Distorted magnetic orders and electronic structures of tetragonal FeSe from first principles

Yong-Feng Li, Li-Fang Zhu, San-Dong Guo, Ye-Chuan Xu and Bang-Gui Liu

Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People’s Republic of China
and
Beijing National Laboratory for Condensed Matter Physics, Beijing 100190, People’s Republic of China

E-mail: bgliu@mail.iphy.ac.cn

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Abstract
We use the state-of-the-art density-functional-theory method to study various magnetic orders and their effects on the electronic structures of FeSe. Our calculated results show that, for the spins of the single Fe layer, the striped antiferromagnetic orders with distortion are more favorable in total energy than the checkerboard antiferromagnetic orders with tetragonal symmetry, which is consistent with known experimental data, and the interlayer magnetic interaction is very weak. We investigate the electronic structures and magnetic property of the distorted phases. We also present our calculated spin coupling constants and discuss the reduction of the Fe magnetic moment by quantum many-body effects. These results are useful in understanding the structural, magnetic and electronic properties of FeSe, and may have some helpful implications for other FeAs-based materials.

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

1. Introduction
The advent of superconducting F-doped LaFeAsO has stimulated a world-wide campaign for more and better Fe-based superconductors [1]. More superconductors were obtained by replacing La by other lanthanides or partly substituting F for O, and higher phase-transition temperatures \( T_c \) were achieved in some of them [2–4]. Furthermore, more series of Fe-based superconductors were found, including the BaFe2As2 series and LiFeAs series [5–8]. The highest \( T_c \) in these series reaches 55–56 K in the case of doped SmFeAsO [4]. Various explorations have been performed to elucidate their magnetic orders, electronic structures, superconductivity, etc [9–15]. Recently, superconductivity was found even in tetragonal FeSe samples under high pressure and \( \alpha \) FeSe phases with Se vacancies [16–20]. Very recently, SrFeAsF was made superconducting by La and Co doping [21–25]. The FeSe system is interesting because its FeSe layer is similar to the FeAs layer of the FeAs-based materials: RFeAsO series (R: rare-earth elements), AFe2As2 series (A: alkaline-earth elements), LiFeAs series and SrFeAsF series. In addition, superconductivity is found even in tetragonal FeSe samples under high pressure and \( \alpha \) FeSe phases with Se vacancies [16–20]. Very recently, SrFeAsF was made superconducting by La and Co doping [21–25]. The FeSe system is interesting because its FeSe layer is similar to the FeAs layer of the FeAs-based materials: RFeAsO series (R: rare-earth elements), AFe2As2 series (A: alkaline-earth elements), LiFeAs series and SrFeAsF series. In addition, superconductivity is found even in tetragonal FeSe samples under high pressure and \( \alpha \) FeSe phases with Se vacancies [16–20]. Very recently, SrFeAsF was made superconducting by La and Co doping [21–25]. The FeSe system is interesting because its FeSe layer is similar to the FeAs layer of the FeAs-based materials: RFeAsO series (R: rare-earth elements), AFe2As2 series (A: alkaline-earth elements), LiFeAs series and SrFeAsF series. In addition, superconductivity is found even in tetragonal FeSe samples under high pressure and \( \alpha \) FeSe phases with Se vacancies [16–20]. Very recently, SrFeAsF was made superconducting by La and Co doping [21–25].
the corresponding electronic structures and magnetic property
for them. Our calculated result means that the striped
antiferromagnetic order is favorable for the spins of the Fe
layer, which is consistent with the main known experimental
data. We also discuss the reduction of the Fe magnetic moment
by quantum many-body effects. More detailed results are
presented in the following.

This paper is organized as follows. In section 2, we
give our computational details. In section 3, we present our
main DFT calculated results, including optimized magnetic
structures and corresponding electronic density of states and
energy bands. In section 4, we discuss spin interactions and
many-body effects on the Fe magnetic moments. Finally, we
present our main conclusion in section 5.

