Magnetic interactions in FeSe studied by first principle calculations

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Based on first principle calculations we have investigated the evolution of magnetism in free-standing monolayer FeSe with respect to lattice constant and magnetism in bulk FeSe. The computational results show that the magnetic order in free-standing monolayer FeSe will change from anti-ferromagnetic pair-checkboard order to stripe collinear order along with enlarging lattice constant. The magnetic order in bulk FeSe will change from stripe collinear order to anti-ferromagnetic pair-checkboard order only if structure reconstruction is allowed. We use J$_{1}$-J$_{2}$-K$_{1}$ model to fit the calculated total energies of different magnetic orders to study magnetic interaction strengths in FeSe. The fitting results of J$_{1}$-J$_{2}$-K$_{1}$ indicate that magnetic interactions in FeSe are quite strong and highly frustrated, and increase slowly with enlarging lattice parameter.

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I. INTRODUCTION

In recent years up to 20meV superconducting gap has been observed in monolayer FeSe grown on SrTiO$_3$(STO) substrate by scanning tunneling spectroscopy(STM) [1] and angle-resolved photoemission spectroscopy(ARPES) [2-4]. Moreover, Jian-Feng Ge et al. [5] reported the observation of over 100K superconductivity in FeSe/STO systems by in situ four-point probe electrical transport measurements, where the superconducting critical temperature(T$_c$) is almost twice of the T$_c$ record in FeAs-based superconductors[6, 7] and ten times of T$_c$ measured in bulk FeSe under ambient pressure[8, 9]. Several possible mechanisms have been proposed to explain the T$_c$ enhancement. The first possible mechanism is charge transfer indicated by the ARPES observation of only electron Fermi pockets in FeSe/STO systems by in situ four-point probe electrical transport measurements, where the superconducting critical temperature(T$_c$) is almost twice of the T$_c$ record in FeAs-based superconductors[6, 7] and ten times of T$_c$ measured in bulk FeSe under ambient pressure[8, 9]. Several possible mechanisms have been proposed to explain the T$_c$ enhancement. The first possible mechanism is charge transfer indicated by the ARPES observation of only electron Fermi pockets in FeSe/STO systems by in situ four-point probe electrical transport measurements, where the superconducting critical temperature(T$_c$) is almost twice of the T$_c$ record in FeAs-based superconductors[6, 7] and ten times of T$_c$ measured in bulk FeSe under ambient pressure[8, 9].

A. First principle calculations

In this paper, we have studied the evolution of magnetism in free-standing monolayer FeSe with respect to lattice constant and magnetism in bulk FeSe[22] by means of first principle calculations. Lattice constants 3.765Å, 3.905Å and 4.045Å were chosen for monolayer FeSe during the calculations. The three kinds of lattice constants were taken from previous DFT work[19], which are supposed to be close to lattice constants of bulk FeSe, STO substrate and KTaO$_3$ substrate respectively. The calculated results show that anti-ferromagnetic pair-checkboard order is magnetic ground state of free-standing monolayer FeSe with lattice constant 3.765Å and bulk FeSe under structure reconstruction, and that stripe collinear order is magnetic ground state of free-standing monolayer FeSe with lattice constant 3.905Å and 4.045Å. The anti-ferromagnetic pair-checkboard order in bulk FeSe was first found by Hai-Yuan Cao et al.[21] via first principle calculations. Furthermore, we used J$_{1}$-J$_{2}$-K$_{1}$ model[23, 24] to fit calculated total energies of different magnetic orders to study magnetic interactions in FeSe and the relations between magnetic interaction and lattice constant. The results indicate that magnetic interaction strengths increase slowly as enlarging lattice constant. The ratio of fitted J$_{2}$/J$_{1}$ is close to 0.5 for both bulk FeSe and monolayer FeSe, which implies strong magnetic frustration in FeSe. Based on J$_{1}$-J$_{2}$-K$_{1}$ model with fitted exchange parameters we calculated spin wave dispersions of bulk FeSe, which can be tested in inelastic neutron scattering experiments.

