

Why T_c of $(\text{CaFeAs})_{10}\text{Pt}_{3.58}\text{As}_8$ is twice as high as $(\text{CaFe}_{0.95}\text{Pt}_{0.05}\text{As})_{10}\text{Pt}_3\text{As}_8$

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Recently discovered $(\text{CaFe}_{1-x}\text{Pt}_x\text{As})_{10}\text{Pt}_3\text{As}_8$ and $(\text{CaFeAs})_{10}\text{Pt}_{4-y}\text{As}_8$ superconductors are very similar materials having the same elemental composition and structurally similar superconducting FeAs slabs. Yet the maximal critical temperature achieved by changing Pt concentration is approximately twice higher in the latter. Using angle-resolved photoemission spectroscopy (ARPES) we compare the electronic structure of their optimally doped compounds and find drastic differences. Our results highlight the sensitivity of critical temperature to the details of fermiology and point to the decisive role of band-edge singularities in the mechanism of high- T_c superconductivity.

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A new class of high temperature superconductors,¹⁻³ $(\text{CaFe}_{1-x}\text{Pt}_x\text{As})_{10}\text{Pt}_3\text{As}_8$ (1038) and $(\text{CaFePtAs})_{10}\text{Pt}_{4-y}\text{As}_8$ (1048), in the family of iron pnictides⁴⁻⁸ has been discovered recently. Although these two compounds are almost similar, both consisting of tetrahedral FeAs planes sandwiched between the planar Pt_nAs_8 ($n = 3, 4$) intermediary layers, differences in their crystal structure and electronic properties have been found. The parent Ca-Pt-Fe-As compound in the 1038 phase has a triclinic crystal structure and is semiconducting, whereas the parent 1048 has a tetragonal crystal structure and is metallic^{2,3} with the band structure calculations pointing to the increased metallicity of the PtAs layers.⁹ Furthermore, parent 1038 is ordered antiferromagnetically (AFM) below a Néel temperature 120 K¹⁰ and unlike in other known iron pnictides the magnetic transition does not lead to any further reduction in the crystal symmetry, but breaks the tetrahedral symmetry of FeAs layers. Superconductivity in 1038 and 1048 systems can be obtained in several ways, either doping FeAs layers directly or via interstitial PtAs layers.^{2,11} In addition, superconductivity can also be induced by doping electrons through a La substitution at the Ca site.¹¹ By changing only Pt content, up to date a maximum T_c of 38 K is obtained in $(\text{CaFeAs})_{10}\text{Pt}_{4-y}\text{As}_8$ superconductor,¹ and a maximum of 15 K is observed in $(\text{Ca}_{1-x}\text{Pt}_x\text{FeAs})_{10}\text{Pt}_3\text{As}_8$.¹¹ One of the proposals to explain this difference was based on an analogy with the cuprates and attributes high T_c s to the increased interlayer hopping induced by high density of states at the Fermi level (E_F) from PtAs layers.³ While the recent ARPES data on 1038 suggesting that the interlayer hopping in these materials is weak thus supporting the conjecture,¹² the data on 1048 are still absent. It is therefore interesting to study the electronic structure of both optimally Pt doped materials under the same experimental conditions.

In this Rapid Communication we report on the electronic structure and Fermi surface topology of both superconductors by means of high-resolution ARPES. We find that while the electronic structures have the same components as the majority of the iron-based superconductors (IBS), i.e., hole pockets near the Brillouin zone center and electron pockets near the zone corner, there are pronounced differences. In particular, we observe three band-edge singularities located in the immediate vicinity of E_F in 1048 ($T_c = 35$ K), where

only one is present in the case of 1038 ($T_c = 15$ K). We also discuss the possible implications of these findings. We call the band-edge singularity a situation when the local top (bottom) of a band is very close to the Fermi level.

