Novel Interplay between High-\(T_c\) Superconductivity and Antiferromagnetism in Tl-based Six-CuO\(_2\)-Layered Cuprates: \(^{205}\)Tl- and \(^{63}\)Cu-NMR Probes

Hidekazu Mukuda\(^1\), Nozomu Shiki\(^1\), Naoki Kimoto\(^1\), Mitsuharu Yashima\(^1\), Yoshiro Kitaoka\(^1\), Kazuyasu Tokiwa\(^2\), and Akira Iyo\(^3\)

\(^1\)Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
\(^2\)Department of Applied Electronics, Science University of Tokyo, Noda, Chiba 278-8510, Japan
\(^3\)National Institute of Advanced Industrial Science and Technology (AIST), Umezono, Tsukuba 305-8568, Japan

(Received June 28, 2016)

We report \(^{63}\)Cu- and \(^{205}\)Tl-NMR studies on six-layered (\(n=6\)) high-\(T_c\) superconducting (SC) cuprate TlBa\(_2\)Ca\(_2\)Cu\(_6\)O\(_{14+\delta}\) (Tl1256) with \(T_c \sim 100\) K, which reveal that antiferromagnetic (AFM) order takes place below \(T_N \sim 170\) K. In this compound, four underdoped inner CuO\(_2\) planes (\(n=4\)) sandwiched by two outer planes (OPs) are responsible for the onset of AFM order, whereas the nearly optimally-doped OPs responsible for the onset of bulk SC. It is pointed out that an increase in the out-of-plane magnetic interaction within an intra-unit-cell causes \(T_N \sim 45\) K for Ti1245 with \(n=3\) to increase to \(\sim 170\) K for Tl1256 with \(n=5\). It is remarkable that the marked increase in \(T_N\) and the AFM moments for the OPs does not bring about any reduction in \(T_c\), since \(T_c \sim 100\) K is maintained for both compounds with nearly optimally doped OP. We highlight the fact that the SC order for \(n \geq 5\) is mostly dominated by the long-range in-plane SC correlation even in the multilayered structure, which is insensitive to the magnitude of \(T_N\) and the AFM moments at the IPs or the AFM interaction among the IPs. These results demonstrate a novel interplay between the SC and AFM orders when the charge imbalance between the OPs and SC is significantly large.

The parent materials of hole-doped high-\(T_c\) cuprates are antiferromagnetic (AFM) Mott insulators characterized by a large in-plane superexchange interaction \(J_{\text{in}} \sim 1300\) K among the \(S=1/2\) spins at the Cu sites. Since the theory demonstrates that no long-range order takes place at finite temperature for two-dimensional (2D) antiferromagnets,\(^1\) the onset of AFM order is actually mediated by three-dimensional (3D) magnetic interactions such as \(J_{\text{out}}(n)\) among the CuO\(_2\) layers within an intra-unit-cell and \(J_{\text{CRL}}\) among an inter-unit-cell through the blocking charge reservoir layer (CRL). Note that \(J_{\text{out}}(n)\) and \(J_{\text{CRL}}\) are much smaller than \(J_{\text{in}}\). As a matter of fact, as the number of CuO\(_2\) planes (\(n\)) increases in the unit cell, the Néel temperature (\(T_N\)) of 325 K for single-layered La\(_2\)CuO\(_4\)(\(n=1\)) increases to 410 K for bilayered YBCO(\(n=2\)) and to 537 K for infinite-layered (Ca,Sr)CuO\(_2\)(\(n=\infty\)); nevertheless the size of the AFM moment does not depend on \(n\).\(^2\)

