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# Enhanced superconductivity in surface electron doped iron-pnictide $\text{Ba}(\text{Fe}_{1.94}\text{Co}_{0.06})_2\text{As}_2$

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**The transition critical temperature ( $T_C$ ) in a FeSe monolayer on  $\text{SrTiO}_3$  is enhanced up to  $100 \text{ K}^{1-4}$ . High  $T_C$  is also found in bulk iron chalcogenides with similar electronic structure<sup>5-7</sup> to that of monolayer FeSe, which suggests that higher  $T_C$  may be achieved**

**through electron doping, pushing the Fermi surface (FS) topology towards leaving only electron pockets. Such observation, however, has been limited to chalcogenides and is in contrast with the iron pnictides for which the maximum  $T_C$  is achieved with both hole and electron pockets forming considerable FS nesting instability<sup>8-11</sup>. Here, we report angle-resolved photoemission (ARPES) characterization revealing a monotonic increase of  $T_C$  from 24 to 41.5 K upon surface doping on optimally doped  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ . The doping changes the overall FS topology towards that of chalcogenides through a rigid downward band shift. Our findings suggest that higher electron doping and concomitant changes in FS topology are favorable conditions for the superconductivity, not only for iron chalcogenides but also for iron pnictides.**

An unconventional superconductivity in iron-based superconductor (IBS) was first discovered in iron pnictides, when additional charge carriers were doped into antiferromagnetic mother compounds<sup>12,13</sup>. Regardless of the carrier type, for each type there is an optimum doping level for the  $T_C$  with the  $T_C$  decreasing away from the optimum doping level. The maximum  $T_C$  was found to occur when a good nesting condition is satisfied among hole and electron pockets at the Brillouin zone (BZ) center and corner, respectively<sup>8,9</sup>. This led to a belief that the FS nesting instability was an important ingredient for the superconductivity<sup>8-11</sup>.

The discovery of a relatively high  $T_C \sim 37$  K in an iron chalcogenides  $\text{AFe}_2\text{Se}_2$  (A=alkali metal)<sup>5,6</sup> came as a surprise due to a largely different FS topology: no hole pockets at the zone center, leaving only electron pockets at the zone corner without any nesting condition. The overall

electronic structure of such chalcogenides resembles that of over-electron-doped iron pnictides. Furthermore, the striking discovery of superconductivity above 65 K in electron doped monolayer FeSe on SrTiO<sub>3</sub><sup>1-4,14,15</sup> and a recent report of 40 K (20 K) superconductivity in intercalated (surface doped) bulk FeSe<sup>7,16,17</sup> consistently strengthen the notion of higher  $T_C$  with increased electron doping and following changes in the FS topology.

While these findings may have brought new insights into the superconducting mechanism, however, such observation - increasing  $T_C$  with electron doping with changes in FS topology, is so far only limited to chalcogenides. It thus poses a challenging task in revealing the true nature of superconductivity in IBS; whether pnictides and chalcogenides have different superconducting mechanisms or such enhanced superconductivity simply has not been realized in pnictides. Finding out which is the case would provide key information on the main factors behind the superconductivity in IBS, thus calls for similar experiments on pnictides. Unfortunately, bulk doping of iron pnictide superconductors usually involves changes in other parameters affecting the superconductivity and electronic structure, such as the arsenic (As) height relative to the Fe-plane<sup>18-20</sup>.

To achieve electron doping without much affecting the underlying local structures or parameters affecting the superconductivity, we applied surface electron doping<sup>21-23</sup> to the prototypical pnictide system, optimally doped Ba(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub>As<sub>2</sub> ( $x = 0.06$ )<sup>24</sup> (see Methods). We observe monotonic enhancement of  $T_C$  upon electron doping of optimally doped Ba(Fe<sub>1-x</sub>Co<sub>x</sub>)<sub>2</sub>As<sub>2</sub> (OP). Our results imply that the superconductivity in pnictides also favors higher electron doping at the expense of the nesting condition as in chalcogenides. Such similarity between pnictides and

chalcogenides demands further studies towards a unified picture for the entire IBS family.

Surface electron doping was carried out by deposition of potassium (K) on the sample surface. Figure 1 shows the electronic structure of pristine (left, OP) and surface electron doped  $\text{Ba}(\text{Fe}_{1.94}\text{Co}_{0.06})_2\text{As}_2$  (right, OPD), respectively. The band structure in Fig. 1a does not show any significant change except a rigid downward band shift, as determined by comparing the band dispersions of OP and OPD along the  $\Gamma$ -M high symmetry line (indicated by the black and yellow dashed lines in Fig. 1a). The electronic structure of pnictides has been found to be highly sensitive to the change in the As height<sup>25,26</sup>. Even a change in the height less than  $0.1 \text{ \AA}$  should result in recognizable modification in the dispersion<sup>25</sup>. The observed rigid band shift without modification of the band dispersion thus implies that K deposition indeed does not alter the As height which plays the key role in the IBS physics<sup>18-20</sup>.

