Title
Tuning electronic correlations in transition metal pnictides: Chemistry beyond the valence count

Permalink
https://escholarship.org/uc/item/1nn0v4bx

Journal
PHYSICAL REVIEW B, 91(21)

ISSN
2469-9950

Authors
Razzoli, E
Matt, CE
Kobayashi, M
et al.

Publication Date
2015-06-03

DOI
10.1103/PhysRevB.91.214502

License
https://creativecommons.org/licenses/by/4.0/ 4.0

Peer reviewed
Tuning electronic correlations in transition metal pnictides: Chemistry beyond the valence count

E. Razzoli,1,2,* C. E. Matt,1,3 M. Kobayashi,1,4 X.-P. Wang,5 V. N. Strocov,1 A. van Roekeghem,5,6 S. Biermann,6,7,8 N. C. Plumb,1 M. Radovic,1 T. Schmitt,1 C. Capian,5 Z. Fisk,9 P. Richard,5,10 H. Ding,5,10 P. Aebi,2 J. Mesot,1,3,11 and M. Shi1

1Swiss Light Source, Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland
2Département de Physique and Fribourg Center for Nanomaterials, Université de Fribourg, CH-1700 Fribourg, Switzerland
3Laboratory for Solid State Physics, ETH Zürich, CH-8093 Zürich, Switzerland
4Department of Applied Chemistry, School of Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-865 6, Japan
5Beijing National Laboratory for Condensed Matter Physics, and Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China
6Centre de Physique Theorique, Ecole Polytechnique, CNRS, F-91128 Palaiseau Cedex, France
7Collège de France, 11 place Marcealin Berthelot, F-75005 Paris, France
8European Theoretical Synchrotron Facility, Europe
9Department of Physics and Astronomy, University of California Irvine, Irvine, California 92697, USA
10Collaborative Innovation Center of Quantum Matter, Beijing, China
11Institut de la Matière Complex, EPF Lausanne, CH-1015 Lausanne, Switzerland

(Received 6 February 2015; revised manuscript received 15 May 2015; published 3 June 2015)

The effects of electron-electron correlations on the low-energy electronic structure and their relationship with unconventional superconductivity are central aspects in the research on iron-based pnictide superconductors. Here we use soft x-ray angle-resolved photoemission spectroscopy to study how electronic correlations evolve in different chemically substituted iron pnictides. We find that correlations are intrinsically related to the effective filling of the correlated orbitals, rather than to the filling obtained by valence counting. Combined density functional theory and dynamical mean-field theory calculations capture these effects, reproducing the experimentally observed trend in the correlation strength. The occupation-driven trend in the electronic correlation reported in our paper supports and extends the recently proposed connection between cuprate and pnictide phase diagrams.

DOI: 10.1103/PhysRevB.91.214502 PACS number(s): 74.70.Xa, 74.25.Jb

I. INTRODUCTION

Many recent studies have focused on the importance of the occupancy of the bands close to the Fermi level \(E_F\) in promoting the superconducting state of iron-based superconducting pnictides [1,2]. Most interestingly, when the filling is expressed with respect to the half-filled \(3d^5\) bands, a striking similarity of the iron pnictide phase diagram to that of high-temperature superconducting cuprates has been pointed out [1,3], suggesting links between strongly correlated Mott insulating behavior and unconventional superconductivity. In iron pnictides, electronic Coulomb correlations are largely driven by Hund’s exchange coupling [4–6], leading to a strong dependence even of the normal state properties on doping [7] and possible orbital selectivity in the strong coupling regime [8]. Theoretical models including the fivefold orbital manifold and Hund’s rule coupling in addition to local Hubbard interactions [9,10] reproduce the main consequences of the change of filling induced by doping, in particular, a regime with strongly enhanced effective masses when approaching the \(d^0\) configuration, even at local Hubbard interactions much smaller than the critical one. However, while this picture works well in the case of substitution of Ba with K or of Fe with Co [11], it fails in the case of isovalent substitution, e.g., for BaFe2As2, Fe, where the correlations change with \(x\) but the nominal filling of the correlated bands does not [2]. Quite generally, the link between the correlation strength in the Fe pnictides and the valence count remains elusive.

