NMR study of magnetism and superconductivity in high-T_c oxides

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The results of ^{139}La and ^{63}Cu nuclear quadrupole resonance (NQR) on La–Ba,Sr–Cu–O, Y–Ba–Cu–O, and Bi–Pb–Sr–Ca–Cu–O compounds and of ^{17}O nuclear magnetic resonance (NMR) on Y–Ba–Cu–O are extensively reviewed. As for the magnetism, the phase diagram for the La system studied by a ^{139}La NQR experiment is presented, with evidence of the disordered magnetic state between the 3D-antiferromagnetic (AF) ordered state and the superconducting state. With respect to its superconducting nature, the nuclear spin-lattice relaxation behavior (T_1) of Cu in the CuO_2 plane has been found to be unconventional above and below T_c for all compounds, with no signatures expected for a nonmagnetic metal and a BCS superconductor, respectively. The behavior of T_1 of Cu above T_c is shown to be dominated by AF fluctuation of Cu *d* spins. In contrast, an enhancement of $1/T_1$ of ^{17}O has been observed just below T_c, which is similar to a BCS case.

1. Introduction

A fascinating subject in solid-state physics is to elucidate the origin of high-temperature superconductivity. Many experimental and theoretical efforts have been applied to this study [1]. It is believed that superconductivity is closely related to antiferromagnetism. With respect to the overall electronic structure, photoemission studies have revealed that doped holes are predominantly O 2*p*-like rather than Cu 3*d*-like, due to the strong on-site Coulomb interaction among Cu 3*d* electrons [2, 3]. The important problem in high-T_c materials is thus to explore separately the respective role of each atomic site in superconductivity and magnetism from a microscopic point of view. The nuclear magnetic (NMR) and quadrupole (NQR) resonance studies are suitable tools with which to obtain information on the electronic state at each atomic site. It is well known that the study of nuclear spin-lattice relaxation has been one of the crucial experiments in establishing BCS theory [4].

As for the magnetism, the ^{139}La NQR experiment has shown a disordered magnetic phase with AF coherency over a long distance only within the CuO_2 plane between the 3D AF state and the superconducting state [5].

With respect to superconductivity, the nuclear relaxation behavior of Cu in the CuO_2 plane tells us that both the normal and the superconducting states are quite unconventional compared to those of a BCS superconductor [6–9]. The behavior of $1/T_1$ of Cu above T_c is dominated by AF fluctuation of Cu spin on the CuO_2 plane [9]. In

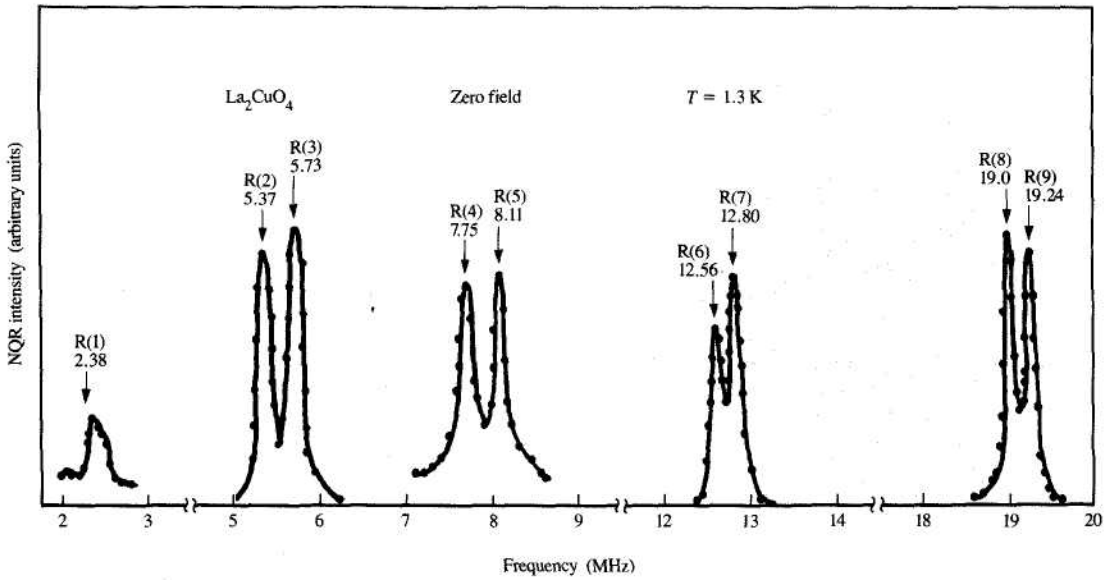

Figure 1

^{139}La NQR spectra of La_2CuO_4. Calculated frequencies are shown by arrows [R(1)–R(9)].

contrast, $1/T_1$ of ^{17}O in the Y–Ba–Cu–O system has been found to exhibit a different feature from that of Cu. Thus, NMR studies have demonstrated that the high-T_c superconductors are unusual, with Cu and O possessing different electronic states.

