Symmetry-broken electronic structure and uniaxial Fermi surface nesting of untwinned CaFe$_2$As$_2$


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(Received 23 June 2013; revised manuscript received 27 November 2013; published 26 December 2013)

We used angle-resolved photoemission spectroscopy to make direct measurements of the electronic structure of the untwinned uniaxial state of CaFe$_2$As$_2$, the parent compound of an iron-based superconductor. The very small photon beam size, combined with the relatively large single-domain area on the crystal surfaces, allowed us to obtain the intrinsic symmetry-broken dispersions and Fermi surface (FS) geometries along the orthogonal Fe-Fe bond directions without any mechanical or magnetic detwinning processes. Comparing the optimized local density approximation calculations, an orbital-dependent band shifting is introduced to obtain better agreement, which is consistent with the development of orbital ordering. More interestingly, unidirectional straight and flat FS segments are observed near the zone center, which indicates the existence of a unidirectional charge density wave order. Our results indicate strong electronic anisotropy in CaFe$_2$As$_2$ and put strong constraints on theories for the iron-pnictide system.

I. INTRODUCTION

The recently discovered iron-pnictide superconductors provide a new platform for studying the unconventional superconductivity and have attracted massive attention in the condensed matter community. Similar to the cuprate superconductors, the iron pnictides are layered systems with transition metal $d$ electrons and have nonsuperconducting parent compounds exhibiting antiferromagnetic (AFM) order. Unlike the cuprates whose parent compounds are Mott insulators, the pnictides parent compounds are metals, yet the transport and optical measurements on iron pnictides show a very large resistivity and a small Drude weight. This indicates that the iron pnictides may not be conventional metals, and the electron correlations could also play a crucial role as they do in the cuprates.

It has been proposed that in cuprates the strong electron correlations could lead the system into exotic quantum electronic liquid crystalline phases with translational and rotational symmetries broken (stripes or smectic phase) or only rotational symmetry broken (nematic phase) and cause the strong in-plane anisotropies observed by transport measurements, neutron scattering studies, and scanning tunneling microscope (STM) studies. As for iron pnictides, the recent inelastic neutron scattering and transport measurements indicate large in-plane anisotropy. The STM studies also reveal unidirectional electronic nanostructures, which are explained as evidence of the existence of a nematic phase. These observations of broken C4 tetragonal symmetry have been proposed to stem from the development of nematic orbital ordering and could be also explained as the result of pure spin interactions. Furthermore, the recent STM studies on Ca(Fe$_{1−x}$Co$_x$)$_2$As$_2$ and transport measurements on Ba(Fe$_{1−x}$Co$_x$)$_2$As$_2$ both indicate that the anisotropy of the in-plane resistivity originates from the anisotropic scattering by dopant-induced impurity states.

In this paper, we report a systematic angle-resolved photoemission spectroscopy (ARPES) study on high-quality CaFe$_2$As$_2$ single crystals, the parent compound of an iron-based superconductor. Unlike the previous ARPES studies either on twinned iron-pnictide single crystals or mechanically detwinned single crystals, we measured the high-quality CaFe$_2$As$_2$ crystals with a very small photon beam size ($\sim 50 \mu m \times 50 \mu m$). This, together with the relatively large single-domain area on the crystal surfaces, allowed us to make measurements of monodomain regions of the cleaved sample surfaces without any detwinning processes. The ability to deconvolve the twinned structure combined with our detailed polarization-dependent studies, $k$-dependent studies, and local density approximation (LDA) calculations, enabled us to make a comprehensive analyses of the electronic structure of a pnictide to date, which indicates strong electronic anisotropy in CaFe$_2$As$_2$ and puts strong constraints on theories for describing the iron-pnictide system.

II. EXPERIMENTAL DETAILS

High-quality single crystals of CaFe$_2$As$_2$ with large untwinned regions were grown by the Sn-flux method and good quality of the samples has been verified by multiple techniques, as described in Ref. 27. The magnetic susceptibility, resistivity, and heat capacity all show a first-order phase transition at $T_0 = 171$ K. The crystals were cleaved in situ and measured in an ultrahigh vacuum better than $3 \times 10^{-11}$ torr. The ARPES experiments were performed at beamline 7.0.1 and 10.0.1 at the Advanced Light Source (ALS), Berkeley. The angular resolution of the experiments was approximately 0.3º, and the energy resolution was 20–35 meV (depending upon photon energy). The photon beam spot size at sample is about 50 $\mu m \times 50 \mu m$ for beamline 7.0.1 and about 150 $\mu m \times 150 \mu m$ for beamline 10.0.1 by choosing proper...
III. RESULTS

