Three- to Two-Dimensional Transition of the Electronic Structure in CaFe$_2$As$_2$: A Parent Compound for an Iron Arsenic High-Temperature Superconductor

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We use angle-resolved photoemission spectroscopy (ARPES) to study the electronic properties of CaFe$_2$As$_2$—parent compound of a pnictide superconductor. We find that the structural and magnetic transition is accompanied by a three- to two-dimensional (3D-2D) crossover in the electronic structure. Above the transition temperature ($T_s$), Fermi surfaces around $\Gamma$ and $X$ points are cylindrical and quasi 2D. Below $T_s$, the $\Gamma$ pocket forms a 3D ellipsoid, while the $X$ pocket remains quasi 2D. This finding strongly suggests that low dimensionality plays an important role in understanding the superconducting mechanism in pnictides.

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The dimensionality of electronic structure plays an important role in the superconductivity of solids. The cuprate superconductors have the highest known transition temperatures, and they have quasi-two-dimensional (2D) electronic structure. In contrast, the borocarbides [1], another class of relatively high transition temperature superconductors, have a strictly three dimensional (3D) electronic structure [2]. The situation in the newly discovered iron-arsenic high-temperature superconductors is less clear. Both RFeAsO (R1111, $R$ being the rare earth element) [3] and AFe$_2$As$_2$ (A122, A being Ca, Sr, Ba) [4] have strongly layered structures, with the iron-arsenic layers believed to be mainly responsible for the electronic properties and superconductivity. The A122 family share the same ThCr$_2$Si$_2$ structure as the borocarbides, and both display interesting interplay between magnetism and superconductivity. Some band structure calculations predict strong $k_z$ dispersion and 3D Fermi surfaces (FSs) [5] in the magnetic state of the parent compounds; however, so far this has not been observed by angle-resolved photoemission spectroscopy (ARPES) [6–12]. On the other hand, a number of physical properties display an anisotropy that is a few orders of magnitude smaller than that found in the cuprates [13–15], which hints at a strong hopping of electrons between the layers. In terms of the pairing mechanism, most theoretical models depend on nesting between the $\Gamma$ and $X(M)$ pockets [16,17], for which the dimensionality of the FSs is very important.

The parent compounds of the two iron pnictide families undergo a tetragonal-to-orthorhombic structural-magnetic transition at elevated temperatures [13,18]. Superconductivity appears in the A122 materials when the high-temperature tetragonal phase is stabilized down to low enough temperatures (e.g., by doping with K in a Ba position or Co substitution for Fe) [19]. Determining the differences between these phases is key to gaining a full understanding and control of the superconductivity in the iron pnictides. In particular, CaFe$_2$As$_2$, shows a first-order tetragonal-orthorhombic transition with a transition temperature (160 $\rightarrow$ 170 K) depending on the growth method [20–22]. Superconductivity is found when moderate (possibly not purely hydrostatic) pressure is applied [23], or by doping with cobalt [21], or sodium [22]. Such a rich phase diagram makes CaFe$_2$As$_2$ an ideal system for studying the electronic properties of the parent compounds. In this Letter, we present ARPES data which demonstrates that the electronic structure in the parent compound of the A122 iron-arsenic family undergoes a 3D to 2D crossover associated with the structural-magnetic transition. The cylindrical, quasi-2D FS surrounding the $\Gamma$ point becomes highly dispersive (3D) and forms an ellipsoid upon cooling below the transition temperature into the orthorhombic phase. The observation of the 3D FS is consistent with recent results from quantum oscillation measurements [24,25]. The FSs around the $X$ pocket remain quasi 2D and unaffected by the structural transition.

