d-wave superconducting gap observed in protect-annealed electron-doped cuprate superconductors $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$

M. Horio,[1,*] K. Koshiishi,[1] S. Nakata,[1] K. Hagiwara,[1] Y. Ota,[2] K. Okazaki,[2] S. Shin,[2] S. Ideta,[3] K. Tanaka,[3] A. Takahashi,[4] T. Ohgi,[4] T. Adachi,[5] Y. Koike,[4] and A. Fujimori[1,6]

[1]*Department of Physics, University of Tokyo, Bunkyo-ku, Tokyo 113-0033, Japan*
[2]*Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan*
[3]*UVSOR Facility, Institute for Molecular Science, Okazaki 444-8585, Japan*
[4]*Department of Applied Physics, Tohoku University, Sendai 980-8579, Japan*
[5]*Department of Engineering and Applied Sciences, Sophia University, Tokyo 102-8554, Japan*
[6]*Department of Applied Physics, Waseda University, Tokyo 169-8555, Japan*

(Received 16 May 2019; revised manuscript received 12 August 2019; published 28 August 2019)

For electron-doped cuprates, the strong suppression of antiferromagnetic spin correlation by efficient reduction annealing by the "protect-annealing" method leads to superconductivity not only with lower Ce concentrations but also with higher transition temperatures. To reveal the nature of this superconducting state, we have performed angle-resolved photoemission spectroscopy measurements of protect-annealed electron-doped superconductors $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ and directly investigated the superconducting gap. The gap was found to be consistent with d-wave symmetry, suggesting that strong electron correlation persists and hence antiferromagnetic spin fluctuations remain a candidate that mediates Copper pairing in the protect-annealed electron-doped cuprates.

DOI: 10.1103/PhysRevB.100.054517

I. INTRODUCTION

The symmetry of the superconducting (SC) gap provides a clue for the origin of superconductivity. It is now firmly established that the SC gap of the hole-doped cuprate superconductors has d-wave symmetry, reflecting the fact that electrons are strongly correlated and tend to avoid double occupation [1]. As for the electron-doped cuprate superconductors with the Nd_2CuO_4 (so-called T'-type) structure, many previous studies have also supported d-wave symmetry [2–10]. In particular, electronic Raman scattering [6] and angle-resolved photoemission spectroscopy (ARPES) [8] studies have revealed that the SC gap exhibits d-wave momentum dependence as well as a maximum near the hot spot, where the antiferromagnetic (AF) Brillouin zone boundary and the Fermi surface cross. Thus, a large contribution of AF spin fluctuations to the superconductivity has been proposed, although the intrinsic momentum dependence of the SC gap still remains elusive since the coexistence with the AF order would also modulate the SC gap from the monotonic d-wave form [11].

The AF correlation in the electron-doped cuprates strongly depends on the postgrowth annealing conducted in a reducing atmosphere [12,13]. By the reduction annealing, impurity oxygen atoms at the apical site, which exist in as-grown samples and act as a strong scattering center [14], are presumably removed [15,16]. Recently, a new annealing method, which is called protect annealing, was demonstrated to induce superconductivity in electron-doped cuprates with lower Ce concentration and higher T_c [17] than those in previous studies [18]. There, while annealing, single crystals were covered with polycrystalline powders with the same composition, allowing the application of a more strongly reducing condition without surface decomposition. With this improved annealing method, the impurity apical oxygen atoms can probably be more efficiently removed. Our ARPES study on the protect-annealed $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ (PLCCO, $x = 0.10$) crystals has revealed strong suppression of the hot spot, namely, the AF pseudogap, suggesting a dramatic reduction of the AF spin correlation length and/or the magnitude of the magnetic moments [19]. A question arising here is what the character of this superconductivity under suppressed antiferromagentism is. Several penetration depth studies [20,21] have reported the observation of an s-wave SC gap for optimally doped electron-doped cuprate superconductors. Biswas *et al.* [22] claimed, by use of point-contact spectroscopy, that the SC gap symmetry changes from d-wave to s-wave in going from the underdoped to overdoped regime. These results point toward the possibility of s-wave superconductivity in the optimal to overdoped samples where the AF order becomes less relevant. In this context, the SC gap symmetry of protect-annealed samples with suppressed antiferromagnetism is of great interest.

