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This article is available at IRis: http://iris.lib.neu.edu/physics_fac_pubs/521
Fermi-surface topology and low-lying electronic structure of the iron-based superconductor \( \text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_2\text{As}_2)_5 \)

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(Received 25 October 2011; revised manuscript received 3 February 2012; published 20 March 2012)

We report a study of low-energy electronic structure and Fermi surface topology for the recently discovered iron-based superconductor \( \text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_2\text{As}_2)_5 \) (the 10-3-8 phase, with \( T_c \sim 8 \) K), via angle-resolved photoemission spectroscopy (ARPES). Despite its triclinic crystal structure, ARPES results reveal a fourfold symmetric band structure with the absence of Dirac-cone-like Fermi dots (related to magnetism) found around the Brillouin zone corners in other iron-based superconductors. Considering that the triclinic lattice and structural supercell arise from the \( \text{Pt}_3\text{As}_8 \) intermediary layers, these results indicate that those layers couple only weakly to the FeAs layers in this new superconductor at least near the surface, which has implications for the determination of its pairing mechanism.

DOI: 10.1103/PhysRevB.85.094510 PACS number(s): 74.70.Xa, 74.25.Jb, 74.10.+v, 74.70.Dd

I. INTRODUCTION

The recent discovery and characterization of superconducting phases in the Ca-Fe-Pt-As system \( \text{Ca}_{10}(\text{Pt}_3\text{As}_8)(\text{Fe}_2\text{As}_2)_5 \) (Refs. 1–4) has potentially significant impact on the field of iron-based high-\( T_c \) superconductors.\(^5\)–\(^12\) Most importantly, these phases serve as ideal platforms for systematic studies of the physics of the intermediary layers and their impact on the superconducting properties, which is an important yet open question in the field of arsenide superconductivity. In high-\( T_c \) cuprates,\(^13\)–\(^17\) such a study is made possible by the availability of materials such as the \( \text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+x} \) \( (n = 1–3) \) series,\(^16,17\) within which one finds a drastic correlation between the number of intermediary layers and the superconducting transition temperature \( (T_c) \). In the iron pnictides, a similar type of survey has been previously unavailable due to the lack of appropriate systems: One needs to search for a series of stoichiometric materials with different but systematically adjusted chemical compositions in either the iron-containing layers or the intermediary layers. The unique crystal structures in the Ca-Fe-Pt-As systems, on the other hand, yield drastically different symmetries and periodicities for the layers of FeAs tetrahedra and the intermediary layers. Therefore, the intralayer (hopping within the FeAs layers) and interlayer (hopping between the FeAs and Ca-PT-As layers) contribution to the density of states at the Fermi level \( (E_F) \) can be uniquely distinguished. Studies of the electronic structure of the Ca-Fe-Pt-As system are thus of crucial importance toward the understanding of the interlayer physics and the microscopic mechanism of high-\( T_c \) superconductivity in the iron pnictides.

In this paper we report a study of the electronic structure of the Ca-Fe-Pt-As system \( n = 3 \) [the 10-3-8 phase with \( T_c \sim 8 \) K] using angle-resolved photoemission spectroscopy (ARPES) as well as first-principles calculations. ARPES measurements reveal the three-dimensional Fermi surface topology and the band structure close to \( E_F \). We observe well-defined Fermi surfaces with tetragonal symmetry that are similar to those of other iron-based superconductors, even though arising from an unambiguously triclinic crystal structure with a larger in-plane unit cell. First-principles band calculations find very small contribution of the platinum density of states at \( E_F \) for the 10-3-8 phase. These results are indicative of a weak interlayer hopping between the FeAs and the PtAs intermediary layers in this Ca-Fe-Pt-As system.

