Fermi Surface Topology of LaFePO and LiFeP

Johannes Ferber,* Harald O. Jeschke, and Roser Valentí

Institut für Theoretische Physik, Goethe-Universität Frankfurt, Max-von-Laue-Strasse 1, 60438 Frankfurt am Main, Germany

(Received 30 June 2012; published 5 December 2012)

We perform charge self-consistent density functional theory combined with dynamical mean field theory calculations to study correlation effects on the Fermi surfaces of the iron pnictide superconductors LaFePO and LiFeP. We find a distinctive change in the topology of the Fermi surface in both compounds where a hole pocket with Fe d_{z^2} orbital character changes its geometry from a closed shape in the localdensity approximation to an open shape upon inclusion of correlations. The opening of the pocket occurs in the vicinity of the Γ (Z) point in LaFePO (LiFeP). We discuss the relevance of these findings for the low superconducting transition temperature and the nodal gap observed in these materials.

DOI: 10.1103/PhysRevLett.109.236403

PACS numbers: 71.27.+a, 71.18.+y, 74.20.Pq, 74.70.Xa

The iron pnictides are an intensively studied new class of superconductors with superconducting transition temperatures up to currently 56 K [1]. They show a variety of distinct properties in the normal as well as superconducting state like the absence or presence of magnetic ordering, weak to strong electronic correlations, and nodal or nodeless superconducting gaps. Most parent compounds exhibit a nonsuperconducting ground state with antiferromagnetic order and become superconducting upon doping or application of external pressure.

LaFePO is the iron pnictide in which superconductivity was reported [2] for the first time at a critical temperature of about 6 K. In LaFePO superconductivity arises without doping or application of pressure, there is no long-range magnetic order [3], and the superconducting gap is nodal [4–6]. As a measure of electronic correlations, mass enhancement values have been reported from a number of different experiments including angle-resolved photoemission spectroscopy (ARPES) [7], optical conductivity [8], de Haas–van Alphen (dHvA) [9], and specific heat measurements [10]; all point to a range $m^*/m_{\rm LDA} \approx 1.7-2.2$, consistent also with existing local-density approximation plus dynamical mean field theory (LDA + DMFT) studies [11,12].

Recently, LiFeAs received particular attention due to a number of features that make it very attractive for both theoretical and experimental studies: like LaFePO, it exhibits superconductivity without doping or pressure at $T_c = 18$ K [13] and is nonmagnetic; furthermore, it cleaves between adjacent Li layers mitigating the issue of polar surfaces for surface-sensitive probes.

LiFeP shares these properties, yet its lower superconducting transition temperature of 5 K [14] did not trigger as much research. LiFeP shows contrasting behavior to LiFeAs in some respects, though. Most importantly, its superconducting order parameter is nodal [15] compared to the nodeless gap in LiFeAs. This is unexpected, as previous works suggested a relation between the lack of a third hole pocket at the Γ point and the formation of gap nodes [16–19], but both LiFeAs and LiFeP show three hole sheets at Γ . Effective masses in LiFeP were extracted from resistivity and upper critical field measurements [20] where the mass enhancements are estimated to be smaller by a factor of ~2 compared to LiFeAs; this corresponds to a mass enhancement of 1.5–2 over the LDA value. De Haas–van Alphen experiments [21] give values 1.6–3.3 for the mass enhancements. However, so far no theoretical studies investigating the effects of correlations on LiFeP have been reported.

Thus, both compounds are considered rather weakly correlated. However, in the present work we argue that the inclusion of correlations has a profound impact on the Fermi surface topology of both materials, which in the case of LaFePO agrees with ARPES [7] observations; for LiFeP, ARPES measurements are not yet reported and the available dHvA [21] data do not allow one to unambiguously decide on the k_z extension of the Fermi surface sheets, as will be discussed below. The features presented here have not been touched upon in the reported LDA + DMFT calculations on LaFePO [11,12]; for LiFeP we present, to our knowledge, the first LDA + DMFT study in the literature.