ARPES measurements were carried out at the UE-112 beamline equipped with ^{13}C -ARPES end station located in BESSY II (Helmholtz zentrum Berlin) synchrotron radiation center.¹³ Photon energies for the measurements were varied between 20 and 80 eV. The energy resolution was set between 5 and 10 meV depending on the excitation energy. Data were recorded at a chamber vacuum of the order of 9×10^{-11} mbar and the sample temperature was kept at 1 K during the measurements. We employed various photon polarizations in order to probe the symmetry of the electronic bands. The preparation of single crystals, $(\text{CaFe}_{0.95}\text{Pt}_{0.05}\text{As})_{10}\text{Pt}_3\text{As}_8$ and $(\text{CaFeAs})_{10}\text{Pt}_{3.58}\text{As}_8$, and their elemental analysis are reported elsewhere.^{2,10} The former compound shows superconductivity at a transition temperature $T_c = 15$ K, and the latter shows it at $T_c = 35$ K. From now on we refer to the former compound as 1038-15 and the latter as 1048-35.

Figure 1(a) shows the Fermi surface (FS) map of superconducting 1048-35 compound measured using p -polarized light with an excitation energy $h\nu = 80$ eV. The map was extracted over an integration window larger than the size of the superconducting gap so that its influence on the intensity distribution is negligible. In order to identify all features of the electronic structure, which sometimes are hidden because of the strong influence of the matrix element effects, one needs to record the map in a big portion of the k space and use the light of various polarizations and energies. We therefore have measured a part of the map using s -polarized light and detected the “missing” spectral weight (white dashed contour). In the map we could thus observe the signatures of the hole pockets at the zone centers [near (0,0), (1.5, 0.5), and (2,-1) and partially near (0.5, -1.5), (-1.5, -0.5)] and electron pockets at the zone corners [near (1, -0.5), (-0.5, -1), (-1, 0.5), and (0.5, 1)], as is typically the case for all IBSs.

The spectral intensity near the zone center is formed by holelike features as shown in the energy distribution maps (EDM) [see Figs. 1(b) and 1(c)]. From the figures we can clearly see that only one of the three features, α_3 , crosses E_F and thus alone contributes to the Fermi surface. We

