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\cite{1,2,3}. As for the electron-doped cuprate superconductors with the Nd$_2$CuO$_4$ (so called T'-type) structure, many of previous studies have also supported d-wave symmetry\cite{4,5,6}. In particular, electronic Raman scattering\cite{7} and angle-resolved photoemission spectroscopy (ARPES)\cite{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, large contribution of AF spin fluctuations to the superconductivity has been proposed though 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\cite{9,10,11,12}.

The AF correlation in the electron-doped cuprates strongly depends on the post-growth annealing conducted in the reducing atmosphere\cite{13,14,15}. By the reduction annealing, impurity oxygen atoms at the apical site, which exist in as-grown samples and act as a strong scattering center\cite{16,17}, are presumably removed\cite{18,19,20}. Recently, a new annealing method, which is called protect annealing, has been demonstrated to induce superconductivity in electron-doped cuprates with lower Ce concentration and higher $T_c$\cite{21,22} than those in previous studies\cite{23,24}. This is probably because the impurity apical oxygen atoms can be more efficiently removed with the improved annealing method. Our ARPES study on the protect-annealed Pr$_{1.3-x}$La$_{0.7}$Ce$_x$CuO$_4$ (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\cite{25,26}. A question arising here is what the character of this superconductivity under suppressed antiferromagnetism is. Several penetration depth studies\cite{27,28} have reported the observation of s-wave SC gap for optimally doped electron-doped cuprate superconductors. Biswas et al.\cite{29} have claimed, by use of point-contact spectroscopy, that the SC-gap symmetry changes from d-wave to s-wave in going from 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 about the surface degradation, we have succeeded in the direct observation of momentum-dependent SC gap. The obtained SC gap has 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.

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 hours at 800 $\text{°C}$\cite{30}. After the annealing, samples with $x = 0.10$ and $x = 0.15$ showed $T_c$ values of 27 K 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 resolution was set at 8 meV. 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 the pressure better than $1 \times 10^{-10}$ Torr. Considering the relatively quick surface degradation of the T’-type...
ARPES spectra of protect-annealed PLCCO ($x = 0.10, 0.15$) recorded within 1 hour after cleavage. (a)–(c) ARPES spectra of sample #2 with $x = 0.10$ along cuts A–C indicated in (i). The spectra were recorded at $T = 12$ K with $hν = 16.5$ 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 $x = 0.15$. (i) Positions of the momentum cuts.

The T'-type cuprates ARPES spectra were recorded within 4 hours 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 the repetition rate of 240 MHz). The total energy resolution was set at 1.5 meV. The measurements were carried out in a vacuum better than $4 \times 10^{-11}$ Torr, and several momentum cuts were measured.

Figure 1 displays ARPES spectra of protect-annealed PLCCO ($x = 0.10, 0.15$) measured at $hν = 16.5$ eV near ($\pi/2, \pi/2$), hot spot, and ($0.3\pi, \pi$). The spectra were recorded within 1 hour after cleavage, when the cleaved surface remained fresh. Energy distribution curves (EDCs) were extracted at the Fermi momentum ($k_F$) points and plotted in Figs. 1(d) and (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.18

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 the T'-type cuprates do not show clear SC coherence peaks in their ARPES spectra and the position of the leading-edge midpoint at $T < T_c$ referenced to $E_F$ is neither clear nor necessarily reflecting the magnitude of the SC gap, we compared the spectra taken above and below $T_c$ and estimated the magnitude of the leading-edge shift $\Delta_{LE}$ between the two temperatures. Here, $\Delta_{LE}$ is defined as an energy shift with decreasing temperature referenced to $E_F$-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 $\Delta_{LE}$ is 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. The leading-edge shift of similar magnitude near ($0.3\pi, \pi$) was also observed in the measurements of another $x = 0.10$ sample reproducibly on different cleavage surfaces as shown in Fig. 2(h), 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 7 eV laser due to the low photon energy, but the laser-ARPES spectra also show negligibly small $\Delta_{LE}$ near ($\pi/2, \pi/2$) and finite $\Delta_{LE}$ 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 $\Delta_{LE}$ near ($0.3\pi, \pi$) was slightly smaller than that.
against the drift of the reference gold film and indicated by an error bar, while the error bars for the x = 0.10 samples.

The \( \Delta_{LE} \) values estimated from Fig. 2 are plotted against the \( d_{x^2-y^2} \)-wave order parameter \( \left| \cos k_x - \cos k_y \right|/2 \) 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 indicated by an error bar, while the error bars for the laser-ARPES data were assumed to be constant. The \( \Delta_{LE} \) for the x = 0.10 samples is roughly proportional to the \( d \)-wave order parameter. For more detailed discussion about the momentum dependence of the SC gap such as the deviation from the monotonic \( d_{x^2-y^2} \)-wave form, 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. In Fig. 3(b), \( \Delta_{LE} \) at \((0.3\pi, \pi)\) is plotted as \( \Delta_{LE}^0 \) against \( T_c \). The dependence of the antinodal \( \Delta_{LE} \) on \( T_c \) has been satisfactorily fitted to the equation of \( 2\Delta_{LE}^0 = \alpha k_B T_c \). 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 under the same mechanism, although obtained value of \( \alpha = 1.18 \), which represents the paring strength, is somewhat smaller than \( \alpha = 2.14 \) by \( d \)-wave BCS theory assuming the empirical relationship for the SC gap \( \Delta_{\text{gap}} = 2\Delta_{LE}^0 \), or \( \alpha = 1.70 \) derived for the antinodal \( \Delta_{LE} \) in the previous ARPES study on \( \text{Pr}_{1-x}\text{LaCe}_x\text{CuO}_4 \) \( (x = 0.11) \). The reason for this small \( \alpha \) is not clear at the moment.

The present result suggests that \( d \)-wave pairing, which arises from strong electron correlation and is associated with AF spin fluctuations, persists after the strong reduction of AF correlation length and/or magnitude of the local magnetic moment by protect annealing. Studies on protect-annealed PLCCO samples using muon spin relaxation and NMR, which are sensitive to spins, have also revealed that while the long-range AF order was...
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. These results are consistent with a phenomenological model in which the 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\textsuperscript{10,22}. Considering the fact that the efficient removal of the apical oxygen atoms by protective annealing results in the increase of $T_c$ compared to the conventional annealing\textsuperscript{15}, the short-range AF order induced around the apical oxygen atoms is harmful for superconductivity although strong correlation itself may drive the $d$-wave superconductivity in the T'-type cuprates.

In conclusion, we have performed ARPES measurements on protect-annealed PLCCO single crystals ($x = 0.10, 0.15$) and estimated the leading-edge shift $\Delta_{LE}$ as a measure of the SC gap. Observed momentum dependence of $\Delta_{LE}$ was consistent with $d$-wave symmetry, suggesting that superconductivity in the 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 protective annealing.

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