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Annealing condition dependence of the superconducting property and the pseudo-gap in the protect-annealed electron-doped cuprates

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Abstract

Annealing as-grown electron-doped cuprates under a low oxygen-partial-pressure condition is a necessary step to achieve superconductivity. It has been recently found that the so-called protect annealing results in much better superconducting properties in terms of the superconducting transition temperature and volume fraction. In this article, we report on angle-resolved photoemission spectroscopy studies of a protect-annealed electron-doped cuprate $Pr_{0.9}La_{1.0}Ce_{0.1}CuO_4$ on annealing condition dependent superconducting and pseudo-gap properties. Remarkably, we found that the one showing a better superconducting property possesses almost no pseudo-gap while others have strong pseudo-gap feature due to an anti-ferromagnetic order.

Keywords : protect-annealed electron-doped cuprate, angle-resolved photoemission spectroscopy, pseudo-gap

1. INTRODUCTION

Electron-doped cuprate superconductors such as $Nd_{2-x}Ce_xCuO_4$, $Pr_{2-x}Ce_xCuO_4$ and $Sm_{2-x}Ce_xCuO_4$ were found in 1989 [1]. The nature of the charge carrier in $Nd_{2-x}Ce_xCuO_4$ being electron-like was soon confirmed by X-ray absorption spectroscopy [2]. The as-grown electron-doped cuprates do not show any superconductivity and it is necessary to anneal the as-grown electron-doped cuprates under a low oxygen-partial-pressure condition for inducing superconductivity. The reason for such necessity for the annealing process is still under controversy. On the other hand, the annealing process concomitantly generates defects or disorder in the electron-doped cuprates and these defects are not desired for better superconducting properties [3, 4]. People believe that better superconducting properties can be achieved if one can avoid the defects or disorders induced by the annealing.

The so-called protect annealing gives better superconducting properties in terms of the superconducting transition temperature and volume fraction in the electron-doped cuprates [5]. The key points of the protect annealing is that single crystals of the electron-doped cuprate are imbedded in electron-doped cuprate powder with the same composition and that the annealing can be performed at a relatively low temperature in a high vacuum.

Remarkably, angle-resolved photoemission spectroscopy (ARPES) studies on a protect-annealed electron-doped cuprate $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ (x=0.10) revealed no pseudo-gap at hot spots where the Fermi surface and the anti-ferromagnetic Brillouin zone boundary intersect [5]. The pseudo-gap in the electron-doped cuprates is believed to originate from coupling to anti-ferromagnetic (AFM) order [6, 7]. Disappearance of the pseudo-gap in the protect-annealed electron-doped cuprates is thus interpreted to be due to a drastic reduction of AFM. Therefore, the protect-annealing reinforces the superconductivity in electron-doped cuprates as the superconductivity and AFM may compete each other in electron-doped cuprates [8].

In this article, we report on ARPES studies on a protect-annealed electron-doped cuprate $Pr_{0.9}La_{1.0}Ce_{0.1}CuO_4$ (PLCCO) which is different from the previously studied material in the ratio between Pr and La concentrations. Especially, we prepared two samples, which are annealed in different temperatures. Annealing condition dependence of the superconducting and pseudo-gap properties are studied by using ARPES. Remarkably, one that shows a clearly better superconducting property in terms of the superconducting transition temperature and volume fraction has almost no pseudo-gap. This is consistent with previous ARPES results on protect-annealed electron-doped cuprates [5].

2. EXPERIMENTAL DETAILS

PLCCO single crystals were grown by the traveling-solvent floating-zone method. All the crystal rods were cleaved into small pieces. One group of pieces (PLCCO#1) is embedded by the same material powder and annealed in

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vacuum for 24 h at 750 ℃, and the other group of pieces (PLCCO#2) is embedded by the same material powder and annealed in vacuum for 20 h at 740 ℃. ARPES measurements were performed on both PLCCO#1 and PLCCO#2 at the beam line 7U of UVSOR-II. 16.5 eV of incident photon energy were used. The total energy resolution was better than 15 meV. Samples were cleaved in situ and the chamber pressure was better than 5×10^{-11} Torr.

3. RESULTS AND DISCUSSION

The magnetization of PLCCO#1 and PLCCO#2 as a function of temperature was measured by SQUID to investigate superconducting property. The samples were cooled down to the base temperature of 5 K without applied magnetic field, and magnetization was measured under 1 Oe of the magnetic field while the temperature was raised. The magnetization normalized by the sample mass is shown in figure 1. The data clearly show higher superconducting transition temperature for PLCCO#2. The saturated value for the diamagnetic signal below the superconducting transition temperature is almost twice larger in PLCCO#2. That indicates a larger superconducting-volume fraction in PLCCO#2.

