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NMR Study on La and Tl-based High-T_C Cuprates*

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NMR study on three types of high-T_C cuprates $TlBa_2CaCu_2O_{7+\delta}$ (Tl1212), $La_{2-x}Ba_xCuO_4$ (LBCO) and $(La_{1-y}Y_y)_{2-x}Ce_xCuO_4$ (LYCCO) is reported. First, the Knight shift in the superconducting state was investigated for the Zn-substituted $TlBa_2Ca(Cu_{1-z}Zn_z)_2O_{7+\delta}$, which belongs to the over-doped region. The temperature dependence of the Knight shift was successfully explained in terms of the partially closed *d*-wave model proposed by Kitaoka et al. The reduction in T_C by Zn-substitution was also consistent with Miyake's theoretical calculation on the potential scattering of the unitarity limit in the *d*-wave superconductors. Next, the impurity effect on the anomalous suppression of the superconductivity in $La_{2-x}Ba_xCuO_4$ (LBCO) around $x \cong 1/8$ was investigated by La-NMR and ultrasonic measurements. The transition temperatures of the magnetic order and of the structural phase transformation in Zn^{2+} and Ce^{4+}-doped LBCO have shown that the main and direct force to the suppression in the superconductivity is the magnetic ordering, and that the role of the structural phase transformation is the enhancement of the suppression. Lastly, the new electron doped cuprate free from 4*f*-spins has been synthesized and studied by NMR. Observed spectra of $^{63/65}Cu$ without quadrupolar splitting similar to other conventional electron-doped cuprates indicate that the doped carrier in this system is electron like.

KEYWORDS: NMR, $TlBa_2CaCu_2O_{7+\delta}$, gapless superconductivity, $La_{2-x}Ba_xCuO_4$ ($x \cong 1/8$), magnetic order, $(La_{1-y}Y_y)_{2-x}Ce_xCuO_4$, electron-doped cuprate.

1. Introduction

From the vast accumulation of studies on the high-T_C cuprates so far, one may consider safely that most physical properties of the cuprates is scaled by the single parameter of the carrier concentration. With doping the carrier, most high-T_C cuprates undergo the three regions: 1) non doped oxides are antiferromagnets with the Néel point comparable to the room temperature, which are well described as the two dimensional Heisenberg model, 2) with a small number of carriers doped, they show high-T_C and many anomalous properties in the normal state such as the non Korringa behavior of NMR-T_1 or as the temperature dependent Hall coefficient, and 3) further doping of excess carriers reduces T_C to zero, the region of which is called as the over-doped region, where the observed physical properties suggest that the conduction carriers in this region is Fermi liquid like.

On the contrary to this unified picture, there still are many unresolved problems. Even an origin for the paring interaction is not clear at present. The universal behavior of T_C with the hole concentration does not hold always: for La-based cuprates, T_C is anomalously suppressed around a specific hole concentration, suggesting the competitive behavior between the superconductivity and other phase transitions. Furthermore, physical properties of the superconducting carrier in electron-doped cuprates have scarcely been studied, because of the disturbance of the 4*f*-spins to NMR study.

We show in this paper our approach in this five years to the selected three topics in those unresolved problems. First, we studied the problem of the paring interaction by investigating the non magnetic impurity effect on Tl-based high-T_C cuprates in the over-doped region. Next, the anomalous suppression of the superconductivity in $La_{2-x}Ba_xCuO_4$ around $x \cong 1/8$ was investigated by utilizing La-NMR and ultrasonic measurements as probes for the magnetic order and the structural phase transformation. Lastly, we show the successful synthesis of a new electron-doped cuprate which does not contain any lanthanides. We start from describing the background for each topic in the following.

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1.1 Non magnetic impurity effect in Tl-based high-T_C cuprate Tl1212

The significant reduction in the superconducting transition temperature T_C by substituting non-magnetic impurities in high-T_C cuprates has been reported recently by many groups $La_{2-x}Sr_xCuO_4$ (LSCO) and $YBa_2Cu_3O_7$ (YBCO)[1,2]. This phenomenon has attracted much interest, because T_C of the conventional BCS-type superconductors is not disturbed by the potential scattering which does not break the time reversal symmetry.

Many proposals to explain the anomalous impurity effect for the high-T_C cuprates have been accumulated so far, such as the magnetic pair breaking due to the local moment induced by Zn-doping[1,3], or as the localization effect[4]. Among them, Kitaoka *et al.*[5,6,7] claim that those high-T_C cuprates have the anisotropic gap like the *d*-wave symmetry, the superconductivity of which is easily destroyed by the potential scattering.[8] By measurements of Cu-NMR Knight shift for YBCO, they demonstrated that the node of the superconducting gap is easily smeared out by the potential scattering due to Zn impurities.[5] The relation between the residual density of states and the reduction in T_C is in accordance with the theory by Miyake et al. in terms of the pair breaking effect by the potential scattering in the unitarity limit.[6] So far, investigations on this impurity effect have been limited in the lightly-doped or optimum-doped region. In order to investigate the impurity effect in over-doped region[9], we have performed Cu/Tl-NMR on the Zn-substituted $TlBa_2CaCu_2O_{7+\delta}$ (Tl1212), the as-sintered samples of which is reported to be in the slightly over-doped region, while the treatment of Ar-anneal reduces the hole concentration, and raises its T_C to the optimum value.[12]

In this paper, we show the Zn-doping effect on T_C in optimum-doped and over-doped Tl1212 samples. The comparison with reported results on LSCO and YBCO is also demonstrated. The temperature dependence of ^{63}Cu-NMR Knight shift was analyzed by the partially closed *d*-wave superconducting gap model proposed by Ishida and Kitaoka[5]. Measurements of the nuclear spin-lattice relaxation rate of Tl site were also worked out to confirm the gap-less superconductivity in Zn-doped Tl1212.

1.2 Impurity effect on the anomalous suppression of the superconductivity in LBCO around $x \cong 1/8$

While most high-T_C cuprates show the simple bell-shaped dependence of T_C on the hole concentration, the La-based cuprate $La_{2-x}Ba_xCuO_4$ (LBCO) shows a singular suppression of the superconductivity around $x \cong 1/8$.[21] So far, three phenomena associating with this anomaly have been reported: 1) the structural phase transformation from the orthorhombic phase (*Cmca*) to the low temperature tetragonal phase ($P4_2/ncm$) at $T_{d2} \cong 70$K, 2) anomaly in the transport properties such as the polarity inversion in the thermoelectric power[22] at $T^* \cong 60$K, and 3) the magnetic ordering[23,25] at $T_N \cong 35$K. In order clarify the causality between these three phenomena and the anomaly in T_C, a detailed investigation on the carrier concentration dependence of these transition temperatures is essential. However, little consensus in experimental results has been obtained until now, because of the large ambiguity in determination of the transition temperatures due to the fact that the system is solid solution, and that another structural phase transition from $I4/mmm$ to *Cmca* get closer to T_{d2} at high Ba-concentration region. In order to overcome the obstacle, we provided the two external parameters other than Ba-concentration by the substitution of the hetero-valent Ce^{4+} to La^{3+} site, and of non-magnetic Zn^{2+} to Cu^{2+} site. By manipulating the substituent concentration, we expect to decouple those phase transitions and clarify the causality. In this article, we report the behavior of T_{d2} and T_N with Zn and Ce substitution, by measurements of the ultrasonic velocity and La-NMR spectra.[24,25]

1.3 The electron-doped cuprate LYCCO free from 4f-spins

The magnetization of 4*f*-spins in the electron-doped high-T_C cuprate with T′-type structure $M_{2-x}Ce_xCuO_4$ (M=Nd, Pr, Sm, Eu) has so far prevented the NMR study[32] on the Cu 3*d*-spin and on the conduction carrier. It has been believed that the synthesis of the T′-type structure is restricted by the ionic radius of the lanthanide site, and is possible only when the ionic radius is in between Pr^{3+} (1.14Å) and Eu^{3+} (1.07Å). Actually, the conventional method of the solid state reaction under 1 atm is *not* capable of the synthesis of $La_{2-x}Ce_xCuO_4$ or $Y_{2-x}Ce_xCuO_4$.[33,34] In order to get rid of this restriction and to proceed the NMR study on electron-doped cuprates, we have tried the synthesis of $(La_{1-y}Y_y)_{2-x}Ce_xCuO_4$, the lanthanide site of which is a solid solution, so that the mean ionic radius satisfies the condition.