Plate-like single crystals of CaFe$_2$As$_2$ were grown out of a FeAs flux as well as Sn flux using conventional high-temperature solution growth techniques [20] with typical dimensions ranging from 2 $\times$ 2 mm$^2$ up to 10 $\times$ 10 mm$^2$. Following the growth, the samples were annealed at 500 °C for 24 hours. Resistivity measurements showed a first-order tetragonal-orthorhombic transition at $\sim$160 K for the FeAs flux grown samples and $\sim$170 K when using Sn flux. The ARPES measurements are performed at beam lines 10.0.1 and 7.0.1 of the Advanced Light Source (ALS), Berkeley, California, and the SIS beam line of the Swiss Light Source, Switzerland. Energy resolution was set at 20–30 meV; vacuum conditions were better than 5 $\times$ 10$^{-11}$ torr. All samples were
cleaved in situ along the a-b plane, yielding mirrorlike, clean surfaces. Lattice constant values from Ref. [26] are used to determine the k-space positions. The high symmetry points X and Z for both two phases are defined to be \([\pi/a, \pi/a(b), 0]\) and \((0, 0, 2\pi/c)\), respectively, with \(k_x (k_{(100)})\) and \(k_y (k_{(010)})\) axes along the Fe-As bonds.

FS maps of CaFe_2As_2 obtained at several different photon energies in the orthorombic phase are shown in Fig. 1 along with ARPES intensity plots and energy distribution curves (EDCs). Varying the photon energy in ARPES effectively changes the momentum offset along the direction perpendicular to the sample surface (in our case, this direction corresponds to \(k_z\)—perpendicular to the Fe-As layers) [27,28]. The striking feature of Fig. 1 is that the dispersion of one of the bands that form the “Γ pocket” (Fermi contour around the zone center \(k_x = k_y = 0\)) changes dramatically with photon energy. At \(h\nu = 40\) eV, three different bands \(\alpha, \beta, \gamma\) cross the chemical potential (\(\mu\)) as seen in Figs. 1(e) and 1(g), and this gives rise to three FS sheets. The \(\gamma\)-band crosses \(\mu\) again near the X point, forming a characteristic flower shape of the X pocket. The other two bands (\(\alpha, \beta\)) are relatively close to each other. They form two hole pockets around Γ. Similar behavior has been reported in Ba_{1-x}K_xFe_2As_2 [6,7,29–31]. However, at \(h\nu = 50\) eV, the top of the \(\alpha\) band is located below \(\mu\) and the corresponding \(\alpha\) pocket disappears. The \(\beta\) and \(\gamma\) pockets continue to cross \(\mu\) at about the same \(k_F\) as for 40 eV photons [Figs. 1(c), 1(f), and 1(h)]. These data conclusively demonstrate that the electronic structure in the orthorombic phase of CaFe_2As_2 is 3D. On the other hand, no obvious change is seen for the X pocket at these four energies.

A comprehensive study of the evolution of the Γ- and X-pocket with different incident photon energies is shown in Fig. 2 for the orthorombic phase of CaFe_2As_2. The photon energy ranges from 35 to 105 eV. The FS map along the \(k_z\) direction is shown in Fig. 2(a) over a range corresponding to several Brillouin zones. The \(\alpha\) Fermi pocket forms an ellipsoid centered at Γ in the respective Brillouin zones with a \(4\pi/c\) periodicity. It should be noted that the observation of \(k_z\) dispersion with such periodicity clearly demonstrates that ARPES data from these samples reveals intrinsic, bulk electronic properties. In Fig. 2(b), we extract the Fermi crossing momenta (\(k_F\)) from the momentum distribution curve (MDC) peaks at \(\mu\) for each photon energy. It is clear that only the \(\alpha\) band (black solid dots) but not the \(\beta\) and \(\gamma\) bands show a strong \(k_z\) dispersion. Almost no dispersion of the X pocket is observed, which indicates its quasi 2D nature. The consistency of this map with that of Fig. 1 is better seen at Figs. 2(c)–2(e) where ARPES intensity maps are shown for three high symmetry points. At \(h\nu = 58\) eV (\(k_z = 16\pi\)), the \(\alpha\) band does not cross \(\mu\), while at \(h\nu = 80\) and 41 eV (\(k_z = 18\pi\) and \(14\pi\)), all three bands form Fermi pockets.

