An insulating ground state with novel antiferromagnetic order in FeSe monolayer

Hai-Yuan Cao, Shiyou Chen, Hongjun Xiang, Xin-Gao Gong

Key Laboratory for Computational Physical Sciences (MOE), State Key Laboratory of Surface Physics, and Department of Physics, Fudan University, Shanghai 200433, China

Abstract

Monolayer FeSe thin film grown on SrTiO$_3$(001) (STO) shows the sign of $T_c > 77$ K, which is higher than the $T_c$-record of 56 K for the bulk FeAs-based superconductors. However, little is known about the magnetic ground state of monolayer FeSe, which should be closely related to its unusual superconductivity. Previous studies regard the collinear stripe antiferromagnetic (AFM) state as the ground state of FeSe, same to that in FeAs superconductors. Here we find a novel magnetic order named “block-checkboard AFM” as the ground state of monolayer FeSe. In this novel state, monolayer FeSe shows an unexpected insulating behavior with a Dirac-cone-like band structure relating to the specific orbital order of $d_{xz}$ and $d_{yz}$ characters of Fe atoms. This insulating ground state of FeSe monolayer could explain recent experimentally observed insulator-superconductor transition. These results cast new insights on the magnetic ordering in FeSe monolayer and its derived superconductors, and more experiments are called for investigating the magnetic properties in high-quality FeSe thin film and related bulk materials.

PACS number: 74.25.Ha, 75.70.Ak, 74.70.-b, 73.22.-f
The high temperature (high-$T_c$) superconductivity discovered in the iron-based superconductors [1–3] breaks the conventional knowledge that the magnetic atoms like Fe should not contribute to the superconductivity. This inspires that the magnetism plays an important role in the mechanism of the high-$T_c$ superconductivity in iron-based superconductors [4]. Although the electronic properties for different families of iron-based superconductors can be somehow different [5], they all are believed to share the common feature of AFM ordered parent compound [6].

While the magnetism contributing to the high-$T_c$ superconductivity has attracted wide attention [7], the ground magnetic states for the parent compounds of iron-based superconductors remain unclear. Recently, the sign of over 77 K unconventional high $T_c$ superconductivity [8–11] has been observed in monolayer FeSe grown on STO substrate [12–17], which is much higher than the highest $T_c$ record in the intensively studied FeAs systems [18, 19]. For FeAs-based materials, the collinear AFM (or the stripe AFM) has been verified as the ground magnetic order for the parent compounds by neutron scatterings [7]. However, the ground magnetic order for the compound based on FeSe is still waiting to be clarified. Previous theoretical studies presumed that FeSe has the same ground magnetic order as FeAs-based materials [20–24]. From the obtained experimental results, the electronic properties of FeSe-based materials are much different from that of FeAs-based materials [25], especially for that in monolayer FeSe on STO substrate [8–17]. Recent ARPES experiment observed that the insulator-superconductor transition via doping in the monolayer FeSe grown on the STO substrate [17], which indicates that the ground state of monolayer FeSe could be insulating. Besides, in the recent discovered molecular-intercalated iron-selenide Li$_x$(ND$_2$)$_y$(ND$_3$)$_{1-y}$Fe$_2$Se$_2$ [26], the neutron-inelastic-scattering measurements found that the magnetic scattering in momentum space is unusually closer to wave-vector $(\pi, \pi/2)$ [27], which means that there could be an unexpected magnetic order other than collinear AFM. Above experimental observations imply that monolayer FeSe could have some unique electronic and magnetic properties. As yet, unveiling the ground-state properties of monolayer FeSe would be crucial for understanding the mechanism of novel high-$T_c$ superconducting.
Here, based on the first-principles calculations, we find a novel magnetic order, named as the block-checkboard AFM, which is clearly different from previously proposed magnetic order in iron based compounds, to be the ground magnetic state (Fig. 1(a)) for the monolayer FeSe. This ground state has a Dirac-cone like band structure with a non-zero band gap induced by the spin-orbit interaction. The Dirac-cone like band structure relates to a specific orbital order of $d_{xz}$ and $d_{yz}$ characters of Fe atoms. The block-checkboard AFM would also induce a $2 \times 1$ reconstruction in FeSe monolayer due to the different distance of the Se atom to the Fe plane. Furthermore, we confirm that this novel block-checkboard AFM not only exists in the simplest FeSe monolayer but also in its derived superconductors, like the recently synthesized bulk LiFeO$_2$Fe$_2$Se$_2$ [28]. This is the first time to reveal that the ground magnetic order of FeSe monolayer is different from that of FeAs-based materials, which could well explain several recent intriguing experimental observations.