In this paper, we review the magnetism and the superconductivity of high-T_c materials investigated by NMR.

2. Magnetism in the $(La_{1-x}Ba_x)_2CuO_4$ system

La_2CuO_4 is an antiferromagnet, with $T_N = 240$ K. When La is replaced by Ba, T_N drops rapidly and then the superconductivity appears for $x = 2.5\%$ [10]. **Figure 1** shows NQR spectra of ^{139}La at 4.2 K. The complicated structure is well interpreted by a large electric quadrupole interaction together with a small Zeeman energy due to the magnetic order [5]:

$$\mathcal{H}_Q = \frac{e^2qQ}{4I(2I-1)}\left\{3I_z^2 - I(I+1) + \frac{\eta}{2}(I_+^2 + I_-^2)\right\},$$

$$\mathcal{H}_Z = -\gamma\hbar H_\perp(I_+e^{-i\phi} + I_-e^{i\phi}) - \gamma\hbar H_\parallel I_Z.$$

Here, $H_\parallel$ and $H_\perp$ are the parallel and perpendicular components of the internal field at the La site with respect to the c-axis. Taking e^2qQ/h, $H_\perp$, $H_\parallel$, and η as 89.3 MHz, 1000 Oe, 200 Oe, and zero, the calculated energy levels up to the second order of $\mathcal{H}_Z$ to $\mathcal{H}_Q$ reproduce the experiment quite well [5]. The internal field is the dipole field from the magnetic moments on Cu whose direction is in the c-plane with a small component parallel to the 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 against the Ba concentration. T_N agrees with the temperature at which the transversal relaxation rates of signals R(6) and R(7) diverge [11]. 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 drastically over $x \sim 0.008$. On the other hand, no anomaly in the specific heat is observed at T_N for $x > 0.008$ [5]. From these results, it is considered that the three-dimensional antiferromagnetic ordering exists up to $x = 0.008$, and then a spin-glass-type ordering appears, where the AF coherency in the CuO_2 plane remains, although the long-range ordering along the c-axis is lost. Aharony et al. have proposed a spin-glass-type ordering in the intermediate state between the 3D AF state and the superconducting state [12]. In their scheme, a local ferromagnetic interaction is induced

by the holes introduced at oxygen sites when Ba is substituted in La sites. This interaction destroys the three-dimensional ordering, although the two-dimensional antiferromagnetic correlation still remains, due to the strong superexchange interaction among Cu spins. This model explains well the phase diagram obtained in Figure 3 [12]. The characteristic feature that the nuclear relaxation rate diverges at T_N [11] means that the spin fluctuation is slowing down with decreasing temperature, its frequency passing through the resonance frequency of La nuclei. These spin dynamics seem to be strongly correlated with the motion of the holes introduced on the oxygens, which start to localize with decreasing temperature. Thus, doped holes which are more or less mobile govern the spin dynamics through the exchange interaction between Cu d spins and hole spins.

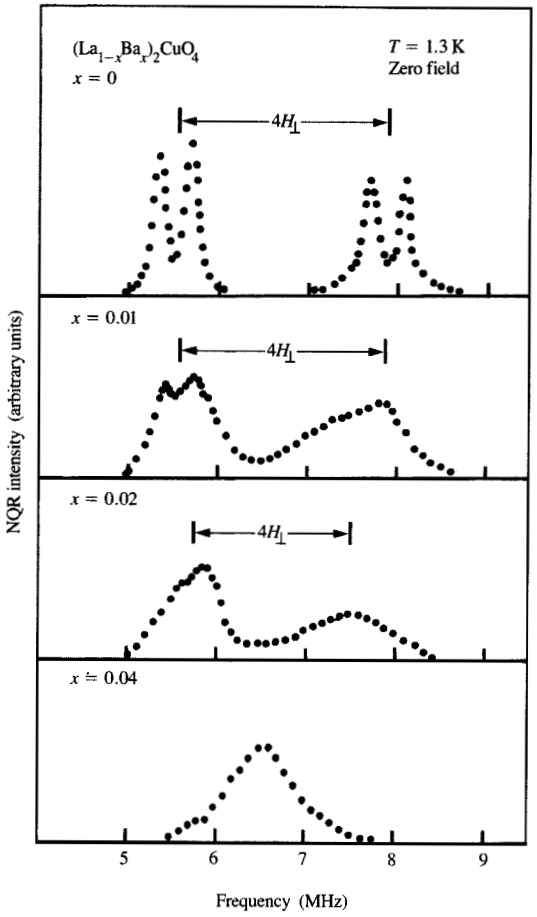

Figure 2

Spectra in $(La_{1-x}Ba_x)_2CuO_4$ corresponding to R(2), R(3), R(4), and R(5) in Figure 1.

