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, $(La_{1-x}Sr(Ba)_x)_2CuO_4$, $YBa_2Cu_3O_7$, $(Bi-Pb)_2Sr_2Ca_2Cu_3O_{10}$, $Tl_2Ba_2Ca_2Cu_3O_{10}$ and $(Nd_{1-x}Ce_x)_2CuO_4$ 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_2CuO_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 $\sim 0.01 \geq x \geq 0.025$, 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 $Bi_2Sr_2(Ca_xY_{1-x})_1Cu_2O_8$ 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 $(La_{1-x}Sr_x)_2CuO_4$ (La compound) has been observed first by Ishida et al. for $x > 0.06$ [7]. The

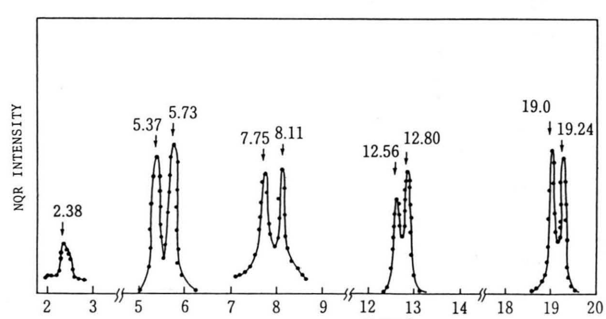

Fig. 1. Spin echo spectrum of ^{139}La in La_2CuO_4 in zero external field at 1.3 K [2].

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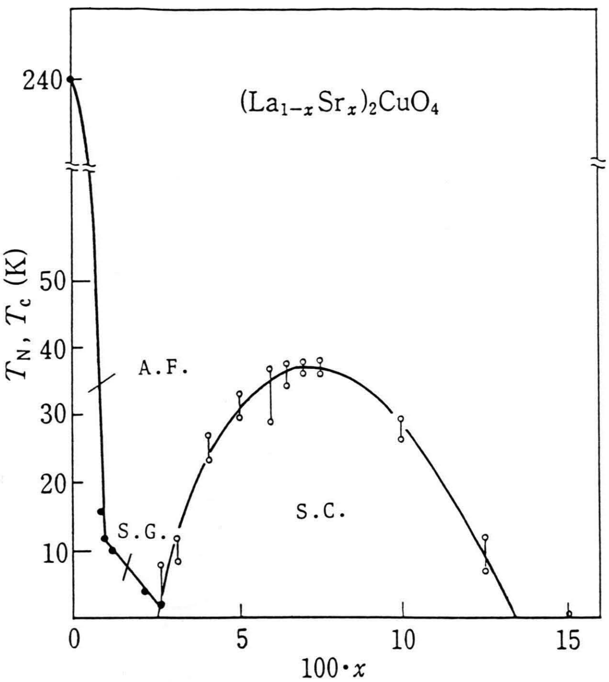

Fig. 2. Phase diagram of $(La_{1-x}Sr_x)_2CuO_4$. The magnetic and superconducting transition temperatures, T_N and T_c, are plotted against x. A.F., S.G. and S.C. mean antiferromagnetic, short range magnetic ordered (spin glass), and superconducting, respectively.

