Electronic Structure and Mott Localization in Iron Deficient TlFe$_{1.5}$Se$_2$ with Superstructures

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Electronic structure and magnetic properties for iron deficient TlFe$_{2-x}$Se$_2$ compounds are studied by first-principles calculations. We find that for the case of $x = 0.5$ with a Fe-vacancy ordered orthorhombic superstructure, the ground state exhibits a stripe-like antiferromagnetic ordering and opens a sizable band gap if the short-ranged Coulomb interaction of Fe-3d electrons is moderately strong, manifesting a possible Mott insulating state. While increasing Fe-vacancies from the $x = 0$ side, where the band structure is similar to that of a heavily electron-doped Fe-3Se system, the Mott localization can be driven by kinetic energy reduction as evidenced by the band narrowing effect. Implications of this scenario in the recent experiments on TlFe$_{2-x}$Se$_2$ are discussed.

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The discovery of superconductivity (SC) with critical temperatures up to 56 K in iron pnictides [1-6] has triggered renewed interest in searching new routes to high-temperature SC. Considerable concerns have been focused on the nature of the parent compounds which show variable bad metal behavior[7] and a universal strip-like antiferromagnetic (SDW) order[8]. The magnetic ordering was proposed to be the consequence of the low energy states (or itinerant electrons) within the nearly nested Fermi surfaces, and hence the Fermi surface nesting is responsible to SC when the SDW order is suppressed [9–11]. An alternative possibility is that the magnetic structure is due to the strong correlation among the Fe-3d electrons, so that the states far away from the Fermi surfaces should be taken into account as well. To this end, Fermi surface nesting is not a necessary ingredient and the $J_1$-$J_2$ Heisenberg model based on the local moment picture could be an appropriate starting point. [12,14,16]

Most recently, Fung et al. [17] reported that the Fe-deficient compounds (Tl,K)Fe$_{2-x}$Se$_2$ exhibit SC with $T_c$ up to 31 K for $x = 0.12 \sim 0.3$. Special interest in this class of materials is that the SC emerges in proximity to an insulating phase. It is yet unknown whether this insulating phase is a Mott insulator driven by Fe-3d electron correlations. Theoretically, this possibility is mysterious, as previous first-principle calculations on both TlFe$_{2}$Se$_2$ [18] and KFe$_{2}$Se$_2$ [19,20] with the ThCr$_2$Si$_2$ structure (122-type) suggest that the parent compounds of the ternary iron chalcogenides should be metallic with either checkerboard antiferromagnetic (AFM) (for Ti$_{122}$) [14] or SDW (for K$_{122}$) [20] order, much like the electron overdoped 11-type iron selenides. Experimentally, it has been reported recently that the alkali intercalated compounds K$_{0.8}$Fe$_2$Se$_2$ [21] and Cs$_{0.8}$Fe$_2$Se$_{1.96}$ [22] (both iso-structural to BaFe$_2$As$_2$), while superconducting under 30 K and 27 K respectively, exhibit the metallic behavior in their normal states.

Two closely related questions thus arise: What is the ground state of the "parent" compound of these superconducting ternary iron chalcogenides of 122-type structure, and how can a Mott-insulating phase develop and then diminish with increasing Fe-content or electron doping giving way to SC?

In this paper, we suggest partial answers to the questions by first-principles study on TlFe$_{2-x}$Se$_2$. We start from and pay special attention to the case with $x = 0.5$, which is stoichiometrically equivalent to Tl$_2$Fe$_3$Se$_4$ but with the 122-type structure. Hence, Fe$^{2+}$ is the nominal valence as in other iron pnictides/chalcogenides. Our calculation shows that the ground state of TlFe$_{1.5}$Se$_2$ with Fe-vacancy ordered orthorhombic superstructure is an SDW phase which can open a sizable gap if a moderately strong electron correlation is imposed. The quantitative change of the bandwidth of Fe-3d electrons further supports the Mott localization driven by kinetic energy reduction due to Fe-vacancies. This scenario is quite similar to the Mott localization proposed for iron oxy-chalcogenides La$_2$O$_2$Fe$_2$O(Se,S)$_4$ [23], where the reduction of kinetic energy or the band narrowing is due to the expanded interatomic Fe-Fe distance. We will discuss the implications of this scenario in the recent experiments on TlFe$_{2-x}$Se$_2$.

