Extended superconducting dome of electron-doped cuprates after protect annealing revealed by ARPES

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The discovery of the electron-doped cuprates guides a new way in unveiling the controversial physics of high-temperature superconductivity and motivates extensive experimental and theoretical studies for decades [1, 2]. Other than the structure differences, the most dramatic distinction between the hole- and electron-doped cuprates embodies in their temperature-doping phase diagram as shown in Fig. 1. On the hole doping side, a tiny amount ∼3% of hole doping suppresses the antiferromagnetic (AFM) insulating phase and the systems become superconducting (SC) at ∼5% hole doping in most cuprate families [3–6]. On the other hand, on the electron doping side, previous numerous studies revealed that electron doping side, previous numerous studies revealed that superconductivity emerges at a Ce doping level varying from ∼10% to 14% in bulk crystals [7–11, 15, 16], and ∼6% to 14% in thin films [17–19]. The doping range of the SC dome, which varies from ∼5% to ∼15% for electron-doped cuprates [7–11, 15, 17–19], is also considerably more restricted than that of ∼22% in the hole-doped case [3–6]. These differences of the phase diagram between the hole- and electron-doped cuprates imply that hole doping and electron doping may affect the electronic structure in different manners.

The electron-doped cuprates are usually characterized by a more robust antiferromagnetic phase and a much narrower superconducting (SC) dome than those of the hole-doped counterparts. Recently, bulk single crystals of Pr1.3−xLa0.7Ce0.2CuO4 (PLCCO) prepared by the protect annealing method have been studied extensively and revealed many intriguing properties that were different from those obtained from samples annealed by the conventional methods. Here, we report on a systematic angle-resolved photoemission spectroscopy study of PLCCO single crystals after protect annealing. The results indicate that the actual electron concentration (nFS) estimated from the Fermi-surface area is significantly larger than the Ce concentration x and the new nFS-based SC dome of PLCCO is more extended towards the overdoped side than the x-based SC dome derived for samples prepared using the conventional annealing method. The similarity between the new nFS-based SC dome and that of the hole-doped cuprate La2−xSrxCuO4 further provides a clue for understanding the reported electron-hole symmetry/asymmetry of the cuprate phase diagram.

The electron-doped cuprates are characterized by the T'-type structure, in which the Cu atom is surrounded by four oxygen atoms in the square-planer manner, instead of octahedral manner by six oxygen atoms in the T'-type structure of the hole-doped counterparts La2−xSrxCuO4 (LSCO). Another hallmark of the electron-doped cuprates is the indispensable role of annealing, i.e., as-grown samples are AFM regardless of dopant concentration and superconductivity emerges only after annealing [1]. Nevertheless, the precise effects of the reduction annealing remain unclear [2, 20]. Historically the most widely acknowledged impact of annealing is the removal of excess and superconductivity-harmful [21] apical oxygen atoms in the T'-type structure [2], even though the fraction of reduced oxygen is small [22–24]. Meanwhile another scenario has also been proposed that annealing may create a secondary phase and repair Cu vacancies which may exist in as-grown samples [25–27].

Since the reduction annealing is crucial for realizing the superconductivity in the electron-doped cuprates, different annealing methods may result in distinct physical properties. For bulk single crystals, conventional annealing procedures [2] can lead to over-reduction of the surfaces and even decompose the crystals under strong reduction conditions. Differently from the conventional processes, Adachi et al. [28–30] recently synthesized bulk SC single crystals of Pr1.3−xLa0.7Ce0.2CuO4 (PLCCO, x = 0.05, 0.10, and 0.15) with Tc as high as ∼27 K, by

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TABLE I. Sample compositions and annealing conditions.

