Uniform Mixing of High-T_c Superconductivity and Antiferromagnetism on a Single CuO_2 Plane of a Hg-Based Five-Layered Cuprate

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We report a site selective Cu-NMR study on underdoped Hg-based five-layered high-T_c cuprate $HgBa_2Ca_4Cu_5O_{12+\delta}$ with a $T_c = 72$ K. Antiferromagnetism (AFM) has been found to take place at $T_N = 290$ K, exhibiting a large antiferromagnetic moment of 0.67–0.69μ_B at three inner planes (IP). This value is comparable to the values reported for nondoped cuprates, suggesting that the IP may be in a nearly nondoped regime. Most surprisingly, the AFM order is also detected with $M_{AFM}(\mathrm{OP}) = 0.1\mu_B$ even at two outer planes (OP) that are responsible for the onset of superconductivity (SC). The high-T_c SC at $T_c = 72$ K can uniformly coexist on a microscopic level with the AFM at OP's. This is the first microscopic evidence for the uniform mixed phase of AFM and SC on a single CuO_2 plane in a simple environment without any vortex lattice and/or stripe order.

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A remarkable aspect of high-T_c superconductivity (HTSC) is that there are many indications that its unique characteristics result from the competition between more than one type of order parameter. The possible coexistence of antiferromagnetism (AFM) and HTSC is one of the remaining interesting problem in high-T_c cuprates. Although AFM and HTSC are intimately related in high-T_c cuprates [1–8], some HTSC compounds show an AFM/SC mixed phase, while others show microscopic separation between these two phases. Evidence for the AFM/SC mixed phase exists in the excess oxygen doped La_2CuO_{4+y} materials. Neutron scattering measurement detects the onset of the AFM or spin-density-wave orders at the same temperature as the T_c [9]. On the other hand, microscopic probes such as STM revealed inhomogeneities of local electronic state and superconductivity (SC) characteristics in nanoscale [10]. Therefore, depending on material details, some HTSC compounds show an AFM/SC mixed phase, while others show microscopic separation between these two phases. Since such different physical effects can be obtained in materials that are so similar, it is still unclear if two phases coexist uniformly in these materials.

Multilayered HTSC offers a naturally prepared heterostructure of AFM planes and SC planes, which is a unique laboratory to investigate such an underlying issue. Evidence for the coexistent phase of SC and AFM in a unit cell has also been obtained recently in the five-layered HTSC $HgBa_2Ca_4Cu_5O_{12+\delta}$[Hg-1245(OPT)] by Kotegawa *et al.* [11] [Fig. 1(c)]. The series of multilayered HTSC includes two types of CuO_2 planes, an outer CuO_2 plane (OP) in a pyramidal coordination and an inner plane (IP) in a square one with no apical oxygen, as shown in Fig. 1(a). A site selective Cu-NMR study enables us to unravel the layer-dependent electronic characters microscopically as follows [11,12]: (1) The flat CuO_2 layers are homogeneously doped, ensured by the narrowest NMR linewidth among the previous examples with very high quality to date; (2) Hole density distributes with a larger doping level at OP than at IP. Its charge imbalance increases as either a total carrier content and/or number of CuO_2 layers in-

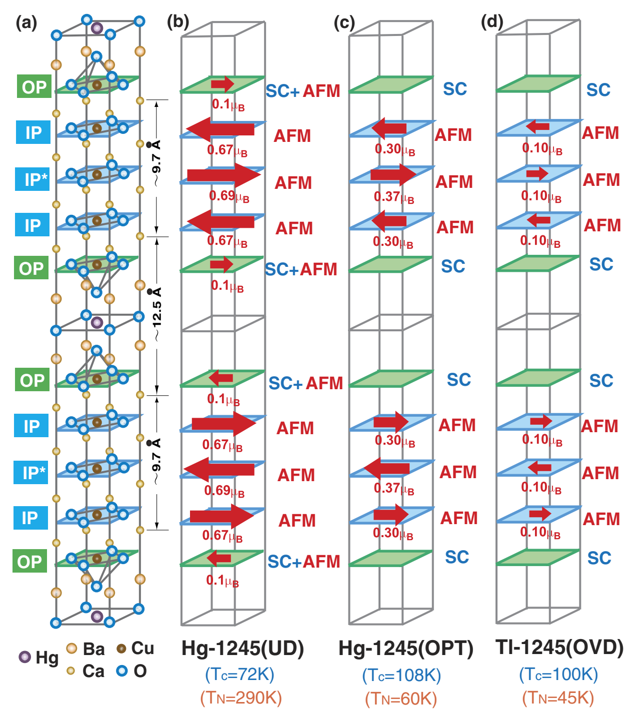

FIG. 1 (color online). (a) Crystal structure of Hg-based five-layered cuprates. Illustration of physical properties at each layer for (b) Hg-1245(UD), (c) Hg-1245(OPT) [11], and (d) Tl-1245(OVD). Here the AFM moments(M_{AFM}) are in the basal plane with an AFM vector $(\pi/a, \pi/a)$ [29].

