The interfacial effects on the spin density wave in FeSe/SrTiO$_3$ thin film

Hai-Yuan Cao, 1 Shiyong Tan, 1, 2 Hongjun Xiang, 1 D. L. Feng, 1, 2 and Xin-Gao Gong 1

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

Abstract

Recently, the signs of both superconducting transition temperature ($T_c$) beyond 60 K and spin density wave (SDW) have been observed in FeSe thin film on SrTiO$_3$ (STO) substrate, which suggests a strong interplay between superconductivity and magnetism. With the first-principles calculations, we find that the substrate-induced tensile strain tends to stabilize the SDW state in FeSe thin film by enhancing of the next-nearest-neighbor superexchange antiferromagnetic interaction bridged through Se atoms. On the other hand, we find that when there are oxygen vacancies in the substrate, the significant charge transfer from the substrate to the first FeSe layer would suppress the magnetic order there, and thus the high-temperature superconductivity could occur. In addition, the stability of the SDW is lowered when FeSe is on a defect-free STO substrate due to the redistribution of charges among the Fe 3d-orbitals. Our results provide a comprehensive microscopic explanation for the recent experimental findings, and build a foundation for the further exploration of the superconductivity and magnetism in this novel superconducting interface.

PACS number: 74.70.Xa, 68.35.-p, 74.78.-w, 75.30.Fv
I. INTRODUCTION

Magnetism seems to be always involved in the superconducting mechanism of high-$T_c$ superconductors. Often, the superconductivity occurs when the long-range magnetic order is suppressed somehow, and yet there are underlying spin fluctuations and antiferromagnetic (AFM) interactions that could mediate the Cooper pairing of the electrons \[1\]. Recently, a large superconducting gap in monolayer FeSe thin film grown on STO substrate was observed by both scanning tunneling spectroscopy (STS) \[2\] and angle-resolved photoemission spectroscopy (ARPES) \[3-5\], with the superconducting transition likely at 65 K. This would establish a new $T_c$ record for the iron based superconductors. Intriguingly, it is well known that the bulk FeSe only exhibits a $T_c$ around 8 K \[6, 7\], or 37 K under compressional pressure \[8\]. It is thus remarkable to observe a higher $T_c$ in monolayer FeSe on STO, which is under the tensile strain imposed by the substrate.

For FeSe bulk material and thin film, a collinear $2 \times 1$ SDW order is theoretically predicted to be the ground state, similar to that in the iron pnictides \[9-12\]. Tan et al. have substantiated the presence of spin density wave (SDW) in multilayer FeSe thin films which were grown layer by layer on the STO substrate with molecular beam expitaxy, and they showed that when the tensile strain decreases as the lattice relaxes with increasing thickness, the strength of the SDW decreases as well \[4\]. To our knowledge, no previous theoretical study has been focused on the evolution of the magnetism with the lattice constant in this system. According to the strong interplay between superconductivity and magnetism, the study on how the interfacial effect influences the magnetism in FeSe/STO thin film should be helpful for the understanding of the superconductivity there.

The SDW would have been the most prominent in monolayer FeSe next to the STO due to the most pronounced strain from the substrate, had it not been suppressed by the charge transferred from the oxygen-vacant substrate, as suggested by both the experiment \[4\] and theory \[13\]. However, previous theoretical studies were not conclusive. Liu et al. analyzed the orbital-resolved partial density of states (PDOS) from the density functional theory (DFT) calculations, and did not find substantial charge transfer between FeSe and the STO substrate \[11\]. On the other hand, Zheng et al. predicted a considerable charge transfer from surface O atoms of STO substrate to Fe atoms of FeSe monolayer \[14\]. Another recent theoretical paper excluded the Se vacancy in FeSe as the source of electron doping.
for superconductivity \[15\], which further indicates that the oxygen vacancy on the STO substrate should play indispensable role in the Fe-HTS. For these reasons, it is necessary to further investigate how the STO substrate and the oxygen vacancies there influence the magnetic order in the monolayer FeSe.

