The absence of surface states for LiFeAs

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We investigate the cleaving behavior of LiFeAs and determine its surface electronic structure by detailed density functional calculations. We show that due to the neutral surface of LiFeAs after cleaving, barely any influence of the surface on the electronic states is present. Therefore the data of surface sensitive probes such as angle resolved photoemission spectroscopy (ARPES) represent to a high degree the bulk electronic structure. This we highlighted by a direct comparison of the calculations to ARPES spectra.

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The use of angle-resolved photoemission (ARPES) and scanning tunneling spectroscopies to study the electronic structure of iron pnictides can turn out to be crucial to understand the superconductivity in these materials. One hand, both methods are very informative by providing the detailed distribution of electron density in real and reciprocal spaces, but on the other hand it is not clear whether the obtained information is related to the bulk or surface.

In a recent paper we found a pronounced surface electronic structure in LaOFeAs, which appears to be present in published angle-resolved photoemission (ARPES) data. LaOFeAs single crystals cleave between the La and As layers forming a polar surface. In contrast LiFeAs, of which clean large single-crystals are now available, can be expected to cleave between adjacent Li layers and hence to produce a neutral surface. This is confirmed by results of density functional (DFT) calculations presented below.

Although LiFeAs in bulk is found much more three dimensional (3D) compared to LaOFeAs in DFT calculations, its surface electronic structure is much more bulk-like. Surface sensitive probes are therefore expected to directly yield information on the bulk behavior. Also, undoped stoichiometric LiFeAs is superconducting below 18 K and does not order magnetically.

Recent ARPES experiments on LiFeAs have revealed several interesting features. Although the low-energy electronic structure is qualitatively similar to other Fe-pnictides, the Fermi surface of LiFeAs is remarkably different. It shows a strongly reduced tendency to $\pi$, $\pi$-nesting, which is present in most of the new iron superconductors and often believed to be characteristic for all of them. As shown in Fig. 6 the radii of the hole and electron cylinders are quite different here. Another observation is the renormalization of the conduction bands by a factor up to 3 as compared to DFT calculations with an extended van Hove singularity (flat maximum of the $h_2$ band) in the center of the Brillouin zone. The four bands supporting the Fermi surface were found to be differently, though isotropically, gapped in the superconducting state. These observations can have important implications for understanding the mechanism of superconductivity in the Fe-pnictides. Here we show that there is no surface driven electronic structure in LiFeAs and therefore surface sensitive measurements represent the bulk electronic structure as opposed to the situation in the 1111 (e.g. LaOFeAs) compounds.

Non-spin-polarized scalar relativistic DFT total energy and Kohn-Sham band structure calculations were performed with the full-potential local-orbital code version FPLO9.00. All considered structures were fully relaxed with the generalized-gradient-approximation (GGA) functional using the force tool of FPLO9.00. Forces were minimized to less then $5 \times 10^{-3}$ eV/$\AA$ for bulk and $10^{-1}$ eV/$\AA$ for slab calculations. This is necessary since no detailed surface structure is known from experiment.

The calculations were carefully converged with the number of k-points, and finally 12,12,4 regular k-point meshes were used in the full Brillouin zone (BZ). The densities were converged down to $10^{-6}$ for the corresponding parameter in FPLO (rms($\rho^{\text{out}} - \rho^{\text{in}}$)/u.c.). Table II shows the results for the bulk lattice parameters compared to experiment.

One can observe a decrease in volume of the cell, compared to experimental data, which is reflected in a $c$-lattice parameter reduction due to the softness of the lattice in $z$-direction (cf. LaOFeAs in Ref. 1). This slight underestimation of the lattice parameters even in GGA calculations is a common feature for non-spin-polarized calculations in the pnictide family due to the strong coupling of magnetism to the lattice. However, the differences remain acceptable although the deviation for the distance in $z$-direction between adjacent Fe and As layers $d_{\text{Fe-As}}$ is approximately 3%. The local density approximation (LDA), would result in even further reduced $a$- and $c$-values (results not shown), hence GGA was used throughout this work.

After relaxation, the next step was to calculate the cleaving behavior of LiFeAs by the same approach as in Ref. 1. We had to use an orthorhombic Pmm2 space
group instead of P4/nmm, in order to allow all atom layers to relax in $z$-direction, unconstrained by symmetry.

In order to study the cleaving behavior we constructed a super-cell with two unit cells in $z$-direction, with lattice constant $2c$. For $c = c_{\text{bulk}}$ this just represents a bulk calculation. Now, we apply tensile strain in $z$-direction, by increasing $c$. We performed a set of calculations for $c$-values, which correspond to 0, 10, 20 and 30\% strain.

