



Proximity of antiferromagnetism and superconductivity in $\text{LaFeAsO}_{1-x}\text{F}_x$: Effective Hamiltonian from *ab initio* studies

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We report density functional theory calculations for the parent compound LaFeAsO of the recently discovered 26 K Fe-based superconductor $\text{LaFeAsO}_{1-x}\text{F}_x$. We find that the ground state is an ordered antiferromagnet, with staggered moment of about $2.3 \mu_B$, on the border with the Mott insulating state. We fit the bands crossing the Fermi surface, derived from Fe and As, to a tight-binding Hamiltonian using maximally localized Wannier functions on Fe $3d$ and As $4p$ orbitals. The model Hamiltonian accurately describes the Fermi surface obtained via first-principles calculations. Due to the evident proximity of superconductivity to antiferromagnetism and the Mott transition, we suggest that the system may be an analog of the electron-doped cuprates, where antiferromagnetism and superconductivity coexist.

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The recent discovery of superconductivity with onset temperature of 26 K in $\text{LaFeAsO}_{1-x}\text{F}_x$ (Ref. 1) has generated considerable interest because of a number of unusual aspects of this material. First, with the exception of some of the A-15 materials, Fe is never found in superconductors at zero pressure (although Fe itself superconducts at 10 GPa). Second, both ferromagnetic *and* antiferromagnetic fluctuations are apparently present in the material, suggesting possible analogies to ternary rare earth, heavy fermion, borocarbide, ruthenate and cuprate superconductors. Finally, the discovery of superconductivity at the relatively high critical temperature of 26 K implies that another pairing mechanism may be in play. The analog system $\text{LaFePO}_{1-x}\text{F}_x$ has a critical temperature of 7 K, so there appears to be a novel class of superconducting materials with no obvious limit on T_c .

Naively, ferromagnetic order is inimical to superconductivity since the exchange field of the ferromagnetic ion breaks singlet pairs. Ferromagnetic order was therefore found only very recently to coexist with superconductivity in UGe_2 (Ref. 2) and URhGe ,³ in situations where the order is quite weak. Coexistence of antiferromagnetic order, on the other hand, is less pairbreaking if the coherence length is much larger than the wavelength of the magnetic modulation, which is generally the case. Thus, many examples of superconductors coexisting with antiferromagnetic order are known, and have been recently reviewed.⁴

The structure of the above-mentioned material consists of LaO layers sandwiching a layer of FeAs, and doping with F appears to occur on the O sites. Since the Fe is arranged in a simple square lattice, the analogy with the cuprates, where electrons hop on a square lattice and doping occurs via a nearby oxide charge reservoir layer, is tempting to draw. Early electronic structure calculations for both the P (Ref. 5) and the As materials⁶⁻⁸ have presented a somewhat different picture, however. While experimentally a low charge density was measured for this material,⁹ these calculations suggest that five bands, of primarily Fe-As character, cross the Fermi level and give rise to a multi-sheet, quasi-2D material. No evidence for long-range order was found in these studies, although proximity to both antiferromagnetic and ferromagnetic ordered states was noted.

The weak coupling of the LaO layers to the FeAs layers found here and in previous works also suggests that insight may be gained by examining iron monoarsenide FeAs, a layered metallic helimagnet¹⁰ with large pitch angle in the zincblende structure with low-temperature effective moment $\sim 0.5 \mu_B$. The electronic structure and spin moment for this compound have been calculated by density functional theory.¹¹ While the theory is successful in the sense that an antiferromagnetic ground state is found, it does not distinguish the complicated magnetic structure and finds a moment of order $\sim 2 \mu_B$.