The electronic structure calculations were performed with the Vienna Ab-initio Simulation Package (VASP) [24,25]. All structures were optimized so that the forces on individual atoms were smaller than 0.02 eV/Å and the pressure convergence criterion is chosen to be 0.5 kbar. For the optimization and ground state calculations, a $8 \times 4 \times 4$ Monkhorst-Pack k-grid [26] was employed, while $16 \times 8 \times 8$ Monkhorst-Pack k-grid was used for the density of states (DOS) calculations. The PBE flavor of general gradient approximation (GGA) to the exchange-correlation functional [27] was applied throughout the calculations.

We first discuss the possible crystal structure and spin configurations of TlFe$_{1.5}$Se$_2$. The Mössbauer experiment suggests a body-centered orthorhombic (BCO) crystal structure [28], where the Fe sheets form superstructure due to Fe-deficiency (FIG. 1). There are four possible stacking configurations for the two neighbouring Fe-layers [32], as shown in FIG. 1. We consider the AFM and SDW configurations within each layer, while the interlayer coupling along c-axis can be either ferromagnetic (FM) or AFM. The relative energies for...
different stacking and ordering patterns are listed in Table I. 

We find that the ground state ( for \( x = 0.5 \) ) should be of essentially two-dimensional SDW, as the energy differences among the different inter-layer magnetic orderings are very small (< 5 meV/Fe), indicating the negligible inter-layer magnetic coupling at this state. Hence, without losing generality, we shall focus on the AA-stacking pattern in the following discussions.

We also notice that for the NM state, the full structural optimization leads to the well-known \( c \)-collapse problem; while for the SDW state, the resulting structure \( (c \text{ and } z_{\text{Se}}) \) is within the expectation. Thus, unless otherwise specified, the electronic structure calculations in the following discussions were performed with the geometry relaxed in the SDW configuration. The calculated local magnetic moment of Fe atom is then \( m_{\text{Fe}} \approx 2.6 \sim 2.7 \mu_B \).

We now examine the DOS of the AA-stacking SDW\(^a\) plotted in Fig. 2(a), which exhibits a sharp dip around the Fermi energy. We find that the band gap \( E_{\text{g}} \) is vanishingly small for the fully optimized system under the GGA method. Furthermore, the \( AB \)- and \( AC \)-stacking SDW\(^a\) states, which are almost degenerate to the AA-stacking SDW\(^a\), are both metallic, with 0.216 states/(eV·Formula) and 0.656 states/(eV·Formula) respectively. Hence, the three stacking patterns may coexist at low temperatures. The SDW band gap, if exists, is too small to compare with the activation gap \( E_a \approx 57.7 \) meV observed in the \( x = 0.5 \) sample \([17]\). It indicates that the observed activation gap in TlFe\(_{2−x}\)Se\(_2\) ( at least for \( x = 0.5 \) ) is not due to the SDW ordering itself.

