A Study of High $T_c$ Oxide Superconductors by NQR and NMR Measurements

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Results of NQR, NMR and nuclear relaxation measurements in normal and superconducting states of high $T_c$ superconductors, $(La_x-Sr)_{y}Cu_4O_{9+x}$, $YBa_2Cu_3O_7$, $\text{(Ba-Sr)}$, $\text{(Ca,La)}$, $\text{(Nd,Ce)}$, and $\text{(Nd,Ce)}$, $\text{CuO}_4$ are reviewed.

1. Introduction

Since the discovery of high transition temperature ($T_c$) superconductors [1] many experimental and theoretical studies have been carried out but still the theories are controversial.

In the high $T_c$ superconductors, magnetism is considered to play an important role. NMR measurements are suitable to investigate both the magnetic and superconducting properties at each atomic site microscopically. In this paper a review will be given on our NQR and NMR results of high $T_c$ oxide superconductors.

2. Magnetism and Superconductivity – Phase Diagram

La$_2$CuO$_4$ is an antiferromagnet with a Neel temperature, $T_N$, of 240 K. Corresponding to this, $^{139}$La NQR split by the internal field from the Cu magnetic moment has been observed below $T_N$ as shown in Fig. 1 [2]. The spectra have been explained in terms of the arrangement of the Cu spins, aligned antiferromagnetically in the (CuO$_2$) plane with a small component along the c axis [2]. This magnetic structure has been confirmed by a neutron scattering experiment.

With increasing Ba(Sr) fraction $x$, $T_N$ decreases rapidly [3]. In the $x$-region $\sim 0.01 > x > 0.025$, there appears a magnetically ordered state, which is confirmed by the internal field at the La site [2]. The temperature at which the internal field disappears is the transition temperature as shown in Figure 2. This temperature coincides with that where the transverse relaxation rate diverges [4]. At this temperature no anomaly in the specific heat or in the magnetic susceptibility has been observed. The magnetically ordered state appearing in this region is concluded to be of short range [2]. The oxygen p-holes introduced by Ba(Sr) doping gives rise to destruction of the long range magnetic ordering [5].

With further increase of $x$, superconductivity appears after the disappearance of the magnetic order. The regions of the superconductive and magnetically order states are in contact with each other. The competing behavior of superconductivity and antiferromagnetic order is also seen in $YBa_2Cu_3O_{6+x}$ and $Bi$_2$Sr$_2$(Ca,La)$_2$Cu$_4O$_8 system. $T_c$ increases with increasing $x$ having a maximum around $x \sim 0.075$ and then decreases, becoming zero around $x \sim 0.15$ [6]. Cu NQR in $(La_{1-x}Sr_x)Cu_4O_4$ (La compound) has been observed first by Ishida et al. for $x > 0.06$ [7]. The

![Fig. 1. Spin echo spectrum of $^{139}$La in La$_2$CuO$_4$ in zero external field at 1.3 K [2].](image)

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Fig. 2. Phase diagram of \((La_{1-x}Sr_x)_{2}CuO_4\). The magnetic and superconducting transition temperatures, \(T_N\) and \(T_c\), are plotted against \(x\). A.F., S.G. and S.C. mean antiferromagnetic, short range magnetic ordered (spin glass), and superconducting, respectively.

NQR spectra are shown in Fig. 3 [7, 8]. Similar results have been obtained by Kumagai et al. [9]. The NQR frequency increases with \(x\) for the La compound.

Cu NQR in \((Bi-Pb)_{2}Sr_{2}Ca_{2}Cu_{2}O_{8}\) (Bi compound) has been observed by Fujiwara et al. and is shown in Fig. 4 [10]. Cu NQR in \(BiSr(Ca-Y)Cu_{2}O_8\) has been observed by Oashi et al. [11]. The NQR frequencies of Cu in high \(T_c\) compounds are listed in Table 1. There is a tendency that the frequency is the higher, the lower \(T_c\).

3. Nuclear Relaxation

The nuclear spin lattice relaxation rate \(T_1^{-1}\) of \({}^{63}\text{Cu}\) is shown in Fig. 5 in La [7], Bi [10] and Y [12–15] (YBa\(_2\)Cu\(_4\)O\(_y\)) compounds. The characteristic properties of \(T_1^{-1}\) are as follows. \(T_1^{-1}\) in the normal state does not follow the Korringa law \((T_1 T = \text{const.})\), but changes more slowly. In the La compound \(T_1^{-1}\) seems to follow the \(T_1 T = \text{const.} \) law from \(T_c\) to about 70 K. Below \(T_c\), \(T_1^{-1}\) decreases monotonously without BCS type enhancement.
We first discuss the behavior in the normal state. The temperature dependence of $T_1^{-1}$ is not conventional as observed in normal superconductors, and the absolute value is much larger than that estimated from the static susceptibility [16]. This suggests that the antiferromagnetic spin fluctuations enhance $T_1^{-1}$.