crease; (3) The study on Hg-1245(OPT) has revealed that the optimally doped two OP's are predominantly superconducting with $T_c = 108$ K, whereas the underdoped three IP's show the AFM at $T_N = 60$ K, indicating the AFM/SC mixed phase in a unit cell [see Fig. 1(c)]. A theoretical approach to the coexistent phase of SC and AFM was proposed recently by Mori and Maekawa, where Josephson coupling between the SC planes through the AFM plane leads to the coexistence of both phases with a rather high-T_c value [13]. However, no mixing of SC and AFM was reported in the heterostructures artificially grown by stacking integer numbers of layers of superconducting $La_{1.85}Sr_{0.15}CuO_4$ and antiferromagnetic insulator La_2CuO_4 [14]. This type of AFM/SC proximity effect was not observed in the artificially grown layer structures.

In this Letter, we report systematic Cu-NMR studies on five-layered cuprates from underdoped Hg-1245(UD) to slightly overdoped Tl-1245(OVD), and compare with optimally doped Hg-1245(OPT) in Ref. [11].

Polycrystalline samples of Hg-1245 were prepared by the high-pressure synthesis technique as described elsewhere [15]. In order to reduce the carrier density, the as-prepared sample of Hg-1245 was annealed in Ar gas atmosphere for 280 h. Figure 2 shows the dc susceptibility measurement on Hg-1245(UD) after annealing, together with that of the as-prepared one, optimally doped Hg-1245 [Hg-1245(OPT)] [11]. The T_c for the former is determined to be 72 K from a very sharp and single transition, indicating the successful removal of the excess oxygen uniformly from charge-reservoir layers. This evidences that the superconducting volume fraction is kept similar for both compounds. Figure 1(a) indicates the crystal structure of Hg-(Tl-)1245 including five CuO_2 layers (two pyramidal OP's and three square IP's). Note that IP* is the middle plane of three IP's.

The nuclear Hamiltonian is described in terms of the Zeeman interaction $\mathcal{H}_Z = -\gamma_N \hbar \mathbf{H} \cdot \mathbf{I}$ and the nuclear quadrupole interaction $\mathcal{H}_Q = e^2qQ/4I(2I-1)(3I_z^2 - I(I+1))$, where γ_N is the nuclear gyromagnetic ratio of Cu and $3e^2qQ/2I(2I-1) \equiv h\nu_Q$ is the nuclear quadrupole frequency. Figure 3 shows the zero-field NMR spectrum at 1.6 K for Hg-1245(UD), together with that for Hg-1245(OPT) in the lower panel [11]. Two resonance peaks from 140 to 180 MHz arise from two isotopes ^{63}Cu and ^{65}Cu with slightly different nuclear gyromagnetic ratio $^{63,65}\gamma_N$ at each site. This is the case for $\mathcal{H}_Z \gg \mathcal{H}_Q$. These spectra for Hg-1245(UD) allow to estimate the respective internal fields to be $H_{\rm int}(IP) = 13.8$ T and $H_{\rm int}(\mathrm{IP}^*) = 14.2$ T at IP and IP* by fitting the spectra with the intensity ratio for two isotopes at IP and IP*. By using the hyperfine-coupling constant to be $H_{\rm hf}(\mathrm{IP}) = -20.7\ \mathrm{T}/\mu_B$ [16], the AFM ordered moments $M_{\rm AFM}$ at IP and IP* are estimated to be 0.67 and $0.69\mu_B$, respectively. Note that these values are almost comparable to the respective $M_{\rm AFM} = 0.50$ and $0.64\mu_B$ in the nondoped La_2CuO_4 [17] and $YBa_2Cu_3O_6$ [18]. From the μSR measurement, the AFM has been found to take place at $T_N = 290$ K [19] that is also comparable to $T_N = 325$ K and 415 K reported in the nondoped La_2CuO_4 [17] and $YBa_2Cu_3O_6$ [18], respectively. These values are larger than $M_{\rm AFM}(\mathrm{IP}) = 0.30\mu_B$, $M_{\rm AFM}(\mathrm{IP}^*) = 0.37\mu_B$, and $T_N = 60$ K for Hg-1245(OPT) which is in the metallic AFM regime [11]. It is hence likely for the IP and the IP* in Hg-1245(UD) to be in a nondoped AFM regime. On the other hand, from the spectra in Fig. 3(c), $M_{\rm AFM}(\mathrm{IP}'\mathrm{s}) = 0.1\mu_B$ is estimated for Tl-1245(OVD) with $T_N \sim 45$ K [11], suggesting that the hole density at IP's is located

