Tetragonal-phase SnOFeSe: A possible parent compound of FeSe-based superconductor

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Recent experiments have reported that inserting metal atoms or small molecules in between the FeSe layers of β-FeSe can significantly enhance the superconducting transition temperature. Here, based on first-principles electronic structure calculations, we propose a stable compound SnOFeSe by alternatively stacking the SnO and β-FeSe layers. The predicted SnOFeSe has the same tetragonal structure as the well-known FeAs-based compound LaOFeAs, meanwhile their electronic structures in the nonmagnetic state are quite similar. The magnetic ground state of SnOFeSe is predicted to be the dimer antiferromagnetic (AFM) state, which is energetically only 2.77 (2.15) meV/Fe lower than the trimer (dimer-trimer-dimer-trimer) AFM state, indicating that strong magnetic fluctuations might be induced via slight modulation. Interestingly, SnOFeSe is at the verge of metal-insulator transition in these low-energy magnetic states, hence bridging the metallic parent compounds of iron-based superconductors and the insulating ones of cuprate superconductors. With the reduced dimensionality, monolayer SnOFeSe also shows great similarities in the electronic and magnetic properties to its bulk phase. Given that SnOFeSe is adjacent to magnetic frustration and resembles LaOFeAs in both crystal and electronic structures, we suggest that SnOFeSe is a possible superconductor parent compound, which may provide a promising platform to study the interplay between magnetism and unconventional superconductivity in FeSe-derived materials.

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I. INTRODUCTION

Iron-based superconductors have inspired intensive interests both experimentally and theoretically since their discovery in 20081–7. With the simplest crystal structure but the mysterious magnetic property among the iron-based superconductors ever found1–7, the anti-PbO-type β-FeSe has become a prototypical system to study the physical properties of iron-based superconductors. The superconducting transition temperature \( T_c \) of bulk β-FeSe is about 8 K at ambient pressure2, and numerous works, therefore, have been devoted to improve the \( T_c \) via high pressure8,9, chemical substitution10, gate voltage11, or epitaxial film growth12. In addition, intercalation of metal atoms or molecules into β-FeSe is another effective approach to enhance the superconductivity. For instance, metal-intercalated FeSe compounds, \( A_xFe_{2-y}Se_2 \) \((A = Li, Na, K, Rb, Cs, Ca, Sr, Ba, Yb, Eu, Tl/K, or Tl/Rb)\), have shown the superconducting \( T_c \)'s around 30 K13–21. With the intercalation of \( Li_x(NH_2)_y(NH_3)_1\)22, \((Li/Na)_x(NH_3)_2\)23, \(Li_x(C_5H_5N)_y\)24, or \(Li_{0.5}Fe_{0.2}OH\)25–27 layers into β-FeSe, the \( T_c \)'s can be significantly lifted above 40 K. The enhanced superconductivities in the FeSe-based compounds are believed to be intimately correlated with the modulation of electronic and magnetic properties of the FeSe layers.

We notice that the PbO-type SnO (space group: \(P4/nmm\)) has the same tetragonal structure as the anti-PbO-type β-FeSe28–30 [Fig. 1(a)], although their metallic and nonmetallic elements are interchanged in atomic positions30. The experimental in-plane lattice constant of SnO \((a = 3.803\ \text{Å})\)28 matches quite well with that of β-FeSe \((a = 3.765\ \text{Å})\)2. It is thus very likely to form the 1111-type FeSe-based compound SnOFeSe by alternatively stacking the SnO and FeSe layers [Fig. 1(d)], which is structurally identical to the FeAs-based compound LaOFeAs4. Since SnO is reported to be a semiconductor with an indirect band gap of 0.7 eV31,32, the SnO layers can serve as insulating spacers in SnOFeSe and may make the FeSe layers more two-dimensional (2D) in electronic behavior. In addition, SnOFeSe has the equal valence electrons as LaOFeAs, thus it may resemble the latter in electronic properties and might also become superconducting via appropriate modulation1,5,33–37. Based on these preliminary inferences, the physical properties of the 1111-type FeSe-based compound SnOFeSe deserve further in-depth theoretical investigation.