Figure 1(a) shows a schematic of the in-plane crystal structure of AFe$_2$As$_2$-type ($A =$ Ba, Sr, or Ca) iron pnictides. In the magnetic phase, the AFM spin ordering happens along the $x$ direction in the crystal coordination, while the ferromagnetic (FM) spin ordering happens along the $y$ direction. Figures 1(b) and 1(c) show the corresponding three-dimensional (3D) Brillouin zones (BZ) in the tetragonal and the AFM-orthorhombic (AFMO) state, respectively. Selected high-symmetry points in the momentum space are labeled on the plots, while $\Gamma-X/\gamma-x$ is along the AFM direction and $\Gamma-Y/\gamma-y$ is along the FM direction. Figures 1(d) and 1(e) show the experimental Fermi surfaces (FSs) of CaFe$_2$As$_2$ taken with 80 eV photons in the nonmagnetic tetragonal state and the AFMO state, respectively. The photon energy-dependent studies (details discussed later) indicate that the 80 eV photons probe the electronic structure in the $Z$ plane in momentum space. At high temperature, the FS of the nonmagnetic tetragonal state shows a very uniform spectral weight distribution near the zone center. At low temperature, on the contrary, the FS of the AFMO state shows a drastic FS reconstruction with very complex fine structure. In particular, it does not show a fourfold symmetry: there are closed small Fermi pockets along one Fe-Fe bond direction, while they are absent along the orthogonal direction. By comparing our LDA calculation (details discussed later), we assign the direction that contains the small Fermi pockets to the $y$ direction (FM direction) and the orthogonal direction to the $x$ direction (AFM direction). Figures 1(f)–1(j) show the FS and intensity maps at different binding energies (BE). They cleanly show that along the $y$ direction, the small Fermi pockets are electronlike, while along the $x$ direction there are only holelike features, i.e., when going to deeper BE the spectral weight spreads further away from the zone center. Hence, the plots shown in Fig. 1 present a clear uniaxial electronic structure of CaFe$_2$As$_2$ in the AFMO phase.

To further understand the electronic structure of CaFe$_2$As$_2$, a polarization-dependent ARPES study using three different experimental geometries has been performed. Figures 2(a), 2(e), and 2(i) are the schematics of three different experimental configurations. In Figs. 2(a) and 2(e), the incident photon beam’s polarization is in the mirror plane of the sample, and the sample is placed so that the beam’s polarization is perpendicular to the mirror plane. Here, we note that for setup in Figs. 2(a) and 2(e), the small beam size at beamline 7.0.1 gives us a chance to probe the untwinned electronic structure along different directions in the crystal, while for setup in Fig. 2(i), the relatively large beam spot at beamline 10.0.1 always gives out the twinned result.

The polarization-dependent study allows us to emphasize or deemphasize different states according to their orbital symmetries—for example, we turn on the flat portions of FS near the zone center in Fig. 2(j) but turn these off and turn on complementary portions of the FS in Fig. 2(f). Experimental dispersions along high-symmetry cuts [white lines in Figs. 2(b), 2(f), and 2(j)] are shown in Figs. 2(c), 2(g), and 2(k), while Figs. 2(d), 2(h), and 2(l) show the extracted dispersions along these cuts as well as the allowed orbital symmetries (here, we utilize the tetragonal BZ so as to be able to utilize standard orbital symmetry labels): since the $Z'X'/Z'Y'$ cuts lie in the plane of mirror symmetry ($xz/yz$ plane) in the crystal, the electronic states that are even (odd) under reflection with respect to this mirror plane can only be excited by light with the electric field polarization pointing in (out of) the mirror plane. Then, in the Fig. 2(a) setup, the dispersions observed along the high-symmetry direction should have $xz/x^2-y^2/z^2$ symmetry, while the dispersions observed along the high-symmetry direction in the Fig. 2(e) setup should contain $yz/x^2-y^2/z^2$ symmetry. For the Fig. 2(i) setup, the dispersion should contain $xy/yz$ and/or $xy/xz$ symmetry due to the domain-averaging effect. Here, we note that the shadow areas in Figs. 2(d) and 2(h) indicate the spectral weights whose dispersion could not be resolved in the experiment.