![FIG. 1: Superstructure of TlFe\(_{1.5}\)Se\(_2\). A, B, and C correspond to three different sites directly above the Fe-vacancy, the 3-coordinated Fe site, and the 2-coordinated site, respectively. Another stacking pattern \( A' \) is that the upper-layer is rotated 90° around c-axis.](image1)

![FIG. 2: Total and projected density of states of TlFe\(_{2−x}\)Se\(_2\). (a) \( U \)-dependent DOS. (b) \( x \)-dependent DOS.](image2)

### Table I: Configuration energies of TlFe\(_{1.5}\)Se\(_2\) ( in unit of meV ).

|        | AA   | AB   | AC   | AA’  |
|--------|------|------|------|------|
| NM     | 0.0  | 9    | 3    | 12.7 |
| AFM\(^f\) | -200 | -177 | -172 |
| AFM\(^a\) | -273 | -268 | -270 |
| SDW\(^f\) | -268 | -268 | -270 |
| SDW\(^a\) | -273 | -268 | -269 |

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Here, we suggest that the sizable activation gap can be attributed to the Mott localization driven by the moderately strong electron correlation. To seek for this possibility, we extended our calculations by using the GGA+U method. The calculated DOS for $U = 0$ eV and $U = 4.0$ eV are compared in FIG. 2(a). Within GGA+U, an insulating gap develops immediately with increasing $U$, which turns out to be 40, 60, 80, 140, and 230 meV for $U = 1, 2, 3, 4$, and 5 eV, respectively. The projected DOS associated with Fe-3d electrons move to higher energies mainly distributed around 1 eV above the Fermi energy (for $U = 4$ eV).

![Diagram of Fe and Se atoms and band structure](image)

FIG. 3: The Fermi surfaces (for $x = 0.5$ and $U = 0$) reconstructed using the MLWFs shown in the $\Gamma$-centered reciprocal BCO lattice.

We also performed calculations for $x = 0, 0.4$, keeping the Fe-vacancy ordered tetragonal superstructure in the latter case. For $x = 0$ the AFM state becomes more stable than the SDW state (in agreement with Ref. [18]), while the overall band structure and Fermi surface (FS) of TlFe$_2$As$_2$ are similar to that of KFe$_2$Se$_2$ [20]. For illustration, the band structures for $x = 0, 0.5$ in the NM states are fitted to a tight-binding model Hamiltonian by using the maximally localized wannier function (MLWF) [29, 30] method. The results are plotted in Fig. 4 where the color indicates the percentage of $d_{2z^2}(y)$ and $d_{2z^2}$ composition, from 0% (blue) to 100% (red). For $x = 0$, the Hamiltonian is particularly simple with 5-bands. The nearest neighbor hopping parameters and the on-site energies are listed in TAB. 4. The bands near $E_F$ are dominated by $d_{2z^2}(y)$ and $d_{2z^2}$ orbitals except for one empty band around X. For $x = 0.5$, the Hamiltonian is too complicated due to the structural distortion, and all 5 d-orbitals are entangled considerably around $E_F$. Nevertheless, the FS of TlFe$_{1.5}$Se$_2$ can be reconstructed as shown in Fig. 3.

The apparent different band structures for $x = 0$ and 0.5, together with the drastic change in their FS topologies, provide an indication for the transition at certain $0 < x_c < 0.5$, i.e., when $x > x_c$, the Mott localization takes place. As the Fe-Fe distance increases less than 1% from $x = 0$ to $x = 0.5$ [17], this amount of lattice expansion is not sufficient for the Mott localization in TlFe$_{2-x}$Se$_x$, as compared to iron oxychalcogenides La$_2$OFe$_2$O(Se,S)$_2$ [23]. Here, we argue that the kinetic energy reduction caused by the Fe-vacancies should play an crucial role in driving the system to the insulating phase. An intuitive estimate is that the coordinate number of Fe in the TlFe$_{1.5}$Se$_2$ is reduced to 3 or 2 depending on the Fe site comparing to 4 in a perfect square lattice. Thus the total kinetic energy is substantially reduced by the Fe-vacancies, enhancing the normalized electron correlation $U/W$, with $W$ being the bandwidth proportional to the kinetic energy.