2. Computational detail

Our calculations are performed by using a full-potential
linearized augmented plane wave (FLAPW) method within
the density-functional theory (DFT) [26], as implemented in
the Vienna package WIEN2k [27]. The generalized gradient
approximation (GGA) is used for the exchange and correlation
potentials [28]. We take the 3d and 4s states of Fe and the 4s
and 4p states of Se as valence states, and the 3p states of Fe
and 3d states of Se are treated as semicore states. The core
states include all the lower states. The core states are treated in
terms of the radial Dirac equation and thus the full relativistic
effect is included. For the valence and semicore states, the
relativistic effect is calculated under the scalar approximation,
with spin–orbit interaction being neglected [29]. The radii of
Fe and Se muffin-tin spheres are 2.05 and 2.00 au, respectively.
To get more accurate results, we take $R_{\text{mt}} \times K_{\text{max}} = 9.0$
and make the angular expansion up to $l = 10$ in the muffin-
tin spheres. We use 1000 $k$ points in the calculations. For
different magnetic orders the $k$ points in the first Brillouin zone
are chosen differently because of the different symmetry. The
self-consistent calculations are controlled by the charge density
and the convergence standard is that the difference between
the input charge density and output is less than 0.000 05 per
unit cell.

We show the unit cell of the tetragonal FeSe (PbO
structure) in figure 1(a). It is a layered structure, in which
an Fe atom occupies the 2a position and an Se atom the 2c
position. There are six possible magnetic configurations for
the Fe ions if the tetrahedral FeSe structure is allowed to
distort into orthorhombic structures. Figure 1(e) shows the
first Brillouin zone with the representative points and lines.
The Fe moments in the Fe plane can be arranged to form
ferromagnetic or antiferromagnetic orders. The AFM orders
can be checkerboard-like (figure 1(c)) or striped (figure 1(d)).
For the successive (001) planes, the Fe moments can couple
ferromagnetically or antiferromagnetically. As a result, we
have four different antiferromagnets, namely (a) checkerboard-
FM, (b) checkerboard-AF, (c) stripe-FM and (d) stripe-AF. In
addition, when we force Fe moments in the Fe plane to have
FM order, the self-consistent calculations yield zero moments
for the Fe moments, which means that FM order is unstable
for FeSe, independent of the interlayer spin arrangements.
Therefore, we can actually construct five magnetic orders for
this system.

3. Main calculated results

The parameters in our calculations are taken from the
experimental values. We use $a = 3.76$ Å and $c = 5.52$ Å.

![Figure 1](image-url)
The positions of Se atoms are optimized fully and the force of the Se atom is made less than 2 mRyd au⁻¹. Calculated results of total energy, magnetic moment and Se position parameter are summarized in Table 1. It makes little difference in total energy to arrange interlayer Fe moments in FM or AF order. The total energy results reveal that the intralayer Fe–Fe interaction is strong and the interlayer interaction weak. Actually, the striped arrangement of the Fe moments lowers the total energy of the FeSe layer by approximately 70 meV with respect to the checkerboard arrangement. On the other hand, the nonmagnetic order is 154 meV higher than the lowest striped AF order. Therefore, the striped AF spin order is the magnetic ground state in the FeSe layer, but the actual interlayer magnetic interaction is too weak for any density-functional-theory calculation to determine. The moment in the Fe muffin-tin sphere is about 1.8 μB for the two checkerboard orders and about 2.0 μB for the two striped orders. The total moment for one Fe atom is estimated to be a little larger for the striped AF orders. For the striped AF orders, the Se position parameter remains almost the same when the interlayer spin coupling is changed from FM to AF. Because it is impossible to distinguish between FM and AF spin alignment in the z direction by density-functional-theory calculation, we present calculated results for both FM and AF arrangements in the z direction in the following.

We present the spin-dependent density of states (DOS) of the FeSe in the two stripe-AF orders in Figure 2. There is no energy gap near the Fermi levels and therefore the FeSe for each AF order shows a metal feature. The Fe atom has a different crystalline environment for different magnetic orders, and thus its states are reformulated in different ways. It can be seen that the main peaks occupy the states in the energy window from −2.2 to −1.5 eV. Almost all the partial DOS of the Fe atom comes from the 3d states and the DOS of the Se atom (dotted–dashed) and the interstitial region (pink or gray solid lines). The black thin solid line indicates the spin-dependent total DOS and the others are projected DOS in the muffin tin sphere of the Se atom (dotted–dashed) and the interstitial region (pink or gray thin solid).