Figure 3 shows a compilation of the FS data, dispersion data, and orbital data, as well as a comparison of our LDA calculations. Figures 3(a) and 3(d) are the experimentally
extracted dispersions and FS, with symmetry information color coded. Here, we ignore the possible $x^2-y^2$ and $z^2$ symmetry component for simplification, consistent with the band calculation that indicates that the near $E_F$ states are dominantly the $xy$ and $xz/yz$ states. Figures 3(b) and 3(e) are raw data taken with mixed polarizations so as to show all symmetry states. Figures 3(c) and 3(f) present the FS and dispersions along the high-symmetry directions (at $k_z = 2\pi/c$) from our LDA calculations (based on the Korging-Kohn-Rostocker (KKR) methodology for complex crystals). Here, we found that with a bandwidth renormalization factor of 2.5, the LDA calculations with magnetic moment of 0.19 $\mu_B$ give us the best match to the experimental result. The renormalization factor of 2.5 that is similar to what has been determined from other experiments is one of the aspects that indicate the importance of the electron correlations in the pnictides. To further improve the agreement between the theory and experiment, we shift the two calculated bands with $yz$ symmetry (green dashed lines) up by 0.1 eV (green solid lines) to match the bands $\gamma_1$, $\gamma_2$ in Fig. 3(d). After this modification, the overall band calculation matches the experimentally determined dispersions reasonably well, though it is certainly not perfect. Here, we note that the upshifting of the bands with specific orbital property may be a sign of the developing of the orbital ordering, which has been advanced by recent theoretical studies.

If one takes a closer look at the small Fermi pockets along the $y$ direction, two long, parallel, and straight FS segments can be found, which indicates an incommensurate FS nesting as indicated by $\mathbf{q}_1$ in Fig. 3(b). Figures 4(a) and 4(b) show the FS in the AFMO phase taken with 80 and 99 eV photons, corresponding to $k_z = Z$ and $\Gamma$ at the zone center, respectively. We found that both FS contain the straight segments with the incommensurate nesting $q_1 \approx 0.33(-\frac{\pi}{a}, \frac{\pi}{a})$. Figures 4(c) and 4(d) show the band structure with the $yz$ bands upshifted by 0.1 eV. The overall band structure matches the experimentally determined dispersions reasonably well.
FIG. 4. (Color online) (a) and (b) FS taken with 80 and 99 eV photons at $T = 20$ K. The incommensurate FS nesting vector $\vec{q}_1$ is labeled on both plots, $\vec{q}_0$ represents the AFM nesting vector. (c) and (d) $k_z$ dispersions of the Fermi crossings along the blue and yellow cuts of (a) and (b). The dashed lines are guides for the eyes of the $k_z$ dispersions, while the blue solid lines indicate the persistence of the nesting vector $\vec{q}_1$, in momentum space. (e) The measured FS of Ca(Fe$_{1-x}$Co$_x$)$_2$As$_2$ sample with $x \sim 3.5\%$ at 40 K. (f) Second-derivative image of the FS topology shown in panel (e). Possible nesting along $ZY'$ direction with nesting vector $\vec{q}_1''$ is indicated by the white dashed lines. (g) Dispersions along the high-symmetry cuts ($ZX'$ and $ZY'$) of Co-doped sample.

and 4(d) show the $k_z$ dispersions of the Fermi crossings along $\Gamma X/ZX'$ and $\Gamma Y/ZY'$ directions, as indicated by the yellow and blue cuts in Figs. 4(a) and 4(b), respectively. Consistent with the asymmetric electronic structure, Figs. 4(c) and 4(d) exhibit very different $k_z$ dispersions. More importantly, along the $\Gamma Y/ZY'$ direction, where the incommensurate FS nesting happens, the Fermi crossings of the nesting bands with nesting vector $\vec{q}_1$ have minimal $k_z$ variation, as indicated by the solid blue lines in Fig. 4(d). This result confirms that the incommensurate FS nesting observed along $\Gamma Y/ZY'$ direction (FM direction) persists through the whole momentum space with an essentially unchanged nesting vector $\vec{q}_1 \approx 0.33(-\frac{\pi}{4}, \frac{\pi}{4})$. Here, we note that among the ARPES studies of the other materials in the AFe$_2$As$_2$ family,21–26,34–39 a fourfold incommensurate FS nesting near $\Gamma$ point with nesting vector $\vec{q} \approx 0.3(\frac{\pi}{4}, -\frac{\pi}{4})$ was also reported in BaFe$_2$As$_2$ recently.24 This fourfold symmetric nesting could be explained as the averaged result due to sample twinning. Furthermore, our measurements on Ca(Fe$_{1-x}$Co$_x$)$_2$As$_2$ ($x = 3.5\%$) give a similar symmetry-broken electronic structure and a slightly smaller FS nesting vector $\vec{q}_1 \approx 0.24(-\frac{\pi}{4}, \frac{\pi}{4})$, as shown in Figs. 4(e)–4(g). The difference of the nesting vector between CaFe$_2$As$_2$ and its Co-doped compound is fully consistent with the electron-doped effect based on a rigid band-shifting picture.