In this paper, we emphasize the conceptual difference between the nominal valence count corresponding to the band filling and the effective orbital occupancies of the correlated states. Based on a combined experimental and theoretical spectroscopic study, we show that the latter is a more reliable tuning parameter for electronic correlations. We perform soft x-ray angle-resolved photoemission spectroscopy (SX-ARPES) for a series of stoichiometric 122 pnictides, namely, LaFe3P2, CaFe2P2, and BaFe2As2. The use of SX-ARPES, with its increased probing depth compared to ARPES performed with ultraviolet light as the excitation source (UV-ARPES), is essential for the determination of the bulk electronic structure of these materials since it has been demonstrated that they show a surface state when measured in the UV range [12–14]. Moreover, we combine the SX-ARPES results with combined density functional theory and dynamical mean-field theory (DFT+DMFT) calculations to show how the electronic correlation effects are associated with the detailed electronic structure and filling in the studied series of stoichiometric 122 pnictides. In particular, when \(d\)-orbital occupations are considered rather than nominal chemical valences, a clear link between the evolution of the strength of electronic correlations and filling emerges. Indeed, contrarily to naive valence counting arguments, we find that the substitution of La with Ca does not change the \(d\)-orbital occupation, whereas the seemingly isovalent substitution of As by P does. Furthermore, we identify the source of the latter change in the occupation, namely, the change in bonding (BB) antibonding splitting of the pnictogen atoms due to the isovalent substitution. Our results reveal that the changes in the correlation strength are mainly driven by unexpected changes in the orbital-resolved occupancy of the bands close to \(E_F\), suggesting that such changes may be fundamental in determining the superconducting properties of a given compound.
FIG. 1. (Color online) DFT band structure and SX-ARPES intensity maps of \( \text{LaFe}_2\text{P}_2 \). (a) Band structure along high symmetry lines. The thickness of the colored line is proportional to the corresponding character of the band. (b) Fermi surface plotted using XCRYSDEN visualization package [17]. (c) FS map with \( h \nu = 575 \) eV. The superimposed dashed lines are the DFT FS sheets. (d) FS map along cut 2 in (c), taken with \( h \nu = 440–640 \) eV in steps of 2.5 eV. The superimposed dashed lines in (c) and (d) are the FS from DFT calculations for \( k_z < 0 \). (e), (f) ARPES spectra along cut 1 in (c) at \( h \nu = 575 \) and 525 eV, respectively. The cut at \( h \nu = 575 \) eV (\( h \nu = 525 \) eV) is close to the \( Z \- \Gamma \) (\( \Gamma \- M \)) direction. (g), (h) ARPES spectra along cut 2 in (c) at \( k_z = 21 \) and 20, respectively. The DFT bands are renormalized by a factor (\( W_{\text{DFT}} / W_{\text{ARPES}} \) = 1.5).

II. EXPERIMENTAL DETAILS

The SX-ARPES experiments were performed at the Advanced Resonant Spectroscopies (ADDRESS) beamline at the Swiss Light Source (SLS). The experimental geometry is described in Ref. [15]. Data were collected using circularly polarized light with an overall energy resolution of 50–80 meV. The samples were cleaved in situ at 11 K and measured in a vacuum always better than \( 5 \times 10^{-11} \) mbar. The \( k \) values are determined by taking into account the photon momentum and are expressed in units of \((2\pi/a, 2\pi/a, 2\pi/c)\). The \( k_z \) values were extracted by using the free-electron final-state approximation with an inner potential \( V_0 = 13 \) for \( \text{LaFe}_2\text{P}_2 \) and \( V_0 = 14 \) for \( \text{BaFe}_2\text{As}_2 \). All the intensity maps shown in the main text are obtained by integrating the ARPES spectral weight in an energy window of \( E_F \pm 10 \) meV.

III. EXPERIMENTAL RESULTS

Figure 1(a) shows the band structure of \( \text{LaFe}_2\text{P}_2 \) obtained using the \textsc{wien2k} software package [16]. The lattice constants used in the calculations are listed in Table I. The calculated Fermi surface (FS) [Fig. 1(b)] is similar to that of \( \text{LaRu}_2\text{P}_2 \) presented in Ref. [13] with the exception that there is an additional band (\( y \) in Fig. 1) that crosses \( E_F \) along the \( \Gamma \- X \) direction in \( \text{LaFe}_2\text{P}_2 \) and forms a small hole pocket at the zone corner. In Figs. 1(c) and 1(d) we plot the ARPES spectral weight mapping at \( E_F \) near the \((k_x, k_y, 21)\) and in the \((k_x, 2 - k_x, k_z)\) plane. The \( k_z \) values were extracted by using the free-electron final-state approximation (FEFSA) [22]. The overlaid dashed lines show the FS from DFT calculations for \( k_z < 0 \) (the FS for \( k_z > 0 \) is obtained by reflection with respect to the \( k_z = 0 \) axis). The \( k_z \) variation as a function of \( (k_x, k_y) \) in the ARPES measurements with fixed photon energy has been taken into account according to the FEFSA. The observed FS is in good agreement with DFT calculations and it is highly three dimensional, similarly to the case of \( \text{LaRu}_2\text{P}_2 \) [13].