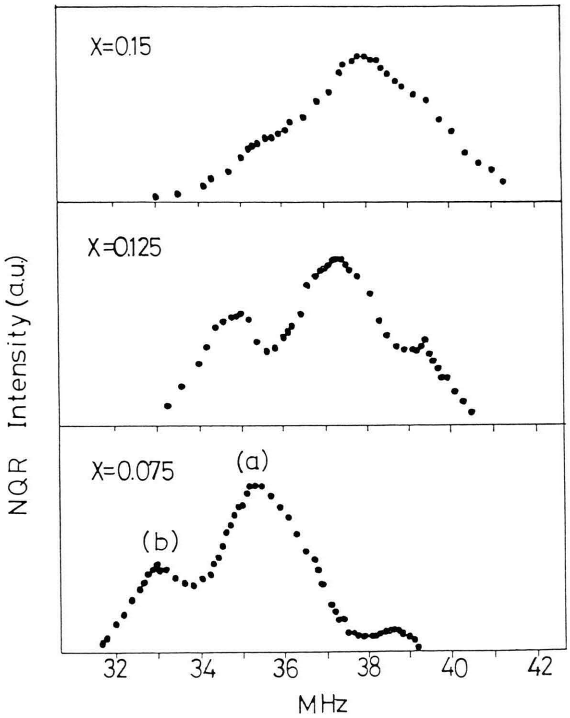

Fig. 3. Spin echo spectrum of Cu NQR in $(La_{1-x}Sr_x)_2CuO_4$ [8]. The peaks (a) and (b) correspond to ^{63}Cu and ^{65}Cu, respectively.

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 $(Bi-Pb)_2Sr_2Ca_2Cu_3O_{10}$ (Bi compound) has been observed by Fujiwara et al. and is shown in Fig. 4 [10]. Cu NQR in $Bi_2Sr_2(Ca-Y)Cu_2O_8$ 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.

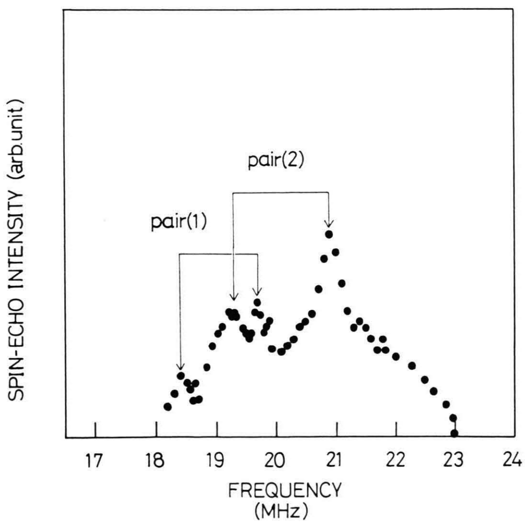

Fig. 4. Spin echo spectrum of Cu NQR at 1.3 K and zero field in $(Bi-Pb)_2Sr_2Ca_2Cu_3O_{10}$ [10]. Pair (1) corresponds to ^{63}Cu and ^{65}Cu in the (CuO_2) layer sandwiched by (CaO) layers, while pair (2) corresponds to those by (CaO) and (SrO) layers.

3. Nuclear Relaxation

The nuclear spin lattice relaxation rate T_1^{-1} of ^{63}Cu is shown in Fig. 5 in La [7], Bi [10] and Y [12–15] $(YBa_2Cu_3O_7)$ compounds. The characteristic properties of T_1^{-1} are as follows. T_1^{-1} in the normal state does not follow the Korringa law ($T_1\ T=$const.), but changes more slowly. In the La compound T_1^{-1} seems to follow the $T_1\ T=$const. law from T_c to about 70 K. Below T_c, T_1^{-1} decreases monotonously without BCS type enhancement.

