A first principles study on FeAs single layers

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FeAs− single layer is tested as a simple model for LaFeAsO and BaFe2As2 based on first-principles calculations using generalized gradient approximation (GGA) and GGA+U. The calculated single-layer geometric and electronic structures are inconsistent with that of bulk materials. The bulk collinear antiferromagnetic ground state is failed to be obtained in the FeAs− single layer. The monotonous behavior of the Fe-As distance in z direction upon electron or hole doping is also in contrast with bulk materials. Our results indicate that, in LaFeAsO and BaFe2As2, interactions between FeAs layer and other layers beyond simple charge doping are important, and a single FeAs layer may not represent a good model for Fe based superconducting materials.

Keywords: superconductivity, FeAs layer, magnetism, density functional theory (DFT)

I. INTRODUCTION

The recently discovered high temperature superconductivity in LaFeAs(1−xFx)O has attracted a lot of interests and triggered the research for other iron-based superconductors. Up to now, most of the Fe-based superconductors are based on either RFeAsO (R=La, Ce, Sm, Nd, Pr and Gd) or AFe2As2 (A=Ba, Sr) structures. In the former 1111 series, replacing La with other rare-earth atom increases the transition temperature (Tc) up to 55 K for SmO1−xFxFeAs2. For the latter 122 series, with appropriate alkali metal (K and Cs) doping, Tc can be raised up to 37 K2. Very recently, superconductivity has also been reported for As-free material FeSe1−δ and Fe(8,9) Moreover, replacing RO layer in 1111 materials with Li or Na also leads to Tc of 18 K and 9 K respectively.21,22

The Fe-based superconductors have a quasi two-dimensional tetrahedral structure, where FeAs layers are separated by RO (R=La, Ce, Sm, Nd, Pr and Gd), A (A=Ba, Sr), or Li (Na) layers. Except LiFeAs and NaFeAs, both parent compounds of 1111 and 122 superconductors are metallic but not superconducting. They undergo a phase transition from tetragonal to orthorhombic with the decrease of temperature, which accompanies with a new collinear antiferromagnetic (AFM) order, known the SDW phase. Upon doping the SDW is suppressed, and superconductivity appears. First principles calculations for both 1111 and 122 materials have been reported, using either local spin density (LSDA) or generalized gradient approximations (GGA). The collinear AFM ground state in the parent compounds has been confirmed by theory.24,25

Although the mechanism of superconductivity in these Fe-based materials is still unknown, it is clear the essential physics lies in the common FeAs layer. It serves as the conducting layer, and the interplay between magnetism and superconductivity happens in this layer. Therefore, it is important to investigate its structure change as well as the evolution of electronic properties upon doping.

At low temperature (25 K), in F doped LaFeAsO, with F doping, the Fe-As bond length changes less than 0.1%, while the La-As distance reduces by 1.5% and the La-O distance increases by 0.8%. These results demonstrate that the structure of FeAs layer changes slightly upon doping, in contrast with the significantly modified LaO layer. Besides, the layered structure of Fe-based superconductors is very similar to that of cuprates and NaxCoO2 superconductors. A single CoO2 layer has been successfully used as a model system to investigate

FIG. 1: (Color online) The crystal structure of the $\sqrt{2} \times \sqrt{2} \times 1$ single FeAs layer. The red and yellow balls are Fe and As species respectively. (a) is the side view of single FeAs layer, (b) and (c) are the top view of FeAs layer, where the black arrows signify the FM (b) and collinear AFM (c) configurations on Fe atoms.

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the doping effects on Na$_x$CoO$_2$. Thus, one question comes out, can we use a similar model of single FeAs layer to study the doping effects on Fe-based superconductors?

In this article, we calculate the geometric, electronic, and magnetic properties of a single FeAs$^-$ layer in the framework of density functional theory (DFT). We fail to obtain the collinear AFM phase with both optimized structure and experimental structure. The behavior of $d_{As}$ (Fig. 1b) respecting to the doping level also differs from that of 1111 and 211 materials.