| x  | $T_c$ (K) | Reduction status | Annealing step | Annealing temperature (°C) | Annealing time |
|----|-----------|------------------|----------------|---------------------------|---------------|
| 0.10 | 26        | UR               | PA $\rightarrow$ LTA $\rightarrow$ DA | 800 $\rightarrow$ 400 $\rightarrow$ 500 | 24 h $\rightarrow$ 24 h $\rightarrow$ 4 h $\times$ 6 |
| 0.10 | 28        | OP               | PA $\rightarrow$ LTA $\rightarrow$ DA | 800 $\rightarrow$ 400 $\rightarrow$ 500 | 24 h $\rightarrow$ 24 h $\rightarrow$ 4 h $\times$ 12 |
| 0.15 | 16-19     | OR               | PA $\rightarrow$ LTA $\rightarrow$ DA | 800 $\rightarrow$ 400 $\rightarrow$ 500 | 24 h $\rightarrow$ 24 h $\rightarrow$ 4 h $\times$ 6 |
| 0.17 | 6         |                  | PA $\rightarrow$ LTA  | 900 $\rightarrow$ 500   | 12 h $\rightarrow$ 12 h |

α: UR: under-reduced, OP: optimally-reduced, OR: over-reduced.

β: PA: protect annealing, LTA: low-temperature annealing, DA: dynamic annealing.

e: A number after “×” is the number of cycles in the dynamic annealing.

utilizing an improved “protect annealing” method [31]. In the protect annealing procedures, single crystals are protected from the over-reduction by covering them by polycrystalline powders of the same composition, and one can anneal the samples under stronger reduction conditions without being decomposed and the oxygen content becomes more homogeneous, giving rise to a higher $T_c$. Inspired by the $T_c$ enhancement of PLCCO single crystals after the improved protect annealing, extensive studies using various techniques have been conducted recently [20, 28, 29, 32–35]. For example, angle-resolved photoemission spectroscopy (ARPES) measurements on protect-annealed PLCCO samples have shown that the signature of the AFM correlations, namely, the "AFM pseudogap" is strongly suppressed for $x = 0.10$ [20], the Ce content at which previous studies obtained from conventionally annealed electron-doped cuprates all favored the existence of the AFM pseudogap on the Fermi surface created by the band folding [16, 36–39]. The striking differences between the conventionally annealed and protect-annealed samples demonstrate again the crucial role of reduction annealing in the electron-doped cuprates. As a natural consequence of annealing, one would anticipate the addition of electrons resulting from oxygen reduction. Actually, by improved elaborate annealing methods, superconductivity emerges even at zero Ce doping level in thin films [40–43] and bulk polycrystals [44, 45]. These new annealing methods not only give rise to the realization of superconductivity in the parent compounds without cation substitution [46–49], but may also lead to a total electron concentration that is larger than the Ce doping level [14, 16, 20, 48, 50]. In the ARPES study focusing on the protect-annealed PLCCO with $x = 0.10$ and $T_c \sim 27$ K [20], the actual electron concentration estimated from the Fermi-surface area ($n_{FS}$) was found to be as high as 0.18. A subsequent ARPES study on conventionally annealed Pr$_{1-x}$LaCe$_x$CuO$_4$ [PLCCO (La1.0)] with $x = 0.10, 0.15,$ and 0.18 [16] also indicated that the reduction (oxidization) injects electrons (holes) into the system. While AFM correlation still exists in the entire doping range, a new $n_{FS}$-based phase diagram was proposed and shows a dome-like SC region implying the possible absence of asymmetry between the phase diagrams of hole- and electron-doped cuprates. Comparing these two studies, one can see that, in the protect-annealed PLCCO [20, 28, 29], $T_c$ is higher than that of the conventionally annealed samples [16], and no AFM pseudogap was found. It is also possible that more electrons are doped by utilizing the novel protect annealing method, with less oxygen inhomogeneity not only on surfaces but also in bulk [20]. A systematic ARPES study is then needed to elucidate the possible new phase diagram of protect-annealed electron-doped cuprates.

In this Letter, we report a systematic ARPES study of PLCCO single crystals after protect annealing [$x = 0.10, 0.15,$ and 0.17 (La1.0)]. The results indicate that the actual doped electron concentration $n_{FS}$ is larger than the Ce doping level $x$ by $\sim 0.08$ $e$/Cu. The improved annealing method dopess the system with more electrons and the new $n_{FS}$-based SC dome of PLCCO is more extended towards the overdoped side than that of the conventionally annealed samples [16]. The similarity between the new $n_{FS}$-based SC dome and that of hole-doped LSCO.
has thus become clearer and provides a clue for understanding the symmetry/asymmetry of the cuprate phase diagram.