II. METHODS

High-quality single crystals of the 10-3-8 phase used in this study were grown by a conventional flux method.\(^2\) ARPES measurements were performed in the Synchrotron Radiation Center (SRC), Wisconsin, using a VG-Scienta R4000 electron analyzer. Energy resolution was set to 10–30 meV. Samples were cleaved \( \text {in situ} \) and measured at 10–30 K under a vacuum condition better than \( 4 \times 10^{-11} \) Torr. The samples were found to be very stable and without degradation for the typical measurement period of 20 h. First-principles calculations are based on the density functional theory (DFT) framework plus the local density approximation (LDA), the Ceperley-Alder exchange-correlation functional,\(^18\) and projector augmented wave method,\(^19\) all implemented in the VASP package.\(^20\) The crystal structure of the 10-3-8 phase is taken from Ref. 2, and the off-(\( \text{Pt}_3\text{As}_8 \)) Pt atom is assigned to a position above the \( \text{Pt}_3\text{As}_8 \) plane.\(^2\) The self-consistency of bulk calculation is done with \( 8 \times 8 \times 8 \) \( k \)-point mesh. For in-plane Fermi surface calculation, the \( k \) mesh is increased to \( 201 \times 201 \) in the \( k_x \) and \( k_y \) plane. The total energy convergence with respect to the \( k \) point is 0.3 meV per atom. The kinetic energy cutoff is 280 eV.

III. RESULTS AND DISCUSSION

We begin our discussion with a detailed examination of the crystallographic properties of the 10-3-8 single crystal, as summarized in Fig. 1. This crystal has a triclinic unit cell with primitive vectors of length \( a = b = 8.759 \) Å, \( c = 10.641 \) Å, \( \alpha = 94.744^\circ \), \( \beta = 104.335^\circ \), and \( \gamma = 90.044^\circ \) \( (\text{Ref. }2) \).
The in-plane triclinic unit cell is essentially a \( \sqrt{3} \) of the 10-3-8 phase. (b)–(c) Schematic crystal structure in (b) the \( \alpha \)-\( \beta \) plane and (c) three dimensions. (d) Low-temperature resistivity (right axis) and magnetic susceptibility (left axis) for the 10-3-8 phase. (e) Laue picture of a 10-3-8 single crystal. Reflection peaks for both the triclinic (yellow circles) and tetragonal (orange squares) lattices are clearly observed.

[see Fig. 1(a)–1(e) for definitions]. Markedly, such a triclinic atomic arrangement is experienced only by the platinum atoms in the crystal; the calcium atoms and the FeAs\(_4\) tetrahedra arrange in a tetragonal fashion with lattice parameters \( a_0 = b_0 = 3.917 \) Å, \( c_0 = 20.548 \) Å. From Fig. 1(b) one notices that the in-plane triclinic unit cell is essentially a \( \sqrt{3} \) superlattice that forms along the (210) direction of the tetragonal cell, making an in-plane inclusion angle of \( \theta = \arctan(1/2) = 26.56^\circ \) and a length relation \( \sigma = \sqrt{3}a_0 \) between the two lattices.

Figure 1(c) reveals that the top and bottom surface centers of the triclinic unit cell displace horizontally via an in-plane vector \( (a_0/2, a_0/2) \). Therefore, the height of the tetragonal cell measures \( c_0 = 2\sqrt{c^2 - a_0^2/2} = 20.548 \) Å. If the interlayer hopping between the PtAs and FeAs layers is weak, the ARPES Fermi surface should reflect a similar topology to the other prototype pnictides, with possibly weak FeAs shadow bands associated with superlattice folding and additional features associated with the PtAs layer. Figure 1(d) presents the superconducting properties of the 10-3-8 single crystals used for ARPES measurements. Both the resistivity and magnetic susceptibility data show clear signature of superconductivity at \( T_c \sim 8 \) K. The transition width in temperature is less than 3 K, indicating high quality and spatial homogeneity for the as-grown crystals.