**II. MODEL AND METHOD**

As shown in Fig. 1, FeAs layers are formed by edge-shared FeAs tetrahedras with Fe ions sandwiched between two As sheets. In the undoped parent materials for both the 1111 and 122 series, the FeAs layer is negatively charged with one electron, which means undoped FeAs layer corresponds to FeAs$^−$. Starting from this point, hole or electron doping is realized by simply adding or removing electrons from FeAs layer, with uniform compensated charge background. Doping level $x$ is defined for charged system FeAs$^{-(1+x)}$. In this work, doping level $x$ ranging from $-1.00$ to $+1.00$ is investigated.

Most of the theoretical works on the electronic and magnetic properties of Fe-based superconductors in the literature are based on the high-temperature tetrahedral structure, with $a=b$. One attempt to obtain the low-temperature orthorhombic lattice constants used an alternative strategy with the magnetic moments fixed to experimental value instead of optimizing on ground state potential energy surface. For single layer in our case, if we directly scan the orthorhombic structure parameters, we obtain $a$ and $b$ around 4.64 Å, which is significantly lower than the experimental values (by more than 1.0 Å). Therefore, in the following calculations, we fix $a$ and $b$ to their experimental values 5.683 and 5.710, respectively. In order to exclude interactions between neighboring layers, $c$ is set to 14 Å, corresponding to about 10 Å’s distance between two neighboring FeAs layers. The positions of all atoms are allowed to relax until forces on each atoms are smaller than 0.01 eV/Å. Due to the symmetry of the system, the only degree of freedom of the atoms is the $z$ coordinate of As. As shown in Fig. 1, $z$ coordinate of As related to the Fe plane is marked as $d_{As}$.

The electronic structure calculations are carried out using the Vienna ab initio simulation package. The electron-ion interactions are described in the framework of the projected augment waves method and the frozen core approximation. The energy cutoff is set to be 600 eV, the same as previously used for LaOF$_2$. For density of states (DOS) calculation, we used a 12x12x6 Monkhorst-Pack $k$-point grid to sample the Brillouin zone, while for geometry optimization, a 8x8x4 grid have been used.

For magnetic property calculations, initial magnetic moments are set according to non-spin polarized (NM), ferromagnetic (FM), and collinear antiferromagnetic (AFM) ordering. The FM and collinear AFM configurations are illustrated in Fig. 1b and c. The latter is the experimentally observed ground state for parent compounds.

In GGA+U calculations, we adopt a simplified model, where the on-site Coulomb repulsion $U$ and the atomic-orbital intra-exchange energy $J$ are simplified to one parameter $U_{eff} = U - J$. For simplicity, we will call $U_{eff}$ as $U$ hereafter.

**III. RESULTS AND DISCUSSIONS**

First we performed structure optimization and electronic structure calculations for FeAs$^-$. From GGA results, the total energy of FM state is about 0.002 eV lower than that of NM state, and the magnetic moment on Fe in FM state is about 0.18 $\mu_B$. The collinear AFM state, which is reported to be the ground state of 1111 and 122 materials, is not stable at all.

The optimized $d_{As}$ is 1.19 Å, which is significantly lower than the experimental value for LaFeAsO (about 1.31 Å at 4 K). The electronic structure as well as the magnetic moments on Fe in 1111 and 122 parent compounds are very sensitive to $d_{As}$, so the discrepancy between the calculated magnetic structure and the ex-
different magnetic behavior.

0.48 lower than the NM state, with a magnetic moment of to see if we can get correct magnetic properties. The cal-

(\text{FeAs})_\text{PDOS} of \text{LaFeAsO}, (b) DOS of FeAs single layer with experimental values of \text{Fe} and \text{As} positions. The Fermi level is aligned to 0.00 eV.

Experimental one may cause by the heavily underestimated $d_{\text{As}}$.

