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First Principles Study on FeAs Single Layers†

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$FeAs^-$ single layer is tested as a simple model for LaFeAsO and $BaFe_2As_2$ 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 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. The results indicate that, in LaFeAsO and $BaFe_2As_2$, 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.

Key words: Superconductivity, FeAs layer, Magnetism, Density functional theory

I. INTRODUCTION

The recently discovered high temperature superconductivity in $LaFeAs[O_{1-x}F_x]$ [1] 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 AFe_2As_2 (A=Ba, Sr) structures. In the former 1111 series, replacing La with other rare-earth atom increases the transition temperature (T_c) up to 55 K for $SmO_{1-x}F_xFeAs$ [2,3]. For the latter 122 series, with appropriate alkali metal (K and Cs) doping, T_c can be raised up to 37 K [4,5]. Very recently, superconductivity has also been reported for As-free material $FeSe_{1-\delta}$ and $Fe(Te_xSe_{1-x})_{1-\delta}$ with T_c around 27 K under pressure [6,7]. Moreover, replacing RO layer in 1111 materials with Li or Na also leads to T_c of 18 and 9 K respectively [8,9].

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 [10-13]. 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) [14-19]. The collinear AFM ground state in the parent compounds has been confirmed by theory.

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% [21]. 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 Na_xCoO_2 superconductors. A single CoO_2 layer has been successfully used as a model system to investigate the doping effects on Na_xCoO_2 [22,23]. 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 work, we calculate the geometric, electronic, and magnetic properties of a singe $FeAs^-$ 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 Fe−As distance in z direction (d_{As} as in Fig 1.(a)) respecting to the doping level also differs from that of 1111 and 211 materials.

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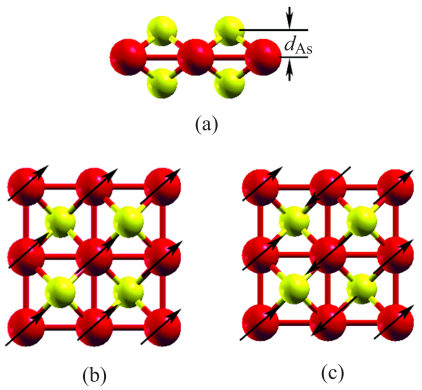

FIG. 1 The crystal structure of the $\sqrt{2}\times\sqrt{2}\times1$ single FeAs layer. The red and yellow balls are Fe and As species respectively. (a) The side view of single FeAs layer, (b) and (c) the top views of FeAs layer, where the black arrows signify the FM (b) and collinear AFM (c) configurations on Fe atoms. For interpretation of the color in this figure legend, the reader can refer to the web version of this article.

II. MODEL AND METHOD

As shown in Fig.1, FeAs layers are formed by edge-shared $FeAs_4$ 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 are based on the high-temperature tetrahedral structure, with a=b in the Refs.[14-16,18,28]. One attempt to obtain the low-temperature orthorhombic lattice constants using an alternative strategy with the magnetic moments fixed to experimental value instead of optimizing on ground state potential energy surface [17]. 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 Å, respectively [21]. 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(a), 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 [24]. PBE functional is used [25]. The electron-ion interactions are described in the framework of the projected augment waves method and the frozen core approximation [26]. The energy cutoff is set to be 600 eV, the same as previously used for LaOFeP [27]. For density of states calculation, we used a $12\times12\times6$ Monkhorst-Pack k-point grid to sample the Brillouin zone, while for geometry optimization, a $8\times8\times4$ 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.1 (b) 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 $U_{\rm eff}$=$U-J$. For simplicity, we call $U_{\rm eff}$ as U hereafter.

III. RESULTS AND DISCUSSION

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 $0.18\mu_{\rm B}$. The collinear AFM state, which is reported to be the ground state of 1111 and 122 materials, is not stable at all.

The optimized $d_{\rm As}$ is 1.19 Å, which is significantly lower than the experimental value for LaFeAsO (about 1.31 Å at 4 K) [10]. The electronic structure as well as the magnetic moments on Fe in 1111 and 122 parent compounds are very sensitive to $d_{\rm As}$ [28,29], so the discrepancy between the calculated magnetic structure and the experimental one may occur by the heavily underestimated $d_{\rm As}$.

Considering the possible electron correlation in FeAs, GGA+U may be a useful strategy to correct $d_{\rm As}$. Different U values are used to test the 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 Fe will be quenched, which is consistent with the trend that negative U delocalize electron. As shown in Fig.2, $d_{\rm As}$ decreases monotonously with U. To get the experimental $d_{\rm As}$ value, an unphysical U as low as -13.0 eV should be used.

Since DFT+U also fail to give the correct $d_{\rm As}$, another thing we can try is to directly adopt the experimental $d_{\rm As}$ to see if we can get correct magnetic properties. The calculated total energy of FM state is about

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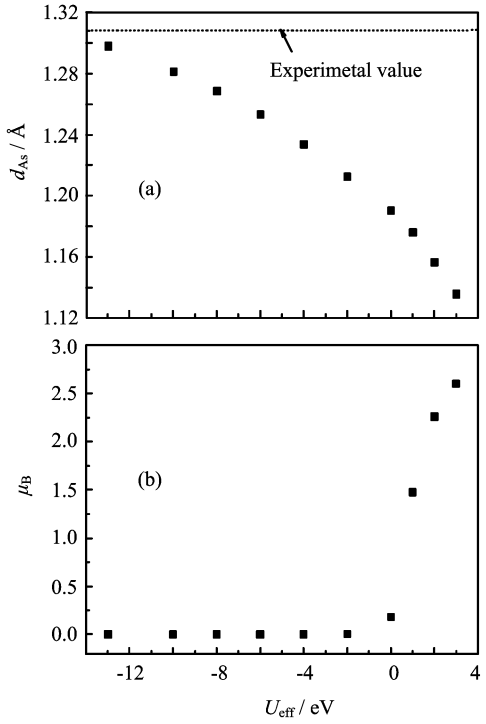

FIG. 2 Dependence of (a) $d_{\rm As}$ and (b) magnetic moment (μ_B, magnetic moment of $0.48\mu_{\rm B}$ per Fe atom) on Hubbard parameter U. The experimental value of $d_{\rm As}$ for LaFeAsO is marked by a dotted line.

