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MAGNETISM AND SUPERCONDUCTIVITY BY NMR STUDY

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Abstract. Results of NMR measurement on high $T_c$ oxide superconductor are reviewed together with heavy electron superconductor. In high $T_c$ compounds, superconductivity and antiferromagnetism compete with each other, while in heavy electron systems both coexist or compete. The property of Cooper pair is discussed in high $T_c$ superconductor together with the heavy electron superconductor.

In the several systems where superconductivity and magnetism interact with each other, heavy electron superconductor and high $T_c$ oxide superconductor are of particular interest. There are several similar aspects in both systems. In these systems antiferromagnetic ordering and superconductivity appear in coexistence or in competition [1]. The property of superconductivity is unconventional in heavy electron system [1] which is also seen in high $T_c$ superconductor in NMR measurement. There is a possibility of non-phonon mechanism, an attractive interaction through a magnetic fluctuations, being responsible for the occurrence of superconductivity, although any direct evidence for this is not proved.

In this paper a recent review on NMR measurements of high $T_c$ superconductor will be presented together with a brief review on heavy electron systems [2].

1. Heavy electron system

1.1 MAGNETISM. The neutron diffraction measurements have observed the antiferromagnetic correlation, sometimes static antiferromagnetic ordering, appearing in the ground state of heavy electron system, which seems to be a general property of this system [1]. The static antiferromagnetic ordering is reflected in the line broadening associated with the internal field and in the anomaly in the nuclear spin-lattice relaxation rate $T_1^{-1}$ in NMR. In CeAl$_2$ NMR line broadening due to antiferromagnetic ordering has been reported [3]. A rapid decrease of $T_1^{-1}$ due to a gap opening associated with SDW ordering is observed in URu$_2$Si$_2$ [4]. Recent NMR measurements have revealed that the systems CeCu$_2$Si$_2$ [5], CeAl$_3$ [6] and CeInCu$_2$ [7] are ordered at low temperature.

1.2 SUPERCONDUCTING PROPERTY. $T_1$ in CeCu$_2$Si$_2$ [8], UBe$_{13}$ [9], URu$_2$Si$_2$ [4] and UPt$_3$ [10] in superconducting state all show an unconventional behavior. $T_1^{-1}$ below $T_c$ decreases monotonously and in proportion to $T^3$ at low temperature. These behaviors are explained in terms of an anisotropic superconductivity, the gap disappearing on lines at the Fermi surface.

2. High $T_c$ oxide superconductor

2.1 MAGNETISM.

2.1.1 $(La_{x}Ba_{1-x})_2CuO_4$. $La_2CuO_4$ is an antiferromagnet with $T_N \approx 240$ K. With replacing La by Ba, $T_N$ decreases rapidly [11] and then superconductivity appears for $x \gtrsim 2.5\%$ [12]. Figure 1 shows a NQR spectrum of La at 4.2 K [13]. The complicated structure is well explained by a large electric quadrupole interaction together with a small Zeeman energy due to the magnetic order. Here, $H_{//}$ and $H_{\perp}$ are the parallel and perpendicular component of the internal field at La site with respect to the c axis respectively. Taking $e^2qQ / h$, $H_{//}$, $H_{\perp}$ and $\eta$ as 89.3 MHz, 200 Oe, 1000 Oe and zero, the calculated energy levels up to second order of $H_{//}$ to $H_{Q}$ reproduces the experiment quite well. The internal field is the dipole field from the magnetic moments.

\[ H_Q = \frac{e^2qQ}{4I(2I-1)} \left\{ 3I_2^2 - I(I+1) + \frac{7}{2} \left( I_2^2 + I_3^2 \right) \right\} \]

\[ H_Z = -\gamma h H_{\perp} (I_+ e^{-i\phi} + I_- e^{i\phi}) - h H_{//} I_Z. \]

Here, $H_{//}$ and $H_{\perp}$ are the parallel and perpendicular component of the internal field at La site with respect to the c axis respectively. Taking $e^2qQ / h$, $H_{//}$, $H_{\perp}$ and $\eta$ as 89.3 MHz, 200 Oe, 1000 Oe and zero, the calculated energy levels up to second order of $H_{//}$ to $H_{Q}$ reproduces the experiment quite well. The internal field is the dipole field from the magnetic moments.