Now we turn our attention to the high-temperature tetragonal phase of CaFe_2As_2. We demonstrate in Fig. 3 the 2D character of the band structure in the tetragonal phase. Panel 3(a) shows the FS map at \(h\nu = 100\) eV. An arrow represents the Γ-Z direction along which data in panels 3(d) and 3(e) were obtained. Schematic arrangement of the Brillouin zones along in-plane and out-of-plane directions for the tetragonal phase are shown in
FIG. 2 (color online). $k_\zeta$ dispersion data for CaFe$_2$As$_2$ low temperature orthorhombic phase ($T = 40$ K). (a) $k_\zeta$ dispersion data obtained by plotting ARPES intensity integrated within 10 meV about $\mu$ as a function of $k_{1(10)}$ and the energy of the incident photons (which corresponds to different values of $k_\zeta$). The photon energy range used was from 35 to 105 eV. (b) Fermi momentum $k_F$ was extracted from the data in panel (a) using the peak positions of the MDCs. (c)–(e) Band dispersion data along the $\Gamma$-$X$ direction for $k_\zeta = 18$, 16, and $14\pi$ at $k_{1(10)} = 0$ (corresponding to photon energies of $h\nu = 80$, 58, and 41 eV, respectively). The locations of these cuts are marked by green (gray) arrows in panel (a).

Panels 3(b) and 3(c). Panels 3(d) and 3(e) present the actual $k_\zeta$ intensity data integrated within 10 meV about $\mu$ as a function of $k_\zeta$ and $k_\xi$ and the FS extracted using MDC peaks, respectively. The photon energy range used here is 80–190 eV, which corresponds to $18\pi \leq k_\zeta \leq 25\pi$. The most important observation here is that the bands around $\Gamma$ cross $\mu$ at all $k_\xi$s measured, no apparent $k_\zeta$ dispersion is visible. For further clarification, in panels 3(f)–3(i), we show ARPES intensity maps divided by the resolution convoluted Fermi function for $k_\zeta = 18, 19, 20$, and $21\pi$, respectively. The band crosses $\mu$ for all these $k_\zeta$ points, in clear contrast with the situation for the low temperature orthorhombic phase. The data in Fig. 3 is consistent with a quasi-2D nature of the FS in the high-temperature tetragonal phase of CaFe$_2$As$_2$.

In Fig. 4, we directly compare the band dispersion of low- and high-temperature phase for the two $k_\zeta$ values that correspond to high symmetry points. The data is taken along $\Gamma$-$X$ direction on the same sample under exactly the same experimental conditions to avoid possible complications due to scattering matrix elements or polarization of incident photons. Though the data in Fig. 4 is taken from different samples and beam lines than that in Fig. 2, the 3D nature of the low-temperature orthorhombic phase reproduces nicely. At high temperature, we divided the data by the resolution convoluted Fermi function to better see the location of the band in the proximity of $\mu$. At low temperature, this is not necessary, as the width of the Fermi edge is much sharper than the leading edge of the peaks, and band crossings are clearly visible. At $T = 200$ K, the $\alpha$ band crosses $\mu$ at both points [$k_\zeta = 16\pi$ and $k_\zeta = 18\pi$—Figs. 4(a) and 4(b)]. At low temperature in the orthorhombic phase, the same band crosses $\mu$ at $k_\zeta = 18\pi$ [Fig. 4(d)], but is located several tens of meV below $\mu$. 
at \( k_z = 16\pi \) [Fig. 4(c)]. This dramatic change of the FS shape with temperature may be the origin of the sudden drop in the electric resistivity found by transport measurements when the material is heated above the transition temperature [20,22].

In conclusion, we have measured the in-plane and out-of-plane band dispersion for both the orthorhombic and tetragonal phase of the iron-arsenic A122 parent compound CaFe\(_2\)As\(_2\). A number of theoretical models of the pairing mechanism and magnetic ordering in these materials are based on nesting between different sheets of the Fermi surface [16,17]. Our results demonstrate that some FS sheets are three dimensional, therefore put significant constrains on possible nesting scenarios since the degree of nesting will strongly depend on the dimensionality of the FSs. Our finding also has important implications for understanding a number of other physical properties such as the anisotropy in electrical and thermal conductivity [32] which depend on the dimensionality of the electronic structure.

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