

## Correlation-Induced Self-Doping in the Iron-Pnictide Superconductor $\text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O}$

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The electronic structure of the iron-based superconductor  $\text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O}$  ( $T_c^{\text{onset}} = 23.5$  K) has been investigated by using angle-resolved photoemission spectroscopy and combined local density approximation and dynamical mean field theory calculations. The electronic states near the Fermi level are dominated by both the Fe  $3d$  and Ti  $3d$  orbitals, indicating that the spacer layers separating different FeAs layers are also metallic. By counting the enclosed volumes of the Fermi surface sheets, we observe a large self-doping effect; i.e., 0.25 electrons per unit cell are transferred from the FeAs layer to the  $\text{Ti}_2\text{As}_2\text{O}$  layer, leaving the FeAs layer in a hole-doped state. This exotic behavior is successfully reproduced by our dynamical mean field calculations, in which the self-doping effect is attributed to the electronic correlations in the  $3d$  shells. Our work provides an alternative route of effective doping without element substitution for iron-based superconductors.

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In iron-based superconductors (IBSCs), the most common way to suppress long-range antiferromagnetic order and obtain high- $T_c$  superconductivity is to introduce carriers [1–3] and/or internal strain [4–6] by element substitution. However, an inevitable problem is that element substitution also introduces disorder, and impurity scattering is believed to be detrimental to superconductivity [7], though not as seriously as in cuprate superconductors. It has been revealed that the impurity scattering effects are site dependent and the scattering strength is gradually reduced when the dopants move away from the Fe plane [8,9]. This may partially explain why the maximum  $T_c$  is much higher and the superconducting dome is much wider in  $(\text{Ba}, \text{K})\text{Fe}_2\text{As}_2$  as compared with  $\text{Ba}(\text{Fe}, \text{Co})_2\text{As}_2$  [8]. Therefore, finding an alternative way to dope carriers without introducing disorder would be a promising path for reaching higher  $T_c$  superconductivity.

A remarkable feature in the IBSCs is that there is an intimate relationship between the electronic correlations and the  $d$ -shell occupancy. For hole doping, extremely low coherence temperatures are expected, while electron doping reinforces Fermi-liquid properties [10,11]. Moreover, the orbital polarization can be tuned by the magnitudes of

the Coulomb interaction  $U$  and the Hund's rule coupling  $J$ , leading to a redistribution of electrons among the five Fe  $3d$  orbitals [12]. Electronic correlations weaken the hybridization between Fe and ligand atoms, reducing the effective occupancy of the Fe  $3d$  orbitals [13]. However, as the total electron count on the Fe and ligand atoms in crystals, such as  $\text{BaFe}_2\text{As}_2$ , is conserved, such charge redistribution between them does not produce any doping effect on the Fermi surfaces (FSs).

In this work, we prove that doping can be induced by electronic correlations in the IBSC  $\text{Ba}_2\text{Ti}_2\text{Fe}_2\text{As}_4\text{O}$  ( $\text{Ba}22241$ ,  $T_c^{\text{onset}} = 23.5$  K) due to the presence of metallic  $\text{Ti}_2\text{As}_2\text{O}$  layers.  $\text{Ba}22241$  can be regarded as a superlattice consisting of alternating stacking of  $\text{BaFe}_2\text{As}_2$  and  $\text{BaTi}_2\text{As}_2\text{O}$  layers [Fig. 1(a)] [14]. Compared with other IBSCs, the most distinctive characteristic of  $\text{Ba}22241$  is the metallic nature of the spacer layers, which contributes distinctly to the density of states (DOS) at the Fermi level ( $E_F$ ) [15]. Our angle-resolved photoemission spectroscopy (ARPES) measurements suggest that the low-energy band dispersions can be regarded as a superposition of the band structures of the FeAs and  $\text{Ti}_2\text{As}_2\text{O}$  layers. By counting the volumes of the FSs, we find that about 0.25 electrons per