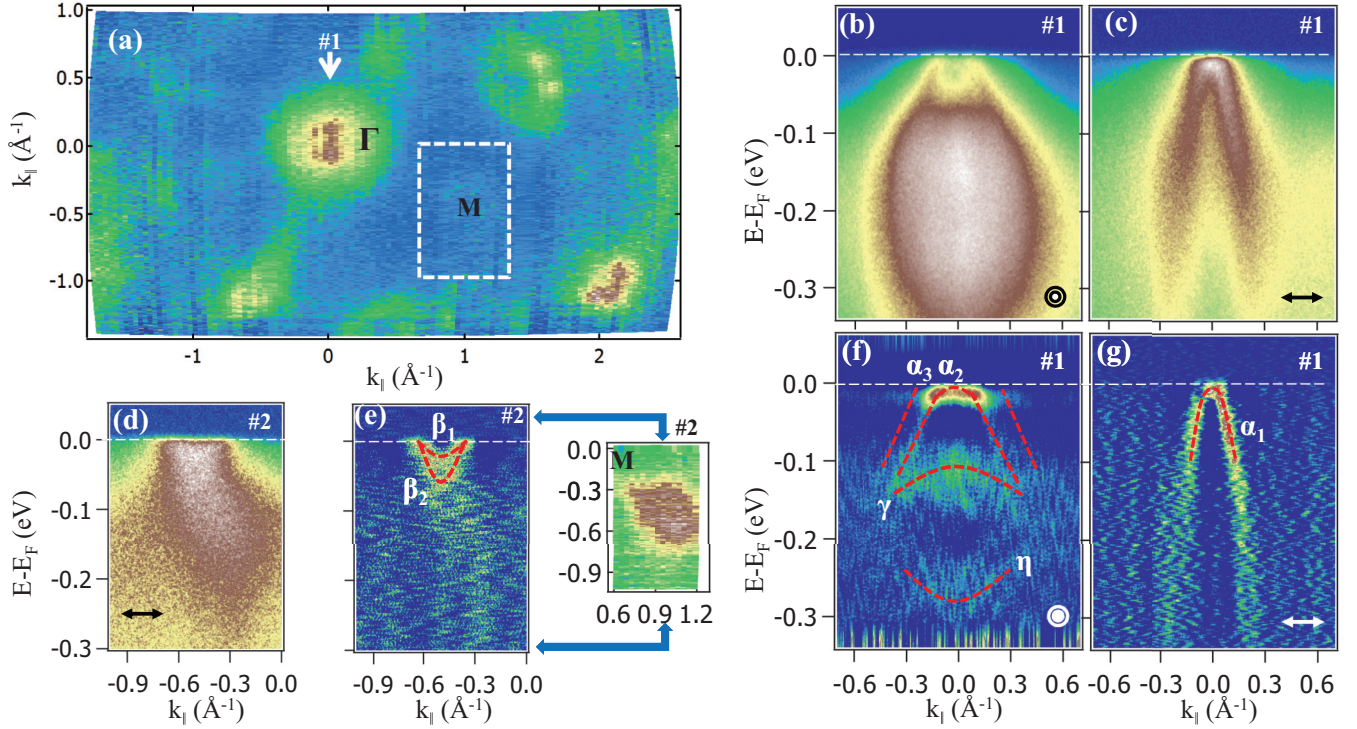


FIG. 1. (Color online) ARPES data taken on 1048-35. (a) shows the FS map measured using p -polarized light with an excitation energy of 80 eV. (b) and (c) show energy distribution map (EDM) cuts taken at Γ along the direction shown by arrow on the FS map, measured using p - and s -polarized lights, respectively. (d) shows EDM cut taken at M along the direction shown by a blue arrow on the FS (inset) map, measured using s -polarized light. (e) is the second derivative of EDM shown in (d). (f) and (g) are second derivatives of EDMs shown in (b) and (c), respectively. In the figure double circles and double sided arrow represent p - and s -polarized lights, respectively.

calculated a Fermi vector $k_F \approx 0.29 \text{ \AA}^{-1}$ and Fermi velocity $v_F \approx 0.4 \text{ eV-\AA}$ for the band α_3 . The two other bands, α_1 and α_2 , only approach E_F but do not cross it. This observation is similar to the case of LiFeAs at particular k_z values [for instance see Fig. 2(d) in Ref. 14]. With the help of polarization dependent measurements, near Γ we could assign Fe $3d_{yz,xz,xy}$ orbital characters to α_1 , α_2 , and α_3 bands, respectively.^{15,16} In Fig. 1(f) one can observe that the top of α_2 forms a band-edge singularity at E_F and this, as we will see later, is remarkably different from 1038-15 compound (see Fig. 3). We further notice two more bands γ and η at the zone center as shown in Fig. 1(b). The former is located at around 105 meV below E_F and disperses towards higher binding energy, while the latter disperses towards lower binding energy and its bottom lies at around 280 meV from E_F . The γ band is most likely resulted

from a hybridization between Pt $5d$ and As $4p$ in the Pt_nAs_8 layers,⁹ while the η band originates from Fe $3d_{z^2}$ states.¹⁵

From the FS maps we can see that the electron pockets are elongated in the Γ - M direction, indicating that these pockets are shallow. Indeed, this is further confirmed by the panels 1(d) and 1(e). Electron pocket dispersions are faint in Fig. 1(d) though, from its second derivative, in Fig. 1(e) we could see the presence of shallow (β_1) and deep (β_2) electron pockets near the zone corner, where one of them (β_1) forms a band edge near E_F . Thus, another singularity is located at the zone corner close to E_F in the case of 1048-35. The presence of hole pockets at the zone center and electron pockets at the zone corner is consistent with the electronic structure of other iron pnictides.¹⁷⁻¹⁹ Apart from the above mentioned features we do not observe any spectral intensity near E_F that could ratify the Pt-related states, which is in good agreement with the reported DFT calculations.²