Here, we report on an ARPES study of protect-annealed PLCCO ($x = 0.10, 0.15$) single crystals conducted to reveal the nature of the SC state with the enhanced T_c and suppressed AF correlation. With special care regarding the surface degradation, we have succeeded in the direct observation of a momentum-dependent SC gap. The obtained SC gap suggests its d-wave symmetry for both samples, suggesting that AF correlation arising from strong electron correlation remains an essential ingredient for the superconductivity in efficiently annealed electron-doped cuprates.

*horio@physik.uzh.ch

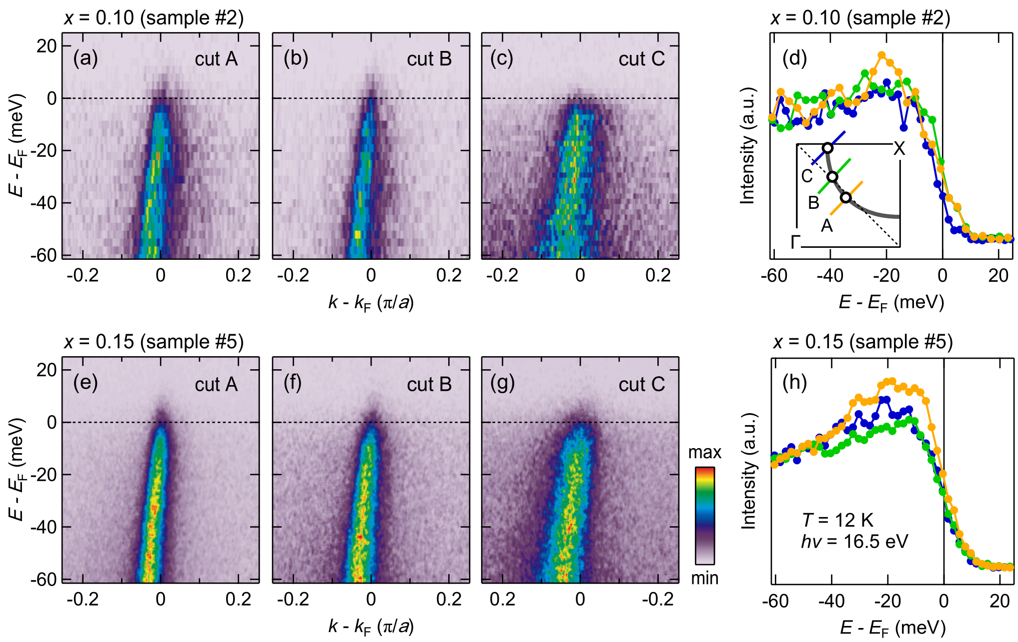

FIG. 1. ARPES spectra of protect-annealed PLCCO ($x = 0.10, 0.15$) recorded within 1 h after cleavage. (a)–(c) ARPES spectra of sample 2 with $x = 0.10$ along cuts A–C indicated in the inset of (d). The spectra were recorded at $T = 12$ K with $h\nu = 16.5$ eV incident photons. (d) EDCs at k_F points extracted from (a)–(c). The spectra have been normalized to the intensity at the high binding energies of 45–60 meV. (e)–(h) The same as (a)–(d), but for sample 5 with $x = 0.15$.