To understand the electronic structure properties of the new Fe-based superconductors and the interplay with structure and magnetic states, we have performed first-principles density functional theory simulations on the undoped and $x=0.0625$ as well as $x=0.125$ doped $\text{LaFeAsO}_{1-x}\text{F}_x$. Most of the reported results on the electronic structure and model Hamiltonian have been obtained using the PWSCF package,¹² which employs a plane-wave basis set and ultrasoft pseudopotentials.¹³ We have also used VASP^{14,15} to confirm our calculations when the same calculations can be performed, as described in the following sections in detail. The local spin density approximation and generalized gradient approximation of Perdew, Burke and Ernzerhof¹⁶ potentials have been incorporated for the simulation. For density of states (DOS) calculations, we have used a $16 \times 16 \times 8$ Monkhorst dense grid¹⁷ to sample the Brillouin zone; while for structural relaxation and self-consistent calculations, a $8 \times 8 \times 4$ Monkhorst grid has been used. All structures have been fully optimized until internal stress and forces on each atom are negligible. Our GGA+ U calculations have been performed via the VASP code. The existing literature uses an on-site Coulomb energy that varies from 4.0 eV to 6.9 eV,¹⁸⁻²⁰ and we have explored the parameter space within the range $U=2.0-5.0$ eV and $J=0.89$ eV on Fe in our calculations.

Our calculations show an unambiguous antiferromagnetic (AFM) ground state with staggered moment $2.3 \mu_B$ for undoped LaFeAsO , which is 84 meV per Fe lower than paramagnetic (PM) and ferromagnetic (FM) states. The energy

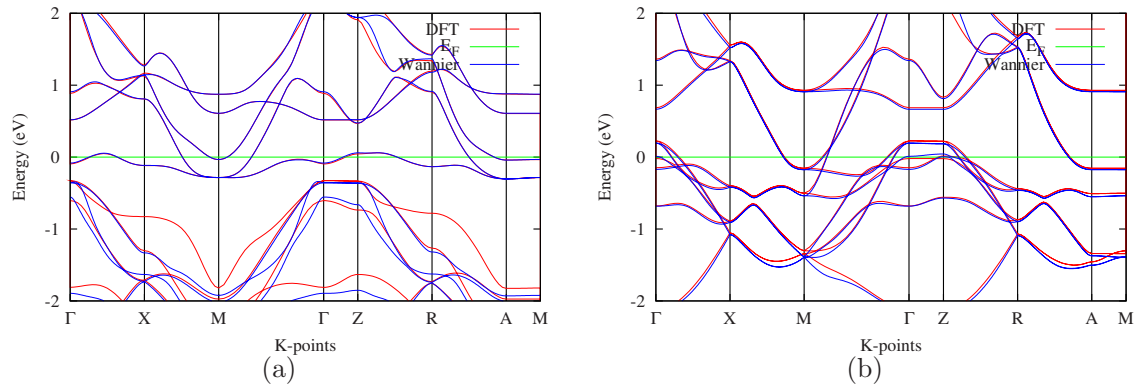


FIG. 1. (Color online) Undoped LaFeAsO band structure of (a) AFM state and (b) PM state. The red lines represent DFT calculation results; blue lines are band structures reconstructed from the tight-binding model using maximally localized Wannier functions (MLWF). Since spin-up and spin-down bands are degenerate for the AFM state, we plot only spin-up bands here. For both figures, Fermi energies are indicated by the green line at 0 eV.

difference between the latter two is found to be negligible. In fact, the FM state has a very small magnetic moment (~ 0.05 per Fe); therefore, it can be regarded as a PM state. The AFM ground state has been confirmed by independent VASP calculations using the projector augmented wave method.²¹ The optimized structure has a lattice constant of $a=4.0200$ Å and $c=8.7394$ Å, and the bond lengths for Fe-As and La-O are 2.35 Å and 2.40 Å, respectively. For reference, the paramagnetic state has an optimized lattice constant of $a=3.9899$ Å, while the bond lengths for Fe-As and La-O are 2.34 Å and 2.33 Å, respectively. Both the AFM and PM band structures are shown in Fig. 1 with red curves. In both states, a small dispersion along the c -axis (from Γ to Z and from A to M) indicates interactions between layers are weak and thus, the separation of the electronic structure into LaO and FeAs layers is possible. The PM state band structure reproduces previous DFT calculation results,^{5,6} exhibiting five bands across the Fermi level. The AFM state band structure is qualitatively different, exhibiting only three bands across E_F . In VASP calculations, AFM states are 14 meV per Fe lower than PM and FM states. Similar to PWSCF calculations, the band structures of the AFM state are very different from the PM state. These results indicate the delicacy of the magnetic states in this system, and that the magnetism strongly affects the electronic structure.

