

NQR and NMR in High T_c Superconductors

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Recent NQR and NMR experiments on $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+y}$ and other compounds are reviewed. The antiferromagnetic spin fluctuations decrease in the order of La, Y, Tl compounds. In the normal state the T -dependence of $(T_1 T)^{-1}$ is considered to follow the Curie-Weiss law at high temperature and the $(T_1 T) = \text{const}$ law at low temperature. The T dependence of $1/T_1$ below T_c suggests strongly d-wave pairing. Correlations of the NQR frequency of ^{63}Cu and ^{17}O with the antiferromagnetic spin fluctuations and the superconducting transition temperature are discussed.

§ 1. Introduction

In spite of much effort, the mechanism of high T_c superconductivity is still not clear. Even the problem how to describe the normal state is controversial. NQR and NMR provide important information on the microscopical properties of the normal and superconducting states. In this paper a review is given on our recent NQR and NMR studies of high T_c cuprates, mainly $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+y}$.

§ 2. Experimental Results and Discussion

Figure 1 shows the T -dependence of $1/T_1$ of ^{63}Cu in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ obtained by NQR [1]. The result for $\text{YBa}_2\text{Cu}_3\text{O}_7$ is also shown for comparison. $1/T_1$ in the normal state decreases with x , indicating antiferromagnetic spin fluctuations (AFSF) that enhance $1/T_1$ to decrease with x . $(T_1 T)^{-1}$ follows a Curie-Weiss law, $c/(T + \theta)$, at high temperatures, becoming constant near T_c [2]. Below T_c , $1/T_1$ decreases rapidly with temperature and finally shows saturation. This saturation occurs earlier for the lower x and is not to be attributed to impurities but presumably to the localized nature of Cu d holes at low hole concentrations. Figure 2 shows the T -dependence of $1/T_1$ of ^{63}Cu in

$\text{Tl}_2\text{Ba}_2\text{CuO}_{6+y}$, which is obtained in an external field of 11 T perpendicular to the c axis [3, 4]. As seen in the figure, $1/T_1$ follows a $(T_1 T) = \text{const}$ law over a wide T range. At high temperature $(T_1 T)^{-1}$ follows a Curie-Weiss law with large θ of about 200 K. With increasing hole concentration, associated with the increasing oxygen, T_c decreases from 72 K to 0 K. The $(T_1 T) = \text{const}$ law extends to the lower temperature region. When the external field is applied in parallel to the c axis, T_c drops remarkably (for example from 40 to 10 K) [4]. Then, as shown in Fig. 2, the $(T_1 T) = \text{const}$ law holds until 10 K. Thus it is concluded that in the Tl compound, $1/T_1$ follows the $(T_1 T) = \text{const}$ law at low temperature when the superconductivity is destroyed.

As seen in Fig. 2, $1/T_1$ above T_c does not change appreciably with hole content, although T_c changes from 72 K to 0 K. This result seems to indicate that the spin fluctuations do not correlate with T_c . However, recent analysis shows that this is not the case [4]. As seen in Fig. 3, both the parallel and perpendicular components of the Knight shift associated with the spin susceptibility in Tl compounds, which are larger than in Y and La compounds, increase with hole content. Furthermore, the anisotropy of $1/T_1$, $T_{1\parallel}/T_{1\perp}$, which amounts to 3.8 and 2.8 in Y and La compounds, respectively, decreases to ~ 1.6 in the Tl compound with $T_c = 72$ K, becoming ~ 1 in the compound with $T_c \sim 0$. Now the hyperfine coupling at Cu is due to the on-site d-spin and the supertransferred part from the neighbouring Cu d-spins [5], the latter one being isotropic. Thus the above results in Fig. 3 are explained consistently by assuming an increase in the transferred part, which is positive and isotropic [4].