II. METHODS

Non-collinear magnetic calculations implemented in Vienna Ab initio Simulation Package(VASP)[25-27] were performed to study the electronic and magnetic structures of free-standing monolayer FeSe with different lattice constants and bulk FeSe. The project augmented wave(PAW) pseudopotential[28, 29] with generalized gradient approximation(GGA) of Perdew-Burke-Emrzerhof(PBE)[30] for exchange-correlation potential were adopted in the calculations. We used 24×24×1 k-mesh and 18×18×18 k-mesh for reciprocal space sampling in monolayer FeSe and bulk FeSe respectively[31],
FIG. 1: Schematic diagram of different magnetic orders in top view. NAFM, CAFM, SM, TM, BAFM, PAFM represent Néel anti-ferromagnetic order, collinear anti-ferromagnetic order, spiral magnetic order, tetrahedron magnetic order, bicollinear anti-ferromagnetic order and pair-checkboard antiferromagnetic order respectively. The tetrahedron magnetic order means that the moments of the four Fe atoms in the unit cell form a tetrahedron. The solid grey lines enclose magnetic unit cell of corresponding magnetic order used in the calculations.

500eV for plane wave energy cut-off, and Gaussian Smearing with broadening width of 0.01eV to capture converged results in meV scale. Over 15Å vacuum layer was added to decouple interlayer couplings. We chose $\sqrt{2} \times \sqrt{2} \times 1$ supercell in the calculations of non-magnetic(NM) state, Néel anti-ferromagnetic(NAFM) state, collinear anti-ferromagnetic(CAFM) state, spiral magnetic(SM) state, and tetrahedron magnetic(TM) state. $2 \times 1 \times 1$ supercell and $2\sqrt{2} \times \sqrt{2} \times 1$ supercell were chosen in the calculations of bi-collinear antiferromagnetic(BAFM) state and anti-ferromagnetic pair-checkboard(PAFM) state respectively. All the calculated magnetic states are schematically shown in the Figure 1. We used the following frustrated $J_1$-$J_2$-$K_1$ model[23, 24] to describe magnetic interactions, where the superexchange parameters are fitted to the total energies with variable moment sizes of different magnetic orders.

\[
H_{spin} = \sum_{\langle i,j \rangle} J_1 S_i \cdot S_j + \sum_{\langle i,j \rangle} J_2 S_i \cdot S_j - \sum_{\langle i,j \rangle} K_1 [S_i \cdot S_j]^2
\]

\[
= \sum_{\langle i,j \rangle} \frac{J_1}{g^2 \mu_B^2} M_i \cdot M_j + \sum_{\langle i,j \rangle} \frac{J_2}{g^2 \mu_B^2} M_i \cdot M_j
\]

\[
- \sum_{\langle i,j \rangle} \frac{K_1}{g^4 \mu_B^4} [M_i \cdot M_j]^2
\]

where $M_i$ ($M_j$) labels the magnetic moment of atom on site $i$ ($j$), $\langle i,j \rangle$, $\langle \langle i,j \rangle \rangle$ denote all the summations over nearest, next-nearest neighbor respectively. $g$ labels the Landé g-factor. $\mu_B$ represents Bohr magneton.

### III. RESULTS AND DISCUSSION

In the calculations we used crystal structure after only relaxing ionic positions under CAFM order. Since the energy difference in bulk FeSe is quite small(1.5 meV per Fe atom under CAFM order) between ferromagnetic stacking and anti-ferromagnetic stacking in the c axis direction, we just considered ferromagnetic stacking in the c axis direction for simplicity during the calculations.