Considering the possible electron correlation in \text{FeAs}, GGA+U may be a useful strategy to correct $d_{\text{As}}$. Different U values are used to test it effects. In all DFT+U calculations, we get either an FM or a NM ground state. The magnetic moment increase with $U$ for medium value of $U$, and when $U$ goes to relative large negative value, the magnetic moment on \text{Fe} will be quenched, which is consistent with the trend that negative $U$ delocalize electron. As shown in Fig. 3, $d_{\text{As}}$ decreases monotonously with $U$. To get the experimental $d_{\text{As}}$ value, an unphysi-

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To be specific, increases with the level of electron doping, and decreases with the level of hole doping. In exper-

iment, at 120 K for \text{LaFeAsO}, $d_{\text{As}}$ do increase slightly from 1.319 to 1.323 Å when 14% F is doped.\textsuperscript{21,30} However, in the case of hole doping, for $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ at 10 K, $d_{\text{As}}$ increases from 1.344, to 1.351 Å and 1.358 Å when hole doping increases from zero to 10% and 20%, respectively.\textsuperscript{21,22} So the calculated trend of $d_{\text{As}}$ using the single layer \text{FeAs} model is insufficient to describe the doping effects on geometrical properties of \text{Fe}-based superconduc-

FIG. 3: (Color online) Density of states of \text{FeAs} and the con-

tributions of \text{Fe} d states and \text{As} p states to \text{FeAs} DOS. (a)

DOS of \text{FeAs} in \text{LaFeAsO}, (b) DOS of \text{FeAs} single layer with experimental values of \text{Fe} and \text{As} positions. The Fermi level is aligned to 0.00 eV.

FIG. 4: (Color online) The evolution of $d_{\text{As}}$ with the doping level $x$.

The doping effect for single \text{FeAs} layer is also studied. Experimentally, the structure transition from tetra-

hedral phase to orthorhombic phase is suppressed when sufficient electron or hole doping is applied, and the $d_{\text{As}}$ in tetrahedral and orthorhombic phases in undoped \text{LaFeAsO} is almost the same.\textsuperscript{24} Therefore, the optimization for \text{FeAs} single layer with doping level from -1.0 to 1.0 is carried out using the experimental tetrahedral phase lattice parameters ($a=b=5.706$ Å). As shown in Fig. 4, the $d_{\text{As}}$ changes monotonously with doping level, to be specific, increases with the level of electron doping, and decreases with the level of hole doping. In experi-

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IV. CONCLUSION

We have performed first-principles calculations on single layer \text{FeAs}. In this model where the inter layer interaction is ignored, we find the structure of the \text{FeAs} layer in \text{RFeAsO} and \text{AFe}_2\text{As}_2 cannot be reproduced accurately in the framework of GGA and GGA+U. Besides, with both optimized and experimental lattice parameters, the collinear AFM ground state of \text{RFeAsO} and \text{AFe}_2\text{As}_2 cannot be obtained in \text{FeAs} single layer.

In the simple single layer model, the inter-layer interactions between \text{ReO} (R) layers and \text{FeAs} layers are excluded. Our results suggest that this interactions may need to be considered to obtain correct geometry. This conclusion is important for choosing a proper theoretical model in future investigation of \text{Fe} based superconduc-
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Note added after submission: A recent experiment suggested a nearly isotropic superconductivity in (Ba,K)Fe$_2$As$_2$.\(^{32}\)

