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Crystal, spin, and electronic structure of the superconductor LiFeAs

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The crystal, spin, and electronic structure of the "111"-type LiFeAs superconductor has been investigated by first-principles calculations based on the density-functional theory. It is found that the crystal structure and weak magnetism of metallic LiFeAs can be described by general gradient approximation and local spin-density approximation (LSDA). Both methods show LiFeAs is a weak correlated system with a striped antiferromagnetic ground state and the easy axis of magnetization is along the *b* direction of the magnetic unit cell. The magnetic unit cell is distorted from the tetragonal into an orthorhombic structure. The spin moment/Fe calculated by the LSDA method is $0.121\mu_B$.

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I. INTRODUCTION

The discovery of $LaO_{1-x}F_xFeAs$ (Ref. 1) with a superconducting transition temperature (T_c) of 26 K have stimulated extensive experimental and theoretical investigations.[2–12] The parent compound, LaFeAsO, is known to be nonsuperconducting. It was found that the emergence of superconductivity upon fluorine doping is associated with the suppression of the spin-density-wave (SDW) state.[5,6] A SDW ordered state with a stripe-type spin configuration has been found in LaFeAsO (Ref. 2) ("1111" type) at 137 K and $BaFe_2As_2$ (Ref. 4) ("122" type) at 140 K. Recently, a related compound, LiFeAs, has been synthesized and found to be a 18 K superconductor. LiFeAs has a simple crystal structure and therefore is a convenient model to investigate the pairing mechanism of the iron arsenide family of superconductors. Surprisingly, no SDW ordered state was observed in LiFeAs.[13–15] However, a very weak spin moment was measured by electron-spin-resonance (ESR) experiments close to the superconducting critical temperature.[14] Moreover, superconducting quantum interference device (SQUID) measurement found no sign of magnetization at low temperature.[15] LiFeAs is certainly not nonmagnetic as the estimated $T_c < 1$ K (Refs. 16 and 17) from electron-phonon coupling calculations assuming a nonmagnetic ground state is much lower than the experimental value.

From x-ray diffraction, LiFeAs was found to have a Cu_2Sb (Ref. 18) type tetragonal structure with space group $P4/nmm$. The structure is composed of stacks of [FeAs] layers interlaced with Li atoms. LiFeAs is metallic with itinerant electrons.[13] It is well known that the Stoner model can describe the ground state of metal very well, but the model fails to explain the temperature-dependent behavior as it neglects the fluctuation in the directions of spin moments. Spin-spin interactions between itinerant electrons are much more complex than that between localized *d* electrons in insulator. There are already many reports on the calculations of the magnetic states of iron arsenide superconductors by density-functional theory (DFT).[19–22] A general consensus is that these systems possess low localized moments suggesting that spin fluctuations may play an important role on the superconductivity. In view of this suggestion, spin orderings and electronic structure in LiFeAs are investigated in this paper. The present work is the first study of spin order using first-principles method including spiral spin.[23–25] As will be shown below, LiFeAs has a collinear stripped antiferromagnetic ground state with a very small spin moment.

II. METHOD OF CALCULATION

Calculations of the equation of state (EOS) and spin moments were performed with spin-polarized generalized gradient (GGA) and local spin-density approximations (LSDAs). Projected augment potentials (PAWs) (Refs. 26 and 27) as implemented in the Vienna *ab initio* simulation package (VASP) (Refs. 28) were used to replace the core electrons. The plane-wave cutoff energy was set at 600 eV. A $6\times6\times4$ Monkhorst-Pack *k*-points grid was used. To investigate effects of electron correlation, calculations employing rotationally invariant GGA+*U* and LSDA+*U* methods[29] were performed and the results are compared to the corresponding GGA and LSDA calculations. Two sets of effective Hubbard parameters, $U_{eff}=U-J$ (2.5 and 3.6 eV) and $J=0.9$ eV, on the Fe atom were used in the calculations.