The ARPES intensity as a function of energy and \( k \) along cut 1 in Fig. 1(c) at \( h \nu = 575 \) eV \((k_z \sim 21)\) and 525 eV \((k_z \sim 20)\) are shown in Figs. 1(e) and 1(f), respectively. Since the value of \( k_z \) changes substantially along cut 2 in Fig. 1(c) \((\Delta k_z \sim 0.5)\), to trace the band dispersion along the \( \Gamma \- X \) and \( Z \- A \) symmetry axes we made interopolations between spectra at different photon energies to obtain the spectra with constant \( k_z \) shown in Figs. 1(g) and 1(h). The DFT band structures (dashed lines) are superimposed on the data. Contrary to the case of \( \text{LaRu}_2\text{P}_2 \), where DFT reproduces the measured band dispersion quite well, the overall agreement between the ARPES spectra and the calculated electronic structure of \( \text{LaFe}_2\text{P}_2 \) becomes reasonable, for the bands close to \( E_F \) \((|E_F - E_F| \lesssim 0.6 \text{ eV})\), only once the DFT bands are renormalized by a factor (\( W_{\text{DFT}} / W_{\text{ARPES}} \) = 1.5 ± 0.1 (red dashed lines). Assuming a purely local and orbital-independent many-body self-energy to be at the origin of this renormalization, we estimate a quasi-particle residue of \( Z_{\text{ARPES}} = 0.67 \pm 0.05 \) [23]. All the bands close to the \( E_F \) are renormalized by this same factor, as evident from the curvature [24], energy distribution curve (EDC), and momentum distribution curve (MDC) analyses of Fig. 2.

The decrease of the bare bandwidth, due to the change in the principal quantum number of the electrons close to the \( E_F \), as well as the increase of the Hubbard interaction \( U \) and Hund’s coupling \( J \) (see Table II) upon isostructural substitution of Ru with Fe significantly contributes to the increasing correlations in the system. However, the observed band renormalization factor in \( \text{LaFe}_2\text{P}_2 \) is smaller than in the antiferromagnetic (AFM) compound (e.g., \( \text{BaFe}_2\text{As}_2 \)) and in the superconducting 122 Fe-based pnictides (e.g., \( \text{Ba}_1\text{−}_x \text{K}_x \text{Fe}_2\text{As}_2 \)), indicating that the above changes induced by the Ru → Fe substitution are not the only mechanisms responsible for the increase of the strength of the electronic correlations observed in these systems.

To investigate the effect of hole doping in the system, we performed a similar study for \( \text{CaFe}_2\text{P}_2 \), which has one

| Sample          | \( a (\text{Å}) \) | \( c (\text{Å}) \) | \( z_{\text{pu}} \) |
|-----------------|-------------------|-------------------|-------------------|
| \( \text{LaRu}_2\text{P}_2 \) | 4.031             | 10.675            | 0.3593            |
| \( \text{LaFe}_2\text{P}_2 \)  | 3.841             | 10.982            | 0.3554            |
| \( \text{CaFe}_2\text{P}_2 \)  | 3.855             | 9.985             | 0.3643            |
| \( \text{BaFe}_2\text{As}_2 \) | 3.957             | 12.969            | 0.354             |
more hole per unit cell compared to LaFe$_2$P$_2$ and LaRu$_2$P$_2$. Similar to these compounds, the three-dimensional (3D) FS of CaFe$_2$P$_2$ is in good agreement with the DFT calculations [see Figs. 3(a)–3(d)], while the band structure has to be renormalized by a factor of ($W_{\text{DFT}}/W_{\text{ARPES}} = 1.5 \pm 0.1$ [Figs. 3(e) and 3(f)]. This result is quite surprising, since the bandwidth renormalization is not influenced by the formal decrease in the number of the electrons due to the La to Ca substitution, contrary to the expected behavior of a system moving toward half filling [28]. However, this is explained once the multiband nature of these systems is taken into account. Comparison between Figs. 1(a) and 3(a) shows that the substitution of La with Ca does not result in a rigid shift of all the bands. Rather, only one band [γ in Fig. 1(a)] is fully pushed above $E_F$, while the others (with Fe d character) crossing $E_F$ are qualitatively unchanged. This is mainly due to the fact that the γ band is very sensitive to the La to Ca substitution since it is essentially a La (Ca) band hybridizing (strongly in the case of La) with Fe d and P p states. The filling of the d bands is thus barely changed even if the total number of electrons in the unit cell is decreased by 1. We note here that the comparison between our finding and the mass enhancement measured by various quantum oscillation experiments ($m/m_{\text{DFT}}$ in Table II) shows that while the electron-phonon interactions are responsible for the main contribution to the mass enhancement in LaRu$_2$P$_2$, most likely causing its low-T$_C$ superconducting state, they are negligible in LaFe$_2$P$_2$ and CaFe$_2$P$_2$, which are indeed not superconducting.

