ARPES Study of the Superconducting Parent Compound Pr_2CuO_4 in Thin Film Form

In high-temperature cuprate superconductors, carrier doping has been regarded as essential for superconductivity. Recent studies demonstrated that reduction annealing alone can induce superconductivity in thin films of *T*'-type cuprates without nominal electron doping through Ce substitutions. In order to reveal the low-energy electronic states relevant to the superconductivity, we have conducted angle-resolved photoemission spectroscopy measurements on thin films of the superconducting Ce-free *T*'-type cuprate Pr_2CuO_4. The obtained band structure and Fermi surface of the superconducting Pr_2CuO_4 are similar to those of superconducting Ce-doped bulk single crystals, suggesting that the superconducting Pr_2CuO_4 is doped with electrons despite the absence of Ce substitutions.

High-temperature superconductivity emerges in cuprates when an antiferromagnetic (AF) Mott-insulating parent compound is doped with carriers. In the electron-doped cuprates $Ln_{2-x}Ce_xCuO_4$ (Ln: rare earth) with a so-called *T*'-type structure, where Cu atoms are coordinated by four O atoms in the square-planar configuration, electron doping is achieved by substituting Ce^{4+} for Ln^{3+}. Recently, the electronic structure of *T*'-type cuprates has attracted renewed interest since superconductivity is realized without Ce substitutions in thin-film samples [1]. This fact challenges the common belief that the parent cuprates are Mott insulators. An indispensable treatment to realize superconductivity in the *T*'-type cuprates is post-growth reduction annealing. The primary role of reduction annealing is the removal of impurity apical oxygen atoms [2], thereby suppressing the quasi-particle scattering rate and AF correlation. Furthermore, recent angle-resolved photoemission spectroscopy (ARPES) studies on bulk crystals have found a significant increase of the doped electron concentration after reduction annealing from estimates of the Fermi surface area [3, 4]. The increase of the electron concentration is associated with the loss of oxygen atoms not only from the apical sites but also from the regular sites. Indeed, the possibility of oxygen-vacancy creation has been pointed out by previous infrared and Raman spectroscopy studies [5]. In this case, Ce concentration no longer represents the doped electron concentration. It is thus imperative to determine the electron concentration of the superconducting (SC) Ce-free *T*'-type cuprates from direct measurements.

The fact that the superconductivity can only be realized in thin films has impeded studies of the electronic structure of Ce-free *T*'-type cuprates. Once thin-film surfaces are contaminated upon being taken out from the growth chamber, surface-sensitive probes such as ARPES cannot be applied. To overcome this issue, we have developed a capping method. Specifically, two Pr_2CuO_4 thin films [T_c = 0 (non-SC), 25.5 K (SC)] for ARPES measurements were first synthesized at NTT Basic Research Laboratories using the molecular beam epitaxy method on $GdScO_3$ (110) substrates [6]. After the growth, the films were rapidly cooled down to 70°C and amorphous Se was evaporated onto the film surfaces up to a thickness of ~ 50 nm. The films were transferred in air from NTT Basic Research Laboratories to BL-2A. Then, the films were heated inside the preparation chamber at 150°C for 30 minutes under a vacuum of better than 2×10^{-9} Torr to desorb the Se cap, and transferred in vacuo to the measurement chamber. X-ray core-level photoemission spectroscopy measurements performed prior to each ARPES measurement confirmed negligible contamination on the surface after the desorption of the Se layers.