Multilayered copper oxides TlBa\(_2\)Ca\(_{n-1}\)Cu\(_n\)O\(_{2n+2+\delta}\) (Tl12(\(n=1\))-1) with \(n \geq 3\) include two types of CuO\(_2\) planes, an outer CuO\(_2\) plane (OP) with fivefold oxygen coordination and an inner plane (IP) with fourfold coordination with no apical oxygen, as shown in Fig. 1(a). The hole density \(p(\text{OP})\) is always larger than \(p(\text{IP})\), since the OP is closer to the CRL than to the IPs. In other words, the spatially dependent Madelung potential for hole carriers from the apical oxygen \(O^{2-}\) becomes smaller as IPs are apart from the CRL.\(^3\)-\(^6\) Accordingly, as \(n\) increases, the \(p(\text{IP})\) tends to decrease. As a result, the AFM order was observed at underdoped IPs of Tl1245(\(n=5\)) with \(T_N=45\) K and an AFM moment of \(M_{\text{AFM}} \sim 0.1\) \(\mu_B\). The most important outcome from this result is evidence that the AFM order at each IP coexists uniformly below \(T_N=45\) K with the SC state below \(T'_c=87\) K.\(^3\)-\(^7\) Further reduction of the hole density in the series results in the uniform coexistence of AFM and SC orders even at an OP where \(p(\text{OP})\) is less than the critical hole density \(p_c\) for the onset of AFM order.\(^3\)-\(^4\)-\(^8\) Regarding the \(n\) dependence of \(p_c\), previous works revealed that as \(n\) increases from \(n=3\) to 4 to 5, \(p_c(n)\) increases from 0.075 to 0.08 to 0.10,\(^3\)-\(^4\) which demonstrates that the interlayer magnetic interaction \(J_{\text{out}}(n)\) becomes stronger with increasing \(n\). It is noteworthy that once an AFM order emerges, \(M_{\text{AFM}}\) is dependent on the doping level \(p\) but independent of \(n\), whereas \(T_N\) depends on \(n\) or \(J_{\text{out}}(n)\). These results have enabled us to present the ground-state phase diagram of SC and AFM orders as a function of the hole doping level for the multilayered cuprates with \(3 \leq n \leq 5\) and to compare it with the theoretically deduced phase diagrams for 2D doped Mott insulators.\(^3\)-\(^4\)

In this Letter, we report on \(^{63}\)Cu- and \(^{205}\)Tl-NMR studies of the six-layered cuprate Tl1256 with \(T_c \sim 100\) K, which provide evidence that an AFM order takes place below \(T_N \sim 170\) K. In the homologous series of Ti12(\(n-1\))\(n=6\) in the optimally doped regime, we find that \(T_N\) is four times larger for \(n=6\) than for \(n=5\), whereas no trace of AFM order was observed for \(n \leq 4\). This is considered to be because \(J_{\text{out}}(n)\) for \(n=6\) is significantly larger than that for \(n=5\). Since \(T_c\) for both compounds is almost the same, we remark that even in the multilayered cuprates, the SC order is mostly dominated by the long-range in-plane SC correlation, which is insensitive to the magnitude of \(T_N\) and AFM moments at the IPs. This is the unique interplay between the high-\(T_c\) SC and AFM orders observed in the six-layered cuprates.
of the plot of \( f_0 - \gamma_N H_{\text{res}} \)/\( \gamma_N H_{\text{res}} \) against \( 1/(\gamma_N H_{\text{res}})^2 \) gives the value of \( \nu_Q \) at the IPs and OP. The estimated values of \( \epsilon_{\nu Q} = 9.7 \) and 16.6 MHz allow us to assign the two peaks in the spectra of Fig. 1(b) to the IPs and OP, respectively, since the similar values of \( \epsilon_{\nu Q} \) have been reported for the IPs and OP previously.\(^6\) Note here that, as shown in Fig. 1(a), the four IPs include two inequivalent IPs, IP(1) and IP(2), but it is not possible to resolve each spectrum associated with IP(1) and IP(2) owing to their comparable values of \( \nu_Q \).

Figure 1(e) indicates the \( T \) dependence of the spin component of the \( ^{63}\text{Cu} \) Knight shift \( ^{63}\text{K}_{\text{ab}} \), which is evaluated by subtracting the orbital part of the Knight shift \( ^{63}\text{K}_{\text{ab}} \sim 0.21(\pm 0.01)\% \) from \( ^{63}\text{K}_{\text{ab}} \). The marked decrease in \( ^{63}\text{K}_{\text{ab}} \) below \( T_c \) reveals the decrease in the spin susceptibility owing to the formation of a spin-singlet Cooper pairing. The empirical relationship between the hole density \( p \) and the value of \( ^{63}\text{K}_{\text{ab}} \) at 300 K\(^10\) enables us to evaluate \( p(\text{OP}) \) to be \(~0.152\) and \( p(\text{IP})s \) to be \(~0.076\). Here, the \( p(\text{IP})s \) represents the average value of \( p(\text{IP}(1)) \) and \( p(\text{IP}(2)) \). Provided that \( p \) at each \( \text{CuO}_2 \) plane follows the spatial dependence of the Madelung potential from the apical oxygen \( O^2− \) [see Fig. 2(d)], the relation \( \rho(\text{IP}(1)) > p(\text{IP}(1)) > \rho(\text{IP}(2)) \) is expected and \( p(\text{IP}(1)) \sim 0.086 \) and \( p(\text{IP}(2)) \sim 0.07 \) are tentatively estimated using \( p(\text{OP}) = 0.152 \). The average value \( \rho(\text{IP})s \) of \( p(\text{IP}(1)) \) and \( p(\text{IP}(2)) \) almost coincides with \( \rho(\text{IP})s \sim 0.076 \) extracted experimentally from \( ^{63}\text{K}_{\text{ab}} \). As possible evidence for the AFM order at IPs, we note that the \( ^{63}\text{Cu-NMR} \) spectra at the IPs disappear below \(~200\) K owing to the development of AFM correlations upon cooling toward \( T_c \), but the \( ^{63}\text{Cu-NMR} \) spectrum at the OP is observable down to low temperatures, suggesting that the OP does not play a primary role in the onset of AFM order.