### Table 1. The magnetic order, the relative total energy per formula unit (ΔE in meV, with the lowest stripe-FM set as reference), the magnetic moment in the Fe muffin-tin sphere (M in μB) and the internal Se position parameter u_{Se} of the two striped antiferromagnetic orders and the two checkerboard ones. The results of the nonmagnetic order are presented for comparison.

| Magnetic order        | ΔE (meV) | Moment M (μB) | u_{Se} |
|-----------------------|----------|---------------|--------|
| Checkerboard-FM       | 72       | 1.82          | 0.2570 |
| Checkerboard-AF       | 72       | 1.81          | 0.2426 |
| Stripe-FM             | 0        | 1.98          | 0.2590 |
| Stripe-AF             | 5        | 2.00          | 0.2592 |
| Nonmagnetic           | 154      | 0.00          | 0.2471 |

Figure 2. Spin-dependent density of states (DOS, in units of states/eV per formula unit) of the stripe-FM (a) and stripe-AF (b). The upper part of each panel is the majority-spin DOS and the lower part the minority-spin DOS. The Fe1 DOS is emphasized by thick red (or gray) solid lines and the Fe2 DOS by thick blue (or gray) dotted lines. The black thin solid line indicates the spin-dependent total DOS and the others are projected DOS in the muffin tin sphere of the Se atom (dotted–dashed) and the interstitial region (pink or gray thin solid).

4. Spin interactions and many-body effects on the magnetic moments

In order to further investigate the magnetic moment, we use the following AFM Heisenberg spin model to describe the spin properties of the Fe atoms in the striped AFM phase:

\[
H = \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j
\]

where \( \vec{S}_i \) is the quantum spin operator for site \( i \) and \( J_{ij} \) is the exchange coupling constants between the two spins at sites \( i \) and \( j \). For the striped AFM phase, the nearest coupling constant in the \( x \) direction is \( J_x \), and that in the \( y \) direction \( J_y \). For the tetrahedral phase, we should have \( J_x = J_y \), but for the striped phase we have \( J_x \neq J_y \) because of the crystalline distortion in the \( xy \) plane. We limit non-zero exchange coupling constants up to the next-nearest-neighbor spins, \( J' \). For convenience, we define \( J = (J_x + J_y)/2 \) and \( \delta = J_x - J_y \). Our DFT calculation yields \( J_x = 10 \) meV, \( J_y = 8 \) meV and \( J' = 5 \) meV. This means \( J = 9 \) meV and
\( \delta = 2 \) meV. The \( J_x \) and \( J_y \) comes from the superexchange through the two nearest Se atoms and \( J' \) from that through the one nearest the Se atom and, as a result, we should have \( J \approx 2J' \), which supports our DFT results.

We treat the spin Hamiltonian (1) with the above parameters with spin wave theory [30]. As usual, the average spin for zero temperature, \( \langle S^z \rangle \), can be given by \( \langle S^z \rangle = S - \Delta S \), where \( S \) is the spin value of the Fe atom in FeSe and \( \Delta S \) the correction due to quantum many-body effects. Presented in figure 4 are our calculated results for \( \langle S^z \rangle \) and \( \Delta S \) as functions of the parameter \( J'/J \). It is clear that \( \langle S^z \rangle \) decreases with decreasing \( J'/J \), getting to zero at \( J' = J/2 \). In fact, the striped AFM structure is not the magnetic ground state of FeSe anymore if \( J' \) is smaller than \( J/2 \). For real samples of FeSe, one should have the parameter relations \( J' \approx J/2 \) and \( \delta \) is small but finite, and therefore the experimental spin value is small compared to the DFT value \( S \).

5. Conclusion

In summary, we have used the full-potential density-functional-theory method to study various magnetic orders and their effects on the electronic structures of FeSe. We find that, for the spins of the single Fe layer, the striped antiferromagnetic orders with the broken symmetry are more favorable in total energy than the checkerboard...
antiferromagnetic orders with tetragonal symmetry, and the interlayer magnetic interaction is very weak. Then, we investigate the corresponding electronic structures and magnetic property of the distorted phases with the striped antiferromagnetic orders. Our calculated result that the striped antiferromagnetic order is favorable for the spins of the Fe layer is consistent with the main known experimental data. We also present our calculated spin coupling constants and conclude that the reduction of the Fe magnetic moment is caused by quantum many-body effects. These results are useful in understanding the structural, magnetic and electronic properties of FeSe, and may have some helpful implications for other FeAs-based materials.