III. RESULTS AND DISCUSSIONS

To determine the magnetic states of LiFeAs, it is necessary to perform the calculations in a model cell commensurate with the magnetic unit cell. For this purpose, a model for the magnetic cell (Fig. 1) constructed from $\sqrt{2}\times\sqrt{2}\times1$ replication of the primitive cell (represented by red dash line in Fig. 1) was constructed. In view of the large interlayer Fe-Fe distance along the *c* direction, LiFeAs can be viewed as a quasi-two-dimensional (2D) system. Therefore, it is not unreasonable to expect that the spin arrangement along the *c* direction will not have a significant effect on electron paring. To this point, the spin arrangement along *c* direction is assumed to be ferromagnetic, but the interplanar coupling is extremely weak and easily destroyed at low temperature. The nonmagnetic (NM) and three types of magnetic order states FM, A′, C′ types were considered. The arrangement of the spin moment for A′ and C′ types are depicted in Fig. 1. The FM type is ferromagnetic and the A′ type is antiferromag-

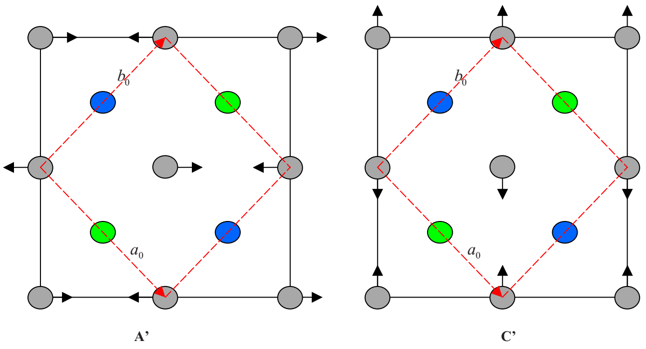

FIG. 1. (Color online) The arrangements of the spin moment for A′ and C′ types. The As atom above the Fe plane is labeled by a green sphere and the As atom below the FeAs plane labeled by a blue sphere. The Fe atom (with spin) is labeled by a gray sphere.

netic in the *ab* plane, respectively. The C′-type magnetic state is a striped antiferromagnetic state.

EOSs of the magnetic and nonmagnetic states of LiFeAs obtained from spin-polarized GGA calculations are compared in Fig. 2(a). The results show the C′ type is the most stable. The calculated equilibrium volume of 22.62 Å^3/LiFeAs is in good agreement with experimental value of 22.51 Å^3/LiFeAs at 300 K.[13] However, the optimized magnetic unit cell becomes orthorhombic *Cmma* with crystal axes $|b|>|a|$ due to the lost of a fourfold rotation symmetry from the tetragonal $P4/nmm$ space group with C′-type magnetic structure.[2,30,31] The optimized structural parameters are a=5.294 Å, b=5.408 Å, and c=6.237 Å, with Li at (0.25,0.25,0.662), Fe at (0,0,0), and As at (0.25,0.25,0.231), respectively. The distortion was only found in the C′-type magnetic structure. There are no distortion in the nonmagnetic unit cell and other selected magnetic unit cells. The predicted GGA Fe spin moment 1.5μ_B is much smaller than the S=2 obtained from a recent multiconfiguration Hartree-Fock (MCSCF) calculations[32] on a cluster model. MCSCF includes static electron correlation effects that may be important in LiFeAs. To investigate this possibility, spin-polarized GGA+U calculations using two different values of U_{eff} (2.5 and 3.5 eV) were performed. The C′-type spin structure is still predicted to be the most stable. Using U_{eff}=2.5 eV, the calculated equilibrium volume 24.46 Å^3/LiFeAs is much larger than experiment and a very large spin moment of 3.04μ_B. The high spin moment is in apparent agreement with a MCSCF (Ref. 32) calculation. However, experimentally, the exact spin state of Fe in LiFeAs is still controversial. A large spin moment has been reported in x-ray absorption experiment.[33] In contrast, all observations made from spin-specific probes suggest a much smaller local spin moment. For example, a very low magnetization in LiFeAs was reported by the ESR experiment.[14] This result is consistent with SQUID measurements that found close to zero magnetization[15] at low temperature. The results strongly suggest that the GGA+U method is not needed to describe the ground state of LiFeAs. The GGA +U method tends to overemphasize the on-site Coulomb repulsion at the Fe atom and does not favor two electrons occupying the same orbital with opposite spin.