In this paper, based on DFT calculations we reveal how the strain, the interfacial coupling and the oxygen-vacant STO substrate affect the magnetism in the FeSe thin film. We find the strain could enhance the Fe-Se-Fe superexchange by increasing the Fe-Se-Fe bond angle. With the increasing superexchange interaction, the local AFM exchange interaction would be enhanced. The interaction between the STO substrate and the monolayer FeSe would reduce the charge density in the spin-majority $d_{xz}/d_{yz}$-orbital states of the Fe atoms, which suppresses the effect of superexchange and reduces the stability of SDW in the monolayer FeSe. If the oxygen vacancies exist on the surface of STO substrate, a certain amount of charge would be transferred from the substrate to the spin-minority $d_{xz}/d_{yz}$-orbital states of the Fe atoms in the monolayer FeSe, which would suppress the SDW and allow the superconductivity to occur. Meanwhile, the original symmetry of spin configuration in monolayer FeSe would also be disturbed due to the oxygen vacancies on the substrate. All of our results are in close agreement with the recent experiment \[4\]. It thus provides a detailed microscopic understanding of the interfacial effects in this intriguing system. More importantly, our results suggest that the high $T_c$ in the monolayer FeSe is closely related to the large underlying superexchange interactions caused by its expanded lattice, which again highlight the pivotal role of magnetism in the high temperature superconductivity of iron-based superconductors.

II. METHODS

To study how the substrate affects the monolayer FeSe grown on STO (001) surface, we carry out the spin-polarized first-principles calculations using the project augmented wave pseudopotential \[16, 17\] implemented in the VASP code \[18, 19\]. We employ the generalized gradient approximation (GGA) of Perdew-Burke-Ernzerhof for the exchange-correlation-potentials \[20\]. The kinetic energy cutoff of the plane-wave basis is chosen to be 400 eV. The force on all relaxed atoms after the optimization is smaller than 0.01 eV/Å. A $6 \times 6 \times 1$ k-point mesh \[21\] for the Brillouin zone sampling and a width of 0.1 eV for the Guassian
Figure 1: (a) Top view of atomic structures of $2 \times 2$ supercell monolayer FeSe and spin patterns of Fe in the AFM state and the SDW state. (b) Side view of atomic structure of monolayer FeSe on TiO$_2$ terminated STO (001) surface.

smearing are adopted. In all the calculations we employ a local Coulomb repulsion GGA+U approach for Ti 3d electrons with $U_{Ti} = 2$ eV \cite{22,24}. The electric field induced by the asymmetric relaxed STO is compensated by a dipole correction \cite{25}. We also use the $J_1 - J_2$ Heisenberg model to describe the magnetic interactions, while the exchange parameters are fitted to the total energy of the first principle calculations.

As shown in Figure 1(a), we use the $2 \times 2 \times 1$ supercell to describe the magnetic order of the monolayer and bulk FeSe. To model the interface with monolayer FeSe on STO, we use a seven-layer STO (001) slab with the $2 \times 2$ monolayer FeSe supercell on the top side plus a vacuum layer about 10 Å as shown in Figure 1(b). According to previous results \cite{11}, the most stable interfacial configuration is the monolayer FeSe on the TiO$_2$ terminated STO surface. In the present calculation, we fix the lattice constant $a$ to be 3.905 Å, the lattice constant of the bulk STO \cite{26}. In the structural optimization, the top two layers of STO substrate and all FeSe atoms are allowed to relax, while the atoms in bottom layers of STO
substrate are fixed at their bulk positions. To study the effect of the oxygen vacancies on the STO substrate, we choose one, two, four vacancies out of eight oxygen atoms on the $2 \times 2$ supercell of TiO$_2$ terminated surface, corresponding to 12.5%, 25% and 50% vacancy concentration, respectively.

III. RESULTS AND DISCUSSION

For both free-standing FeSe and epitaxial monolayer FeSe on STO substrate, we have calculated four magnetic states, including the nonmagnetic state (NM state), the ferromagnetic state, the checkboard AFM state (AFM state) and the collinear AFM state (SDW state). The spin texture of the AFM state and the SDW state in FeSe are shown in Figure 1(a) [10, 11], respectively. By calculating and comparing the energy difference between these four states, we find that the ground state is the SDW state with a large magnetic moment of $\sim 2.4 \mu_B$ on each Fe atom for both free-standing FeSe and epitaxial FeSe on STO. The ferromagnetic state has very high energy, $\sim 0.2$ eV per Fe atom higher than the NM state, so we ignore the ferromagnetic state in the following discussions. This has also been proved in the previous theoretical studies [11, 12].