In this letter, we performed extensive study on the electronic and magnetic properties of the block-checkboard AFM in monolayer FeSe and LiFeO$_2$Fe$_2$Se$_2$ based on the first-principles simulations. We employed the plane-wave basis set and the projected augmented wave method [29, 30] which is implemented in the VASP code [31, 32] to calculate the electronic and magnetic properties. We adopted the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) formula [33] for the exchange-correlation functional. A plane-wave cutoff energy of 450 eV and a Monkhorst-Pack mesh of $16 \times 8$ $k$-points [34] for monolayer FeSe and $18 \times 9 \times 9 \times 9$ $k$-points for LiFeO$_2$Fe$_2$Se$_2$ with 0.1 eV Gaussian smearing were used in magnetic unit cell calculations. A supercell of 16 Fe atoms was used to calculate the magnetic exchange coupling parameters. The vacuum layer more than 20 Å thick was used to ensure decoupling between neighboring FeSe layers. For structural relaxation, all the atoms were allowed to relax until atomic forces are smaller than 0.01 $eV/Å$. The density of states calculations were performed based on the tetrahedral method [35] with a much denser k-grid of $24 \times 12$ and $24 \times 12 \times 12$ for the magnetic unit cell of monolayer FeSe and LiFeO$_2$Fe$_2$Se$_2$, respectively.

Our results show that the ground magnetic state of monolayer FeSe should be the block-checkboard AFM, rather than the collinear AFM which was supposed to be. We have calculated the relative energy of various phases, including the nonmagnetic state, the checkboard AFM order (or the Ni$_{\text{coe}}$ AFM), the bicollinear AFM order, the collinear AFM order and the block-checkboard AFM. Table I lists all the relaxed structure parameters as well
as their relative energies. One can clearly see that the energy of block-checkboard AFM is lower than that of the collinear AFM order by 12 meV/f.u., while the magnetic moments of these two magnetic orders are quite similar. The breaking of the C4 symmetry after lattice-constant optimization is found in the block-checkboard AFM order as well as in the collinear AFM, which is caused by the ferro-orbital order of Fe atoms in FeSe [36]. Furthermore, we find that the bulk FeSe also energetically prefers the block-checkboard AFM order.

The block-checkboard AFM is different from the collinear AFM order that each spin of Fe atom has one neighbor spin aligned ferromagnetically while the other neighbor spins all aligned antiferromagnetically (Fig. 1a). More interestingly, we find apparent difference between the charge-density distribution of the block-checkboard AFM and the collinear AFM (Fig. 1b, 1c). Both Fe and Se atoms in the block-checkboard AFM order has a unique orbital order which does not appear in other AFM orders. The Se atoms could be divided into two groups (labeled as Se1 and Se2 in Fig. 1(b)), while each group has the same orbital order. The orbital order of Se atoms is in consistent with the different distances of the Se atoms to the Fe plane (zSe). The zSe for Se1 is 1.48 Å and that for Se2 is 1.46 Å which can be regarded as a 2 × 1 reconstruction in monolayer FeSe.

The block-checkboard AFM has a feature of exotic Dirac-cone-like band structure as shown in Fig. 2. If regarding the spin-orbit coupling, monolayer FeSe with the block-checkboard AFM becomes insulated, with a band gap around 27 meV, while that with the other magnetic orders are all metallic. It is worth to note that such gap is an indirect band gap, although both the valence band maximum (VBM) and the conduction band minimum (CBM) of the band structure located very closed to the k-point (0.2, 0.0, 0.0) in Γ − X boundary of the first magnetic Brillouin zone. Inspecting throughout the Brillouin zone confirms that this is a single gap at the boundary, as is the Dirac point in graphene.