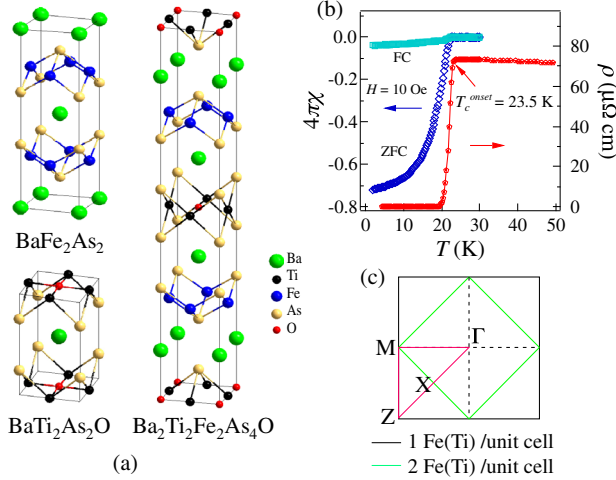


FIG. 1 (color online). (a) Crystal structures of BaFe<sub>2</sub>As<sub>2</sub>, BaTi<sub>2</sub>As<sub>2</sub>O, and Ba<sub>2</sub>Ti<sub>2</sub>Fe<sub>2</sub>As<sub>4</sub>O. (b) Temperature dependence of the dc susceptibility (left axis) and resistivity (right axis). The dc susceptibility data were obtained using the zero-field-cooling (ZFC) and field-cooling (FC) modes with a dc magnetic field of 10 Oe. The resistivity data were obtained under zero field. The onset superconducting transition temperature  $T_c^{\text{onset}}$  is determined to be 23.5 K from the resistivity data. (c) Schematic Brillouin zones for one and two Fe (Ti) per unit cell. Red lines indicate the measurement locations in Fig. 2(a).

unit cell are transferred from the FeAs layer to the Ti<sub>2</sub>As<sub>2</sub>O layer. This exotic behavior is successfully reproduced by dynamical mean field-based electronic structure calculations, which allow us to identify electronic Coulomb correlations in the 3d shells as the main cause for this self-doping effect.

High-quality single crystals of Ba22241 were synthesized by the flux method [16]. ARPES measurements were performed at beam lines PGM and APPLE-PGM of the Synchrotron Radiation Center (Wisconsin) with Scienta R4000 and SES 200 analyzers, respectively, as well as at beam line SIS of the Swiss Light Source (PSI) with Scienta R4000. The energy and angular resolutions were set at 15–30 meV and 0.2°, respectively. The samples were cleaved *in situ* and measured in the temperature range between 25 and 150 K in a vacuum better than  $3 \times 10^{-11}$  Torr. The ARPES data were taken under horizontal (HP) or vertical (VP) polarized lights.

Figure 2(a) shows the experimental band dispersions along the high-symmetry lines  $M \rightarrow Z \rightarrow X \rightarrow \Gamma \rightarrow M$  in an energy range within 2.2 eV below  $E_F$ . The band dispersions are much more complex than those of other IBSCs due to the contribution of the metallic Ti<sub>2</sub>As<sub>2</sub>O layers. To understand the multiband electronic structure, we superimpose the Kohn-Sham band structure of density functional theory within the local density approximation (LDA) as calculated within WIEN2K [17] on top of the experimental data in Fig. 2(a). We use the experimental crystal structure of Ref. [14] as input. The experimental band dispersions

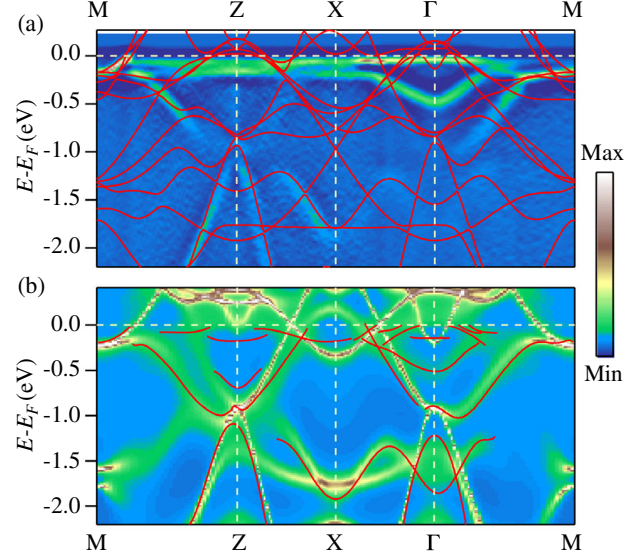


FIG. 2 (color online). (a) Two-dimensional (2D) curvature intensity plot [24] of the ARPES data along  $M$ - $Z$ - $X$ - $\Gamma$ - $M$  recorded at 150 K and photon energy  $h\nu = 55$  eV with HP. The LDA bands are also plotted without renormalization for comparison. (b) Momentum-resolved spectral function calculated within LDA + DMFT at 145 K. Red curves represent the extracted experimental band dispersions.

