Electronic band structure of BaCo$_2$As$_2$: a fully-doped ferropnictide with reduced electronic correlations

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We report an angle-resolved photoemission spectroscopy investigation of the Fermi surface and electronic band structure of BaCo$_2$As$_2$. Although its quasi-nesting-free Fermi surface differs drastically from that of its Fe-pnictide cousins, we show that the BaCo$_2$As$_2$ system can be used as an approximation to the bare unoccupied band structure of the related BaFe$_2$-As$_2$ and Ba$_{1-x}$K$_x$Fe$_2$As$_2$ compounds. However, our experimental results, in agreement with dynamical mean field theory calculations, indicate that electronic correlations are much less important in BaCo$_2$As$_2$ than in the ferropnictides. Our findings suggest that this effect is due to the increased filling of the electronic 3$d$ shell in the presence of significant Hund’s exchange coupling.

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Although the role they play in ferropnictide superconductivity is still unsettled, there is sufficient evidence indicating that these materials exhibit non-negligible electronic correlations. Hence, previous angle-resolved photoemission spectroscopy studies reported typical overall bandwidth renormalization of about 2-5 [1]. Interestingly, Hund’s rule coupling was identified as an efficient tuning parameter for electronic correlations [2-4], thus indicating the importance of local moments in the physics of these materials. Very recently [5], a study of holed-doped BaFe$_2$As$_2$ including dynamical screening effects evidenced an unusual non-Fermi liquid metallic phase in which partially-screened local moments are frozen above the ordering temperature. Interestingly, the doping-temperature phase diagram of these materials exhibits exotic fractional power-law behaviors of the many-body self-energies assimilated to the phase diagram of the “spin-freezing” model [6], where fractional behaviors occur in some temperature range at fillings close to half-filling. Following this logic, one would expect the weaker correlation effects evidenced an unusual non-Fermi liquid metallicity from that of its Fe-pnictide cousins, we show that the BaCo$_2$As$_2$ system can be used as an approximation to the bare unoccupied band structure of the related BaFe$_2$-As$_2$ and Ba$_{1-x}$K$_x$Fe$_2$As$_2$ compounds. However, our experimental results, in agreement with dynamical mean field theory calculations, indicate that electronic correlations are much less important in BaCo$_2$As$_2$ than in the ferropnictides. Our findings suggest that this effect is due to the increased filling of the 3$d$ shell in the presence of significant Hund’s exchange coupling.

High quality single crystals of BaCo$_2$As$_2$ were grown by the flux method [7]. ARPES experiments were performed at beamlines PGM and Apple-PGM of the Synchrotron Radiation Center (WI) equipped with a Scienta SES 200 analyzer and a Scienta R4000 analyzer, respectively. The energy and angular resolutions were set at 15-30 meV and 0.2°, respectively. The samples were cleaved in situ and measured at 20 K in a vacuum better than 5×10$^{-11}$ Torr. We label the momentum values with respect to the 1 Fe/unit cell Brillouin zone (BZ), and use $c'/c= c'/2$ as the distance between two Fe planes.

Wide energy photoemission spectra of BaCo$_2$As$_2$ (red) and BaFe$_2$As$_2$ (blue) are compared in Fig. 1(a). A well-defined Co 3p core level observed at a binding energy of 59.2 eV in the BaCo$_2$As$_2$ spectrum (inset I) in contrast to 52.7 eV for the Fe 3p core level in BaFe$_2$As$_2$ confirms the Fe→Co substitution. As expected from a previous ARPES study [9] and confirmed by band structure calculations [10], this substitution is accompanied by an upward shift of the chemical potential. Consequently, the As 3$d$ core levels (inset II) are observed 200 meV towards higher binding energy in BaCo$_2$As$_2$ as compared with BaFe$_2$As$_2$. We note that the As 3$d$ peaks have asym-
FIG. 1. (Color online): (a) Core level spectra of BaCo$_2$As$_2$ (red) and BaFe$_2$As$_2$ (blue) recorded with 195 eV photons. Insets I and II are zooms on the Fe/Co 3p and As 4d levels, respectively. (b) and (c) EDCs measured at 20 K along Γ-M ($k_z = 0$) and Z-A ($k_z = \pi$), respectively. (d) Photon energy dependence of the EDCs taken at the BZ center. (e) and (f) 2D curvature intensity plots [8] along high-symmetry lines in the $k_z = 0$ and $k_z = \pi$ planes, respectively. Non-renormalized LDA bands are overlapped for comparison.

metric profiles, which is consistent with the enhanced coherence of the BaCo$_2$As$_2$ valence electrons.