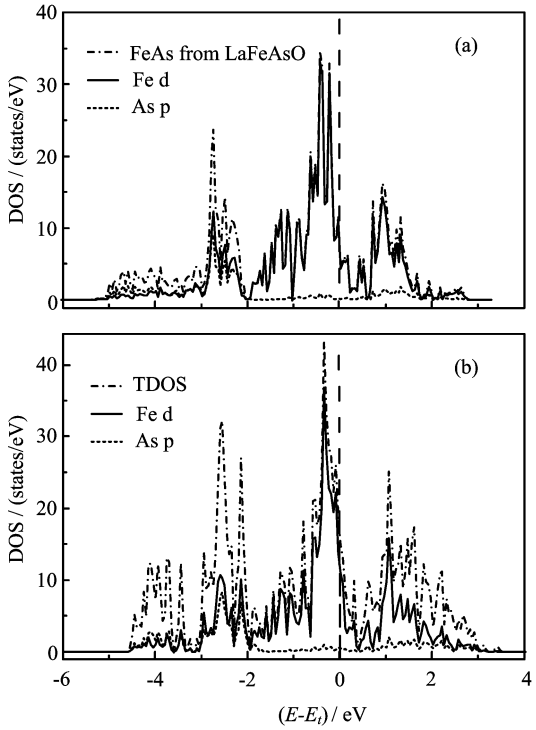

FIG. 3 Density of states of FeAs and the contributions of Fe d states and As p states to FeAs DOS. (a) PDOS of FeAs in LaFeAsO, (b) DOS of FeAs single layer with experimental values of Fe and As positions. The Fermi level is aligned to 0.00 eV.

27.8 meV/cell lower than the NM state, with a magnetic moment of $0.48\mu_{\rm B}$ per Fe atom. The collinear AFM state does not exist again in single FeAs layer with experimental $d_{\rm As}$. The resulting electronic density of states of undoped FeAs layer is shown in Fig.3, comparing to the FeAs partial DOS (PDOS) of LaFeAsO obtained with experimental structure parameters at low temperature [10,21]. The main structures of the DOS and PDOS are very similar. In energy ranges from -2 eV to 2 eV near the Fermi level, Fe 3d states dominate. The peaks from -3 eV to -2 eV are mixed Fe and As states. The density of states at Fermi level ($N(E_{\rm f})$) for single FeAs layer is significantly larger than that of FeAs PDOS of LaFeAsO ($\sim$16.13 eV^{-1} *vs.* $\sim$7.15 eV^{-1}), which may result in different magnetic behavior.

The doping effect for single FeAs layer is also studied. Experimentally, the structure transition from tetrahedral phase to orthorhombic phase is suppressed when sufficient electron or hole doping is applied, and the $d_{\rm As}$ in tetrahedral and orthorhombic phases in undoped LaFeAsO is almost the same [21]. Therefore, the optimization for 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 $d_{\rm As}$ changes monotonously with doping level, to be specific, increases with the level of electron doping, and decreases with the level of hole

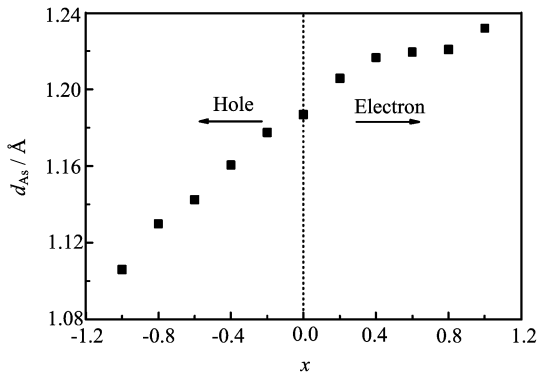

FIG. 4 The evolution of $d_{\rm As}$ with the doping level x.

doping. In experiment, at 120 K for LaFeAsO, $d_{\rm As}$ do increase slightly from 1.319 Å to 1.323 Å, when 14% F is doped [21,30]. However, in the case of hole doping, for $Ba_{1-x}K_xFe_2As_2$ at 10 K, $d_{\rm As}$ increases from 1.344 Å, to 1.351 and 1.358 Å, when hole doping increases from zero to 10% and 20%, respectively [11,31]. So the calculated trend of $d_{\rm As}$ using the single layer FeAs model is insufficient to describe the doping effects on geometrical properties of Fe-based superconductors.

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IV. CONCLUSION

We have performed first-principles calculations on single layer FeAs. In this model where the inter layer interaction is ignored, we find the structure of the FeAs layer in RFeAsO and AFe_2As_2 can not 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 RFeAsO and AFe_2As_2 can not be obtained in FeAs single layer.

In the simple single layer model, the inter-layer interactions between RO (R) layers and 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 Fe based superconductors.

V. ACKNOWLEDGMENTS

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VI. NOTE ADDED AFTER SUBMISSION

A recent experiment suggested a nearly isotropic superconductivity in $(Ba,K)Fe_2As_2$ [32].

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