In the measured Fermi surfaces in Fig. 1b, it is seen that the hole pocket shrinks almost to the hole-electron Lifshitz transition point while the electron pocket enlarges. These observed changes in the FS topology are mostly due to the rigid band shift. The band shift was determined by monitoring the electron band bottom position at  $M$  that gradually shifts to a higher binding energy with the increasing doping level. The maximum achievable band shift is around 14 meV as the band shift saturates when the K coverage reaches up to 1 monolayer (ML) (see Fig. S1 in the Supplementary Information). Another noticeable change in the FS topology is the disappearance of the surface states from the surface reconstruction associated with Ba atoms (the weak intensity at (0.5,0.5) of OP in Fig. 1b). The states are found to completely disappear around 0.5 ML of K

coverage which was estimated from the core level spectra from both surface Ba and deposited K (see Fig. S2).

With the new Fermi surface topology, the next step is to investigate how the  $T_C$  changes upon the electronic structure change associated with the surface electron doping. As the system has a doping level away from the optimal value, the  $T_C$  for OPDs should decrease considering the phase diagram of bulk  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ . However, as summarized in Fig. 2, the superconducting gap size as well as the  $T_C$  turn out to increase in OPDs. Figures 2a-d show symmetrized energy distribution curves (EDCs) from various surface doping levels (0, 0.33, 0.5, and 0.67 ML) taken at different temperatures. The EDCs are from the momentum points where the electron band crosses the Fermi level. The symmetrized EDCs in Fig. 2a-d show a clear gap feature at the lowest temperature which increases with the doping level. Fitting the spectra with a Dynes function<sup>27</sup> gives a doping dependent gap size at 10 K as plotted in Fig. 2e. Starting from  $\Delta=4.8$  meV ( $\pm 0.8$ ) for the pristine system which is consistent with the reported value<sup>9</sup>, the gap size increases up to 7.2 meV ( $\pm 1.1$ ) for 0.67 ML case.

As indicated by the gap size, the  $T_C$  determined from the temperature dependent gap profile also increases in OPDs. The temperature dependent gap opening, plotted in Figs. 2f-h, shows enhanced  $T_C$ 's, essentially following the Bardeen-Cooper-Schrieffer mean-field temperature dependence<sup>28,29</sup>. Both the  $T_C$  and gap size gradually increase, from  $T_C = 24.0$  K and  $\Delta = 4.5$  meV ( $\pm 0.6$ ) for OP to  $T_C = 41.5$ K and  $\Delta = 6.8$  meV ( $\pm 0.8$ ) for 0.67 ML OPD. These results give  $2\Delta/(k_B T_C)$  ratios of 4.35 for OP and 3.77, 3.86 and 3.8 for 0.33, 0.5 and 0.67 ML OPDs,

respectively. The temperature dependence as well as similar values of  $2\Delta/(k_B T_C)$  ratio indicate that the gaps in OPDs is also of superconducting origin. The back bending dispersion observed at low temperatures, which is typically due to the Bogoliubov quasiparticles, further supports the superconducting origin of the gaps in OPDs (see Fig. S3d-g in Supplementary Information).

Our observation of the  $T_C$  enhancement in OPDs via surface doping is summarized in Fig. 3. The coverage is converted into effective bulk doping level in order to compare the results with the bulk  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$  phase diagram (see Supplementary Information S4), and is labeled in white text.  $T_C$ 's in OPDs are overlaid on the phase diagram with red square marks for the corresponding effective bulk doping levels. The observed doping dependent  $T_C$  upon surface doping (red dashed line) is in a clear contrast with the known doping dependence of the bulk doping (blue dashed line). The difference in the doping dependence of  $T_C$  should be attributed to the Co induced impurity effects in over-doped bulk sample (OV) compared to that in OPD. This also suggests that  $T_C$  in the bulk could have gone up for OV without the impurity potential generated by Co atoms and that the intrinsic optimal doping level might be higher than 6% Co in  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ . It is interesting to note that the Co concentration level of 6 % needed for the highest  $T_C$  in Co-doped  $\text{BaFe}_2\text{As}_2$  is far lower than any other dopants, such as 30 % for Ru- and 40 % for K-doped  $\text{BaFe}_2\text{As}_2$ <sup>30,31</sup>, suggesting a strong impurity effect from Co-doping.

This may also provide an important implication for the gap symmetry in  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ . Since superconductivity with an  $s_{+-}$  gap symmetry is expected to be suppressed by impurity effects, the relatively high  $T_C$  in  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$  has been viewed as either lack of or weak

pair-breaking role of Co atoms. These observations were used to propose  $s_{++}$  as the superconducting gap symmetry in  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$  system<sup>32</sup>. However, our results on suppressed superconductivity in OV from impurity effects indicate that the gap symmetry is more consistent with the  $s_{+-}$ .