Figure 1(e) shows the x-ray Laue picture of a 10-3-8 crystal. Reflection peaks are clearly resolved, and corresponding high-symmetry directions are marked and labeled. It is very important to point out here that crystal twinning effect is unlikely to hinder the ARPES observation of the PtAs superlattice. It is true that a sufficiently large crystal must contain structural domains in which the triclinic superlattice is rotated by either \( \theta \) or \( -\theta \) with respect to the tetragonal lattice. Thus, the ARPES signal for the triclinic PtAs lattice contains ingredients from both domains, and the intensity for signal from each domain is weakened. We argue here, based on the x-ray Laue picture, that this effect should not be the main reason for the invisibility of the ARPES superlattice signal. In Fig. 1(e) reflection peaks for the triclinic lattice (yellow circles) are clearly observed at a clockwise angle of \( \theta \) (±0.1° accuracy) with respect to the tetragonal lattice (orange squares). In the counterclockwise angle of \( \theta \), however, reflection peaks are not present (or the intensity is very weak). This observation points out that the domains may have a preferred orientation, which limits the possible influence on the ARPES visibility. We further state here that, even if there is no preferred orientation for the structural domains, the ARPES signal for both domains will still be visible given a large enough interlayer hopping, since these domains are well defined by bright peaks in x-ray diffraction. Therefore, the corresponding ARPES intensity will be comparable to that of the tetragonal lattice.

We now present the ARPES data for the Fermi surface topology of the 10-3-8 phase. Figure 2(a) shows the Fermi surface plots for four different photon energies. The circular or diamond-shaped \( \alpha_1 \) and \( \alpha_2 \) Fermi pockets around the zone center as well as the elliptical \( \beta_1 \) Fermi pocket around the zone corners are clearly observed. Raw ARPES intensity maps in Fig. 2(b) and the corresponding energy distribution curves (EDCs) in Fig. 2(c) (cuts nos. 1 and 2) verify the holelike nature of the \( \alpha_1 \) and \( \beta_2 \) bands and the electronlike nature of the \( \beta_1 \) band. There is a less dispersive but clearly visible band at a binding energy of \( \sim 0.2 \) eV [tracked by brown markers in Fig. 2(c)]. First-principles calculation shows a considerable contribution of the Pt \( d \) orbitals to the total density of states (DOS) at about 0.2–0.3 eV below \( E_F \). Thus, this band may be influenced to some extent by the Pt \( 5d \) orbitals. Figure 2(a) also reveals that the shape and sizes of the X electron pockets at the Brillouin zone corners are different than those of the observed holelike Fermi surfaces at the zone center. As a result, the nesting condition among these Fermi surfaces is not perfect. Based on the ARPES \( k-E \) maps [Fig. 2(b)], we also calculate the Fermi velocities for the three Fermi crossing bands \( \alpha_1, \alpha_2, \) and \( \beta_1 \). The values are \( v_F(\alpha_1) \sim 0.494 \) eV Å.

FIG. 1. (Color online) Crystallographic and superconducting properties of Ca_{12}(Pt3As5)(Fe2As2)\(_x\) (10-3-8). (a) Crystal structure of the 10-3-8 phase. (b)–(c) Schematic crystal structure in (b) the \( \alpha \)-\( \beta \) plane and (c) three dimensions. (d) Low-temperature resistivity (right axis) and magnetic susceptibility (left axis) for the 10-3-8 phase. (e) Laue picture of a 10-3-8 single crystal. Reflection peaks for both the triclinic (yellow circles) and tetragonal (orange squares) lattices are clearly observed.
with blue (dark gray), green (medium gray), and pink (light gray) in Fig. 2(b)–2(c).

Intensity variation is observed for the kα pockets with photon energy, i.e., dispersion along the kz axis of the Brillouin zone. For other Fermi crossing bands, a weak dispersion proves the bulk sensitivity for the ARPES data (Fermi surface map in the Γ-Z plane). Since these dots are direct consequences of the PtAs intermediary layers and those from the FeAs layers are absent in the 10-3-8 phase [seen most clearly in the 42 eV panel of Fig. 2(a)]. The two hole pockets around Γ and the electron pocket around X0 are labeled as kα, kβ, and kγ, respectively and are tracked with blue (dark gray), green (medium gray), and pink (light gray) in Fig. 2(b)–2(c).

$v_F(\alpha_2) \sim 0.182 \text{ eV Å}$, and $v_F(\beta_1) \sim 0.587 \text{ eV Å}$, which are very similar to the ones obtained for BaFe2As2 (Ref. 30).