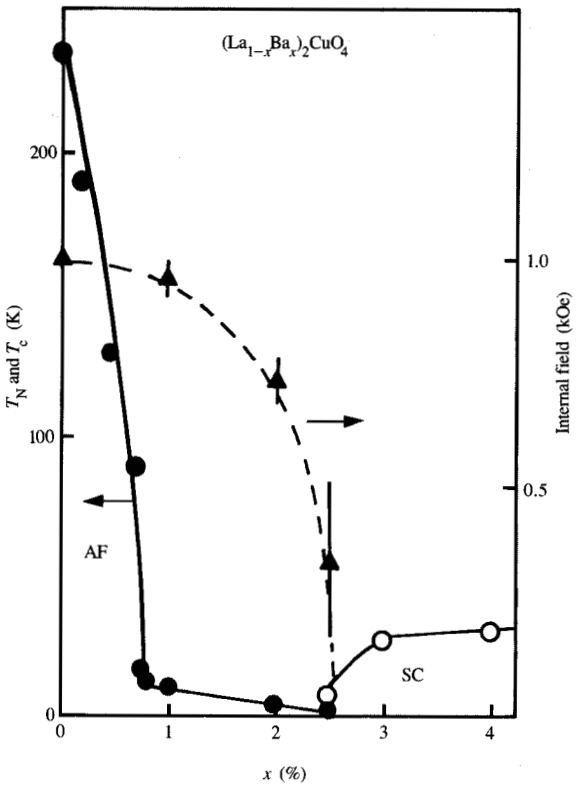

Figure 3

Phase diagram of $(La_{1-x}Ba_x)_2CuO_4$ system. ●: T_N from NQR; ▲: $H_\perp$.

3. Cu nuclear relaxation behavior

Figures 4(a) and **4(b)** show the Cu NQR spectra for Y and La compounds, respectively. The spectra were obtained at 1.3 K and zero magnetic field by changing frequency. The Cu NQR for the La system has recently been observed for the first time by Ishida et al. [13]. [Following us [13] (received October 20, 1988), K. Kumagai and Y. Nakamura also observed Cu nuclear quadrupole resonance—*Physica C* **157**, 307–314 (1989) (received December 15, 1988).] Each pair of spectra correspond to two ^{63}Cu and ^{65}Cu isotopes. For Y compounds, it is well known that there are two Cu sites, i.e., CuO_2 plane and CuO chain. For a La system including one CuO_2 sheet, ^{63}Cu NQR has been discovered at about 35.3 MHz [13]. As seen in Figure 4(b), the resonance frequency for the La compound is close to that for the Y compound.

In **Figure 5**, we show the temperature dependences of $1/T_1$ of ^{63}Cu for $La_{1.85}Sr_{0.15}CuO_4$ ($T_c = 38$ K) and $YBa_2Cu_3O_7$ ($T_c = 92$ K), indicated by solid and open circles,

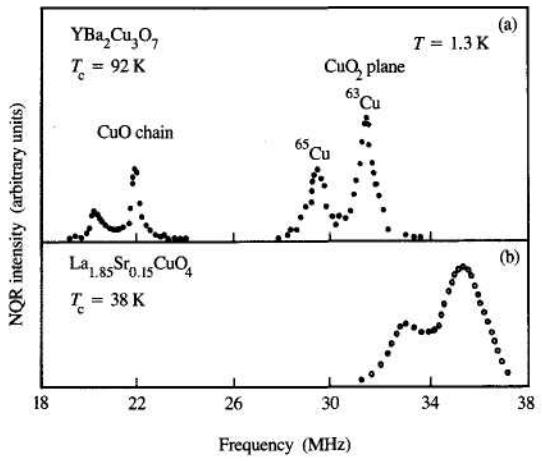

Figure 4

Cu NQR spectra of (a) $YBa_2Cu_3O_7$ and (b) $La_{1.85}Sr_{0.15}CuO_4$ at 1.3 K and zero magnetic field.

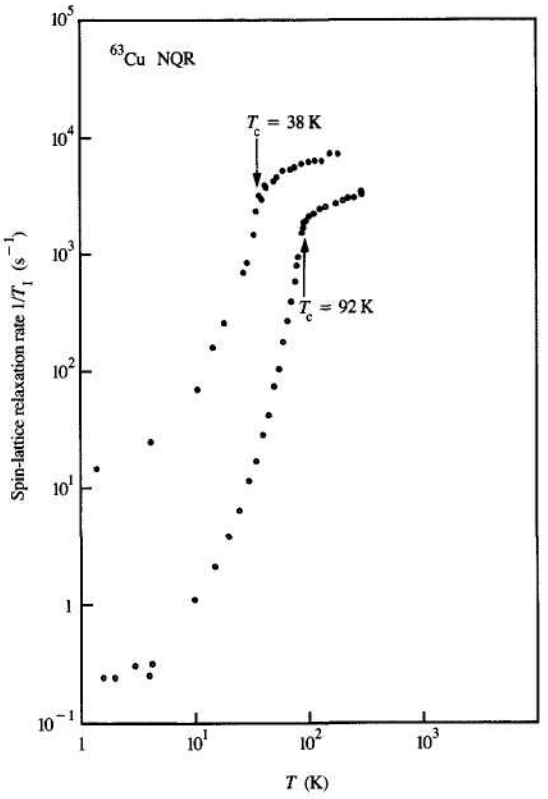

Figure 5

Temperature dependences of $1/T_1$ obtained for ^{63}Cu. Closed circles: $1/T_1$ of $(La_{0.925}Sr_{0.075})_2CuO_4$ (T_c = 38 K). Open circles: $1/T_1$ in the CuO_2 plane of $YBa_2Cu_3O_7$ (T_c = 92 K).