II. EXPERIMENT

Single crystals of PLCCO with $x = 0.10$ (samples 1–4) and $x = 0.15$ (samples 5 and 6) were synthesized by the traveling-solvent floating-zone method and were protect annealed for 24 h at 800 °C [17]. After the annealing, samples with $x = 0.10$ and $x = 0.15$ showed T_c values of 27 and 22 K, respectively. Most of the ARPES measurements were performed at beamline 7U of UVSOR-III Synchrotron (samples 1–3, 5, and 6). At UVSOR-III, linearly polarized light with $h\nu = 16.5$ eV was used for the measurements. The total energy and momentum resolutions were set at 8 meV and 0.005 Å^{-1}, respectively. Sample 3 was measured three times, while each of the other samples was measured once. Prior to each measurement, the sample was cleaved *in situ* under pressure better than 1×10^{-10} Torr. Considering the relatively quick surface degradation of the T'-type cuprates [4], ARPES spectra were recorded within 4 h after cleavage at only one momentum cut at two temperatures below and above T_c for each sample. Just before or after taking every single spectrum of the sample, a gold film evaporated near the sample was measured to determine the Fermi level E_F of the sample at that moment. Sample 4 was measured using a laser-ARPES apparatus developed at the Institute for Solid State Physics (ISSP) with a 7-eV quasi-cw laser (with a repetition rate of 240 MHz). The space-charge effect was confirmed to be negligibly small. The total energy and momentum resolutions were set at 1.5 meV and 0.002 Å^{-1}, respectively. The measurements were carried out in a vacuum better than 4×10^{-11} Torr, and several momentum cuts were measured. Energy distribution curves (EDCs) at Fermi momentum k_F positions presented in Figs. 1 and 2 were obtained by integration within $k_F \pm 0.006\pi/a$, where $a = 3.98$ Å is the in-plane lattice constant.

III. RESULTS AND DISCUSSION

Figure 1 displays ARPES spectra of protect-annealed PLCCO ($x = 0.10, 0.15$) measured at $h\nu = 16.5$ eV near $(\pi/2, \pi/2)$, the hot spot, and $(0.3\pi, \pi)$. The spectra were recorded within 1 h after cleavage, when the cleaved surface remained fresh. EDCs were extracted at k_F points and plotted in Figs. 1(d) and 1(h) after normalization to the intensity at binding energies of 45–60 meV. For both the $x = 0.10$ and $x = 0.15$ samples, one cannot recognize remarkable intensity suppression at the hot spot near E_F. This suggests a strong suppression of AF spin correlation length and/or the magnitude of the magnetic moment by protect annealing, consistent with the previous ARPES study on the protect-annealed crystals [19].

In order to examine the SC gap of protect-annealed PLCCO samples, in Fig. 2(a), EDCs of PLCCO ($x = 0.10$) near $(\pi/2, \pi/2)$ and $(0.3\pi, \pi)$, i.e., near the node and antinode in the case of $d_{x^2-y^2}$ symmetry, are plotted. Because T'-type cuprates do not show clear SC coherence peaks in their ARPES spectra [4,5,8] and the position of the leading-edge midpoint at $T < T_c$ referenced to E_F is not clear and does not necessarily reflect the magnitude of the SC gap [5], we compared the spectra taken above and below T_c and estimated the magnitude of the leading-edge shift Δ_{LE} between the two temperatures. Here, Δ_{LE} is defined as an energy shift with decreasing temperature referenced to the E_F-crossing point at $T > T_c$. As shown in Fig. 2(a), the EDCs near $(\pi/2, \pi/2)$ taken above and below T_c cross almost at E_F, and Δ_{LE} is