In Fig. 3 we present the variation of the electron and hole pockets with photon energy, i.e., dispersion along the kz axis of the Brillouin zone. Figure 3(a) shows the kz dispersion data (Fermi surface map in the Γ-X-Z plane). In Fig. 3(b) we plot the momentum distribution curves (MDCs) at $E_F$ for each photon energy. The variation of $\alpha_1$ and $\alpha_2$ Fermi pockets is tracked by blue and green markers. In Fig. 3(d) we plot the raw ARPES k-E maps across the zone center at selected photon energies (kz values). The presence of multiple Fermi crossings is further verified by the MDCs (yellow curves at the top of each intensity plot) at $E_F$. The inner holelike Fermi surface ($\alpha_1$) shows considerable kz dispersion. In particular, the $\alpha_1$ pocket is essentially closed at kz values 19.4 and 20.6π/σ0, while the two MDC peaks at other kz values signify its opening. This dispersive pattern results in ellipsoidal Fermi pockets with a periodicity of 4π/σ0. These observations are captured in the schematic three-dimensional Fermi surface [Fig. 3(c)]. It is worthwhile to point out that the presence of kz dispersion proves the bulk sensitivity for the ARPES data in this compound. For other Fermi crossing bands, a weak intensity variation is observed for the $\alpha_2$ pocket, and almost no kz dispersion is observed for the $\beta_1$ pockets, indicating the quasi-two-dimensional nature of these bands.

The most important observation from Figs. 2 and 3 is that the ARPES electronic structure has a tetragonal symmetry, and the experimental Brillouin zone size is proportional to $\pi/\sigma_0$ rather than $\pi/\alpha$ in the kx-kz plane [Fig. 2(a)]. In other words, the ARPES signal reveals that the electronic system is tetragonal, with the periodicity of the FeAs layer sublattice. This observation is noteworthy for two reasons. First, it points out directly that the triclinic arrangement and larger supercell periodicity of the platinum atoms have very little influence on the electronic structure. If the platinum orbitals had a strong contribution at $E_F$, then the observation of Fermi pockets arranged according to the triclinic Brillouin zone is expected. From this we deduce that the hybridization between bands from the PtAs intermediary layers and those from the FeAs layers has to be weak. Although this is only a qualitative statement, the unique crystal structure of the 10-3-8 phase does provide an important estimation of the interlayer hopping strength that is otherwise hard to obtain from experiment in the FeAs superconductors: Interlayer hopping must be so weak that it renders the triclinic lattice invisible by photoemission. Second, the ARPES electronic structure mimics the electronic structures of other prototype pnictides like $AEFe_2As_2$ (“122”, $A = Ca$, Sr, Ba, etc.). Not only the in-plane lattice parameter $\sigma_0$ but also the shapes, sizes, and Fermi velocities of the Γ and X0 Fermi pockets show very little difference with those of the 122 parent compounds.21–30 This indicates that a universal electronic structure capturing the underlying superconducting mechanism may exist for different subfamilies of the Fe-based superconductors (except for the KαFe2-βSe2 series, where electron pockets instead of hole pockets are observed around the Γ point31,32).

Despite the overall similarity, there are observable differences between the Fermi surface of the 10-3-8 phase and that of the prototype pnictides. In Fig. 4 we compare explicitly the in-plane ARPES Fermi surfaces for the 10-3-8 phase, BaFe2As2 (Ref. 33), and LaFeAsO (Ref. 34). First, the Dirac-cone-like Fermi dots around the X points in BaFe2As2 are absent in the 10-3-8 phase [seen most clearly in the 42 eV panel of Fig. 2(a)]. Since these dots are direct consequences
of the long range antiferromagnetic order present in the 122 compound,\textsuperscript{33,35} their absence is consistent with the absence of an antiferromagnetic signature in transport measurements up to room temperature.\textsuperscript{2} It is important to point out that the 10-3-8 phase is a superconductor, whereas no sign of superconductivity is found in BaFe\textsubscript{2}As\textsubscript{2}. Related to the absence or presence of the Fermi dots near the X point, our finding is consistent with the idea that superconductivity can be found in the iron pnictide compounds only if the in-plane electronic structure reduces to its paramagnetic appearance\textsuperscript{33} (except for the case of K\textsubscript{0.3}Fe\textsubscript{2−δ}Se\textsubscript{2}). Second, extended ARPES intensity along one of the Γ-X_0 directions is seen only for the 10-3-8 phase. A close look into the k-E maps (data of cut no. 3 in Fig. 2) reveals that there is a Fermi crossing in these locations and that the band is hololekale. We point out that this band also originates from the Fe orbitals, since it shows reflective symmetry along the high-symmetry directions of the iron unit cell rather than the triclinic platinum cell. Third, from the k_z dispersion data [Fig. 3(a)–3(b)], one notices that ellipsoidal hole pockets are observed around both the Z_0 and X_0 points for the 10-3-8 phase, while in the 122 parent compounds only Z ellipsoids are observed.\textsuperscript{28,29} According to band calculation (Fig. 5), this signifies the weak but existent Pt influence on the Fermi surface topology.