Firstly, we calculate the Fermi surface of bulk FeSe, the obtained result shown in Figure 2(a) is in close agreement with previous calculations [9] which is composed of several hole pockets around the $\Gamma$ point and two electron pockets around the M point. For the Fermi surface of the monolayer FeSe on STO substrate with lattice constant 3.905 Å, as showing in Figure 2(b), we shift the Fermi level according to the 0.12 e$^{-}$ per Fe atom as suggested by the experiment [4]. It is in good agreement with that observed in the ARPES experiments [3–5] which is composed of two nearly degenerate electron pockets around the M point and the hole pockets around the $\Gamma$ point are absent. These results confirm that our method can well reproduce the electronic structures for both bulk FeSe and monolayer FeSe on STO substrate observed in experiments.

A. How the Tensile Strain Affects the SDW in FeSe

We firstly study how the external strain could affect the stability of the SDW state. We use the energy difference between the SDW state and other two states, the AFM state and
Figure 2: The calculated Fermi surface of (a) bulk FeSe and (b) monolayer FeSe on STO substrate. The center is M point and the corner is Γ point. The electron pockets are denoted as red while the hole pockets are denoted as blue. The hole pockets are absent in the Fermi surface of monolayer FeSe on STO substrate [3–5].

the NM state, to assess the stability of the SDW state [10, 11]. In Figure 3, we can see that the energy difference relative to the SDW state increases with the expanding of lattice constant, which indicates that the tensile strain can enhance the stability of the SDW state in both bulk and monolayer FeSe. Moreover, the energy difference in the monolayer and bulk FeSe with the same lattice constant is almost the same, therefore the relative stability of the SDW is insensitive to the thickness of the FeSe, but sensitive to the lattice constant.

To investigate why the tensile strain can affect the stability of SDW, we would model the magnetic interaction in FeSe with different lattice constant. We assume that the interaction between the Fe spins dominates the energy difference between different magnetic orders. We could map the magnetic interaction to the following Heisenberg model which is described by the nearest-neighbor and next-nearest-neighbor coupling parameters $J_1$ and $J_2$ [12]:

$$H = J_1 \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j + J_2 \sum_{\langle\langle ij \rangle\rangle} \vec{S}_i \cdot \vec{S}_j$$  \hspace{1cm} (1)

whereas $\langle ij \rangle$, $\langle\langle ij \rangle\rangle$ denote the summation over the nearest-neighbors and the next-nearest-neighbors, respectively. Using the method proposed by previous theoretical work [27], we can determine the value of $J_1$ and $J_2$. In bulk FeSe, we find $J_1 = 74$ meV/$S^2$ and $J_2 = 43$.
Figure 3: The calculated energy difference (relative to the SDW state) of the AFM state (red circle) and the NM state (black circle) versus the lattice constant of FeSe, (a) for bulk FeSe and (b) for monolayer FeSe, respectively. In both the bulk and monolayer FeSe, the SDW state tends to be energetically more stable with increasing lattice constant.

$\text{meV}/S^2$, in close agreement with the previous results$^{[12]}$.

As shown in Table 1, $J_1$ increases only slightly with increasing lattice constant, but $J_2$ increases about 40% when the lattice constant increases just a few percent. More clearly, $J_2/J_1$ increases monotonously with lattice constant expanding, suggesting that the SDW state is getting more and more stable. According to the frustrated Heisenberg model, the magnetic exchange energy in the unit cell of FeSe with four Fe atoms is $-2J_1 + 2J_2$ for the AFM state and $-2J_2$ for the SDW state (assuming $S = 1$). It is known that the frustration between $J_1$ and $J_2$ destructs the stability of the AFM state and induces the SDW state when $J_2 > J_1/2$ for a square lattice$^{[12]}$.

