Effects of annealing on the electronic structure of the electron-doped high-$T_c$ superconductor Nd$_{1.85}$Ce$_{0.15}$CuO$_4$

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Abstract. We have performed an angle-resolved photoemission spectroscopy (ARPES) study of as-grown Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ (ag-NCCO) and annealed Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ (an-NCCO) samples in order to elucidate how the superconductivity is induced by the annealing process in Nd$_2$Ce$_2$CuO$_4$. In the ARPES spectra of ag-NCCO, a gap opens in the nodal region due to the effects of antiferromagnetism. This nodal gap is closed in an-NCCO, indicating that the effects of antiferromagnetism become weaker by annealing, similar to the previous ARPES results on Pr$_{1.85}$Ce$_{0.15}$CuO$_4$. However, while in as-grown Pr$_{1.85}$Ce$_{0.15}$CuO$_4$ the gap opens on the entire Fermi surface, in ag-NCCO the gap does not open around ($\pi$, 0).

1. Introduction

Since the discovery of the electron-doped high-$T_c$ superconductors (HTSCs) with the $T'$-type structure [1], their similarity and dissimilarity to the hole-doped HTSCs has been under dispute [2, 3, 4]. In addition, the electron-doped HTSCs show interesting physical properties in their own right. Materials where Nd$^{3+}$ in Nd$_2$Ce$_2$CuO$_4$ is replaced by La$^{3+}$, Pr$^{3+}$, Sm$^{3+}$, or Eu$^{3+}$ are also electron-doped HTSCs with the $T'$-type structure and show systematic changes in the lattice constant [5, 6], $T_c$ [5, 7], and electronic structure [8], induced by the changes in the ionic radius of the substituted lanthanide ion. In electron-doped HTSCs, in addition to the Ce-atom substitution for the lanthanide ion, it is necessary to anneal the samples in order to induce superconductivity, unlike the hole-doped HTSCs, but the precise role of the annealing has been controversial. Shortly after the discovery of the electron-doped HTSCs, the effect of annealing was only regarded as the removal of oxygen [1, 9, 10, 11, 12]. However, subsequent studies by transport [13, 14, 15], neutron [16, 17], infrared-transmission [18, 19], optical [20, 21], and ultrasound [22] experiments have provided more information about the mechanism of the annealing process. The neutron and infrared-transmission studies have elucidated the crystallographic position of the removed oxygen, suggesting that the oxygen defects induce the superconductivity through destroying the long-range antiferromagnetic order and increasing the mobility of charge carriers [16, 17, 18, 19]. In the optical studies, the pseudogap was observed in as-grown samples and
these were filled with increasing temperature, which was not observed in annealed samples [20, 21]. Furthermore, recent neutron studies have demonstrated that the impurity phase, which lacks in the as-grown samples, was created during the annealing process [23, 24, 25]. Recently, the electronic structure of Pr$_{1.85}$Ce$_{0.15}$CuO$_4$ (PCCO) before and after annealing was investigated by angle-resolved photoemission spectroscopy (ARPES) [26]. The observed photoemission spectra showed that in as-grown PCCO samples the gap opens on the entire Fermi surface, where the gap size becomes maximum around the hot spot. On the other hand, in annealed PCCO the gap was filled. In addition, shadow bands due to antiferromagnetism disappeared with annealing. In order to confirm that these observations are characteristic of the electron-doped HTSCs, it is necessary to perform ARPES studies on other electron-doped HTSCs.

In this paper, we report on an ARPES study of as-grown Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ (ag-NCCO) and annealed Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ (an-NCCO) and compare the results with other experimental results. The observed Fermi surface and band dispersion in ag-NCCO showed that the gap was observed around the nodal direction while in an-NCCO the gap was closed, confirming that the effects of antiferromagnetic interaction become small with annealing process.

2. Experiment

High-quality single crystals of optimally doped Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ were grown by the traveling solvent floating zone method. Annealing was carried out at 920°C for 24 hours in an Ar gas. The $T_c$ of an-NCCO was ~22 K while ag-NCCO did not show superconductivity. The ARPES measurements were performed at beamline 28A of Photon Factory (PF), Institute of Materials Structure Science, High Energy Accelerators Research Organization (KEK), using incident photons with 55 eV with circularly polarization. We used a five-axis manipulator [27] and a SCIENTA SES-2002 electron-energy analyzer in the angle mode, with which one can collect spectra over ~14 degree, corresponding to the momentum width of ~1.1$\pi$ (in units of 1/$a$, where $a$ ~ 3.9 Å is the lattice constant). The total energy resolution and angular (momentum) resolution were 15 meV and 0.2 degree (0.01$\pi$), respectively. Samples were cleaved in situ in an ultrahigh vacuum of 10$^{-11}$ Torr to obtain clean surfaces. The incident photon beam angle was at approximately 45 degree to the sample surface. The measurements were made at ~10 K. The Fermi edge of gold was used to determine the Fermi level ($E_F$) position and the instrumental resolution before and after the ARPES measurements.

3. Results and Discussion

Figure 1 shows the plot of ARPES intensity near $E_F$ in an-NCCO and ag-NCCO as a function of two-dimensional momentum. Spectral weight has been integrated within a ±30 meV window. White circles in Fig. 1 represent the peak positions of momentum distribution curve (MDC) and represent the Fermi surface or the “underlying” Fermi surface. The shape of the Fermi surface is similar to that predicted by the LDA band-structure calculation [28]. However, the suppression of the intensity is seen near the hot spot, which is the intersecting point of the underlying Fermi surface and the antiferromagnetic Brillouin zone boundary. This is due to the ($\pi$, $\pi$) scattering as discussed in the previous ARPES studies [29, 30]. From Fig. 1(a) and (b), one can recognize that the spectral intensity around ($\pi$/2, $\pi$/2) in an-NCCO is stronger than that in ag-NCCO. In order to understand the difference of the nodal spectral intensity between an-NCCO and ag-NCCO, we represent the energy distribution curves (EDCs) at the nodal point in Fig. 2(b), and the ARPES intensity plot in the nodal direction in Figs. 3(c) and (d). From these plots, particularly from Fig. 2(b), one can see that at the nodal point the gap opens in ag-NCCO and not in an-NCCO.