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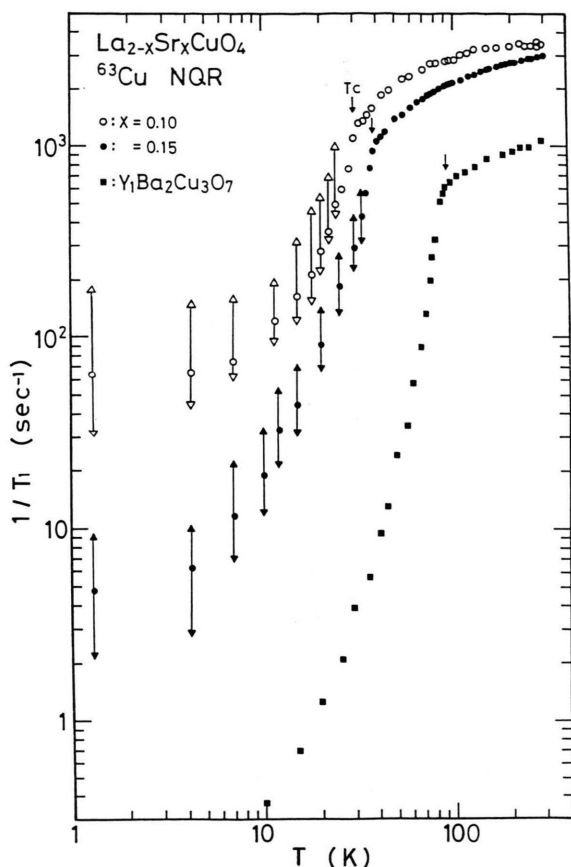


Fig. 1. Temperature dependence of $1/T_1$ of ^{63}Cu in the CuO_2 plane in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_7$ [1].

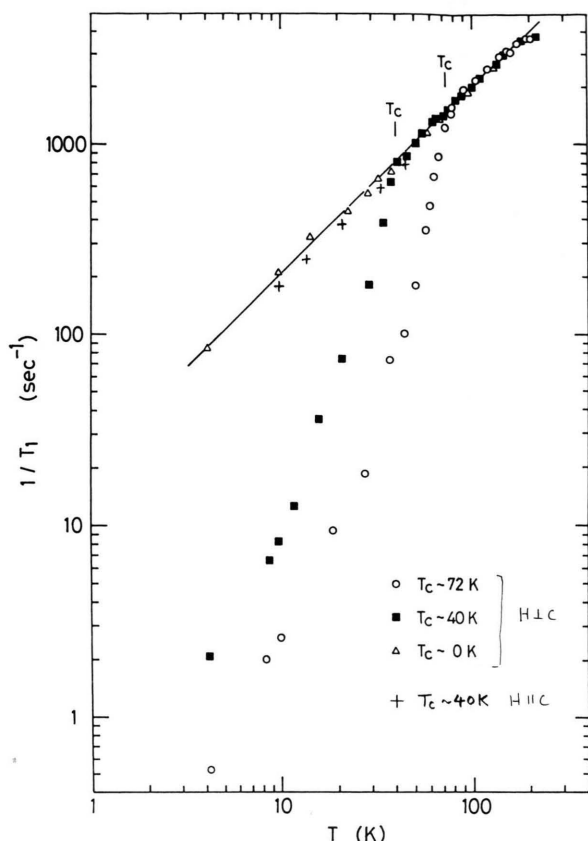


Fig. 2. Temperature dependence of $1/T_1$ of ^{63}Cu in $\text{Tl}_2\text{Ba}_2\text{CuO}_{6+y}$ [3, 4].

From the apparent invariant of $(T_1 T)^{-1}$ in spite of the increase of the hyperfine field with hole content, the AFSF may be concluded to decrease with hole content. The AFSF in the Tl system have been concluded to be reduced compared with the Y system and to decrease further with hole content [4]. Furthermore, the analysis shows that the antiferromagnetic correlation almost disappears and the Cu spins fluctuate independently in the Tl compound with $T_c = 0$ [4]. Thus we conclude that the AFSF decrease in the order La-, Y-, Tl-system with increasing hole content.