To explore the origin of the changing of $J_1$ and $J_2$ with the lattice constant, we have
Table I: Structural parameters, calculated nearest-neighbor and next-nearest-neighbor coupling parameters of monolayer FeSe. The definition of Fe-Se-Fe angle is shown in Figure 4(b). Here we assume S = 1 for Fe atoms.

calculated the charge distribution around Fe and Se atoms. As shown in Figure 4(a) and 4(b), there is almost no charge density between two nearest-neighbor Fe atoms but the bonds are formed between Fe and Se atoms. Similar to the previous calculation of LaFeAsO, \( J_2 \) here is dominated by the superexchange bridged by Se atoms [27, 28]. According to the mechanism of superexchange and the band structure of FeSe, we find that the superexchange interaction is from the half-filled Fe \( d_{xz} / d_{yz} \) orbitals bridged by the Se p-orbitals, and Goodenough-Kanamori rules state that this is AFM coupling [29]. With the expanding of the lattice constant, the out of plane height of Se atoms tends to decrease and the Fe-Se-Fe angle (defined in Figure 4(b)) tends to increase as shown in Table I. The increase of the Fe-Se-Fe angle increases the overlapping of the Fe \( d_{xz} / d_{yz} \) orbitals and Se p-orbitals, while the Fe-Se-Fe superexchange interaction would be maximized if the Fe-Se-Fe angle is 180° according to Goodenough-Kanamori rules [29]. From the above discussions, we can conclude that the tensile strain enhances the superexchange interaction and then enlarges the next-nearest-neighbor coupling \( J_2 \), which directly stabilize the SDW state in monolayer and bulk FeSe.

The recent experiment by Tan et. al. used the band separation at M point to characterize the strength of the SDW in FeSe thin films. The observed band separation increases with expanding of the lattice constant, which is essentially caused by the different band dispersions along the AFM and FM directions in the SDW state [4]. Here we observe a linear relation between our calculated relative stability of the SDW and the experimental band separation as shown in Figure 5. It indicates that our calculation results of the energy difference is closely correlated to the experimental observation, and it further implies that the band separation is a relevant energy scale to characterize the strength of the SDW in FeSe thin films. This relation with the lattice constant is directly ascribed to the enhancement of the

| Lattice Constant (Å) | \( J_1 \) (meV) | \( J_2 \) (meV) | \( J_2/J_1 \) | Fe-Se-Fe Angle |
|---------------------|---------|---------|----------|----------------|
| 3.765               | 74      | 43      | 0.58     | 105°           |
| 3.905               | 78      | 53      | 0.68     | 109°           |
| 4.045               | 82      | 60      | 0.73     | 113.5°         |
Figure 4: (a) The top view and the side view of the charge distribution in monolayer FeSe. In the top view, there is almost no bond between Fe atoms. In the side view, we can clearly observe that there exists a bond (black line) between Se and Fe. (b) The top view of the nearest as well as the next-nearest magnetic exchange interacting $J_1$ and $J_2$ (red arrow) and the side view of the defined Fe-Se-Fe angle between two next-nearest Fe atoms (blue line).

next-nearest superexchange interaction due to the increased Fe-Se-Fe angle with the lattice expansion. Recent theoretical work predicts that a strong next-nearest AFM interaction could lead to a high temperature superconductor [1]. According to this prediction, our result shows that strain enhanced superexchange interaction should play important role in the over 60 K high temperature superconductivity observed in FeSe-STO.
Figure 5: The experimental band separations for FeSe films at various lattice constants versus the calculated energy difference between the AFM state and the SDW state. The dash line is a linear fitting. The error bar for the experimental band separations is $\pm 2$ meV.