Table 1. NQR frequencies of $^{63}$Cu in high $T_c$ superconductors.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_c$ (K)</th>
<th>$\nu_0$ (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(La_{0.85}Sr_{0.15})_2CuO_4$</td>
<td>0</td>
<td>$\sim$38</td>
</tr>
<tr>
<td>$(La_{0.92}Sr_{0.075})_2CuO_4$</td>
<td>38</td>
<td>35.3</td>
</tr>
<tr>
<td>$YBa_2Cu_3O_7$</td>
<td>92</td>
<td>31.5 CuO$_2$ plane</td>
</tr>
<tr>
<td>Bi$_2$Sr$_2$Ca$_2$Cu$<em>3$O$</em>{10}$</td>
<td>80</td>
<td>$\sim$24</td>
</tr>
<tr>
<td>$(Bi-Pb)$_2Sr$_2$Ca$_2$Cu$<em>3$O$</em>{10}$</td>
<td>109</td>
<td>20.9</td>
</tr>
<tr>
<td>$(Nd_{0.85}Ce_{0.15})_2CuO_4$</td>
<td>24</td>
<td>0, 30 $\sim$ 50</td>
</tr>
<tr>
<td>$(Nd_{0.85}Th_{0.15})_2CuO_4$</td>
<td>-</td>
<td>0, 20 $\sim$ 70</td>
</tr>
</tbody>
</table>

In Fig. 7 we plot $\ln \frac{M(\infty) - M(t)}{M(\infty)}$ against $t/T$ for $x = 0.15$, where $M(t)$ is the nuclear magnetization at time $t$ after the saturating pulses, and $T$ is the temperature. The experimental points are distributed on a line, indicating each component of $T_1$ to follow the $T_1 T = \text{const.}$ law in a wide temperature range. If we tentatively decompose the relaxation curve into two exponentials, $A \exp(-t/T_{1L}) + B \exp(-t/T_{1S})$ we obtain the longer and shorter components $T_{1L}$ and $T_{1S}$ which are plotted in Fig. 8. In Fig. 9 we plot the $x$ dependence of $(T_1 T)^{-1}$ obtained in the temperature range.

Figure 6 shows $T_1^{-1}$ of $^{63}$Cu in $(La_{1-x}Sr_x)_2CuO_4$. Here the longest components of $T_1$ are plotted, when the recovery is not exponential. The solid lines correspond to the relation $T_1 T = \text{const.}$...
Fig. 7. In $\frac{M(\infty) - M(t)}{M(\infty)}$ is plotted against $t \cdot T$ for $(La_{0.85}Sr_{0.15})_2CuO_4$ [8].

Fig. 8. Temperature dependence of $T_1^{-1}$ for $x = 0.075$ and $x = 0.15$ in $(La_{1-x}Sr_x)_2CuO_4$. For $x = 0.15$ the longer and shorter components, $T_{1L}$ and $T_{1S}$, are plotted.

Fig. 9. $x$ dependence of $(T_1 T)^{-1}$ in $(La_{1-x}Sr_x)_2CuO_4$. Closed and open circle show the longer and shorter component.

Fig. 10. $x$ dependence of the spin echo decay time constant $T_2$ in $(La_{1-x}Sr_x)_2CuO_4$ at 4.2 K.
region where the relation $T_1 T = \text{const.}$ holds, although the region for $x = 0.075$ is narrow. As seen in Figs. 6, 8, and 9, $T_1^{-1}$ decreases and develops multi-exponential-components, with the increase of Sr doping, and the region expands, where $T_1 T = \text{const.}$ holds. The longer component of $T_1$ arises from the region where the holes are effectively doped. The result shows that the spin fluctuations are easily suppressed by the hole doping and that a metallic character or a Fermi liquid behavior becomes remarkable. The shorter component for $x = 0.15$ indicates that the spin fluctuations still remain partly even at this concentration.

Next we discuss the transverse relaxation time. The spin echo decay time constant $T_2$ at 4.2 K is plotted against $x$ in Fig. 10 [8, 17]. Here the spin echo decay is exponential, and $T_2^{-1}$ decreases with increasing $x$. A similar result was obtained by Kumagai et al. [9]. The absolute value of $T_2^{-1}$ around $x \sim 0.075$ is much larger than that expected from the classical dipole interaction. The result shows that $T_2$ is determined by a strong nuclear magnetic indirect coupling through the Cu spin fluctuations which decreases with Sr doping.