Now, we shall compare the ARPES results with other experimental results. The electrical resistivity of an-NCCO is smaller than that in ag-NCCO [13, 14, 15, 20]. From the Fermi surface mapping and EDCs in Figs. 1 and 2, in an-NCCO a gap does not open both in the ($\pi$, 0) and nodal regions while in ag-NCCO the gap does not open around the ($\pi$, 0) region but opens around the nodal region. We consider that because of this difference, the electrical resistivity in an-NCCO is low compared with that in ag-NCCO. Also, according to the optical studies, the pseudogap in ag-NCCO is
filled with increasing temperature while in an-NCCO the pseudogap feature was not clearly observed [20]. We surmise that since the gap opens in a wide region of $k$-space in ag-NCCO compared with an-NCCO, the pseudogap feature was clearly observed in the optical conductivity of ag-NCCO.

**Figure 1.** Plot of ARPES intensity at $E_F$ in an-NCCO (a) and ag-NCCO (b) as a function of the two-dimensional wave vector ($k_x$, $k_y$). Energy distribution curves have been integrated within a ±30 meV window around $E_F$. The data were taken over a Brillouin zone octant and symmetrized with respect to the (0,0) - ($\pi$, $\pi$) line. White circles show peaks in momentum distribution curves, indicating the Fermi surface. Red solid curves and green dashed curves show the Fermi surface obtained by tight-binding fit assuming the antiferromagnetic and paramagnetic states, respectively.

**Figure 2.** EDCs on the Fermi surface in the ($\pi$, 0) region (a) and in the nodal region (b) of an-NCCO (black dotted curves) and ag-NCCO (red solid curves). The momentum position is shown in the inset. In the ($\pi$, 0) region, the gap was not observed for both samples while in the nodal region the gap was observed in ag-NCCO.
Figure 3. ARPES intensity plot of an-NCCO and ag-NCCO in the energy-momentum space for two cuts in the Brillouin zone. White squares and white circles denote EDC peak positions and MDC peak positions, respectively. Green solid curves and dotted curves represent the paramagnetic energy band and shadow band obtained by tight-binding fit, respectively. The red dashed curves represent the calculated antiferromagnetic band. (a) an-NCCO near the ($\pi$, 0) region. (b) ag-NCCO in the ($\pi$, 0) region. (c) an-NCCO in the nodal region. (d) ag-NCCO in the nodal region.

In order to quantitatively evaluate the difference between an-NCCO and ag-NCCO, we have performed a tight-binding analysis as follows. We have assumed the single-band model and two-dimensional antiferromagnetic ordering and obtained the band structure:

$$E = \varepsilon_0 \pm \sqrt{\Delta E^2 + 4t^2 (\cos k_x a + \cos k_y a)^2 - 4t' \cos k_x a \cos k_y a - 2t'' \cos 2k_x a + \cos 2k_y a},$$

where $t$, $t'$, and $t''$ represent transfer integrals between the nearest-neighbor, second-nearest-neighbor, and third-nearest-neighbor Cu sites, respectively, $\varepsilon_0$ represents the center of the band relative to the chemical potential, and $2 \Delta E$ the energy difference between the spin-up and spin-down sites. We have fitted the calculated band to the white circles in Fig. 1 by adjusting the parameter $-t'/t$, which represents the curvature of the Fermi surface. Note that we have fixed the parameter $-t''/t'$ as -0.50. As a result, we have obtained $-t'/t = 0.20$ for both an-NCCO and ag-NCCO. Also, we have fitted the
calculated band to the white squares in Fig. 3 and obtained $\Delta E = 0.07$ eV and $\Delta E = 0.09$ eV for an-NCCO and ag-NCCO, respectively, quantitatively indicating that the effects of antiferromagnetism in ag-NCCO is stronger than those in an-NCCO.

Finally, we compare the present ARPES results on Nd$_{1.85}$Ce$_{0.15}$CuO$_4$ with the previous study on PCCO [26]. In both samples, the gap was observed in as-grown samples and this gap was filled through the annealing process. However, in as-grown PCCO, the gap was open on the entire Fermi surface while in ag-NCCO the gap was open only around the nodal region, and not around $(\pi, 0)$. One possible origin of this difference is that the as-grown PCCO has more excess oxygen compared with ag-NCCO and that the excess oxygen causes a disorder of the electrostatic potential and hence carrier localization. Further systematic annealing dependence study is necessary to confirm the gap opening around the $(\pi, 0)$ region.

4. Conclusion

We have performed an ARPES study of an-NCCO and ag-NCCO in order to investigate the effects of annealing on the electronic structures. Around the nodal point in two dimensional $k$-space, the gap opens in ag-NCCO and not in an-NCCO, which we attribute to the effects of antiferromagnetism. On the other hand, around the $(\pi, 0)$ region the gap does not open both in an-NCCO and ag-NCCO. The behavior of the gap opening in ag-NCCO is consistent with the observations in the transport and optical measurements. Also, the difference in the electronic structure between ag-NCCO and as-grown PCCO was observed possibly due to the difference of the oxygen content in the as-grown state. We therefore consider that the electronic states around the nodal point should be important for the superconductivity.

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