Cu NQR Study on Transverse Relaxation Rate below $T_c$ in YBa$_2$Cu$_3$O$_7$ *

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The transverse relaxation rate $T_2^{-1}$ was measured in YBa$_2$Cu$_3$O$_7$ 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$_2$Cu$_3$O$_{7-\delta}$ 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$_2$Cu$_3$O$_{7-\delta}$ samples were mostly prepared by the gel method [3]. $y$ was determined as $\sim$0.1 by I$_2$-metry. The spray-dry method and the conventional

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Fig. 1. JB pulse sequence of the $T_2$ measurement.
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.
rate $T^{-1}_1$. One has
\begin{align}
(1/T_2)_{\text{ls}} &= \gamma_n^2 k_{zz}(0), \\
(1/T_1)_{\text{ls}} &= \gamma_n^2 k_{yy}(\omega_0),
\end{align}
where
\[ k_{q\alpha}(\omega) = \frac{1}{2} \int H_q(t) H_q(t\tau) e^{-i\omega\tau} d\tau. \]
For NQR, (1) should be modified as follows:
\[ 1/T_2 = \beta(1/T_2)_{\text{ls}} + (1/T_2)_{\text{hs}} + \beta(1/T_1)_{\text{hs}}, \]
where
\[ \beta = I(I+1) - m(m+1) = 3 \text{ for } I=2/3. \]
Pennington et al. [1] have analyzed the NMR data above $T_c$ as follows:
\begin{align}
(1/T_2)_{\text{exp}} &\sim 1.4 \times 10^4 \text{ s}^{-1}, \\
(1/T_2)_{\text{hs}} &\sim (1.8 \pm 1.0) \times 10^3 \text{ s}^{-1}, \\
(1/T_2)_{\text{ls}} &\sim 1.1 \times 10^4 \text{ s}^{-1}, \\
(1/T_1)_{\text{hs}} &\sim 5.3 \times 10^2 \text{ s}^{-1},
\end{align}
With (5), for our NQR case the corresponding terms are changed as follows
\begin{align}
(1/T_2)_{\text{exp}} &\sim 2.1 \times 10^4 \text{ s}^{-1}, \\
\beta(1/T_2)_{\text{hs}} &\sim 6.7 \times 10^3 \text{ s}^{-1}, \\
(1/T_2)_{\text{ls}} &\sim 1.2 \times 10^4 \text{ s}^{-1}, \\
\beta(1/T_1)_{\text{hs}} &\sim 1.6 \times 10^3 \text{ s}^{-1}. \\
\end{align}
On the other hand, below $T_c$, typically at 10 K, the experimental data are given by
\[ (1/T_2)_{\text{exp}} \sim 6.7 \times 10^3 \text{ s}^{-1} \sim \beta(1/T_2)_{\text{hs}}, \]
where \( (1/T_2)_{\text{hs}} \) is given by (7.2) above $T_c$. This means that \( (1/T_2)_{\text{hs}} \) 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 \((1/T_2)_{\text{hs}} + (1/T_1)_{\text{hs}}\) 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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