Effect of carrier distribution on superconducting characteristics of the multilayered high-T_c cuprate $(Cu_{0.6}C_{0.4})Ba_2Ca_3Cu_4O_{12+y}$: ^{63}Cu-NMR study

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We report Cu-NMR studies of the multilayered high-T_c cuprate $(Cu_{0.6}C_{0.4})Ba_2Ca_3Cu_4O_{12+y}$ (Cu1234) with $T_c = 117$ K. In the normal state, the Knight shift (K) and the nuclear spin-lattice relaxation rate ($1/T_1$) of ^{63}Cu give evidence that the inner CuO_2 planes (IP) are underdoped, whereas the outer ones (OP) are heavily overdoped. In the superconducting (SC) state, both K and $1/T_1$ decrease markedly below $T_c = 117$ K in the IP, whereas in the OP they decrease moderately below $T_c = 117$ K, but markedly below $T_{c2} = 60$ K. The unusual NMR results in the OP reveal that the SC gap does not fully develop down to $T_{c2} = 60$ K. From comparison with a conventional d-wave model, it is shown that the SC gap in the OP increases linearly below T_c and follows the mean-field type of T dependence below T_{c2}. We propose that these dissimilarities are caused by the large difference of doping levels between the IP and the OP. The bulk SC transition at $T_c = 117$ K is considered to be triggered by the underdoped IP in Cu1234.

Copper oxide high-T_c superconductors commonly include corner-sharing CuO_2 planes forming a two-dimensional square lattice. Doping hole carriers into the plane is essential for the occurrence of high-T_c superconductivity. Various anomalies of physical properties in the normal state as well as the superconducting transition temperature T_c strongly depend on the in-plane carrier content N_h.

The carriers are homogeneously doped into the planes in mono- or bilayer high-T_c cuprates, since all the planes are crystallographically equivalent. This is not the case, however, in multilayered high-T_c cuprates, which include three or more CuO_2 planes in a unit cell. In these compounds, there exist two inequivalent CuO_2 planes, that is, the outer CuO_2 planes (denoted as OP) with a pyramidal (five) oxygen coordination and the inner planes (IP) with a square (four) oxygen coordination. The NMR studies reported thus far on the multilayered cuprates Bi2223,[1] Hg1223,[2,3] and Hg1234 (Ref. 4) reveal that the carrier content in the OP $[N_h(\mathrm{OP})]$ is slightly larger than $N_h(\mathrm{IP})$ in the IP. The difference between $N_h(\mathrm{IP})$ and $N_h(\mathrm{OP})$ is reported to increase in going from the under- to the optimally doped region; however, T_c is uniquely determined.[5,6] Therefore, this raises the question of which planes can determine the bulk T_c of multilayer cuprates, if the doping levels are significantly different between the IP and the OP. Understanding of this issue will give valuable information for considering the role of interlayer coupling in high-T_c superconductivity, as well as provide a basis for investigating the superconducting (SC) characteristics of multilayer cuprates.

In this paper we report Cu-NMR studies in the multilayered high-T_c cuprate superconductor, $(Cu_{1-x}C_x)Ba_2Ca_3Cu_4O_{12+y}$ (Cu1234) which comprises two IP's and the OP's.[7–9] From measurement of the Hall coefficient, it was inferred that the formal N_h average per one CuO_2 plane in Cu1234 ranges from 0.35 to 0.60, which is significantly larger than those in other multilayered cuprates reported thus far, e.g., $N_h \sim 0.21$ in Hg1234.[10]

In the normal state, the Knight shift (K) and the nuclear spin-lattice relaxation rate ($1/T_1$) of ^{63}Cu have proved that the magnetic properties in the OP (IP) are typical of those in heavily overdoped (underdoped) compounds, indicative of a significant difference between $N_h(\mathrm{OP})$ and $N_h(\mathrm{IP})$. In the SC state, it has been revealed that the SC gap does not develop simultaneously in the IP and the OP. The SC gap in the IP fully develops below T_c, but that in the OP increases linearly down to $T_{c2} = 60$ K below $T_c = 117$ K. We propose that this dissimilarity is caused by the large difference between $N_h(\mathrm{IP})$ and $N_h(\mathrm{OP})$. Noting that $N_h(\mathrm{OP})$ is compatible with those in the overdoped Tl1212 ($T_c = 64$ K) and Tl2201 (43 K), it is suggested that the inherent transition temperature in the OP is reduced to $T_{c2} = 60$ K due to its heavily overdoped level, and thus the bulk SC transition at $T_c = 117$ K is triggered by the underdoped IP in Cu1234.