Fig. 1 shows the inter and intra unit-cell layer distances of different atomic layers, such as Li-Li (straight and dashed lines), Fe-As (dotted line) and Li-As (dashed-dot line) for this periodic superstructure of two unit cells in $z$-direction as a function of tensile strain. At large enough strain the original periodicity of period $c$ in $z$-direction is broken by forming slits. By our adopted superstructure of two unit cells, slits form between every other Li-Li layer pair. (\textit{Inter} indicates the distance crossing the slit, when it is formed, while \textit{intra} corresponds to distances within the two unit cell slab $\{\text{Li} | \text{As} | \text{Fe}_2 \text{As} | \text{Li} | \text{As} | \text{Fe}_2 \text{As} | \text{Li}\}$.)

For small strain the whole slab is more or less uniformly stretched with all the layer distances increasing compared to their bulk values. From the calculated forces of about $0.2 \, \text{eV/Å}$ one infers a tensile stress in $z$-direction of 2.1 GPa for 10\% tensile strain. For a strain between 10 and 20\%, LiFeAs cleaves between two Li layers in our calculations with a resulting neutral surface and consequently a non-polar slab, as we pointed out above (see also Ref. [13]). Cleavage here means that the layers are no longer uniformly stretched but that the two unit cells relax back to bulk like distances, while a slit (vacuum) opens up between two Li layers such that we have a repeated slab setup with a slab thickness of two unit cells.

In the doubled unit cell the interior Li-Li layer distance (termed \textit{intra}cell in Fig. 1) relaxes back even below the bulk value. Also the topmost Li-As layer distance close to the slit reduces appreciably while the Fe-As layer distance hardly changes. (It should be pointed out that our simulation of the cleaving process only provides its qualitative behavior, because the chosen supercell may not be large enough to simulate true bulk like behavior in the interior layers.)

To obtain a reliable lattice and electronic structure of a cleaved crystal surface it is necessary to choose a slab that is thick enough to pin the Fermi level of the slab to the bulk value and to choose a slit that is wide enough so that electronic wave functions from both sides of the slit do not overlap. (Due to the chosen mirror symmetry in the center of the slab ($z$-direction) there is no electric field across the slit.) It turns out that the Fermi level of even a slab thickness of only three unit cells hardly changes compared to the bulk, indicating that this thickness is already sufficient. To check convergence with the vacuum layer width, calculations were done with a slit width of about $c_{\text{bulk}}$ (resulting in a periodicity 4$c$ for the repeated three unit cells slab; termed 3/1 in Table II) and with a slit width of about 3$c$ (resulting in a periodicity of 6$c$ for the whole repeated slab setup, termed 3/3). In order to have $\vec{k}$-integration errors under control, the bulk calculations (used for comparison in Table II) were done with supercells of the same periodicity in $z$-direction (4 and 6 unit cells, respectively) allowing for the same $\vec{k}$-integration.
mash interpolation in both bulk and slab cases. The two different vacuum setups with their corresponding bulk calculations are represented by the left and right double columns in Table \ref{table1}

When comparing the inner layer distances and layer charges of the slab with those of the bulk crystal (lower parts of both sub panels in Table \ref{table1}), one sees that a slab of three unit cells thickness is already giving bulk representative interior layers. From the residual forces the numerical accuracy of the distances is estimated to be better than 0.01Å, while the accuracy of the layer charges is better than 0.005 of the electron charge. Also the positions and charges between a calculation with a vacuum width of c and 3c barely differ, so that in what follows the 3/1 slab is used for the surface band structure analysis.

As is seen from the upper parts of Table \ref{table1} there is a slight outward shift of the topmost As layer beneath the surface and an appreciable inward shift of the Li surface layer. Interestingly, this causes a charge redistribution between the As layer and the Fe layer below of about 0.1 electron charge, but nearly no change of the Li layer charge.

After having justified our model, we will inspect more closely Figs. 2 to 4 which show results for the band-structure and Fermi surface (FS). In Fig. 2 we present the orbital projected band structure for the bulk calculation. The orbital projection is obtained by projecting the Kohn-Sham wave functions onto the chemical orbitals of the FPLO basis. The line width of the colored lines in Fig. 2 indicates the orbital content/character in the vicinity of the Fermi level are within the $\Gamma$-M and $\Gamma$-Z-R-A, which couples to As at higher energies and to Fe at lower energies. This effect is absent in all other families of iron pnictides or chalcogenides i.e., 11 (e.g. FeSe), 1111 (e.g. LaOFeAs) or 122 (e.g. BaFe$_2$As$_2$)\cite{ref11}. In fact, this dispersive feature is responsible for the closed Fermi surface (FS) seen around $\Gamma$ in Fig. 4 (left panel). Of course, in a slab model there is no $k_z$-dispersion and hence this FS is not closed in Fig. 4 (right panel).