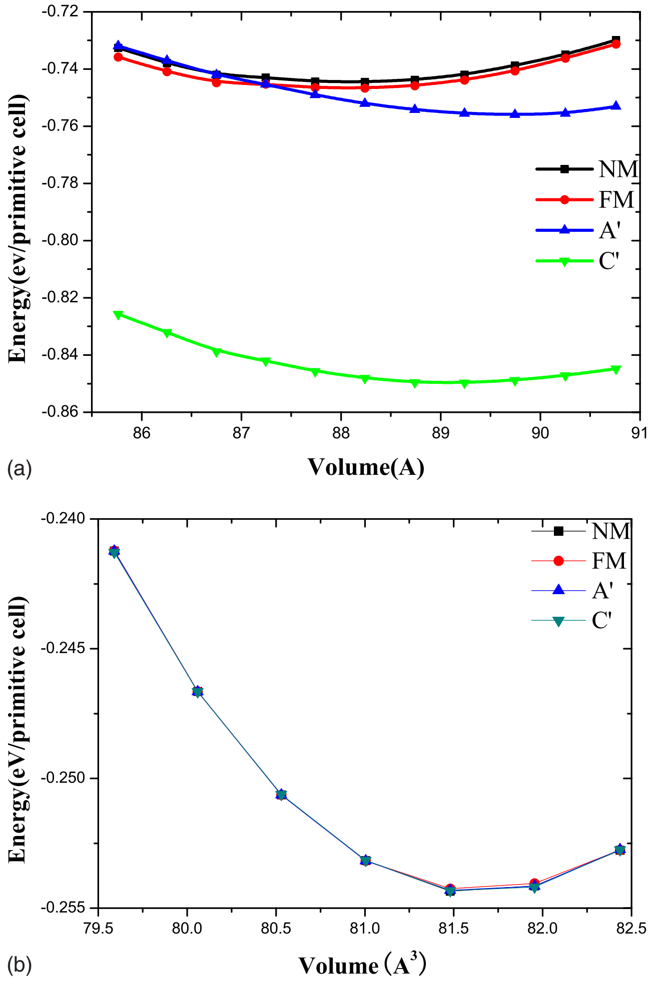

FIG. 2. (Color online) (a) EOS of nonmagnetic and FM-, A′-, C′-type LiFeAs from GGA calculations. (b) EOS of nonmagnetic and FM-, A′-, C′-type LiFeAs from collinear LSDA calculation.

Next, we explore the reliability of the LSDA method. Near the equilibrium volume [Fig. 2(b)], the total energies for the nonmagnetic and magnetic states with FM, A′, and C′ types (Fig. 1) obtained from LSDA calculations are very similar with the C′-type magnetic state marginally most stable. The LSDA Fe spin moments are much smaller than the GGA calculations. The calculated equilibrium volume of the C′-type magnetic crystal structure is somewhat smaller (ca. 10%) than the experimental but the predicted spin moment is negligibly small. The trend obtained from LSDA +U calculation is similar to the GGA+U calculations (*vide supra*). The C′-type structure is still the most stable with large spin moments of 2.6μ_B and 2.7μ_B with U_{eff}=2.5 eV and U_{eff}=3.6 eV, respectively. As mentioned above, a large Fe moment is inconsistent with experiments.[13–15] Since the LSDA gave reasonable ground state structure and spin moment, the ensuing calculations were performed with this method. The trend that GGA results in better geometric parameters but predicted a higher spin moment than LSDA is common in the FeAs superconductors.[34] The Fe d electrons are more delocalized due to Fe-As bonding or perhaps short Fe…Fe contacts that enhanced orbital overlaps. Therefore, GGA is more appropriate to describe the electronic structure than GGA+U. However, the LSDA gave a smaller spin moment in better agreement with experiment.

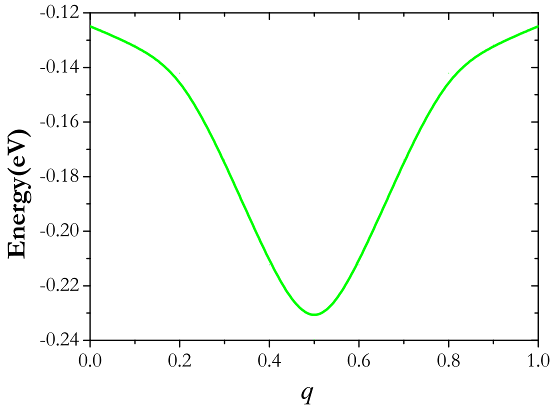

FIG. 3. (Color online) Total energy $E(q)$ calculated with LSDA for the spin spiral states of LiFeAs as a function of $\vec{Q}=\frac{2\pi}{a_0}(q,-q,0)$.

To investigate the possibility of lower energy noncollinear magnetic states, calculations on the spin structure and spin moment with spiral spin structures derived from the C′-type magnetic states were performed on a spin propagation vector $\vec{Q}=\frac{2\pi}{a_0}(q,-q,0)$ ($a_0=3.7741$ Å). The directional indices are defined with respect to the primitive cell. Calculations were performed at primitive cell with experimental cell parameters.[13,18] The total energies $E(q)$ calculated on the spin spiral states are shown in the Fig. 3. An energy minimum was found at $q=0.5$. This spin structure has a ferromagnetic spin arrangement in the Fe-Fe chain along the [110] direction and antiferromagnetic spin arrangement in the Fe-Fe chain along the $[1\bar{1}0]$ direction. This spin arrangement is identical to the C′-type magnetic state depicted in the Fig. 1. The results indicate that there is no need to invoke noncollinear spin structure to describe the ground state of LiFeAs. In passing, it is noteworthy that the calculated spin moment decreases with increasing q.