To fully investigate the dispersive states near $E_F$, we performed ARPES experiments over a wide photon energy range. We show energy distribution curves (EDCs) recorded along the $\Gamma(0,0,0)$−M($\pi,0,0$) and Z($0,0,\pi$)−A($\pi,0,\pi$) directions in Figs. 1(b) and 1(c), respectively. The two sets of data are different, suggesting a strong 3D character of the electronic structure emphasized by the photon energy dependence of the EDCs taken at the BZ center displayed in Fig. 1(d). At the first sight, the results are quite different from that of previous studies on the 122-ferropnictides [1]. In particular, an electron band rather than hole bands crosses $E_F$ around the $\Gamma$ point. This is indeed what is expected from our LDA calculations, which are shown in Figs. 1(e) and 1(f). Actually, an overall band renormalization of only 1.4 is needed to capture the essential dispersive features highlighted in the curvature intensity plots [8] also shown in Figs. 1(e) and 1(f) for high-symmetry directions. In contrast, the electronic correlations in Ba$_{0.6}$K$_{0.4}$Fe$_2$As$_2$ place the compound at the boundary of an exotic non-Fermi liquid state, where coherent quasi-particles are ill-defined quantities. To fit spectral features to a renormalized LDA band structure requires renormalization of at least a factor 2 [11]. We attribute this decrease in the strength of the electronic correlations to the less drastic effects of Hund’s rule coupling [12] in the $d^7$ compound BaCo$_2$As$_2$ as compared to the $d^{5-\delta}$ filling of the $d$-shell in hole-doped BaFe$_2$As$_2$. We come back to this point below.

Photoemission selection rules give further information on the nature of the electronic bands observed. In Figs. 2(a) and 2(b), we show the curvature intensity plots corresponding to data recorded with a $s$ polarization (with a polarization component along the $z$-axis) along the $\Gamma$-M and Z-A high-symmetry lines, respectively. Similarly, the data recorded with a $p$ polarization are displayed in Figs. 2(c) and 2(d) for the $k_z = 0$ plane and in Figs. 2(e) and 2(f) for the $k_z = \pi$ plane. While the $s$ polarization enhances bands with odd symmetries with respect to the photoemission plane, the $p$ polarization highlights
mainly the even symmetries. Two bands, δ and γ, cross $E_F$ at the M(A) point, independently of $k_z$. While both appear clearly with $s$-polarization, only the δ band is detected with $p$-polarization, suggesting that the other one, the γ band, has an odd character. Similarly, two electron bands, called η and θ, cross $E_F$ at the BZ center. The first one is detected at Γ and Z but appears stronger under $s$ polarization, suggesting an odd character. The effect of the polarization is more severe on the $θ$ under $s$

The results are summarized in Figs. 2(g) and 2(h) for the $k_z = 0$ and $k_z = π$ planes, respectively.

We display in Figs. 3(a) and 3(b) our LDA calculations for the FS cuts at $k_z = 0$ and $k_z = π$, respectively. The corresponding ARPES data, obtained by integrating the ARPES intensity within $E_F ± 10$ meV, are shown in Figs. 3(d) and 3(e), respectively. As expected from the previous analysis of the band structure in the vicinity of $E_F$, the FS topology of BaCo$_2$As$_2$ is quite different from that of the Fe-pnictides. For example, the more or less circular hole FS pockets at the Γ point of superconducting BaO$_6$K$_4$Fe$_2$As$_2$ are replaced by star-shape electron FS pockets in BaCo$_2$As$_2$, thus removing all possibility for electron-hole quasi-nesting scattering in this system. In Fig. 3(f) we show the $k_z$ dispersion at $E_F$ approximated by scanning the photon energy over a wide range, and we display the corresponding LDA calculation in Fig. 3(c). We note that the $η$ and $δ$ bands have a strong 2D character, which is consistent with our assignment of their orbital character. On the other hand, the $γ$ band exhibits a small warping that could be caused by a small hybridization with the $p_z$ orbital according to our LDA calculations.