As seen in Fig. 3 all slab bands (thin green lines) in the vicinity of the Fermi level are within the $k_z$-dispersion range of the corresponding bulk bands (pairs of black and red lines). Hence no surface band is found in an energy window free of bulk bands. This is in contrast to the situation found for LaOFeAs in Ref\ref{ref1}. Furthermore, the bulk FS nesting is less pronounced than in LaOFeAs (larger difference between radii of electron and hole FSs), due to a larger $k_z$-dispersion compared to LaOFeAs, which is mainly caused by the extended Li states. This could be related to the absence of magnetic order in this material.

We note that Ref. \ref{ref19} calculated a smaller orbital weight ratio between As 4p and Fe 3d. Although both calculations differ somewhat in the Fe-As layer distance (here 2.345 Å compared to 2.403 Å of Ref. \ref{ref19}) this is mainly caused by different local orbital projections.

In Table III the calculated bulk Fermi radii (averaged over $k_z$) are compared to measured values (see Fig. 5). Of course, in a slab model there is no $k_z$-dispersion and hence this FS is not closed in Fig. 4 (right panel).

ARPES results for the FS are shown on Fig. 5. The FS radii are comparable with the calculated results at least in chosen directions while the shape of the FSs around $\Gamma$ seems to be more complex in experiment. We infer that this finding, just as the band renormalization presented below, is intrinsic to the bulk electronic structure.

Figure 2. Band structure of bulk LiFeAs, orbital projected onto the leading Fe, As and Li orbitals.

Figure 3. Band plot of bulk LiFeAs for $k_z = 0$ (black) and $k_z = \pi$ (red) and slab LiFeAs (green lines).

| $\varepsilon(k)$ [eV] | $n$ |
|------------------------|-----|
| -4                     | 2  |
| -2                     | 1  |
| 0                      | 0  |
| 2                      | 2  |
| 4                      | 2  |
| 6                      | 2  |

Figure 4 (left panel). Of course, in a slab model there is no $k_z$-dispersion and hence this FS is not closed in Fig. 4 (right panel).
with the results of the calculations. The spectra were collected at BESSY. A detailed description of the experiment can be found elsewhere (Ref. 15). In the upper panel, we show the photoemission intensity and in the lower panel the corresponding results for the calculated bulk band structure. The photoemission data have been interpolated by a tight-binding (TB) fit (denoted by the dotted lines). Note, however, that there are uncertainties in TB fits, especially concerning band connectivities. The hole-like structures near the Γ-point are indicated by $h_1$, $h_2$ and $h_3$, and electron-like structures near the corner of the BZ by $e_1$ and $e_2$. These notations are also used in Fig. 5 (except for $h_3$, see below).

The energy scale in both panels is of the same width, which allows to estimate the band renormalization. The overall agreement is remarkable, taking into account that in both cases the low energy electronic structure is formed by five bands and the Fermi surface (FS) is of the same topology. Applying a renormalization factor to the calculations leads to even better, quantitative agreement. All characteristic dispersions and Fermi velocities are reproduced by the calculations. The experimental Fermi surface (Fig. 5) consists of two hole-like FSs around the Γ-point and two electron-like FSs centered at the M-point. The strongly dispersive $h_3$ feature (seen in Fig. 6) barely contributes to the spectral weight at the Fermi level and hence is not indicated in Fig. 5. The relative sizes of the Fermi surfaces differ slightly from the theoretical ones. Notably, the first two hole pockets at the zone center seem to be smaller in the ARPES data compared to the calculations. (The agreement can be improved by applying a small shift of the chemical potential. This would also improve the agreement concerning the $h_3$ feature at the Γ-point.)

In summary, we have investigated the surface structure and surface effects on the electronic structure in LiFeAs.

|     | $M_1$ | $M_2$ | Γ₁  | Γ₂  |
|-----|-------|-------|-----|-----|
| experim. | 0.15  | 0.18  | 0.24 | ≈ 0.07 |
| GGA   | 0.17  | 0.17  | 0.19 | 0.13 |

Table III. Fermi radii in $k_x$-direction of different FS-pockets in units of $\frac{2\pi a}{c}$ from experimental data and from the calculation.
The main finding is that due to the neutral cleaving of the compound between the Li-layers there are no significant surface effects on the electronic states. Consequently, LiFeAs is an ideal compound in the pnictide family for the study by ARPES and STM methods.