Having discussed the role of the La to Ca substitution, it is now important to clarify the origin of the change in the bandwidth renormalization from CaFe$_2$P$_2$ to BaFe$_2$As$_2$. The nominal filling, the screened Coulomb interaction $U$, and the Hund’s coupling $J$ (see Table II) are very similar in the two systems, suggesting similarities in the electronic correlations. However, our measurements for BaFe$_2$As$_2$ (see Fig. 4), for which a similar analysis as above leads to identifying a bandwidth renormalization $\sim 2.1 \pm 0.2$ ($Z_{\text{ARPES}} = 0.48 \pm 0.05$), in agreement with the existent ARPES measurements in the UV range [29], indicate that there is a sizable increase in the bandwidth renormalization. Again, the change in the bandwidth renormalization can be understood once the effective filling of the d bands is considered, instead of the nominal value. A first indication that the actual filling of the d bands is decreased in BaFe$_2$As$_2$ comes from comparing the DFT calculations. Focusing on the $d_{xz}$ ($d_{yz}$) bands, the comparison between Figs. 3(a) and 4(a) reveals that the bands at $-250$ meV in CaFe$_2$P$_2$ are very similar to the ones at $E_F$ in BaFe$_2$As$_2$, i.e., these bands appear shifted by $250$ meV with respect to each other. The change in the band structure in this case is mainly due to the P to As substitution (similarly to the case of CaFe$_2$P$_2$ and CaFe$_2$As$_2$ [26]), which results in a change in the distance between the pnictide atoms Pn (Pn = P, As) of two adjacent Fe-Pn layers. In case of smaller distance (in CaFe$_2$P$_2$) the stronger bonding (BB) antibonding (AB) splitting of the Pn bands results in the AB bands being above $E_F$ [in particular, the band at 0.5 eV at the X point in Fig. 3(a) [30]]. In the case of a larger distance, as in BaFe$_2$As$_2$, the splitting is smaller and the same band now crosses $E_F$. To compensate the increase of the carriers in this band, the other bands shift towards $E_F$. A clear demonstration of this mechanism is shown in Fig. 5(a), where the DFT calculations for CaFe$_2$P$_2$ are performed as a function of the P-P distance for a fixed P-Fe distance. We finally note that the transition from a three-dimensional (in CaFe$_2$P$_2$) into a more two-dimensional FS (in BaFe$_2$As$_2$), induced by the increase of the Pn-Pn distance, may also influence the change of the strength of the electronic correlations between the two systems.

To summarize, we have shown that while the weak strength of correlations in LaRu$_2$P$_2$ is mainly due to its larger bare bandwidth $W_{\text{DFT}}$ [see Table II and Fig. 5(d)], the evolution of the correlation strength in LaFe$_2$P$_2$, CaFe$_2$P$_2$, and BaFe$_2$As$_2$ is driven by the effective filling of the $d$ orbitals crossing the $E_F$. The strength of the correlations remains constant in LaFe$_2$P$_2$ and CaFe$_2$P$_2$ due to the similar filling, and increases in BaFe$_2$As$_2$ when the filling decreases [see Fig. 5b)]. This result differs from what would be naively expected from the nominal

\[ \text{TABLE II. Critical temperature, ground state, bandwidth renormalization with respect to DFT extracted from ARPES, mass enhancements reported in the literature, Hubbard } U \text{ and Hund’s coupling } J \text{ calculated from the constrained random phase approximation (cRPA), bare bandwidth obtained from DFT, vertical pnictogen-pnictogen distance, and nominal occupation of the } 3d \text{ shell for the samples LaRu$_2$P$_2$, LaFe$_2$P$_2$, CaFe$_2$P$_2$, and BaFe$_2$As$_2$.} \]

| Sample     | $T_c$ (K) | Ground state | $W_{\text{DFT}}/W_{\text{ARPES}}$ | $n_{\text{eff}}/n_{\text{DFT}}$ | $U_{\text{RPA}}$ (eV) | $J_{\text{RPA}}$ (eV) | $W_{\text{DFT}}$ (eV) | $z_{\text{Pn-Pn}}$ (Å) | $n_{d_{\text{eff}}}$ |
|------------|-----------|--------------|----------------------------------|----------------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| LaRu$_2$P$_2$ | 4 [19]   | Low T, SC    | 1 [13]                           | 2 [25]                           | 1.89                   | 0.502                  | 9.4                    | 3.00 [19]              | 6.5                    |
| LaFe$_2$P$_2$ | Non-SC    | 1.5          | 1.8 [25]                         | 2.035                            | 0.695                  | 7.55                   | 3.20 [19]              | 6.5                    |
| CaFe$_2$P$_2$ | Non-SC    | 1.5          | 1.5 [26]                         | 2.632                            | 0.723                  | 7.50                   | 2.71 [20]              | 6                      |
| BaFe$_2$As$_2$ | 142 [21] | AFM          | 2.1                              | 2–3 [27]                         | 2.572                  | 0.78                   | 7.4                    | 3.78 [21]              | 6                      |
Fe 3d band filling, i.e., the same strength of correlations in the 3d\textsuperscript{5} LaRu\textsubscript{2}P\textsubscript{2} and LaFe\textsubscript{2}P\textsubscript{2} and bigger (W\textsubscript{DFT}/W\textsubscript{ARPES}) in CaFe\textsubscript{2}P\textsubscript{2} and BaFe\textsubscript{2}As\textsubscript{2}, which are both nominally in the 3d\textsuperscript{6} configuration.