In this paper, we show the search for the possible condition of the synthesis in several different environments of argon and oxygen, as well as in wide range of the compositions.[35,36] The electric resistance and the Cu-NMR Knight shift of obtained samples showed the metallic temperature dependence.

2. Experimental

2.1 Zn-doped Tl1212

Polycrystalline samples of $TlBa_2Ca(Cu_{1-z}Zn_z)_2O_{7+\delta}$ were synthesized from starting materials of Tl_2O_3, BaO_2, CaO, ZnO and CuO by the conventional solid state reaction. The detail in the synthesis is described elsewhere.[12] We prepared five samples: the three as-sintered samples with Zn-concentration of $z=0$, 0.015, 0.03, and the other two Ar-annealed with $z=0$, 0.015. Each sample was confirmed to be single phase by the X-ray powder diffraction. The superconducting transition temperatures were determined by the onset of the diamagnetic signal measured by a SQUID magnetometer

under the applied field of 20 Oe.

Obtained compounds were ground into powder for NQR and NMR measurements. The crystal axis of each grain was aligned by curing the powder mixed with epoxy in the magnetic field of 11 Tesla at the room temperature. Field-swept spectra of $^{63/65}$Cu -NMR were measured by the conventional spin-echo method at temperatures between 4.2 and 200 K. Frequency spectra of $^{63/65}$Cu -NQR were taken at 4.2 K. In all the NMR measurements, the aligned c-axis was set perpendicular to the applied field. Figure 1 shows typical profiles of Cu-NMR and NQR spectra. Note the considerable increase in the NQR resonance line width with the Zn-concentration, which assures that Zn and Cu atoms form a solid solution.

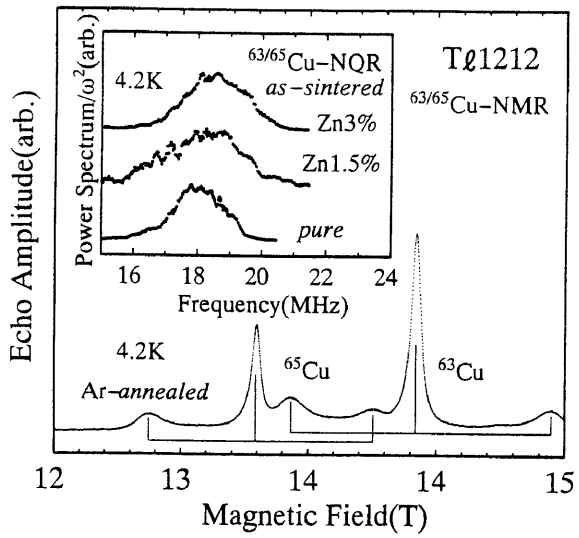

Figure 1. A typical profile of field swept spectrum of $^{63/65}$Cu-NMR, with the inset of profiles of frequency spectra of $^{63/65}$Cu-NQR.

The Knight shift K_S and the electric quadrupolar frequency ν_Q were deduced by the conventional method[13] from resonance line positions taken at several resonance frequencies ν_0. The resonance frequency of the center transition line for the ^{63}Cu nuclear spin (I=3/2) is given by the second order perturbation as

$$\nu_0 = (1+K_S)\gamma_n H_{obs} + \frac{\alpha_\perp \nu_Q^2}{(1+K_S)\gamma_n H_{obs}} \qquad (1)$$

where H_{obs} is the resonance field, which was determined as the top of the peak, and $\alpha_\perp = \frac{3}{16}$, $\gamma_n = 11.285$ MHz/T are constants. By plotting $\nu_0/\gamma_n H_{obs}$ against $(\gamma_n H_{obs})^{-2}$, one can immediately obtain K_S and ν_Q simultaneously. In order to obtain K_S and ν_Q with a high precision, spectra were taken at least ten different frequencies between 125 and 170 MHz. Obtained value for ν_Q at 4.2K agreed with the result by NQR measured at zero-field, indicating that effects of the superconducting diamagnetic shielding and of the third order quadrupolar term were small enough to be neglected.

The nuclear spin-lattice relaxation T_1^{-1} of Tl site was measured with an applied field of approximately 2.8 Tesla at temperatures between 4.2 and 250 K by the saturation-recovery method with a pulse train. Typical profiles of Tl-NMR spectra are given in Fig. 2, where one can see two main peaks for ^{203}Tl and ^{205}Tl, associated with two tiny peaks, the amplitude of which is about 5% of main peaks. We measured T_1^{-1} of the main peak for ^{205}Tl. The origin of the tiny satellite peak is attributed to the partial exchange between Tl and Ca site, as was reported for other Tl-based cuprate.[14]

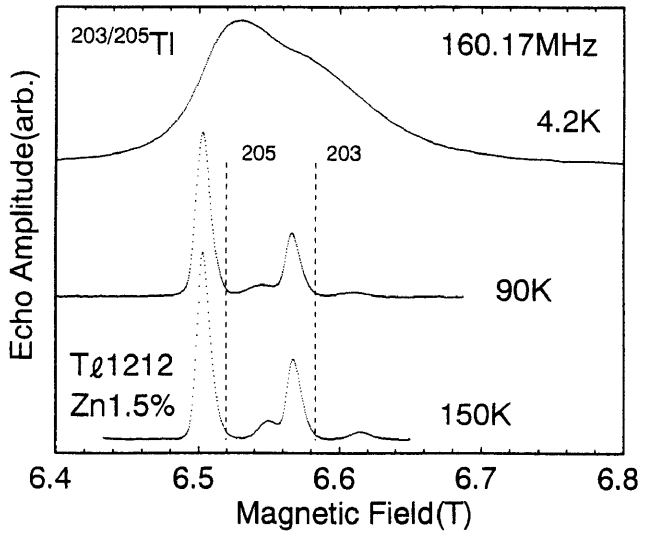

Figure 2. A typical profile of field swept spectrum of $^{203/205}$Tl-NMR.