Figure 4 shows the dependence of $1/T_1$ of several compounds on T/T_c [6]. As seen in spite of different T_c values the points fall approximately on one curve below T_c although the behavior above T_c depends on the material. These results suggest that the nature of the superconductivity is the same in these compounds. From the same T -dependence below T_c it is natural to

expect that the T -dependence in the normal state below about T_c is also the same for these compounds. As mentioned above $(T_1 T) = \text{const}$ from about 150 K down to 10 K, as seen in Fig. 3 for the compound. Thus we may conclude that the $(T_1 T) = \text{const}$ law would hold not only in the Tl system but in all the compounds in Fig. 4 if the superconductivity were destroyed at low temperature below about T_c . A schematic behavior of $1/T_1$ in the normal state is suggested in Figure 5. $(T_1 T)^{-1}$ follows a Curie-Weiss law at high temperature and becomes constant below a characteristic temperature T^* . With increasing hole concentration T^* shifts to higher temperature. There are some cases where $(T_1 T)^{-1}$ decreases even above T_c . Although we cannot give an explanation for this behavior we believe that the essential behavior in high T_c cuprates is that as shown in Figure 5. To know the T -dependence of T_1 in the normal state is very impor-

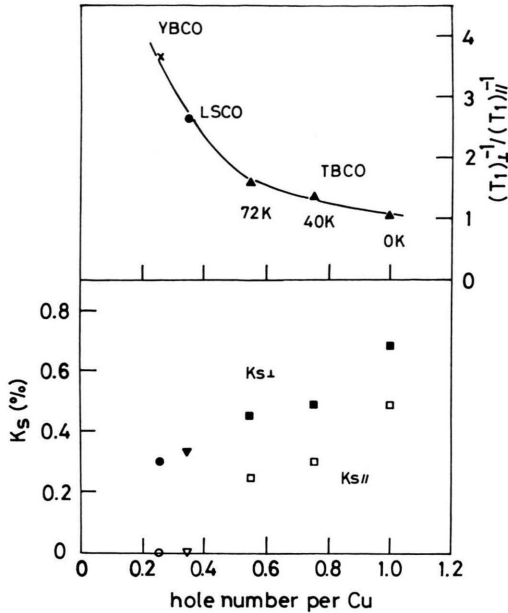


Fig. 3. (a) Anisotropy of $1/T_1$, $T_{1||}/T_{1\perp}$, and (b) $K_{s||}$ and $K_{s\perp}$ due to spin susceptibility (b) of $^{63}\text{CuO}_2$ plane are plotted against hole concentration [4].

tant in discussions of the T -dependence of superconductivity.

As for the sharp drop of $1/T_1$ below T_c , in contrast to the BCS superconductor, there are several efforts to explain it in the BCS s-wave model. The depairing effect by AFSF [8] or the strong scattering by phonons [9] are proposed. However the AFSF depend strongly on the material, as previously mentioned. So the behavior below T_c should be different if the spin fluctuations induce a gapless state. Similarly, the phonon scattering mechanism will also be different for different compounds because this mechanism will be the more effective the higher the temperature. The sharp drop of $1/T_1$ below T_c is commonly seen not only in Cu relaxation but also in O, Tl, and Pb relaxation.

The quite universal behavior in these cuprates suggests a gapless state which is intrinsic and common, that is, a d-wave pairing is promising, although in the measurements of other physical quantities, such as Knight shift [10] and penetration depth λ [11], the s-wave pairing seems to be favorable. If we assume tentatively the gap zero on line as $\Delta(\theta) = \Delta_0 \cos \theta$, $2\Delta_0 \sim 10.5 k_B T_c$, then the calculated $1/T_1$ (dashed line) shows no BCS type peak just below T_c and decreases in proportion to T^3 , reproducing well the experimental values except at low temperature, as seen in Fig-

