Doping Driven (\(\pi, 0\)) Nesting and Magnetic Properties of Fe\(_{1+x}\)Te Superconductors

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To understand newly discovered superconductivity in Fe-based systems, we investigate the electronic structure and magnetic properties of Fe\(_{1+x}\)Te using first-principles density functional calculations. While the undoped FeTe has the same Fermi surface nested at \((\pi, \pi)\) as in Fe arsenides, doping by \(~0.5\) electrons reveals a novel square-type Fermi surface showing a strong \((\pi, 0)\) nesting and leading to a different magnetic structure. Our result strongly supports the same mechanism of superconductivity in chalcogenides as in the arsenides, reconciling theory with existing experiments. The calculated magnetic interactions are found to be critically dependent on doping and notably different from the arsenides.

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Shortly after the discovery of the novel high temperature superconductor LaFeAsO\(_{1−x}\)F\(_x\) with \(T_c \approx 27 \text{ K}\) [1], many different types of iron-based superconductors have been reported. Now the highest \(T_c\) reaches up to \(~55 \text{ K}\) [2], and there are four different structural classes: so-called 122-[3], 111-[4], and 11-type [5] structures, in addition to the 1111 type. Although a tremendous amount of research activity devoted to this field over the years has shed light on their intriguing physical properties, our understanding of superconductivity here, and its interplay with magnetism, is still far from being complete. One of the most important properties which was found in these systems is the Fermi surface nesting, whose nesting vector corresponds to the antiferromagnetic (AFM) ordering vector of the undoped magnetic phase [6–9]. Density functional theory (DFT) calculations show that all of the four classes of these materials share this common feature in their electronic structure [7,10,11], which strongly suggests the superconductivity is exotic and is mediated by spin fluctuations [9].

Along this line, one of the most interesting questions arises in the 11-type Fe chalcogenide family: Fe(S,Se,Te) [5,12–18]. In spite of their same crystal structure represented by the two-dimensional Fe square lattice and the same Fermi surface nesting predicted by DFT calculations [11], Fe chalcogenide superconductors exhibit notable differences from the arsenides. The magnetic structure found in their parent compound, Fe\(_{1+x}\)Te, strongly tackles the spin fluctuation theory because the experimentally observed magnetic ordering is clearly different from that of parent arsenide compounds. Although DFT calculations predict the same Fe surface topology, a recent neutron experiment [19] shows that, at a small \(x \approx 0.068\), Fe\(_{1+x}\)Te has a rotated and double-stripe AFM order. Importantly, this magnetic structure cannot be matched with the \((\pi, \pi)\) nesting as found in all the arsenide materials and predicted by previous calculations, but requires \((\pi, 0)\) nesting which has never been reported. This “missing nesting” remains as a puzzle in the study of Fe-based superconductors. Therefore it is not a big surprise that some papers speculate about a different superconducting mechanism for Fe chalcogenides from the arsenides, and the reinvestigation of the electronic structure and magnetic properties for Fe\(_{1+x}\)Te is of crucial importance [15,20–22].

To address these issues, we study electronic structure and magnetic interactions of Fe\(_{1+x}\)Te using first-principles DFT calculations. Since it is noted experimentally [19] that FeTe has always some amount of excess Fe atoms we perform doping dependent calculations to understand their effect on the electronic and magnetic properties. Our results show that Fe\(_{1+x}\)Te has a different Fermi surface topology as a function of doping, and eventually a novel \((\pi, 0)\) nesting appears at a doping level of \(\delta \sim 0.5\) electrons while the \((\pi, \pi)\) nesting is largely suppressed. This \((\pi, 0)\) nesting exactly matches with the double-stripe AFM order found in neutron experiments. Our result strongly supports the spin fluctuation mediated superconductivity for Fe chalcogenides, reconciling theory to existing experiments which showed significant differences between pnictides and chalcogenides. It is also found that magnetic interactions depend on doping, and, at the same level of doping \(\delta \sim 0.5\), the calculated exchange couplings become consistent with the double-stripe phase. While the second nearest neighbor AFM coupling \((J_{2b})\) is strongest, the first \((J_{1b})\) and second neighbor ferromagnetic (FM) interactions \((J_{2a})\) are also significant, which is different from arsenides.