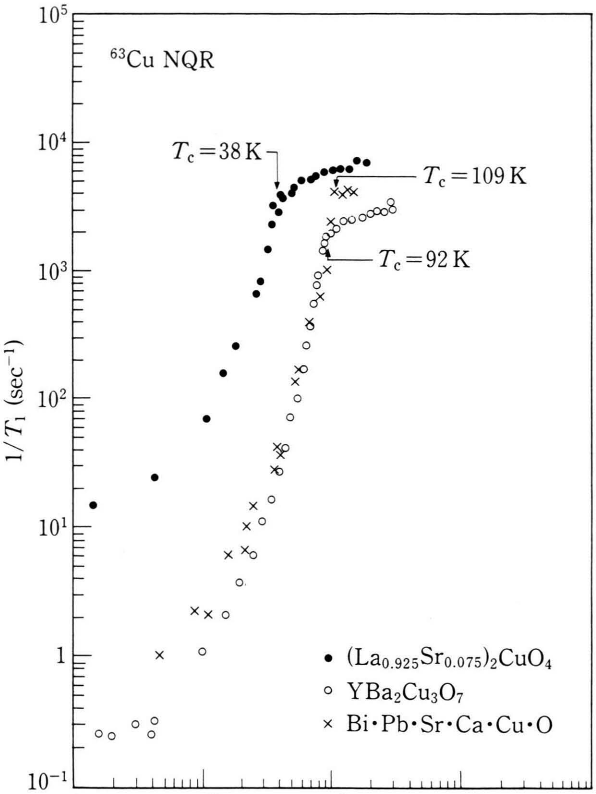

Fig. 5. T_1^{-1} of ^{63}Cu in $(La_{0.925}Sr_{0.075})_2CuO_4$ [7], $YBa_2Cu_3O_7$ (CuO_2 plane) [14] and $(Bi-Pb)_2Sr_2Ca_2Cu_3O_{10}$.

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

Compound	T_c (K)	ν_Q (MHz)
$(La_{0.85}Sr_{0.15})_2CuO_4$	0	~38
$(La_{0.925}Sr_{0.075})_2CuO_4$	38	35.3
$YBa_2Cu_3O_7$	92	31.5 CuO_2 plane
		20.2 CuO chain
$Bi_2Sr_2CaCu_2O_8$	80	~24
$(Bi-Pb)_2Sr_2Ca_2Cu_3O_{10}$	109	20.9
		19.7
$(Nd_{0.85}Ce_{0.15})_2CuO_4$	24	0, 30~50
$(Nd_{0.85}Th_{0.15})_2CuO_4$	–	0, 20~70

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}.

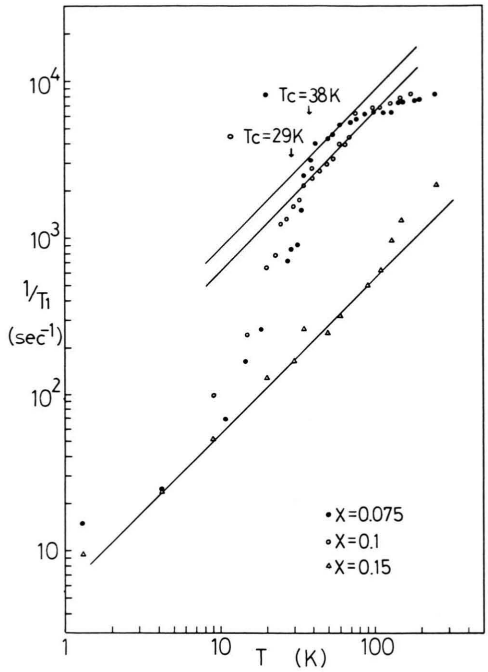

Fig. 6. T_1^{-1} of ^{63}Cu in $(La_{1-x}Sr_x)_2CuO_4$. Here the longest components of T_1 are plotted, when the recovery is not exponential. The solid lines correspond to the relation $T_1\,T$=const.

Figure 6 shows T_1^{-1} of ^{63}Cu in the La system with several x [8, 17]. For $x=0.075$ the relaxation behavior is exponential above 30 K, while non-exponential behavior appears gradually below 30 K. In Fig. 6 the longest components are plotted. With increasing x, multi-exponential behavior becomes remarkable as shown in Fig. 7. This indicates that the enhancement due to the antiferromagnetic spin fluctuations is not uniform in space but distributed from site to site. The Cu atoms surrounded by many Sr atoms are much affected by hole doping, which suppresses the fluctuations giving rise to the increase in T_1.