A polycrystalline sample of $(Cu_{0.6}C_{0.4})Ba_2Ca_3Cu_4O_{12+y}$ was prepared by the high-pressure synthesis technique described elsewhere.[7] The superconducting transition tempera-

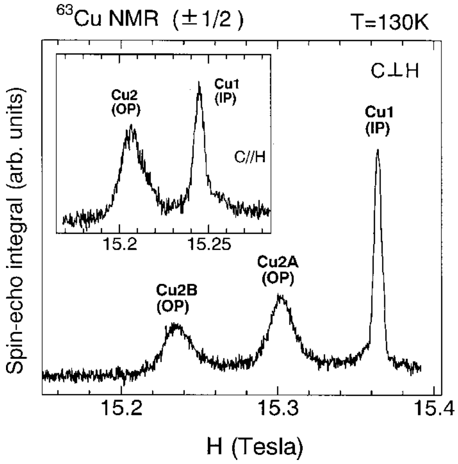

FIG. 1. The ^{63}Cu-NMR spectrum for the $(1/2 \leftrightarrow -1/2)$ central transition at $f = 174.2$ MHz and $T = 130$ K on the c-axis aligned polycrystal Cu1234 with $H \perp c$ axis. Inset: $H \| c$ axis.

ture T_c was determined as 117 K, below which a diamagnetic signal appears in the ac susceptibility, and N_h was estimated to be 0.5–0.6 from Hall coefficient measurements. A powder sample, confirmed to be almost a single phase by x-ray diffraction, was magnetically aligned along the c axis. K and $1/T_1$ of ^{63}Cu were measured in the range $T = 4.2$–300 K at 174.2 MHz and a magnetic field ($H \sim 15.5$ T) parallel ($H \| c$) and perpendicular ($H \perp c$) to the c axis. T_1 was measured as a single component by the saturation-recovery method at the $(1/2 \leftrightarrow -1/2)$ central transition (CT).

The NMR spectrum for $H \| c$ is shown in the inset of Fig. 1 where the two peaks corresponding to the IP and the OP are well resolved. The results for NMR intensity, K, and T_1 reveal that the sharp peak at a higher field arises from the Cu(1) site in the IP, and the broad one at a lower field from the Cu(2) site in the OP. Figure 1 shows the ^{63}Cu-NMR spectrum for the CT at 130 K for $H \perp c$. The Cu(2)-NMR spectrum for $H \perp c$ splits into two peaks, proving the presence of two Cu(2) sites in the OP with a different second-order quadrupole shift for $H \perp c$. A neutron-powder-diffraction experiment revealed that the CO_3 unit introduced into the charge reservoir layers elongates the distance between the apical oxygen and the Cu(2) site in the OP, and suggested the appearance of two inequivalent Cu sites, Cu(2A) and Cu(2B), with the apical oxygens in the original and displaced positions, respectively.[8] The NMR experiment is consistent with this neutron diffraction result. We note, however, that any difference in the K and T_1 results is not appreciable between the Cu(2A) and Cu(2B) sites, which assures that the magnetic properties are uniform in the OP. The nuclear quadrupole frequency ν_Q for the Cu(2A) and Cu(2B) sites are estimated to be ~ 14.7 and 30.0 MHz, respectively, and $\nu_Q = 11.1$ MHz for the Cu(1) site from the frequency (f) dependence of the total shift for $H \perp c$. Unfortunately, we have not succeeded in observing any Cu-NMR signal associated with the (Cu-C) charge reservoir layers. This suggests that some large crystal inhomogeneity may be introduced into these layers due to the partial substitution of CO_3 units.