respectively. We skip the CuO chain result for the Y compounds because the data are strongly sample-dependent due to some difference of the oxygen deficiency in the CuO chain [6–9]. As seen in the figure, the two $1/T_1$ are similar. Thus, the relaxation of ^{63}Cu in the La systems is considered to arise from the same mechanism as that of the CuO_2 plane in the Y compounds. $1/T_1$ above T_c shows a weak temperature dependence, being saturated at higher temperature. The difference between the two behaviors is that $1/T_1$ for the La system is proportional to the temperature in the narrow temperature range between T_c and 70 K and about three times larger than $1/T_1$ of the Y compound.

Quite recently, Fujiwara et al. have found Cu NQR signals around 20 MHz in the high-T_c oxides Bi–Pb–Sr–Ca–Cu–O with T_c = 109 K [14]. Two ^{63}Cu NQR lines have been observed. Noting that this compound possesses three CuO_2 planes (two of them being CuO_2 planes with five pyramid-like oxygens as in the Y compound and one CuO_2 plane with four oxygens in the basal plane sandwiched between two CaO layers), two NQR lines are associated with these Cu sites. T_1 of ^{63}Cu in the same CuO_2 plane as in the Y compound has been measured between 4.2 K and 150 K. The temperature dependence of $1/T_1$ is shown by the solid circles in **Figure 6**. Above T_c, $1/T_1$ follows no Korringa relation of T_1T = constant, as in the case of La and Y compounds. The behavior of $1/T_1$ above T_c tends to be less temperature-dependent, with T_c increasing.

In order to look at the relaxation behavior below T_c, we plot in **Figure 7** the $1/T_1$ normalized by the value at $T = T_c$ against the temperature normalized by T_c. As seen in the figure, the $1/T_1$ of each compound decreases markedly without an enhancement just below T_c characteristic of a BCS superconductor. At low temperature, $1/T_1$ saturates, implying that the intrinsic magnetic relaxation is masked. The relaxation behavior of ^{63}Cu in the CuO_2 plane possesses a common feature for three different types of high-T_c oxides discovered thus far, suggesting that the same mechanism is responsible for the relaxation process. As for the saturation of $1/T_1$ at low temperature, the quadrupole relaxation process was confirmed to come up at low temperature for both Y and La compounds [13, 15]. As shown already [15], we can, however, discriminate an intrinsic magnetic relaxation rate from the observed T_1 by measuring precisely the ratio of T_1 of two isotopes ^{63}Cu and ^{65}Cu with the different nuclear magnetic moment and the electric

quadrupole moment. Then $1/T_1$ for the Y compound was found to approach a T^3 behavior at low temperature [15], which is not of the exponential type expected for a BCS case.

The behavior of T_1 in the superconducting state is apparently in contrast to that of the usual BCS superconductor. $1/T_1$ below T_c is expressed [4] as

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

where A is the hyperfine coupling constant, $N_s(E)$ and $M_s(E)$ are

$$\frac{N_0 E}{\sqrt{E^2 - \Delta^2}} \quad \text{and} \quad \frac{N_0 \Delta}{\sqrt{E^2 - \Delta^2}},$$

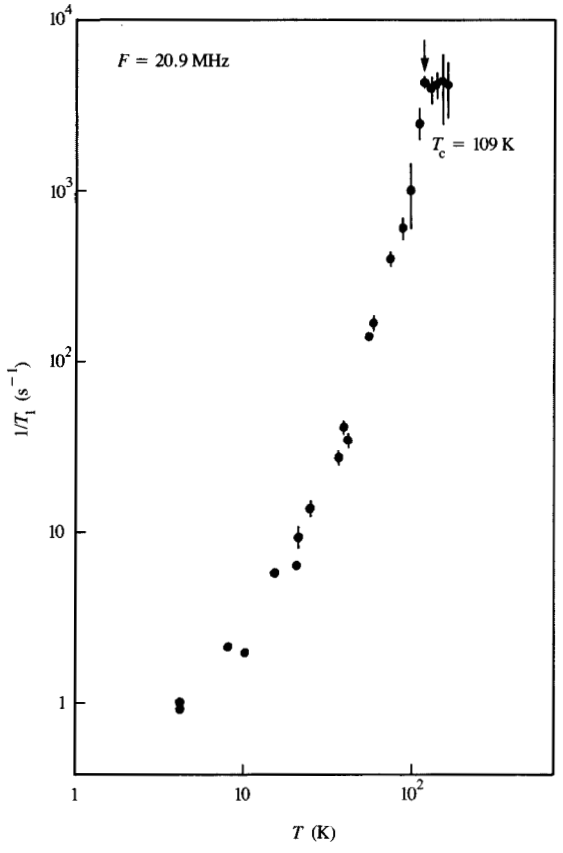

Figure 6

Temperature dependence of $1/T_1$ in the CuO_2 plane with the same oxygen pyramid as in Y compounds in Bi–Pb–Sr–Ca–Cu–O.