2.2 Ce- and Zn-doped LBCO

Polycrystalline samples of $La_{1.98-x}Ba_xCe_{0.02}CuO_4$ (x=0.10~0.16) and $La_{2-x}Ba_xCu_{1-y}Zn_yO_4$ (y=0~0.08) have been obtained by the conventional solid state reaction from the nominal compositions of the starting materials with four nines purity. Samples were confirmed to be of phase pure by the X-ray powder diffraction pattern. The superconducting transition temperature was determined as an onset of the diamagnetic signal, that is, the temperature where the Meissner volume fraction becomes one percent of the perfect diamagnetism. Magnetic measurements were performed by the SQUID magnetometer under the applied field of 20 Oe. Field-swept spectra of ^{139}La-NMR were measured for axially-aligned powder samples with the aligned c-axis set perpendicular to the applied field. The resonance line width was defined empirically as the full width at the 70 or 80 percent of the maximum intensity for the central transition line.[24,25] The magnetic ordering temperature was determined as the onset of the increase in the width at low temperatures. The ultrasonic velocity was measured for rod-shaped sintered samples by the conventional pulse superposition method with 7 MHz longitudinal wave. The structural phase transition temperature T_{d2} in Zn-doped samples was determined as a onset of the hardening at low temperatures, the definition of which is the same as that for LBCO without Zn-doping. For Ce-doped samples, where

another intervening phase *Pccn* appears between *Cmca* and $P4_2/ncm$, T_{d2} was defined as the mid point of the velocity jump, which corresponds to the appearance of $P4_2/ncm$. These two definitions have been previously confirmed to be consistent with the X-ray analysis by our group.[26]

2.3 Electron-doped cuprate LYCCO

Polycrystalline samples of $(La_{1-y}Y_y)_{2-x}Ce_xCuO_4$ was synthesized from La_2O_3, Y_2O_3, CeO_2 and CuO by the conventional solid state reaction. Surveyed nominal compositions are extended over the region for the two parameters x=0.1, 0.15, 0.18, 0.2, 0.21, 0.22, 0.23, 0.24, 0.25, 0.26, and y=0.1, 0.2, 0.3. Starting powder materials with the purity of four nines were pressed into pellets, and were sintered twice with the intermediate grinding, under the temperature 1100 °C for 24 or 32 hours in the flowing gas of 100%Ar, 99%Ar+1%O_2, 100%O_2 or in the air. Calcined compounds were annealed in the flowing gas of Ar under 900 °C for 24 hours, the reduction treatment of which has so far been believed to be necessary for the electron-doped cuprate with the T′-type structure. We also tried for Ca^{2+}-doping to reduce the carrier concentration explicitly.

Obtained compounds were tested by X-ray powder diffraction for the T′-type structure and impurity phases. The mass fraction of the impurity phases was determined by comparing the intensity of Bragg peaks with calibration curves which we made from standard materials in advance. The lattice parameters of the tetragonal structure were obtained from the diffraction pattern by Cohen's method.

The electric resistance was measured before and after the Ar-anneal treatment by the standard four probe dc method in the temperature between 1.5 and 300 K. The possibility of the superconductivity was tested also by magnetic measurements with the SQUID magnetometer under the applied field of 20 Oe. Field-swept spectra of $^{63/65}$Cu -NMR were measured by the conventional spin-echo method. The Knight shift was determined as the position of the top of the resonance line peak.

3. Results and Discussion

3.1 Non magnetic impurity effect in Tl1212 system

We show the Zn-concentration dependence of T_C for Tl1212 in Table I with reported results for LSCO[1] and YBCO.[2] One must immediately note that $\Delta T_C/c$, the reduction rate of T_C, where $c = z/2$, for as-sintered Tl1212 is much smaller than that of Ar-annealed one, from which we can immediately draw out the first conclusion that the impurity effect becomes smaller in the over-doped region. Next, note that $\Delta T_C/c$ for the Ar-annealed Tl1212 is much smaller than that of LSCO ($x = 0.15$) and the same as that of 90K-class YBCO.

Table 1. The list of samples with T_C determined as the onset of the superconducting diamagnetization. The reduction rate of T_C with Zn-doping is also shown with results on LSCO[1] and YBCO.[2]

	pure	Zn 1.5%	Zn 3%	$-\Delta T_C/c$ (K/%)
as-sintered	78 K	73 K	71 K	2.3
Ar-annealed	96 K	87 K	---	6
$La_{1.85}Sr_{0.15}CuO_4$[1]				12.4
$YBa_2Cu_3O_7$[2]				6

These two observations are qualitatively explained with the pair breaking theory by the potential scattering of the unitarity limit.[8,9] In the small concentration limit of the impurity, the reduction in T_C is given by the theory[8] as

$$\Delta T_C \cong \chi \frac{\pi}{4} \frac{\Gamma_N}{k_B}, \qquad (2)$$

where $\chi \leqq 1$ is a constant depending on the gap anisotropy, and Γ_N is the scattering rate of the normal state electrons. For the case of the unitarity scattering, or the strong scattering limit, Γ_N is known to be proportional to the inverse of the density of states as $\Gamma_N \propto c/\pi N_0$, which clearly explains our result that $\Delta T_C/c$ becomes smaller in the over-doped region. We mention here that Kluge and Koike's group has recently reported the similar behavior in the over-doped LSCO and Bi-system.[9] Furthermore, we emphasize that this relation holds in comparing $\Delta T_C/c$ of Tl1212 with other systems. As was revealed by Uemura's μSR experiments[10], the concentration of the superconducting quasi-particles in 90K-class YBCO is much higher than that in LSCO ($x = 0.15$), though both the two are optimum-doped. By the NMR investigation, Kitaoka and Zheng[11] also reached the similar conclusion that the carrier concentration in Tl1212 is higher than LSCO. Thus, we can see that the difference in $\Delta T_C/c$ for LSCO, YBCO and Tl1212 is explained, if qualitatively, in terms of the carrier concentration.

For the next step, in order to see whether or not 1) the proportionality between ΔT_C and $1/N_0$ holds rigorously, and 2) the superconducting gap is smeared by the strong scattering, we utilized NMR, which is a nice probe for the density of states. Figure 3 shows a plot of $\nu_0/\gamma_n H_{obs}$ vs. $(\gamma_n H_{obs})^{-2}$ to obtain the Knight shift K_S and the quadrupolar frequency $^{63}\nu_Q$ from the linear fitting, which is fairly well for the entire temperature range of our measurements. The temperature dependence of thus obtained K_S and $^{63}\nu_Q$ are given in Fig. 4 for three samples: as-sintered (*pure*), as-sintered (Zn-3%), and Ar-annealed (*pure*). In the normal state above T_C, the Knight shift stays constant against the temperature, which is a hallmark for the optimum-doped and over-doped cuprates.[11,13] Note that there is no change in K_S with Zn-doping in the normal state, indicating that the density of states is not modified by Zn-doping. The slightly smaller shift for the

Ar-annealed sample reflects the decrease in the hole number by the reduction treatment.

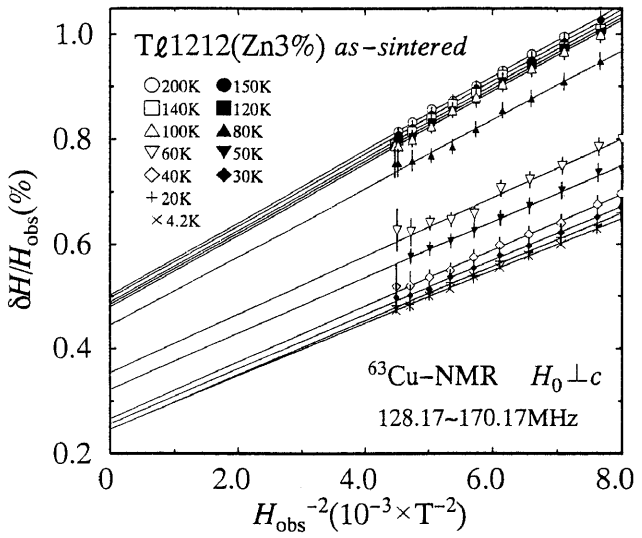

Figure 3. A typical plot of the resonance shift $\delta H/H_{obs} \equiv (\gamma^{-1}\nu_0 - H_{obs})/H_{obs}$ against the inverse of squared resonance field H_{obs}^{-2}.