The Dirac-cone-like band structure relates to a specific orbital order of dxz and dyz characters of Fe atoms, which can be seen from the decomposed band structure near the Fermi level (Fig. 3). The spin-majority d-orbitals of Fe atoms are almost all filled, while the density of states (DOS) near the Fermi level is mostly contributed by the spin-minority d-orbitals of the Fe atoms. For the spin-minority part of Fe atoms, dx2−y2, dz2 and dxz orbitals are mostly filled while dyz and dxy orbitals are slightly filled [37]. The two bands cross over the Fermi level are mainly composed of spin-minority dxz and dyz characters of Fe atoms, respectively. If neglecting the spin-orbit coupling, dxz and dyz belong to different symmetry-groups
which allows them to cross without hybridization at the Fermi level. Then turning on the
spin-orbit coupling could lead to the mixing between $d_{xz}$ and $d_{yz}$ orbitals, resulting a gap
opening. While opening the gap, the charge density at the VBM is mainly composed of $d_{xz}$
hybridized with $d_{xy}$ and $d_{z}$ of Fe atoms, while that at the CBM is mainly composed of $d_{yz}$
hybridized with $d_{xy}$ (Fig. 4). The charge density at the VBM and CBM is in agreement with
the ferro-orbital order of $d_{xz}$ and $d_{yz}$ orbitals. The emerging Dirac-cone-like band structure
in the block-checkboard AFM should be directly related to the novel ground magnetic order
in the monolayer FeSe, which means the orbital order and the magnetic order are strongly
coupled together here.

LiFeO$_2$Fe$_2$Se$_2$, a FeSe-based superconductor with $T_c \sim 43$ K and neutral LiFeO$_2$ anti-
PbO-type spacer layers intercalated between FeSe layers, was recently synthesized by the
hydrothermal method [28]. The relative energy difference between various magnetic orders
and the nonmagnetic order in LiFeO$_2$Fe$_2$Se$_2$ is similar to that in monolayer FeSe as shown in
Table I. The calculation shows that the block-checkboard AFM is not only the ground mag-
netic order for LiFeO$_2$Fe$_2$Se$_2$, but its relative stability to other magnetic states is even more
robust comparing to that of monolayer FeSe [37]. This reveals that the block-checkboard
AFM could be the possible universal ground magnetic order for undoped FeSe layer and its
derived structures. Besides that, we also find that the Dirac-cone like band structure still
be kept in the bulk LiFeO$_2$Fe$_2$Se$_2$.

The predicted block-checkboard AFM order could be confirmed experimentally by per-
forming neutron-scattering measurements in the high-quality FeSe thin films grown on STO
substrate by molecular beam epitaxy and the single crystal bulk LiFeO$_2$Fe$_2$Se$_2$. Although
this novel AFM order has not been observed directly yet, there were several experimental
evidences indicating the existence of this unusual magnetic order. Firstly, the 27 meV band
gap we observed in FeSe monolayer with block-checkboard AFM order is quite closed to
the ARPES experimentally observed insulating gap, while the insulating gap for the slightly
doped FeSe monolayer is around 20~25 meV [17]. Our results provide a possible explanation
for the observed insulating gap by including the block-checkboard AFM order and the effect
of spin-orbit coupling. Besides, the block-checkboard AFM matches perfectly to the un-
usual magnetic scattering with wave-vector ($\pi$, $\pi$) in iron selenide Li$_x$(ND$_2$)$_y$(ND$_3$)$_{1-y}$Fe$_2$Se$_2$
[27]. It highly suggests that the block-checkboard AFM is also the ground magnetic order
in Li$_x$(ND$_2$)$_y$(ND$_3$)$_{1-y}$Fe$_2$Se$_2$. Another STM experiment observed a $2 \times 1$ reconstruction
would occur in monolayer FeSe on STO substrate [38], which could also be explained by
the block-checkboard AFM induced two types of Se atom with different height $z_{Se}$. Very
recent electric transport measurements observed the Dirac-cone-like ultrafast carriers in the
single crystal FeSe superconductor [39], which could be interpreted as originating from our
proposed block-checkboard AFM order induced Dirac-cone-like band structure.