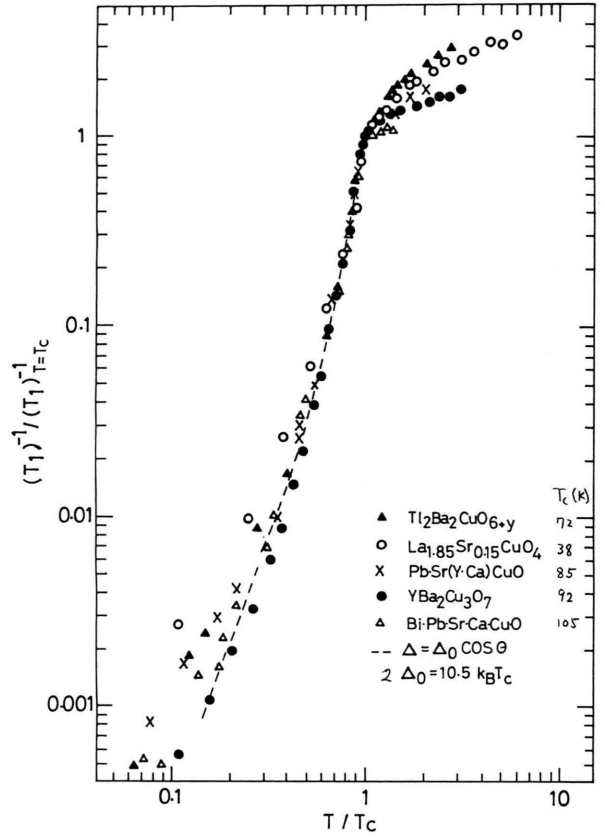


Fig. 4. $1/T_1$ of ^{63}Cu in the CuO_2 plane is plotted against T/T_c for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $\text{YBa}_2\text{Cu}_3\text{O}_7$, BiPbSrCaCuO , $\text{PbSr}_2\text{CaCuO}$ ($H=0$), and $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+y}$ ($H=11\text{ T}$) [6].

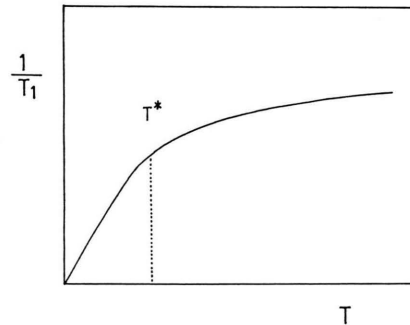


Fig. 5. Typical temperature dependence of $1/T_1$ of Cu in the CuO_2 plane in high T_c cuprate.

ure 4. Here it should be noted that we assume the $(T_1 T) = \text{const}$ relation in the normal state.

Recently Ishida *et al.* [12] investigated the Zn impurity effect both on T_1 and the Knight shift in YBCO_7 and observed a gapless effect at low temperature, al-

though the effect is very small near T_c . The behavior of $(T_1 T) = \text{const}$ and the increase of the residual Knight shift at low temperature become remarkable with Zn content, which is consistent with the d-wave model with an additional gapless state induced by impurities [12]. In this case, there appears a finite density at low lying excitation energy in addition to a density of states depending linearly on the energy associated with a gap zero on line. Then the Knight shift remains even at $T = 0$ K. The approach to $T = 0$ is no more linear with T even in d-wave pairing but seems BCS like if the residual part is subtracted from the raw data. Thus it is considered that in all the high T_c materials the states are more or less gapless due to impurities, dislocations and so on in the d-wave pairing. The T -dependence observed in the Knight shift [10] and λ [11], which seem to be BCS like, can also be explained by the d-wave model with an impurity induced gapless state. From the low temperature behavior it is difficult to distinguish s- or d-pairing. The deviation of $1/T_1$ from T^3 -dependence at the lowest temperature is attributed to the impurity induced gapless state. The saturation observed in the La system will be attributed to the gaplessness and the localized character of Cu d-holes. The Knight shift has a residual spin part in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ [15].

The NQR frequency ν_Q proportional to the electric field gradient q also provides important information. q is in general a sum of q_{int} and q_{ext} where q_{int} is due to the non-spherical distribution of on-site electrons and q_{ext} is due to the charges in the outside. Many authors analysed q on the assumption that q_{int} is coming from the $3d^9$ state and explained the observed values by multiplying q_{ext} by the so called Sternheimer factor [13]

$$q = q_{\text{int}} + q_{\text{ext}}(1 - \gamma).$$

Hanzawa *et al.* [14] analysed and explained consistently ν_Q of ^{63}Cu and ^{17}O in YBCO_7 excluding γ . So in their analysis the main part of q is q_{int} . According to their analysis, the ratio of the hole numbers of Cu and O in the CuO_2 plane is about 0.5.