In Fig. 7 we plot $\ln \frac{M(\infty)-M(t)}{M(\infty)}$ against tT 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 $T_1\,T$=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

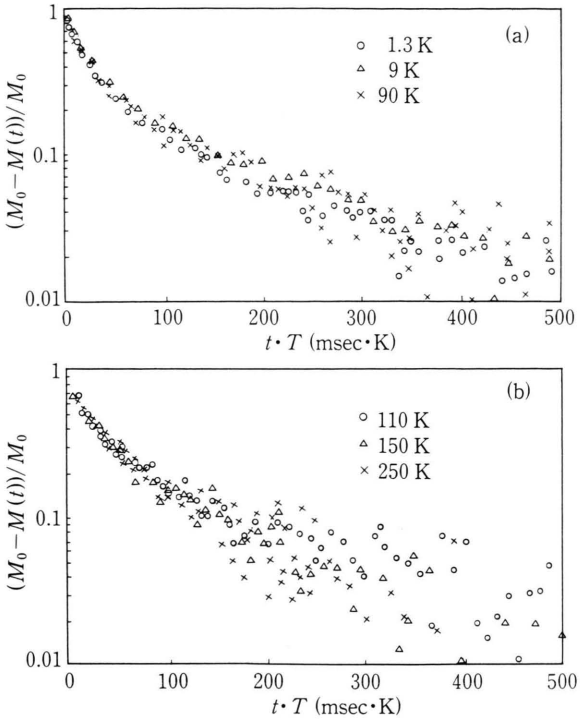

Fig. 7. $\ln \frac{M(\infty)-M(t)}{M(\infty)}$ is plotted against tT for $(La_{0.85}Sr_{0.15})_2CuO_4$ [8].

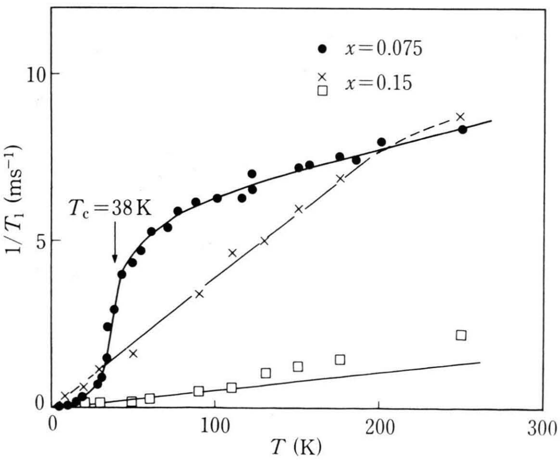

Fig. 8. Temperature dependence of T_1^{-1} for $x=0.075$ and $x=0.15$ in $(La_{1-x}Sr_x)_2CuO_4$. For $x=0.15$ the longer and shorter components, T_{1L} and T_{1S}, are plotted.

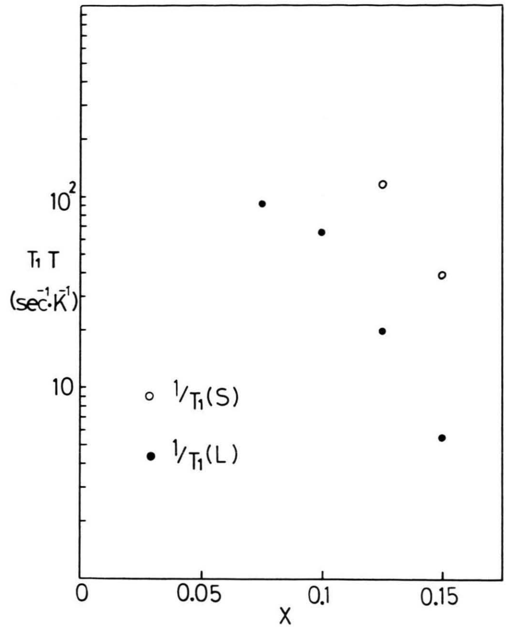

Fig. 9. x dependence of $(T_1 T)^{-1}$ in $(La_{1-x}Sr_x)_2CuO_4$. Closed and open circle show the longer and shorter component.