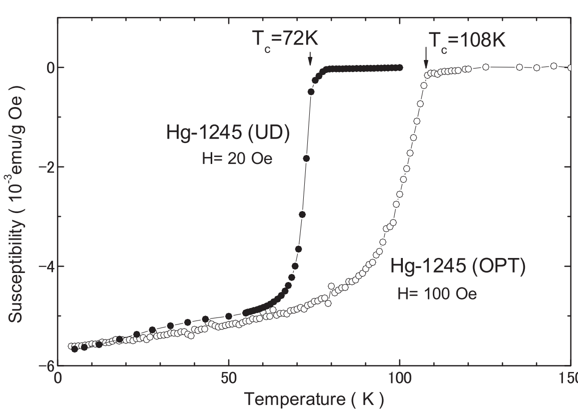

FIG. 2. dc susceptibility for Hg-1245(UD) after annealing and as-prepared Hg-1245(OPT) [11]. T_c is determined to be 72 K by a very sharp and single transition, indicating the successful removal of the excess oxygen uniformly from the charge reservoir. It was ensured by the similar superconducting volume fraction for both compounds.

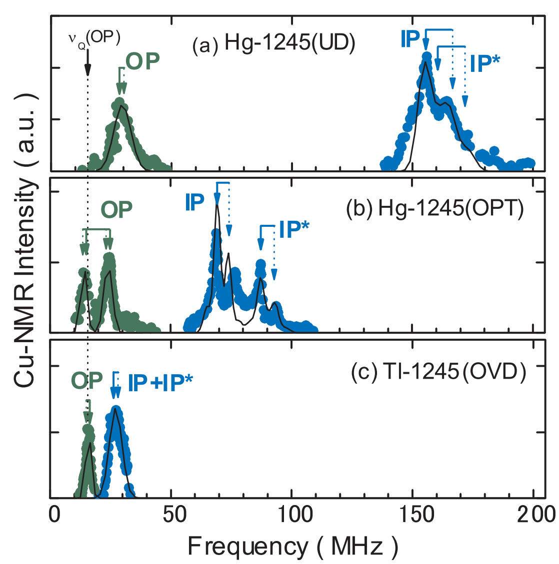

FIG. 3 (color online). Zero-field NMR spectra at 1.6 K for (a) Hg-1245(UD), (b) Hg-1245(OPT) [11], and (c) Tl-1245(OVD). The resonance spectrum from 140 to 180 MHz arises from IP's and IP*, and the broad spectrum at 20–40 MHz arises from OP. Solid and broken arrows show the signals from two isotopes ^{63}Cu and ^{65}Cu, respectively. The solid line indicates the calculated spectrum using the parameters in this text.

near a critical value above which AFM collapses as discussed later.

