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2010 J. Phys.: Condens. Matter 22 046006

(http://iopscience.iop.org/0953-8984/22/4/046006)

J. Phys.: Condens. Matter **22** (2010) 046006 (4pp) doi:10.1088/0953-8984/22/4/046006

# First-principles study of the magnetic, structural and electronic properties of LiFeAs

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Received 30 September 2009, in final form 11 December 2009
Published 12 January 2010
Online at stacks.iop.org/JPhysCM/22/046006

**Abstract**

By first-principles calculations we found the magnetic ground state of LiFeAs is striped antiferromagnetically with the Fe layers antiferromagnetically coupled along the $z$ axis in the orthorhombic $Cmma$ structure. This $Cmma$ structure can be obtained from a structural distortion of the striped antiferromagnetic tetragonal $P4/nmm$ structure. The lattice dynamics calculations suggested the orthorhombic $Cmma$ is stable. The density of states at the Fermi level is mainly from the contribution of Fe 3d orbitals. These results suggest that LiFeAs has similar magnetic, structural and electronic properties to NaFeAs at low temperature.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The recently discovered high temperature superconductors—layered iron pnictides—have received a great deal of research interest. These discovered parent compounds of iron pnictides can be divided into four different classes: ReOFeAs [1–6] (Re = rare earth elements) (abbreviated as 1111), $AeFe_2As_2$ [7–10] (Ae = alkali earth metals) (122), AFeAs [11–15] (A = Li, Na) (111) and FeSe [16, 17] (11). They share a similar $Fe_2As_2$ tetrahedral layer structure and become superconducting by properly doping or applying pressure. The low temperature phase transition (from the tetragonal to orthorhombic) and SDW ordered state with the striped antiferromagnetic order had been found in 1111, 122 and 11 compounds [18–22]. In 111 type iron pnictides, the nearly stoichiometric NaFeAs had been found to undergo a structural phase transition from tetragonal $P4/nmm$ to orthorhombic $Cmma$ structure at ∼50 K [23, 24] and turn out to be antiferromagnetic ordering at 41 K [23]. However, there is no experimental evidence about the SDW and the phase transition reported in LiFeAs at low temperature [11–13]. Only a weak spin moment was detected by electron spin resonance (ESR) as the temperature was lowered below 50 K [25]. Some theoretical studies suggested a magnetic ordered structure is energetically favored [26–28]. But the magnetic ground state of LiFeAs at low temperature was not confirmed by experiments up to now. It is well known that the magnetic, electronic and structural properties are the keys to understanding the underlying superconducting mechanism, especially in iron-based superconductors. Thus it is highly desirable to study such basic issues of LiFeAs.

In this paper, we report the *ab initio* calculations on the magnetic, structural and electrical properties of LiFeAs. We found the striped antiferromagnetic tetragonal $P4/nmm$ structure distorted to an orthorhombic $Cmma$ structure that is similar to the low temperature structure of NaFeAs and LaOFeAs. By comparing the total energy of several possible magnetic ordered configurations in this orthorhombic $Cmma$ structure, we confirmed the striped antiferromagnetic configuration, with the Fe layers coupled antiferromagnetically in the $z$ direction to be the most stable.

## 2. Calculation details

The calculations of the magnetic properties and electronic structures were performed within the generalized gradient approximation (GGA) [29] using Perdew–Burke–Ernzerhof (PBE) as implemented in the Vienna *ab initio* simulation package (VASP) code [30]. The projector augmented wave (PAW) [31] method was adopted and the PAW potentials were

