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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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 Pt\text{As} 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.

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I. INTRODUCTION

The recent discovery and characterization of superconducting phases in the Ca-Fe-Pt-As system \( \text{Ca}_{10}(\text{Pt}_n\text{As}_8)(\text{Fe}_2\text{As}_2)_5 \) (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 for \( n = 3 \) [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 \textit{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-(Pt\text{As}) Pt atom is assigned to a position above the (Pt\text{As}) plane.2 The self-consistency of bulk calculation is done with \( 8 \times 8 \times 8 \) \textit{k}-point mesh. For in-plane Fermi surface calculation, the \( k \) mesh is increased to \( 201 \times 201 \) in the \( k_x-k_y \) 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 \( \gamma = 90.044^\circ \sim 90^\circ \) (Ref. 2).
The in-plane triclinic unit cell is essentially a \( a \times b \times c \) with \( c \neq 0 \), which is different from the tetragonal cell measures \( c_0 = 2\sqrt{a_0^2 - a_0^2/2} = 20.548 \) 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 \( T_c \approx 8 \) 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 \( \theta \) (\( \pm 0.1^\circ \) 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 \( \alpha_2 \) 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 \( v_F(\alpha_1) \approx 0.494 \) eV Å, \( v_F(\alpha_2) \approx 0.494 \) eV Å, \( v_F(\beta_1) \approx 0.494 \) eV Å.
**FIG. 2.** (Color online) ARPES Fermi surface maps and $k$-$E$ cuts for selected incident photon energies. (a) Fermi surface maps for four different photon energies (lower right corner in each panel). Inset of the 31 eV panel shows definition of high symmetry points and a schematic in-plane electronic structure. Brillouin zone sizes are determined based on the tetragonal cell [see Fig. 3(c) for relations between momenta in the triclinic and tetragonal cells]. (b) Raw $k$-$E$ maps and (c) corresponding energy distribution curves along directions marked by cut nos. 1–3 in Fig. 2(a). The two hole pockets around $\Gamma/Z_0$ and the electron pocket around $X_0$ are labeled as $\alpha_1$, $\alpha_2$, and $\beta_1$, respectively and are tracked with blue (dark gray), green (medium gray), and pink (light gray) in Fig. 2(b)–2(c).

$v_F(\alpha_2) \sim 0.182$ eV Å, and $v_F(\beta_1) \sim 0.587$ eV Å, which are very similar to the ones obtained for BaFe$_2$As$_2$ (Ref. 30).

In Fig. 3 we present the variation of the electron and hole pockets with photon energy, i.e., dispersion along the $k_z$ axis of the Brillouin zone. Figure 3(a) shows the $k_z$ dispersion data (Fermi surface map in the $\Gamma$-$X$-$Z$ 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 ($k_z$ 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 $k_z$ dispersion. In particular, the $\alpha_1$ pocket is essentially closed at $k_z$ values 19.4 and 20.6$\pi/c_0$, while the two MDC peaks at other $k_z$ values signify its opening. This dispersive pattern results in ellipsoidal Fermi pockets with a periodicity of $4\pi/c_0$. These observations are captured in the schematic three-dimensional Fermi surface [Fig. 3(c)]. It is worthwhile to point out that the presence of $k_z$ 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 $k_z$ 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 $\pi/a_0$ rather than $\pi/a$ in the $k_x$-$k_y$ 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 $AECaFe_2As_2$ (“122”, $AE = Ca, Sr, Ba$, etc.). Not only the in-plane lattice parameter $a_0$ but also the shapes, sizes, and Fermi velocities of the $\Gamma$ and $X_0$ Fermi pockets show very little difference with those of the 122 parent compounds. 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 K$_n$Fe$_{2-\beta}$Se$_2$ series, where electron pockets instead of hole pockets are observed around the $\Gamma$ point$^{1,32}$).

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, BaFe$_2$As$_2$ (Ref. 33), and LaFeAsO (Ref. 34). First, the Dirac-cone-like Fermi dots around the X points in BaFe$_2$As$_2$ 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 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{0.9}Fe\textsubscript{2−δ}Se\textsubscript{2}). Second, extended ARPES intensity along one of the Γ-X\textsubscript{0} directions is seen only for the 10-3-8 phase, while in the 122 parent compounds only Z ellipsoids are observed.\textsuperscript{38,39} 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

FIG. 3. (Color online) Analysis of \( k_z \) dispersion data. (a) \( k_z \) dispersion data for the 10-3-8 phase, taken along the Γ-X\textsubscript{0} direction with photon energies 15 to 64 eV. Inner potential is set to 9.5 eV. (b) Momentum distribution curves (MDCs) for different \( k_z \) values. Fermi crossing bands are consistent with the same colors as in Fig. 2. (c) Schematics of an experiment-derived Fermi surface construction in three dimensions. (d) Raw ARPES \( k\)-\( E \) maps across the zone center (\( k = 0 \)) for selected photon energies. Yellow (light gray) curves are MDCs at \( E_F \). The \( \alpha \) band evolves below \( E_F \) around 19.4 and 20.6 \( \pi / c \), and crosses \( E_F \) for other photon energies, forming a bigger ellipsoidal hole pocket centering at \( Z_0 / \Gamma \) and a smaller hole pocket centering at \( \Gamma / Z_0 \).

FIG. 4. Comparison of in-plane ARPES Fermi surfaces of the 10-3-8 phase, BaFe\textsubscript{2}As\textsubscript{2} (Ref. 33), and LaFeAsO (Ref. 34). Incident photon energies are 22, 105, and 45 eV, respectively. The “Fermi dots” seen around the \( \Gamma \) pockets of BaFe\textsubscript{2}As\textsubscript{2} come from antiferromagnetic reconstructions of the electronic structure,\textsuperscript{33} and the large \( \Gamma \) hole pocket in LaFeAsO originates from surface effects.\textsuperscript{34}
From Fig. 5(b) we see that the innermost orbitals. In Fig. 5(b)–5(c), the calculated LDA band structure into the tetragonal zone. (d) Fermi surfaces unfolded (gray) dots indicate the contribution of platinum orbitals. (c) Fermi surfaces sketched in the triclinic zone. (d) Fermi surfaces unfolded into the tetragonal zone.

We assume that the potential from the 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.

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