IV. DFT+DMFT DETAILS

The qualitative description above can be confirmed by theoretical calculations using the combined DFT+DMFT method which gives access to the spectral properties of these compounds. The DMFT calculations were performed in the implementation of Ref. [31], using the hybridization expansion continuous-time quantum Monte Carlo algorithm [32] as implemented in the TRIQS toolkit [33]. Localized Wannier orbitals were built by truncating the expansion of the initial atomiclike orbitals to an energy window \( W \), chosen here as \( W = [-7.5, 3] \) eV (see Ref. [31] for details). Calculations have been carried out at an inverse temperature of \( \beta = 40 \) eV\textsuperscript{-1}, in the paramagnetic phases of the compounds. The calculations of the Hubbard interactions and Hund’s coupling (or more generally the Slater integrals \( F_0, F_2, F_4 \)) have been performed using the constrained random phase approximation (cRPA) method in the implementation of Ref. [34].

V. DFT+DMFT RESULTS

The values obtained for the interactions are shown in Fig. 5(d). The DMFT spectral functions for the various samples are presented in Figs. 6(a)–6(d). The DFT band structures, overlaid on the respective spectral functions, are renormalized by a factor \((W\textsubscript{DFT}/W)\textsubscript{DMFT}\). The renormalized bands agree well with the DFT+DMFT spectral function at low binding energies, while they overestimate the correlation strength at higher binding energies, in agreement with our ARPES data. The resulting quasiparticle residues (denoted \( Z\textsubscript{DMFT} \)) agree well with the \( Z_m \) values \((m = z^2, x^2 - y^2, xy, xz, yz)\) directly extracted from the self-energy on the Matsubara
grid as $Z_m = \{1 - \text{Im}[\frac{\sum_e (i\omega_n)}{d_{\text{nom}}}]\}_{\omega_n=0}^{-1}$ [see Fig. 5(b)]. The calculated behavior agrees well with the experimental one; the correlations are negligible in LaRu$_2$P$_2$, increase in LaFe$_2$P$_2$, remain constant in CaFe$_2$P$_2$, and reach a maximum in BaFe$_2$As$_2$. Figures 6(e)–6(h) show the imaginary parts of the local many-body self-energy on the imaginary frequency axis, a quantity which in the Fermi liquid regime exhibits linear behavior at low energies (and a slope related to the quasiparticle residues as above). These curves show that the DMFT calculations display the trend of correlation strength for our series of compounds in two ways: Not only do the self-energies increase in overall value, with the steeper slopes for BaFe$_2$As$_2$ corresponding to the stronger quasiparticle renormalizations (smaller $Z_m$), but also the energetic extent of the linear regime decreases. In BaFe$_2$As$_2$, coherent quasiparticles exist only on very low-energy scales, while the other compounds display larger coherence scales. In the spectral functions, the signature of this effect is the overall quite substantial broadening observed in BaFe$_2$As$_2$, as compared to the other compounds. The small understimation of $(W_{\text{DFT}}/W)$ in the DMFT calculations as compared to experiment might be due to the local nature of the DMFT method [35] or the absence of dynamical screening in the calculations [7,36,37]. We also note that there is a sizable change in $U_{\text{RPA}}$ and $J_{\text{RPA}}$ only upon the Ru to Fe substitution and that, even in this case, it does not have a large influence on the correlations in our calculations. Indeed, the calculated $Z_m$ for the LaRu$_2$P$_2$ are slightly changed by an increase in $U_{\text{RPA}}$ and $J_{\text{RPA}}$ (values obtained using the same $U_{\text{RPA}}$ and $J_{\text{RPA}}$ used for BaFe$_2$As$_2$ are $Z_{\text{m}} = 0.90$, $Z_{\text{m}} = 0.91$, $Z_{\text{m}} = 0.92$, $Z_{\text{m}} = 0.90$). The evolution of the filling of the Wannier $d$ orbitals, $n_{\text{W}}$, both before and after the DFT-DMFT calculations, is shown in Fig. 5(c). The filling of the orbitals is constant in LaFe$_2$P$_2$ and CaFe$_2$P$_2$ and decreases in BaFe$_2$As$_2$, in agreement with the qualitative conclusions drawn from the band structure calculations. We underline that the observed occupation-driven trend in the correlations confirms the link between cuprate and pnictide phase diagrams. In Ref. [1], a unified phase diagram for hole-doped cuprates and both hole- and electron-doped Fe-based pnictides was proposed by plotting $T_C$ as a function of the nominal average orbital filling ($y_{\text{nom}}$), expressed as the deviation from half filling of the Fe $d$ bands (i.e., $n_{\text{W}} = 5 + 5y_{\text{nom}}$). To extend this picture in LaFe$_2$P$_2$ and CaFe$_2$P$_2$, we propose to use the Wannier orbital filling instead of the nominal value. We can calculate the average orbital filling with respect to the half-filled case for $i = \text{LaFe}_2\text{P}_2, \text{CaFe}_2\text{P}_2$ as $y_i = y_{\text{nom}} + K \times (y_{\text{W}} - y_{\text{BaFe}_2\text{As}_2})$, with $y_{\text{W}} = (n_{\text{d}} - 5)/5$. The use of a linear relation between $y_{\text{nom}}$ and $y_{\text{W}}$, with $K \approx 1$, is supported by our DFT-virtual crystal approximation (VCA) calculations of $y_{\text{W}}$ for BaFe$_{1-x}$Co$_x$As$_2$. The resulting $y_{\text{LaFe}_2\text{P}_2} = 0.27$ and $y_{\text{CaFe}_2\text{P}_2} = 0.28$, obtained using $n_{\text{d}}$ from our DFT calculations, places them in the overdoped nonsuperconducting side of the unified phase diagram proposed in Ref. [1]. At this doping the correlations are not strong enough to allow the development of unconventional superconductivity and to display differentiation of bandwidth renormalization, i.e., selective Mottness, for electrons with different band characters. These results are in agreement with our observation of moderated electronic correlations and absence of selective Mottness in LaFe$_2$P$_2$ and CaFe$_2$P$_2$.