In general, K consists of a T-dependent spin part $K_s(T)$ and a T-independent orbital part K_{orb}, $K_\alpha(T) = K_{s,\alpha}(T) + K_{orb,\alpha}(\alpha = ab, c)$. $K_{orb,ab}$ is estimated to be 0.20% (0.25%) for the IP (OP) from the residual shift at 4.2 K. Figure 2(a) shows the T dependence of $K_{s,ab}(T)$. $K_{s,ab}(T)$ in the IP decreases gradually with decreasing T in the normal state, typical for underdoped high-T_c cuprates, whereas that in the OP is greatly enhanced with a nearly T-independent value, typical for overdoped cuprates. It is well established that $K_{s,ab}$, proportional to the uniform susceptibility χ_s, increases progressively as N_h increases. The values of $K_{s,ab}$ in the IP and OP in Cu1234 are compatible with those in the IP of the optimally doped Hg1223 ($T_c = 133$ K),[3] and those in the heavily overdoped Tl1212 ($T_c = 64$ K)[11] and Tl2201 ($T_c = 42$ K),[12] respectively. This contrasting behavior in $K_{s,ab}(T)$ evidences a significant difference between N_h(IP) and N_h(OP) in Cu1234.

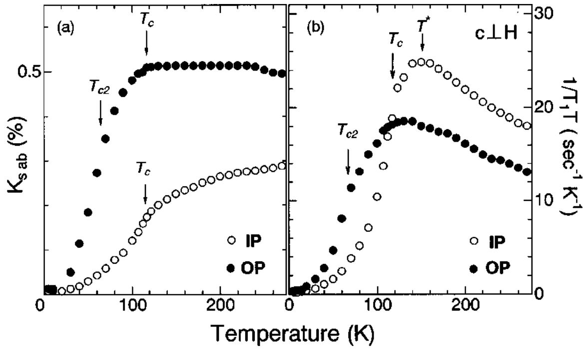

FIG. 2. T dependences of (a) the spin part of the Knight shift, $K_{s,ab}(T)$ and (b) $1/T_1T$ of ^{63}Cu for the inner and outer CuO_2 planes at $H \sim 15$ T.

Figure 2(b) shows the T dependence of $1/T_1T$ for $H \perp c$. In the normal state, $1/T_1T$ in the IP is larger than that in the OP. This is because the antiferromagnetic (AF) spin correlation in the underdoped IP is more pronounced than in the overdoped OP. $1/T_1T$ in the IP exhibits a broad maximum around $T^* \sim 150$ K, consistent with the spin-gap behavior observed in underdoped high-T_c cuprates. By contrast, $1/T_1T$ in the OP continues to increase down to T_c, typical of overdoped cuprates. Both the K and $1/T_1T$ results verify that the OP (IP) is overdoped (underdoped). This is in contrast with results in other multilayered high-T_c cuprates, Bi2223,[1] Hg1223,[2,3] Hg1234,[4] and Tl2223.[13,5] In these compounds, the difference between N_h(IP) and N_h(OP) does not alter the magnetic and SC properties in the OP and IP. In Cu1234, however, it is anticipated that the large difference between N_h(IP) and N_h(OP) will bring about a distinct difference not only in the magnetic properties but also in the SC characteristics.

We next focus on the T dependences of K_s and $1/T_1$ in the SC state, which reflect the T dependence of the SC gap $\Delta(T)$ in the different planes. As shown in Fig. 2(a), $K_s(T)$ in the underdoped IP undergoes a sharp drop below $T_c = 117$ K due to the opening of the SC gap. On the other hand, $K_s(T)$ in the overdoped OP decreases gradually below $T_c = 117$ K, followed by a sharp decrease below $T_{c2} \sim 60$ K. In order to unravel the detailed T dependence of K_s below T_c, its T-derivative value $d(K_{s,ab})/dT$ is plotted against T in Fig. 3(a). It should be noted that $d(K_{s,ab})/dT$ in the IP shows a clear peak just below $T_c = 117$ K, but that in the OP shows the peak not just below $T_c = 117$ K but just below $T_{c2} = 60$

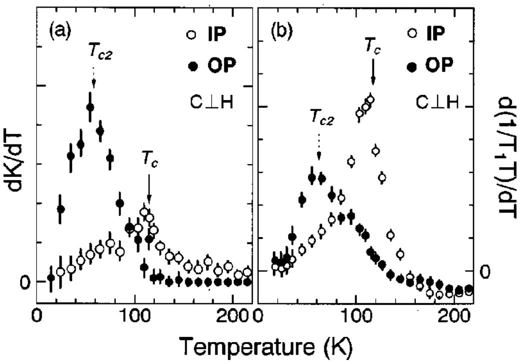

FIG. 3. T dependences of the T-derivative changes of (a) $K_{s,ab}(T)$, $dK_{s,ab}/dT$, and (b) $1/T_1T$, $d(T_1T)^{-1}/dT$, for the inner and outer CuO_2 planes.