In summary, the present studies reveal that monolayer FeSe does not share the same
collinear AFM ground magnetic order with the FeAs-based materials. The ground state of
monolayer FeSe is block-checkboard AFM, which is a new insulating ground state with a
27 meV band gap and completely different from the magnetic states found in other iron su-
perconductors. The Dirac-cone-like band structure would appear in monolayer FeSe induced
by the block-checkboard AFM order, which relates to a specific orbital order of $d_{xz}$ and $d_{yz}$
characters of Fe atoms. Such novel magnetic order is found to be robust against tensile strain
up to a few percent and also robust against electron doping to a certain level [37]. We pre-
dict that bulk LiFeO$_2$Fe$_2$Se$_2$ superconductor could probably share the same novel magnetic
order, in which the neutron scattering measurement can easily be performed. The existence
of the gapped insulating ground state could well explain the recently observed insulating
behavior of monolayer FeSe on STO substrate by ARPES. Besides that, our results could
explain some intriguing experimental observations including the unusual magnetic signal in
the molecular-intercalated iron selenide, the $2 \times 1$ reconstruction in monolayer FeSe on STO
substrate and the Dirac-cone-like ultrafast carriers in FeSe. The block-checkboard AFM
order with the insulating behavior found in FeSe layer shed new lights on the understand-
ing of high-$T_c$ superconductivity in FeSe monolayer on the oxides substrates and FeSe-layer
derived superconductors.

Acknowledgments

We acknowledge professor D. L. Feng, Dr. Rui Peng and Dr. Shiyong Tan for stimulating
discussions. The work was partially supported by the Special Funds for Major State Basic
Research, National Natural Science Foundation of China (NSFC), Program for Professor
of Special Appointment (Eastern Scholar) and the National Basic Research Program of
China (973 Program). Computation was performed in the Supercomputer Center of Fudan
University.
Figure 1: (a) Schematic top view of the block-checkboard AFM in FeSe monolayer. Each spin of Fe atom has only one neighbor spin aligned ferromagnetically while the other neighbor spins all aligned antiferromagnetically. The rectangle enclosed by the dashed lines denotes the magnetic unit cell. (b) The charge density difference between the block-checkboard AFM and the nonmagnetic state. (c) The charge density difference between the collinear AFM and the nonmagnetic state. The isosurface depicted by the red and green colors represents the lost and gained charge density comparing to the nonmagnetic state. Se atoms in the block-checkboard AFM order show an orbital order which are labeled with Se1 (blue) and Se2 (yellow), respectively.
Table I: Lattice constant, energy difference $\Delta E$ (reference to the energy of nonmagnetic order) and magnetic moments $M_{Fe}$ of monolayer FeSe with different magnetic order. The unit cell of monolayer FeSe is shown in Fig. 1(a).

| Magnetic Order               | a (Å) | b (Å) | $\Delta E$ (meV/f.u.) | $M_{Fe}$ ($\mu_B$) |
|------------------------------|-------|-------|-----------------------|------------------|
| Nonmagnetic Order            | 5.200 | 10.399| 0                     | 0                |
| Collinear AFM                | 5.279 | 10.455| -87                   | 1.9              |
| Checkboard AFM               | 5.239 | 10.477| -62                   | 1.7              |
| Bicollinear AFM              | 5.192 | 10.383| -37                   | 2.2              |
| Block-checkboard AFM         | 5.285 | 10.452| -99                   | 2.0              |