Zero-field \( ^{63}\text{Cu-NMR} \) measurements were performed at 1.8 K for \( \text{Tl1256} \) \((n = 6) \) to gain an insight into the AFM ordered state. Figure 2 indicates the NMR spectra for (a) \( \text{Tl1256} \), (b) \( \text{Tl1254} \) \((n = 5) \) with \( T_c = 100 \) K,\(^3\) and (c) \( \text{Tl1223} \) \((n = 3) \) with \( T_c = 133 \) K. The nuclear Hamiltonian \( \mathcal{H}_N \) for the \( \text{Cu} \) nucleus \((I = 3/2) \) at zero external field is described in terms of the Zeeman interaction \( \mathcal{H}_Z = \gamma_N \hbar H_{\text{int}} \cdot \mathbf{I} \) and the nuclear quadrupole interaction \( \mathcal{H}_Q = (\nu_Q/2)(I_z^2 - 5/4) \), where \( H_{\text{int}} \) is the internal field at the \( \text{Cu} \) site induced by AFM moments. In the case that the IPs and OP are in the nonmagnetic state with \( H_{\text{int}} = 0 \), the Cu-NQR spectra should be observed at \( \epsilon_{\nu Q} \) \((\text{IPs}) \sim 9.7 \) and \( \epsilon_{\nu Q} \) \((\text{OP}) \sim 16.6 \) MHz, as shown by the dotted lines in Fig. 2. As a matter of fact, such the spectra are observed in Fig. 2(c) for \( \text{Tl1223} \) \((n = 3) \), which does not have an AFM order. Accordingly, the spectrum with a peak at \(~16\) MHz in Fig. 2(a) is assigned to the OP, which is in the paramagnetic state. For the IPs, the peaks around \(~25\) and \(42\) MHz in the spectra are assigned to IP(1) and IP(2), respectively, revealing that both are in the AFM ordered state. This is because these frequencies are much higher than \( \epsilon_{\nu Q} \) \((\text{IPs}) \sim 9.7 \) MHz, pointing to the presence of an internal field \( H_{\text{int}} \) at the IPs. In fact, on the basis of the nuclear Hamiltonian of \( \mathcal{H}_N = \mathcal{H}_Z + \mathcal{H}_Q \), a simulation of these spectra gives \( H_{\text{int}} = 2.1 \) and 3.6 T for IP(1) and IP(2), respectively. Using the relation \( H_{\text{int}} = |A_{\text{ab}} - 4B| \gamma M_{\text{AFM}} \) spon-
As shown in Fig. 3(a), the rapid decrease in the CRL and determine $T_n$ means that the on-site hyperfine field is $B(\text{IP}) \approx 6.1 \, T/\mu_B$ and $B(\text{OP}) \approx 7.4 \, T/\mu_B$.\cite{note2} As a result, the AFM order with $M_{\text{AFM}}(\text{IP}(1))=0.10 \, \mu_B$ and $M_{\text{AFM}}(\text{IP}(2))=0.17 \, \mu_B$ emerges at the respective hole densities of $p(\text{IP}(1)) \sim 0.086$ and $p(\text{IP}(2)) \sim 0.07$. We highlight the fact that the present relationship between $M_{\text{AFM}}$ and $p$ in Ti1256$(n=6)$ coincides with the groundstate phase diagram of the SC and AFM orders as a function of $p$ for the multilayered cuprates with $3 \leq n \leq 5$,\cite{note3} ensuring that this phase diagram is independent of $n$.