Pennington et al. have demonstrated that in the Y compound the nuclear indirect coupling through the exchange coupled Cu spins is important to produce short $T_2$ [18]. $T_2^{-1}$ is larger in the La compound than in the Y compound. With decreasing $x$, $T_2^{-1}$ increases, making the observation of Cu NQR finally difficult.

Thus the behavior both of $T_1$ and $T_2$ indicates that the antiferromagnetic spin fluctuations existing clearly around $x \sim 0.075$ are suppressed by Sr doping, which is accompanied by a decrease of $T_1$. The antiferromagnetic spin fluctuations are suggested to play an important role for the occurrence of the superconductivity.

A similar behavior is seen in Zn substituted YBa$_2$Cu$_3$O$_7$. Zn doping in the Y system decreases $T_c$ remarkably [19]. Figure 11 shows the temperature dependence of $T_1^{-1}$ of $^{63}$Cu in YBa$_2$(Cu$_{0.98}$Zn$_{0.02}$)$_3$O$_7$. Closed and open circle correspond to $T_{1S}$ and $T_{1L}$, respectively [20]. ($T_c = 65$ K, $\nu = 31.5$ MHz).

Figure 12 shows the temperature dependence of $T_1$ of $^{205}$Ti in Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ [21]. $T_1^{-1}$ in the normal state nearly follows the Korringa law. This behavior is similar to those of $^{89}$Y [22] and $^{17}$O [23] in YBa$_2$Cu$_3$O$_7$ and $^{139}$La [24] in (La−Sr)$_2$CuO$_4$, in contrast with Cu. For $^{139}$La, $(T_1 T)^{-1}$ increases slightly with $T$. The antiferromagnetic spin fluctuations at the Cu site are considered to be cancelled at other sites.

Next we discuss the superconducting state. $T_1^{-1}$ in the superconducting state is expressed by

\[ 1/T_1 = \frac{\pi}{\hbar} \int A^2 \left( N_s^2(E) + M_s^2(E) \right) f(E) \left( 1 - f(E) \right) dE, \]

where $A$ is the hyperfine coupling constant, $f(E)$ the Fermi function, $N_s(E)$ the density of states of the quasi particles in the superconducting state and $M_s(E)$ the anomalous density of states due to the coherence effect.
In the BCS s-wave superconductor, both $N_{S}(E)$ and $M_{S}(E)$ diverge at the gap edge owing to a uniform energy gap. Thus $T_{1}^{-1}$ shows an enhancement just below $T_{c}$, followed by an exponential decrease at low temperature. The relaxation of Cu, Ti, Y and La does not behave in this way. We have no enhancement of $T_{1}^{-1}$ just below $T_{c}$.

In the case of d-wave pairing, where the gap is anisotropic and disappears on lines, $M_{S}(E)$ becomes zero and $N_{S}(E)$ at the gap edge is suppressed. This gives rise to a suppression of the enhancement of $T_{1}^{-1}$ which is seen in the heavy Fermion superconductors CeCu$_2$Si$_2$, UBe$_{13}$, UPt$_3$ and URu$_2$Si$_2$ [26]. The relaxation behavior of Cu, Y, La and Ti does not behave in this way. We have no enhancement of $T_{1}^{-1}$ just below $T_{c}$.

Finally, we comment on the measurement of $^{63}$Cu NMR in (Nd$_{1-x}$Ce$_x$)$_2$CuO$_4$ where superconductivity has been found below 24 K [30]. For $x=0$ the compound shows an antiferromagnetism with $T_{N}$ of 300 K [31]. With Ce doping the antiferromagnetism disappears and superconductivity sets in. The Hall effect measurement shows that the electrons act as charge carriers [30]. Zheng et al. have found an NMR signal of Cu for $x=0.15$ which has an anomalously small electric quadrupole interaction [32]. In addition to this signal, Kumagai et al. have found an NQR signal of $^{63}$Cu around 30 ~ 60 MHz [33]. Furthermore, Kohori et al. have found two groups of $^{63}$Cu signals in (Nd$_{1-x}$Th$_x$)$_2$CuO$_4$: one having almost no $e^2 Q$, the other being distributed around 20 ~ 70 MHz [34]. These two groups of signals may be attributed to two kinds of Cu atoms which are surrounded by larger and smaller amounts of Ce(Th). The reason why the electric quadrupole interaction disappears in a dense Ce(Th) region in spite of the non-cubic environment around Cu is not clear.
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