We performed full charge self-consistent calculations following the scheme from Ref. [22] using a combination of electronic structure calculations in the full potential linearized augmented plane wave framework as implemented in WIEN2K [23] with DMFT. For solving the impurity problem we employed the hybridization expansion continuous-time quantum Monte Carlo method [24] as implemented in the ALPS code [25,26]; only densitydensity terms of Hund's coupling were considered. We performed calculations on all available experimental crystal structures as reported in Refs. [2,3] (LaFePO) and Refs. [14,21] (LiFeP) with space group P4/nmm; results are shown for the structures from Ref. [2] (LaFePO) and Ref. [14] (LiFeP). The energy window for the construction of a localized Wannier basis was chosen to range from -5.4 eV to 2.7 eV (-6 eV to 3.15 eV) with respect to the Fermi energy for LaFePO (LiFeP). The Monte Carlo

sampling was done at an inverse temperature $\beta = 40 \text{ eV}^{-1}$ with 3×10^6 sweeps.

For the interaction parameters, we use the definitions of $U = F^0$ and $J = (F^2 + F^4)/14$ in terms of Slater integrals [27] F^k with U = 4 eV, J = 0.8 eV, and the aroundmean-field [28] double counting correction. Some low energy features, in particular, the size and shape of the Fermi hole pockets which are of central interest here, turn out to be rather sensitive to details of the LDA + DMFT calculation like the choice of double counting; however, we tested variations in these technical aspects and found the reported features—while being affected quantitatively—qualitatively consistent with calculations using the fully localized limit [29] double counting, as well as among different interaction parameters and reported crystal structures (see the Supplemental Material [30]).

In the following, orbital characters are labeled in a coordinate system which is 45° rotated with respect to the crystallographic axes, i.e., *x* and *y* point to nearest Fe neighbors in the Fe-P plane.

In Table I we list the orbital-resolved mass enhancements for both compounds as inferred from the self-energy on the Matsubara axis, $m^*/m_{\text{LDA}} = 1 - \partial \text{Im}\Sigma(i\omega)/\partial \omega|_{\omega \to 0^+}$. The mass enhancements for LaFePO are in line with the measured values $\sim 1.7-2.2$ from the various experiments [7-10] as well as previous LDA + DMFT studies where mass enhancements $\sim 1.6-2.2$ were calculated [11,12]. Note that for LaFePO the effective masses are higher for the e_g orbitals, whereas in LiFeP (and most other iron pnictides) the t_{2g} orbitals show stronger renormalization. This is because of the crystal field splitting which in LaFePO puts the t_{2g} orbitals below the e_g orbitals thereby promoting a ground state with configuration $e_g^2 t_{2g}^4$ in the atomic limit. This suppresses interorbital fluctuations among the e_g states, rendering these orbitals more correlated in effect [12,31]. As a consequence, the d_{z^2} orbital is the most strongly correlated one in LaFePO.

The values for LiFeP range between 1.4 and 1.7, which is roughly a factor of 2 smaller than in LiFeAs where ARPES [32] and dHvA [21] experiments yield mass enhancements of 3–4. This is in agreement with resistivity and upper critical field measurements [20] which also give a factor of 2 reduction with respect to LiFeAs.

The momentum-resolved spectral function of the two materials is presented in Fig. 1 in comparison with the LDA band energies. The excitations around the Fermi energy are well defined, revealing the Fermi liquid nature in accordance with resistivity measurements [20]. Most

TABLE I. Orbital-resolved mass enhancements m^*/m_{LDA} .

Orbital		d_{z^2}	$d_{x^2-y^2}$	d_{xy}	$d_{xz/yz}$
LaFePO	$\frac{m^*}{m_{\rm IDA}}$	1.85	1.70	1.54	1.69
LiFeP	$\frac{m^*}{m_{\text{LDA}}}$	1.52	1.39	1.71	1.62



FIG. 1 (color online). Momentum-resolved spectral function $A(\mathbf{k}, \boldsymbol{\omega})$ together with LDA bands in the vicinity of the Fermi surface topology change.

importantly, both compounds feature a band placed just below the Fermi energy E_F in LDA which gets shifted above E_F upon inclusion of correlations in the vicinity of the Γ (Z) point in LaFePO (LiFeP). In both compounds this band has d_{z^2} orbital character around E_F for the path shown in Fig. 1 and originates from the hybridization with phosphorus p states.