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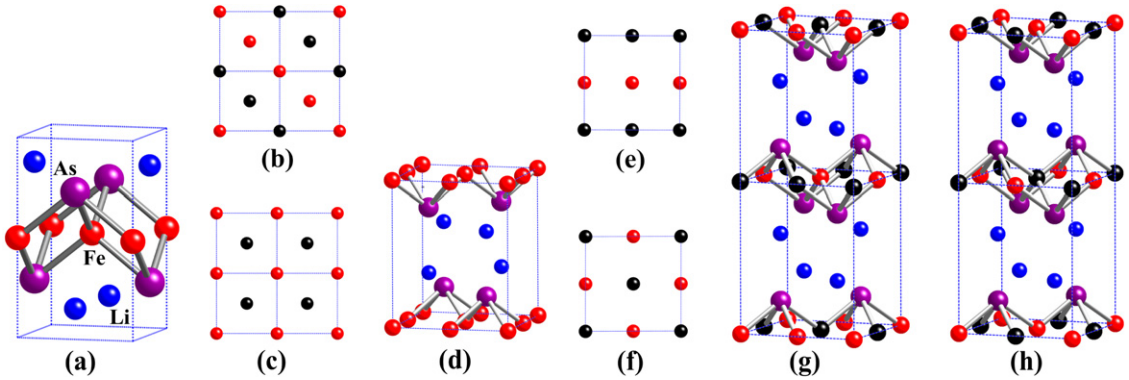


**Figure 1.** The crystal structures and magnetic configurations. (a) and (d) are the unit cells of the $P4/nmm$ and $Cmma$ structure, respectively. (b) and (c) are the top view of Fe layers in AFM-1a and AFM-1b configurations of $P4/nmm$. Fe layers in AFM-1a, AFM-1b, AFM-2a and AFM-2b configurations of $Cmma$ are shown in (e), (f), (g) and (h), respectively. The red and black balls represent the two antiparallel Fe spins, respectively. The optimized lattice parameters of orthorhombic $Cmma$ structure are $a = 5.26$ Å, $b = 5.41$ Å and $c = 6.24$ Å with atomic positions: Li at 4a (0, 0.25, 0.66424), Fe at 4g (0.25, 0, 0) and As at 4a (0, 0.25, 0.2364).

**Table 1.** The magnetic moment and total energy of various magnetic configurations (per formula unit) relative to NM $P4/nmm$ structure. Previous theoretical results from [26–28] are also shown for comparison.

| | $P4/nmm$ | | | $Cmma$ | |
|---|---|---|---|---|---|
| | | $M$ ($\mu_B$) | | | |
| | $E$ (meV/f.u.) | This work | Other calculations | $E$ (meV/f.u.) | $M$ ($\mu_B$) |
| NM | 0 | — | — | −0.032 | — |
| FM | −3.165 | 0.4 | 0.38[a], | −3.197 | 0.402 |
| AFM-1a | −56.110 | 1.514 | 1.50[a], 0.62[b], 1.76[c], 0.7[d] | −61.878 | 1.507 |
| AFM-1b | 1.782 | 1.102 | 1.11[a] | 2.175 | 0.433 |
| AFM-2a | −57.913 | 1.571 | 1.58[a], 0.63[b] | −62.967 | 1.562 |
| AFM-2b | −0.122 | 0.009 | 0.01[a] | 2.957 | 0.258 |

[a] Reference [27]: LAPW-GGA calculation.
[b] Reference [27]: LAPW-LSDA calculation.
[c] Reference [26]: LAPW-GGA calculation.
[d] Reference [28]: LAPW-LDA calculation.

taken from the VASP library [32], where the $2s^1$, $3p^6 4s^1 3d^7$ and $4s^2 4p^3$ are treated as the valence for Li, Fe and As atoms, respectively. The energy cutoff of 500 eV was used. The Monkhorst–Pack (MP) grids of $8 \times 8 \times 6$ for NM, FM and AFM-1b configurations in the $P4/nmm$ structure, $4 \times 4 \times 4$, $4 \times 4 \times 2$, $8 \times 8 \times 3$ for the AFM-1a, AFM-2a and AFM-2b configurations in the $P4/nmm$ structure, $8 \times 8 \times 6$ for the NM and FM configurations in the $Cmma$ structure, and $6 \times 6 \times 4$, $6 \times 6 \times 2$ for the AFM-1a (1b) and AFM-2a (2b) configurations in the $Cmma$ structure, respectively, were used to ensure the total energy converged to 0.2 meV/f.u. For all structures, we have optimized the volume, geometry and internal position parameters. The phonon frequencies of the nonmagnetic $P4/nmm$ and $Cmma$ structures were calculated using the Parlinski–Li–Kawazoe method and FROPHO program [33].

