**SUPERCONDUCTIVITY**

Observation of small Fermi pockets protected by clean CuO$_2$ sheets of a high-$T_c$ superconductor

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In cuprate superconductors with high critical transition temperature ($T_c$), light hole-doping to the parent compound, which is an antiferromagnetic Mott insulator, has been predicted to lead to the formation of small Fermi pockets. These pockets, however, have not been observed. Here, we investigate the electronic structure of the five-layered Ba$_2$Ca$_2$Cu$_4$O$_8$(F,O)$_2$, which has inner copper oxide (CuO$_2$) planes with extremely low disorder, and find small Fermi pockets centered at $(\pi/2, \pi/2)$ of the Brillouin zone by angle-resolved photoemission spectroscopy and quantum oscillation measurements. The d-wave superconducting gap opens along the pocket, revealing the coexistence between superconductivity and antiferromagnetic ordering in the same CuO$_2$ sheet. These data further indicate that superconductivity can occur without contribution from the antinodal region around $(\pi, 0)$, which is shared by other competing excitations.

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Fig. 1. Small Fermi pockets revealed by laser-ARPES. (A) FS mapping obtained by integrating ARPES intensities within an energy window of 10 meV about $E_F$. The arrows point to FSs dominated by the innermost plane (IP$_0$), the second inner planes (IP$_1$), and the outermost planes (OP), which are depicted in (C). (B) Magnified image of the area enclosed by a white dashed rectangle in (A). The scales for the horizontal and vertical axes are noted with white double-headed arrows. (C) Five CuO$_2$ sheets in the crystal structure of Ba$_2$Ca$_4$Cu$_5$O$_{10}$F,O$_2$. (D) The EDCs at the nodes [marked by colored circles in (B)] for the smaller and larger Fermi pockets (IP$_0$ and IP$_1$, respectively) and Fermi arc (OP). The inset plots the energy width of the spectral peaks ($\Delta E$) for each FS (or each CuO$_2$ sheet). The broad peak around $0.03$ eV in the red spectrum comes from the energy state of the band for IP$_0$, which stays energetically below the band of IP$_1$ [for example, see (H) and (K)]. (E to G) MDCs at $E_F$ for (H) to (J). The vertical axis values are decreased to clearly exhibit peaks for the back sides of Fermi pockets; the peaks for the pockets (fitted by Lorentzian curves) are clearly visible, whereas the one corresponding to the Fermi arc is missing (green dashed arrow). (H to J) The same images as in (K) to (M), but the color scale is changed to emphasize the folded bands; the white color is displayed at intensities greater than 0.019, 0.031, and 0.160 times those in (H), (I), and (J), respectively. (K to M) ARPES dispersions obtained along the momentum cuts indicated in (B) by white dashed lines (cut1, cut2, and cut3). (N and O) ARPES dispersions extracted along the momentum cuts indicated in (B) by green and purple arrows, respectively. (P) MDCs along the dashed lines in (O). All the data presented here were measured at 5 K.
Fig. 2. Small Fermi pockets revealed by quantum oscillations. (A) Magnetic torque signals (dHvA) at several temperatures where smooth backgrounds are subtracted (21). The angle between the field direction and the crystallographic c axis was set to be 7° during the measurements. a.u., arbitrary units. (B) The FFT spectra of the observed quantum oscillations in (A). Arrows mark the two main peaks ($F_0$ and $F_1$). The inset shows the area of the two Fermi pockets, estimated by means of dHvA and ARPES, as a percentage of the Brillouin zone area. The small peaks other than $F_0$ and $F_1$ arise owing to trivial reasons. For frequencies higher than $F_1$, the small peaks could represent higher harmonics of $F_0$ and $F_1$; however, the peak positions change with temperature, indicating that these peaks must be affected by or might even just be artifacts of noise in the raw data. The small peaks below $F_0$ are stable with temperature but are sensitive to the method of background subtraction and thus are not intrinsic (see the raw data before background subtraction in fig. S4B); we assumed a polynomial curve as the background for each quantum oscillation spectrum. Hence, artificial intensities of a wave-like structure with a low frequency are inevitably left after background subtraction. Most importantly, we have confirmed that the frequencies of the two main peaks ($F_0$ and $F_1$) are robust against both the noise in data and the method of background subtraction.

Bi2212; see fig. S3L). This indicates that the inner planes are indeed very clean and have carriers with long lifetimes; the suppression of AF fluctuations may be another factor that causes less scattering in the inner planes. To confirm the same Fermi pockets by bulk sensitive probes, we measured the de Haas-van Alphen effect (dHvA) (Fig. 2A and fig. S4B) and the Shubnikov–de Haas effect (SdH) (fig. S4A) through torque and contactless resistivity measurements, respectively; both experiments detected quantum oscillations, indicating two-dimensional pockets (fig. S5). In the fast Fourier transformation (FFT) spectra for dHvA (Fig. 2B), we find mainly two peaks at frequencies $F_0 = 147 T$ and $F_1 = 318 T$, which correspond to the FS area covering 2.1 and 4.3% of the Brillouin zone, respectively. Importantly, these values almost perfectly agree with the ARPES results (2.2 and 4.7%). The charge carriers are found to always be hole type regardless of temperature, with no sign inversion even at high magnetic fields, as confirmed by the behavior of Hall resistance against the magnetic field [see fig. S6 and related discussion (21)]. Therefore, the Fermi pockets captured by quantum oscillations are the same as those detected by ARPES, rather than the reconstructed FSs with electron-type carriers as reported for Y123 and Y124 (13).