All the calculated total energies and moments of free-standing monolayer FeSe with different lattice constants and bulk FeSe are illustrated in the Table I.

| $a$(Å) | 3.765 | 3.905 | 4.045 | bulk |
|-------|-------|-------|-------|------|
| $Z_{Se}$(Å) | 1.444 | 1.393 | 1.326 | 1.418 |
| NAFM E(eV) | -49.628 | -49.374 | -48.968 | -49.547 |
| M($\mu_B$) | 1.94 | 2.22 | 2.42 | 1.88 |
| CAFM E(eV) | -49.761 | -49.647 | -49.396 | -49.690 |
| M($\mu_B$) | 2.13 | 2.42 | 2.63 | 2.05 |
| PAFM E(eV) | -49.808 | -49.614 | -49.234 | -49.728 |
| M($\mu_B$) | 2.12 | 2.35 | 2.52 | 2.09* |
| BAFM E(eV) | -49.392 | -49.122 | -48.736 | -49.333 |
| M($\mu_B$) | 2.01 | 2.35 | 2.67 | 1.80 |
| SM E(eV) | -49.505 | -49.366 | -49.143 | -49.458 |
| M($\mu_B$) | 1.96 | 2.43 | 2.63 | 1.80 |
| TM E(eV) | -49.548 | -49.346 | -49.033 | -49.394 |
| M($\mu_B$) | 1.89 | 2.29 | 2.52 | 1.90 |

TABLE I: Total energies and magnetic moments for free-standing monolayer FeSe with different lattice constants and bulk FeSe under different magnetic orders.

As the results shown in the Table I, PAFM state is stable in monolayer FeSe with lattice constant 3.765Å, where the energy is lower than CAFM order by 12meV per Fe atom. The total energies of CAFM order are still lowest among calculated states in monolayer FeSe with lattice constant 3.905Å, 4.045Å, and bulk FeSe are -49.113eV, -48.638eV, -47.960eV respectively. Energy and moment of bulk FeSe labeled with * are obtained after relaxing the height of Se atoms. Due to the reconstruction under PAFM order, the total energies and moments under PAFM order were not used in fitting exchange parameters.
schematically shown in the Figure 2. In bulk FeSe the reconstruction leads to the magnetic ground state changing from CAFM order to PAFM order with total energy lower by 9.5meV per Fe.

Although no long range magnetic order has been observed in bulk FeSe, it does not mean that the magnetic interaction can be ignored. Previous studies in iron-based superconductors used local spin model to describe the magnetic interactions[18, 32–35]. Here we also employ a frustrated $J_1$-$J_2$-$K_1$ model[23, 24] to describe the magnetic interactions. Since the values of moment sizes are not strictly $2\mu_B$, we fitted total energies with variable moment sizes to obtain superexchange parameters (see equation (1)). Table II lists the fitting results.

| a(Å)       | 3.765  | 3.905  | 4.045  | bulk       |
|------------|--------|--------|--------|------------|
| $Z_{Se}(\text{Å})$ | 1.444  | 1.393  | 1.326  | 1.418      |
| $J_1/g^2$(meV) | 21.5±2.8 | 24.0±3.2 | 29.5±4.9 | 17.9±1.7  |
| $J_2/g^2$(meV) | 10.9±1.4 | 13.2±1.6 | 17.4±2.4 | 9.9±0.9   |
| $K_1/g^4$(meV) | 1.4±0.3  | 1.3±0.3  | 1.2±0.3  | 1.5±0.2   |
| $J_2/J_1$    | 0.51    | 0.55    | 0.59    | 0.55       |

TABLE II: Fitting values of $J_1$, $J_2$, $K_1$ for monolayer FeSe with different lattice constants and bulk FeSe.

The fitting values of superexchange parameters have been divided by the square or fourth power of Landé g-factor. If the Landé g-factor is 2, the given exchange parameters should multiply by 4 or 16. The data in the Table II indicates that the magnetic interactions in FeSe are quite strong and that magnetic interactions in monolayer FeSe is stronger than that in bulk FeSe. We can also see that the magnetic interaction strengths increase slowly with enlarging lattice parameter in monolayer FeSe.