Most surprisingly, the zero-field NMR spectrum at OP for Hg-1245(UD) was observed over a broad frequency range 20–40 MHz that is about twice larger than the Cu-NQR frequency ($\nu_Q(\mathrm{OP}) = 16$ MHz) observed for the case of paramagnetic OP in Tl-1245(OVD) and Hg-1245(OPT)(shown by the broken line in Fig. 3). The observed broad spectrum was reproduced by an internal field of about $H_{\mathrm{int}}(\mathrm{OP}) = 2.4$ T with a fixed parameter of $\nu_Q(\mathrm{OP}) = 16$ MHz [16], as indicated in Fig. 3. This internal field is larger than not only the calculated dipole field (~180 Oe) but also 0.54 T for the case of proximity effect at the OP from AFM ordered IP [11]. A size of ordered moment $M_{\mathrm{AFM}}(\mathrm{OP}) = 0.1\mu_B$ is estimated using the relation of $H_{\mathrm{hf}}(\mathrm{OP}) = -26\,\mathrm{T}/\mu_B$ for the OP for Hg-1245(UD) [16]. The distribution of M_{AFM} is illustrated in Fig. 1. The $H_{\mathrm{int}}(\mathrm{OP}) = 2.4$ T at OP's is about 5 times larger than $H_{\mathrm{int}}(\mathrm{OP}) = 0.54$ T for Hg-1245(OPT), while $M_{\mathrm{AFM}}(\mathrm{IP}) \sim 0.67\mu_B$ is about twice larger than $M_{\mathrm{AFM}}(\mathrm{IP}) \sim 0.3\mu_B$ for Hg-1245(OPT). Therefore, it is concluded that $H_{\mathrm{int}}(\mathrm{OP}) = 2.4$ T at the OP's for Hg-1245(UD) is not only transferred from $M_{\mathrm{AFM}}(\mathrm{IP})$, but also AFM order manifests itself in the OP at low temperatures. When noting that no NMR signal was observed in the vicinity of $\nu_Q(\mathrm{OP}) = 16$ MHz that would be expected for the paramagnetic OP, a possibility of phase separation into paramagnetic SC domains and AFM domains is experimentally excluded. Instead, all of the Cu sites at OP are microscopically demonstrated to undergo a uniform AFM order with about $M_{\mathrm{AFM}}(\mathrm{OP}) \sim 0.1\mu_B$. This is the first microscopic evidence for the uniform mixed phase of AFM and SC on a single CuO_2 plane (OP) in a simple environment without any vortex lattice [20] and/or stripe order [21].

We consider that a nearly perfect flatness of CuO_2 planes is a key for the first observation of uniform mixed state of AFM and SC in the cuprates. In mono- and bi-layered cuprates, the phase separation has been found by microscopic probes due to inhomogeneity of the electronic state at CuO_2 plane [10,22], because the buckling of CuO_2 planes may be inevitable owing to doping holes for LSCO, for instance. On the other hand, the CuO_2 layers in the multilayered cuprates are not directly affected by some disorder effect introduced into the charge-reservoir layers through the carrier doping process. The flatness is guaranteed by the narrowest Cu-NMR linewidth about 50 Oe (150 Oe) for the IP (OP) in the polycrystalline of Hg-based systems [11].

We here address a novel phase diagram in Fig. 4(b) that is derived from the systematic Cu-NMR studies on the Hg-, Tl-, and Cu-based five-layered HTSC via using the local hole density at OP and IP [23]. This phase diagram differs from the global phase diagram of the HTSC reported so far, for instance, such as LSCO. It should be noted that the nearly nondoped AFM in IP and IP* takes place, whereas inhomogeneous magnetic phases such as spin-glass phase

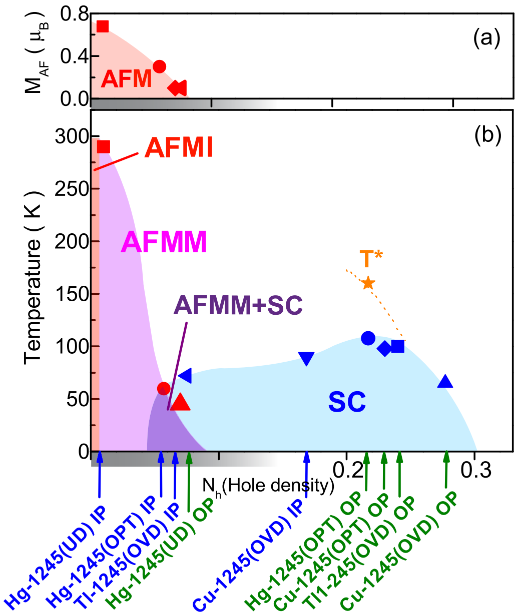

FIG. 4 (color online). (b) A phase diagram derived from the physical properties at the IP and the OP for various five-layered HTSC. Here we denote the AFM insulator and the metal phase as AFMI and AFMM. T^* is a pseudogap temperature deduced from a decrease of $1/T_1T$ at the OP for Hg-1245(OPT). The panel (a) shows the variation in the size of the AFM ordered moment M_{AFM} as the function of hole density. Since the hole density of the underdoped region indicated by the gray line could not be determined precisely, we plot by using the relative hole density as described in the text [23].