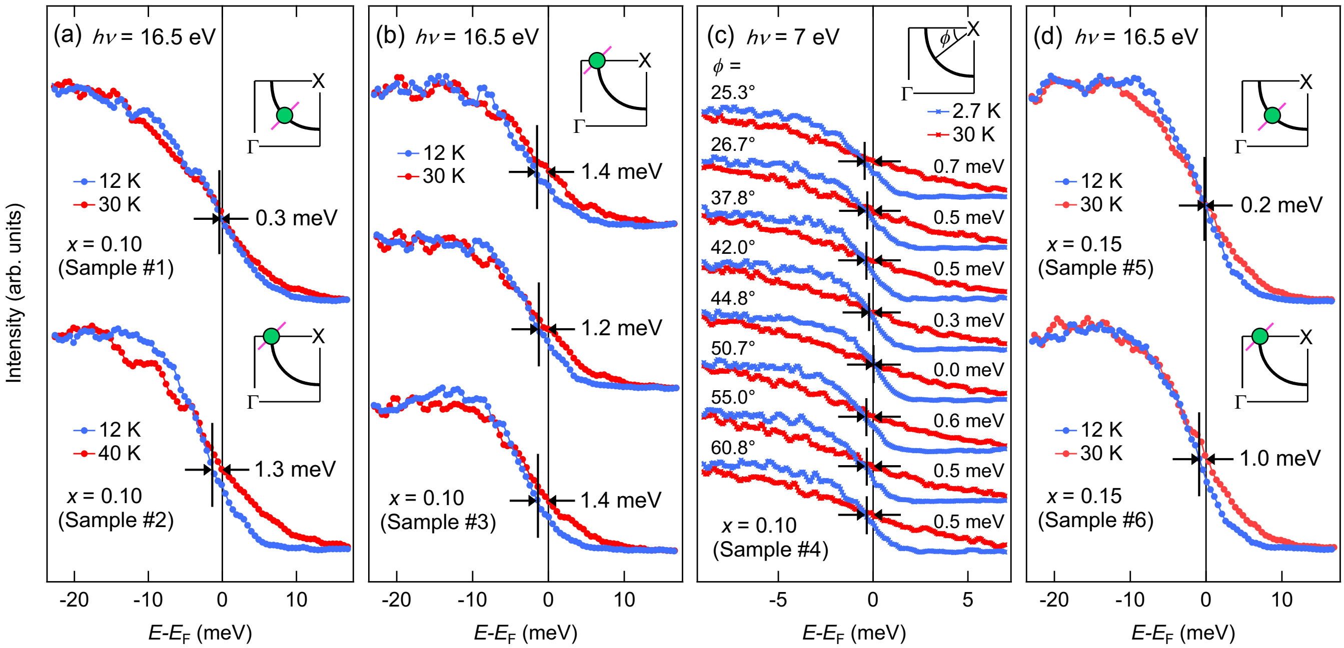

FIG. 2. Leading-edge shift Δ_{LE} observed for PLCCO samples. EDCs of (a) samples 1 and 2 with $x = 0.10$, (b) sample 3 with $x = 0.10$ measured three times on different cleavage surfaces, (c) sample 4 with $x = 0.10$, and (d) samples 5 and 6 with $x = 0.15$ measured at temperatures above (red curves) and below (blue curves) T_c. Insets of (a), (b), and (d) indicate the momentum cuts and k_{F} positions where the EDCs were measured. For each EDC in (c), the Fermi surface angle ϕ defined in the inset is indicated. Estimated Δ_{LE} values are shown beside each set of the EDCs.

as small as 0.3 meV, whereas those near $(0.3\pi,\ \pi)$ cross appreciably below E_{F}, and a leading-edge shift of 1.3 meV was observed. A leading-edge shift of similar magnitude near $(0.3\pi,\ \pi)$ was also reproducibly observed in the measurements of another $x = 0.10$ sample on different cleavage surfaces, as shown in Fig. 2(b), clearly indicating the SC gap opening near $(0.3\pi, \pi)$. The momentum region near $(0.3\pi, \pi)$ cannot be reached in the ARPES measurement using a 7-eV laser due to the low photon energy, but the laser-ARPES spectra also show negligibly small Δ_{LE} near $(\pi/2,\ \pi/2)$ and finite Δ_{LE} away from $(\pi/2,\ \pi/2)$ [Fig. 2(c)]. The same tendency is also observed for the $x = 0.15$ samples [Fig. 2(d)], although Δ_{LE} near $(0.3\pi, \pi)$ was slightly smaller than that of the $x = 0.10$ samples.