## 3. Results and discussions

At room temperature, LiFeAs adopts the tetragonal $P4/nmm$ structure, as shown in figure 1(a). To explore the possible magnetic state in the $P4/nmm$ structure, we considered six different configurations: nonmagnetic configuration (hereafter we denoted it as NM), ferromagnetic order (FM) with all the Fe atoms having the same parallel spins, and four antiferromagnetic configurations (AFM). Two kinds of antiferromagnetic orders in the Fe layers are striped-type and checkerboard-type, as shown in figures 1(b) and (c), respectively. By coupling the striped-type Fe layers ferromagnetically and antiferromagnetically, respectively, we get the AFM-1a and AFM-2a. In the same way, for the checkerboard-type Fe layer, we obtain the AFM-1b and AFM-2b configurations. The total energy of the six possible magnetic configurations with respect to the NM tetragonal $P4/nmm$ structure was calculated and labeled in table 1. It can be clearly seen that the AFM-2a configuration has the lowest energy, which is in agreement with the previous calculations [27]. We note that the total energy of AFM-1a is only ∼1.8 meV higher than AFM-2a and much lower than the other magnetic configurations, which indicate the striped-AFM coupling in Fe layers is energetically favored in LiFeAs.

After optimization, both AFM-1a and AFM-2a configurations showed a structural distortion from tetragonal to orthorhombic structure with the $\gamma$ angle deviating from 90°, the distance of two nearest parallel Fe spins decreasing and

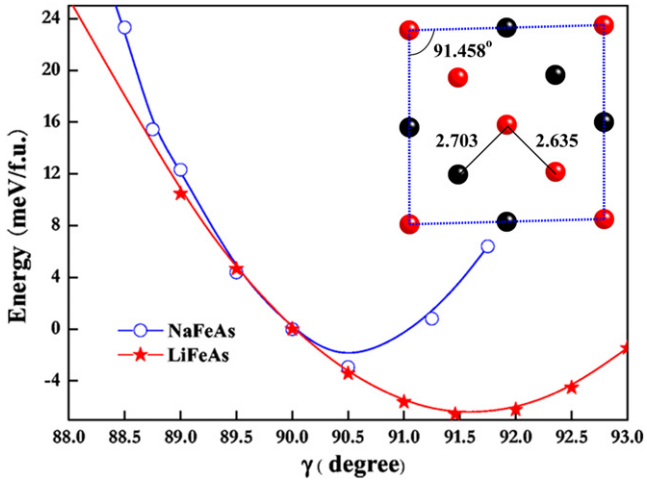


**Figure 2.** The total energy per cell versus the angle $\gamma$ for AFM-1a configuration of $P4/nmm$ in LiFeAs and NaFeAs. The inset shows the distorted Fe layers of LiFeAs when $\gamma = 91.458°$. It can be seen that the total energy is lowest when $\gamma \approx 90.5°$ in NaFeAs, which is consistent with experiment ($\gamma \approx 90.3°$). The ferromagnetically aligned Fe spins get closer while the antiferromagnetically aligned Fe spins move apart, which finally induced $a$ and $b$ not equal in the orthorhombic $Cmma$ structure.

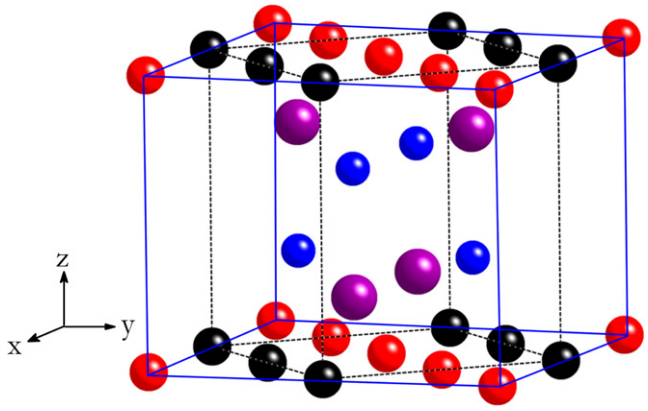


**Figure 3.** The AFM-1a magnetic cell of $P4/nmm$ and its relation to orthorhombic $Cmma$ unit cell. The AFM-1a magnetic cell and orthorhombic $Cmma$ unit cell are outlined by blue solid lines and black dashed lines, respectively. The $\sqrt{a^2+b^2} \times \sqrt{a^2+b^2} \times 1$ supercell of orthorhombic $Cmma$ is basically the AFM-1a magnetic cell.