We performed the first-principles DFT calculations within local density approximation (LDA) for the exchange-correlation energy functionals [23]. The full potential linearized-muffin-tin-orbital (LMTO) method has been used [24]. To estimate the exchange interaction strengths between Fe moments, we performed a linear response calculation [25–27], which has been successfully applied earlier to \(3d\) transition-metal oxides, \(5f\) metallic alloys [27,28], and the other Fe arsenides [29]. To simulate electron doping a rigid-band approximation is utilized. The calculation of band dispersions, Fermi surfaces, and Stoner response functions have been done with the nonmagnetic unit cell (dotted squares in Fig. 1) and using experimental lattice parameters as in the previous study [11]. To estimate the exchange constants we performed a spin-polarized...
calculation with an enlarged unit cell containing four Fe atoms, and the experimental $z$(Te) was used, which well reproduces the observed moment and is consistent with our previous study of Fe arsenides [29].

Figure 1 summarizes spin structures found in the parent materials of arsenide superconductors [Fig. 1(a)] and Fe$_{1+x}$Te for small $x$ [Fig. 1(b)] [19]. In Fe$_{1+x}$Te, the FM spin stripes are doubled and rotated by 45° with respect to the nonmagnetic unit cell (smallest dotted squares). According to the neutron scattering experiment by Li et al. [19], this double stripe phase realizes at the smallest possible $x \approx 0.068$, i.e., close to the stoichiometric FeTe ($x = 0$). The $J_{1a}$, $J_{1b}$, $J_{2a}$, and $J_{2b}$ represent the first nearest neighbor AFM, FM, second nearest AFM, and FM interactions, respectively. While the second neighbor coupling is always AFM in arsenides [Fig. 1(a)], both FM and AFM second neighbor couplings exist in FeTe [Fig. 1(b)]. As $x$ increases further, the spin ordering becomes incommensurate at $x \approx 0.141$ and the incommensurate ordering vector depends on $x$. Importantly this different magnetic structure found in Fe$_{1+x}$Te cannot be matched with the $(\pi, \pi)$ nesting which is common for AFM parent materials of all the arsenide superconductors. The different spin structure found in Fe$_{1+x}$Te remains as a puzzle because DFT calculation predicts the same Fermi surface topology and the same $(\pi, \pi)$ nesting [11].

Figure 2 shows the calculated band dispersions of a typical arsenide material, LaFeAsO [Fig. 2(a)], and FeTe [Fig. 2(b)]. As discussed by Subedi et al. [11], the two band structures are similar. The Fe-3$d$ states are dominant around the Fermi level while the anion $p$ bands depicted by “fat” bands are located fairly well below the Fermi level, and the similar band structure around the Fermi level produces the same Fermi surface topology. As a result, the same kind of $(\pi, \pi)$ nesting is obtained for FeTe as in the other arsenide materials [11]. Here we focus on the differences found in the electronic structure. First, Te-$p$ bands hybridize with Fe-$d$ at around $-2.5$ eV along $\Gamma - Z$ line while As-$4p$ is well separated from the Fe-3$d$ states. Different features along $\Gamma - Z$ are also found at energies above the Fermi level in FeTe, there are significant band crossings at about +0.3 eV. Another notable difference exists at around the $X$ point above the Fermi level where the parabolic band along $X - M - \Gamma$ is flattening at about +0.5 eV in FeTe. It is also noted that there are no band crossings across the $X$ point in the range of +0.5 $-$ +1.8 eV. These differences above the Fermi level suggest that possibly different Fermi surface topology is induced by electron doping as excess Fe atoms appear in stoichiometric FeTe host.