In Fig. 2 we show photon energy dependent measurements performed to reveal band dispersion in the k_z direction. Figures 2(a)–2(d) show EDMs measured at the zone center using photon energies 20, 30, 40, and 80 eV and corresponding k_z values are given by $8.55 \pi/c$, $10.11 \pi/c$, $11.46 \pi/c$, and $15.7 \pi/c$ ($c = 10.46 \text{ \AA}$ and the inner potential is taken as 9.5 eV),¹² respectively. In Fig. 2(e) we show momentum distribution curves (MDCs) taken from the EDMs shown in Figs. 2(a)–2(d) over an integration range of 10 meV with respect to E_F . As obtained MDCs are fitted using a function of four Lorentzians. From the fits we extracted peak position of the bands α_2 and α_3 , marked by vertical blue lines as shown in Fig. 2(e). We

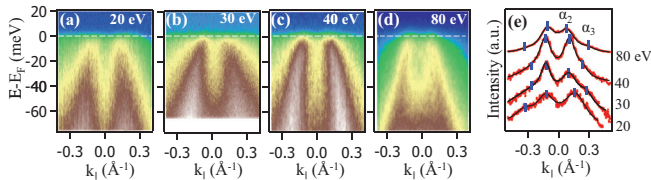


FIG. 2. (Color online) ARPES data taken on 1048-35. (a)–(d) show photon energy dependent EDMs measured at the zone center. (e) shows momentum distribution curves taken over an integration range of 10 meV with respect to the Fermi level, derived from EDMs shown in (a)–(d). Vertical blue lines in the figure (e) represent peak positions of the bands α_2 and α_3 .

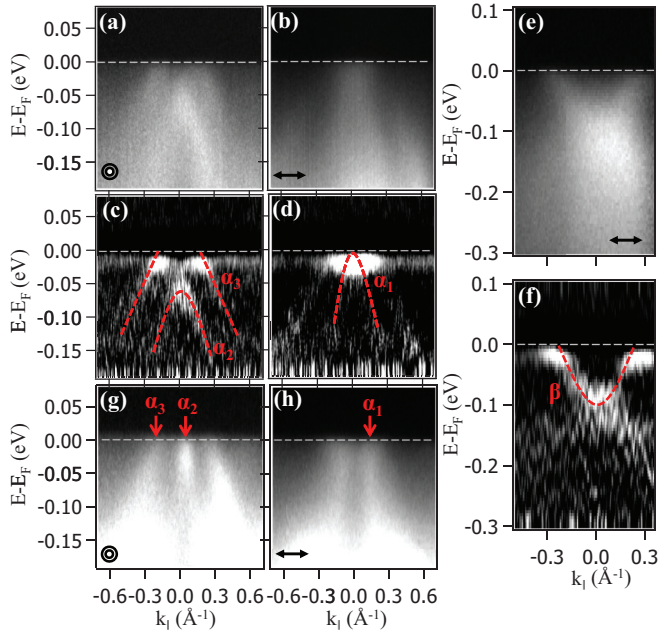


FIG. 3. (Color online) ARPES data taken on 1038-15. (a) and (b) show EDMs taken at the zone center measured using an excitation energy of 70 eV with p - and s -polarized lights, respectively. (c) and (d) are second derivatives of EDMs shown in (a) and (b), respectively. (e) is EDM taken at the zone corner and (f) is second derivative of (e). (g) and (h) are EDMs measured with the same photon energy and polarization of (a) and (b), respectively but from a different polar angle which corresponds to a different k_z . In the figure double circles and double sided arrow represent p - and s -polarized lights, respectively.

