field of electron spins, the origin of which is the same for the longitudinal relaxation rate T_1^{-1}. One has

$$(1/T_2')_{\text{IS}} = \gamma_n^2\, k_{zz}(0), \tag{2}$$

$$(1/T_1')_{\text{IS}} = \gamma_n^2\, k_{yy}(\omega_0), \tag{3}$$

where

$$k_{qq'}(\omega) = \tfrac{1}{2} \int \overline{H_q(t)\, H_{q'}(t+\tau)}\, e^{-i\omega t}\, dt \,. \tag{4}$$

For NQR, (1) should be modified as follows:

$$1/T_2 = \beta (1/T_2)_{\text{II}} + (1/T_2')_{\text{IS}} + \beta (1/T_1')_{\text{IS}} \,, \tag{5}$$

where

$$\beta = I(I+1) - m(m+1) = 3 \quad \text{for} \quad I = 2/3 \,. \tag{6}$$

Pennington et al. [1] have analyzed the NMR data above T_c as follows:

$$(1/T_2)_{\text{exp}} \sim 1.4 \times 10^4\ \text{s}^{-1}, \tag{7.1}$$

$$(1/T_2)_{\text{II}} \sim (1.8 \pm 1.0) \times 10^3\ \text{s}^{-1}, \tag{7.2}$$

$$(1/T_2')_{\text{IS}} \sim 1.1 \times 10^4\ \text{s}^{-1}, \tag{7.3}$$

$$(1/T_1')_{\text{IS}} \sim 5.3 \times 10^2\ \text{s}^{-1}. \tag{7.4}$$

With (5), for our NQR case the corresponding terms are changed as follows

$$(1/T_2)_{\text{exp}} \sim 2.1 \times 10^4\ \text{s}^{-1}, \tag{8.1}$$

$$\beta (1/T_2)_{\text{II}} \sim 6.7 \times 10^3\ \text{s}^{-1}, \tag{8.2}$$

$$(1/T_2')_{\text{IS}} \sim 1.2 \times 10^4\ \text{s}^{-1}, \tag{8.3}$$

$$\beta (1/T_1')_{\text{IS}} \sim 1.6 \times 10^3\ \text{s}^{-1}. \tag{8.4}$$

On the other hand, below T_c, typically at 10 K, the experimental data are given by $(1/T_2)_{\text{exp}} \sim 6.7 \times 10^3\ \text{s}^{-1} \sim \beta (1/T_2)_{\text{II}}$, where $(1/T_2)_{\text{II}}$ is given by (7.2) above T_c. This means that $(1/T_2)_{\text{II}}$ is essentially temperature independent. The observed isotope effect at 10 K was consistent with the relation $(T_2^{-1})_{63}/(T_2^{-1})_{65} \sim (\gamma_{63}/\gamma_{65})^2 = 1.15$. This indicates that T_2^{-1} is not due to electric quadrupolar but to nuclear magnetic origin at least at temperatures lower than 20 K. The sudden change of T_2^{-1} just below T_c is attributed to the disappearance of the relaxation mechanism by the d-electron spin fluctuation, resulting in $(1/T_2')_{\text{IS}} + (1/T_1')_{\text{IS}}$ given by (8.3) and (8.4). The same effect changes T_1^{-1}, that is a suppression of the spectral density of the local field at $\omega \sim 0$.

The origin of the cusp-shaped sharp peak at 35 K is not exactly known. From an X-ray diffraction analysis on the same sample no sign of a structural change was observed across 35 K. Anomalies at 35 K have been reported by a neutron diffraction experiment [5] and a magneto-resistance experiment. However, their oxygen content was $O_{6.35}$ and $O_{6.5}$, respectively, i.e. different from ours of $O_{6.9}$. We are continuing a detailed experiment including variation of the oxygen content to explore the origin of the observed sharp peak at 35 K.

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[1] C. H. Pennington, D. J. Durand, C. P. Slichter, J. P. Rice, E. D. Bukowski, and D. M. Ginsberg, Phys. Rev. B **39,** 274 (1989). – C. H. Pennington, D. J. Durand, C. P. Slichter, E. D. Bukowski, and D. M. Ginsberg, Phys. Rev. B **39,** 2902 (1989).

[2] M. Mali, J. Roos, and D. Brinkmann, Physica C **153–155,** 737 (1988).

[3] M. Hirabayashi, Bulletin of the Japan Institute of Metals (in Japanese) **26,** 943 (1987).

[4] J. Jeener and P. Broekaert, Phys. Rev. **157,** 232 (1967).

[5] H. Kadowaki, M. Nishi, Y. Yamada, H. Takeya, H. Takei, S. M. Shapiro, and G. Shirane, Phys. Rev. B **37,** 7932 (1988).