By using first-principles electronic structure calculations, here we propose a stable intercalation compound SnOFeSe formed by inserting SnO layers into β-FeSe, which is isosstructural to the well-known LaOFeAs. We find that the electronic structure of SnOFeSe in the nonmagnetic state is quite similar to that of LaOFeAs. And we determine the magnetic ground state of SnOFeSe to be a dimer antiferromagnetic state, in which the system is at the verge of metal-insulator transition. The monolayer SnOFeSe in the ultrathin limit has also been investigated in theory, which might be fabricated experimentally via epitaxial growth or mechanical exfoliation. Our calculation results suggest that SnOFeSe could be an ideal parent compound for studying the relationship between magnetism and unconventional superconductivity in FeSe-based superconductors.
II. COMPUTATIONAL DETAILS

To study the crystal structure, electronic structure, and magnetic properties of SnOFeSe, fully spin-polarized density functional theory (DFT) calculations were performed with the projector augmented wave (PAW) method, as implemented in the Vienna Ab initio Simulation Package (VASP). The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) type was adopted for the exchange-correlation functional. The kinetic energy cutoff of the plane-wave basis was set to 520 eV. The DFT-D2 method was used to account for the van der Waals (vdW) interaction in the layered materials. The 16 × 16 × 8 and 4 × 12 × 8 Monkhorst-Pack k-point meshes were adopted to sample the Brillouin zones (BZs) of the unit cell and the supercell, respectively. The Fermi surface was broadened by the Gaussian smearing method with a width of 0.05 eV. The internal atomic positions and the cell parameters were fully optimized until the residual forces on all atoms were smaller than 0.01 eV/Å. The energy convergence criterion was set to 10^{-6} eV. For monolayer SnOFeSe, a vacuum layer larger than 20 Å was utilized to eliminate the interaction between image slabs along the (001) direction. The interlayer binding energy $E_b$ of SnOFeSe was calculated according to the formula $E_b = E_{SnOFeSe} - E_{FeSe} - E_{SnO}$, where $E_{SnOFeSe}$ is the energy of SnOFeSe, and $E_{FeSe}$ ($E_{SnO}$) is the energy of the FeSe (SnO) after removing the SnO (FeSe) layers from SnOFeSe. To check the dynamical stability, phonon spectra were calculated within the framework of density functional perturbation theory (DFPT) as implemented in the Quantum ESPRESSO (QE) package. For the thermal stability, ab initio molecular dynamics simulations were carried out with the VASP package. An NVT ensemble with a temperature $T$ of 300 K controlled by the Nosé-Hoover thermostat was simulated. The total simulation time was set to 9 ps with a time step of 3 fs.

III. RESULTS AND ANALYSIS

The crystal structures of the tetragonal-phase SnO and β-FeSe (space group: P4/nmm) are shown in Fig. 1(a). The experimental in-plane lattice constant of SnO is $a = 3.803 \text{ Å}$, which is only 1.0% larger than that of β-FeSe ($a = 3.765 \text{ Å}$). The rather small lattice mismatch between SnO and β-FeSe indicates that they might form the 1111-type FeSe-based compound SnOFeSe by alternatively intercalating the SnO and FeSe layers. Before finding out the most stable intercalation structure, we considered six nonequivalent stacking sites for the SnO layer on the FeSe plane [Fig. 1(b)], among which there are three top sites (Fe1 top, Fe2 top, and Se1 top) lab-
We next examine the structural stabilities of SnOFeSe. The calculated phonon dispersion of SnOFeSe in the NM state along the high-symmetry paths of the BZ [Fig. 1(c)] is shown in Fig. 2(a), in which no imaginary phonon mode is observed, indicating the dynamical stability. Furthermore, we carried out \textit{ab initio} molecular dynamics simulations for the NM state of SnOFeSe, and obtained the time evolution of the free energy at 300 K as shown in Fig. S2(a) of the SI\textsuperscript{48}. From a snapshot at 9 ps [Figs. S2(b) and S2(c) in the SI\textsuperscript{48}], we can see that the structure remains intact without the bond breaking, suggesting that SnOFeSe is also thermodynamically stable at room temperature. The interlayer binding energy of SnOFeSe is calculated to be 112 meV/atom in the NM state, which is approximately two to three times that of graphite\textsuperscript{49–52}. Such small interlayer binding energy indicates that SnOFeSe has a relatively weak interlayer interaction. To figure out the charge transfer between the SnO and FeSe layers in SnOFeSe, we then calculated the one-dimensional (1D) and three-dimensional (3D) differential charge densities as plotted in Figs. 2(b) and 2(c), respectively. It can be seen clearly that there are some electrons accumulated in the interlayer region. These calculation results show that SnOFeSe is a dynamically and thermodynamically stable material that is very likely to be synthesized experimentally.