B. How The Interfacial Coupling Affects the SDW in FeSe

For the monolayer FeSe on a defect-free STO substrate, we did not find apparent charge transfer at the interface from Bader analysis, and we did not yet find any obvious structural distortion occurred in monolayer FeSe. However, after detailed calculations of the charge difference between the epitaxial and free-standing monolayer FeSe, we find that the interfacial coupling would induce the redistribution of the charge density in epitaxial monolayer FeSe, which would decrease the charge density in the spin-majority $d_{xz}/d_{yz}$-orbital states of Fe atoms as shown in the inset of Figure 6. If we gradually increase the interface distance from the equilibrium position 3.1 Å to 5.6 Å, the energy difference between the SDW state and the AFM state rises from 37 meV/f.u. to 52 meV/f.u. as shown in Figure 6. In the meantime, the charge redistribution occurring in monolayer FeSe
Figure 6: The calculated energy difference between the SDW state and the AFM state as a function of the interface distance. With the decrease of the interface distance, the SDW state becomes less stable relative to the AFM state. The blue arrow shows the equilibrium distance as 3.1 Å. Inset shows the charge redistribution on Fe atoms in epitaxial FeSe at the equilibrium distance (left side). The blue part represents the charge density lost while the green part represents the charge density gained. The inset also shows there is almost no charge redistribution on Fe atom if the interface distance is 5.6 Å (right side).

becomes smaller and smaller, which suggests that the charge redistribution is attributed to the interfacial interaction. The decrease of the charge density in the spin-majority $d_{xz}/d_{yz}$-orbital states with decreasing interface distance would reduce the charge overlapping between the Fe $d_{xz}/d_{yz}$-orbitals and the Se p-orbitals, and then lower the superexchange interaction. As we have discussed in Sec. III A, a smaller superexchange interaction would bring about the weaker next-nearest-neighbor coupling $J_2$, and degrade the stability of the SDW in FeSe. So the interfacial interaction between monolayer FeSe and STO substrate could decrease the stability of the SDW.

We find that the change of the $d_{xz}/d_{yz}$-orbital states could be induced by the dipolar field along the direction perpendicular to the interface. The plane-averaged charge density difference between the monolayer FeSe-STO, free-standing monolayer FeSe and STO substrate are shown in Figure 7(a). Although there is no charge transfer between the monolayer FeSe
Figure 7: The plane-averaged charge density difference (black line) and the local potential (red line) for (a) the monolayer FeSe/defect-free STO interface and (b) the monolayer FeSe/oxygen-vacant STO interface. The position of the surface TiO$_2$ layer of STO substrate and FeSe atomic layers are denoted by the dotted vertical lines. Significant charge transferred from the top TiO$_2$ layer of the oxygen-vacant STO substrate to the Fe atomic layer can be observed here.

and the STO substrate, the charge redistribution near the interface can be observed clearly. It forms a charge dipole at the interfacial region due to the interfacial coupling, which has been previously explained by the metal-insulator band alignment [31, 32]. The interfacial dipole formed at the monolayer FeSe-STO interface could induce the electric field along the direction perpendicular to the interface which induces the change of the d-orbital order of Fe atom.
C. How The Oxygen Vacancy Affects the SDW in FeSe

Oxygen vacancy on the STO surface is experimentally unavoidable due to the heat treatment in preparing the STO substrate \[2\]. In order to understand how the oxygen vacancy affects the property of monolayer FeSe, we have simulated monolayer FeSe on STO substrate with different concentration of oxygen vacancies.

Firstly, we calculate the energy difference between the NM state, the AFM state and the SDW state, as well as the charge density distribution in monolayer FeSe on the STO substrate with different concentration of oxygen vacancies. The results are shown in Fig. 8. We find that the oxygen vacancy can induce charge transfer from the STO substrate to monolayer FeSe, the higher concentration of the oxygen vacancy, the more the charge is transferred (Fig. 8(b)). As more and more charge transferred to the monolayer FeSe, the stability of the SDW state relative to the AFM state and the NM state decreases monotonously (Fig. 8(a)). We also calculate the plane-averaged charge difference obtained by subtracting the valence charge densities of the free-standing FeSe layer and isolated STO substrate from the monolayer FeSe on STO. The results presented in Fig. 7(b) clearly show the monolayer FeSe on STO substrate with oxygen vacancies inducing significant charge transferred to Fe atoms while almost no charge transfer existing when it is on the defect-free STO substrate as shown in Fig. 7(a).