the antiparallel Fe spins increasing. The total energy of the AFM-1a configuration with the change of $\gamma$ angle was calculated and shown in figure 2. It is evident that the structure indeed has the lowest energy when $\gamma = 91.458°$, corresponding to the orthorhombic $Cmma$ structure. The relationship between the AFM-1a magnetic cell and the $Cmma$ unit cell is shown in figure 3. It can be seen that the distorted AFM-1a structure is basically the $\sqrt{a^2+b^2} \times \sqrt{a^2+b^2} \times 1$ supercell of orthorhombic $Cmma$. Besides, our calculations for NaFeAs suggested that the tetragonal $P4/nmm$ distorted to the orthorhombic $Cmma$ structure (figure 2) at 0 K, which agrees well with experiment [23, 24].

It is not hard to understand this structural distortion in view of that the AFM-1a and AFM-2a configurations are magnetically frustrated [34]. In these structures, each Fe has four nearest Fe atoms forming a square with two pairs of antiparallel spins to minimize the interactions. The Fe spin in the middle of a square, whichever direction it points in, could not keep all the interactions minimized simultaneously—that is, the Fe spins will not exist in their lowest energy states simultaneously. Previous investigations have shown that a structural distortion, thermal or quantum fluctuations will help to remove the frustration in the system and make it more stable [34–36]. Thus, the structural distortion occurring in the AFM-1a and AFM-2a configurations of tetragonal LiFeAs is reasonable during a structural optimization at 0 K. The similar structural distortion of striped antiferromagnetic configuration in tetragonal $P4/nmm$ had also been observed and analyzed in LaOFeAs [34].

At zero temperature a stable crystalline structure requires all phonon frequencies to be positive. The phonon dispersion relations were calculated for the $Cmma$ structure. No imaginary phonon frequency was observed in the whole of the Brillouin zones, indicating the dynamical stability. We have to note that the calculation for the phonon frequencies of the $Cmma$ structure was done without considering the magnetism. Based on this dynamically stable $Cmma$ structure, we continue to discuss the magnetic and electronic properties.

For this orthorhombic $Cmma$ structure, we also investigated the possible magnetic configurations: NM, FM and four different AFMs: AFM-1a, AFM-1b, AFm-2a and AFM-2b. Figures 1(e) and (f) show the Fe layer in the AFM-1a and AFM-1b configurations, respectively. Figures 1(g) and (h) depict the AFM-2a and AFM-2b structures, respectively. The calculated total energies of these six possible magnetic configurations in the $Cmma$ structure were shown in table 1. Among these configurations, AFM-2a has the lowest total energy compared to the other magnetic configurations indicating that it is the magnetic ground state of LiFeAs. We note that the AFM-2a configuration in the orthorhombic $Cmma$ structure is the magnetic ground state of NaFeAs at low temperature [24].

The magnetic moment of the Fe atom in each magnetic structure is given in table 1. Besides, the calculated Fe moment in striped antiferromagnetic NaFeAs is 0.78 $\mu_B$, which is much larger than that of the experimental value ($0.09 \pm 0.04$ $\mu_B$) [24]. The magnetic moments in our calculations are in good agreement with previous GGA results, whereas it is larger than that of LDA, as shown in table 1. It is well known that the DFT calculations on iron-based superconductors always overestimated the magnetic moment [28, 34, 37, 38]. One possible reason for the small magnetic moments in the iron-based superconductors was suggested to be the hybridization of the iron 3d and the arsenic 4p orbitals [39]. Therefore, the real experimental magnetic moment of Fe in LiFeAs may be smaller than our calculated value. More investigations are in need to give the accurate magnetic moment of Fe.