To investigate the electronic structure of SnOFeSe in the NM state, we calculated the band structure, the partial density of states (PDOS), as well as the Fermi surface (FS). From the band structure shown in Fig. 3(a), we can see that there are five bands crossing the Fermi level, indicating a metallic behavior of SnOFeSe. The overall band characteristics look very similar to those of LaOFeAs\textsuperscript{53,54} [Fig. S3(a) in the SI\textsuperscript{48}], especially for the bands near the Fermi level. The calculated PDOS of SnOFeSe in Fig. 3(b) demonstrates that the Fe 3d orbitals contribute most in the energy range from -2 to 2 eV around the Fermi level, which is also similar to that of LaOFeAs [Fig. S3(b) in the SI\textsuperscript{48}]. Figure 3(c) shows five FS sheets of SnOFeSe in the NM state, among which there are three hole-type pockets around the BZ center (Γ point) and two electron-type pockets around the BZ corner (M point). The perfect cylindrical shape of these FS sheets indicates the prominent 2D feature of SnOFeSe. Based on the information of FS, we then calculated the electron susceptibility \( \chi(q) \). The real part \( \chi'(q) \) shows a broad peak around the M point [Fig. 4(a)], suggesting the electronic instability of the NM state. Meanwhile, the imaginary part \( \chi''(q) \) [Fig. 4(b)] also has considerable intensity around the M point, which reflects the FS nesting that can be discerned intuitively by shifting the Fermi pockets from Γ to M in Fig. 3(c). These results indicate that besides the crystal structure [Fig. 1(d)], the electronic properties of SnOFeSe in the NM state also resemble those of LaOFeAs\textsuperscript{55}.

The existence of strong FS nesting in Fe-based superconductors may induce magnetic instabilities\textsuperscript{56–60}, thus we have further studied the magnetic properties of SnOFeSe. In addition to the aforementioned NM
TABLE I: Relative energies $\Delta E$ (in unit of meV/Fe) of the FM, checkerboard AFM Néel, stripe AFM, dimer AFM, trimer AFM, and dimer-trimer-dimer-trimer (di-tri-di-tri) AFM states with respect to the NM state for bulk SnOFeSe. The corresponding average local moments $M$ (in unit of $\mu_B$) on Fe atoms are also listed.

| State               | NM $\Delta E$ | FM $\Delta E$ | Néel $\Delta E$ | stripe $\Delta E$ | dimer $\Delta E$ | trimer $\Delta E$ | tetramer $\Delta E$ | di-tri-di-tri $\Delta E$ |
|---------------------|---------------|----------------|------------------|-------------------|------------------|-------------------|----------------------|------------------------|
| $\Delta E$          | 0.00          | 168.69         | -33.15           | -67.01            | -86.34           | -83.57            | -77.31               | -84.19                 |
| $M$ (in unit of $\mu_B$) | -2.34 | 1.75 | 1.94 | 2.04 | 2.02 | 1.99 | 2.01 |