The Δ_{LE} values estimated from Fig. 2 are plotted against the $d_{x^2-y^2}$-wave order parameter $|\cos k_x - \cos k_y|/2$ in Fig. 3(a). A tiny but finite drift of the incident photon energy during the synchrotron measurement, which affects the kinetic energy of the photoelectrons, was evaluated from the drift of E_{F} of the reference gold film and is indicated by an error bar, while the error bars for the laser-ARPES data are assumed to be constant. Δ_{LE} for the $x = 0.10$ samples is roughly proportional to the d-wave order parameter. For a more detailed discussion of the momentum dependence of the SC gap, such as the deviation from the monotonic $d_{x^2-y^2}$-wave form [6,8], a more thorough investigation, especially around the hot spot, is required. Still, at this moment, one can conclude that the observed SC gap is consistent with d-wave symmetry. Detection of the sign change using phase-sensitive probes is a future issue. In Fig. 3(b), Δ_{LE} at $\sim(0.3\pi, \pi)$ is plotted as Δ^0_{LE} against T_c. The dependence of the antinodal Δ_{LE} on T_c has been satisfactorily fitted to the equation of $2\Delta^0_{\mathrm{LE}} = \alpha k_{\mathrm{B}} T_c$. This observation suggests that the SC states of the $x = 0.10$ and $x = 0.15$ samples are in the same d-wave symmetry and are realized with the same mechanism. On the other hand, the obtained value of $\alpha = 1.18$, which represents the paring strength, is quite small even compared to $\alpha = 2\Delta/k_{\mathrm{B}} T_c = 4.28$ predicted by d-wave BCS theory. In fact, it was shown in previous ARPES studies that the leading-edge shift underestimates the SC gap magnitude by a factor of $\sim$2 [23–25].

In order to gain more quantitative information, we attempt to apply the recently developed tomographic density of states (TDOS) method [25]. TDOS is defined as the sum of EDCs

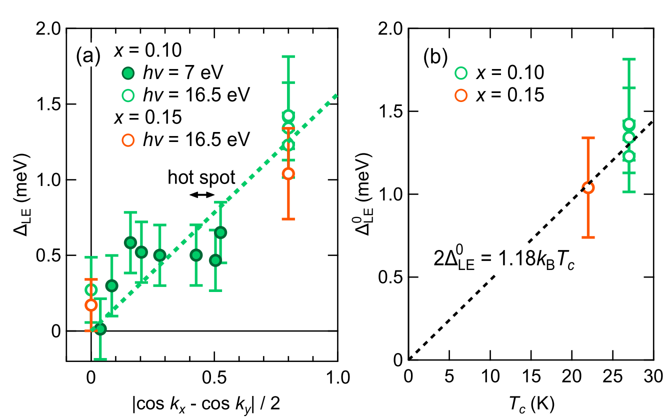

FIG. 3. d-wave SC gap of PLCCO. (a) Leading-edge shift Δ_{LE} plotted against the $d_{x^2-y^2}$-wave order parameter $|\cos k_x - \cos k_y|/2$. A line obtained by fitting the data is also plotted. (b) Δ_{LE} at the antinode $(0.3\pi, \pi)$, Δ^0_{LE}, plotted against T_c values. A line representing $2\Delta^0_{\mathrm{LE}} = 1.18 k_{\mathrm{B}} T_c$ is superimposed.