VI. CONCLUSION

In conclusion, we showed that the evolution of the electronic correlations in the presented series of pnictides differs from the expected behavior inferred from the nominal filling of the correlated orbitals. The experimental trend can be qualitatively understood based on the effective filling of the correlated orbitals and quantitatively reproduced by our DMFT calculations. We also demonstrated that the observed occupation-driven trend in the correlations supports the recently proposed link between the
unconventional superconductivity in cuprates and Fe pnictides. Finally, the high sensitivity of the correlations to small changes in the filling opens different ways of tuning the strength of electronic correlations in transition metal pnictide systems by systematic chemical substitutions, pressure, or constraints.

ACKNOWLEDGMENTS

This project was supported by the Swiss National Science Foundation (Grant No. 200021-137783), through MaNEP (Grant No. 200020-105151) and Division II, the French ANR under Project PNICTIDES, IDRIS/GENCI under Project No. 091393, the European Research Council under Project No. 617196, and the Cai Yuanpei program. P.R. and H.D. acknowledge grants from MOST (No. 2010CB923000, No. 2011CBA001000, No. 2011CB921701, No. 2013CB921700, and No. 2012CB821403) and NSFC (No. 11004232, No. 11234014, and No. 11274362) from China. The DFT+DMFT calculations were performed at DALCO cluster of the University of Fribourg. We thank Pawel Bednarek for support.