below  $-1$  eV match well the LDA bands, which are mainly derived from As 4p of the Ti<sub>2</sub>As<sub>2</sub>O layers (Fig. S3 in the Supplemental Material [18]). Obvious discrepancies between the experimental results and the LDA calculations are observed within 1 eV below  $E_F$ , where the DOS is mainly of Fe 3d and Ti 3d characters. The deviation can be qualitatively attributed to non-negligible correlation effects between the 3d electrons, for which the self-energy leads to strong band renormalizations near  $E_F$ , as observed in other IBSCs [20]. To analyze the effects of Coulomb correlations on the electronic structure, we have performed LDA + dynamical mean field theory (DMFT) calculations of the momentum-resolved spectral function, starting from the above Kohn-Sham band structure and the implementation of Ref. [21] using projected atomic orbitals. Since our target compound contains two different atomic species with partially filled narrow  $d$  shells, we have generalized the usual LDA + DMFT scheme to include effective local Coulomb interactions on both the Fe 3d and Ti 3d shells. We use  $U = 2.64$  eV [3.50 eV] and  $J = 0.96$  eV [0.74 eV] for the Hubbard interactions (monopole Slater integral  $F_0$  and Hund's coupling on Fe [Ti]), and a multiorbital around mean field double counting based on the LDA electron count [22]. The resulting 10-orbital many-body problem was solved within a continuous-time quantum Monte Carlo scheme, as implemented in the TRIQS toolbox [23]. The corresponding results are presented in Fig. 2(b), which reproduce well the experimental band dispersions. The Fe 3d derived bands are strongly renormalized compared with the LDA results and their spectral intensities are very

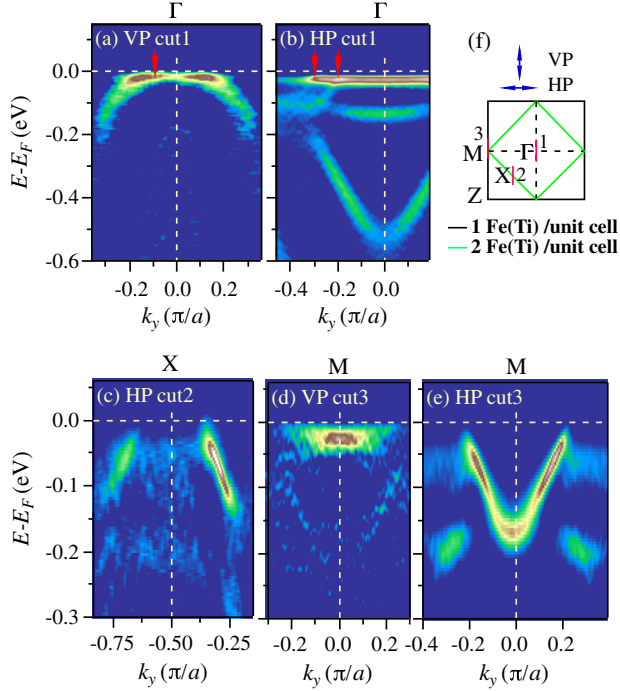


FIG. 3 (color online). (a)–(e) 2D curvature intensity plots of the near- $E_F$  ARPES data recorded at  $h\nu = 55$  eV. The momentum locations are indicated as red vertical lines in panel (f). To illustrate the Fe 3d related band dispersions more clearly, the data taken at 30 K are shown in panels (a), (b), and (d). As the Ti 3d related band dispersions are dramatically changed across the transition at 125 K (Fig. S2 in the Supplemental Material [18]), the data taken at 150 K are shown in panels (c) and (e).

diffuse due to a large quasiparticle broadening encoded in the imaginary part of the DMFT self-energy.