Here, we show the $^{205}\text{Tl-NMR}$ results at the CRL, which enable us to gain an insight into the 3D magnetic interaction $J_{\text{CRL}}$ among the inter-unit-cells through the CRL and determine $T_N$. Figure 1(c) shows the $T$-dependence of the $^{205}\text{Tl-NMR}$ spectra. The spectra for $H||c$ and $H\parallel ab$ (see the data at 200 K) are well resolved and the $T$ dependences of $^{205}\text{Tl Knight shift}$ for $H||c$ and $H\parallel ab$ are presented in Fig. 3(a). $^{205}K_{s}^{ab(c)}$ comprises the spin component $^{205}K_{s}^{ab(c)}$ and the $T$-independent orbital component $^{205}K_{s}^{ab(c)}$.\cite{note4} $^{205}K_{s}^{ab(c)}$ is associated with an anisotropic hyperfine field supertransferred by the $6s$- and $6p$-spin polarizations at the Tl site, originating from the spin polarization at the IPs and OP. As shown in Fig. 3(a), the rapid decrease in $^{205}K_{s}^{ab(c)}$ below $T_c$ is attributed to that in $^{205}K_{s}^{ab(c)}$ due to the formation of spin-singlet Cooper pairs. Since $^{205}K_{s}^{ab(c)}$ approaches zero well below $T_c$, the values of $^{205}K_{s}^{ab}$ and $^{205}K_{s}^{c}$ at $T\ll T_c$ give $\sim 0.29$ and $\sim 0.07\%$, respectively. Furthermore, it is anticipated that the anisotropic spin part in the Knight shift exhibits $^{205}K_{s}^{c} > ^{205}K_{s}^{ab}$, suggesting that the dipole hyperfine field from the spin polarization at the $6p_z$ orbital is larger than those at the $6p_{x,y}$ orbitals. By contrast, the anisotropy in the orbital part exhibits $^{205}K_{s}^{L} < ^{205}K_{s}^{ab}$. In general, $K_{s}^{L}$ originates from the van Vleck susceptibility, which is proportional to $\langle | L| \rangle / |e_s - e_e|$. Here, $\langle | L| \rangle$ and $e_s (|e_e|)$ denote the energies (wave functions) for the ground state and the excited states, respectively, and $L$ is the orbital angular momentum operator.\cite{note5} Provided that $6p_z$ and $6p_{x,y}$ are in the ground and excited states, respectively, it is expected that $^{205}K_{s}^{c} \propto \langle p_z | L | p_{x,y} \rangle / \langle p_{x,y} | p_z | p_{x,y} \rangle > 0$. As a result, the spin densities on the $6s$ and $6p_z$ orbitals at the Tl site are responsible for the anisotropy in the spin and orbital parts, playing a significant role in the interlayer magnetic coupling $J_{\text{CRL}}$ through the possible covalency with the $4s$ and $3d_{x^2-y^2}$ orbitals of Cu via the $2p_x$ and $2s$ orbitals of apical O. This event is schematically drawn in the inset of Fig. 3(a). These microscopic outcomes resemble the previous $^{205}\text{Tl-NMR}$ results for single-layered Ti1201,\cite{note6,note7} indicating that the local electronic state at the Tl site, and hence $J_{\text{CRL}}$, does not vary from $n=1$ to 6.

Next, we estimate $T_N$ from the measurements of $^{205}(1/T_1 T)$. Its $T$ dependence exhibits a peak at 170 K, as shown in Fig. 3(c). The distinct peak in $^{205}(1/T_1 T)$ gives evidence that an AFM order occurs in a long-range manner. Below $T_N$, as shown in Fig. 3(b), the linewidth in the $^{205}\text{Tl-NMR}$ spectra starts to increase, similar to the case for Ti1245, giving another evidence for the onset of the AFM order. These similar behaviors were observed in the $^{205}\text{Tl-NMR}$ spectra of Ti1245($n=5$) at $T_N(\tilde{g}) = 45$
where the charge imbalance between the IP and OP is significantly large.