K. Likewise, the peak of $d(1/T_1T)/dT$ in the IP, as seen in Fig.3(b), appears around T_c, whereas that in the OP appears around T_{c2}. In Fig. 4, the T dependences of $1/T_1$ in the IP and the OP are plotted on logarithmic scales. $1/T_1$ in the IP decreases sharply just below T_c, followed by a T^3-like dependence in the low-T regime. These relaxation behaviors share common features with those observed in other high-T_c cuprates, consistent with the d-wave model with a gapless line node. By contrast, $1/T_1$ for the OP decreases gradually below $T_c = 117$ K but sharply below $T_{c2} \sim 60$ K. In the inset of Fig. 4, $(1/T_1)/(1/T_1)_{T=T_{c2}}$ vs T/T_{c2} is indicated for the OP together with $(1/T_1)/(1/T_1)_{T=T_c}$ vs T/T_c for the IP. Here $(1/T_1)_{T=T_{c2}}$ is $1/T_1$ at $T_{c2} = 60$ K and $(1/T_1)_{T=T_c}$ at $T_c = 117$ K. The plot in the OP for $0.4 < T/T_{c2} < 1$ is on almost the same line as that in the IP for $0.4 < T/T_c < 1$, suggesting that the d-wave SC gap in the OP fully develops not below T_c but below T_{c2}.

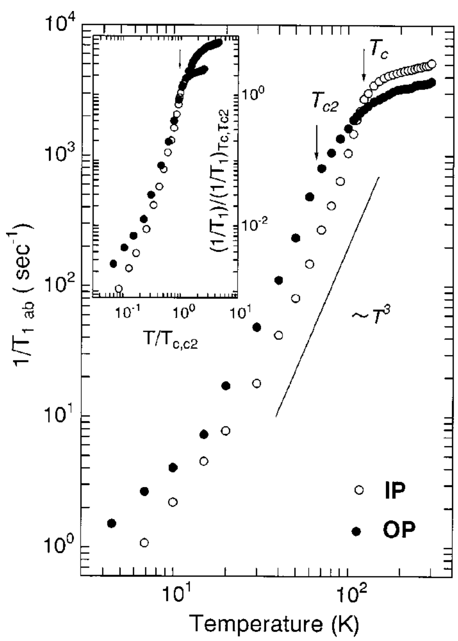

FIG. 4. $1/T_1$ vs T both in logarithmic scales for $H \perp c$ axis. Inset shows $(1/T_1)/(1/T_1)_{T_c}$ vs T/T_c and $(1/T_1)/(1/T_1)_{T_{c2}}$ vs T/T_{c2} plots for the inner and outer CuO_2 planes, respectively. $(1/T_1)_{T_c}$ at $T_c = 117$ K and $(1/T_1)_{T_{c2}}$ at $T_{c2} \sim 60$ K.

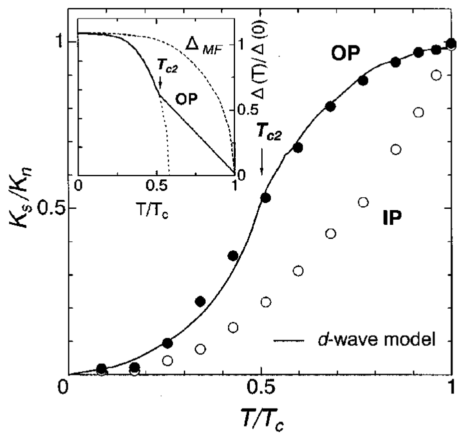

FIG. 5. $K_s(T)/K_n$ vs T/T_c plot for the IP and the OP. $K_s(T)$ and K_n are the Knight shifts in the superconducting state and at T_c, respectively. $K_s(T)/K_n$ for the OP is reproduced by the d-wave model assuming a T-linear increase of $\Delta(T)$ below T_c and follows the BCS form below T_{c2} as shown in the inset.