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on Cu whose direction is in the c plane with a small component to c axis. Figure 2 shows the change of the spectra with $x$ for R(2)R(3) and R(4)R(5) in figure 1. The splitting due to $H_{\perp}$ exists up to about $x = 0.025$ where the superconductivity starts to appear. With increasing temperature $H_{\perp}$ decreases becoming zero at $T_N$, which is plotted in figure 3. The change of $H_{\perp}$ is also plotted. $T_N$ agrees with the temperature at which the transversal relaxation rate of signals R(6) and R(7) diverges [14]. $T_N$ decreases first rapidly and then slowly. It should be noticed that no abrupt change in $H_{\perp}$ is observed in spite of the discontinuous change of $T_N$ around $x \sim 0.008$. This fact indicates that the magnetic arrangements surrounding La do not change over $x \sim 0.008$ drastically. On the other hand no anomaly in the specific heat is observed at $T_N$ for $x > 0.008$ [15]. From these results it is considered that the three dimensional antiferromagnetic ordering appears exists up to $x = 0.008$ and then a spin glass type ordering appears where the two dimensional ordering still exists although the long range ordering along c axis is lost. Recently Aharony et al. [16] proposed a spin glass type ordering. In their scheme, a local ferromagnetic interaction induced by the holes introduced at oxygen sites when Ba is substituted to La. This interaction destroys the three dimensional ordering, whereas the two dimensional antiferromagnetic correlation still remains. This model explains well the obtained magnetic phase diagram in figure 3.

2.1.2 YBa$_2$Cu$_3$O$_{7-y}$. - There are two inequivalent Cu sites in CuO$_2$ plane Cu(II) and in CuO chain Cu(I) for this compound. Since Cu has two isotopes both having $I = 3/2$, two pairs of NQR signals are expected. The NQR signals of Cu are observed as shown in figure 4a [17-21]. The signals around $30 \sim 32$ MHz and $20 \sim 22$ MHz are assigned to Cu at (II) and (I), respectively after several discussions [19, 20, 22-25]. When Y is replaced by Gd, Sm, and Nd, two pairs of Cu signals appear in almost the same frequency range as in Y case. In these replaced systems, $T_1$ of the signal around 32 MHz is much shorter than at 20 MHz which supports the above assignment [23]. Furthermore, analyses of Cu NMR spectra in the external field in the grain oriented sample also confirm the above assignment [24, 25].

Figure 4b, c and d show NQR spectra for $y = 0.35$, 0.7 [26] and 0.9 [25, 27, 28]. The line broadens below 20 K for $y = 0.7$ [25] and splits at 4.2 K for $y = 0.8$ [27]. For $y \approx 1$ an antiferromagnetic ordering was already reported by $\mu$SR [29] and neutron diffraction measurement [30] with $T_N \simeq 400 \sim 540$ K. Furthermore, the neutron diffraction in single crystal for $y \simeq 0.65$ shows...
an antiferromagnetic order at Cu(II) site appearing below 405 K and then the second ordering at Cu(I) site with small moment below 40 K [31]. Recently, NMR signals due to Cu(II) site are observed around 100 MHz for $y = 0.9 \sim 0.7$ [32]. Thus the signals observed around 30 MHz in figures 4c and d are demonstrated to be due to Cu(I) site. The broadening and splitting observed for $y = 0.7$ and 0.8 correspond to modifications of the magnetic ordering. The phase diagram obtained by neutron diffraction [31, 33] pSR [35] is shown in figure 5.

Fig. 5. – Phase diagram of YBa$_2$Cu$_3$O$_{7-y}$. Neutron diffraction [30, 31], (○) [31], (●) [33], μSR (▲) [34], NQR (●) [35]. The solid line in antiferromagnetic phase indicates a change of the magnetic ordering.

2.2 SUPERCONDUCTING PROPERTY. – $T_1$ of Cu in YBa$_2$Cu$_3$O$_{7-y}$ system was measured by several groups [17, 19, 20, 36-38]. The results agree qualitatively with each other. Figure 6 shows $T_1$ at Cu(II) site [37]. The characteristic aspects are as following: $T^{-1}_1$ above $T_c$ is not linear to $T$ but changes more slowly. Below $T_c$, $T^{-1}_1$ decreases rapidly and then shows a saturation behavior at low temperature. By comparing $T_1$ of $^{63}$Cu and $^{65}$Cu the relaxation above 20 K has been confirmed to be magnetic in origin whereas below 20 K the electric quadrupole relaxation begins to participate. By using a relation [37]

$$1/T_1 = 1/^{63}T_1 \text{obs} \times \frac{Z - 65Q/^{63}Q}{(65Q/^{63}Q)^2 - (65Q/^{63}Q)^2}$$

with $Z = ^{63}T_1 \text{obs} / ^{65}T_1 \text{obs}$ the magnetic relaxation $T_1 M$ has been separated from the observed $T_1$ as shown in the figure by open dot circle. Thus $T^{-1}_1$ associated with the magnetic relaxation decreases nearly in proportion to $T^3$ at low temperature.