A prominent feature in the calculations is that the  $\text{Ti}_2\text{As}_2\text{O}$  intermediate layers contribute significantly to the DOS at  $E_F$ , demonstrating the metallic nature of the spacer layers in this system. To clarify the effects on the low-energy electronic states of the FeAs layers, we show the band dispersions near  $E_F$  in Fig. 3. All the cuts are parallel to the  $\Gamma M$  direction, as schematically plotted in Fig. 3(f). We identify three holelike bands near  $\Gamma$  [Figs. 3(a) and 3(b)], one holelike band near  $X$  [Fig. 3(c)], and two electronlike bands near  $M$  [Figs. 3(d) and 3(e)], which cross  $E_F$ . The band dispersions can be regarded as a superposition of the band structures of the FeAs and  $\text{Ti}_2\text{As}_2\text{O}$  layers. We assign the three holelike bands near  $\Gamma$  [Figs. 3(a) and 3(b)] and the shallow electronlike bands near  $M$  [Fig. 3(d)] to the Fe 3d orbitals, while the holelike band near  $X$  [Fig. 3(c)] and the deep electronlike band near  $M$  [Fig. 3(e)] are attributed to the Ti 3d orbitals. The Fe-3d related band structure resembles those of other IBSCs. In the IBSCs, there are generally two electronlike bands from Fe 3d near  $M$ . Only one electronlike band from Fe 3d is observed in our experiments [Fig. 3(d)], while another one from Fe 3d is not identified, most likely due to its extremely

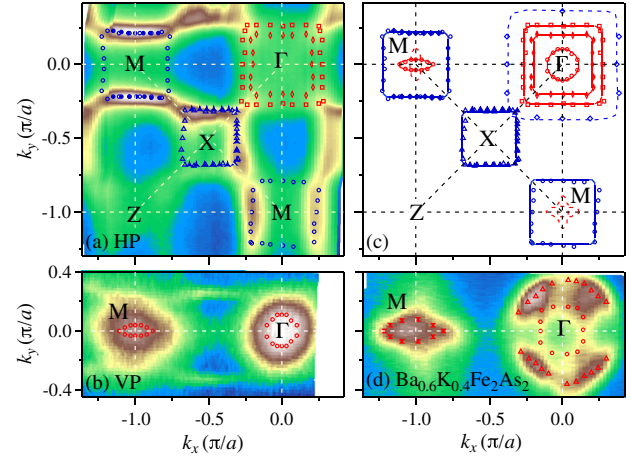


FIG. 4 (color online). (a) FS intensity plot of Ba22241 recorded at 150 K and  $h\nu = 55$  eV with HP. The intensity is obtained by integrating the spectra within  $\pm 10$  meV with respect to  $E_F$ .  $a$  represents the nearest neighbor Fe(Ti)-Fe(Ti) distance. (b) Same as (a) but taken with VP. (c) Extracted FSs of Ba22241. Red and blue symbols represent the extracted  $k_F$  points related to the FeAs and  $\text{Ti}_2\text{As}_2\text{O}$  layers, respectively. Solid and hollow symbols are extracted from the data taken at 150 and 30 K, respectively. Solid curves are guides for the eye. (d) FS intensity plot of  $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$  recorded with He I $\alpha$  resonance line ( $h\nu = 21.218$  eV), which measured the  $k_z \sim 0$  plane of this compound.

low spectral weight as it is folded from the adjacent  $M$  due to inequivalent As sites around Fe. The Ti 3d related band structure is similar to that of  $\text{BaTi}_2\text{As}_2\text{O}$  [25]. In  $\text{BaTi}_2\text{As}_2\text{O}$ , there is one electronlike band near  $\Gamma$ , one holelike band near  $X$ , and one electronlike band near  $M$ , which cross  $E_F$ . We do observe one electronlike band with a bottom of  $-0.5$  eV at  $\Gamma$  [Fig. 3(b)] and our photon energy dependence measurements suggest it originates mainly from Ti 3d states (Fig. S1 in the Supplemental Material [18]), in agreement with the observation in  $\text{BaTi}_2\text{As}_2\text{O}$  [25]. The spectral intensity of this band is smeared out as dispersing towards  $E_F$ , and its wave vector is estimated to be close to  $0.4\pi/a$  along  $\Gamma M$  by extrapolating the band dispersion to  $E_F$ .

