Genuine Phase Diagram of high-$T_c$ superconductors Based on Site-selective Cu-NMR Studies on Five-layered Cuprates

H. Mukuda$^1$, Y. Yamaguchi$^1$, S. Shimizu$^1$, Y. Kitaoka$^1$, P. M. Shirage$^2$, A. Iyo$^2$

$^1$Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
$^2$National Institute of Advanced Industrial Science and Technology (AIST), Umezono, Tsukuba 305-8568, Japan

E-mail: mukuda@mp.es.osaka-u.ac.jp

Abstract. We report a genuine phase diagram for a disorder-free CuO$_2$ plane based on the evaluation of the local hole density ($N_h$) by site-selective Cu-NMR studies on five-layered cuprates. It has been unraveled that (1) the antiferromagnetic (AFM) metallic state is robust up to $N_h \approx 0.17$, (2) the uniformly mixed phase of SC and AFM metal (AFMM) is realized at $N_h \leq 0.17$, (3) the tetracritical point for the AFMM/(AFMM+SC)/SC/PM(Paramagnetism) phases may be present at $N_h \approx 0.15$ and $T \approx 75$ K, (4) $T_c$ is maximum just outside a quantum critical point (QCP) at which the AFM order collapses, suggesting the intimate relationship between the high-$T_c$ SC and the AFM order. Our finding experimentally suggests that the AFM interaction plays the vital role as the glue for the Cooper pairs.

1. Introduction
A high-$T_c$ superconductivity (SC) in cuprates emerges on a CuO$_2$ plane when an antiferromagnetic (AFM) Mott insulator is doped with mobile carriers. A strong relationship between AFM order and SC is believed to be a key to understand the origin of their remarkably high SC transition. Experimentally, however, in a prototype high-$T_c$ cuprate La$_{2-x}$Sr$_x$CuO$_4$ (LSCO), the AFM and SC phases are separated by the spin-glass phase in association with the carrier localization [1]. Multilayered cuprates, which is composed of a pyramid-type outer CuO$_2$ plane (OP) and a square-type inner plane (IP), allow us to extract the characteristics of the disorder-free doped CuO$_2$ plane[2, 3, 4, 5]. In the multilayered cuprates, since the IPs are farther from a charge reservoir layers than the OPs, the carrier density at IPs is lower than that at OPs. The disorder introduced along with the chemical substitution in the charge reservoir layer is effectively shielded on an OP, as a result of which ideally flat CuO$_2$ planes are realized, especially at IPs, differentiating multilayered cuprates from mono-layered cuprate LSCO.

2. Experimental
A polycrystalline sample of Hg-based five-layered cuprate HgBa$_2$Ca$_4$Cu$_5$O$_{12+d}$(Hg-1245(OPT)22) has been synthesized at a pressure (temperature) of 2.5 GPa (950°C), which is lower than that applied in the sample synthesis in the previous studies [4, 6], i.e., 4.5 GPa (1050°C), and referred
to as ”Hg-1245(OPT)♯1” in this study. The SC transition temperature $T_c$ has been determined to be 110 K from the onset of a sharp diamagnetic signal in dc susceptibility.

3. Results and discussions

Figures 1(a) and 1(b) show the temperature ($T$) dependences of $K^{ab}_s$ ($K^{ab}_s$ in a field parallel to the ab-plane) for OPs and IPs of Hg-1245(OPT)♯2, respectively. Here, $K^{ab}_s$ is obtained by subtracting temperature-independent $K^{orb}_s$, which is approximately 0.2-0.21%, irrespective of IP or OP for Hg-based cuprates [7, 8]. $K^{ab}_s$ of OPs decreases rapidly below $T_c = 110$ K. We note that a distinct peak in the temperature derivatives of $K^{ab}_s$(OP) coincides with $T_c = 110$ K. On the other hand, $K^{ab}_s$(IP) decreases significantly at $T < 85$ K in addition to its observed decrease at bulk $T_c$ of 110 K, which has been corroborated by the two peaks at 85 and 110 K in the temperature derivatives of $K^{ab}_s$(IP). This result reveals that the bulk SC transition is driven primarily by an optimally doped OP, but the SC transition inherent in underdoped IPs manifests itself at $T_c$(IP) ≈ 85(±5) K due to a large imbalance in the carrier densities between OPs and IPs. It is naturally expected that IPs exhibit superconductivity between 85 and 110 K due to the proximity effect, which has been observed in other multilayered cuprates [2, 3].