To further examine and confirm these findings, we have performed two series of additional calculations. First, we have performed GGA+ U calculations using VASP. Haule *et al.* (Ref. 8) used a dynamical mean field theory (DMFT)-LDA approach, and found that a critical value of $U=4.5$ eV led to a Mott transition with a gap at the Fermi surface. We have calculated the electronic structure using VASP's implementation of GGA+ U , and also found a Mott transition for the LaFeAsO system at a critical $U\sim 3$ eV for Fe. Note that the lower bound of the empirical value of U chosen in calculation is 3.5–4.0 eV for Fe d orbitals.¹⁸ The ground state is found to be always AFM for all tested U within 0.0–5.0 eV in our calculations, but the DOS changes dramatically (Fig. 4). A Mott gap of about 1.0 eV is observed in the GGA+ U calculation at $U=4.5$ eV. Experimentally, it is observed that below 100 K, the resistivity of undoped

LaFeAsO increases when temperature decreases, but appears to remain metallic,¹ suggesting that the system is in fact on the edge of a Mott transition.⁸

Second, we have investigated bulk FeAs. The AFM state is again found to be the ground state, in agreement with the experiment,¹⁰ as well as with previous calculations based on full-potential linearized augmented planewave (FLAPW) method.¹¹ In addition, an isolated layer of FeAs has also been simulated, and the system again has an AFM ground state. The calculated AFM states of bulk and the isolated layer are 53 meV and 408 meV per Fe atom lower than their PM states, respectively. Compared to FLAPW calculations, our results have shown a smaller energy difference between the AFM and PM states, indicating that our calculations do not have an artificial bias for the AFM state.

The electron DOS derived from the AFM band structure and the corresponding projected DOS (PDOS) onto LaO and FeAs planes are presented in Fig. 2. It is clear from the PDOS analysis that Fe $3d$ orbitals dominate the DOS around E_F (-2 to 2 eV relative to E_F) and from -12 to -10 eV; whereas DOS below -13 eV is almost completely derived from LaO layers. This clear separation in the DOS confirms that this material can be viewed as a layered structure. However, both LaO and FeAs layers contribute approximately the same from -6 to -2 eV, suggesting a hybridization between layers within this energy window. For the AFM state, the calculations give a $2.30\mu_B$ local magnetic moment on Fe by integrating the PDOS to E_F , which is similar to the value obtained from calculations for the bulk FeAs crystal.

To further understand the physics within the FeAs layers and connect our calculations to model calculations, we have used the maximally localized Wannier functions (MLWF) method^{22,23} to analyze the atomic orbitals which dominate the electronic structure near the Fermi surface. Sixteen MLWFs, including $10d$ -type MLWFs on Fe and $6p$ -type MLWFs on As, have been used to obtain a tight-binding effective Hamiltonian $H_{\text{eff}}=\sum_i \epsilon_i c_i^\dagger c_i + \sum_{i,j} t_{ij} c_i^\dagger c_j$ by fitting the band structure around E_F . These MLWFs are then used to construct a model Hamiltonian matrix, from which we can regenerate the band structure using a tight-binding framework (blue curves in Fig. 1). In both AFM and PM cases, the

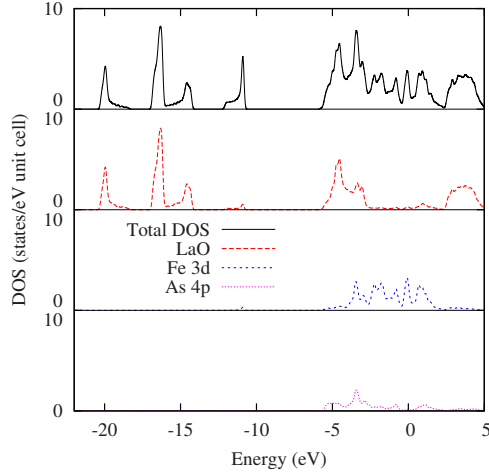


FIG. 2. (Color online) DOS (top panel) and PDOS (FeAs and LaO planes: middle panel and bottom panel, respectively) of undoped LaFeAsO. Since the spin-up and spin-down states are degenerate for the AFM state, we plot spin-up states only. The Fermi level is aligned to 0.0 eV.