As shown in Figs. 2 and 3, this crossing of the Fermi energy is naturally accompanied by the appearance at the Fermi surface of an outer hole pocket centered at Γ in LaFePO [see Fig. 2(b)] and an inner hole pocket centered at *Z* in LiFeP [see Fig. 3(b)]. As has been suggested [33] for the iron pnictides, appearance of a pocket with d_{z^2} character may alter the superconducting pairing function to a nodal state and reduce the strength of the pairing as it is observed in LaFePO and LiFeP in contrast to their arsenic counterparts LaFeAsO and LiFeAs.

Because of the hybridization with the phosphorus states, the position of the crossing band in LDA is sensitive to the phosphorus z position and doping. Therefore, although the large outer hole pocket appearing in LaFePO has been observed in ARPES [7], it has been suspected [7,9] that the appearance of this pocket is caused by surface doping indicated by a too small electron count obtained in ARPES. In contrast, our calculations yield the change in the Fermi surface topology as a result of electronic correlations only. Note that the total charge in the crystal is conserved in our calculations and the opening of the pocket (i.e., increase of the Fermi surface volume) merely amounts to a charge transfer from the d_{z^2} orbitals to the t_{2g} orbitals. Despite the sensitivity of the band position in LDA (for LaFePO the band energies differ by approximately 12 meV between the two published structures [2,3]), we found the opening of the pocket in both structures and with very similar pocket sizes. As for the electron deficiency in ARPES, the huge size of the measured pocket [> 12 kT] as compared to <5 kT in our calculations, cf., orbit 3a in Fig. 4(a) probably still results from a charge effect.

As a result, the calculated dHvA frequencies for LaFePO experience significant shifts as shown in Fig. 4(a).



FIG. 2 (color online). Fermi surfaces of LaFePO in the $k_z = 0$ and $k_z = \pi$ plane (left-hand panels) and the $k_x = k_y$ plane (right-hand panels) for (a) LDA and (b) LDA + DMFT. The colors give the dominating orbital character.

The frequencies correspond to extremal pocket sizes (orbits) that are observed at a given angle θ with respect to the k_z axis. The outer hole pocket experiences a large increase compared to LDA and the opening at Z adds a new frequency 3a for the minimal orbit. As a result of charge conservation, the outer electron pocket (4a and 4b) is also greatly increased. The enlargement of the electron pocket seen in our calculations is not observed in the dHvA experiment [9]. The hole pocket itself is not measured in dHvA (7 out of the 10 predicted frequencies are present in the measurements). In LDA, inclusion of spin-orbit coupling reduces the size of the inner hole pocket (1a and 1b),

but spin-orbit coupling is not included in our LDA + DMFT calculations. It is therefore likely that this pocket shrinks even more than predicted by us, thereby reducing the total Fermi surface volume enclosed by the hole pockets; this could approximately compensate for the added volume from the opened hole pocket without enlargement of the electron pocket.

For LiFeP, the inclusion of interactions induces only moderate changes in the sizes of the Fermi surface sheets; see Fig. 4(b). The frequency shifts with respect to LDA are in qualitative agreement with the experimental dHvA data from Ref. [21]: the middle hole pocket (2a and 2b) shifts



FIG. 3 (color online). Fermi surfaces of LiFeP in the $k_z = 0$ and $k_z = \pi$ plane (left-hand panels) and the $k_x = k_y$ plane (right-hand panels) for (a) LDA and (b) LDA + DMFT. The colors give the dominating orbital character. The arrows indicate the k points for the calculation of the effective masses in Table II.