Figure 2: Electronic band structure of monolayer FeSe with the block-checkboard AFM order including spin-orbit coupling. Inset shows the first Brillouin zone with the special $k$ points: $\Gamma(0 \ 0 \ 0)$, $X(0.5 \ 0 \ 0)$, $M(0.5 \ 0.5 \ 0)$, and $X'(0 \ 0.5 \ 0)$. The Dirac-point appears at the Fermi level, while including SOC would open (highlighted) a 27 meV indirect band gap.
Figure 3: Decomposed band structure around the Fermi level for the different spin-minority d-orbital characters of Fe atoms in different colors. The size of the symbol represents the relative proportion for different character of each band. The two bands crossing at the Fermi level are mainly composed of the $d_{xz}$ or $d_{yz}$ character near the Fermi level, respectively.
Figure 4: The band decomposed charge density of the block-checkboard AFM at the VBM and CBM: (a) and (b) projections of the charge density of the VBM along [001] and [010] directions; (c) and (d) projections of the charge density of the CBM along [001] and [010] directions.
[1] Y. Kamihara et al., J. Am. Chem. Soc, 130, 3296 (2008).
[2] M. Rotter et al., Phys. Rev. Lett. 101, 107006 (2008).
[3] F.-C. Hsu et al., Proc. Natl. Acad. Sci. U.S.A 105, 14262 (2008).
[4] D. J. Scalapino, Rev. Mod. Phys. 84, 1383 (2012).
[5] D. C. Johnston, Adv. Phys. 59, 803 (2010).
[6] Y. J. Uemura, Nat. Mater. 8, 253 (2009).
[7] P. Dai et al., Nat. Phys. 8, 709 (2012).
[8] Q. Y. Wang et al., Chin. Phys. Lett. 29, 037402 (2013).
[9] L. Z. Deng et al., arXiv:1311.6459.
[10] R. Peng et al., arXiv:1402.1357
[11] J.-F. Ge et al., arXiv:1406.3435
[12] D. F. Liu et al., Nat. Commun. 3, 931 (2012).
[13] S. L. He et al., Nat. Mater. 12, 605 (2013).
[14] S. Y. Tan et al., Nat. Mater. 12, 634 (2013).
[15] H. W. Zhang et al., Chin. Phys. Lett. 31, 1(2014).
[16] Xu Liu et al., arXiv:1402.1400.
[17] Junfeng He et al., arXiv:1401.7115.
[18] Z. A. Ren et al., Chin. Phys. Lett. 25, 2215 (2008).
[19] C. Wang et al., Europhys. Lett. 83, 67006 (2008).
[20] A. Subedi et al., Phys. Rev. B 78, 134514 (2008).
[21] T. Bazhirov and M. L. Cohen, J. Phys.: Condens. Matter 25, 105506 (2013).
[22] K. Liu, Z.-Y Lu, and T. Xiang, Phys. Rev. B 85, 235123 (2012).
[23] F. Ma et al., Phys. Rev. Lett 102, 177003 (2009).
[24] Hai-Yuan Cao et al., Phys. Rev. B 89, 014501 (2014).
[25] E. Dagotto, Rev. Mod. Phys. 85, 849 (2013).
[26] M. Burrard-Lucas et al., Nat. Mater. 12, 15 (2013).
[27] A. E. Taylor et al., Phys. Rev. B 87, 220508(R) (2013).
[28] X. F. Lu et al., Phys. Rev. B 89, 020507(R) (2013).
[29] P. E. Blochl, Phys. Rev. B 50, 17953 (1994).
[30] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
[31] G. Kresse and J. Furthmüller, Comput. Mat. Sci. 6, 15 (1996).
[32] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
[33] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865, (1996).
[34] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
[35] Peter E. Blöchl, O. Jepsen, and O. K. Andersen, Phys. Rev. B 49, 16223 (1994).
[36] Chi-Cheng Lee, Wei-Guo Yin, and Wei Ku, Phys. Rev. Lett. 103, 267001 (2009).
[37] See Supplemental Material for the calculated projected density of states, the calculated relative energy of bulk LiFeO$_2$Fe$_2$Se$_2$ with different magnetic order and stability of block-checkboard AFM order against strain and charge-doping.
[38] Junhyeok Bang et al., Phys. Rev. B 87, 220503(R) (2014).
[39] K. K. Huynh et al., arXiv:1405.3815.