In order to deduce the T dependence of the SC gap $\Delta(T)$ in the OP, $K_s(T)/K_n$ normalized by the value K_n at $T_c = 117$ K is plotted against T/T_c in Fig. 5, together with $K_s(T)/K_n$ for the IP. It is clear that $\Delta(T)$ in the OP does not fully develop down to T_{c2} in contrast to that in the IP. A two-dimensional d-wave model[14–16] has been applied to fit the data for the OP since K_n is independent of the temperature, but not to the data in the IP since $K_n(T)$ decreases with decreasing T. A model with $\Delta_{MF}(T)$ following a conventional mean-field (MF) pattern is not in accord with the slow decrease of $K_s(T)/K_n$ in the OP between $T_{c2} = 60$ K and $T_c = 117$ K. Alternatively, as indicated by the solid line in the inset of Fig. 5, the agreement between the experiment and the calculation seems to be satisfactory when it is assumed that $\Delta(T)/\Delta(0)$ increases linearly down to $T_{c2} = 60$ K and follows the MF type of behavior below T_{c2}. This result shows that the gap in the OP does not fully develop below $T_c = 117$ K but below $T_{c2} = 60$ K.

In the SC state, the appearance of bulk superconductivity indicates that the SC phase has a coherent character below T_c. However, the present NMR study reveals that the SC gap does not develop simultaneously in the IP and the OP. We propose that this dissimilarity is caused by the large difference between N_h(IP) and N_h(OP). Note that N_h(OP) is compatible to those in the overdoped Tl1212 ($T_c = 64$ K)[11] and Tl2201 (43 K).[12] This suggests that the inherent transition temperature in the OP is reduced to $T_{c2} = 60$ K due to its heavily overdoped level, although the bulk SC transition is triggered by the underdoped IP at $T_c = 117$ K. In this case, the unusual $\Delta(T)$ behavior in the OP between T_c and T_{c2} may be interpreted as a kind of ''proximity effect'' induced by the superconductivity in the IP. This is because the coherent length along the c axis is reported to be $\xi_c \sim 10$ Å in Cu1234, which is much larger than the distance between the IP and the OP, i.e., ~ 3.2 Å.[17]

We note that a further dissimilarity relevant to the large difference between N_h(OP) and N_h(IP) is seen in the normal state. As seen in Fig. 2(b), spin-gap behavior in the IP is extracted from the broad maximum of $1/T_1T$ around $T^* = 150$ K, but not in the OP. In the underdoped and optimally doped Hg1223's (Refs. 2,3) and Hg1234,[4] the OP and the IP retain similar SC characteristics as well as magnetic properties, although N_h(OP) and N_h(IP) are different. In this context, we suppose that there is a threshold in the difference between N_h(OP) and N_h(IP) to bring about dissimilarities in the SC and magnetic properties.

In Cu1234, it has been reported that T_c keeps a rather high value above $T_c = 117$ K and stays nearly constant regardless of the variation of N_h in the overdoped region, $N_h = 0.35–0.6$, which is almost three times larger than $N_h \sim 0.2$ in the optimum region.[10] The fact that T_c does not depend on the carrier doping seems to be unique compared with other cuprates in which the T_c value decreases drastically on increasing N_h in the overdoped region. What the present NMR studies have suggested is that the doping level in the OP is heavily overdoped; however, the IP remains underdoped and sustains a high T_c value above 117 K in Cu1234.

In conclusion, the measurements of ^{63}Cu Knight shift and $1/T_1T$ in the overdoped multilayered cuprate Cu1234 reveal that the outer (inner) CuO_2 planes are heavily overdoped (underdoped). In the normal state, spin-gap behavior is observed in the IP but not in the OP. In the SC state, it was found that the SC gap in the OP does not fully develop below $T_c = 117$ K but below $T_{c2} = 60$ K. We propose that these dissimilarities are caused by the large difference of doping level between the IP and the OP. Noting that the doping level in the OP is compatible with those in the overdoped Tl1212 ($T_c = 64$ K) and Tl2201 (43 K), it is suggested that the T_c inherent to the OP is reduced to $T_{c2} = 60$ K due to its heavily overdoped level, although the bulk SC transition is triggered by the underdoped IP at $T_c = 117$ K. We would remark that the low anisotropy of SC characteristics[17] in Cu1234 is associated with the heavily overdoped level in the OP and the bulk T_c is kept unchanged since the IP remains underdoped.