We have also confirmed a good agreement in the mass of conduction electrons: 0.69 $m_0$ for $IP_0$ and 0.74 $m_0$ for $IP_1$ by dHvA (fig. S4C) and ~0.7 $m_0$ for the two pockets by ARPES. Another consistency is seen in the Dingle temperature ($T_D$), proportional to the scattering rate (fig. S4D), and the inverse of the mean free path ($\hbar/2\pi t_D$); the $T_D$ and $I_1$ values are estimated to be lower and longer, respectively, for the smaller pocket ($T_D = 6.5 K$, $l = 210 Å$) than those for the larger pocket ($T_D = 11.8 K$, $l = 160 Å$), which is consistent with ARPES spectra showing sharper peaks for the smaller pocket (Fig. 1D) and with the argument that $IP_0$ is cleaner than $IP_1$. We also note that these values are comparable to those of Y123 ($T_D = 6.2 K$, $l = 200 Å$) (10, 22) and lower and longer, respectively, than those of Hg1201 ($T_D = 18 K$, $l = 85 Å$) (12, 22), which further verifies that the carriers of protected inner planes have an exceptionally high mobility even in such a lightly doped regime.

The Fermi pockets are revealed by quantum oscillations and are robust against both the noise in data and the method of background subtraction. The small peaks below $F_0$ are stable with temperature but are sensitive to the method of background subtraction and thus are not intrinsic (see the raw data before background subtraction in fig. S4B); we assumed a polynomial curve as the background for each quantum oscillation spectrum. Hence, artificial intensities of a wave-like structure with a low frequency are inevitably left after background subtraction. Most importantly, we have confirmed that the frequencies of the two main peaks ($F_0$ and $F_1$) are robust against both the noise in data and the method of background subtraction.

The energy dispersion along ($\pm \pi$) of the main band ($\pm \pi/2$); the two pockets observed by laser-ARPES cannot be resolved separately because of limited resolutions in the synchrotron ARPES.

The energy dispersion along ($\pm \pi$) to ($\pi, -\pi$) crossing the pocket (Fig. 3B) can be contrasted with the large parabolic dispersion seen at $hv = 100 eV$ (fig. S7B), which selectively observes the Fermi arc band (fig. S7, A to G). To unveil the whole band shape for the Fermi pockets, we also extracted the ARPES dispersion along AFZB over multiple Brillouin zones (Fig. 3D); a periodic pattern has been obtained. The band determined by a tight-binding fit to our ARPES data is plotted in Fig. 3E. We find that the saddle point at the zone edge (25), a famous feature in cuprates, is missing. Instead, a parabola disperses down below ~1 eV at ($\pi, 0$) (see Fig. 3D). Therefore, the CDW and pseudogap states known to emerge around ($\pi, 0$) with the energy scale of ~100 meV (26–29) cannot develop in the inner planes, which lack electrons required to generate these excitations in the band structure; this is in stark contrast to the situation in the outer planes, where the pseudogap opens around ($\pi, 0$) as in other underdoped cuprates, and thus the CDW state is likewise expected to occur (30–32).

The band shape we observed is compatible with that of Mott insulating CCOC (33) and Sr$_2$CuO$_2$Cl$_2$ (SCOC) (3); however, our sample is metallic, and hence the chemical potential crosses the lower Hubbard band (Fig. 3F). In our sample, the bandwidth ($W$) is about 1.5 eV, and a kink structure is observable around ~0.5 eV in the band dispersion (see Fig. 3, B and D). Such a water-like dispersion with a large energy width of 1.3 to 2.0 eV has been commonly observed in many cuprate compounds (34), including the insulating CCOC ($W \approx 1.8$ eV) with the lower Hubbard band fully occupied (35). The Fermi pockets in the carrier-doped Mott band of our sample seem to persist above the Neel temperature $TN$ (~135 K), given that the temperature dependence of the Hall coefficient (fig. S6C) exhibits no notable variation across $TN$. This agrees

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with the ARPES studies of Mott-insulating CCOC ($T_N = 245$ K) and SCOC ($T_N = 256$ K), where the band folding has been clearly observed at room temperature ($24^\circ$) or even 100 K higher than $T_N$ ($3$).