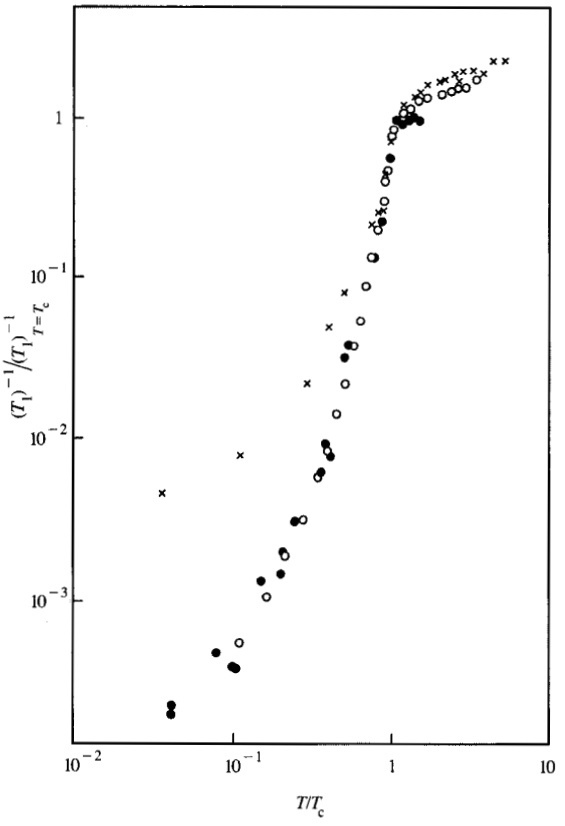

Figure 7

Temperature dependences of $1/T_1$ obtained for ^{63}Cu in the CuO_2 plane. Cross marks: La compound (T_c = 38 K). Open circles: Y compound (T_c = 92 K). Solid circles: Bi compound (T_c = 109 K). Here the temperature is normalized by T_c. $1/T_1$ is also normalized by $1/T_1$ at $T = T_c$.

respectively, with normal density of state N_0. $f(E)$ is the Fermi function, and 2Δ is the energy gap. Owing to a uniform energy gap in BCS superconductors, which gives rise to a divergence of both $N_s(E)$ and $M_s(E)$ at the gap edge, $1/T_1$ shows an enhancement just below T_c and then decreases exponentially [4]. The absence of the enhancement just below T_c and the nonexponential behavior (nearly T^3 dependence at low temperature for the Y compounds) suggest the unconventional nature of the superconductivity of the high-T_c oxides, implying an anisotropic energy gap on the Fermi surface [8, 15]. In the above expression of $1/T_1$ below T_c, the Korringa law of T_1T = constant is implicitly

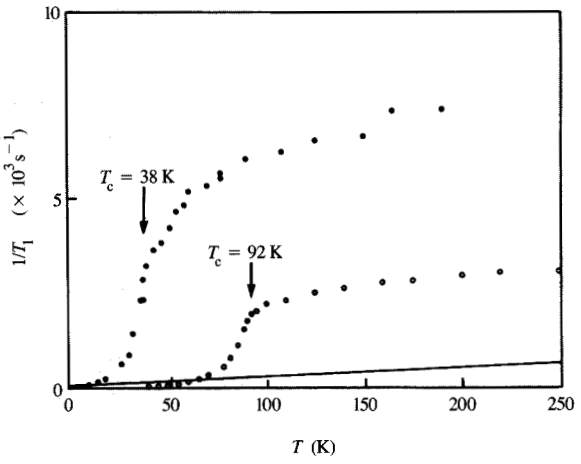

Figure 8

Temperature dependences of $1/T_1$ of ^{63}Cu in both La and Y compounds in a linear scale for both values. A solid line indicates a T_1T = constant law for the Cu metal.

involved in the normal state. However, this is not the case for the high-T_c materials, as previously noted. Accordingly, first of all, we should discuss the origin of the relaxation process above T_c, which is not of the type expected for a nonmagnetic metal.