The total density of states in the NM tetragonal $P4/nmm$ structure and the one in the AFM-2a configuration in the orthorhombic $Cmma$ structure were calculated and shown in figure 4. It seems that the AFM-2a state of the orthorhombic

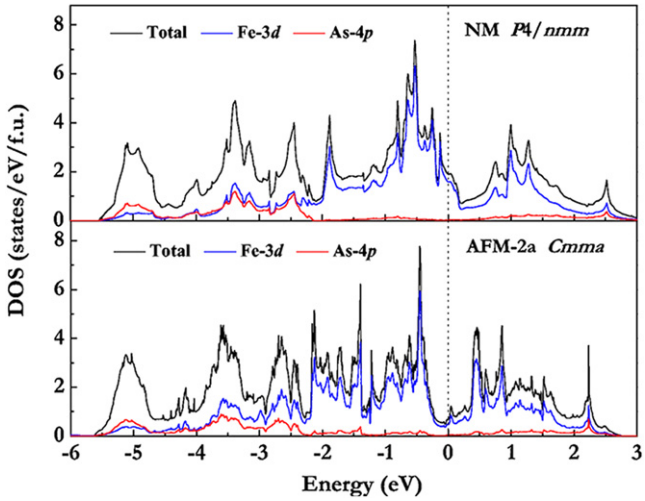


**Figure 4.** The density of states of AFM-2a configuration of *Cmma* structure and nonmagnetic $P4/nmm$ structure. Fermi energy is set to 0.

*Cmma* structure is more stable due to shifting of the Fermi energy ($E_f$) into a valley in the density-of-states curve. In both of these structures, the contribution of Li orbitals to the states near $E_f$ is rather small and not depicted in our picture. The density of states at $E_f$ is mainly from the contribution of Fe 3d orbitals. The weak hybridization of Fe 3d orbitals with As 4p orbitals between −4 and −2 eV indicates the bonding between Fe and As. We also found that the valence charge density distributed mainly around the FeAs layers by charge density distribution calculations.

## 4. Conclusions

In conclusion, by first-principles calculations we found the striped antiferromagnetic configuration with the Fe layers antiferromagnetically coupled in the orthorhombic *Cmma* structure is the magnetic ground state of LiFeAs. This *Cmma* structure is derived from a distortion of the striped antiferromagnetic configuration of the tetragonal $P4/nmm$ structure. In NaFeAs, the similar structural distortion was found in our calculation. Thus, LiFeAs, NaFeAs, $BaFe_2As_2$ and LaOFeAs have similar low temperature structural and magnetic properties. We believe that our findings can help understanding the basic physical properties in these iron-based superconductors.

## Acknowledgments

This work is supported by the China 973 Program under grant no. 2005CB724400, the NSAF of China under grant no. 10676011, the National Natural Science Foundation of China under grant no. 10874054, the Program for 2005 New Century Excellent Talents in University and the 2007 Cheung Kong Scholars Program of China.