FIG. 4 (color online). dHvA frequencies with respect to magnetic field angle obtained within LDA (dashed thin lines) and LDA + DMFT (solid lines). Orbits 1, 2, and 3 refer to the inner, middle, and outer hole pocket, and orbits 4 and 5 to the outer and inner electron pocket. kT denotes kilo Tesla.

most and shrinks in size by approximately 0.39 kT (compared to approximately 0.95 kT in the experiment), the other sheets are less affected (orbit 4b also shrinks substantially, but is not measured in dHvA). For comparison, in LiFeAs inclusion of correlations leads to shifts up to 0.51 kT [34] in LDA + DMFT (for orbit 2b). This is another indication that LiFeP is less correlated than LiFeAs. However, due to the details of the band structure, the band generating the topology change in LiFeP stays below E_F in LiFeAs.

The opening of the inner hole pocket in LDA + DMFT has almost no effect on the dHvA frequencies: also in LDA, two frequencies for the inner hole pocket are expected due to a weak peanutlike distortion which gives a minimal orbit around Γ and a maximal orbit at $k_z \approx \frac{\pi}{2}$. In LDA + DMFT, the size of the pocket at Z (the new maximal orbit) essentially equals the maximal orbit size from LDA, thereby mimicking the LDA orbits. Since the position of the orbits in the Brillouin zone cannot be determined from dHvA, no clear distinction between the predictions from LDA and LDA + DMFT can be made from the published data. Measurements up to $\theta = 90^{\circ}$, which in principle allow us to differentiate between open and closed pockets ($F\cos\theta$ drops to zero for a closed pocket), have been performed and indicate a tendency of $F\cos\theta$ towards small values but are not conclusive because of the very weak signal [35].

While a good qualitative agreement is reached between our results and dHvA observations, our calculations do not lead to a sufficient shift to attain complete agreement with the experimental frequencies in LiFeP; in particular, the calculated reduction of the middle hole pocket is not pronounced enough. Note that spin-orbit coupling helps with the size reduction of this pocket, its effect is

TABLE II. Mass enhancements of the maximal and minimal Fermi surface orbits in LiFeP. The mass enhancements are measured at the k points indicated in Fig. 3.

Orbit	1a	1b	2a	2b	3a	3b	4a	4b	5a	5b
Pocket	Inner Hole		Middle Hole		Outer Hole		Outer Electron		Inner Electron	
$\frac{m^*}{m_{\text{LDA}}}$	1.47	1.34	1.48	1.47	1.69	1.70	1.49	1.46	1.52	1.37

comparatively small here, though (about 0.2 kT). Limitations of our approach are also revealed by a comparison of the effective masses in LiFeP. The effective masses obtained from the dHvA measurements are rather uniform among all orbits except for the orbits 2a and 2b which show only half the mass enhancement of the other orbits. Since these mass enhancements refer to the Fermi surface orbits rather than the localized orbitals, we calculated the LDA + DMFT mass enhancements in the same basis by projecting the self-energy in the localized Wannier basis $|\chi_m(\mathbf{k})\rangle$, Σ_{mm} , to the basis of Bloch states $|\psi_{\nu}(\mathbf{k})\rangle$, $\Sigma_{\nu\nu'}(\mathbf{k})$,

$$\Sigma_{\nu\nu'}(\mathbf{k}) = \sum_{mm'} P^*_{\nu m}(\mathbf{k}) \Sigma_{mm'} P_{m'\nu'}(\mathbf{k}), \qquad (1)$$

where $P_{m\nu}(\mathbf{k}) = \langle \chi_m(\mathbf{k}) | \psi_\nu(\mathbf{k}) \rangle$. From the diagonal elements $\Sigma_{\nu\nu}$ we obtain the mass enhancements of the respective Fermi surface pocket at the *k* points indicated in Fig. 3; the values are given in Table II.

The significantly smaller mass enhancements of the middle hole pocket (orbit 2) measured in the quantum oscillation experiments are not seen in LDA + DMFT. This suggests that this pocket is differently affected by the coupling to some scattering channel like spin fluctuations or nonlocal correlations which are not captured by our LDA + DMFT approach.