Compared with the value of $1/T_1$ for Cu metal shown by a solid line in **Figure 8**, $1/T_1$ of both La and Y compounds are strongly enhanced in spite of the low density of the carrier concentration of these materials. Combining the weak temperature dependence and the large enhanced behavior of $1/T_1$ above T_c, we suppose that $1/T_1$ of ^{63}Cu in the CuO_2 plane is dominated by a spin fluctuation characteristic of a highly correlated system. In general, $1/T_1$ is described by the imaginary part of a dynamic susceptibility $\chi(q, \omega)$ as

$$1/T_1 = k_B T \Sigma_q A_q^2 \, \mathrm{Im}\, \chi(q, \omega_n)/\omega_n,$$

where A_q is the hyperfine coupling constant and ω_n is the resonance frequency. If we express $\mathrm{Im}\,\chi(q, \omega)$ by using the magnetic relaxation rate Γ_q of the electron spin system as

$$\mathrm{Im}\,\chi(q, \omega) = \frac{\chi(q)\omega\Gamma_q}{\omega^2 + \Gamma_q^2},$$

taking a relation of $\omega_n \to 0$, we have the expression

$$1/T_1 = k_B T \Sigma_q A_q^2 \chi(q)/\Gamma_q,$$

where $\chi(q)$ is a wavenumber-dependent spin susceptibility. The point is that $1/T_1$ reflects the q-dependent magnetic response averaged over a whole reciprocal space. This means that even if the uniform susceptibility $\chi(0)$ is temperature-independent, as in Pauli paramagnets (just corresponding to the high-T_c materials), $1/T_1$ is dominated by an antiferromagnetic (AF) spin fluctuation. In the case where the AF spin correlation is developing in the CuO_2 plane owing to a strong superexchange interaction among Cu d-spins with decreasing temperature below $T_0 \sim J/k_B \sim 1000$ K, it is expected that the staggered susceptibility $\chi(Q)$ is larger and more temperature-dependent even if the uniform susceptibility is unaffected. Then, $1/T_1$ integrated over the whole q-space has a large contribution from the AF spin fluctuation around $q = Q$ (Q: AF q vector), which is considered to be responsible for the weak temperature dependence and the enhanced behavior of $1/T_1$ of Cu in the CuO_2 plane. This type of discussion has been presented by several groups [9, 16].

With the above scheme, the marked decrease of $1/T_1$ below T_c may also be associated with a strong depression of the AF spin fluctuation due to the appearance of superconductivity if the Cu d electron is nearly localized on the Cu sites. That is, when the superconducting energy gap appears in the excitation spectrum of the mobile hole carriers (quasiparticles with spin) below T_c, it is likely that the frequency spectrum of the Cu d spin fluctuation may also have some gap in the low-frequency part because the spins are strongly coupled; $1/T_1$ enhanced above T_c may be suppressed below T_c, as pointed out by the theory [17]. Thus, the unconventional behavior of $1/T_1$ of ^{63}Cu may be due to the strong correlation of Cu d electrons.

On the other hand, if the Cu d electrons form the quasiparticle with doped hole carriers and then contribute to the pairing as superconducting carriers below T_c, as expected for the marked decrease of $1/T_1$ of Cu, it might be deduced from the unusual relaxation behavior of Cu that the superconductivity is highly anisotropic in nature. Under such circumstances, in order to further characterize the superconducting property of high-T_c oxides, it is of substantial importance to investigate the electronic state at oxygen sites by the ^{17}O NMR technique. Below, we present preliminary ^{17}O NMR results [18, 19].

4. ^{17}O nuclear relaxation behavior

The sample of the ^{17}O substituted system is prepared as follows [20]. First, $YBa_2Cu_3O_7$ was prepared by a solid-state reaction of Y_2O_3, $BaCO_3$, and CuO, all at least 99.99% pure, at 950°C in air for 24 h. The gas-exchange process consists of (1) removing ^{16}O from the sample at 700°C; (2) keeping the pellet in $^{17}O_2$ atmosphere (51.244 at. % ^{17}O) at 950°C for 24 h; (3) cooling to 550°C at a rate of 50°C/h; (4) keeping at 550°C for 12 h; and (5) cooling to room temperature at a rate of 50°C/h. There are three inequivalent oxygen sites: CuO_2 plane, CuO chain, and BaO layer. The Raman

scattering experiments showed that the oxygen isotope is equally distributed in these sites [21].

Figure 9 curve (a) shows the NMR spectrum of ^{17}O in a field of ~ 3 T in $YBa_2Cu_3O_7$. The spectrum indicates a powder pattern of the first-order electric quadrupole interaction with nonzero asymmetry parameter η. We first discuss which oxygen sites the observed signal comes from. Figure 9 curves (b) and (c) show, respectively, the spectra of ^{17}O in $YBa_2Cu_3O_{6.65}$ (T_c = 60 K) and $YBa_2Cu_3O_6$ (antiferromagnet), where the ^{17}O is replaced in almost the same procedure [19]. As seen in the figure, the signal intensity in $YBa_2Cu_3O_{6.65}$ is nearly the same as in $YBa_2Cu_3O_7$ in spite of the deficiency of oxygen at the CuO chain. Furthermore, even in $YBa_2Cu_3O_6$ [Figure 9(c)] which has no CuO chain, we have ^{17}O signal. No appreciable decrease in the integrated intensity was observed compared with $YBa_2Cu_3O_7$. In the oxygen exchange process in $YBa_2Cu_3O_6$, the concentration of ^{17}O was about half that in O_7 and $O_{6.65}$ compounds, which is the main reason for the slight decrease of the apparent integrated intensity in Figure 9(c) compared with 9(a) and 9(b).