tight-binding band structure fits the DFT band structure well, showing the validity of our model Hamiltonian. We show the most important hopping terms in Fig. 3, and the corresponding values are listed in Table I together with the on-site energies. Due to the S_4 symmetry of the FeAs tetrahedra, the Fe 3d orbitals split into three non-degenerate ($3d_{x^2-y^2}$, $3d_{xy}$, $3d_{z^2}$) and one doubly degenerate energy state ($3d_{x(y)z}$) in both PM and AFM states. Interestingly, the lowest lying $3d_{z^2}$ state in PM is the highest in AFM state, leaving the order of the other three states unchanged. The energy difference between lowest 3d states and highest 4p orbitals ($4p_{x(y)}$) are ~ 1.2 eV and 1.6 eV in PM and AFM states, respectively, which is about the same magnitude as the Cu-O splitting in cuprates. In the PM state, the strongest hoppings come from Fe $3d_{x^2-y^2}$, $3d_{z^2}$ and As $4p_z$ orbitals, followed by the coupling

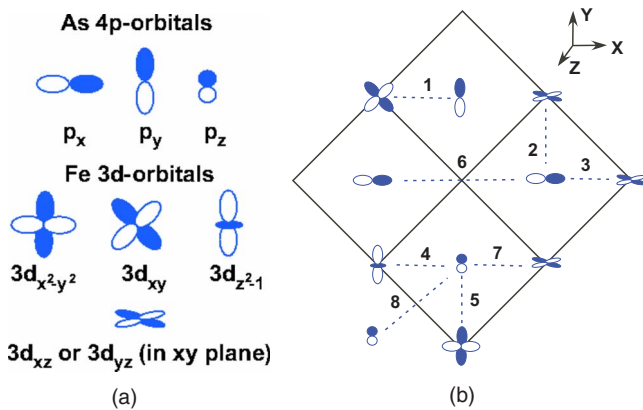


FIG. 3. (Color online) Diagrams for (a) atomic-type MLWFs and (b) strongest hoppings in the system. The diagram is presented on the x-y plane with the most important hoppings labeled. Iron atoms and arsenic atoms are located at the vertices and centers of the square lattice, respectively. Note that (b) depicts an irreducible subset of hoppings, and the z-displacement of As atoms is not shown.

TABLE I. Electron hopping t_{ij} and on-site energy ϵ_i (in eV) matrix elements calculated from MLWFs. In the AFM state, hoppings will be different for iron atoms on different sublattices.

type		PM	AFM	
On-site energies				
	$3d_{x^2-y^2}$	11.35	11.67	9.85
	$3d_{x(y)z}$	11.26	11.56	9.76
	$3d_{xy}$	11.18	11.49	9.60
	$3d_{z^2}$	11.14	11.96	10.06
	$4p_{x(y)}$	9.97	9.33	9.33
	$4p_z$	6.35	3.17	3.17
Hoppings				
1	$3d_{xy}-4p_y$	0.79	0.80	0.62
2	$3d_{xz}-4p'_x$	0.60	0.67	0.48
3	$3d_{xz}-4p_x$	0.81	0.79	0.74
4	$3d_{z^2-1}-4p_z$	1.02	0.83	0.46
5	$3d_{x^2-y^2}-4p_z$	1.26	1.21	1.00
6	$4p_x-4p_x$	0.68	0.68	0.68
7	$3d_{xz}-4p_z$	0.49	<0.1	0.68
8	$4p_z-4p_z$	0.17	0.55	0.55

from Fe $3d_{xz}$, $3d_{xy}$, and As $4p_x$ orbitals. Remarkably, the direct hopping between As $4p_{x(y)}$ in the same x-y plane are as large as the Fe-As hopping. In the AFM state, since the mirror symmetry within the unit cell is removed, these hopping matrix elements split into two groups for spin-up electrons and spin-down electrons on Fe sites, respectively. Furthermore, the hopping between two neighboring As $4p_z$ and $4p_z$ orbitals are greatly enhanced in AFM states. The direct hoppings between Fe 3d orbitals are finite, but are much smaller compared to Fe-As and As-As hopping in both cases.