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1. Y. Kamihara, T. Watanabe, M. Hirano and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
2. X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen and D. F. Fang, Nature 453, 761 (2008).
3. Z.-A. Ren et al., Chin. Phys. Lett. 25, 2215 (2008).
4. M. Rotter, M. Tegel and D. Johrendt, Phys. Rev. Lett. 101, 107006 (2008).
5. K. Sasmal, B. Ev, B. Lorenz, A. Guloy, F. Chen, Y. Xue and C. W. Chu, Phys. Rev. Lett. 101, 107007 (2008).
6. F. C. Hsu et al., PNAS 105, 14262 (2008).
7. Z.-A. Ren et al., Chin. Phys. Lett. 25, 2215 (2008).
8. M. Rotter et al., Phys. Rev. Lett. 101, 107006 (2008).
9. C. de la Cruz et al., Nature 453, 899 (2008).
10. M. Rotter et al., Phys. Rev. B 78, 020503 (2008).
11. Q. Huang et al., arXiv:0806.2776 (2008).
12. G. F. Chen, Z. Li, G. Li, W. Z. Hu, J. Dong, X. D. Zhang, P. Zheng, N. L. Wang and J. L. Luo, Chin. Phys. Lett. 25, 3403 (2008).
13. F. Ma and Z.-Y. Lu, arXiv:0803.3280 (2008).
14. Z. P. Yin et al., Phys. Rev. Lett. 101, 047001 (2008).
15. T. Yildirim, Phys. Rev. Lett. 101, 057010.
16. I. I. Mazin, D. J. Singh, M. D. Johannes and M. H. Du, Phys. Rev. Lett. 101, 057003 (2008).
17. D. J. Singh and M. H. Du, Phys. Rev. Lett. 100, 237003 (2008).
18. L. Boeri, O. V. Dolgov and A. A. Golubov, Phys. Rev. Lett. 101, 026403 (2008).
19. H.-H. Wen, Gang Mu, Lei Fang, Huan Yang and Xiyu Zhu, Eur. Phys. Lett. 82, 179009 (2008).
20. T. Nomura et al., Supercond. Sci. Technol. 21, 125028 (2008).
21. Peihong Zhang, Weidong Luo, Marvin L. Cohen, and Steven G. Louie, Phys. Rev. Lett. 93, 236402 (2004).
22. Peihong Zhang, Weidong Luo, V. H. Crespi, M. L. Cohen and Steven G. Louie, Phys. Rev. B 70, 085108 (2004).
23. K. Sasmal, B. Ev, B. Lorenz, A. Guloy, F. Chen, Y. Xue and C. W. Chu, Phys. Rev. Lett. 101, 107006 (2008).
24. C. de la Cruz et al., Nature 453, 899 (2008).
25. M. Rotter et al., Phys. Rev. B 78, 020503 (2008).
26. Q. Huang et al., arXiv:0806.2776 (2008).
27. G. F. Chen, Z. Li, G. Li, W. Z. Hu, J. Dong, X. D. Zhang, P. Zheng, N. L. Wang and J. L. Luo, Chin. Phys. Lett. 25, 3403 (2008).
28. F. Ma and Z.-Y. Lu, arXiv:0803.3280 (2008).
29. Z. P. Yin et al., Phys. Rev. Lett. 101, 047001 (2008).
30. T. Yildirim, Phys. Rev. Lett. 101, 057010.
31. I. I. Mazin, D. J. Singh, M. D. Johannes and M. H. Du, Phys. Rev. Lett. 101, 057003 (2008).
32. L. Boeri, O. V. Dolgov and A. A. Golubov, Phys. Rev. Lett. 101, 026403 (2008).
33. H.-H. Wen, Gang Mu, Lei Fang, Huan Yang and Xiyu Zhu, Eur. Phys. Lett. 82, 179009 (2008).
34. T. Nomura et al., Supercond. Sci. Technol. 21, 125028 (2008).
35. Peihong Zhang, Weidong Luo, Marvin L. Cohen, and Steven G. Louie, Phys. Rev. Lett. 93, 236402 (2004).
36. Peihong Zhang, Weidong Luo, V. H. Crespi, M. L. Cohen and Steven G. Louie, Phys. Rev. B 70, 085108 (2004).
37. G. Kresse and D. Joubert, Phys. Rev. B 59, 1578 (1999).
38. G. Kresse and J. Furthmuller, Phys. Rev. B 54, 11169 (1996).
39. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
40. P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
41. S. Lebegue, Phys. Rev. B 75, 035110 (2007).
42. T. Yildirim, arXiv:0807.3936 (2008).
43. V. Vildosola et al., Phys. Rev. B 78, 064518 (2008).
44. G. Mu, L. Fang, H. Yang, X. Y. Zhu, P. Cheng and Hai-Hu Wen, arXiv:0806.2104 (2008).
45. M. Rotter et al., arXiv:0812.2827 (2008).
46. H. Q. Yuan, J. Singleton, F. F. Balakirev, S. A. Baily, G. F. Chen, J. L. Luo, and N. L. Wang, Nature 457, 565 (2009).