We next investigated the electronic structures of SnOFeSe in the above low-energy magnetic states. Figures 6(a) and 6(b) show the total and partial DOSs of SnOFeSe in the dimer and trimer AFM states, respectively. It can be seen that in these two AFM states, the Fe 3$d$ orbitals have the main contributions near the Fermi level. With a close inspection of the total DOS in the lowest-energy dimer AFM state, SnOFeSe shows a bad-metal character with very low density of states at the Fermi level. In comparison, there is a rather small energy gap ($\sim$0.07 eV) for SnOFeSe in the trimer AFM state. These results demonstrate that SnOFeSe is at the verge of metal-insulator transition when the magnetism is taken into account.
TABLE II: Relative energies $\Delta E$ (in unit of meV/Fe) of the magnetic states (AFM Néel, stripe AFM, dimer AFM, trimer AFM, tetramer AFM, and di-tri-di-tri AFM) with respect to the NM state for monolayer SnOFeSe. The corresponding average local moments $\overline{M}$ (in units of $\mu_B$) on Fe atoms are also listed.

| State       | NM          | Néel      | stripe  | dimer      | trimer    | tetramer  | di-tri-di-tri |
|-------------|-------------|-----------|---------|------------|-----------|-----------|---------------|
| $\Delta E$  | 0.00        | -41.12    | -73.39  | -90.04     | -88.23    | -83.42    | -89.30        |
| $\overline{M}$ | -          | 1.77      | 2.01    | 2.07       | 2.08      | 2.04      | 2.05          |

In addition to the bulk phase, the monolayer form is also worth investigation for the layered materials. Likewise, we studied the dynamical stability as well as the electronic and magnetic properties of monolayer SnOFeSe. The calculated phonon dispersion of monolayer SnOFeSe in the NM state along the high-symmetry paths of the BZ is shown in Fig. S4 of the SI. A rather tiny imaginary frequency in the acoustic branch appears near the $\Gamma$ point, which is common for the calculated phonon spectra of 2D materials. It is not a sign of structure instability, but may originate from the difficulties in accurately calculating the rapid decaying interatomic forces. The band structure and PDOS of monolayer SnOFeSe in the NM state are shown in Figs. 7(a) and 7(b), respectively. The electronic band dispersion of SnOFeSe along the $\Gamma$-X-M-$\Gamma$ path [Fig. 7(a)] is similar to that of bulk phase [Fig. 3(a)], demonstrating the metallic behavior. Meanwhile, the DOS near the Fermi level is mainly contributed by Fe 3d orbitals [Fig. 7(b)]. We have further studied several typical spin configurations (Fig. 5) for monolayer SnOFeSe. After full relaxation, the FM state converges to the NM state, suggesting that the former is unstable. The calculated relative energies of the AFM magnetic states with respect to the NM state for monolayer SnOFeSe are listed in Table II. Like bulk SnOFeSe (Table I), the dimer AFM state is also the lowest-energy spin configuration for the monolayer form. Besides, the energy of the trimer (dimer-trimer-dimer-trimer) AFM state is merely 1.81 (0.74) meV/Fe higher than that of the dimer AFM state, suggesting that via slight tuning there may also exist magnetic frustration among the low-energy magnetic states in monolayer SnOFeSe. From the calculated total DOSs of the low-energy magnetic states (Fig. S5 in the SI), we can see that in both the dimer and trimer AFM states, monolayer SnOFeSe possesses tiny band gaps. Overall, the electronic and magnetic properties of monolayer SnOFeSe show great similarities to those of the bulk form.