further notice peak positions of α_2 and α_3 at high symmetry points Γ and Z are almost equivalent within the experimental errors, which suggests a quasi-2D hole dispersion along the Γ - Z direction for these compounds. If the interlayer coupling between FeAs layers was enhanced by the intermediary PtAs planes, as proposed in Ref. 3, we should observe a strong dispersion of the bands along the Γ - Z direction.¹⁵ On the contrary, we observe typically weak (but finite) k_z dispersion for the hole pockets. We further observe a low spectral weight for α_3 . This could be due to the dominant in-plane xy orbital contribution to α_3 , as they have low scattering cross sections in the photoemission process.^{16,20}

Next, in Fig. 3 we show the ARPES data taken on the superconducting 1038-15 compound. All the data were recorded with an excitation energy of 70 eV. We observe three holelike band dispersions α_1 , α_2 , and α_3 at the zone center [see Figs. 3(a) and 3(b)] and an electronlike band dispersion β at the zone corner [see Fig. 3(c)]. In Figs. 3(a) and 3(c) we observe top of the band α_2 is approximately 75 meV below E_F , while α_1 disperses to E_F and touches it. Therefore, only α_3 crosses E_F in this 70 eV data near zone center. We calculated a Fermi vector $k_F = 0.18 \text{ \AA}^{-1}$ and Fermi velocity $v_F = 0.45 \text{ eV-\AA}$ for α_3 . In order to confirm the presence of all three bands, we also show the data [Figs. 3(g) and 3(h)] on hole pockets from a different polar angle measured with the same photon energy which corresponds to a different k_z . Our 1038-15 sample appears to be more electron doped than the one presented in Ref. 12, where already two holelike bands crossed

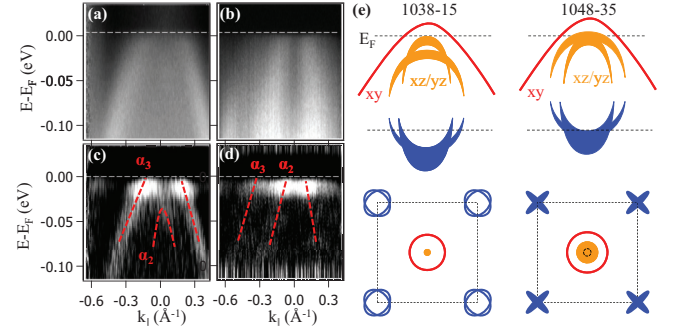


FIG. 4. (Color online) (a) and (b) are EDMs measured using p -polarized light with an excitation energy of 20 eV from 1038-15 and 1048-35, respectively. (c) and (d) are second derivatives of (a) and (b), respectively. (e) shows schematic representation of the experimentally determined electronic structure near Γ for both compounds.

the Fermi level. It is clearly seen in Figs. 3(e) and 3(f) that both electron pockets (though not clearly resolved) have their band bottoms much farther away from E_F than in 1048-35.

We now switch to comparison of the electronic structure between higher- and lower- T_c compounds in order to identify the basic elements for enhancement in the critical temperature. In Fig. 4 we show EDMs taken at the zone center measured using p -polarized light with an excitation energy of 20 eV. We can see that the band α_3 crosses E_F in both cases, while supporting a slightly larger Fermi surface in 1048-35. On the other hand in 1038-15 the top of the band α_2 is much deeper (≈ 40 meV from E_F), therefore, hardly playing any role in transport or superconductivity. In contrast, α_2 in 1048-35 approaches E_F and its top virtually coincides with it for a range of momenta. We calculated $v_F = 0.33 \text{ eV-\AA}$ and $k_F = 0.15 \text{ \AA}^{-1}$ for α_3 in 1038-15. Similarly, we found $v_F = 0.3 \text{ eV-\AA}$ and $k_F = 0.25 \text{ \AA}^{-1}$ for α_3 in 1048-35. Constant Fermi velocity of the band α_3 suggests similar in-plane interactions in both compounds. By shifting the Fermi level in Fig. 4(a) up to 55 meV towards higher binding energy we can reproduce Fig. 4(b). At a glance one can think of rigid-band scenario in these compounds. However, the presence of α_1 close to E_F in both 1038-15 and 1048-35 [see Figs. 1(c) and 3(b)] excludes such a behavior. Currently we cannot offer a reasonable explanation for this effect, but we do not exclude a possible influence of the triclinic crystal structure of the 1038 compounds which can lift the degeneracy of the xz, yz states at the Γ point, which otherwise can be lifted only by inclusion of the spin-orbit interaction.²¹