In the superconducting state, the behavior of K_S shows a significant difference for the three samples. While the Ar-annealed sample without Zn-doping shows a monotonic decrease of K_S with temperature down to 4.2 K, both the two as-sintered samples with and without Zn-doping showed a saturating behavior below 50 K. This saturating behavior becomes significant with Zn-doping, suggesting that the system becomes gapless by Zn-doping, which is just the answer to the first question above. The slightly gapless-like behavior of the as-sintered sample without Zn-doping is *not* surprising, but a simple consequence of the fact that the system is over-doped. The same behavior has been reported[11,13] also for other over-doped systems $TlSr_2CaCu_2O_{7+\delta}$ and LSCO($x \geq 0.2$).

In analyzing the data quantitatively, we adopt the partially closed *d*-wave model proposed by Ishida et al.[5,6] First, we assume the anisotropic superconducting gap $\Delta_k(T) = 2\Delta_0(T)\sin\theta_k\cos\theta_k$ with the $d_{x^2-y^2}$ symmetry and the BCS like temperature dependence, from which the density of states is calculated numerically as

$$N(\omega) = \begin{cases} \sum_k \delta(\omega - E_k) & (\omega > \omega_{res}) \\ N_{res} & (\omega < \omega_{res}) \end{cases}, \quad (3)$$

where we make a further assumption, which is an essential point of their model, that there exists a constant residual density of states N_{res} at the lower energy region, which corresponds to the smearing out of the gap node due to the potential scattering by Zn impurities. Note that the density of states is measured in the unit of N_0, here. The Knight shift is numerically calculated from $N(\omega)$ with the general formula of

$$K_S(T) = K_n \int N(\omega) \frac{\partial f(\omega)}{\partial \omega} d\omega, \quad (4)$$

where K_n is the normal state Knight shift, assumed to be constant, and $f(\omega)$, the Fermi function. Here, the five free parameters $\lambda = 2\Delta_0(0)/T_C^*$, T_C^*, N_{res}, K_n and the orbital shift K_{orb} are determined as such that the calculated $K_S(T) + K_{orb}$ follows the observed temperature dependence.

Though the number of fitting parameters seems to be too many at first sight, the parameter fitting is completed with little ambiguity, because each parameter corresponds to the characteristic point of the Knight shift temperature dependence: K_n to the normal state value, T_C^* to the onset of the reduction, λ to the curvature in the superconducting state, N_{res} and K_{orb} to the saturating behavior at low temperatures. The above assumption of the BCS-like temperature dependence for the gap may also seem to be too rough at first sight. However, one must note that the important point here is whether or not there exists the residual density of states N_{res} which gives the constant Knight shift at the low temperature limit, and that the detailed temperature dependence is not crucial.

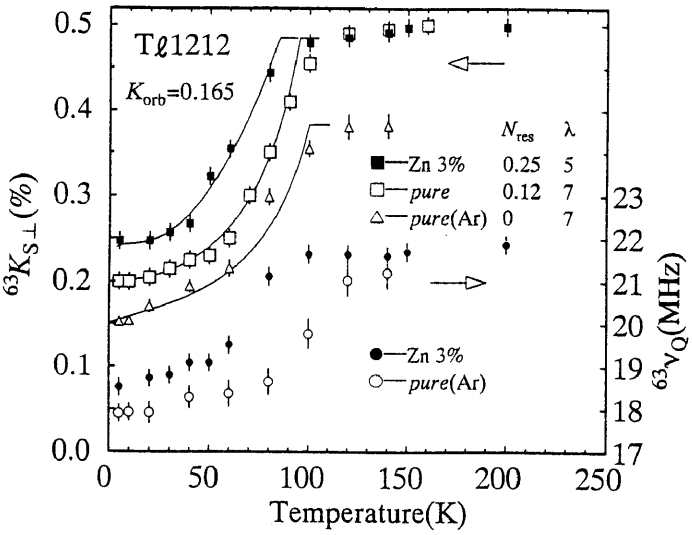

Figure 4. The temperature dependence of Knight shift K_S and the electric quadrupolar frequency $^{63}\nu_Q$.

In Fig. 4, solid curves of the calculated $K_S(T)$ are shown with the fitted parameters. The orbital shifts K_{orb} obtained from fitting are almost the same for all the samples, which is consistent with many observations on other high-T_C cuprates.[13] Thus obtained N_{res} and ΔT_C are compared with the theoretical relation calculated by Miyake for the unitarity scattering limit[6], by which the result on Zn-doped YBCO is explained very well.[5] According to the universal curve for N_{res} and ΔT_C in the theory[6], the sample exhibiting the residual density of states $N_{res} \cong 0.25$ is expected to be with $\Delta T_C \cong 5$ K, which is just comparable to the observed value $\Delta T_C \cong 7$ K for the as-sintered sample (Zn-3%). This correspondence indicates that the potential scattering by Zn-impurities is in the unitarity limit, the result of which is consistent with reports

by Kitaoka[5] and Koike.[9] Noting that both the ΔT_C and N_{res} become smaller in the over-doped region, we can draw out another conclusion that the superconducting gap in the over-doped region is rather robust against the potential scattering.

Next, in order to answer the second question given above, we try to argue the relation between ΔT_C and N_0, the density of states in the normal state, which can be obtained from the measured Knight shift as

$$N_0 = (K_S - K_{orb})/A\mu_B^2, \qquad (5)$$

where A is the hyperfine coupling constant between Cu nuclei and the conduction electrons, and μ_B the Bohr magneton. Though the hyperfine coupling constant of this system has not been reported so far, one can still postpone the resignation of the analysis, by considering many reports on other various high-T_C cuprates, where the experimental consensus seems to be obtained: the hyperfine coupling constant is almost constant in the lightly-doped or optimum-doped region, and is increasing in the over-doped region.[15,16] Consequently, in the case of Tl1212, we can safely assume that the hyperfine coupling constant for the as-sintered sample is the same as or larger than that of Ar-annealed one. With this assumption, we compare $\Delta T_C/c$ and $N_0 \propto K_S - K_{orb}$ to find that the decrease in T_C with the carrier doping is too steep to be explained by the increase in N_0. Note that $\Delta T_C/c$ of the as-sintered samples is approximately 2.6 times larger than that of Ar-annealed samples, while N_0 estimated from the Knight shift is only 1.3 times larger at best. This suggests that there exists another mechanism which breaks the superconductivity in the optimum doped-region. A possible candidate for this mechanism is the magnetic pair breaking due to the induced moment by non-magnetic impurities, as already suggested by Kitaoka.[7]

In Fig. 5, we show the temperature dependence of the nuclear spin relaxation rate for Tl site, which is considered to be driven by the fluctuation of Cu 3*d*-spins through the supertransferred hyperfine interaction.[17] While the pure sample shows a single exponential recovery of the nuclear spin magnetization, the Zn-doped sample does not. We tentatively fit relaxation curves with the two components of the relaxation rates. The fraction of the equilibrium magnetization for the long and short component are 37 and 63 percent, which are almost temperature independent in the whole experimental region.