We now examine the electronic structure of the Ca-Fe-Pt-As system from the results of first-principles calculations.\textsuperscript{18–20} In
From Fig. 5(b) we see that the innermost surfaces sketched in the triclinic zone. (d) Fermi surfaces unfolded (gray) dots indicate the contribution of platinum orbitals. (c) Fermi calculated band structure of 10-3-8 in the triclinic Brillouin zone. Red all elements. Inset shows the integrated DOS (IDOS) near $E_F$ orbitals (Pt1 and Pt2, respectively). Right column: Total DOS for column: partial DOS for in-plane and out-of-plane platinum 5 orbitals. (a) Calculated density of states (DOS) for the 10-3-8 phase. Left off-plane Pt (Pt2) atom in the Pt 3As8 layer assigned to one structure of the 10-3-8 phase is taken from Ref. 2 with the crystal potential from the Fe-based superconductors in the vicinity of $E_F$. Our ARPES observations, reduced tetragonal electronic structure and little $k_z$ dispersion, point to a weak interlayer hopping strength in this system. The Dirac-cone-like Fermi dots around $X$ are absent in the 10-3-8 phase, consistent with the absence of long-range antiferromagnetism in this compound. First-principles calculations agree well with experimental data if the potential from the $\sqrt{3}$ superlattice arising from the PtAs layers is considered to be very weak, and the triclinic band structure can be unfolded onto the tetragonal Brillouin zone. The Ca-Fe-Pt-As superconductors are ideal systems for the study of interlayer hopping in the iron-based superconductors. The present detailed study of the electronic structure of the 10-3-8 phase serves as an important step in that direction.

IV. CONCLUSION

In conclusion, we have presented a systematic study of the band structure and Fermi surfaces of one of the Ca-Fe-Pt-As superconductors in the vicinity of $E_F$. Our ARPES observations, reduced tetragonal electronic structure and little $k_z$ dispersion, point to a weak interlayer hopping strength in this system. The Dirac-cone-like Fermi dots around $X$ are absent in the 10-3-8 phase, consistent with the absence of long-range antiferromagnetism in this compound. First-principles calculations agree well with experimental data if the potential from the $\sqrt{3}$ superlattice arising from the PtAs layers is considered to be very weak, and the triclinic band structure can be unfolded onto the tetragonal Brillouin zone. The Ca-Fe-Pt-As superconductors are ideal systems for the study of interlayer hopping in the iron-based superconductors. The present detailed study of the electronic structure of the 10-3-8 phase serves as an important step in that direction.

ACKNOWLEDGMENTS

M.N. and C.L. contributed equally in this work. C.L. acknowledges T. Kondo and A. Kaminski for provision of data analysis software. Work at Princeton is supported by NSF-DMR-0537588. Work at Northeastern is supported by the Basic Energy Sciences, US Department of Energy (DE-FG02-07ER46352 and AC03-76SF00098), and benefited from the allocation of supercomputer time at NERSC and Northeastern University’s Advanced Scientific Computation Center. M.Z.H. acknowledges Visiting Scientist support from LBNL and additional support from the A. P. Sloan Foundation.