Another clear difference between these two compounds is the total charge in the FeAs slabs. Since the α_3 Fermi sheet is slightly larger and electron pockets are significantly shallower in 1048-35, it appears that this compound is more hole doped compared to 1038-15. Although $(\text{CaFeAs})_{10}\text{Pt}_{3.58}\text{As}_8$ (1048-35) has higher net Pt, in $(\text{CaFe}_{0.95}\text{Pt}_{0.05}\text{As})_{10}\text{Pt}_3\text{As}_8$ (1038-15) it is substituted directly into the FeAs slabs which affects the electronic structure more than in the former where Pt is substituted into the intermediary PtAs layers. Note that the critical temperatures of transition-metal doped compounds are generally much lower than those of charge doped or pure FeAs layers.

Comparing our experimental observations with the published band-structure calculations of these compounds,⁹ we notice a partial agreement. The experimental hole dispersions at the zone center qualitatively agree with the predicted quasi-2D hole pockets along the k_z direction. On the other hand, the predicted electronlike band at the zone corner which has a sharp dispersion along k_z is not observed experimentally in our measurements. Absence of such a band reduces the chance of high degree of interlayer coupling that is argued as a reasonable explanation for the pairing mechanism in these compounds.³ We further note that regardless of the additional disorder induced in 1038-15 due to direct Pt doping into FeAs slabs, we observed (not shown) comparable peak widths of holelike bands from both 1038-15 and 1048-35 compounds.

In Fig. 4(e) we schematically show the experimentally determined electronic structure for both compounds. Here, the key difference is obviously the number of band edges near E_F in higher T_c superconductor (1048-35) compared to the lower one (1038-15). Such singularities, provided that the band edges are not parabolic, can induce high density of states near E_F and thus enhance T_c . These band-edge singularities do exist in every IBS with a significant critical temperature,^{14,22–24} which appear to be eminent for acquiring superconductivity in iron pnictides. In this study, the presence of two additional band edges near the Fermi level in 1048-35 is a plausible explanation for more robust pairing compared

to 1038-15 where we observe only one band-edge singularity. Moreover, in 1038-15 the nesting conditions are not perfect due to different sizes of the hole and electron pockets, and also the intraorbital interactions are suppressed since the “active” xz, yz states are far below E_F . Whereas in 1048-35 the xz, yz states are close to E_F at both zone center and corner, showing the necessity of these states to present as many as near E_F for high T_c superconductivity in iron pnictides.

In conclusion, we have studied the electronic structure of newly discovered Ca-Pt-Fe-As-type iron pnictide superconductors in both 1038 and 1048 phases. We observed, typical for IBS, holelike bands at the zone center and electronlike bands at the zone corner for both compounds. While the degree of interlayer coupling was found to be similar in both materials, the pronounced difference in the low-energy electronic structure itself could offer a very plausible explanation for the enhanced critical temperature in 1048-35 compared to 1038-15. Three band-edge singularities present in the immediate vicinity of the Fermi level in the system that has higher T_c (1048-35) where only one is realized for lower T_c (1038-15) compound. Our experimental findings underline the importance of fine tuning of the electronic structure within the FeAs layers by interstitial atoms, as well as the role played by the band-edge singularities in the mechanism of high T_c superconductivity in iron-based superconductors. Our results provide no evidence for the strong interlayer coupling among the FeAs layers.

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