We find that the charge is transferred from the substrate to the spin-minority \(d_{xz}/d_{yz}\)-orbital states of the Fe atom in monolayer FeSe, so it would decrease the superexchange interaction and reduce the stability of the SDW state. From Table II we find \(J_2\) decreases from 48 meV to 35 meV and \(J_2/J_1\) decreases from 0.63 to 0.59 if 12.5% oxygen vacancy exists on the surface of the STO substrate. Based on the PDOS of Fe atom on STO substrate with 12.5% oxygen vacancy, we do find that about \(\sim 0.1\) charge transferred to the spin-minority \(d_{xz}/d_{yz}\)-orbital states. Since the superexchange between two next-nearest ideally half-field orbitals is the strongest, the increasing charge density in the spin-minority \(d_{xz}/d_{yz}\)-orbital states would decline the AFM superexchange coupling, and it would decrease the stability of the SDW state. Moreover, we find that the oxygen vacancy can magnetically polarize the nearby Ti atoms, and the magnetism of Ti atoms could also decrease the stability of the SDW state. For the concentration of 12.5% oxygen vacancies, the nearby Ti atom would possess a magnetic moment of 0.88 \(\mu_B\) [23, 33]. The ferromagnetism from the Ti atoms
Figure 8: (a) The energy difference between the AFM state (blue circle), the NM state (red circle) and the SDW state with different concentration of oxygen vacancy. (b) The charge transferred to \(2 \times 2\) supercell of monolayer FeSe with the AFM state (blue square) and the SDW state (red square) calculated by Bader analysis. The charge of monolayer FeSe on defect-free STO substrate is set to be the reference. Both the oxygen vacancy and the charge transferred from STO are related to decrease the relative stability of the SDW state.

would break the symmetry of spin in monolayer FeSe, as shown in Figure 9. the PDOS of spin-minority electrons of Fe atom would increase a lot near the Fermi level.

IV. SUMMARY

We have studied the interfacial effect on the stability of the SDW in monolayer FeSe using the GGA+U method. We find that tensile strain can increase the superexchange interaction between the next-nearest Fe atoms by increasing the Fe-Se-Fe bond angle, thus enhance the
Table II: Calculated nearest-neighbor and next-nearest-neighbor coupling parameters of the free-standing monolayer FeSe, monolayer FeSe on defect-free STO and monolayer FeSe on 12.5% oxygen-vacant STO. Here we assume $S = 1$ for Fe atoms.

|                             | $J_1$ (meV) | $J_2$ (meV) | $J_2/J_1$ |
|-----------------------------|-------------|-------------|-----------|
| Free-standing Monolayer FeSe| 82          | 60          | 0.73      |
| Monolayer FeSe on defect-free STO | 76          | 48          | 0.63      |
| Monolayer FeSe on 12.5% oxygen-vacant STO | 59          | 35          | 0.59      |

Figure 9: The partial density of states (PDOS) of $d_{xz}$-orbital for two-type Fe atoms in the unit cell of the SDW state with the up spin-majority and down spin-majority electrons, respectively. The PDOS for Fe atoms in expitaxial monolayer FeSe on (a) the defect-free STO substrate and (b) the 12.5% oxygen-vacant STO substrate. The existance of oxygen vacancies on the surface of STO substrate disturb the symmetry of spin of two-type Fe atoms and increases the density of states near the Fermi energy significantly for spin-minority electrons of Fe atoms.

local AFM coupling and the stability of the SDW. However, we also find that the interfacial coupling between FeSe and STO substrate can change the charge distribution in the 3d orbitals of Fe atoms, leading to less charge density in the spin-majority $d_{xz}/d_{yz}$-orbitals. It decreases the superexchange coupling between the next nearest Fe atoms and suppress the stability of the SDW. In agreement with previous calculation[13], we also observed a
significant charge transferred from the oxygen-vacant substrate to monolayer FeSe. Furthermore, we find that such charge will be transferred to the spin-minority $d_{xz}/d_{yz}$-orbitals of Fe atoms, and the almost fully occupied $d_{xz}/d_{yz}$-orbitals will decline AFM superexchange interaction, thus will also suppress the stability of the SDW.