Although the FS of BaCo$_2$As$_2$ differs substantially from that of the 122-ferropnictides, we found out that the constant energy maps recorded at 470 meV below $E_F$ for the $k_z = 0$ and $k_z = π$ planes, which are respectively displayed in Figs. 3(g) and 3(h), are quite similar to the FSs of BaO$_6$K$_4$Fe$_2$As$_2$. To illustrate this resemblance, we overlap on these figures the FSs obtained for BaO$_6$K$_4$Fe$_2$As$_2$ in Ref. [11]. In a similar fashion, the $k_x$, $k_z$ map at 470 meV binding energy displayed in Fig. 3(i) could be easily mistaken for the $k_z$ dispersion at $E_F$ of some typical 122-ferropnictides [15, 16].

At least qualitatively, the simplest explanation for this behavior is to assume a $≈$ 470 meV upward shift of the chemical potential following a complete Fe–Co substitution. As shown in Figs. 2(g) and 2(h), all the bands in BaCo$_2$As$_2$ below a binding energy of 470 meV find their near-$E_F$ equivalent in the 122-ferropnictides with the same orbital assignment [17]. At the Γ point for example, the $α$ and $α'$ bands are degenerate over a wide momentum range at $k_z = 0$, whereas at $k_z = π$ they merge only at the $Z$ point. Their relative position with respect to the $β$ band is also the same as in BaO$_6$K$_4$Fe$_2$As$_2$ [17]. For a more quantitative comparison, we use for the $k_z = 0$ data a tight-binding model (TBB) model [18] successfully applied previously to BaO$_6$K$_4$Fe$_2$As$_2$ [11]:

$$E^{α,β}(k_x, k_y) = E^{0,α,β} + t_{1}^{α,β} \left(\cos k_x + \cos k_y\right) + t_{2}^{α,β} \cos k_x \cos k_y$$

$$E^{γ,δ}(k_x, k_y) = E^{0,γ,δ} + t_{1}^{γ,δ} \left(\cos k_x + \cos k_y\right) + t_{2}^{γ,δ} \cos(k_x/2) \cos(k_y/2)$$

The results of the fit are overlapped in Fig. 4(a) with the curvature intensity plot at $k_z = 0$. The agreement with the data is quite good. Disregarding a 470 meV shift for the chemical potential, we find that all the fit parameters, except $t_{1}^{γ}$ and $t_{2}^{γ}$ which are 4 times larger, are twice as large as the parameters obtained for BaO$_6$K$_4$Fe$_2$As$_2$ [11]. Our experimental data suggest that BaCo$_2$As$_2$ can be viewed in a first rough approximation as a highly overdoped and non-magnetically ordered BaFe$_2$As$_2$ compound, thus allowing us to visualize the unoccupied

![FIG. 3. (Color online) (a)-(b) LDA cuts of the FS at $k_z = 0$ and $k_z = π$, respectively. (c) LDA FS in the plane defined by $k_y = 0$. (d)-(f) Experimental FS mappings corresponding to the cases described in panels (a)-(c). The open symbols represent extracted FS data. (g)-(i) Same as (d)-(f) but for ARPS data recorded 470 meV below $E_F$. The ARPES FS data [11] for BaO$_6$K$_4$Fe$_2$As$_2$ (red dashed lines) are plotted in (g) and (h) for comparison.](attachment:image.png)
The results given in Fig. 4(c) for BaCo$_2$As$_2$ show a remarkable agreement with the experimental data. We extract a quasi-particle weight $Z$ of 0.8 leading to a bandwidth renormalization of 1.25 that compares well to the experiment. We find a power-law behavior of the self-energy in BaFe$_2$As$_2$ for calculations at the same temperature (120 K), signaling the absence of coherent quasi-particles. However, the corresponding spectral functions are consistent with an apparent renormalisation of the low-energy LDA bands by a factor of 2.9, in agreement with the factor 3 observed experimentally [22].