[1] L. de’ Medici, G. Giovannetti, and M. Capone, Selective Mott Physics as a key to iron superconductors, Phys. Rev. Lett. 112, 177001 (2014).
[2] Z. R. Ye, Y. Zhang, F. Chen, M. Xu, J. Jiang, X. H. Niu, C. H. P. Wen, L. Y. Xing, X. C. Wang, Q. Jin, B. P. Xie, and D. L. Feng, Extraordinary doping effects on quasiparticle scattering and bandwidth in iron-based superconductors, Phys. Rev. X 4, 031041 (2014).
[3] T. Misawa, K. Nakamura, and M. Imada, Ab Initio evidence for strong correlation associated with mott proximity in iron-based superconductors, Phys. Rev. Lett. 108, 177007 (2012).
[4] M. Aichhorn, S. Biermann, T. Miyake, A. Georges, and M. Imada, Theoretical evidence for strong correlations and incoherent metallic state in FeSe, Phys. Rev. B 82, 064504 (2010).
[5] L. de’ Medici, Hund’s coupling and its key role in tuning multiorbital correlations, Phys. Rev. B 83, 205112 (2011).
[6] K. Haule and G. Kotliar, Coherence-incoherence crossover in the normal state of iron oxypnictides and importance of Hund’s rule coupling, New J. Phys. 11, 025021 (2009).
[7] P. Werner, M. Casula, T. Miyake, F. Aryasetiawan, A. J. Millis, and S. Biermann, Satellites and large doping and temperature dependence of electronic properties in hole-doped BaFe2As2, Nat. Phys. 8, 351 (2012).
[8] L. de’ Medici, S. R. Hassan, M. Capone, and Xi Dai, Orbital-Selective mott transition out of band degeneracy lifting, Phys. Rev. Lett. 104, 126401 (2009).
[9] A. Liebsch and H. Ishida, Correlation-induced spin freezing transition in FeSe: A dynamical mean field study, Phys. Rev. B 82, 155106 (2010).
[10] N. Lanata, H. U. R. Strand, G. Giovannetti, B. Hellising, L. de’ Medici, and M. Capone, Orbital selectivity in Hund’s metals: The iron chalcogenides, Phys. Rev. B 87, 045122 (2013).
[11] N. Xu, P. Richard, A. van Roekeghem, P. Zhang, H. Xiao, W.-L. Zhang, T. Qian, M. Ferrero, A. S. Sefat, S. Biermann, and H. Ding, Electronic Band Structure of BaCo2As2: A fully doped ferropnictide analog with reduced electronic correlations, Phys. Rev. X 3, 011003 (2013).
[12] E. van Heumen, J. Vuorinen, K. Koepennik, F. Massee, Y. Huang, M. Shi, J. Klei, J. Goedkoop, M. Lindroos, J. van den Brink, and M. S. Golden, Existence, character, and origin of surface-related bands in the high temperature iron pnictide superconductor BaFe2As2, Phys. Rev. Lett. 106, 027002 (2011).
[13] E. Razzoli, M. Kobayashi, V. N. Strocov, B. Delley, Z. Bukowski, J. Karpinski, N. C. Plumb, M. Radovic, J. Chang, T. Schmitt, L. Patthey, J. Mesot, and M. Shi, Bulk electronic structure of superconducting LaRu2P2 single crystals measured by soft-X-ray angle-resolved photoemission spectroscopy, Phys. Rev. Lett. 108, 257005 (2012).
[14] P. Richard, C. Capan, J. Ma, P. Zhang, N. Xu, T. Qian, J. D. Denlinger, G.-F. Chen, A. S. Sefat, Z. Fisk, and H. Ding, Angle-resolved photoemission spectroscopy observation of anomalous electronic states in EuFe2As2, P., J. Phys.: Condens. Matter 26, 035732 (2014).
[15] V. N. Strocov, X. Wang, M. Shi, M. Kobayashi, J. Krempasky, C. Hess, T. Schmitt, and L. Patthey, Soft-X-ray ARPES facility at the ADRESS beamline of the SLS: Concepts, technical realization and scientific applications, J. Synchrotron Radiat. 21, 32 (2014).
[16] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties (Karlsruhe Schwarz, Techn. Universitat in Wien, Austria, 2001).
[17] A. Kokalj, Computer graphics and graphical user interfaces as tools in simulations of matter at the atomic scale, Comput. Mater. Sci. 28, 155 (2003). Code available from http://www.xcrysden.org/.
[18] W. Jeitschko, R. Glaum, and L. Boonk, Superconducting LaRu2P2 and other alkaline earth and rare earth metal ruthenium and osmium phosphides and arsenides with ThCr2Si2 structure, J. Solid State Chem. 69, 93 (1987).
[19] W. Jeitschko, U. Meisen, H. M. Höller, and M. Reichuis, Ü ber LaCo5P2 und andere Neue Verbindungen mit ThCr2Si2- und CaBe2Ge2-Struktur, Z. Anorg. Allg. Chem. 527, 73 (1985).
[20] A. Mewis, Ternäre Phosphide mit ThCr2Si2-Struktur, Z. Naturforsch. B 35, 141 (1980).
[21] Q. Huang, Y. Qiu, W. Bao, M. A. Green, J. W. Lynn, Y. C. Gasparovic, T. Wu, G. Wu, and X. H. Chen, Neutron-diffraction measurements of magnetic order and a structural transition in the parent BaFe2As2 compound of FeAs-Based high-temperature superconductors, Phys. Rev. Lett. 101, 257003 (2008).
[22] S. Hüfner, Photoelectron Spectroscopy (Springer, Berlin, 1995).
[23] The bandwidth renomalization factor is symbolically indicated as $(W_{\text{DFT}}/W)$, with the index $i$ (i.e., ARPES, DMFT) specifying whether it is obtained by rescaling the DFT bands to match the experimental spectral function or the calculated one. The associated quasiparticle residue $Z$ is defined as $Z_i \equiv (W_{\text{DFT}}/W)^i$.
[24] P. Zhang, P. Richard, T. Qian, Y.-M. Xu, X. Dai, and H. Ding, A precise method for visualizing dispersive features in image plots, Rev. Sci. Instrum. 82, 043712 (2011).
[25] P. J. W. Moli, J. Kanter, R. D. MacDonald, F. Balakirev, P. Blaha, K. Schwarz, Z. Bukowski, N. D. Zhigadlo, S. Katrych, 112, 177001 (2014).
K. Mattenberger, J. Karpinski, and B. Batlogg, Quantum oscillations of the superconductor LaRu2P2: Comparable mass enhancement $\lambda \approx 1$ in Ru and Fe phosphides, Phys. Rev. B 84, 224507 (2011).