At the low temperature limit, both the samples show the residual Korringa behavior $(T_1T)^{-1} \cong$ const., the value of which increases with Zn-doping, that is, the residual value of the short component is larger than that of the pure sample. This fact suggests that the superconducting gap is partially closed, which is consistent, if qualitatively, with the Knight shift result. We must admit here that there still remains a little ambiguity for the origin of the slow and fast relaxation components observed in the Zn-doped sample. At first sight, these two components seem to correspond to Tl-sites near and far from Zn-impurities, the assignment of which is successful in the Cu site relaxation for Zn-doped YBCO.[5] However, this assignment requires that the inequality between the two relaxation rates must be inverted in the normal and superconducting state.[5] In the normal state, those Tl atoms near the Zn-impurity must show slower relaxation rate than those far form the impurity, because the antiferromagnetic 3*d*-spin fluctuation is broken by non-magnetic Zn atoms. On the contrary, in the superconducting state, those Tl atoms near the Zn-impurity must show faster rate than those far from impurity, because the gap-smearing effect must be stronger around the impurity. Apparently, this requirement contradicts our observation in Tl1212 system. A possible explanation of this discrepancy may be that the distinct separation between "near" and "distant" sites is impossible for Tl-site, for the distant location of Tl-site from CuO plane may cause the effect of the impurity rather averaged.[18]

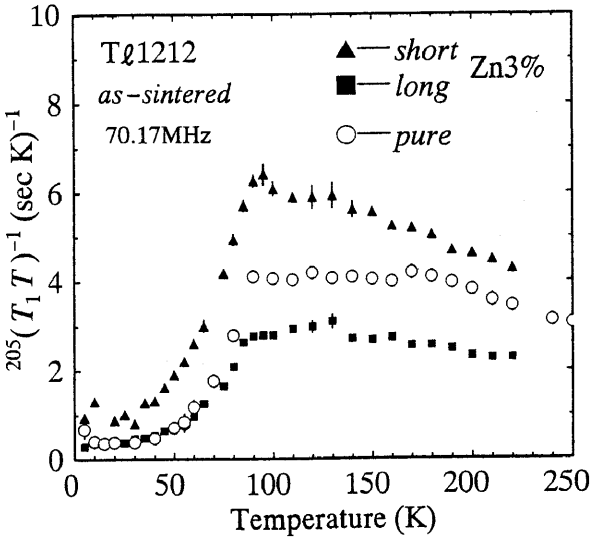

Figure 5. The temperature dependence of $(T_1T)^{-1}$ for the Tl site.

Finally, we shortly state on the significant reduction in $^{63}\nu_Q$ below T_C. As is clearly demonstrated in both Fig. 3 and 4, the reduction is as large as 15 percent for both Zn-doped and pure samples. We emphasize here again that the observed change in $^{63}\nu_Q$ is *not* an artifact due to the superconducting diamagnetization, because $^{63}\nu_Q$ obtained by NMR at 4.2 K agrees with the result by NQR measurements performed in zero-field.

For there are two contributions to the electric field gradient at the Cu site of high-T_C cuprates, the on-site hole carrier and the surrounding ionic lattice, we cannot determine the origin of the reduction in $^{63}\nu_Q$ at this stage. For the qualitative argument, if the reduction comes from the former contribution, there must be a substantial change[19] in the local hole concentration at Cu site below T_C. On the other hand, if it is from the latter, there must be a microscopic structural distortion in the superconducting state, the similar phenomenon is observed

for another Tl-based oxide $Tl_2Ba_2CaCu_2O_8$ by the neutron experiments.[20]

3.2 Zn and Ce doping effects on the magnetic order and the structural phase transformation in $La_{2-x}Ba_xCuO_4$ ($x \cong 1/8$)

Figure 6 shows the temperature dependence of the La-NMR line width for Ce-doped samples. The broadening at low temperatures H_{La} becomes largest at $x \cong 0.145$, where T_N is also the highest. This clearly shows that the Ba-concentration where the magnetic order becomes most significant is shifted from $x \cong 0.125$ to 0.145 by 2% Ce-doping. Next, the structural transition temperature T_{d2} in Fig. 7 shows rather a monotonic increase with Ba-concentration up to $x \cong 0.16$, though it shows a saturating behavior above 0.13. There was little ambiguity in the determination of T_{d2} for Ce-doped samples, because T_{d1} is raised far above T_{d2} for the sake of doped Ce^{4+} ions, the radius of which is much smaller than La^{3+} ions.[26] These results for T_{d2}, T_N, H_{La} and T_C in LBCO with and without Ce-doping are shown together in Fig. 8, where the negative correlation between T_C and T_N is clearly seen.[27] By Ce-doping, the position of the T_C-anomaly moves also to the higher Ba-concentration, the behavior of which is similar to the magnetic order. However, note that the location of the peak in T_N does *not* precisely match to the sharp dip in T_C, which is always located at slightly higher Ba-concentration, irrelevant of Ce-doping.

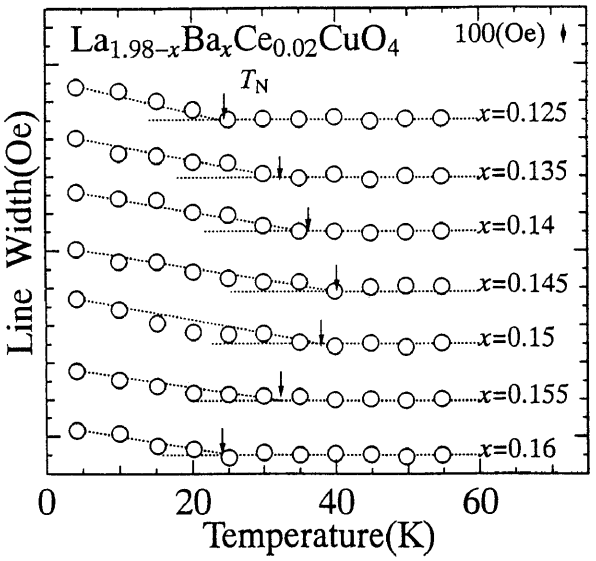

Figure 6. The temperature dependence of the La-NMR line width for 2% Ce-doped samples. Note that the broadening is most significant at $x \cong 0.145$, where the hole concentration is 0.125.

Next, for Zn-doped samples, both H_{La} and T_N shows a significant decrease with Zn-concentration, indicating the disappearance of the magnetic order. The structural phase transition, on the contrary, stays almost constant around $T_{d2} \cong 70$K against the Zn-doping up to 4 %.

Figure 9 shows the Zn-concentration dependence of T_{d2} and T_N, from which one must clearly see the independent behavior between the structural phase transformation and the magnetic order against Zn-doping.[25]

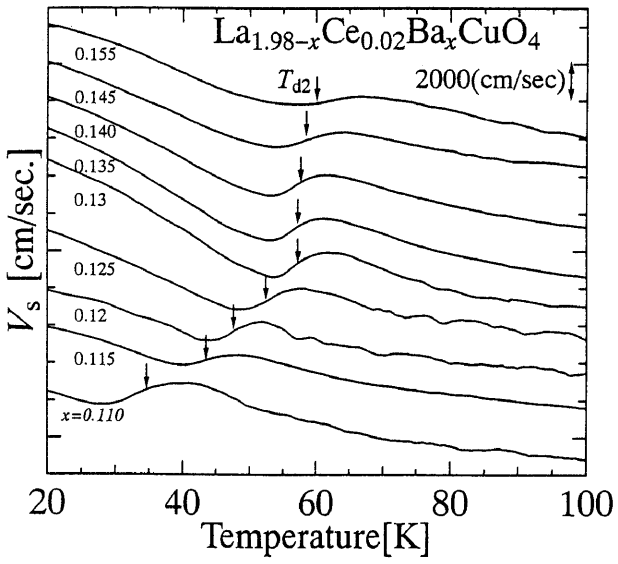

Figure 7. The temperature dependence of the ultrasonic velocity for 2% Ce-doped samples. The definition of T_{d2} is the midpoint at the jump in the velocity.