Below 70 K, the NMR signal of IPs of Hg-1245(OPT)♯2 disappears because of the extremely short relaxation time due to the development of critical AFM spin fluctuations towards a possible Néel ordering $T_N$ even in the SC state. In fact, $T_N = 55$ K has been confirmed by a peak in a plot of $1/T_1$ versus $T$ at an OP. The onset of the AFM order at IPs has been evidenced by the zero-field (ZF) Cu NMR spectrum at 1.5 K without any external field, as shown in Fig. 1(c). The peak at 15 MHz has been attributed to OPs in the paramagnetic state because the peak almost coincides with the nuclear quadrupole resonance (NQR) frequency for OPs, $^{63}ν_Q$(OP) = 16 MHz [4]. It should be noted that the spectrum of IPs is observed at 23 MHz, not at $^{63}ν_Q$(IP) = 8.4 MHz [4]. The spectral analysis of IPs, assuming a Zeeman field, reveals that an internal field ($H_{int}$) of 2.0 T is induced by the spontaneous AFM moments $M_{AFM}$(IP) due to the AFM order at the Cu site in IPs, as displayed by the bars in the figure. The unique value of $M_{AFM}$(IP) is evaluated to be 0.095$μ_B$ per Cu site at IPs by using the relation $H_{int}$(IP) = $|A_{hf}$(IP)|$M_{AFM}$(IP) with the hyperfine coupling constant $A_{hf}$(IP) = −20.7 $T/μ_B$ [4]. It is remarkable that this AFM moment spontaneously emerges at superconducting IPs with a possible commensurate AFM structure. Here, we can exclude the spin-glass state at IPs because the internal field at IPs ($H_{int}$ = 2.0 T) is almost the same at all the Cu(IP) sites and its distribution is less than ± 0.2 T.

The local carrier densities $N_h$ for these layers are evaluated from the Knight shift. It has been established that $N_h$ in various cuprates can be experimentally deduced from the value of $K^{ab}_s$ at room temperature by using the linear relation $N_h = 0.0462 + 0.502K^{ab}_s$(RT)[3, 9]. Note that this relation is valid for various high-$T_c$ cuprates, irrespective of the type (square or pyramid) and/or number of CuO$_2$ planes. In fact, the carrier densities at OPs and IPs have been independently evaluated to be $N_h$(OP) = 0.236 and $N_h$(IP) = 0.157 for Hg-1245(OPT)♯2. The value of $M_{AFM}$(IP) ∼ 0.1$μ_B$ is significantly reduced by the mobile holes with $N_h$(IP) = 0.157 from 0.5-0.7$μ_B$ in undoped cuprates [5, 10], which emphasizes that the AFM metallic (AFMM) phase persists at IPs even in $N_h = 0.157$. As shown in Fig. 2, we obtain the novel phase diagram for the five-layered cuprates by plotting $T_N$ and $T_c$ as functions of $N_h$, which are also estimated from their Knight shift data. The characteristic features are summarized as: (1) the AFM metallic state is robust up to $N_h$ ≈ 0.17, (2) the uniformly mixed phase of SC and AFMM is realized at 0.15 < $N_h$ < 0.17 at least, (3) the $T_c$ is maximum just outside a QCP at which the AFM order collapses, suggesting the intimate relationship between the high-$T_c$ SC and the AFM order. This result also indicates the presence of a tetracritical point for the AFMM/[AFMM+SC]/SC/PM(Paramagnetism) phases at $T$ ≈ 75 K with $N_h$ ≈ 0.15 at zero fields, which is the first observation in the phase diagrams of high-$T_c$ superconductors. It is noteworthy that the phase diagram for 0.14 < $N_h$ < 0.18 including the QCP is precisely...
determined only by ideally flat IPs.

![Figure 1](image1.png)

**Figure 1.** $K^{ab}_{s}$ for (a) OP and (b) IP of Hg-1245(OPT)$_2$. The solid and empty circles represent $K_s$ and its temperature-derivatives, respectively. $K^{ab}_{s}$(OP) decreases rapidly below $T_c = 110$ K, whereas $K^{ab}_{s}$(IP) decreases significantly at $T = 85$ K. (c) Zero-field Cu NMR spectrum of Hg-1245(OPT)$_2$ at 1.5 K is reproduced by assuming the internal field to be 2.0 T for IPs, which is induced by the spontaneous AFM moments of $\sim 0.1 \mu_B$. The peak at 15 MHz is attributed to OPs in the paramagnetic state.