What’s more, the fitting ratio of $J_2/J_1$ in both monolayer FeSe and bulk FeSe is close to 0.5. It is known in $J_1$-$J_2$ heisenberg model of square lattice that the system becomes highly frustrated as the ratio of $J_2/J_1$ close to 0.5. Magnetic frustration has been proposed as the explanation for the absence of magnetic long range order in bulk FeSe[20, 36–39]. So although magnetic order can be obtained in FeSe with DFT calculations, the strong quantum fluctuation can destroy the long range magnetic order[20]. J. K. Glashbrenner et al.[20] and Zhong-Yi Lu et al.[40] found that there exist a series of magnetic states between PAFM order and CAFM order, which also imply strong magnetic frustration in FeSe.

We also calculated electronic structures of monolayer FeSe with the three kinds of lattice constants under NM state to study lattice constant’s influence on band structure. The band structures shown in the Figure 3 indicate that enlarging lattice parameter does not change band structures significantly, except a small change in bandwidth and a small hole fermi pocket located at $\Gamma$. 

FIG. 3: Band structures of free-standing monolayer FeSe with lattice constant $a=3.765\text{Å}, 3.905\text{Å}$ and $4.045\text{Å}$. The band structures are calculated under NM states. The coordinates of special points $\Gamma, X, M$ are $(0,0)$, $(\pi/a,0)$, and $(\pi/a,\pi/a)$ respectively.
point dropping below fermi level. The fact that band structures and magnetic interactions do not dramatically change with enlarging lattice constant implies that $T_c$ enhancement in FeSe/STO is unlikely induced by tensile stress.

To test the validity and accuracy of our approach to fitting exchange parameters, we calculated spin wave dispersions in bulk FeSe based on linear spin wave theory, which can be experimentally measured by inelastic neutron scattering. Since no structure reconstruction in bulk FeSe has been observed by experiments, we then chose CAFM order as magnetic ground state during the spin wave calculations. The magnon dispersions within $J_1$-$J_2$-$K_1$ model can be written as,

$$E_{LSW}(k) = \sqrt{A_k^2 - B_k^2},$$

where

$$A_k = (2J_1 \cos(k_y) + 4J_2)S + 2K_1(4 - 2\cos(k_y))S^3,$$

$$B_k = (2J_1 \cos(k_x) + 4J_2 \cos(k_x) \cos(k_y))S + 4K_1 \cos(k_x)S^3.$$

(3)

**FIG. 4:** Spin wave dispersions of tetragonal BaFe$_2$As$_2$ and bulk FeSe under stripe collinear order, where we chose $g=2$ and $S=1$. The dispersions are drawn in the unfolded Brillouin zone(one Fe atom per unit cell), where the high symmetry points are shown in the inset.

For comparison we also calculated spin wave dispersions of tetragonal BaFe$_2$As$_2$[41] within $J_1$-$J_2$-$K_1$ model, where $J_1$ and $J_2$ are also obtained by fitting total energies with variable moment sizes. The fitted values are $J_1/g^2=13.6\pm2.4$meV, $J_2/g^2=10.0\pm1.1$meV and $K_1/g^4=1.4\pm0.3$meV. The ratio of $J_2/J_1$ is around 0.74, which is larger than that in both monolayer FeSe and bulk FeSe, and thus make CAFM order stable. The magnon dispersions along high symmetry points are shown in the Figure 4. We can see that bulk FeSe has a slightly larger bandwidth of magnon dispersions compared with BaFe$_2$As$_2$, assuming the same $g$-factor and spin size for the two compounds. Although no magnetic long range order has been observed in bulk FeSe, we hope that the spin wave dispersions under CAFM order can still qualitatively describe the magnetic excitations in bulk FeSe.