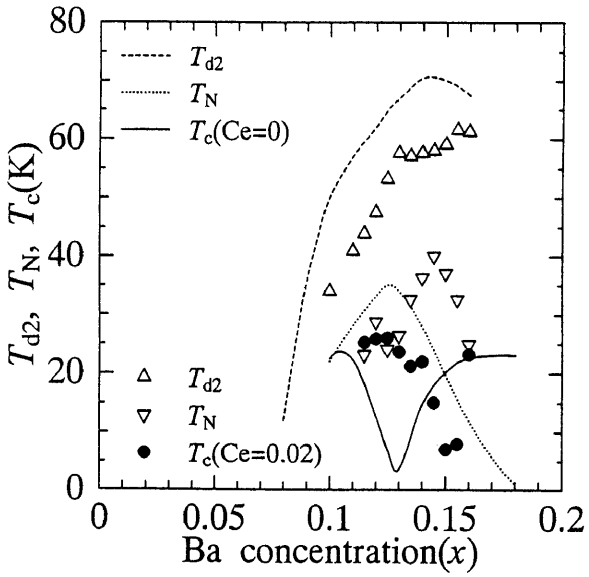

Figure 8. The phase diagram for T_{d2}, T_N and T_C in samples with and without Ce-doping.[27]

From these two observations, one may immediately reach the first conclusion that there exists a competing behavior between the superconductivity and the magnetic ordering around the hole concentration 0.125, and that the main and direct force to the suppression of the superconductivity is the magnetic order. This is justified by the fact that another La-based cuprate $La_{2-x}Sr_xCuO_4$ (LSCO), where no T_{d2} has been reported so far[28], also shows both the magnetic order and the T_C-anomaly, which, however, is much weaker than that for LBCO.[24,25]

Coexistence of the magnetic order and CDW has been reported recently by the neutron scattering experiments for Nd-doped LSCO ($x \cong 0.12$) at low temperatures, though the characteristic wave vector for the magnetic order differs slightly from the one for simple antiferromagnets.[31] The possibility of the magnetic order in carrier-doped cuprates was pointed out theoretically by Bonesteel [30]; the antiferromagnetic ordering can be stabilized at the finite hole concentration in those cuprates with the strong Dzyaloshinsky-Moriya interaction among Cu 3*d*-spins.

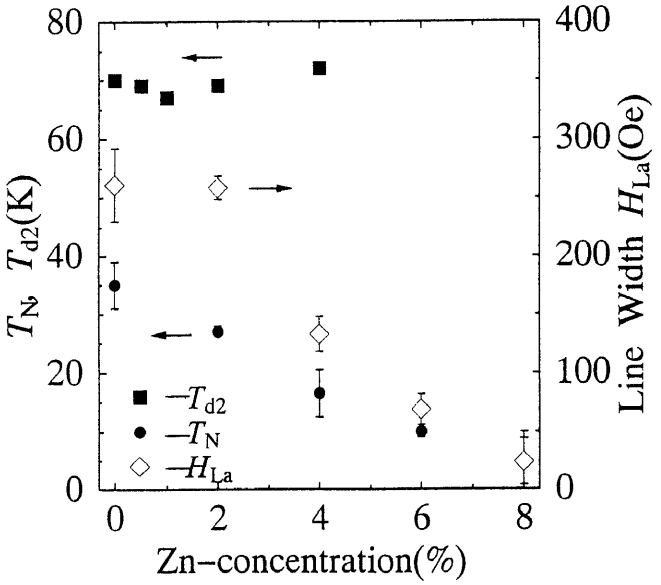

Figure 9. The Zn-concentration dependence of the magnetic and structural phase transition temperatures, the two of which clearly shows the different behavior with Zn-doping.

Next, for the role of the structural phase transition, which is a delicate problem, we must note first that though T_{d2} does not show an evident correlation with the superconductivity, it takes finite value above T_N in rather a wide range of Ba-concentration around the T_C-anomaly. If we now adopt the idea that the structural transformation may enhance, if not essential, the change in the electronic state and the suppression of the superconductivity, it is straightforward to explain the weaker T_C-anomaly in LSCO as a lack of the enhancement by the structural transformation.[24,25]

The small discrepancy between the Ba-concentration of the T_C-anomaly and of the peak in T_N stated above is also explained as the cooperative effect of the structural transformation and the magnetic order to the suppression in the superconductivity in the higher Ba-concentration, where T_{d2} is higher. In LSCO, where no T_{d2} is reported, there is no discrepancy between the two, being in accordance with this explanation.

3.3 Synthesis and NMR study on electron-doped LYCCO with T′-type structure

The existence of the T′-type structure was confirmed with impurities of La_2CuO_4, Y_2O_3 and CeO_2 for the wide range of the nominal composition $x \cong 0.15$~0.25 and $y \cong 0.1$~0.3, when the sintering environments was the air or 99%Ar+1%O_2.

Single phase of the T′-type structure was obtained for the extremely narrow region around $x \cong 0.22$ and $y \cong 0.2$, which, however, did not change for these two environments for sintering. Figure 10 shows a typical profile of X-ray powder diffraction pattern for obtained compounds with T′-type structure. No traces of T′-type structure was observed in products sintered in 100%Ar or O_2. The Ca^{2+}-doping was also found to be impossible; the dominant product was La_2CuO_4 with T-type structure.

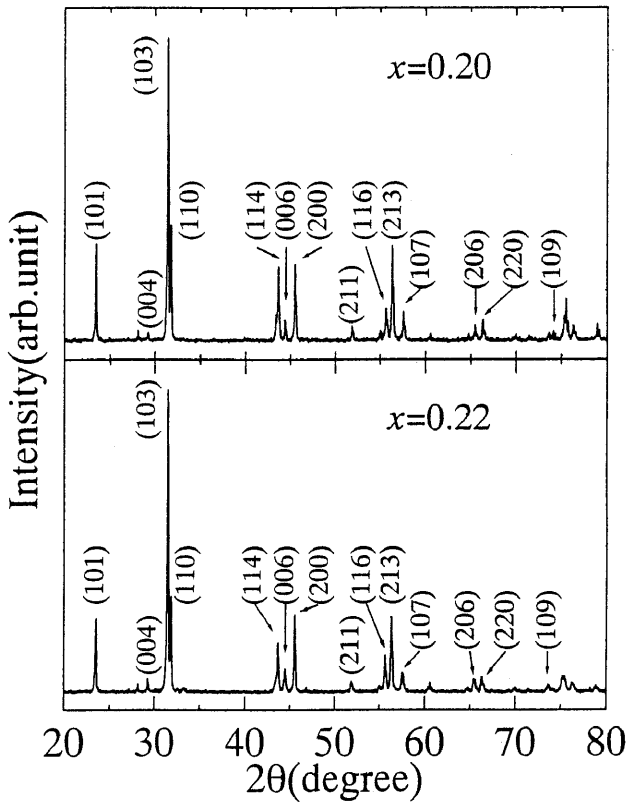

Figure 10. Typical profiles of X-ray powder diffraction pattern for $(La_{1-y}Y_y)_{2-x}Ce_xCuO_4$ with T′-type structure (x=0.22, y=0.2, sintered in air).

Lattice parameters obtained by Cohen's method stayed almost constant around a=3.983(±0.002)Å, c=12.23(±0.01)Å for all the nominal composition surveyed. This anomalous behavior makes a clear contrast against reported results on $M_{2-x}Ce_xCuO_4$ (M=Nd, Pr, Sm, Eu, and the solid solution of each two), where the lattice constants sensitively change with the mean ionic radius of the lanthanides site.[33,35,37] Consequently, observed constant lattice parameters indicate that the synthesis of the single phase is possible only for the restricted region of the nominal composition, and that the nominal composition outside of this region results in the increase of impurity phases.[35,36]

Figure 11 shows the temperature dependence of the electric resistance. All the as-sintered samples exhibit the semiconductor-like temperature dependence at low

temperatures. After the treatment of Ar-anneal, resistance drops drastically. There are two possibilities expected to be the reason at this stage. One is the increase in the electron carrier concentration by the Ar-anneal, and the other, the decrease in defects. We shall discuss this later with the result of the Knight shift.