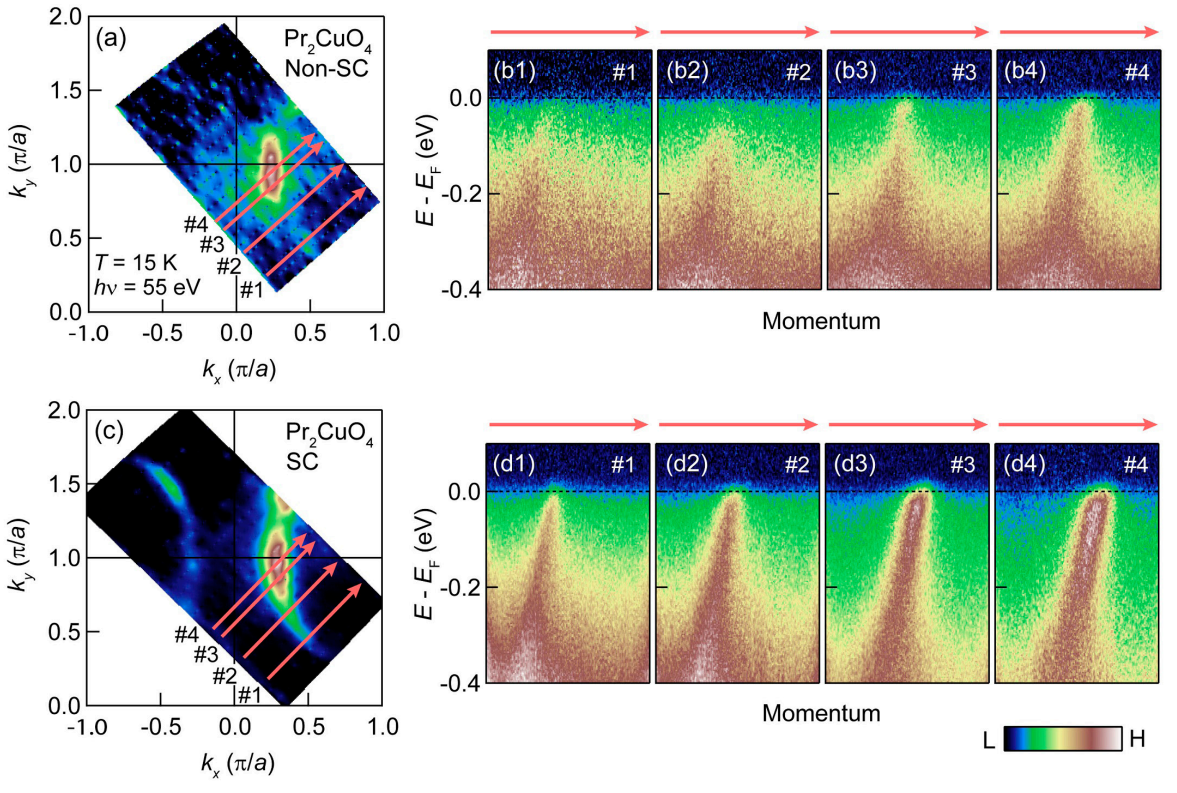

Figure 1: ARPES spectra of Pr_2CuO_4 thin films. (a), (b1)–(b4) Fermi surface and band images along cuts #1–#4, respectively, of the non-SC sample. (c), (d1)–(d4) The same as (a) and (b1)–(b4), respectively, but for the SC sample.

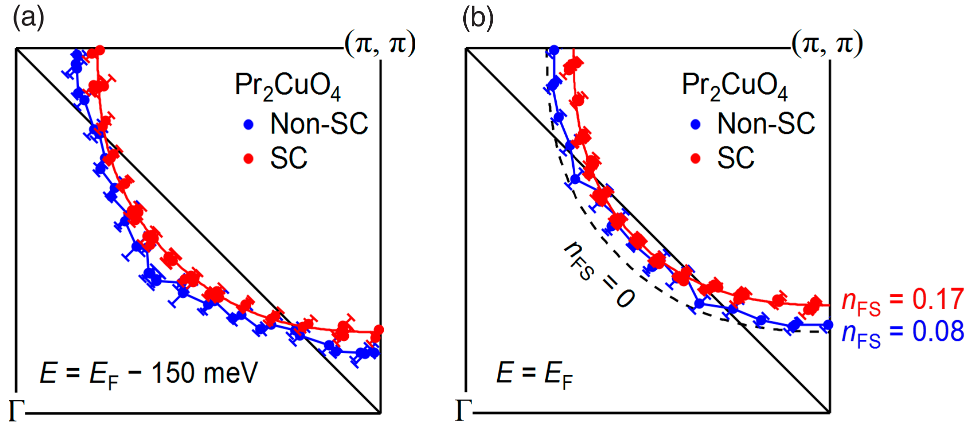

Figure 2: Constant-energy surfaces and Fermi surfaces of Pr_2CuO_4 thin films. (a) Constant energy surfaces of the non-SC (blue) and SC (red) samples at $E = E_F - 150$ meV. (b) Fermi surface displayed in the same color code as (a). Dotted curve represents the hypothetical Fermi surface at half-filling (n = 0) for comparison.