It is perhaps surprising that (collinear) LSDA calculations predict almost degenerate nonmagnetic and magnetic states with FM, A′, and C′ types, yet the spiral spin calculation reproduces the same spin structure as the GGA calculations. The difference between collinear and spiral spin calculations is that the direction of spin moment is considered in the spiral spin calculation but not in the collinear calculation. In the latter method, all magnetic states with C′-type spin structure will have the same total energy regardless of the direction of magnetization. This implies the total energy is invariant if all the magnetic moments are rotated by the same angle. In reality, the direction of the spontaneous magnetization often prefers one specific direction, the easy axis, instead of an isotropic arrangement. Magnetic anisotropy energy (MAE) is defined as the total energy of system on the direction of the spontaneous magnetization. MAE is the consequence of the crystal symmetry of system. Therefore it is important to compute the total energy of the magnetic states with different axes of magnetization. Results obtained by LSDA calculations[35] with axes of magnetization along *a*, *b*, and *c* directions of the undistorted magnetic unit cell constructed with the experimental $P4/nmm$ structure are summarized in Table I. Higher-order corrections from spin-orbit coupling are not included. In Table I, $E_{\parallel a}$, $E_{\parallel b}$, and $E_{\parallel c}$ represent the total energy with magnetization axis along *a*, *b*, and *c* directions, respectively, and $M_{\parallel a}$, $M_{\parallel b}$, and $M_{\parallel c}$ represent the corresponding magnetic moments/Fe. The results show that the most stable spin structure is C′ type and the easy axis of magnetization is along the *b* direction. This result is in complete agreement with the magnetic structure predicted by GGA and spiral spin calculations (*vide supra*). The values for $E_{\parallel a}$ and $E_{\parallel b}$ are the same in the A′ and FM spin structures since the fourfold rotation symmetry is retained in the magnetic group.

Geometry optimization with the easy axis of magnetization and spin structure is performed (C′ type in Fig. 1) using LSDA. In complete agreement with spin-polarized GGA calculations, an orthorhombic *Cmma* magnetic cell was obtained. The optimized cell parameters and atomic positions are $a=5.225$ Å, $b=5.232$ Å, $c=5.968$ Å, Li at (0.25,0.25,0.336), Fe at (0,0,0), and As at (0.25,0.25,0.226). The difference between *a* and *b* axes is so small and may not be easily detected by diffraction experiments.[15,18] The calculated small spin moment of $0.121\mu_B$ is in accord with experimental observations.[13–15] In addition, a low-temperature neutron-diffraction study did not reveal spin moment on the Fe atom.[18]

IV. SUMMARY

In summary, the crystal, spin, and electronic structure of LiFeAs have been studied by first-principles density-functional calculations with consideration of electron correlation effect, collinear and noncollinear spin spiral structures, and magnetic anisotropy. Major findings are (i) LiFeAs is a weak correlation system but superconductivity may be related to spin fluctuations as demonstrated in a recent paper by Yang *et al.*[36] and there is no need introduce *ad hoc* Hubbard model into GGA or LSDA; (ii) the ground state is a stripped antiferromagnetic with a C′-type magnetization (Fig. 1); (iii) the spin arrange is collinear. Both GGA and

TABLE I. Total energy (meV)/LiFeAs and spin moment/Fe calculated in the tetragonal magnetic unit cell by LSDA with magnetic moment along *a*, *b*, and *c* directions, relatively to total energy (meV)/LiFeAs of nonmagnetic state

	$E_{\parallel a}$	$M_{\parallel a}$	$E_{\parallel b}$	$M_{\parallel b}$	$E_{\parallel c}$	$M_{\parallel c}$
A′	−6.04	1.137	−6.04	1.137	0.30	0.285
FM	−5.19	0.599	−5.19	0.599	−5.40	0.618
C′	−21.53	0.882	−48.83	1.347	−28.47	1.187

LSDA methods gave the same C′-type spin magnetic cell which is distorted from tetragonal $P4/nmm$ to an orthorhombic $Cmma$ with the easy axis of magnetization along b. In agreement with experiment, LSDA predicted a very small Fe spin moment. The spin arrangement is similar to that in LaFeAsO and $BaFe_2As_2$.[2,4]

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