Our argument can be checked by fitting band structures of $x = 0, 0.4$ and 0.5 to the tight-binding models. We only need to consider the NM state (and $U = 0$) and calculate the sum of the nearest neighbor hoppings (absolute values) among all five d-orbitals around a specific Fe atom. It serves as an approximate upper limit of the total kinetic energy $E_K$. Using the fitted hopping parameters we obtain $E_K = 15.59$ and 9.98 eV for $x = 0$ and 0.4, respectively. While for $x = 0.5$, we obtain $E_K = 11.34$ or 6.87 eV, corresponding to 3- or 2-coordinated Fe-sites, respectively. As the ratio of their numbers is 2:1, the average kinetic energy is 9.85 eV. For comparison, the DOS at the NM state when $U = 0$ for $x = 0, 0.4$, and 0.5 are plotted in FIG. 2(b). The Fe-3d bandwidths are roughly 4.8 eV, 3.8 eV, and 3.5 eV, respectively. Thus, we indeed find a substantial enhancement of the normalized electron correlation, manifesting the kinetic energy reduction caused by Fe-vacancies.

Finally, we remark that our calculations assume homogeneous formation of the Fe-vacancy ordered superstructures. If this is the case in real materials, the activation gap observed in the $x = 0.5$ sample should be not due to the Anderson localization caused by vacancy disorder effect. As the Mott (de-)localization is sensitive to physical pressure which can lead to monotonous bandwidth expansion by lattice contraction, we expect that the gap dependence on pressure can be used to test this scenario. The numerical results for the pressure dependent band gap $E_g$ with fixed $U = 4.0$ eV are listed in TAB. 3 ($x = 0.5$). From these results we expect that the activation gap, which is about 60 meV or well below 150 meV [17] under ambient pressure, can be completely suppressed by applying pressure up to $\sim 6$ GPa and then the SC may emerge.

| $P$ (GPa) | 0 | 2 | 4 | 6 |
|----------|---|---|---|---|
| $a$ (Å)  | 5.507 | 5.4517 | 5.3716 | 5.3079 |
| $b$ (Å)  | 11.0342 | 10.8842 | 10.7283 | 10.6177 |
| $c$ (Å)  | 13.8027 | 13.5166 | 13.2874 | 13.1102 |
| $E_{cell}$ (eV) | -187.01 | -186.65 | -185.91 | -158.00 |
| $E_g$ (meV) | 140 | 80 | 50 | 0 |
Note added: After completing this work, we became aware of two recent papers by X.W. Yan et al. [31], where independent first-principles studies on the cases of $x = 0$ and $x = 0.5$ were reported.

To summarize, we find that for $\text{TlFe}_{1-x}\text{Se}_2$, the electronic band structure shows a sizable band gap if the short-ranged Coulomb interaction $U$ beyond LDA/GGA is considered. From the experimentally observed activation gap, $U$ should be at least 2eV. The corresponding ground state is then a stripe-like anti-ferromagnetic Mott insulator. The superstructure of various Fe-vacancy ordering patterns is important for the stability of the Mott insulating phase and kinetic energy reduction caused by the vacancies plays a crucial role for the Mott localization. The pressure dependence of the gap behavior could be used to test this possibility.

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TABLE IV: Tight-binding Hamiltonian for $\text{TlFe}_{2-x}\text{Se}_2$. Only the nearest neighbor hoppings and on-site energies (diagonal line in the brackets) are shown here. All numbers are in eV.

| $d_{xz}$ | $d_{yz}$ | $d_{x^2-y^2}$ | $d_{y^2}$ |
|----------|----------|----------------|-----------|
| -0.019 (4.765) | 0 | 0.156 | 0.303 |
| 0 | -0.028 (5.084) | 0 | 0.286 |
| 0.156 | 0 | -0.314 (5.084) | -0.344 |
| 0 | -0.303 | 0 | -0.378 (4.600) |
| 0 | 0.286 | 0 | 0 | -0.047 (5.056) |

FIG. 4: Band structures of $\text{TlFe}_{2-x}\text{Se}_2$ fitted using MLWF.