Profiles of $^{63/65}$Cu -NMR spectra are shown in Fig. 12. Note that *no* electric quadrupolar splittings are observed for ^{63}Cu and ^{65}Cu nuclei with I=3/2 spin, for both as-sintered and Ar-annealed samples. This is an evidence for the fact that the doped carrier is electron like.[32,38] As was shown theoretically by Maekawa et al., the electric field gradient at Cu site is dominated by the local carrier concentration, and is confirmed to be accidentally nearly zero for the electron-doped high-T_c cuprates reported so far, because of the canceling between the terms from Cu-$3d_{x^2-y^2}$ and from Cu-$4p_{x,y}$.[39]

Next, note the huge width of spectra for as-sintered samples at 4.2 K. The hyperfine field estimated from the width is as high as 2~3 Tesla, suggesting the existence of the magnetic order at the low temperature. Judging from the observed profile, which is gaussian like rather than the characteristic powder pattern, the ordered state may be of the short range order rather than the well defined antiferromagnetism. We can estimate the transition temperature to be between 40 and 80 K, where no signals are detected therein, possibly because the spin-spin relaxation rate becomes anomalously large due to the critical slowing down near the transition point.

By the treatment of Ar-anneal, this magnetic order vanishes, and instead, sharp resonance lines are observed down to 4.2 K. The temperature dependence of the Knight shift is nearly constant as shown in Fig. 13, reflecting the Pauli paramagnetism, which is consistent with the observed metallic behavior of the electric resistivity. Figure 13 also shows that the shift is independent of the nominal composition. If we assume that the orbital contribution and the electron correlation effect to the shift does *not* change considerably before and after the Ar-anneal, this result is understood as the invariable carrier concentration against the change in the nominal composition of Ce^{4+}. This is also consistent with the observation on the lattice parameters.

Finally, we discuss the effect of the Ar-anneal treatment to the shift before and after the Ar-anneal treatment. Obviously as in Fig. 13, the shift does not change after the treatment. This result clearly shows that the Ar-anneal does not bring any excess carriers. Consequently, both the two drastic changes, the reduction in the electric resistivity and the disappearance of the

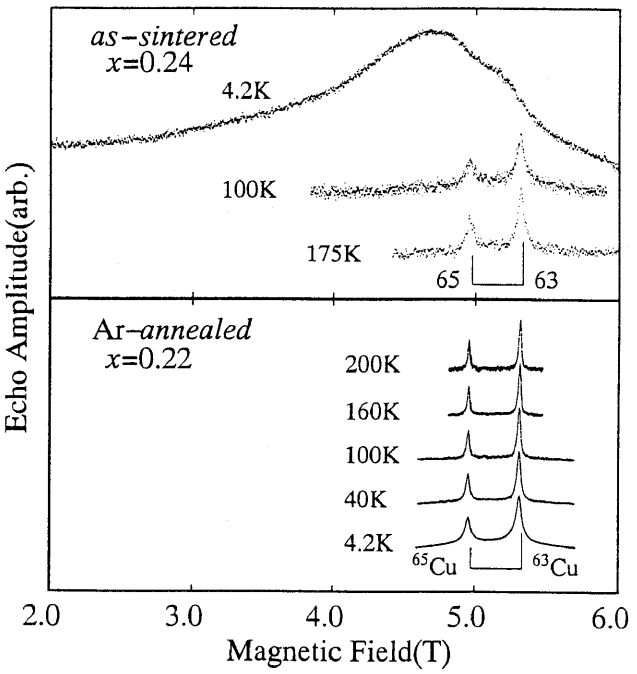

Figure 12. Profiles of Cu-NMR spectra under various temperatures for as-sintered and Ar-annealed samples.

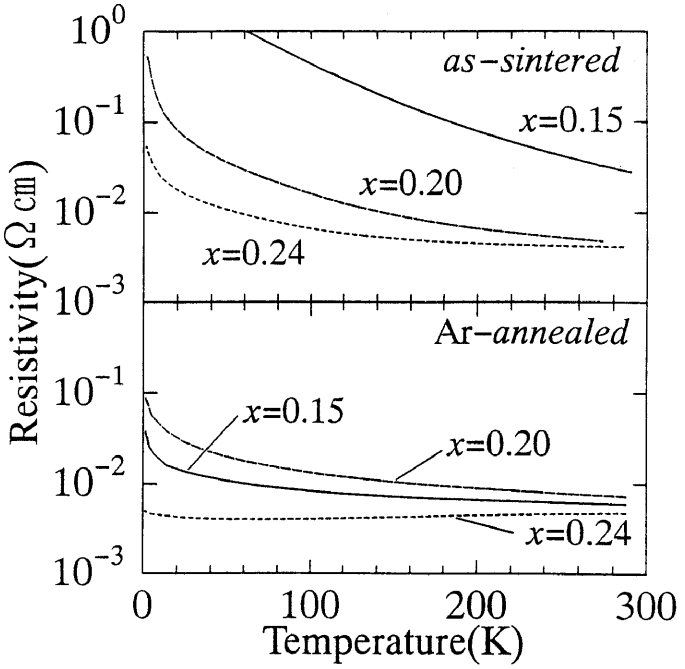

Figure 11. The temperature dependence of the electric resistance for as-sintered and Ar-annealed samples.

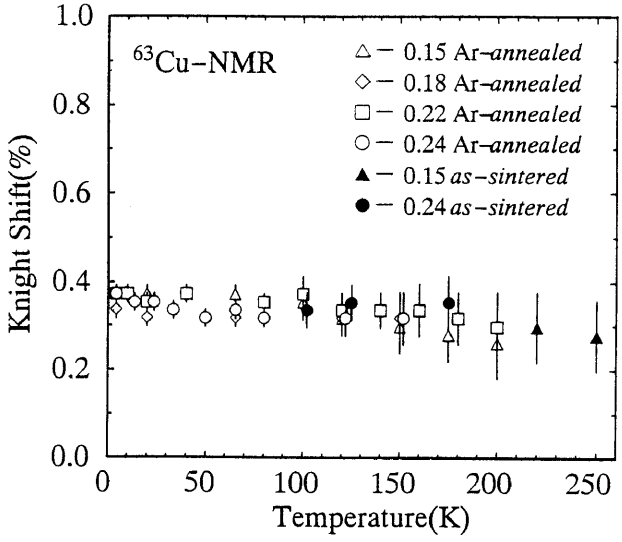

Figure 13. The temperature dependence of the ^{63}Cu Knight shift.

magnetic order observed after the Ar-anneal treatment should be assigned to the decrease in defects in samples by annealing.

Summary

The effect of Zn-impurities on the superconductivity in Tl1212 system has been investigated by NMR technique. The reduction rate of T_C of as-sintered samples was found to be much smaller than YBCO and LSCO. By comparing as-sintered and Ar-annealed samples, the reduction rate of T_C was found to become smaller by the excess carrier doping. We analyzed the temperature dependence of the Knight shift with the model of the partially closed *d*-wave proposed by Ishida to find that there exists the residual density of states N_{res} in the superconducting state, and that N_{res} increases with Zn-doping. The ratio of ΔT_C and N_{res} was found to be in accordance with the universal curve by the theoretical calculation in the unitarity limit by Miyake, suggesting that the superconducting gap in the over-doped region is robust against the impurity doping.

The magnetic and the structural transition temperatures have been investigated by La-NMR and the ultrasonic velocity in Zn^{2+} and Ce^{4+}-doped $La_{2-x}Ba_xCuO_4$, where T_N and T_C clearly showed a competing behavior around the hole concentration 0.125, while T_{d2} increased nearly monotonically with the hole concentration. This behavior is consistently understood by the idea that the direct and main force to the suppression in the superconductivity is the magnetic order, and that the structural phase transformation enhances the suppression.