In summary, the substrate induced tensile strain can enhance the next-nearest antiferromagnetic interaction, while the interfacial coupling and charge transfer will destroy the long range magnetic order. We provide a systematical microscopic description for the interfacial effects on the magnetism and further suggest a strong correlation between the magnetism and the possible high $T_c$ in monolayer FeSe on STO substrate. Our results build the foundation for understanding the prominent role of magnetism in this new kind of iron-based superconductor.

**Acknowledgments**

HY Cao thanks Shiyou Chen for helpful 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.
[1] J. Hu and H. Ding, Sci. Rep. 2, 381 (2012).

[2] Q.-Y. Wang, Z. Li, W.-H. Zhang, Z.-C. Zhang, J.-S. Zhang, W. Li, H. Ding, Y.-B. Ou, P. Deng, K. Chang, et al., Chinese. Phys. Lett. 29, 037402 (2012).

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

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

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

[6] 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., Proc. Natl. Acad. Sci. U.S.A. 105, 14262 (2008).

[7] 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, 20503 (2011).

[8] S. Medvedev, T. M. McQueen, I. A. Troyan, T. Palasyuk, M. I. Eremets, R. J. Cava, S. Naghavi, F. Casper, V. Ksenofontov, G. Wortmann, et al., Nat. Mater. 8, 630 (2009).

[9] A. Subedi, L. Zhang, D. J. Singh, and M. H. Du, Phys. Rev. B 78, 134514 (2008).

[10] T. Bazhirov and M. L. Cohen, J. Phys.: Condens. Matter. 25, 105506 (2013).

[11] K. Liu, Z.-Y. Lu, and T. Xiang, Phys. Rev. B 85, 235123 (2012).

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

[13] J. Bang, Z. Li, Y. Y. Sun, A. Samanta, Y. Y. Zhang, W. Zhang, L. Wang, X. Chen, X. Ma, Q.-K. Xue, et al., Phys. Rev. B 87, 220503 (2013).

[14] F. Zheng, Z. Wang, W. Kang, and P. Zhang, Sci. Rep. 3, 2213 (2013).

[15] T. Berlijn, H. Cheng, P. Hirschfeld, and W. Ku, arXiv:1307.0140 (2013).

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

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

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

[19] G. Kresse and J. Furthmüller, Comp. Mater. Sci. 6, 15 (1996).

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

[21] H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
[22] N. Pavlenko, T. Kopp, E. Y. Tsymbal, G. a. Sawatzky, and J. Mannhart, Phys. Rev. B 85, 020407 (2012).

[23] N. Pavlenko, T. Kopp, E. Y. Tsymbal, J. Mannhart, and G. A. Sawatzky, Phys. Rev. B 86, 64431 (2012).

[24] M. Breitschaft, V. Tinkl, N. Pavlenko, S. Paetel, C. Richter, J. R. Kirtley, Y. C. Liao, G. Hammerl, V. Eyert, T. Kopp, et al., Phys. Rev. B 81, 153414 (2010).

[25] J. Neugebauer and M. Scheffler, Phys. Rev. B 46, 16067 (1992).

[26] F. El-Mellouhi, E. N. Brothers, M. J. Lucero, and G. E. Scuseria, Phys. Rev. B 84, 115122 (2011).

[27] F. Ma and Z.-Y. Lu, Phys. Rev. B 78, 33111 (2008).

[28] F. Ma, Z.-Y. Lu, and T. Xiang, Phys. Rev. B 78, 224517 (2008).

[29] J. B. Goodenough, Phys. Rev. 100, 564 (1955).

[30] W. Tang, E. Sanville, and G. Henkelman, J. Phys.: Condens. Matter 21, 084204 (2009).

[31] J. Tersoff, Phys. Rev. B 30, 4874 (1984).

[32] J. Tersoff, Phys. Rev. B 32, 6968 (1985).

[33] J. Park, B.-G. Cho, K. D. Kim, J. Koo, H. Jang, K.-T. Ko, J.-H. Park, K.-B. Lee, J.-Y. Kim, D. R. Lee, et al., Phys. Rev. Lett. 110, 17401 (2013).