Another important aspect to consider is the nesting instability. As seen in the insets of Fig. 3, the Fermi surface topology of OPD resembles that of OV. As a result, the associated nesting instability of OPD is significantly reduced compared to that of OP, which can be seen from the charge susceptibility estimated from the auto-correlation of the ARPES data<sup>33</sup> (the inset in the upper-right corner of Fig. 3). A higher  $T_C$  with less nesting instability in OPD implies that the FS nesting instability may not play an essential role for the superconductivity even for iron pnictides.

The observed  $T_C$  above 40 K in OPD has never been achieved in bulk doped  $\text{BaFe}_2\text{As}_2$  systems<sup>34</sup>, and the observed doping dependent  $T_C$  behavior in OPD is on par with that of chalcogenides: higher  $T_C$  with higher electron doping with corresponding changes in the electronic structure and the FS topology. Our results provide a guideline towards the unified understanding of the superconducting mechanism for entire IBS family, and calls for a new theoretical and experimental investigations on the role of inter-band scattering<sup>35</sup> in the IBS superconductivity.





## Methods

### Angle-resolved photoemission spectroscopy

The ARPES measurements were performed at the Beamlines (BLs) 10.0.1 and 4.0.3 of the Advanced Light Source, Lawrence Berkeley National Laboratory. Surface electron doping was carried out by evaporation of Na/K on the sample surfaces using commercial SAES alkali metal dispensers. Spectra were acquired with Scienta R4000 (BL 10.0.1) and R8000 (BL 4.0.3) electron analyzers. The overall energy resolution and used photon energy were 8 meV and 49 eV for BL 10.0.1, and 13 meV and 62 eV for BL 4.0.3, respectively. The samples were cleaved and doped at 50 and 10 K, respectively, in an ultra-high vacuum better than  $4 \times 10^{-11}$  Torr. All measurements were performed within an hour for each cleaved sample to avoid the aging effect on the Na/K evaporated sample surface. Data shown in Figs. 1-3 were collected on 7 different samples.

### Sample synthesis and characterization

Single crystals of  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$  ( $x = 0.06$  and  $0.16$ ) were grown using a self-flux method as described in Ref. 24. The actual Co composition was determined by an inductively coupled plasma technique.  $T_C$  of the optimally doped samples ( $x = 0.06$ ) is 24 K, which was determined from the resistivity and magnetic susceptibility measurements. Superconductivity was not observed in the overdoped samples ( $x = 0.16$ ).

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**Figure 1** Electronic structures of pristine (OP) and surface electron doped (OPD) optimal  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ . ARPES intensity plot along the  $\Gamma$ - $M$  direction (a) of OP (left) and OPD (right). White solid lines in panel a indicate energy distribution curves (EDC) at the  $M$ -point which reveal the downward band shift. The dashed lines mark the band dispersion of OP (black) and OPD (yellow), respectively. OP band dispersion is overlaid on the OPD data with a 14 meV downward shift. b, ARPES intensity maps at the Fermi level of OP (left) and OPD (right). While both  $\Gamma$  and  $M$  pockets have a similar size in OP, the FS of OPD shows a much larger electron pocket at the  $M$ -point than the hole pocket at the  $\Gamma$ -point.

**Figure 2** Surface doping and temperature dependence of the superconducting gap. Temperature dependent symmetrized ARPES spectra measured at the  $k_F$  point of the electron pocket around  $M$  for pristine OP (a), 0.4 ML of K covered (b), 0.6 ML (c) and 0.8 ML cases (d). Overlaid blue and red solid lines represent fitting results with Dynes function for OP and OPDs, respectively. e, Doping dependence of the gap (left) and the electron band bottom position shift with respect to OP case (right) at 10K. Temperature dependent gap behaviors of 0.4 ML (f), 0.6 ML (g) and 0.8 ML (h) OPDs. OP is plotted in (h) in blue. Black dotted lines in f-h indicate BCS spectral function<sup>29</sup> drawn by fitting each data. Error bars are estimated from the standard error of the fitting.

**Figure 3** Summary of  $T_C$  enhancement and FS topology change upon surface doping.  $T_C$  of surface doped  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$  is marked as the red rectangle on the phase diagram



of bulk  $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ . FSs of OP, OPD and OV are shown as insets. The surface dosing level was estimated from the electron pocket size with respect to that of OP and OV. The inset on the upper-right corner depicts the charge susceptibility calculated from ARPES intensity at  $E_F$  with autocorrelation method<sup>33</sup>. Blue and red dashed lines highlight the distinct trends of  $T_C$  in bulk- and surface-doped case, respectively. Error bars represent the standard error in the fitting procedure.