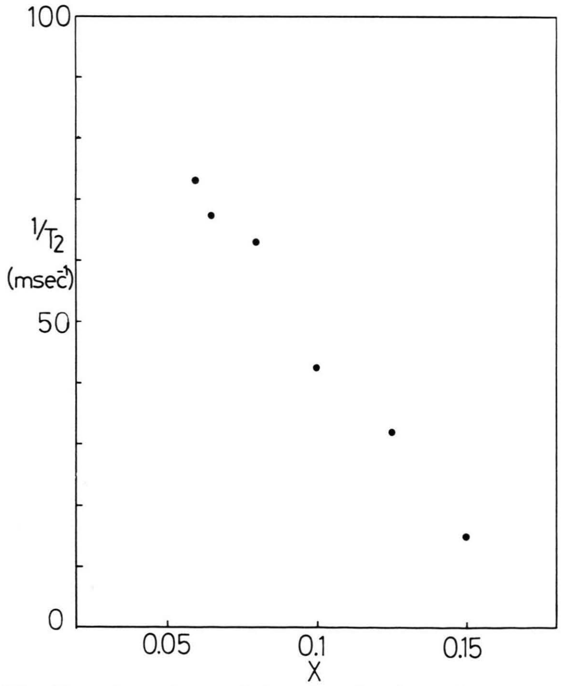

Fig. 10. x dependence of the spin echo decay time constant T_2 in $(La_{1-x}Sr_x)_2CuO_4$ at 4.2 K.

region where the relation $T_1\,T=$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 $T_1\,T=$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 $x\sim0.075$ 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 $x\sim0.075$ are suppressed by Sr doping, which is accompanied by a decrease of T_c. 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 $YBa_2Cu_3O_7$. Zn doping in the Y system decreases T_c remarkably [19]. Figure 11 shows the temperature dependence of T_1^{-1} of Cu in $YBa_2(Cu_{0.98}Zn_{0.02})_3O_7$ [20]. With Zn doping the relaxation behavior becomes multi-exponential. The shortest component of T_1, being almost the same as that for $x=0$ above $\sim$92 K, corresponds to Cu atoms far from Zn, while the longest component corresponds to those close to Zn. This indicates that Zn doping suppresses the Cu-spin fluctuations around Zn to give rise to the increase of T_1. Here we again see the correlation between T_c and the spin fluctuations. The shortest component de-

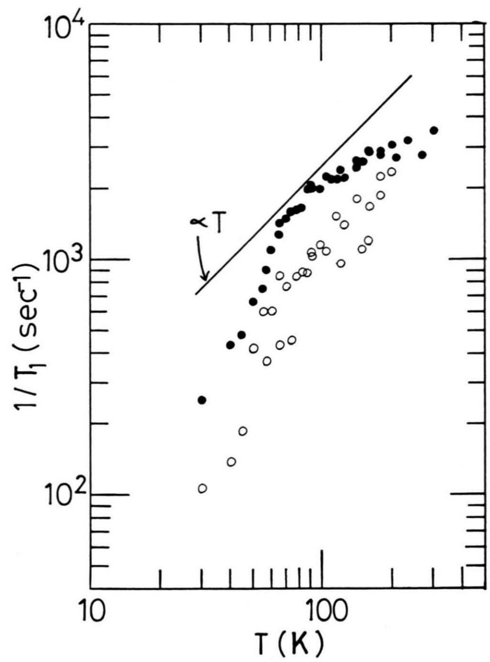

Fig. 11. Temperature dependence of T_1^{-1} of ^{63}Cu in $YBa_2(Cu_{0.98}Zn_{0.02})_3O_7$. Closed and open circle correspond to T_{1S} and T_{1L}, respectively [20]. ($T_c=65$ K, $f=31.5$ MHz).

creases in proportion to T^{-1} from $\sim$95 K down to 65 K (T_c). The longest component changes also as T^{-1}. Thus in both the La and Y compounds the Fermi liquid behavior ($T_1\,T=$const.) appears in Cu nuclear relaxation with decreasing temperature in the normal state, indicating an itinerant character of Cu spins even in the high T_c compounds.