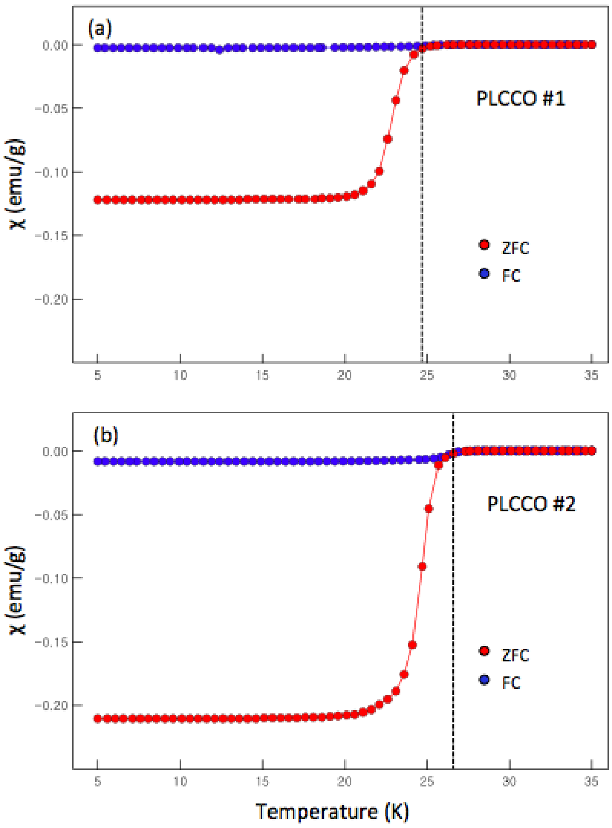

Fig. 1. Magnetization of PLCCO#1 (a) and PLCCO#2 (b) normalized by the sample mass. 1 Oe of the magnetic field was applied for both samples to measure the magnetization by SQUID. The vertical dashed lines indicate the onset of the Meissner effect.

As-grown PLCCO is not superconducting but becomes superconducting after the annealing process. The magnetization data show that superconducting property is very sensitive to the annealing conditions. PLCCO#2 shows better superconducting properties in terms of the transition temperature and volume fraction. There are a couple of candidates for the origin of the better superconducting properties in PLCCO#2. Firstly, less defects or disorder induced by annealing process are expected in PLCCO#2 as the annealing temperature was a little lower. Secondly, PLCCO#2 may be more optimally reduced in terms of the electron doping concentration. The annealing temperature for PLCCO#1 might be too high and over-reduced. We performed ARPES experiments to investigate the microscopic origin of the better superconducting properties in PLCCO#2.

2D momentum mappings of ARPES intensities at the Fermi energy show a quarter of the Fermi surface of PLCCO#1 and PLCCO#2 (figure 2). Fermi surfaces of PLCCO#1 and PLCCO#2 look clearly different. We notice small pockets near (π, 0) and strong ARPES intensity near (π/2, π/2) in the Fermi surface of PLCCO#1, while we cannot see distinguished small-pockets near (π, 0) but a single large pocket centered at (π, π) in the Fermi surface of PLCCO#2. It has been believed that a large hole-pocket without AFM order evolves into small electron pockets near (π, 0) and a small hole pocket near (π/2, π/2) due to the band folding from AFM [6, 7]. The gap at the hot spots where the original Fermi surface and AFM Brillouin zone boundary intersect is called pseudo-gap, since it is not a full gap but has finite spectral weight near the Fermi energy. It is probably because of the finite correlation length of AFM [9]. Therefore, we conclude from Fermi surface data that there is considerable AFM in PLCCO#1, while almost no AFM ordering in PLCCO#2.

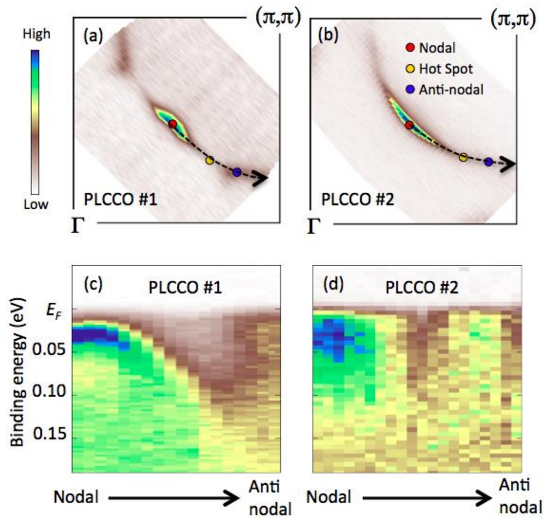

Fig. 2. 2D momentum mappings of ARPES intensities at the Fermi energy show a quarter of the Fermi surface of PLCCO#1 (a) and PLCCO#2 (b). ARPES intensity mapping of PLCCO#1 (c) and PLCCO#2 (d) along the momentum indicated by dashed arrows on Fermi surfaces (a, b) are shown.