With the identification of the near- $E_F$  bands, we extract the corresponding FSs and summarize them in Fig. 4(c). The extracted FSs related to the Fe 3d orbitals resemble those of other IBSCs, indicating that the FS topology of the FeAs layers is not changed by the metallic  $\text{Ti}_2\text{As}_2\text{O}$  intermediate layers. One prominent feature of the Fe-related FSs is that the total enclosed area of the hole pockets near  $\Gamma$  is much larger than that of the electron pockets near  $M$ . Our  $k_z$  dependent measurements suggest that the electronic structure of Ba22241 is quasi 2D (Fig. S1 in the Supplemental Material [18]). By counting the Luttinger volume of 2D FS sheets and assuming a purely 2D FS, we obtain a hole doping of  $\sim 0.25$  per Fe site. Indeed, the Fe-related FSs look similar to those of the optimally doped  $\text{Ba}_{0.6}\text{K}_{0.4}\text{Fe}_2\text{As}_2$  with a hole doping of



TABLE I. Orbital-resolved electron counts of Fe 3*d* and Ti 3*d* in Wannier functions calculated by LDA + DMFT (LDA). Upper table shows the electron counts of Fe 3*d* for Ba22241 (1st column), BaFe<sub>2</sub>As<sub>2</sub> with the same structure as in Ba22241 (2nd column), BaFe<sub>2</sub>As<sub>2</sub> (3rd column), and optimally doped Ba<sub>0.63</sub>K<sub>0.37</sub>Fe<sub>2</sub>As<sub>2</sub> (4th column). LDA + DMFT occupations for Ba22241 and Ba<sub>0.63</sub>K<sub>0.37</sub>Fe<sub>2</sub>As<sub>2</sub> are in bold font to emphasize the similarities between the electronic structures of these two compounds. Lower table shows the electron counts of Ti 3*d* for Ba22241 (1st column) and BaTi<sub>2</sub>As<sub>2</sub>O with the same structure as in Ba22241 (2nd column).

Orbital	Ba22241	BaFe <sub>2</sub> As <sub>2</sub> @Ba22241	BaFe <sub>2</sub> As <sub>2</sub>	Optimally doped 122
Fe $d_{z^2}$	<b>1.30</b> (1.41)	1.33 (1.42)	1.35 (1.43)	<b>1.30</b> (1.43)
Fe $d_{x^2-y^2}$	<b>1.33</b> (1.23)	1.34 (1.23)	1.32 (1.25)	<b>1.32</b> (1.25)
Fe $d_{xy}$	<b>1.20</b> (1.40)	1.23 (1.40)	1.26 (1.40)	<b>1.20</b> (1.33)
Fe $d_{xz} + d_{yz}$	<b>1.27</b> (1.35)	1.30 (1.34)	1.32 (1.34)	<b>1.27</b> (1.29)
Total Fe $d$	<b>6.38</b> (6.76)	6.50 (6.75)	6.56 (6.77)	<b>6.36</b> (6.61)
	Ba22241	BaTi <sub>2</sub> As <sub>2</sub> O @Ba22241		
Ti $d_{z^2}$	0.46 (0.43)	0.41 (0.42)		
Ti $d_{x^2-y^2}$	0.39 (0.39)	0.38 (0.38)		
Ti $d_{xy}$	0.63 (0.69)	0.60 (0.69)		
Ti $d_{xz}$	0.36 (0.15)	0.33 (0.15)		
Ti $d_{yz}$	0.45 (0.45)	0.48 (0.45)		
Total Ti $d$	2.29 (2.09)	2.20 (2.09)		

0.2 per Fe site, as shown in Fig. 4(d). Note that the inner hole pockets are almost doubly degenerate at  $k_z \sim 0$  for Ba<sub>0.6</sub>K<sub>0.4</sub>Fe<sub>2</sub>As<sub>2</sub>. By counting the volumes of the Ti-related FS sheets, we obtain an electron doping of  $\sim 0.25$  per Ti site. Both the  $k_z$  and temperature dependent ARPES results reflect bulk features (Figs. S1 and S2 in the Supplemental Material [18]), thus excluding the possibility of charge polarization on the surface. Therefore, the most significant effect of the introduction of metallic Ti<sub>2</sub>As<sub>2</sub>O layers is that the electrons are transferred from the FeAs layer to the Ti<sub>2</sub>As<sub>2</sub>O layer. The “washed out” nature of the Fe 3*d* bands is then a direct consequence of the interlayer charge transfer, since the effective hole doping places this compound in the regime of strongly doping- and temperature-dependent coherence properties induced by Hund’s rule coupling [10]. Analyzing further the many-body self-energies obtained within our DMFT calculations we find qualitatively similar incoherent behavior for the Fe 3*d* states in Ba22241 and optimally hole-doped BaFe<sub>2</sub>As<sub>2</sub>.