Figure 12 shows the temperature dependence of T_1 of ^{205}Tl in $Tl_2Ba_2Ca_2Cu_3O_{10}$ [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 $YBa_2Cu_3O_7$ and ^{139}La [24] in $(La{-}Sr)_2CuO_4$, 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

$$1/T_1=\frac{\pi}{\hbar}\int A^2\{N_S^2(E)+M_S^2(E)\}\,f(E)\,(1-f(E))\,dE\,, \quad (1)$$

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

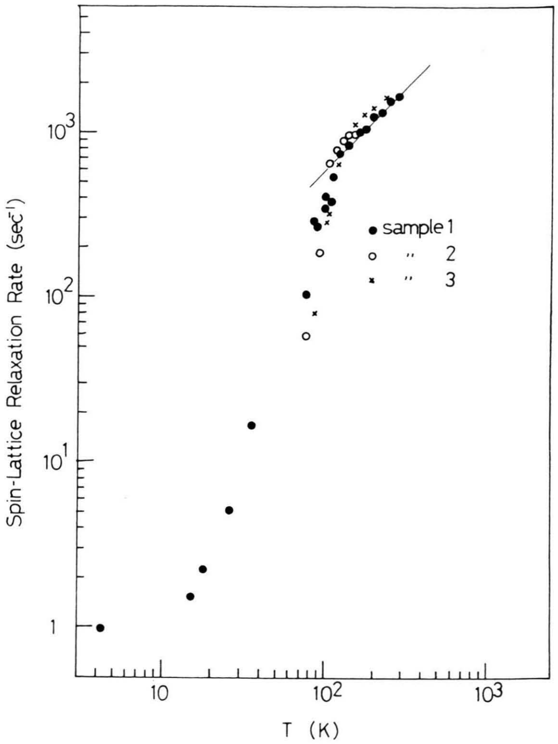

Fig. 12. Temperature dependence of T_1^{-1} of ^{205}Tl in $Tl_2Ba_2Ca_2Cu_3O_{10}$ [21]. ($T_c \sim 115$ K, $f=30.8$ MHz).

[25]. 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, Tl, 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 $CeCu_2Si_2$, UBe_{13}, UPt_3 and URu_2Si_2 [26]. The relaxation behavior of Cu, Y, La and Tl seems to support the d-wave pairing. The possibility of p-wave (triplet) pairing is excluded in our first measurement of the Knight shift of ^{63}Cu in $YBa_2Cu_3O_7$, which decreases below T_c indicating singlet pairing [14].

On the other hand, in our previous measurement we reported an enhancement in T_1^{-1} of ^{17}O in $YBa_2Cu_3O_7$ in an external field of 3 T, which seemed to support the s-wave pairing [23]. A similar enhancement was also reported by Wzietek et al. in the measurement of ^{17}O at 5.5 T [27]. On the contrary, the measurement of ^{17}O by Hammel et al. [28] in a field of 7 T did not show the enhancement. At present the origin of the observed enhancement is not clear.

As for the pairing function, the temperature dependence of the penetration depth in $YBa_2Cu_3O_7$ has been reported to be consistent with the BCS s-wave pairing [29]. The reason for the discrepancy between this and T_1 is still not clear.

4. $(Nd_{1-x}Ce_x)_2CuO_4$

Finally, we comment on the measurement of ^{63}Cu NMR in $(Nd_{1-x}Ce_x)_2CuO_4$ 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 $(Nd_{1-x}Th_x)_2CuO_4$: one having almost no e^2qQ, 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.

Acknowledgements

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