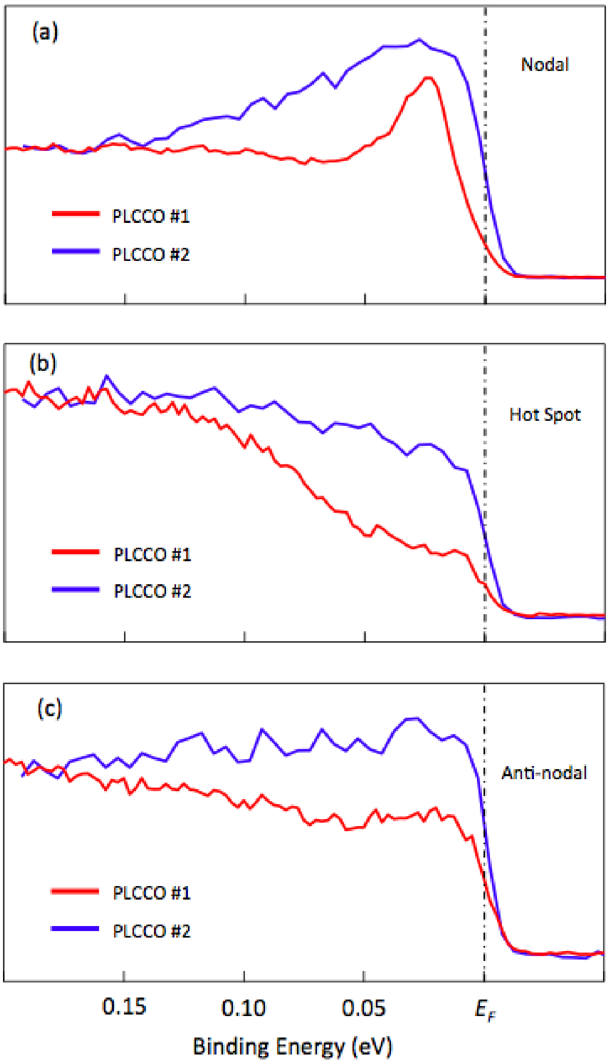

Fig. 3. ARPES intensities of PLCCO #1 and PLCCO #2 as a function of binding energy at the nodal point (a), at a hot-spot point (b) and at an anti-nodal point (c) indicated in figure 2.

ARPES intensity maps of PLCCO#1 and PLCCO#2 along the Fermi momentum indicated by the dashed arrows in figure 2 reveal more details about the pseudo-gap (figure 2). We notice that the depletion of the spectral weight near Fermi energy near hot spot in PLCCO#1. Pseudo-gap energy is about 0.1 eV. In the contrast, there is almost no pseudo-gap in PLCCO#2.

Energy distribution curves (EDCs) at specific momentum points allow us to compare electronic structures of PLCCO#1 and PLCCO#2 in more detail. The EDC of PLCCO#2 for the nodal point shows the Fermi edge that follows the Fermi-Dirac distribution (figure 3a), indicating the band crossing the Fermi energy. The EDC of PLCCO#1 for the nodal point, however, shows that the leading edge is shifted from the Fermi energy. This may be induced by the strong AFM as the Fermi momentum along nodal is very close to the AFM Brillouin-zone boundary [10]. One more thing about which we need to discuss is the line-shape of the EDCs at the nodal point. The EDC of PLCCO#1 is very sharp, indicating weak scattering due to defects or disorder. Therefore, defects or disorder induced during the annealing process is not the origin of the poorer superconducting property in PLCCO#1. Both EDCs for the anti-nodal point (figure 3c) show clear Fermi edges and thus no gap.

We can clearly notice a pseudo-gap behavior in the EDC of PLCCO#1 at hot-spot points (figure 3b). While there is a small Fermi edge, ARPES intensity is depleted down to about 0.1 eV binding energy. The reason why it shows a small Fermi edge instead of a full gap may be attributed to the finite correlation length of AFM [7].

What is the origin of the better superconducting property of PLCCO#2 than of PLCCO#1? Our ARPES data clearly show a strong pseudo-gap, originating from AFM, in PLCCO#1 but weak pseudo-gap effect in PLCCO#2. PLCCO#1 probably has stronger AFM but weaker superconductivity, while PLCCO#2 has weaker AFM but stronger superconductivity. It has been known that as–grown electron-doped cuprates have no superconductivity but strong AFM [3]. Therefore, for a better superconductivity in electron-doped curpates, the annealing process probably has to eliminate the AFM.

3. CONCLUSIONS

We observed that superconducting property of the protect-annealed electron-doped cuprate PLCCO is very sensitive to the annealing condition such as the annealing temperature. We performed ARPES experiments to investigate the origin of the better superconducting property in PLCCO#2. Remarkably, PLCCO#2 shows almost no pseudo-gap induced by AFM, while PLCCO#1 shows strong pseudo-gap. We conclude that the AFM has to be eliminated during through the annealing process to achieve a higher superconducting-transition temperature and larger superconducting-volume fraction in the electron-doped cuprates.

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