The obtained Fermi surface and ARPES spectra of two Pr_2CuO_4 thin films [7] are summarized in Fig. 1. For the non-SC sample, photoemission intensity is suppressed around the hot spot where the Fermi surface and AF Brillouin zone boundary cross [Fig. 1(b2)]. This is called the AF pseudogap and presumably arises from band folding due to AF short-range order. In contrast, for the SC sample, the suppressed intensity recovers [Fig. 1(d2)] and the Fermi surface becomes continuous over the entire Brillouin zone [Fig. 1(c)]. This observation suggests the strong reduction of AF correlation length and/or magnitude of magnetic moments in the SC sample, consistent with the emergence of superconductivity out of competition with the AF order.

Figure 2(a) displays constant energy surfaces of Pr_2CuO_4 thin films at $E = E_F - 150$ meV. These constant energy surfaces are hole-like and centered at (π, π). Apparently, the SC sample has a smaller area of the surface, suggesting a larger electron concentration. By directly measuring the area of the Fermi surface [Fig. 2(b)], the doped electron concentration of the non-SC and SC samples were estimated to be n = 0.08 and 0.17 per Cu, respectively, considerably deviating from half-filling (n = 0). The electron concentration of 0.17 is comparable to that of bulk SC samples (0.13–0.17). Fitting of the band structure to the tight-binding model also yielded nearly the same hopping parameters for the SC Pr_2CuO_4 and SC Ce-doped bulk samples. Therefore, the overall electronic structure is similar between the SC Ce-free *T*'-type cuprates and SC Ce-doped bulk samples. The present study thus highlights the importance of considering the actual doped electron concentration rather than the Ce concentration when discussing the electronic structure of *T*'-type cuprate superconductors.

REFERENCES

[1] A. Tsukada, Y. Krockenberger, M. Noda, H. Yamamoto, D. Manske, L. Alff and M. Naito, *Solid State Commun.* **133**, 427 (2005).
[2] P. G. Radaelli, J. D. Jorgensen, A. J. Schultz, J. L. Peng and R. L. Greene, *Phys. Rev. B* **49**, 15322 (1994).
[3] M. Horio, T. Adachi, Y. Mori, A. Takahashi, T. Yoshida, H. Suzuki, L. C. C. Ambolode, K. Okazaki, K. Ono, H. Kumigashira, H. Anzai, M. Arita, H. Namatame, M. Taniguchi, D. Ootsuki, K. Sawada, M. Takahashi, T. Mizokawa, Y. Koike and A. Fujimori, *Nat. Commun.* **7**, 10567 (2016).
[4] D. Song, G. Han, W. Kyung, J. Seo, S. Cho, B. S. Kim, M. Arita, K. Shimada, H. Namatame, M. Taniguchi, Y. Yoshida, H. Eisaki, S. R. Park and C. Kim, *Phys. Rev. Lett.* **118**, 137001 (2017).
[5] P. Richard, G. Riou, I. Hetel, S. Jandl, M. Poirier and P. Fournier, *Phys. Rev. B* **70**, 064513 (2004).
[6] Y. Krockenberger, M. Horio, H. Irie, A. Fujimori and H. Yamamoto, *Appl. Phys. Express* **8**, 053101 (2015).
[7] M. Horio, Y. Krockenberger, K. Koshiishi, S. Nakata, K. Hagiwara, M. Kobayashi, K. Horiba, H. Kumigashira, H. Irie, H. Yamamoto and A. Fujimori, *Phys. Rev. B* **98**, 020505(R) (2018).

BEAMLINE

BL-2A

M. Horio[1], Y. Krockenberger[2], K. Koshiishi[1], S. Nakata[1], K. Hagiwara[1], M. Kobayashi[3], K. Horiba[3], H. Kumigashira[3], H. Irie[2], H. Yamamoto[2] and A. Fujimori[1] ([1]The Univ. of Tokyo, [2]NTT-BRL, [3]KEK-IMSS-PF)