In summary, we reported LDA + DMFT calculations on LiFeP and LaFePO where we find a change of the Fermi surface topology upon inclusion of correlations in both compounds, namely, the opening of an outer hole pocket at Γ in LaFePO and the opening of an inner hole pocket at Z in LiFeP, both with Fe d_{z^2} orbital character. As discussed by Kemper et al. [33], this might promote the nodal gap and weak pairing strength, i.e., low T_c , in these materials. Whereas this pocket has been observed in ARPES [7] for LaFePO, the current experimental situation for LiFeP does not allow for a conclusive testing of our predictions and further experimental work is desired. Also, we find that the peculiarities of the middle hole pocket in LiFeP observed in dHvA experiments and not reproduced in our LDA + DMFT approach reveal the importance of scattering channels beyond local correlations.

We would like to thank A. Coldea, C. Putzke, A. Carrington, P. J. Hirschfeld, E. Gull, and P. Werner for useful discussions, and the Deutsche Forschungsgemeinschaft

for financial support through Grant No. SPP 1458, the Helmholtz Association for support through HA216/ EMMI, and the centre for scientific computing (CSC, LOEWE-CSC) in Frankfurt for computing facilities.

*ferber@itp.uni-frankfurt.de

- G. Wu, Y. L. Xie, H. Chen, M. Zhong, R. H. Liu, B. C. Shi, Q. J. Li, X. F. Wang, T. Wu, Y. J. Yan, J. J. Ying, and X. H. Chen, J. Phys. Condens. Matter 21, 142203 (2009).
- Y. Kamihara, H. Hiramatsu, M. Hirano, R. Kawamura, H. Yanagi, T. Kamiya, and H. Hosono, J. Am. Chem. Soc. 128, 10012 (2006).
- [3] T. M. McQueen, M. Regulacio, A. J. Williams, Q. Huang, J. W. Lynn, Y. S. Hor, D. V. West, M. A. Green, and R. J. Cava, Phys. Rev. B 78, 024521 (2008).
- [4] M. Yamashita, N. Nakata, Y. Senshu, S. Tonegawa, K. Ikada, K. Hashimoto, H. Sugawara, T. Shibauchi, and Y. Matsuda, Phys. Rev. B 80, 220509 (2009).
- [5] J. D. Fletcher, A. Serafin, L. Malone, J. G. Analytis, J.-H. Chu, A. S. Erickson, I. R. Fisher, and A. Carrington, Phys. Rev. Lett. **102**, 147001 (2009).
- [6] C. W. Hicks, T. M. Lippman, M. E. Huber, J. G. Analytis, J.-H. Chu, A. S. Erickson, I. R. Fisher, and K. A. Moler, Phys. Rev. Lett. 103, 127003 (2009).
- [7] D.H. Lu, M. Yi, S.-K. Mo, A.S. Erickson, J. Analytis, J.-H. Chu, D.J. Singh, Z. Hussain, T.H. Geballe, I.R. Fisher, and Z.-X. Shen, Nature (London) 455, 81 (2008).
- [8] M. M. Qazilbash, J. J. Hamlin, R. E. Baumbach, L. Zhang, D. J. Singh, M. B. Maple, and D. N. Basov, Nat. Phys. 5, 647 (2009).
- [9] A. I. Coldea, J. D. Fletcher, A. Carrington, J. G. Analytis, A. F. Bangura, J.-H. Chu, A. S. Erickson, I. R. Fisher, N. E. Hussey, and R. D. McDonald, Phys. Rev. Lett. 101, 216402 (2008).
- [10] S. Suzuki, S. Miyasaka, S. Tajima, T. Kida, and M. Hagiwara, J. Phys. Soc. Jpn. 78, 114712 (2009).
- [11] S. L. Skornyakov, N. A. Skorikov, A. V. Lukoyanov, A. O. Shorikov, and V. I. Anisimov, Phys. Rev. B 81, 174522 (2010).
- [12] Z.P. Yin, K. Haule, and G. Kotliar, Nat. Mater. 10, 932 (2011).
- [13] J. H. Tapp, Z. Tang, B. Lv, K. Sasmal, B. Lorenz, P. C. W. Chu, and A. M. Guloy, Phys. Rev. B 78, 060505 (2008).
- [14] Z. Deng, X. C. Wang, Q. Q. Liu, S. J. Zhang, Y. X. Lv, J. L. Zhu, R. C. Yu, and C. Q. Jin, Europhys. Lett. 87, 37 004 (2009).
- [15] K. Hashimoto, S. Kasahara, R. Katsumata, Y. Mizukami, M. Yamashita, H. Ikeda, T. Terashima, A. Carrington,