or stripe phase are not observed at both IP's and OP's. Instead, the presence of the doped AFM metallic (AFMM) phase at IP and IP* is remarkable at the boundary between AFM insulating (AFMI) phase and SC [11]. This differs from the case of $La_{2-x}Sr_xCuO_4$ (LSCO) where the disorder-driven magnetic phases exist between the AFMI phase in $N_h < 0.02$ and the SC phase in $N_h > 0.05$. It is noted that the AFM for IP is extended to a higher hole density due to the flatness of CuO_2 plane with no apical oxygen and the homogeneous distribution of carrier density. By contrast, the prototype phase diagrams reported thus far are under the inevitable disorder effect associated with the chemical substitution introduced into the CuO_2 out of planes. Here the hole densities in the underdoped region ($N_h < 0.13$) are determined by using the relative hole density suggested from Knight shift and T_1 measurements. For example, N_h at the IP's for Tl-1245(OVD) is slightly larger than that for Hg-1245(OPT). As for the OP in Hg-1245(UD), N_h may be compatible with that at the IP's of Tl-1245(OVD) because the size of M_{AFM} is the same for both. It is this global phase diagram that convinces us of the presence of the AFM/SC uniformly mixed phase at OP of Hg-1245(UD), where $M_{\mathrm{AFM}} = 0.1\mu_B$ and $T_c = 72$ K. The OP of Hg-1245(UD) and IP's of Tl-1245(OVD) might be located just on a region where AFM and SC confront each other.

Unexpectedly in Hg-1245(UD), it has been revealed that the nearly nondoped AFM IP's and the AFM/SC uniformly mixed OP's are alternatively stacked as (AFM + HTSC)/AFM/(AFM + HTSC) along the c axis, as shown in Fig. 1(b). The T_N for AFM may be determined through the interlayer magnetic coupling. Although the AFM order for IP's occurs below $T_N = 290$ K, T_N inherent to the OP is not known because the T_N of this compound is dominated by the interlayer magnetic coupling between the nearly nondoped AFM IP's and the AFM/SC mixed OP's. Surprisingly, this interlayer magnetic coupling does not prevent the onset of SC with the high value of $T_c = 72$ K, even though the SC uniformly coexisting with the AFM is significantly separated over more than 10 Å by three nearly nondoped AFM IP's below $T_N = 290$ K. It remains a mystery why it keeps a high-T_c value. According to the theoretical studies on multilayered cuprates [13,25], the T_c for SC may be determined through the quantum tunneling of Cooper pairs between the layers. The fact that HTSC can keep a high value of T_c even in the mixed state with AFM on the same CuO_2 plane suggests that HTSC and AFM phases are nearly degenerate and that the mechanism of SC is magnetic in origin. An explanation for the uniform mixing of AFM and SC phases at OP is relevant with the theoretical prediction based on the SO(5) model [7,8], that is, the correlation length for the superconducting proximity effect across an AFM should be very long, and hence supercurrent should flow through the naturally prepared thick heterostructure of (AFM + HTSC)/AFM/(AFM + HTSC) in the present multilayered systems. Thus as long as HTSC and AFM phases are nearly degenerate, the proximity effect ought to be strong.

In conclusion, we have found that the underdoped Hg-1245 has the nearly nondoped three IP's with $T_N = 290$ K and $M_{AFM}(IP) \approx 0.67$–$0.69\mu_B$ and the superconducting two OP's with $T_c = 72$ K. The AFM order was also detected with $M_{AFM}(OP) = 0.1\mu_B$ even at the OP that are responsible for the onset of SC. This finding provides the first microscopic evidence for the uniform mixing of AFM and SC at a single CuO_2 plane in HTSC. Although the AFM/SC mixed CuO_2 planes are significantly separated by three nondoped AFM layers, the onset of AFM does not prevent nearly the occurrence of SC with the high value of $T_c = 72$ K. In a large class of materials including HTSC, organic and heavy-fermion superconductors, AFM and SC occur in close proximity to each other. A genuine uniform mixed phase of AFM and SC has been observed in the pressure versus temperature phase diagrams in several heavy-fermion systems [26–28]. The present results give a hint to gain insight into a mechanism in strongly correlated superconductivity in general.

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[29] The magnetic structure is speculated to be antiparallel between the adjacent layers. If the M_{AFM}'s in the plane were ferromagnetically aligned between the layers, the internal field at each layer should be affected not only by the on-site M_{AFM} but also by the transferred hyperfine fields with negative sign against the on-site one that are induced by M_{AFM}'s at the adjacent layers. In this case, the on-site M_{AFM} is roughly calculated as 0.7–0.8μ_B for the IP* of Hg-1245(UD), that amounts to an unreasonably large value.