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[1] H. Eschrig, A. Lankau, K. Koepernik, Phys. Rev. B 81, 155447 (2010)
[2] D. H. Lu, M. Yi, S.-K. Mo, A. S. Erickson, J. Analytis, J.-H. Chu, D. J. Singh, Z. Hussain, T. H. Geballe, R. R. Fisher and Z.-X. Shen, Nature 455, 81 (2008)
[3] Ch. Liu, T. Kondo, A. D. Palczewski, G. D. Samolyuk, Y. Lee, M. E. Tillman, N. Ni, E. D. Mun, R. Gordon, A. F. Santander-Syro, S. L. Bud’ko, J. L. McChesney, E. Rotenberg, A. V. Fedorov, T. Valla, O. Copie, M. A. Tanatar, C. Martin, B. N. Harmon, P. C. Canfield, R. Prozorov, J. Schmalian and A. Kaminski, Physica C 469, 491 (2009).
[4] D. H. Lu, M. Yi, S.-K. Mo, J. G. Analytis, J.-H. Chu, A. S. Erickson, D. J. Singh, Z. Hussain, T. H. Geballe, I. R. Fisher and Z.-X. Shen, Physica C 469, 452 (2009).
[5] Ch. Liu, Y. Lee, A. D. Palczewski, J.-Q. Yan, T. Kondo, B. N. Harmon, R. W. McCallum, T. A. Lograsso and A. Kaminski, arXiv:1006.0929v1
[6] L. X. Yang, B. P. Xie, Y. Zhang, C. He, Q. Q. Ge, X. F. Wang, X. H. Chen, M. Arita, J. Jiang, K. Shimada, M. Taniguchi, I. Vobornik, G. Rossi, J. P. Hu, D. H. Lu, Z. X. Shen, Z. Y. Lu, D. L. Feng, arXiv:1006.1107v1
[7] H. Liu, G. F. Chen, W. Zhang, L. Zhao, G. Liu, T.-L. Xia, X. Jia, D. Mu, Sh. Liu, Sh. He, Y. Peng, J. He, Zh. Chen, X. Dong, J. Zhang, G. Wang, Y. Zhu, Z. Xu, Ch. Chen and X. J. Zhou, arXiv:0912.2838v4 (2010)
[8] Igor Morozov, Alexander Boltalini, Olga Volkova, Alexandre Vassiliev, Olga Kataeva, Ulrike Stockert, Mahmoud Abdel-Hafiez, Madeleine Fuchs, Hans-Joachim Grafe, Günter Behr, Rüdiger Klingeler, Sergej Borisenko, Sabine Wurmehl, Bernd Büchner, submitted to Cryst. Growth and Design
[9] Y. J. Song, J. S. Ghim, B. H. Min, Y. S. Kwon, M. H. Jung, J.-S. Rhyee, arXiv:1002.2249 (2010)
[10] Joshua H. Tapp, Zhongjia Tang, Bing Lv, Kalyan Sasmal, Bernd Lorenz, Paul C. W. Chu, and Arnold M. Guloy, Phys. Rev. B 78, 060505(R) (2008)
[11] H. Eschrig, K. Koepernik, Phys. Rev. B 80, 104503 (2009)
[12] Takashi Miyake, Kazuma Nakamura, Ryotaro Arita, Masatoshi Imada, J. Phys. Soc. Jpn., 79, 044705 (2010)
[13] Hiroki Nakamura, Masahiko Machida, Tomio Koyama, Noriaki Hamada, J. Phys. Soc. Jpn. 78, 123712 (2009)
[14] C.W. Chu, F. Chen, M. Gooch, A.M. Guloy, B. Lorenz, B. Lv, K. Sasmal, Z.-J. Tang, J.H. Tapp, Y.Y. Xue, Physica C, 469, 326-331 (2009)
[15] 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, B. Büchner Phys. Rev. Lett. 105, 067002 (2010)
[16] K. Koepernik and H. Eschrig, Phys. Rev. B 59, 1743 (1999)
[17] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[18] M. J. Pitcher, D. R. Parker, P. Adamson, S. J. C. Herkelrath, A. T. Boothroyd, R. M. Ibberson, M. Brunelli and S. J. Clarke, Chem. Commun. 45, 5918 (2008)
[19] D. J. Singh, Phys. Rev. B 78, 094511 (2008)