Y. Matsuda, and T. Shibauchi, Phys. Rev. Lett. 108, 047003 (2012).

- [16] K. Kuroki, H. Usui, S. Onari, R. Arita, and H. Aoki, Phys. Rev. B 79, 224511 (2009).
- [17] H. Ikeda, R. Arita, and J. Kuneš, Phys. Rev. B 81, 054502 (2010).
- [18] R. Thomale, C. Platt, W. Hanke, and B. A. Bernevig, Phys. Rev. Lett. **106**, 187003 (2011).
- [19] For a review, see P.J. Hirschfeld, M. M. Korshunov, and I. I. Mazin, Rep. Prog. Phys. 74, 124508 (2011).
- [20] S. Kasahara, K. Hashimoto, H. Ikeda, T. Terashima, Y. Matsuda, and T. Shibauchi, Phys. Rev. B 85, 060503 (2012).
- [21] C. Putzke, A.I. Coldea, I. Guillamón, D. Vignolles, A. McCollam, D. LeBoeuf, M.D. Watson, I.I. Mazin, S. Kasahara, T. Terashima, T. Shibauchi, Y. Matsuda, and A. Carrington, Phys. Rev. Lett. **108**, 047002 (2012).
- [22] M. Aichhorn, L. Pourovskii, and A. Georges, Phys. Rev. B 84, 054529 (2011).
- [23] 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, edited by K. Schwarz (Technische Universität Wien, Austria, 2001).
- [24] P. Werner, A. Comanac, L. de' Medici, M. Troyer, and A. J. Millis, Phys. Rev. Lett. 97, 076405 (2006).
- [25] B. Bauer et al., J. Stat. Mech. (2011) P05001.
- [26] E. Gull, P. Werner, S. Fuchs, B. Surer, T. Pruschke, and M. Troyer, Comput. Phys. Commun. 182, 1078 (2011).
- [27] V.I. Anisimov, F. Aryasetiawan, and A.I. Lichtenstein, J. Phys. Condens. Matter 9, 767 (1997).
- [28] M. T. Czyżyk and G. A. Sawatzky, Phys. Rev. B 49, 14211 (1994).
- [29] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyżyk, and G. A. Sawatzky, Phys. Rev. B 48, 16929 (1993).
- [30] See Supplemental Material at http://link.aps.org/ supplemental/10.1103/PhysRevLett.109.236403 for a brief analysis of the robustness with respect to different double counting corrections, interaction parameters, crystal structures, and the consideration of the rotationally invariant Hund's rule coupling.
- [31] L. de' Medici, Phys. Rev. B 83, 205112 (2011).
- [32] S. V. Borisenko, V. B. Zabolotnyy, D. V. Evtushinsky, T. K. Kim, I. V. Morozov, A. N. Yaresko, A. A. Kordyuk, G. Behr, A. Vasiliev, R. Follath, and B. Büchner, Phys. Rev. Lett. 105, 067002 (2010).
- [33] A.F. Kemper, T.A. Maier, S. Graser, H.-P. Cheng, P.J. Hirschfeld, and D.J. Scalapino, New J. Phys. 12, 073030 (2010).
- [34] J. Ferber, K. Foyevtsova, R. Valentí, and H.O. Jeschke, Phys. Rev. B 85, 094505 (2012).
- [35] C. Putzke (private communication).