Figure 3 shows the Fermi surface for Fe$_{1+x}$Te as a function of doping: (a) without doping and (b) doping by 0.5 electrons per formula unit. Figure 3(a) is in good agreement with previous calculation [11] and clearly shows the existence of $(\pi, \pi)$ nesting as in the arsenides. The most important feature found in Fig. 3(b) is the square-type topology developed at around $\Gamma$ and $(\pi, 0)$ points with...
Fermi surfaces shown in Fig. 3(b) and is driven by the electron doping through the excess Fe atoms. It is noted that the small amount of excess Fe plays the key role in determining the magnetic structure as the result of the Fermi surface change. Since this (\(\pi, 0\)) nesting matches with the rotated-doubled spin stripe found in experiment, our result strongly supports the same spin fluctuation mechanism for superconductivity in Fe chalcogenides as in the Fe arsenides.

The nesting property of Fe\(_{1.063}\)Te at \(q_z \neq 0\), is different from that at \(q_z = 0\). While any notable peak is not found in Im\(\chi_0(q_z \neq 0)\) for the stoichiometric undoped FeTe, the Im\(\chi_0(q_z \neq 0)\) of Fe\(_{1.063}\)Te shows rather complicated features including both \((\pi, \pi)\) and \((\pi, 0)\) peaks with reduced intensities. These features are attributed to a significant variation of the Fermi surface along the Z direction which is also reflected in the band dispersion in Fig. 2. The doping level of \(\delta \sim 0.5\) corresponds to the Fermi level shifted by about 0.76 eV where it can be noted that the FeTe bands along \(\Gamma - Z\) direction around \(\sim +0.76\) eV region are different from those of LaFeAsO (Fig. 2).

By further dopings, the Fermi surface topology once again changes significantly, and the \((\pi, 0)\) nesting disappears. At the doping level of \(\delta \sim 1.1\), which would correspond in our analysis to Fe\(_{1.14}\)Te with the incommensurate spin order as observed in the experiment [19], the \((\pi, 0)\) nesting is largely suppressed. At this doping level, square-type structures are no longer found in the Fermi surface, and the complicated multiple-peak structure is found to be developed in the \(\chi_0\) plot. It might be responsible for the experimentally observed incommensurate spin orderings [15,19]. While, at \(q_z = 0\), neither \((\pi, \pi)\) nor \((\pi, 0)\) peak is found in \(\chi_0\), several prominent peaks exist at around \(\Gamma\) point which are gradually suppressed along the \((\pi, \pi)\) line. At \(q_z = 2\pi/3c\), notable four peaks are found around the \((\pi, \pi)\) points. This structure found at \(q_z \neq 0\) shows another difference of Fe\(_{1.063}\)Te from FeAs materials and is originated from the different band structures and hybridizations around \(Z\) point above the Fermi level as shown in Fig. 2.

The accounting for the excess Fe atoms and the validity of the rigid-band approximation is a highly nontrivial prob-

TABLE I. The calculated Fe moment (in \(\mu_B\)) and exchange parameters (in meV) for double-stripe Fe\(_{1.063}\)Te (doped) and FeTe (undoped) along with the single stripe FeTe (undoped). The results of LaFeAsO are also presented for comparison and the experimental moments are given in parenthesis.

<table>
<thead>
<tr>
<th>System</th>
<th>Moment</th>
<th>(J_{1a})</th>
<th>(J_{1b})</th>
<th>(J_{2a})</th>
<th>(J_{2b})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Double-stripe Fe(_{1.063})Te</td>
<td>2.09 (1.97)</td>
<td>-7.6</td>
<td>-26.5</td>
<td>46.5</td>
<td>-34.9</td>
</tr>
<tr>
<td>FeTe</td>
<td>2.16</td>
<td>-4.2</td>
<td>12.9</td>
<td>-6.2</td>
<td>-15.3</td>
</tr>
<tr>
<td>Single-stripe FeTe</td>
<td>2.09</td>
<td>38.6</td>
<td>21.7</td>
<td>5.0</td>
<td>(\cdots)</td>
</tr>
<tr>
<td>LaFeAsO(^\text{a})</td>
<td>1.69 (0.36)</td>
<td>47.4</td>
<td>-6.9</td>
<td>22.4</td>
<td>(\cdots)</td>
</tr>
</tbody>
</table>