In summary, site-selective $^{63}$Cu-NMR/NQR and $^{207}$TI-NMR studies on six-layered Tl1256 with $T_c=100$ K have revealed that the AFM order with moments of 0.10 and 0.17$\mu_B$ takes place at the inner CuO$_2$ planes IP(1) and IP(2), respectively, below 170 K. This is the consequence of the underdoped hole densities at IP(1) and IP(2) with $p \sim 0.086$ and $\sim 0.07$, respectively. We highlight the fact that the increase in the out-of-plane magnetic interaction within the intra-unit-cell causes $T_N(5) \sim 45$ K for Tl1245 with $n$(IP)=3 to increase to $T_N(6) \sim 170$ K for Tl1256 with $n$(IP)=4, whereas no trace of AFM order was observed for $n \leq 4$. The interesting finding in this work is that the marked increases in $T_N$ and AFM moments for the IPs do not bring about any reduction in $T_c$, since $T_c \sim 100$ K is maintained for both the compounds with a nearly optimally doped OP. We remark that even in the multilayered cuprates, the SC order for $n \geq 5$ is mostly dominated by the long-range in-plane SC correlation, which is insensitive to the magnitude of $T_N$ and the AFM moments at the IPs or the AFM interaction among the IPs, demonstrating the novel interplay between the SC and AFM orders at $n \geq 5$. This is in contrast to the case of $n=3$, for which a higher $T_c$ ($\sim 133$ K) is realized at the three SC layers, where the charge imbalance between the IP and OP is quite small.

This work was supported by JSPS KAKENHI Grant Nos. 26400556, 26610102, and 16H04013.

1) N. D. Mermin and H. Wagner, Phys. Rev. Lett. 17, 1133 (1966).
2) J. M. Tranquada, in Handbook of High-Temperature Superconductivity (Springer, New York, 2007), p. 257.
3) H. Mukuda, S. Shimizu, A. Iyo, and Y. Kitaoka, J. Phys. Soc. Jpn. 81, 011008 (2012).
4) S. Shimizu, S.-i. Tabata, S. Iwai, H. Mukuda, Y. Kitaoka, P. M. Shirage, H. Kito, and A. Iyo, Phys. Rev. B 85, 024528 (2012).
5) H. Kotegawa, Y. Tokunaga, K. Ishida, G.-q. Zheng, Y. Kitaoka, K. Asayama, H. Kito, A. Iyo, H. Ibara, K. Tanaka, K. Tokiwa, and T. Watanabe, Phys. Rev. B 64, 064515 (2001).
6) H. Kotegawa, Y. Tokunaga, Y. Araki, G.-q. Zheng, Y. Kitaoka, K. Tokiwa, K. Ito, T. Watanabe, A. Iyo, Y. Tanaka, and H. Ibara, Phys. Rev. B 69, 014501 (2004).
7) H. Mukuda, Y. Yamaguchi, S. Shimizu, Y. Kitaoka, P. M. Shirage, and A. Iyo, J. Phys. Soc. Jpn. 77, 124706 (2008).
8) H. Mukuda, M. Abe, Y. Araki, Y. Kitaoka, K. Tokiwa, T. Watanabe, A. Iyo, H. Kito, and Y. Tanaka, Phys. Rev. Lett 96, 087001 (2006).
9) A. Iyo, Y. Tanaka, H. Kito, Y. Kodama, P. M. Shirage, D. D. Shivanag, H. Matsuura, K. Tokiwa, and T. Watanabe, J. Phys. Soc. Jpn. 76, 064711 (2007).
10) S. Shimizu, S. Iwai, S.-i. Tabata, H. Mukuda, Y. Kitaoka, P. M. Shirage, H. Kito, and A. Iyo, Phys. Rev. B 83, 144523 (2011).
11) S. Kambe, H. Yasuoka, A. Hayashi, and Y. Ueda, Phys. Rev. B 48, 6593 (1993).
12) O. M. Vyaaslev, N. N. Kolesnikov, M. P. Kulakov, and I. F. Schegolev, Physica C 199, 50 (1992).
13) B. A. Scott, E. Y. Suard, C. C. Tsuei, D. B. Mitzi, T. R. McGuire, B.-H. Chen, and D. Walker, Physica C 230, 239 (1994).
14) S. Shimizu, S.-i. Tabata, H. Mukuda, Y. Kitaoka, P. M. Shirage, H. Kito, and A. Iyo, Phys. Rev. B 83, 214514 (2011).
15) S. Shimizu, H. Mukuda, Y. Kitaoka, H. Kito, Y. Kodama, P. M. Shirage, and A. Iyo, J. Phys. Soc. Jpn. 78, 064705 (2009).
16) M. Mori and S. Maejima, Phys. Rev. Lett. 94, 137003 (2005).