In Fig. 6, we plot the NQR frequency ν_Q of ^{63}Cu and ^{17}O in the CuO_2 plane in La [15], Y, and Tl compounds. ν_Q of ^{63}Cu decreases, while ν_Q of ^{17}O increases in the order La, Y, Tl. We assume that the observed ν_Q 's are approximately proportional to the Cu d-hole number $n(\text{Cu})$ and the O p-hole number $n(\text{O})$, respectively. Thus the number of holes at Cu in the CuO_2 plane, $n(\text{Cu})$, decreases, while that at oxygen

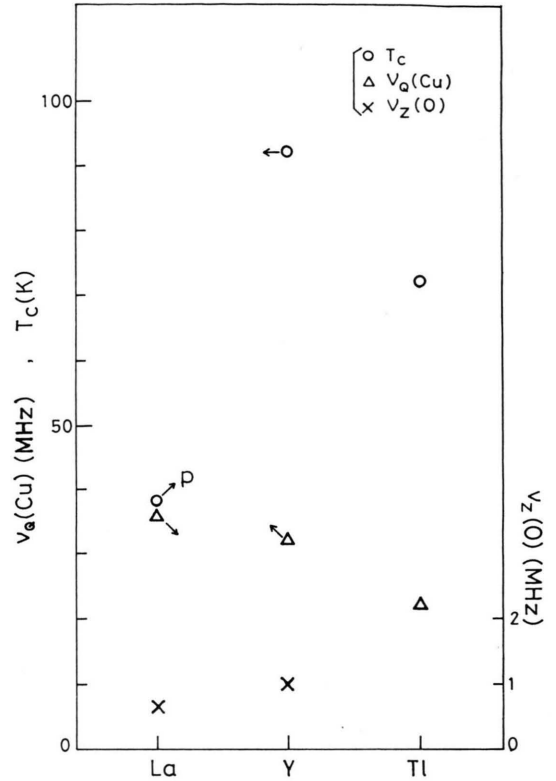


Fig. 6. T_c , $\nu_Q(\text{Cu})$, and $\nu_Q(\text{O})$ are plotted for La, Y, and Tl compounds. The pressure effects on T_c and ν_Q are shown by arrows.

in the CuO_2 plane, $n(\text{O})$, increases from La to Y. $n(\text{O})$ in the Tl system is expected to increase further. Now it is considered that the increase in $n(\text{Cu})$ increases the AFSF, while the increase in $n(\text{O})$ reduces them. If the AFSF play an essential role for the occurrence of superconductivity, T_c should increase with AFSF. On the other hand, the increase of $n(\text{O})$ decreases the AFSF while it increases the carrier density and/or the mobility of holes. The decrease of the AFSF is unfavourable for the superconductivity, while the increase in carrier density and/or the mobility is in favor of it. In fact, the localized behavior of the Cu d-hole observed in T_1 in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with decreasing Sr seems to correlate with the decrease of T_c . Thus values for $n(\text{Cu})$ and $n(\text{O})$ are expected to exist which give a maximum value of T_c .

High pressure measurements by Zheng *et al.* suggest that parameters which are important for T_c may be $n(\text{Cu})/n(\text{O})$ and $n(\text{Cu}) + n(\text{O})$, and that there exists an optimum value of $n(\text{Cu})/n(\text{O})$ [16]. When high

pressure is applied, v_Q of Cu decreases [16] while T_c increases [17] in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$, as seen in Figure 6. $n(\text{Cu})/n(\text{O})$ is considered to be reduced to approach the optimum value under pressure, where the decrement of $n(\text{Cu})$ is assumed to be equal to the increment of $n(\text{O})$ when the total numbers of holes are conserved. In $\text{YBa}_2\text{Cu}_3\text{O}_7$, the pressure dependence of T_c is small [18], indicating that $n(\text{Cu})/n(\text{O})$ is close to the optimum value. Zheng *et al.* observed an increase in v_Q of Cu in $\text{Y}_1\text{Ba}_2\text{Cu}_4\text{O}_8$ [13], which is consistent with the results of Zimmerman *et al.* [19]. This means that $n(\text{Cu})$ increases. In this case dT_c/dp is very large [17]. The sharp increase of T_c with pressure is attributed to the approach of $n(\text{Cu})/n(\text{O})$ to the opti-

mum value, which is caused by the transfer of holes from CuO chains into both Cu and O in the CuO_2 plane [20].

The band calculation shows that the contribution to $v_Q(\text{Cu})$ from 4 p electrons is as important as that from 3 d electrons [21]. So the discussion may not be so simple. However, since the relation between the hole density and the AFSF and/or T_c are very important, it is necessary to make a more systematic study on v_Q .

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