\(^{a}\text{Ref. [29].}\)
\(^{b}\text{Ref. [19].}\)
\(^{c}\text{Ref. [30].}\)
problem even when we tried to simulate the doping by supercell calculations. For the present study, however, our excellent agreement with experiment demonstrates that our simplified treatment well describes this material.

The magnetic properties are summarized in Table I. Note that the calculated magnetic moment based on the experimental $z$(Te) is about 2.09 $\mu_B$ which is in good agreement with the neutron data $\sim 1.97$ $\mu_B$. This result demonstrates another difference between FeTe and Fe arsenides. In the arsenides, it is known that using experimental $z$(As) in the calculation always leads to overestimating the Fe moment [29,31,32]. For comparison, we also present in Table I the data for parent material, LaFeAsO. The numbers in parenthesis are the experimental ones. The origin of this large discrepancy is still under debate [31]. If the small moment observed in experiment is exceptionally large. The good agreement found in experiment is attributed to domain motions as suggested by Mazin and Johannes [33], the transition is achieved for both single- and double-stripe spin order, the spin waves and magnetic interactions are stabilized. While the charge density self-consistency is not achieved for both single- and double-stripe spin order, the spin waves for the undoped FeTe are found to be unstable with respect to the spin angle tilting. For the single-striped FeTe, $J_{1b}$ becomes AFM and its strength is much larger than $J_{2a}$ which is in a sharp disagreement with the single-stripe-stabilized LaFeAsO. In the undoped double stripe FeTe, the overall size of exchange interactions is small, and the signs of $J_{1a}$, $J_{1b}$, $J_{2a}$ do not correspond to the actual ordering. It implies that the stoichiometric FeTe ($x = 0.0$) is hardly stabilized, which partly explains the reason that the FeTe sample always has some amounts of excess Fe atoms [19].

The spin waves and magnetic interactions are stabilized in Fe$_{1.063}$Te being consistent with experiment. In arsenides, the exchange interactions are represented by two major AFM interactions, $J_{1a}$ and $J_{2}$, and their strengths are in the same range as is seen in the entire arsenide family [29]: The $J_{1a}$ $\sim$ 45 meV and $J_{2}$ $\sim$ 20 meV while the ferromagnetic $J_{1b}$, is very small. Based on these exchange interactions, the striped AFM phase is stabilized. In Fe$_{1.063}$Te, on the other hand, $J_{2a}$ is the strongest while $J_{1a}$ is as small as $J_{1b}$ in the arsenides. It is noted that the two FM coupling, $J_{1b}$ and $J_{2b}$, are fairly large which might be responsible for the novel doubled stripe AFM spin order. Our results suggest the spin wave velocities and dispersions for Fe chalcogenides are different from the arsenides, which can be verified by inelastic neutron scattering.

In conclusion, our electronic structure calculations show that a small amount of excess Fe atoms existing in the Fe$_{1+x}$Te samples changes the Fermi surface topology significantly. As a result, a novel ($\pi$, 0) nesting appears at $x \approx 0.063$, and the rotated double-stripe AFM spin structure stabilizes. This is different from Fe arsenide parent materials. Our finding of the “missing nesting” explains the origin of the spin density wave observed by a recent neutron experiment and validates the spin fluctuation theory of superconductivity for Fe chalcogenides. The calculated exchange interactions and spin moment demonstrate the role of excess Fe atoms in stabilizing the magnetic structure, and imply a different magnetic behavior of chalcogenide superconductors from the arsenides.

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