We noticed that our fitting results for monolayer FeSe are different from previous calculations[19], where the following reasons may be responsible for that. (i) We used more dense $k$-mesh and smaller broadening width compared with their calculations. (ii) Non-collinear magnetic states(SM and TM) were included in our calculations. (iii) We calculated the total energies and moments of different magnetic orders with fixed structure to fit the exchange parameters $J_1$, $J_2$, $K_1$, where they optimized structure under different magnetic orders during the calculations. (iv) In addition, we have used the method considering the magnetic moment sizes to fit exchange parameters, which were not taken into account in their fittings. Our $J_1$-$J_2$-$K_1$ fitting results for bulk FeSe are in rough agreement with the results of F. Ma et al.[42], but are significantly smaller than the results of J. Glasbrenner et al.[20].

In conclusion, the computational results show that the magnetic order in monolayer FeSe will change from PAFM order to CAFM order with enlarging lattice constant, and that the magnetic order in bulk FeSe will change from CAFM order to PAFM order only if structure reconstruction is allowed. The fitted exchange parameters within $J_1$-$J_2$-$K_1$ model suggest strong frustration in monolayer FeSe and bulk FeSe, which may provide hint to understand why long range magnetic order has not been observed in FeSe. According to the results, the bandwidth of spin wave dispersions in bulk FeSe would be slightly larger than that in BaFe$_2$As$_2$, which can be verified in inelastic neutron scattering experiments.

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[1] W. Qing-Yan, L. Zhi, Z. Wen-Hao, Z. Zuo-Cheng, Z. Jin-Song, L. Wei, D. Hao, O. Yun-Bo, D. Peng, C. Kai, et al., Chinese Physics Letters 29, 037402 (2012).

[2] S. He, J. He, W. Zhang, L. Zhao, D. Liu, X. Liu, D. Mou, Y.-B. Ou, Q.-Y. Wang, Z. Li, et al., Nature materials 12, 605 (2013).

[3] S. Tan, Y. Zhang, M. Xia, Z. Ye, F. Chen, X. Xie, R. Peng, D. Xu, Q. Fan, H. Xu, et al., Nature materials 12, 634 (2013).

[4] D. Liu, W. Zhang, D. Mou, J. He, Y.-B. Ou, Q.-Y. Wang,
Z. Li, L. Wang, L. Zhao, S. He, et al., Nature communications 3, 931 (2012).

[5] J.-F. Ge, Z.-L. Liu, C. Liu, C.-L. Gao, D. Qian, Q.-K. Xue, Y. Liu, and J.-F. Jia, Nature materials 14, 285 (2014).

[6] R. Zhi-An, L. Wei, Y. Jie, Y. Wei, S. Xiao-Li, C. Guang-Can, D. Xiao-Li, S. Li-Ling, Z. Fang, Z. Zhong-Xian, et al., Chinese Physics Letters 25, 2215 (2008).

[7] C. Wang, L. Li, S. Chi, Z. Zhu, Z. Ren, Y. Li, Y. Wang, X. Lin, Y. Luo, S. Jiang, et al., EPL 83, 67006 (2008).

[8] F.-C. Hsu, J.-Y. Luo, K.-W. Yeh, T.-K. Chen, T.-W. Huang, P. M. Wu, Y.-C. Lee, Y.-L. Huang, Y.-Y. Chu, D.-C. Yan, et al., Proceedings of the National Academy of Sciences 105, 14262 (2008).

[9] C.-L. Song, Y.-L. Wang, Y.-P. Jiang, Z. Li, L. Wang, K. He, X. Chen, X.-C. Ma, and Q.-K. Xue, Phys. Rev. B 84, 020503 (2011).

[10] J. Lee, F. Schmitt, R. Moore, S. Johnston, Y.-T. Cui, W. Li, M. Yi, Z. Liu, M. Hashimoto, Y. Zhang, et al., Nature 515, 245 (2014).

[11] R. Peng, X. P. Shen, X. Xie, H. C. Xu, S. Y. Tan, M. Xia, T. Zhang, H. Y. Cao, X. G. Gong, J. P. Hu, et al., Phys. Rev. Lett. 112, 107001 (2014).