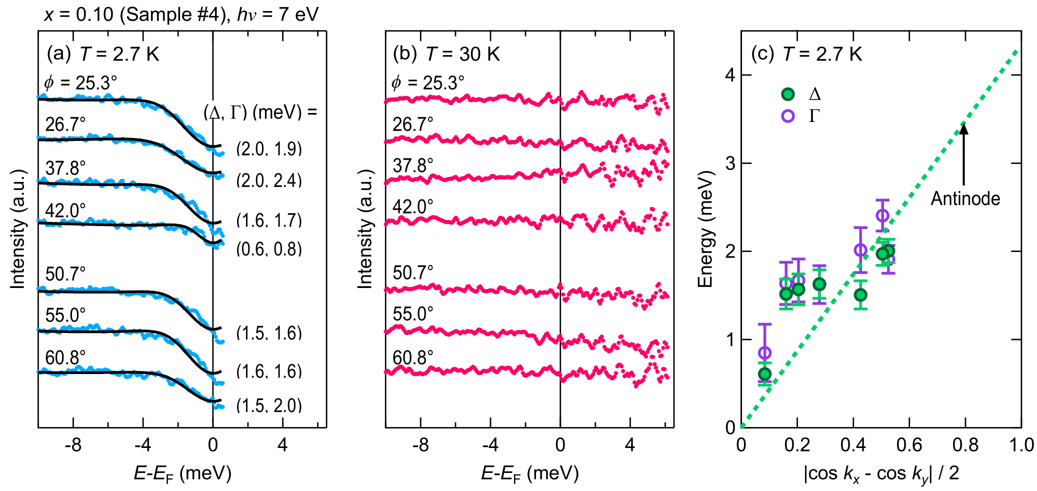

FIG. 4. SC gap estimated from TDOS. (a) and (b) Off-nodal TDOS of the $x = 0.10$ sample derived from laser-ARPES data at $T = 2.7$ and 30 K, respectively. The $T = 2.7$ K spectra are fitted to the Dynes formula (shown in black). (c) SC gap Δ and pair-breaking scattering rate Γ obtained through fitting and plotted against the $d_{x^2-y^2}$-wave order parameter $|\cos k_x - \cos k_y|/2$.

along one momentum cut which is normalized to a similar but ungapped reference sum along the nodal direction. The resulting TDOS can be fitted to the following Dynes formula:

$$I_{\mathrm{TDOS}}(\omega) = \mathrm{Re}\frac{\omega - i\Gamma}{\sqrt{(\omega - i\Gamma)^2 - \Delta^2}}, \quad (1)$$

where I_{TDOS} is the TDOS intensity, Γ is the pair-breaking scattering rate, and Δ is the SC gap [26]. Without further complicated assumptions about fitting, this method is capable of determining SC gap magnitude more precisely than conventional estimates from leading-edge shifts or symmetrized EDCs [25]. Figures 4(a) and 4(b) show TDOS obtained from the laser-ARPES measurement on the $x = 0.10$ sample [same data as in Fig. 2(c)]. While clear gaps are found at all the off-nodal positions at $T = 2.7$ K [Fig. 4(a)], the gaps are closed at $T = 30\ \mathrm{K} > T_c = 27$ K [Fig. 4(b)], consistent with the d-wave SC gap opening below T_c. The SC gap value Δ, obtained by fitting to the Dynes formula, is plotted in Fig. 4(c) as a function of the $d_{x^2-y^2}$-wave order parameter $|\cos k_x - \cos k_y|/2$. The overall trend of the momentum dependence is consistent with that of the leading-edge shift shown in Fig. 3(a). As Δ increases, the pair-scattering rate Γ also increases, thereby suppressing the coherence peak. From linear extrapolation of the obtained Δ values, the antinodal SC gap value at $(0.3\pi, \pi)$ ($|\cos k_x - \cos k_y|/2 \sim 0.8$) can be estimated to be 3.5 meV. This leads to $\alpha = 2\Delta/k_{\mathrm{B}}T_c = 3.0$, which is $\sim$2.5 times larger than the estimate from the leading-edge shift. Still, the value of α is somewhat smaller than what is predicted by d-wave BCS theory, and it remains unclear whether this relatively small α is intrinsic or due to an artifact of the analysis. With any analysis method, the exact size of the SC gap cannot be uniquely determined when the SC coherent peak is not clear, as in the present case.