High-quality single crystals of Pr$_{1.3-x}$La$_{0.7}$Ce$_x$CuO$_4$ ($x = 0.10, 0.15$) with $T_c$ varying from 16 K to 28 K and Pr$_{1.0-x}$La$_{1.0}$Ce$_x$CuO$_4$ ($x = 0.17$) with $T_c$ of 6 K were synthesized by the traveling-solvent floating-zone method [28, 29]. As-grown samples were then annealed in vacuum under a pressure of $10^{-6}$ Torr. $T_c$ is defined as the crossing point of the zero-susceptibility line and the extrapolated line of the steepest part of the susceptibility curve. Table I summarizes key parameters of the annealing conditions and sample properties. The sample reduction status, i.e., under-reduced (UR), optimally reduced (OP), and over-reduced (OR), is judged from the annealing conditions and the $T_c$. Note that the reduction status depends on $x$ for the same annealing conditions. The annealing consists of three steps, namely, protect annealing (PA) [20, 28], low-temperature annealing (LTA) [43], and dynamic annealing (DA) [32, 51, 52]. In the dynamic annealing, the annealing processes are separated into a few cycles providing sufficient time for oxygen atoms to diffuse from bulk to surfaces and thus further improves the oxygen homogeneity of the samples and increases the $T_c$. ARPES measurements were performed at beamline BL-28A of Photon Factory (PF) and BL5U of UVSOR facility with the total energy resolution of 30 meV. The samples were cleaved and measured in situ at temperatures below 10 K and pressure better than $1.5 \times 10^{-10}$ Torr. The photon energy was set at 55 eV with circular polarization at PF and at 60 eV with linear (perpendicular to the cut) polarization at UVSOR.

Figures 2(a) - 2(c) show the ARPES Fermi-surface intensity plots of the protect-annealed PLCCO samples for $x = 0.10$ with $T_c = 28$ K, $x = 0.15$ with $T_c = 19$ K, and $x = 0.17$ with $T_c = 6$ K (La1.0), respectively. One can identify that there is no signature of the AFM pseudogap on the entire Fermi surfaces for the doping range studied in the present work. This is consistent with our previous results [20] that AFM correlation is strongly suppressed in the protect-annealed PLCCO single crystals, unlike those studies on conventionally annealed PLCCO (La1.0) [16, 36] or other electron-doped cuprates [37–39]. According to the Luttinger theorem [53], the number of conduction electrons is proportional to the Fermi surface volume. We then fit the Fermi surfaces to the tight-binding model as shown in Fig. 2(d), and calculate the Fermi-surface area $1 + n_{FS}$ to estimate the actual doped electron concentration $n_{FS}$ [16, 20, 46].