[26] A. I. Coldea, C. M. J. Andrew, J. G. Analytis, R. D. McDonald, A. F. Bangura, J.-H. Chu, I. R. Fisher, and A. Carrington, Topological change of the Fermi surface in ternary iron pnictides with reduced $c/a$ Ratio: A de Haas–van Alphen Study of CaFe2P2, Phys. Rev. Lett. 103, 026404 (2009).

[27] T. Terashima, N. Kurita, M. Tomita, K. Kihou, C.-H. Lee, Y. Tomioka, T. Ito, A. Iyo, H. Eisaki, T. Liang, M. Nakajima, S. Ishida, S.-I. Uchida, H. Harima, and S. Uji, Complete fermi surface in BaFe2As2 observed via shubnikov–de Haas Oscillation measurements on detwinned single crystals, Phys. Rev. Lett. 107, 176402 (2011).

[28] H. Ishida and A. Liebsch, Fermi-liquid, non-Fermi-liquid, and Mott phases in iron pnictides and cuprates, Phys. Rev. B 81, 054513 (2010).

[29] P. Richard, T. Sato, K. Nakayama, T. Takahashi, and H. Ding, Fe-based superconductors: An angle-resolved photoemission spectroscopy perspective, Rep. Prog. Phys. 74, 124512 (2011).

[30] O. K. Andersen, and L. Boeri, On the multi-orbital band structure and itinerant magnetism of iron-based superconductors, Ann. Phys. 1, 8 (2011).

[31] M. Aichhorn, L. Pourovskii, V. Vildosola, M. Ferrero, O. Parcollet, T. Miyake, A. Georges, and S. Biermann, Dynamical mean-field theory within an augmented plane-wave framework: Assessing electronic correlations in the iron pnictide LaFeAsO, Phys. Rev. B 80, 085101 (2009).

[32] P. Werner, A. Comanac, L. de’ Medici, M. Troyer, and A. J. Millis, Continuous-time solver for quantum impurity models, Phys. Rev. Lett. 97, 076405 (2006).

[33] M. Ferrero and O. Parcollet, Continuous-time solver for quantum impurity models TRIQS: A Toolbox for Research on Interacting Quantum Systems, http://ipt.cea.fr/triqs.

[34] L. Vaugier, H. Jiang, and S. Biermann, Hubbard $U$ and Hund exchange $J$ in transition metal oxides: Screening versus localization trends from constrained random phase approximation, Phys. Rev. B 86, 165105 (2012).

[35] A. Georges, G. Kotliar, K. Werner, and M. J. Rozenberg, Dynamical mean-field theory of strongly correlated fermion systems and the limit of infinite dimensions, Rev. Mod. Phys. 68, 13 (1996).

[36] M. Casula, P. Werner, L. Vaugier, F. Aryasetiawan, T. Miyake, A. J. Millis, and S. Biermann, Low-energy models for correlated materials: Bandwidth renormalization from coulombic screening, Phys. Rev. Lett. 109, 126408 (2012).

[37] A. van Roekeghem, T. Ayral, J. M. Tomczak, M. Casula, N. Xu, H. Ding, M. Ferrero, O. Parcollet, H. Jiang, and S. Biermann, Dynamical correlations and screened exchange on the experimental bench: Spectral properties of the cobalt pnictide BaCo2As2, Phys. Rev. Lett. 113, 266403 (2014).

[38] K. Gofryk, B. Saparov, T. Durakiewicz, A. Chikina, S. Danzenbächer, D. V. Vyalikh, M. J. Graf, and A. S. Sefat, Fermi-surface reconstruction and complex phase equilibria in CaFe2As2, Phys. Rev. Lett. 112, 186401 (2014).

[39] J. Diehl, S. Backes, D. Guterding, H. O. Jeschke, and R. Valenti, Correlation effects in the tetragonal and collapsed-tetragonal phase of CaFe2As2, Phys. Rev. B 90, 085110 (2014).

[40] S. Mandal, R. E. Cohen, and K. Haule, Pressure suppression of electron correlation in the collapsed tetragonal phase of CaFe2As2: A DFT-DMFT investigation, Phys. Rev. B 90, 060501(R) (2014).