To see the behavior in normal state in wider temperature range, $T_1$ has been measured in YBa$_2$ (Cu$_{0.98}$Zn$_{0.02}$)$_3$O$_7$ with $T_c = 60$ K [39]. As seen in figure 6, the values above 100 K are almost the same as those for $x = 0$, whereas $T_1 T =$ const. law begins to hold below 100 K. The deviation from $T_1 T =$ const. law above 100 K may be attributed to antiferromagnetic fluctuations [38].

$T_1$ of Y is proportional to $T$ above $T_c$ [36]. Below $T_c$, $T^{-1}_1$ decreases monotonously rapidly.

The behavior of $T_1$ of Cu in superconducting state is in contrast with the usual BCS superconductor. $T^{-1}_1$ in superconducting state is expressed as [40]

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

where $A$ is the hyperfine coupling constant, $N_s (E)$ and $M_s (E)$ are $\frac{N_0 E}{\sqrt{E^2 - \Delta^2}}$ and $\frac{N_0 \Delta}{\sqrt{E^2 - \Delta^2}}$, respectively, with normal density of states $N_0$. $f (E)$ is the Fermi function, and $2 \Delta$ is the energy gap. Owing to a uniform energy gap in BCS superconductor, which gives rise to a divergence of both $N_s (E)$ and $M_s (E)$ at the gap edge, $T^{-1}_1$ shows an enhancement just below $T_c$ and then decreases exponentially. The absence of the enhancement and non-exponential behavior, nearly $T^3$ dependence at low temperature, in the present system suggested the anisotropic nature of the superconductivity (p or d-wave).

On the other hand, the Knight shift of Cu is observed to decrease below $T_c$ indicating the singlet pairing in this system [37]. Thus the superconducting pairing function was considered to be of d-wave due to a strong on-site Coulomb repulsion [37].
In the d wave pairing the gap disappears on lines and/or points which provides $T^3$ or $T^5$ dependence of $T_{c}^{-1}$ at low temperature. Furthermore, $\Delta (\theta)$ takes positive and negative values becoming zero on the average which makes $M_S$ zero. If we assume tentatively $2\Delta (\theta) = 12kT_c \cos \theta$ the experiment is well reproduced as shown by a solid line in the figure.

$T_1$ of Cu in (I) site shows no rapid decrease below $T_c$ as if the gap at this site is small [20]. However, $T_1$ at Cu(I) is sample dependent: an analysis of $T_{c}^{-1}$ by Kitaoka et al. [37] shows that the quadrupole relaxation plays a dominant role which masks the intrinsic relaxation associated with the conduction electrons, whereas Warren et al. show that the relaxation is magnetic [20]. So we cannot say about the superconducting property on site (I).

$T_1^{-1}$ on site (II) for YBa$_2$Cu$_3$O$_{6.65}$ becoming superconducting below 60 K is also shown in figure 6. $T_{c}^{-1}$ in normal state is surprisingly suppressed compared with YBa$_2$Cu$_3$O$_7$ [37, 41]. A sharp peak appearing below $T_c$ is attributed to an extra relaxation due to some impurity electron spins (probably free Cu spins) whose fluctuation rate decreases rapidly below $T_c$ and passes through Cu NMR frequency at about 50 K [42]. It should be noted that the effect of Zn substitution and O deficiency on $T_1$ in normal state are quite different, even when the depressions of $T_c$ are same.

Quite recently, Kitaoka et al. [43] have found that $1/T_1$ of $^{17}$O substituted at CuO$_2$ plane has a clear enhancement just below $T_c$ which suggests strongly the s-wave pairing of the superconductivity. The d-wave like behaviour observed in Cu relaxation may be explained by a rapid reduction of antiferromagnetic fluctuation below $T_c$ which is considered to be localized at Cu site and enhances the $1/T_1$ of Cu in normal state. This suggests that the superconductivity is carried by O p-holes. A remarkable reduction of $1/T_1$ of Cu at CuO$_2$ plane from YBa$_2$Cu$_3$O$_7$ to YBa$_2$Cu$_3$O$_{6.65}$ in normal state may be attributed to a reduction of the antiferromagnetic fluctuations associated with the decrease of oxygen hole number.

In summary, superconductivity and antiferromagnetic ordering in high-$T_c$ compounds appear with their region in contact with each other when the concentration of Ba or O are changed in (La$_{1-x}$Ba$_x$)$_2$CuO$_4$ and YBa$_2$Cu$_3$O$_{7-y}$. This behavior is similar to the heavy electron system where the superconductivity and magnetic ordering coexist or compete.

In YBa$_2$Cu$_3$O$_7$, the nuclear relaxation behavior of Cu is d-wave like as in the case of heavy electron system. However recent study on O suggests s-wave pairing. The d-wave like behavior in Cu may be caused by a reduction of antiferromagnetic spin fluctuations localized on Cu site in superconducting state. This suggests that the superconductivity is carried by oxygen p-holes.

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