Studies on protect-annealed PLCCO samples using muon spin relaxation [27] and NMR [28], which are sensitive to spins, revealed that while the long-range AF order is suppressed, the AF spin susceptibility increases with decreasing temperature for both $x = 0.10$ and $x = 0.15$ samples, and short-ranged AF order sets in at very low temperatures for the $x = 0.10$ sample. Given the presence of the enhanced AF spin susceptibility, a simple but straightforward scenario is to associate the d-wave superconductivity suggested from the present ARPES results with AF spin fluctuations that arise from strong electron correlation. This consideration is consistent with a phenomenological model in which T'-type cuprates are regarded as being in an antiferromagnetically correlated state and a static short-range AF order is induced around the excess apical oxygen atoms [17,27]. Considering the fact that the efficient removal of the apical oxygen atoms by protect annealing results in the increase of T_c compared to the conventional annealing [18], the short-range AF order induced around the apical oxygen atoms is harmful for superconductivity. Once the apical oxygen atoms are removed, AF correlation becomes more short ranged to nurture superconductivity. The emergence of the superconductivity and its relationship to the AF pseudogap have been discussed by ARPES studies in terms of the reduction of spin correlation length [19,29,30]. Thus, strong electron correlation leading to AF spin fluctuations remains a candidate for what drives the d-wave superconductivity in the T'-type cuprates.

IV. CONCLUSION

In conclusion, we have performed ARPES measurements on protect-annealed PLCCO single crystals ($x = 0.10, 0.15$) and estimated the leading-edge shift Δ_{LE} as a measure of the SC gap. The observed momentum dependence of Δ_{LE} was consistent with d-wave symmetry, suggesting that superconductivity in T'-type cuprates may be driven by AF spin fluctuations arising from strong electron correlation regardless of the doping level even after the suppression of the static short-range AF order and the strong reduction of AF spin correlation length and/or the magnitude of the magnetic moment by protect annealing.

ACKNOWLEDGMENTS

ARPES experiments were performed at UVSOR-III Synchrotron (Proposals No. 27-808 and 28-545) and ISSP. This work was supported by JSPS KAKENHI Grants No. JP14J09200, No. JP15H02109, No. JP16K05458, No. JP17H02915, No. JP19H00651, No. JP19H01818, No. JP19H01841, No. JP19H05826, and No. JP19K03741. M.H. acknowledges support from the Advanced Leading Graduate Course for Photon Science (ALPS) and the JSPS Research Fellowship for Young Scientists.

[1] D. J. Scalapino, Rev. Mod. Phys. **84**, 1383 (2012).

[2] C. C. Tsuei and J. R. Kirtley, Phys. Rev. Lett. **85**, 182 (2000).

[3] J. D. Kokales, P. Fournier, L. V. Mercaldo, V. V. Talanov, R. L. Greene, and S. M. Anlage, Phys. Rev. Lett. **85**, 3696 (2000).

[4] T. Sato, T. Kamiyama, T. Takahashi, K. Kurahashi, and K. Yamada, Science **291**, 1517 (2001).

[5] N. P. Armitage, D. H. Lu, D. L. Feng, C. Kim, A. Damascelli, K. M. Shen, F. Ronning, Z.-X. Shen, Y. Onose, Y. Taguchi, and Y. Tokura, Phys. Rev. Lett. **86**, 1126 (2001).

[6] G. Blumberg, A. Koitzsch, A. Gozar, B. S. Dennis, C. A. Kendziora, P. Fournier, and R. L. Greene, Phys. Rev. Lett. **88**, 107002 (2002).

[7] G.-q. Zheng, T. Sato, Y. Kitaoka, M. Fujita, and K. Yamada, Phys. Rev. Lett. **90**, 197005 (2003).

[8] H. Matsui, K. Terashima, T. Sato, T. Takahashi, M. Fujita, and K. Yamada, Phys. Rev. Lett. **95**, 017003 (2005).

[9] Y. Dagan, R. Beck, and R. L. Greene, Phys. Rev. Lett. **99**, 147004 (2007).

[10] A. F. Santander-Syro, M. Ikeda, T. Yoshida, A. Fujimori, K. Ishizaka, M. Okawa, S. Shin, R. L. Greene, and N. Bontemps, Phys. Rev. Lett. **106**, 197002 (2011).