## References

[1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 *J. Am. Chem. Soc.* **130** 3296
[2] Ren Z A *et al* 2008 *Europhys. Lett.* **83** 17002
[3] Jie Y *et al* 2008 *Supercond. Sci. Technol.* **21** 082001
[4] Wei Z, Li H, Hong W L, Lv Z M, Wu H, Guo X and Ruan K 2008 *J. Supercond. Nov. Magn.* **21** 213
[5] Chen G F, Li Z, Wu D, Li G, Hu W Z, Dong J, Zheng P, Luo J L and Wang N L 2008 *Phys. Rev. Lett.* **100** 247002
[6] Zhi An R, Yang J, Lu W, Guang Can C, Xiao Li D, Li Ling S and Zhong Xian Z 2008 arXiv:0806.2452
[7] Rotter M, Tegel M and Johrendt D 2008 *Phys. Rev. Lett.* **101** 107006
[8] Ni N, Nandi S, Kreyssig A, Goldman A I, Mun E D, Bud'ko S L and Canfield P C 2008 *Phys. Rev.* B **78** 14523
[9] Fu C G, Zheng L, Gang L, Zheng H W, Jing D, Jun Z, Dong Z X, Ping Z, Lin W N and Lin L J 2008 *Chin. Phys. Lett.* **25** 3403
[10] Sasmal K, Lv B, Lorenz B, Guloy A M, Chen F, Xue Y Y and Chu C W 2008 *Phys. Rev. Lett.* **101** 107007
[11] Tapp J H, Tang Z, Lv B, Sasmal K, Lorenz B, Chu P C W and Guloy A M 2008 *Phys. Rev.* B **78** 060505
[12] Wang X C, Liu Q Q, Lv Y X, Gal W B, Yang L X, Yu R C, Li F Y and Jin C Q 2008 *Solid State Commun.* **148** 538
[13] Pitcher M J, Parker D R, Adamson P, Herkelrath S J C, Boothroyd A T, Ibberson R M, Brunelli M and Clarke S J 2008 *Chem. Commun.* **2008** 5918
[14] Chu C W, Chen F, Gooch M, Guloy A M, Lorenz B, Lv B, Sasmal K, Tang Z J, Tapp J H and Yue Y Y 2009 *Physica* C **469** 326
[15] Parker D R, Pitcher M J, Baker P J, Franke I, Lancaster T, Blundell S J and Clarke S J 2009 *Chem. Commun.* **2009** 2189
[16] Hsu F C *et al* 2008 *Proc. Natl Acad. Sci. USA* **105** 14262
[17] Fang M H, Pham H M, Qian B, Liu T J, Vehstedt E K, Liu Y, Spinu L and Mao Z Q 2008 *Phys. Rev.* B **78** 224503
[18] Nomura T, Kim S W, Kamihara Y, Hirano M, Sushko P V, Kato K, Takata M, Shluger A L and Hosono H 2008 *Supercond. Sci. Technol.* **21** 125028
[19] Rotter M, Tegel M and Johrendt D 2008 *Phys. Rev.* B **78** 020503
[20] Cruz C d l *et al* 2008 *Nature* **453** 899
[21] McQueen T M, Williams A J, Stephens P W, Tao J, Zhu Y, Ksenofontov V, Casper F, Gelser C and Cava R J 2009 *Phys. Rev. Lett.* **103** 057002
[22] Huang Q, Qiu Y, Bao W, Green M A, Lynn J W, Gasparovic Y C, Wu T, Wu G and Chen X H 2008 *Phys. Rev. Lett.* **101** 257003
[23] Chen G F, Hu W Z, Luo J L and Wang N L 2009 *Phys. Rev. Lett.* **102** 227004
[24] Li S, de la Cruz C, Huang Q, Chen G F, Xia T L, Lou J L, Wang N L and Dai P 2009 *Phys. Rev.* B **80** 020504
[25] Zhang S J *et al* 2009 *Phys. Rev.* B **80** 014506
[26] Jishi R A and Alyahyael H M 2010 *Adv. Condens. Matter Phys.* **2010** 804343
[27] Li Y F and Liu B G 2009 arXiv:0905.3303
[28] Singh D J 2008 *Phys. Rev.* B **78** 094511
[29] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[30] Kresse F and Furthmuller J 1999 *Phys. Rev.* B **54** 11169
[31] Blochl P E 1994 *Phys. Rev.* B **50** 17953
[32] Kresse G and Joubert D 1999 *Phys. Rev.* B **59** 1758
[33] Atsushi F O, Togo A and Tanaka I 2008 *Phys. Rev.* B **78** 134106
[34] Yildirim T 2008 *Phys. Rev. Lett.* **101** 057010
[35] Yildirim T, Harris A B and Shender E F 1996 *Phys. Rev.* B **53** 6455
[36] Lee S H, Broholm C, Kim T H, Ratcliff W and Cheong S-W 2000 *Phys. Rev. Lett.* **84** 3718
[37] Mazin I I and Johannes M D 2009 *Nat. Phys.* **5** 141
[38] Mazin I I and Johannes M D 2008 *Phys. Rev.* B **78** 085104
[39] Jishi R A and Alyahyaei H M 2009 *New J. Phys.* **11** 083030