IV. DISCUSSION AND SUMMARY

The SnOFeSe compound formed by intercalating the SnO layers into the anti-PbO-type $\beta$-FeSe has the following advantages. First, the same tetragonal symmetry and the small lattice mismatch between SnO and $\beta$-FeSe allow for an ideal intercalation without structural reconstruction and hence the formation of a stable crystal. Second, according to our calculations in the NM state (Fig. 3), the 2D characteristics of the electronic structure of SnOFeSe are significantly enhanced compared with those of bulk $\beta$-FeSe. The improved two-dimensionality due to the intercalation of insulating SnO layers facilitates the investigation of the intrinsic property of the FeSe layer. Third, SnOFeSe and $\beta$-FeSe show different magnetic behaviors and can thus be utilized for a comparative study. For $\beta$-FeSe, there is no long-range magnetic order at ambient pressure and the AFM order only emerges under certain high pressures. Our previous calculations indicated that there exist quaside-

FIG. 7: (Color online) (a) Band structure along the high-symmetry paths of the BZ and (b) PDOS for monolayer SnOFeSe in the NM state. The Fermi energy is set to zero.
generate AFM states with tiny energy difference of 0.3 meV/Fe in β-FeSe, which are responsible for the absence of magnetic order. Here, the magnetic ground state (dimer AFM state) of SnOFeSe is energetically 2.77 meV/Fe lower than that of the trimer AFM state, providing an opportunity to detect the AFM order of the FeSe layer at low temperature and ambient pressure. Hence, SnOFeSe would be an interesting platform to study both electronic structure and magnetism of the quasi-2D FeSe layers.

As to the superconducting properties, SnOFeSe has the same crystal structure as the famous parent compound of the 1111-type Fe-based superconductor, namely LaOFeAs. The electronic properties of SnOFeSe in the NM state, including band structure, density of states, and Fermi surface, are all similar to those of LaOFeAs. Moreover, both SnOFeSe and LaOFeAs have the antiferromagnetic ground states, which are often in close proximity to the superconducting phase. Since previous experiments have shown that doping elements (such as F, Sr, Pb, Th, Ca/F, and Ce/F) in LaOFeAs can suppress the AFM order and achieve the superconducting $T_c$’s up to $\sim 30$ K, we infer that the superconductivity in SnOFeSe can also be induced by appropriate modulations, such as element substitution, external pressure, ionic gating, etc.

In summary, by using first-principles electronic structure calculations, we have predicted a stable intercalation FeSe-based superconductor, namely SnOFeSe, which is on the verge of metal-insulator transition, which bridges the respective metallic and insulating parent compounds of iron-based and cuprate superconductors. Further calculations reveal that the electronic and magnetic properties of monolayer SnOFeSe in the ultrathin limit resemble those of its bulk phase. In consideration of the similarities between SnOFeSe and LaOFeAs, we suggest that SnOFeSe is a promising parent compound to explore the FeSe-based superconductivity, which calls for future experimental verification.