The disappearance of the central peak in $YBa_2Cu_3O_6$ is attributed to a broadening associated with the antiferromagnetic ordering. Even at the O site in the CuO_2 plane, which is a magnetically symmetrical position, a canting of the Cu magnetic moments due to the external field and/or an inhomogeneity in the sample will produce a line broadening to smear the central line into the broad satellites. These results indicate that the contribution to the ^{17}O spectrum is relatively small.

To study further the detailed structure of the ^{17}O NMR spectrum, precise NMR measurement has been made quite recently by using an oriented powder sample with the c-axis parallel to the magnetic field [22]. This type of NMR experiment using an oriented powder sample was first performed by Takigawa et al. to obtain the precise data of the Cu Knight shift [23]. The central ($1/2 \leftrightarrow -1/2$) transition of the ^{17}O NMR spectrum of $YBa_2Cu_3O_7$ has been found to consist of three lines corresponding to three different O sites. It is evident that the central peak in Figure 9(a) is not well resolved, and all signals overlap.

The nuclear spin-lattice relaxation time T_1 of ^{17}O for $YBa_2Cu_3O_7$ was measured in the central peak of the spectrum of Figure 9(a) observed in an external magnetic field of about 3 tesla. T_c in the magnetic field is expected to be almost the same as T_c = 92 K in the zero magnetic field, because the powder sample is preferentially oriented with the c-axis perpendicular to the magnetic field due to the anisotropy of the superconducting diamagnetism [24], and the upper critical field H_{c2} has quite a large slope against the temperature near T_c [25]. In the T_1 measurement of ^{17}O, a significant distribution of T_1 has not been found [18], though the ^{17}O NMR spectrum is composed of the signals from three oxygen sites: CuO_2 plane, CuO chain, and BaO layer.

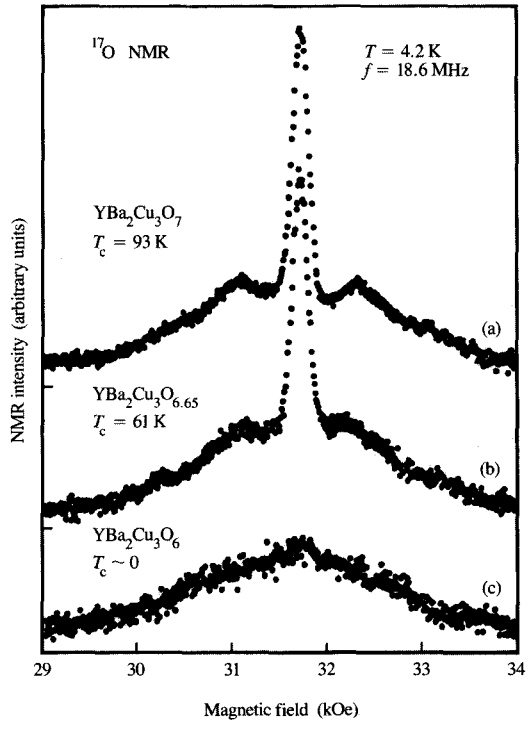

Figure 9

^{17}O NMR spectra in (a) $YBa_2Cu_3O_7$, (b) $YBa_2Cu_3O_{6.65}$, and (c) $YBa_2Cu_3O_6$.

At present, it is not clear to which oxygen sites the measured T_1 is assigned. Nevertheless, we can compare the nuclear relaxation behavior of ^{17}O with that of Cu. **Figure 10** shows the temperature dependence of $1/T_1$ for ^{17}O (solid circles) and ^{63}Cu (open circles) in the CuO_2 plane. Above T_c, $1/T_1$ of ^{17}O looks like a Korringa type (T_1T = constant) up to 150 K, as shown by the solid line, while it deviates upward from a linear temperature dependence above 150 K. This behavior of T_1 of ^{17}O is similar to that of ^{63}Cu in the CuO chain [6–9]. In contrast, $1/T_1$ of ^{63}Cu in the CuO_2 plane shows no Korringa behavior in the whole temperature range, though a T_1T = constant behavior appears in the narrow temperature range between T_c and 70 K for $La_{1.85}Sr_{0.15}CuO_4$ [13].