We finally present our calculations on doped LaFeAsO. The doping is simulated by substituting an oxygen atom in eight primitive cells with a fluorine atom, and then fully relaxing the structure with the optimized lattice constants of the undoped system. Since each primitive cell contains two oxygen atoms, the doping corresponds to $\text{LaFeAsO}_{1-x}\text{F}_x$ with $x=0.0625$. The resulting material turns out to be still AFM, but with an extra total spin. With $x=0.125$ doping, we reduced the number of primitive cells involved by half, so that one oxygen atom in every four primitive cells was replaced with a fluorine atom. The fluorine substitution has an effect on the electronic structure which is primarily concentrated in the FeAs layers at energies near E_F , plus an impurity state at ~ 7.5 eV below E_F . We show the comparison of undoped and $x=0.125$ doped systems in Fig. 5. The $x=0.0625$ doped system has a similar doping effect, but smaller in magnitude. The overall magnetic ordering remains the same, but the magnetic moment is altered by 6%.

In conclusion, we have performed first-principles calculations for LaFeAsO and $\text{LaFeAsO}_{1-x}\text{F}_x$ systems. An AFM ground state has been found for undoped LaFeAsO via DFT calculations. We find that the geometry, electronic structure, and the magnetic state of this system are strongly related. In both AFM and PM states, the band structures around the

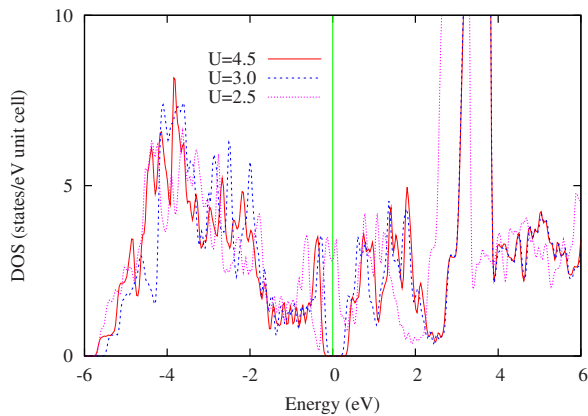


FIG. 4. (Color online) DOS calculated from GGA+ U with different U 's, 2.0, 3.0, and 4.5 eV. E_F is aligned to 0.0 eV in all cases. Due to degeneracy, only the α -spin DOS is plotted.

Fermi level are derived from Fe $3d$ and As $4p$ orbitals, and we have fitted bands crossing the Fermi surface to tight-binding Hamiltonians using MLWFs. The parameters for the model Hamiltonians from the first-principles calculations can be used for modeling transport, magnetic and superconducting phenomena associated with strongly correlated electrons in the system under investigation. While the system exhibits metallic behavior in DFT calculations, an inclusion of an on-site energy of 4.5 eV on Fe turns it into a semiconductor with a gap of 1.0 eV, which implies that the system is close to a Mott-type insulator. Due to the evident proximity of superconductivity to antiferromagnetism and the Mott transition, we suggest that the system may be a large-spin analog of the electron-doped cuprates, where AFM and superconductivity coexist.

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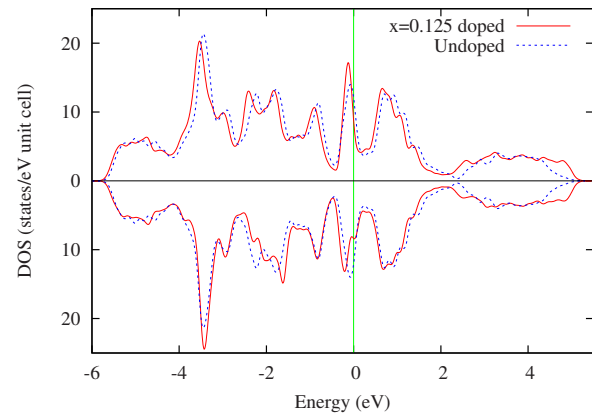


FIG. 5. (Color online) DOS of $\text{LaFeAsO}_{1-x}\text{F}_x$ with $x=0.125$ projected onto FeAs layers. The E_F is aligned to 0.0 eV.

appeared, a linear spin density wave state was predicted in an electronic structure calculation,²⁴ and discovered in neutron scattering experiments,²⁵ then extensively studied in Ref. 26. We have compared the energy of such a magnetic state with the sublattice type AFM state discussed in this work, and can confirm that according to PWSCF calculations it is 109 meV per Fe lower in energy.

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