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[1] A. Trokiner, L. Le Noc, J. Schneck, A. M. Pougnet, R. Mellet, J. Primot, H. Savary, Y. M. Gao, and S. Aubry, Phys. Rev. B **44**, 2426 (1991).
[2] M.-H. Julien, P. Carreta, M. Horvatić, C. Berthier, Y. Berthier, P. Ségransan, A. Carrington, and D. Colson, Phys. Rev. Lett. **76**, 4238 (1996).
[3] K. Magishi, Y. Kitaoka, G.-q. Zheng, K. Asayama, K. Tokiwa, A. Iyo, and H. Ihara, J. Phys. Soc. Jpn. **64**, 4561 (1995).
[4] Y. Tokunaga, K. Ishida, K. Magishi, S. Ohsugi, G.-q. Zheng, Y. Kitaoka, K. Asayama, K. Tokiwa, A. Iyo, and H. Ihara, Physica B **259-261**, 571 (1999).
[5] Y. Piskunov, K. N. Mikhalev, Yu. I. Zhdanov, A. P. Geraschenko, S. V. Verkhovskii, K. A. Okulova, E. Yu. Medvedev, A. Yu. Yakubovskii, L. D. Shustov, P. V. Bellot, and A. Trokiner, Physica C **300**, 225 (1998).
[6] Y. Tokunaga, H. Kotegawa, K. Ishida, G.-q. Zheng, Y. Kitaoka, K. Tokiwa, A. Iyo, and H. Ihara, J. Low Temp. Phys. **117**, 473 (1999).
[7] H. Ihara, K. Tokiwa, H. Ozawa, M. Hirabayashi, A. Negishi, H. Matuhata, and Y. S. Song, Jpn. J. Appl. Phys., Part 1 **33**, 503 (1994); Jpn. J. Appl. Phys., Part 2 **33**, L300 (1994); Physica C **235-240**, 981 (1994).
[8] Y. Shimakawa, J. D. Jorgensen, D. G. Hinks, H. Shaked, R. L. Hitterman, F. Izumi, T. Kawashima, E. Takayama-Muromachi, and T. Kamiyama, Phys. Rev. B **50**, 16 008 (1994).
[9] J. Akimoto, K. Tokiwa, A. Iyo, H. Ihara, H. Hayakawa, Y. Gotoh, and Y. Oosawa, Physica C **279**, 181 (1997).
[10] M. Ogino, T. Watanabe, H. Tokiwa, A. Iyo, and H. Ihara, Physica C **258**, 384 (1996).
[11] G.-q. Zheng, K. Magishi, Y. Kitaoka, K. Asayama, T. Kondo, Y. Shimakawa, T. Manako, and Y. Kubo, Physica B **186-188**, 1012 (1993).
[12] Y. Kitaoka, K. Fujiwara, K. Ishida, K. Asayama, Y. Shimakawa, T. Manako, and Y. Kubo, Physica C **179**, 107 (1991).
[13] G.-q. Zheng, K. Kitaoka, K. Asayama, K. Hamada, H. Yamauchi, and S. Tanaka, Physica C **260**, 197 (1996).
[14] H. Monien and D. Pines, Phys. Rev. B **41**, 6297 (1990).
[15] K. Ishida, Y. Kitaoka, N. Ogata, T. Kamino, K. Asayama, J. R. Cooper, and N. Athanassopoulou , J. Phys. Soc. Jpn. **62**, 2803 (1993).
[16] K. Magishi, Y. Kitaoka, G.-q. Zheng, K. Asayama, T. Kondo, Y. Shimakawa, T. Manako, and Y. Kudo, Phys. Rev. B **54**, 10 131 (1996).
[17] H. Ihara, Adv. Supercond. **7**, 255 (1994).