IV. DISCUSSIONS

The observed symmetry-broken electronic structure at low temperature is roughly duplicated by our LDA calculation based on the spin-density wave (SDW) band-folding and hybridization picture. This provides strong evidence for the validity of the itinerant SDW approach to the pnictide systems, but there are also several very important features that are not caught by our LDA calculation. First, an orbital-dependent band shifting is introduced to get better agreement between the calculation and the experimental dispersion, which is consistent with the development of orbital ordering. We also note that our observed FS topology shows different symmetry properties of inner ($xy/yz$) and outer ($yz$) parts of the electron pockets, as shown in Fig. 3(a). This is consistent with the recent SDW plus orbital-ordering calculation,40 which indicates that the inner and outer pockets will be dominated by different orbitals if a partial orbital ordering was included in the calculations. Recently, it has been proposed that the orbital order could introduce the structural distortion and the long-range SDW order in the pnictides system, while our result provides strong evidence for the existence of the orbital ordering.43 It has been proposed that the in-plane resistivity anisotropy observed by transport measurements could also be explained by developing orbital ordering,40 and one needs to shift $d_{xz}$ orbitals up to give rise to the larger resistivity along $y$ direction (FM direction). Our result indicates an upshifting of $d_{xz}$ orbitals instead of $d_{yz}$ orbitals along $\Gamma X/ZX'$ direction; a similar upshifting of $d_{xz}$ band along the $\Gamma Y$ direction is also reported in mechanically detwinned BaFe$_2$As$_2$ samples.23 This discrepancy indicates that the orbital ordering may not be the main reason for the in-plane resistivity anisotropy. Recently, the STM studies on Ca(Fe$_{1-x}$Co$_x$)$_2$As$_2$ indicate that by introducing dimer impurity state, the quasiparticle interference (QPI) pattern obtained from the STM measurement shows surprising agreement with the QPI pattern obtained from our band structure; thus, the anisotropy of the in-plane resistivity could very likely originate from the anisotropic scattering by dopant-induced impurity states.

Beyond the possible orbital ordering, the unusual uniaxial FS nesting could not be quantitatively duplicated by any theoretical calculations so far. The gapless incommensurate FS nesting observed at low temperature may be explained as the failed charge density wave order, where the nesting instability gives way to other orders, such as SDW or superconductivity. We also noticed a valley density wave picture proposed by Cveticovic and Tesanovic,41 which argues that the iron-pnictide physics can be understood as the competition between superconductivity and a combination of spin, charge, and orbital density waves at the wave vector that connects the valleys (i.e., electron and hole pockets). Although this valley density wave cannot fully explain the FS nesting observed in our experiment, it did open the possibility of the existence of the charge density instability in iron-pnictide systems. Further theoretical efforts are required to understand the FS nesting observed in our experiment.

In summary, our studies on CaFe$_2$As$_2$ indicate that beyond the SDW order and superconducting state, there are also other possible competing orders in the iron-pnictide materials, such as orbital ordering and charge ordering, and both indicate strong electronic anisotropy. The coexistence of all these possible orders puts strong constraints on theories for describing the iron-pnictide materials.
ACKNOWLEDGMENTS

The authors thank David Singh, Igor Mazin, Milan Allan, and J. C. Davis for helpful discussions. This work was supported by the Division of Materials Science and Engineering, Basic Energy Sciences, US Department of Energy (DOE) Grants No. DE-FG02-03ER46066, No. AC03-76SF00098, and No. DE-FG02-07ER46352 and benefited from the allocation of supercomputer time at National Energy Research Scientific Computing and Northeastern University’s Advanced Scientific Computation Center. ALS is supported by the Director, Office of Science (DOE) under Contract No. DE-AC02-05CH11231. The work at Los Alamos National Laboratory was performed under the auspices of the US DOE.