In Fig. 3, by plotting the $T_c$ values against $n_{FS}$ for multiple samples (filled red markers), we show the new $n_{FS}$-based phase diagram (the SC dome shown by a magenta shaded area) of the protect-annealed PLCCO with $x = 0.10, 0.15, \text{and } 0.17 \text{(La1.0)}$. Our previous results on PLCCO samples with $x = 0.02$ (non-superconducting), 0.05 ($T_c = 24$ K), and 0.10 ($T_c = 27$ K) are included as filled dark red circles [20, 33]. Meanwhile, the $T_c$ values of OP protect-annealed PLCCO are also plotted against Ce concentration (empty magenta circles) [30]. One can immediately see the difference between the traditional Ce-based phase diagram (magenta dashed curve) and the $n_{FS}$-based (magenta shaded area), i.e., $n_{FS}$ estimated from the Fermi-surface area is significantly larger than the Ce doping level $x$. The remarkable increase of actual electron concentration by protect annealing yields an extension of the SC dome on the overdoped side. For comparison, the $T_c$ values of conventionally annealed PLCCO and Pr$_{1.0-x}$La$_{1.0}$Ce$_x$CuO$_4$ [denoted as PLCCO (La1.0)] samples are also plotted by blue markers, with empty markers plotted against the Ce concentration [8, 16, 55] and filled markers plotted against $n_{FS}$ [16]. The thick dashed blue curve tracks the data from Fujita et al. [8] showing examples of the traditional phase diagram for electron-doped cuprates (Fig. 1). Owing to the improved annealing method, superconductivity in the protect-annealed PLCCO samples can be realized not only with higher $T_c$ but also at a Ce doping level as low as 0.05, which has never been reported for the conventional annealing method. We also replotted the results from Song et al., who obtained a $n_{FS}$-based SC dome (blue shaded area enclosed by filled blue squares) by conventionally annealing and oxidizing PLCCO (La1.0) samples with three Ce concentrations (empty blue squares tracked by a thin dashed blue line) [16]. Apparently, the SC dome obtained in protect-annealed PLCCO is more extended on the overdoped side than that based on the conventional annealing method. Quantitatively, for protect annealed PLCCO and conventionally annealed PLCCO (La1.0), the addition of actual electron concentration ($n_{FS} - x$) is $\sim 0.08$ and 0.04 $e$/Cu, respectively, in average. This indicates the improved protect (and dynamic) annealing method dopes the system with more...
FIG. 3. New electron-concentration ($n_{FS}$)-based phase diagram of protect-annealed PLCCO. The $T_c$ values of PLCCO with $x = 0.10$ (optimally-reduced (OP) and under-reduced (UR)), $x = 0.15$ (over-reduced (OR)), and PLCCO (La1.0) with $x = 0.17$ are plotted against $n_{FS}$ (estimated from the Fermi-surface area in Fig. 2(d)) as filled red markers. Our previous results on protect-annealed PLCCO with $x = 0.02$, 0.05, and 0.10 are also included (filled dark red circles, Horio et al. [20, 33]), which, together with current results, reveal a $n_{FS}$-based superconducting (SC) dome (magenta shaded area). For the $x = 0.17$ data point, a vertical line is drawn from the $T_c$ defined as described in the text to the $T_c$ onset (see Supplemental Material [54]). For all the other samples, the $T_c$ and $T_c$ onset are close to each other and fall within the size of the markers. The $T_c$ values of OP samples are also plotted traditionally against Ce concentration (empty magenta circles, Adachi et al. [30]). Data based on conventionally annealed PLCCO and PLCCO (La1.0) are included for comparison and indicated by blue markers (the empty are plotted against Ce concentration [8, 16, 55] and the filled are plotted against $n_{FS}$ showing a blue shaded SC dome [16]). The estimated $n_{FS}$ and $T_c$ for annealed T'-type Pr$_2$CuO$_4$ (PCO) thin films [48] is replotted as an orange filled square. The green curve indicates the SC dome of hole-doped T'-type LSCO [56] after scaling the maximum $T_c$ value to that of the protect-annealed PLCCO. The dashed curves and lines are the guide to the eyes.

In summary, we have performed ARPES measurements on protect-annealed PLCCO single crystals with Ce concentrations $x = 0.10, 0.15,$ and 0.17 (La1.0). The actual electron concentration $n_{FS}$ estimated from the Fermi-surface area is significantly larger than the nominal Ce doping level by $\sim 0.08$ $e$/Cu. Owing to the improved protect (and dynamic) annealing method, which dopes the system with electrons, the new $n_{FS}$-based SC dome of PLCCO is more extended on the overdoped side than that based on the conventional annealing method. The reduction of the excess apical oxygen together with those oxygen atoms at the regular sites and the improvement of oxygen homogeneity may be able to account for the significant amount of additional electrons. The present results suggest that employing $n_{FS}$ as the doping axis is a useful way when investigating the temperature-doping phase diagram of electron-doped cuprates. Furthermore, the similarity between the new $n_{FS}$-based SC dome and that of hole-doped LSCO may provide a clue for understanding the electron-hole symmetry/asymmetry of the cuprate phase diagram.

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