As shown in Fig. 2, the phase diagram differs significantly from the well-established phase diagrams of mono-layered LSCO and double-layered YBa$_2$Cu$_3$O$_{6+x}$(YBCO), in which the long-range AFM order collapses completely by doping with an extremely small amount of holes of $N_h \sim 0.02$ [1] and 0.055 [11], respectively. We suggest that the QCP moves to a region of lower carrier density for $n$-layered cuprates with $n \leq 4$. Actually, we have investigated two underdoped Hg-1234 samples ($n = 4$) with $T_c = 95$ K and 110K at $N_h$(IP)$\sim 0.15$ and $\sim 0.16$, respectively, however, any static AFM order has not been evidenced at their IPs even though these carrier densities are lower than $N_h = 0.169$ at QCP for five-layered compounds. Remarkably, the extremely short spin-spin relaxation time was observed in the case of $N_h$(IP)$\sim 0.15$ for underdoped Hg-1234, suggesting the closeness to the QCP of four-layered cuprates. Although the AFM superexchange interaction among spins at the nearest neighbor Cu sites in a CuO$_2$ plane is as large as $J_{ab} \sim 1300$ K [12], the effective interlayer coupling depends on the structural details and number of CuO$_2$ planes. In a five-layered system, three underdoped IPs may stabilize...
the long-range AFM order due to sufficient interlayer coupling. In this context, it is the weak interlayer magnetic coupling that suppresses the AFM order in LSCO [1] and YBCO [11] at such small carrier densities region. As a result, we propose that the antiferromagnetically coupled spontaneous moment may persist up to $N_h \sim 0.16$ in the CuO$_2$ planes in LSCO and YBCO as well, but may be hidden within the plane due to the strong 2D fluctuations brought about by the weak interlayer coupling. In fact, the application of a high magnetic field stabilizes the static AFM order in the vortex state in underdoped samples, but not in the optimally doped samples [13, 14]. Furthermore, the AFM order was also observed in the charge-stripe phases around $x \sim 1/8$ of LSCO[15]. In oxygen-ordered high-quality YBCO6.5, a quantum oscillation revealed the Fermi surface comprising a Fermi pocket [16], which may be understood by assuming that the Fermi surface is folded at the magnetic Brillouin zone due to the presence of the AFM order under a very high field. The Fermi arc observed in the photoemission spectra of underdoped cuprates [17] may also be explained by the Fermi pocket picture under the hidden short-range AFM order and by the collapse of a part of the Fermi surface caused by the very short life time of quasi-particles due to the disorder. Although the phase diagrams of LSCO and YBCO are widely believed thus far as typical phase diagram of cuprates, we claim that these underlying issues in their underdoped region may be affected by the strong 2D fluctuations produced by the weak interlayer coupling, in addition to the disorders caused by the chemical substitution for doping.

4. Conclusion
The site-selective NMR studies on the five-layered cuprates have unraveled the genuine phase diagram of the ideally flat CuO$_2$ plane where carriers are homogeneously doped: (1) the AFM order is robust up to $N_h \approx 0.17$, (2) the uniform mixing of AFM order and SC takes place at least in $0.14 \leq N_h \leq 0.17$, (3) $T_c$ has a peak just outside the QCP at which the AFM order collapses, and (4) the tetracritical point for the AFM/(AFM+SC)/SC/PM phases may be present at $N_h \approx 0.15$ and $T \approx 75$ K. These results suggest the intimate relationship between the high-$T_c$ SC and AFM order, namely, the AFM superexchange interaction plays a vital role not only for the onset of the AFM order but also of SC, which will lead us to a genuine understanding of why the $T_c$ of cuprate superconductors is so high.

References
[1] B. Keimer et al.: Phys. Rev. B 46 (1992) 14034.
[2] Y. Tokunaga et al.: Phys. Rev. B 66 (2000) 9707.
[3] H. Kotegawa et al.: Phys. Rev. B 64 (2001) 064515.
[4] H. Kotegawa et al.: Phys. Rev. B 69 (2004) 014501.
[5] H. Mukuda et al.: Phys. Rev. Lett 96 (2006) 087001.
[6] K. Tokiwa et al.: Czech. J. Phys. 46 (1996) 1491.
[7] M.-H. Julien et al.: Phys. Rev. Lett. 76 (1996) 4238.
[8] K. Magishi et al.: J. Phys. Soc. Jpn. 64 (1995) 4561.
[9] G.-q. Zheng et al.: J. Phys. Soc. Jpn. 64 (1995) 2524.
[10] D. Vaknin et al.: Phys. Rev. Lett. 58 (1987) 2802.
[11] S. Sanna et al.: Phys. Rev. Lett. 93 (2004) 207001.
[12] Y. Tokura et al.: Phys. Rev. B 41 (1990) 11657.
[13] B. Lake et al.: Nature 415 (2002) 299.
[14] R. I. Miller et al.: Phys. Rev Lett. 88 (2002) 137002.
[15] J. M. Tranquada et al.: Nature 375 (1995) 561.
[16] N. Doiron-Leyraud et al.: Nature 447 (2007) 565.
[17] M. R. Norman et al.: Nature 392 (1998) 157.