[11] Q. Yuan, F. Yuan, and C. S. Ting, Phys. Rev. B **73**, 054501 (2006).

[12] P. K. Mang, O. P. Vajk, A. Arvanitaki, J. W. Lynn, and M. Greven, Phys. Rev. Lett. **93**, 027002 (2004).

[13] P. Richard, M. Neupane, Y.-M. Xu, P. Fournier, S. Li, P. Dai, Z. Wang, and H. Ding, Phys. Rev. Lett. **99**, 157002 (2007).

[14] X. Q. Xu, S. N. Mao, W. Jiang, J. L. Peng, and R. L. Greene, Phys. Rev. B **53**, 871 (1996).

[15] P. G. Radaelli, J. D. Jorgensen, A. J. Schultz, J. L. Peng, and R. L. Greene, Phys. Rev. B **49**, 15322 (1994).

[16] A. J. Schultz, J. D. Jorgensen, J. L. Peng, and R. L. Greene, Phys. Rev. B **53**, 5157 (1996).

[17] T. Adachi, Y. Mori, A. Takahashi, M. Kato, T. Nishizaki, T. Sasaki, N. Kobayashi, and Y. Koike, J. Phys. Soc. Jpn. **82**, 063713 (2013).

[18] X. F. Sun, Y. Kurita, T. Suzuki, S. Komiya, and Y. Ando, Phys. Rev. Lett. **92**, 047001 (2004).

[19] 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).

[20] L. Alff, S. Meyer, S. Kleefisch, U. Schoop, A. Marx, H. Sato, M. Naito, and R. Gross, Phys. Rev. Lett. **83**, 2644 (1999).

[21] J. A. Skinta, T. R. Lemberger, T. Greibe, and M. Naito, Phys. Rev. Lett. **88**, 207003 (2002).

[22] A. Biswas, P. Fournier, M. M. Qazilbash, V. N. Smolyaninova, H. Balci, and R. L. Greene, Phys. Rev. Lett. **88**, 207004 (2002).

[23] T. Kondo, T. Takeuchi, A. Kaminski, S. Tsuda, and S. Shin, Phys. Rev. Lett. **98**, 267004 (2007).

[24] T. Yoshida, M. Hashimoto, S. Ideta, A. Fujimori, K. Tanaka, N. Mannella, Z. Hussain, Z.-X. Shen, M. Kubota, K. Ono, S. Komiya, Y. Ando, H. Eisaki, and S. Uchida, Phys. Rev. Lett. **103**, 037004 (2009).

[25] T. J. Reber, N. C. Plumb, Z. Sun, Y. Cao, Q. Wang, K. McElroy, H. Iwasawa, M. Arita, J. S. Wen, Z. J. Xu, G. Gu, Y. Yoshida, H. Eisaki, Y. Aiura, and D. S. Dessau, Nat. Phys. **8**, 606 (2012).

[26] R. C. Dynes, V. Narayanamurti, and J. P. Garno, Phys. Rev. Lett. **41**, 1509 (1978).

[27] T. Adachi, A. Takahashi, K. M. Suzuki, M. A. Baqiya, T. Konno, T. Takamatsu, M. Kato, I. Watanabe, A. Koda, M. Miyazaki, R. Kadono, and Y. Koike, J. Phys. Soc. Jpn. **85**, 114716 (2016).

[28] M. Yamamoto, Y. Kohori, H. Fukazawa, A. Takahashi, T. Ohgi, T. Adachi, and Y. Koike, J. Phys. Soc. Jpn. **85**, 024708 (2016).

[29] S. R. Park, T. Morinari, D. J. Song, C. S. Leem, C. Kim, S. K. Choi, K. Choi, J. H. Kim, F. Schmitt, S. K. Mo, D. H. Lu, Z.-X. Shen, H. Eisaki, T. Tohyama, J. H. Han, and C. Kim, Phys. Rev. B **87**, 174527 (2013).

[30] 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).