To investigate the superconducting gap ($36^\circ-39^\circ$), we used a high-resolution laser-ARPES apparatus. In Fig. 4A, we plot the energy distribution curves (EDCs) along the Fermi pocket for IP$_1$ (red oval in Fig. 4F), especially for the main side of the Brillouin zone (green circles in Fig. 4G). As expected for a d-wave gap structure, the spectral edge reaches $E_F$ with no gap in the diagonal direction ($f = 0^\circ$; $f$ is defined in Fig. 4G), and it shifts to higher binding energies with a gap opening off the node. This gap behavior is visualized in Fig. 4B with the EDCs symmetrized across $E_F$: The nodal spectrum with one peak changes to a two-peak structure off the node, and the gap increases up to the tip of the ellipsoidal Fermi pocket ($f = 90^\circ$).

Notably, we have obtained almost the same results (Fig. 4, C and D) for the folded side of the Brillouin zone (purple circles in Fig. 4G); these results are summarized in Fig. 4E.

These results suggest that the superconductivity occurs in the inner CuO$_2$ plane (IP$_1$), rather than as a consequence of the proximity effect from the superconducting outer planes with the Fermi arc. We demonstrate this with a model calculation (fig. S8) by comparing the spectra calculated with and without a superconducting order in IP$_1$. In the latter case, the EDC at the larger Fermi pocket (mainly contributed by IP$_1$) never shows a finite superconducting gap unlike the experiment; the spectral gap is reproduced only when IP$_1$ itself is superconducting. In the model, the Fermi pockets are formed by band folding stemming from the AF order in the inner planes, so that the results also demonstrate a microscopic coexistence of the AF order and superconductivity in IP$_1$. We also note that the coexistence of the AF order and superconductivity in the lightly doped CuO$_2$ plane has been confirmed by numerical calculations for the Hubbard model ($40$–$42$).

To validate the relationship between the different layers more directly, we compared the superconducting gaps on the Fermi pocket and arc measured by ARPES (fig. S9, A to D) and found that the gap size in the pocket for OP is slightly larger than that in the Fermi arc for OP (fig. S9H). The trend is opposite to what is expected from the proximity scenario, which can therefore be ruled out. Because the Fermi pocket emerges in the doped Mott band with AF ordering (Fig. 3F), the observation of a superconducting gap along the pocket (Fig. 4E) directly demonstrates the coexistence of superconductivity and AF order in a CuO$_2$ sheet (Fig. 4H) ($15$, $16$). It is notable that such a small amount of carriers ($p \sim 0.04$) form superconducting pairs under the majority background of the AF-ordered state.

*Fig. 3. Overall band structure with Fermi pocket revealed by synchrotron-ARPES. (A) ARPES intensity map about $E_F$ over multiple Brillouin zones measured at $T = 10$ K. The data were taken at $h\nu = 70$ eV, which selectively observes the Fermi pocket (fig. S7). (B) ARPES dispersion along a diagonal momentum cut [red double-headed arrow in (A)]. (C) Magnified image of the area enclosed by a black dashed rectangle in (A). (D) ARPES dispersion along AFZB indicated in (C). Band dispersion is traced by dashed red curves, which are extracted from the band shape in (E). (E) Band dispersion determined by tight-binding fitting to our ARPES data (table S1) ($21$). (F) Schematic for the density of states in the lightly hole-doped Mott state. $N(e)$, density of states; UHB, upper Hubbard band; LHB, lower Hubbard band; CTB, charge transfer band.
Along the smallest Fermi pocket, the superconducting gap is found to be almost zero within the experimental resolution (fig. S9, F and H). This extreme difference in the superconductivity between the two pockets has two notable implications. First, the two pockets are almost separately contributed by IP0 and IP1, respectively, because otherwise the mixing of layers would produce superconducting gaps of similar magnitudes for both pockets. Second, the electronic state of IP0 less doped than IP1 should be situated outside of the Tc dome in the phase diagram.

The data showing the larger superconducting gap in the Fermi pocket than in the Fermi arc (fig. S9H) imply that the electron pairing gets more stabilized in the former despite smaller doping by avoiding the competition with other ordered states, which could develop around the zone edge (π, 0). This may be the main reason why superconductivity persists down to dopings in the close vicinity of the half-filled Mott state in the five-layered cuprates, in contrast to single-layered cuprates with disordered CuO2 layers, which are insulating up to about 10% carrier doping (29). Nonetheless, further investigations will be necessary to clarify which layer actually triggers the superconductivity in bulk because the relationship between the value of \( T_c \) and the superconducting gap magnitude in cuprates is still under debate; in the context of the pairing mechanism, it is particularly intriguing that larger pairing gaps open in the CuO2 sheet with the AF-fluctuations suppressed. Our results will contribute to solving the long-standing puzzle of the Fermi arc phenomena and urge the need for revisiting the Mott physics leading to the electron pairing in cuprates, which, up to now, has been based mainly on the research on single- and double-layered compounds with inhomogeneous electronic states.

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**SUPPLEMENTARY MATERIALS**

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Materials and Methods

Supplementary Text

Figs. S1 to S9

Table S1

References (44–49)

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