In Fig. 4(c), we plot the imaginary part of the self-energy $\Sigma''(i\omega_n)$ of both BaCo$_2$As$_2$ and paramagnetic BaFe$_2$As$_2$ as a function of the Matsubara frequencies. While $\Sigma''(i\omega_n)$ varies linearly at low frequency in BaCo$_2$As$_2$, indicating coherent Fermi liquid behavior already at the temperature of the calculation ($T = 120$ K), it follows a nearly square-root behavior characteristic of the "spin-freezing" regime in BaFe$_2$As$_2$. To investigate further the origin of this phenomenon, we artificially added 1 electron per Fe in BaFe$_2$As$_2$ to mimic the effect of substitution, while maintaining the LDA Hamiltonian of this compound. Surprisingly, the self-energy of this hypothetical crystal can hardly be distinguished from that of BaCo$_2$As$_2$, as shown in Fig. 4(c). This strongly suggests that the decrease in the electronic correlations in BaCo$_2$As$_2$ is mainly due to the less drastic effects of Hund’s exchange in the Co-compound whose $t^2$ filling is further away from the case of a half-filled shell. An analogous effect has recently been studied in a three-orbital Hubbard model [9], where Hund’s exchange was found to induce an exotic “spin-freezing” regime at finite temperatures for incommensurate fillings close to the half-filled case. This explanation rules out any significant influence from structural variations [23]. Indeed, this huge change in the level of correlations cannot be linked to a variation of the Coulomb parameter $U$. In both cases, we find $U = F_0$ around 2.8 - 2.9 and $J_H = (F_2 + F_4)/14$ around 0.85, with even a small increase of $U$ in the Co case. We furthermore performed additional calculations where we artificially set $J_H$ to 0. In this case, we see a sudden drop of the renormalisation and the suppression of the non-Fermi liquid behavior in BaFe$_2$As$_2$. However, BaCo$_2$As$_2$ only gets slightly less correlated.

Our results emphasize the importance of local moments in the ferropnictides. In the spin-freezing regime, these unscreened local moments have a long lifetime and spin-spin correlations increase with the local moments. Thus, correlations in the ferropnictides can be interpreted as the interaction of local moments with itinerant electrons, as in the Kondo problem. In the present study, we com-
pare two compounds with small orbital polarization (due to the strength of Hund’s coupling): BaFe$_2$As$_2$, with six electrons in five bands, and BaCo$_2$As$_2$, which has seven electrons in five bands. In the former case, Hund’s exchange drastically reduces the available channels for Kondo screening, thus enhancing the consequences of electronic correlations, while in the latter screening is quite efficient and reestablishes a largely uncorrelated picture. We stress that this effect is not primarily due to the density of states. Indeed, a calculation with 5 degenerate bands gives qualitatively the same conclusion, and the reduction of orbital polarization by Hund’s coupling is likely to push the compound close to that model case. Yet, the overlap of $E_F$ with the pseudogap of the $e_g$ orbitals in BaFe$_2$As$_2$ is possibly the cause for orbital-dependent renormalization. This is not the case in BaCo$_2$As$_2$ since $E_F$ locates above the pseudogap, and the $e_g$ orbitals in that case are actually slightly more correlated than the $t_{2g}$ orbitals.

In summary, we used ARPES to characterize the electronic band structure of BaCo$_2$As$_2$. We showed that this material can be used as a first approximation to investigate the unoccupied states of the 122-ferropnictides. However, supported by LDA+DMFT calculations, our study indicates that BaCo$_2$As$_2$ is significantly less correlated than BaFe$_2$As$_2$ due to the Hund’s rule coupling and the filling of the $d$ electron shell. Our results reveal clearly the importance of local moments in the physics of the Fe-based superconductors.

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near the crossover between Fermi liquid and non-Fermi liquid. For instance, trying to hole-dope the BaCo$_2$As$_2$ compound gives a very different picture, with a finite part of $\Sigma''(0)$, indicating that this compound is pushed even further into the spin-freezing phase.