The new compound with T′-type structure $(La_{1-y}Y_y)_{2-x}Ce_xCuO_4$, which does not contain any lanthanides with 4*f*-spins, has been synthesized in the narrow region of the nominal composition around $x \cong 0.22$, $y \cong 0.2$. Observed spectra of Cu-NMR with no quadrupolar splittings show that the doped carrier in the system is electron like. The existence of the magnetic order was found at low temperatures by Cu-NMR in as-sintered samples, which showed the semiconductor-like behavior of the electric resistivity. After the Ar-anneal treatment, this magnetic order disappeared, and the drastic reduction in the resistivity was observed. However, the Knight shift did not change before and after the Ar-anneal, suggesting that the Ar-anneal does not change the carrier concentration in the system.

Acknowledgments

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1) G. Xiao, M. Z. Cieplak, J. Q. Xiao and C. L. Chien: Phys. Rev. **B42** (1990) 8752.
2) S. T. Ting, P. Pernambuco-Wise and J. E. Crow: Phys. Rev. **B50** (1994) 6375.
3) A. V. Mahajan, H. Alloul, et al.: Phys. Rev. Lett. **72** (1994) 3100.
4) C. S. Jee, D. Nichols, A. Kebede, S. Rahman, J. E. Crow, A. M. Ponte Conclavers, T. Mihalisin, G. H. Myer, I. Perez, R. E. Salomon, P. Schlottmann, S. H. Bloom, M. V. Kuric, Y. S. Yao and R. P. Guertin: J. Supercond. **1** (1988) 63.
5) K. Ishida, Y. Kitaoka, N. Ogata, T. Kamino, K. Asayama, J. R. Cooper and N. Athanassopoulou: J. Phys. Soc. Jpn. **62** (1993) 2803.
6) S. Schmitt-Rink, K. Miyake and C. M. Varma: Phys. Rev. Lett. **57** (1986) 2575; *ibid. unpublished.*
7) Y. Kitaoka, K. Ishida and K. Asayama: J. Phys. Soc. Jpn. **63** (1994) 2052.
8) L. S. Borkowski and P. J. Hirschfeld: Phys. Rev. **B49** (1994) 15404; R. Fehrenbacher and M. R. Norman: Phys. Rev. **B50** (1994) 3495.
9) T. Kluge, Y. Koike, A. Fujiwara, M. Kato, T. Noji, Y. Saito: Phys. Rev. **B52** (1995) R727; *and references therein.*
10) Y. J. Uemura, L. P. Le, G. M. Luke, B. J. Sternlieb, J. H. Brewer, J. Carolan, W. Hardy, R. Kadono, R. F. Kiefl, S. R. Kreitzman, T. M Riseman, C. L. Seaman, J. J. Neumeier, M. B. Maple, G. Saito, H. Yamochi, H. Takagi, S. Uchida, J. Gopalakrishnan, M. A. Subramanian, A. W. Sleight and Gang Xiao: Hyperfine Interactions **63** (1990) 131.
11) G.-q. Zheng, K. Magishi, Y. Kitaoka, K. Asayama, T. Kondo, Y. Shimakawa, T. Manako and Y. Kubo: Physica **B186-188** (1993) 1012.
12) S. Nakajima, M. Kikuchi, Y. Syono, K. Nagase, T. Oku, N. Kobayashi, D. Shindo and K. Hiraga: Physica **C170** (1990) 443.
13) S. Ohsugi, Y. Kitaoka, K. Ishida, G.-q. Zheng and K. Asayama: J. Phys. Soc. Jpn. **63** (1994) 700.
14) K. Fujiwara, Y. Kitaoka, K. Asayama, H. Katayama-Yoshida, Y. Okabe and T. Takahashi: J. Phys. Soc. Jpn. **57** (1988) 2893.
15) Y. Yoshinari, H. Yasuoka, Y. Ueda, K. Koga and K. Kosuge: J. Phys. Soc. Jpn. **59** (1990) 3698.
16) Y. Kitaoka, K. Fujiwara, K. Ishida, K. Asayama, Y. Shimakawa, T. Manako and Y. Kubo: Physica **C179** (1991) 107.
17) T. Goto, T. Shinohara, T. Sato, S. Nakajima, M. Kikuchi, Y. Syono and T. Fukase: Jpn. J. Appl. Phys. Series 7, *Mechanisms of Superconductivity* (1992) 197. *See also* H. B. Brom, D. Reefman, J. C. Jol, D. M de Leeuw and W. A. Groen: Phys. Rev. **41** (1990) 7261.
18) K. Ishida: private communication.

19) M. Matsumura, H. Yamagata: in preparation.
20) B. H. Tobby, T. Egami, J. D. Jorgensen and M. A. Subramanian: Phys. Rev. Lett. **64** (1993) 2414.
21) J. D. Axe, A. H. Moudden, A. R. Moodengaugh, et al.: Phys. Rev. Lett. **62** (1989) 2751.
22) M. Sera, Y. Ando, S. Kondoh, K. Fukuda, M. Sato, I. Watanabe, S. Nakashima and K. Kumagai: Solid State Commun. **69** (1989) 851.
23) G. M. Luke, L. P. Le, B. J. Sternlieb, W. D. Wu, Y. J. Uemura, J. H. Brewer, T. M. Riseman, S. Ishibashi, S. Uchida: Physica **C185-189** (1991) 1175.
24) T. Goto, S. Kazama, K. Miyagawa and T. Fukase: J. Phys. Soc. Jpn. **63** (1994) 3493.
25) T. Goto, K. Seki, S. Kazama, H. Koizumi and T. Fukase: Physica **C235-240** (1994) 1663.
26) T. Suzuki, M. Sera, T. Hanaguri and T. Fukase: Phys. Rev. **B49** (1994) 12392.
27) T. Fukase, T. Hanaguri, T. Nomoto, T. Goto, Y. Koike, T. Shinohara, T. Sato, I. Tanaka and H. Kojima: Jpn. J. Appl. Phys. Series 7, (1992) 213.
28) Y. Maeno, A. Odagawa, N. Kakehi, T. Suzuki and T. Fujita: Physica **C173** (1991) 322.
29) T. Goto, S. Kazama, K. Miyagawa, M. Fukunaga and T. Fukase: Physica **B194-196** (1994) 2173.
30) N. E. Bonesteel, T. M. Rice and F. C. Zhang: Phys. Rev. Lett. **68** (1992) 2684. *See also,* B. Büchner, M. Breuer, A. Freimuth, A. P. Kampf: Phys. Rev. Lett. **73** (1994) 1841.
31) J. M. Tranquada, B. J. Sternlieb, J. D. Axe, Y. Nakamura, S. Uchida: Nature **375** (1995) 561.
32) G.-q. Zheng, Y. Kitaoka, Y. Oda and K. Asayama: J. Phys. Soc. Jpn **58** (1989) 1910.
33) E.-T. Muromachi, Y. Uchida and K. Kato: Physica **C165** (1990) 147.
34) H. Takahashi, N. Mori, M. Azuma, Z. Hiroi, M. Takano: Physica **C227** (1994) 395.
35) T. Goto, M. Fukunaga, K. Miyagawa, T. Hanaguri and T. Fukase: *Advances in Superconductivity V* (1992) Springer-Verlag, 267.
36) M. Fukunaga, T. Goto and T. Fukase: Physica **B194-196** (1994) 2279.
37) N. Kobayashi, A. Ito, M. Hiroi, H. Iwasaki: Physica **C185-189** (1991) 741.
38) K. Hanzawa: J. Phys. Soc. Jpn. **62** (1993) 3302.
39) Y. Ohta, W. Koshibae and S. Maekawa: J. Phys. Soc. Jpn. **61** (1992) 2198.