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1. Y. Kamihara, T. Watanabe, M. Hirano, and H. Hosono, J. Am. Chem. Soc. 130, 3296 (2008).
2. 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, and M.-K. Wu, Proc. Natl. Acad. Sci. USA 105, 14262 (2008).
3. X. C. Wang, Q. Q. Liu, Y. X. Lv, W. B. Gao, L. X. Yang, R. C. Yu, F. Y. Li, and C. Q. Jin, Solid State Commun. 148, 538 (2008).
4. M. Rotter, M. Tegel, and D. Johrendt, Phys. Rev. Lett. 101, 107006 (2008).
5. H. Takaishi, K. Igawa, K. Arri, Y. Kamihara, M. Hirano, and H. Hosono, Nature (London) 453, 376 (2008).
6. X. H. Chen, T. Wu, G. Wu, R. H. Liu, H. Chen, and D. F. Fang, Nature (London) 453, 761 (2008).
7. G. F. Chen, Z. Li, D. Wu, G. Li, W. Z. Hu, J. Dong, P. Zheng, J. L. Luo, and N. L. Wang, Phys. Rev. Lett. 100, 247002 (2008).
8. Y. Mizuguchi, F. Tomioka, S. Tsuda, T. Yamaguchi, and Y. Takano, Appl. Phys. Lett. 93, 152505 (2008).
9. M. Bendele, A. Ishisyan, Y. Pashevich, L. Keller, T. Strässle, A. Gusev, E. Pomjakushina, K. Conder, R. Khasanov, and H. Keller, Phys. Rev. B 85, 064517 (2012).
10. M. Abdel-Hafiez, Y.-Y. Zhang, Z.-Y. Cao, C.-G. Duan, G. Karapetkov, V. M. Pudalov, V. A. Vlasenko, A. V. Sadakov, D. A. Knazyev, T. A. Romanova, D. A. Chareev, O. S. Volkova, A. N. Vasiliev, and X.-J. Chen, Chin. Phys. B 16, 156109 (2015).
11. B. Lei, J. H. Cui, Z. J. Xiang, C. Shang, N. Z. Wang, G. J. Ye, X. G. Luo, T. Wu, Z. Sun, and X. H Chen, Phys. Rev. Lett. 116, 077002 (2016).
12. 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, J. Wen, C.-L. Song, K. He, J.-F. Jia, S.-H. Ji, Y.-Y. Wang, L.-L. Wang, X. Chen, X.-C. Ma, and Q.-K. Xue, Chin. Phys. Lett. 29, 037402 (2012).
13. J. J. Ying, X. F. Wang, X. G. Luo, A. F. Wang, M. Zhang, Y. J. Yan, Z. J. Xiang, R. H. Liu, P. Cheng, G. J. Ye, and X. H. Chen, Phys. Rev. B 83, 212502 (2011).
14. J. G. Guo, S. F. Jin, G. Wang, S. C. Wang, K. X. Zhu, T. T. Zhou, M. He, and X. L. Chen, Phys. Rev. B 82, 180520(R) (2010).
15. A. Krzton-Maziopa, Z. Shermadini, E. Pomjakushina, E. Pomjakushina, M. Bendele, A. Amato, R. Khasanov, H. Luetsens, and K Conder, J. Phys.: Condens. Matter 23, 052203 (2011).
16. L. L. Sun, X.-J. Chen, J. Guo, P. W. Gao, Q.-Z. Huang, H. D. Wang, M. H. Fang, X. L. Chen, G. F. Chen, Q. Wu, C. Zhang, D. C. Gu, X. L. Dong, L. Wang, K. Yang, A. G. Li, X. Dai, Ho-kwang Mao, and Z. X. Zhao, Nature 67,
Y. Zhu, V. Ksenofontov, F. Casper, C. Felser, and R. J. Cava, Phys. Rev. Lett. 103, 057002 (2009).

J.-P. Sun, B.-S. Wang, and J.-G. Cheng, Chinese Science Bulletin 62, 3925 (2017).

M. Bendele, A. Amato, K. Conder, M. Elender, H. Keller, H.-H. Klauss, H. Luetkens, E. Pomjakushina, A. Raselli, and R. Khasanov, Phys. Rev. Lett. 104, 087003 (2010).

C. de la Cruz, Q. Huang, J. W. Lynn, J.-Y. Li, W. R. II, J. L. Zarestky, H. A. Mook, G.-F. Chen, J.-L. Luo, N.-L. Wang, and P.-C. Dai, Nature 453, 899 (2008).

J. Yang, X.-L. Shen, W. Lu, W. Yi, Z.-C. Li, Z.-A. Ren, G.-C. Che, X.-L. Dong, L.-L. Sun, F. Zhou, and Z.-X. Zhao, New J. Phys. 11, 025005 (2009).

L. Gao, Y.-Y. Xue, F. Chen, Q. Xiong, R.-L. Meng, D. Ramirez, and C.-W. Chu, Phys. Rev. B 50, 4260 (1994).

C.-W. Chu, L. Gao, F. Chen, Z.-J. Huang, R.-L. Meng, and Y.-Y. Xue, Nature 365, 323 (1993).

K. Taniguchi, A. Matsumoto, H. Shimotani, and H. Takagi, Appl. Phys. Lett. 101, 042603 (2012).