Below T_c, there appears a further marked difference in relaxation behavior between ^{17}O and ^{63}Cu. As seen in Figure 10, $1/T_1$ of ^{17}O exhibits an enhancement just below T_c, whereas $1/T_1$ of ^{63}Cu in the CuO_2 plane shows a strong reduction with no hump below T_c. Thus, the relaxation behaviors of ^{17}O and ^{63}Cu have been found to be different,

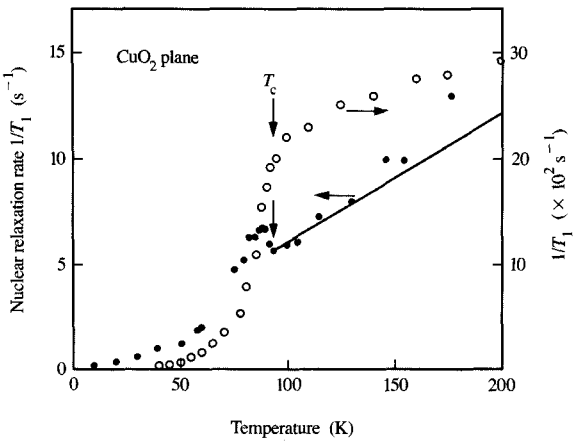

Figure 10

Temperature dependences of $1/T_1$ of ^{17}O (solid circles) and of ^{63}Cu (open circles) in $YBa_2Cu_3O_7$. T_1 data of ^{17}O and ^{63}Cu were measured in a magnetic field of 3 tesla and zero magnetic field, respectively. Note that each scale of $1/T_1$ is different. A solid line indicates a T_1T = constant law for the reference.

despite their relatively close locations. Since the oxygen sites where T_1 was measured are not clear, we cannot remark about the origin of the different nuclear relaxation behaviors of ^{17}O and ^{63}Cu. The important feature independent of the site assignment is, however, an observation of an enhancement of $1/T_1$ just below T_c similar to that of a BCS case. In contrast to the behavior of $1/T_1$ of Cu, this may provide a signature that the superconductivity is of the *s*-wave type if the Cu *d* electrons are nearly localized. Here, if we remember the electronic structure of the cuprate proposed by the photoemission studies (i.e., the doped holes are predominantly oxygen *p*-like, while the Cu *d* holes are nearly localized [2, 3]), we may associate the nuclear relaxation behaviors of ^{17}O and ^{63}Cu with the doped oxygen *p* holes and the Cu *d* holes, respectively, with a freedom of spin fluctuation. There then seems to be a possibility that the superconductivity is formed by the *p*-hole pairing with a dominant *s*-wave symmetry. In order to establish the above scheme, we need further precise measurements of T_1 at each oxygen site; this is now in progress.

5. Conclusion

The magnetic phase diagram of $(La_{1-x}Ba_x)_2CuO_4$ has been established from a microscopic point of view [5]. A crossover from the 3D AF ordered state to a disordered magnetic state occurs around $x = 0.008$. This disordered magnetic phase, continuing to $x = 0.025$, is of a short-range type along the successive plane, and of a long-range type in the plane. The superconductivity appears just after the disappearance of the disordered magnetic phase. The obtained phase diagram is well interpreted in terms of a model proposed by Aharony et al. [12]. The important feature of this model is that it takes into account a local ferromagnetic interaction induced by the holes introduced at oxygen sites when Ba is substituted at La sites. This interaction destroys the 3D AF order while the AF correlation within the plane still remains, due to the strong superexchange interaction among Cu spins. We would like furthermore to stress that this local ferromagnetic interaction not only induces frustration in the AF state, but also governs the dynamics of Cu *d* spins, since the holes can move in the crystal. Unless this aspect is missed, we cannot explain the divergent behavior of the nuclear spin-lattice relaxation rate [11].

As for the superconductivity, the nuclear relaxation behavior of ^{63}Cu in the CuO_2 plane of $La_{1.85}Sr_{0.15}CuO_4$ ($T_c = 38$ K) [13], $YBa_2Cu_3O_7$ ($T_c = 92$ K) [8, 9, 15], and Bi–Pb–Sr–Ca–Cu–O ($T_c = 109$ K) [14] have been found to be unconventional above and below T_c, affected strongly by the antiferromagnetic spin fluctuation [9, 16]. These findings indicate that the high-T_c superconductor is not of the usual BCS type, and constitute important evidence testing the theory of high-T_c superconductivity. Another striking feature is that the nuclear spin relaxation behavior of ^{17}O is different from that of Cu. At the present stage, there is an ambiguity about the site assignment of the oxygen where T_1 was measured. Independent of this problem, the observation of the enhancement of $1/T_1$ just below T_c seems to be important, because this behavior is expected for a BCS case. Combining the ^{17}O NMR result with the photoemission result that doped holes are predominantly oxygen *p*-like [23], it may be possible that the superconductivity is caused by *p*-hole pairing. To further characterize the superconducting nature definitely, we need to investigate the electronic state of each oxygen site separately. This is now in progress. Together with the results of Cu NMR, the ^{17}O NMR study has demonstrated that the role of oxygen is crucial for high-T_c superconductivity.

Note added in proof

Quite recently, Wzietek et al. have measured T_1 of ^{17}O with the sample exposed to $^{17}O_2$ gas (51 at. % ^{17}O) at 300°C for five days and have also observed a hump of $1/T_1$ just below T_c [*Europhys. Lett.* **8**, 363–368 (1989)]. On the other hand, Takigawa et al. have reported that there is no hump of $1/T_1$ for all oxygen sites (in preparation). At present, the experimental results are inconsistent. It is necessary to do further detailed measurements of T_1 concerning the magnetic field and the sample dependence.

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