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References

[1] Kamihara Y, Watanabe T, Hirano M and Hosono H 2008 J. Am. Chem. Soc. 130 3296
[2] Takahashi H, Igawa K, Arii K, Kamihara Y, Hirano M and Hosono H 2008 Nature 453 376
[3] Chen X H, Wu T, Wu G, Liu R H, Chen H and Fang D F 2008 Nature 453 761
[4] Ren Z-A, Lu W, Yang J, Yi W, Shen X-L, Li Z-C, Che G-C, Dong X-L, Sun L-L, Zhou F and Zhao Z-X 2008 Chin. Phys. Lett. 25 2215
[5] Rotter M, Tegel M and Johrendt D 2008 arXiv:0805.4630
[6] Sasmal K, Ly B, Lorenz B, Guloy A M, Chen F, Xue Y-Y and Chu C-W 2008 arXiv:0806.1301
[7] Alireza P L, Gillett J, Chris Ko Y T, Sebastian S E and Lonzarich G G 2008 arXiv:0807.1896
[8] Pitcher M J, Parker D R, Adamson P, Herkelrath S J C, Boothroyd A T and Clarke S J 2008 arXiv:0807.2228
[9] de la Cruz C, Huang Q, Lynn J W, Li J, Ratcliff W II, Zareskiy J L, Mosk H A, Chen G F, Luo J L, Wang N L and Dai P 2008 Nature 453 899
[10] Ishibashi S, Terakura K and Hosono H 2008 J. Phys. Soc. Japan 77 053709
[11] Yin Z P, Lebegue S, Han M J, Neal B P, Savrasov S Y and Pickett W E 2008 Phys. Rev. Lett. 101 047001
[12] Yildirim T 2008 Phys. Rev. Lett. 101 057010
[13] Singh D J and Du M H 2008 Phys. Rev. Lett. 100 237003
[14] Mazin I I, Singh D J, Johannes M D and Du M H 2008 Phys. Rev. Lett. 101 057003
[15] Sefat A S, McGuire M A, Sales B C, Jin R, Howe J Y and Mandrus D 2008 Phys. Rev. B 77 174503
[16] Mizuguchi Y, Tomioka F, Tsuda S, Yamaguchi T and Takano Y 2008 Appl. Phys. Lett. 93 152505
[17] Li L, Yang Z R, Ge M, Li P, Xu J T, Wang B S, Sun Y P and Zhang Y H 2008 arXiv:0809.0128
[18] Zhang S B, Sun Y P, Zhu X D, Wang X B, Li G, Lei H C, Luo X, Yang Z R, Song W H and Dai J M 2008 arXiv:0908.1905
[19] Lee K W, Pardo V and Pickett W E 2008 arXiv:0808.1733
[20] Subedi A, Zhang L, Singh D J and Du M H 2008 arXiv:0807.4312
[21] Matsuishi S, Inoue Y, Nomura T, Hirano M and Hosono H 2008 arXiv:0810.2351v1
[22] Zhu X Y, Han F, Cheng P, Mu G, Shen B and Wen H H 2008 arXiv:0810.2351
[23] Tegel M, Johansson S, Weiss V, Schellenberg I, Hermes W, Potignan R and Johrendt D 2008 arXiv:0810.2120v1
[24] Han F, Zhu X Y, Mu G, Cheng P and Wen H H 2008 arXiv:0810.2475v1
[25] Zhu L-F and Liu B-G 2008 arXiv:0810.5049v1
[26] Hohenberg P and Kohn W 1964 Phys. Rev. 136 B864
[27] Kohn W and Sham L J 1965 Phys. Rev. 140 A1133
[28] Blaha P, Schwarz K, Sorantin P and Trickey S B 1999 Comput. Phys. Commun. 59 399
[29] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[30] Koelling D D and Harmon B N 1977 J. Phys. C: Solid State Phys. 10 3107
[31] Liu B-G 1990 Phys. Rev. B 41 9563
[32] Liu B-G, Pu F-C and Czycholl G 1996 J. Magn. Magn. Mater. 154 369