[12] P. Dai, J. Hu, and E. Dagotto, Nature Physics 8, 709 (2012).

[13] C. de La Cruz, Q. Huang, J. Lynn, J. Li, W. Ratcliff II, J. L. Zarateky, H. Mook, G. Chen, J. Luo, N. Wang, et al., Nature(London) 453, 899 (2008).

[14] J. Zhao, Q. Huang, C. de La Cruz, S. Li, J. Lynn, Y. Chen, M. Groen, G. Chen, G. Li, Z. Li, et al., Nature materials 7, 953 (2008).

[15] J. Dong, H. J. Zhang, G. Xu, Z. Li, G. Li, W. Z. Hu, D. Wu, G. F. Chen, X. Dai, J. L. Luo, et al., EPL 83, 27006 (2008).

[16] Y. J. Uemura, Nature materials 8, 253 (2009).

[17] F. Ma and Z.-Y. Lu, Phys. Rev. B 78, 033111 (2008).

[18] T. Yildirim, Physical Review Letters 101, 057010 (2008).

[19] H.-Y. Cao, S. Tan, H. Xiang, D. Feng, and X.-G. Gong, Physical Review B 89, 014501 (2014).

[20] J. Glashrenner, I. Mazin, H. O. Jeschke, P. Hirschfeld, R. Fernandez, and R. Valentí, Nature Physics (2015).

[21] H.-Y. Cao, S. Chen, H. Xiang, and X.-G. Gong, Phys. Rev. B 91, 020504 (2015).

[22] T. M. McQueen, A. J. Williams, P. W. Stephens, J. Tao, Y. Zhu, V. Ksenofontov, F. Casper, C. Felser, and R. J. Cava, Phys. Rev. Lett. 103, 057002 (2009).

[23] A. N. Yaresko, G.-Q. Liu, V. N. Antonov, and O. K. Andersen, Phys. Rev. B 79, 144421 (2009).

[24] A. L. Wysocki, K. D. Belashchenko, and V. P. Antropov, Nature Physics 7, 485 (2011).

[25] D. Hobbs, G. Kresse, and J. Hafner, Phys. Rev. B 62, 11556 (2000).

[26] G. Kresse and J. Furthmüller, Computational Materials Science 6, 15 (1999), ISSN 0927-0256.

[27] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).

[28] P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).

[29] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).

[30] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).

[31] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 56401 (2008).

[32] Q. Si and E. Abrahams, Physical Review Letters 101, 076401 (2008).

[33] D.-X. Yao and E. W. Carlson, Phys. Rev. B 78, 052507 (2008).

[34] C. Fang, H. Yao, W.-F. Tsai, J. Hu, and S. A. Kivelson, Phys. Rev. B 77, 224509 (2008).

[35] F. Ma, Z.-Y. Lu, and T. Xiang, Physical Review B 78, 224517 (2008).

[36] H. C. Jiang, F. Krüger, J. E. Moore, D. N. Sheng, J. Zaanen, and Z. Y. Weng, Phys. Rev. B 79, 174409 (2009).

[37] F. Wang, S. A. Kivelson, and D.-H. Lee, Nature Physics (2015).

[38] R. Yu and Q. Si, Phys. Rev. Lett. 115, 116401 (2015).

[39] A. V. Chubukov, R. M. Fernandes, and J. Schmalian, Phys. Rev. B 91, 201105 (2015).

[40] Presentation by Zhong-Yi Lu at Chinese Physics Society Meeting (2015).

[41] Q. Huang, Y. Qiu, W. Bao, M. Green, J. Lynn, Y. Gasparovic, T. Wu, G. Wu, and X. Chen, Physical Review Letters 101, 257003 (2008).

[42] F. Ma, W. Ji, J. Hu, Z.-Y. Lu, and T. Xiang, Phys. Rev. Lett. 102, 177003 (2009).