We analyze the electron transfer from Fe to Ti by comparing LDA and LDA + DMFT calculations for Ba22241 with experimental crystal structure, BaFe<sub>2</sub>As<sub>2</sub>, Ba<sub>0.63</sub>K<sub>0.37</sub>Fe<sub>2</sub>As<sub>2</sub> and the compounds derived by splitting Ba22241 into BaTi<sub>2</sub>As<sub>2</sub>O and BaFe<sub>2</sub>As<sub>2</sub>, while keeping the same distance and angle between atoms within one layer. We construct localized Wannier-like orbitals within the same window [−8.16 eV, 8.16 eV] for all the compounds and extract the number of electrons, and the orbital-resolved electron counts for Fe *d* and Ti *d*, which are displayed in Table I. For Ba<sub>0.63</sub>K<sub>0.37</sub>Fe<sub>2</sub>As<sub>2</sub> we have taken the band structure of BaFe<sub>2</sub>As<sub>2</sub> with the experimental crystal structure of optimally doped BaFe<sub>2</sub>As<sub>2</sub> and calculated the chemical potential such as to obtain the correct total number of electrons. The number of electrons in the

different orbitals of Ba22241 obtained from LDA is independent of the particular stacking structure of this material, as we can see by comparing the calculation on Ba22241 to calculations on BaFe<sub>2</sub>As<sub>2</sub> and BaTi<sub>2</sub>As<sub>2</sub>O crystals. Two effects are contributing to the global hole doping of the Fe-*d* orbitals when going from BaFe<sub>2</sub>As<sub>2</sub> to Ba22241. The effect of correlations in BaFe<sub>2</sub>As<sub>2</sub> is to reduce the number of electrons in the correlated shell. If the Fe-As hybridization is weaker, electrons are more localized and this effect is enhanced. In Ba22241, the Fe-As distance is about 1% larger than in BaFe<sub>2</sub>As<sub>2</sub>, thus lowering the hybridization with As. The consequence can be seen by comparing the number of electrons in the Fe-*d* Wannier orbitals in BaFe<sub>2</sub>As<sub>2</sub> in the structure of Ba22241 to BaFe<sub>2</sub>As<sub>2</sub> in the experimental crystal structure: There is already a loss of 0.05 electrons per Fe in Ba22241. The second effect is a transfer of electrons from Fe to Ti due to correlations. In BaTi<sub>2</sub>As<sub>2</sub>O, correlations tend to increase the number of electrons in the Ti *d* orbitals. This effect is enhanced when BaTi<sub>2</sub>As<sub>2</sub>O and BaFe<sub>2</sub>As<sub>2</sub> are put together, leading to a transfer of about 0.1 electrons from Fe to Ti. That transfer happens notably (but not exclusively) through the Fe- $d_{z^2}$  – Ti- $d_{z^2}$  hybridization, as Ti and Fe are on top of each other. We stress that the band with bottom around −0.5 eV at the  $\Gamma$  point is of mixed Ti  $d_{z^2}$  and Fe  $d_{z^2}$  characters, and wrongly predicted by LDA while correctly captured by our two-correlated shells LDA + DMFT.

In conclusion, we studied the electronic structure of Ba22241 and revealed a large charge transfer between the FeAs and metallic Ti<sub>2</sub>As<sub>2</sub>O layers, which is identified as a consequence of electronic correlations in the 3*d* shells by the LDA + DMFT calculations. This provides an alternative route of effective doping without element substitution for the IBSCs and thus without introducing disorder. We noticed

that several IBSCs with perovskite- or skutterudite-type intermediate layers were also claimed to have metallic spacer layers [26–31], suggesting that metallic spacer layers may in fact be less rare than generally thought. Since electronic correlations are believed to play an important role in most IBSCs, there should be high chances to find other “correlation-induced self-doped” superconducting compounds with metallic spacer layers. Furthermore, our results prove the presence of strong interlayer coupling in Ba22241 arising from the Fe- $d_{z^2}$  – Ti- $d_{z^2}$  hybridization and the metallic nature of the Ti<sub>2</sub>As<sub>2</sub>O intermediate layer. It has been argued that, as in the high- $T_c$  cuprate superconductors, the FeAs interlayer coupling can play a crucial role in enhancing  $T_c$  in the IBSCs [28]. Further studies for the IBSCs with metallic spacer layers may be a fruitful path for reaching higher  $T_c$  in the IBSC family.

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