Density Functional Study of Excess Fe in Fe_{1+x}Te: Magnetism and Doping

Lijun Zhang, D.J. Singh, and M.H. Du
Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6114
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The electronic and magnetic properties of the excess Fe in iron telluride Fe_{1+x}Te are investigated by density functional calculations. We find that the excess Fe occurs with valence near Fe^{+}, and therefore provides electron doping with approximately one carrier per Fe, and furthermore that the excess Fe is strongly magnetic. Thus it will provide local moments that interact with the plane Fe magnetism, and these are expected to persist in phases where the magnetism of the planes is destroyed for example by pressure or doping. These results are discussed in the context of superconductivity.

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Recently, iron chalcogenides α-FeSe and α-FeTe, another new family of Fe-based superconductors have been reported. The superconducting transition temperature \( T_c \) has increased from initial 8 K  to 148 \( (15.2 \text{ K}) \) with appropriate Te substitution, and 27 K at high pressures \( (1.48 \text{ GPa}) \). While the presently known maximum critical temperatures are lower than in the Fe-As families \( (8,9,11,12) \) this binary system has drawn considerable attention due to the apparent simplicity of the structure, the fact that it is As free, and the fact that large crystals of Fe_{1+x} (Se,Te) can be grown enabling detailed characterization by neutron and other measurements. These compounds the \( \alpha \)-PbO structure, which consists of a c-axis stack of FeTe sheets, with each sheet consisting a square planar layer of Fe, tetrahedrally coordinated by Te, similar to the FeAs sheets of LaFeAsO or LiFeAs. In fact from a structural point of view these compounds are very similar to LiFeAs, with As replaced by a chalcogen and the Li replaced by a site with a low partial filling of excess Fe. According to literature, these compounds always form with excess Fe, \( (\text{13,14,15,16,17,18}) \).

Electronic structure calculations for the stoichiometric iron chalcogenides, \( \text{FeX,19} \) show electronic structures and Fermi surface topologies very similar to those of the other Fe-based superconductors. \( (\text{20,21,22,23,24,25,26}) \) There is a general proximity to magnetism, especially in FeTe, as well as a substantially nested Fermi surface, which favors a spin density wave (SDW) instability at the 2D \((\pi,\pi)\) point. While the mechanism for superconductivity in the Fe-based superconductors is yet to be established, there is a strong association between the occurrence of the SDW and superconductivity in the phase diagrams, with superconductivity generally occurring when the SDW is destroyed either by doping or by pressure. The SDW is observed in most of the undoped Fe-As superconducting materials, and is accompanied by a lattice distortion\( (\text{27,28,29,30,31}) \). For the chalcogenides, a structural distortion with decreasing temperature was detected in \( \text{FeSe}_{(1-x)} \text{Te}_x \) and superconductivity was found to be close to magnetic instability in \( \text{FeSe}_{(1-x)} \text{Te}_x \) (the formula does imply chalcogen vacancies but reflects excess Fe). Furthermore, Fe_{1+x}Te is reported as magnetic, with properties depending on stoichiometry in several older papers. Bao et al.\( (\text{18}) \) based on neutron results suggested a more complex incommensurate antiferromagnetic order for the Fe(Se_{1-x}Te_x) system than in the Fe-As based SDW phases. On the theoretical side, magnetism driven by Se vacancies\( (\text{33}) \) non-collinear\( (\text{14}) \) and bi-collinear\( (\text{35}) \) antiferromagnetic state have been suggested.

Here we report supercell calculations investigating the role of the excess Fe focusing on Fe_{1+x}Te. We find that as might be expected, excess Fe donates charge to the FeTe layers, acting as an electron dopant. Interestingly, it occurs with a valence near Fe^{+} with each Fe donating one carrier. Furthermore, there is a very strong tendency towards moment formation on the excess Fe. These moments will then interact with the magnetism of the FeTe layers, perhaps complicating the magnetic order. They would also be expected to persist into the regime where FeTe magnetism is suppressed by doping or pressure, perhaps extending the range of magnetic order in the phase diagram, and providing pair breaking in the superconducting state.
were performed with the projector augmented wave method\textsuperscript{23} as implemented in VASP code.\textsuperscript{24,25} The generalized gradient approximation\textsuperscript{26} was employed for the exchange-correlation functional. A kinetic energy cutoff of 268 eV and augmentation charge cutoff of 511 eV were used to obtain converged energy (within 1 meV). To simulate the partially occupied excess Fe, we used a 2x2 supercell of α-FeTe (two formula per cell) with one Fe atom (labeled as Fe\textsubscript{2}) placed at the 2c (0.5,0,z) site, as shown in Fig. 1. This corresponds to a stoichiometry of Fe\textsubscript{1.125}Te. The experimental lattice parameters a = 3.8245 and c = 6.2818 for Fe\textsubscript{1.125}Te\textsubscript{17} were used in our calculations. 

An 8x8x10 grid was used for the k-point sampling of the Brillouin zone, and a denser 16x16x20 k-mesh was used for density of state (DOS) calculations. The internal coordinates were relaxed to minimize the forces to below 0.01 eV/Å. The calculated coordinate of Fe\textsubscript{2} is z\textsubscript{Fe\textsubscript{2}} = 0.703. This is in reasonable agreement with the experimental results in Ref.\textsuperscript{14} (z\textsubscript{Fe\textsubscript{2}} = 0.692) and Ref.\textsuperscript{18} (z\textsubscript{Fe\textsubscript{2}} = 0.721), but significantly higher than that in Ref.\textsuperscript{17} (z\textsubscript{Fe\textsubscript{2}} = 0.561).

We begin by showing that the excess Fe atom is strongly magnetic. Fig. 2 shows the DOS for Fe\textsubscript{1.125}Te obtained in a nonmagnetic calculation. The electronic states near the Fermi level (E\textsubscript{F}) are mostly of 3d character of the Fe\textsubscript{1} layers with small contribution from the excess Fe\textsubscript{2} atom. The result that the Fermi level lies exactly at a sharp peak of the Fe\textsubscript{2} 3d DOS indicates the magnetic instability. The calculated Fe\textsubscript{2} partial DOS at E\textsubscript{F} is 6.2 states/eV/Fe (both spins). Within the Stoner theory the magnetism occurs when N(E\textsubscript{F})I > 1, where N(E\textsubscript{F}) is the DOS at the Fermi level per atom per spin and I is the Stoner parameter, typically in the range of 0.7 \~ 0.9 eV for Fe. The large Fe\textsubscript{2} 3d DOS at E\textsubscript{F} easily satisfies the Stoner criterion for the magnetic instability. Indeed, when considering the spin polarization for the Fe\textsubscript{2} atom (not Fe\textsubscript{1} layers), the total energy is reduced by 48.9 meV as shown in Table I. A pseudogap is opened with the Fermi level falling into its bottom, as shown in Fig. 4. The calculated Fe\textsubscript{2} DOS at the Fermi level is reduced to 0.8 states/eV/Fe. The calculated magnetic moment for Fe\textsubscript{2} is 2.5 μ\textsubscript{B}.

Based on integration of the partial Fe\textsubscript{2} DOS up to the Fermi level and normalization with the total Fe\textsubscript{2} DOS we find 4.7 electrons in the majority spin states and 2.2 electrons in the minority spin states. Thus, the excess Fe occurs as Fe\textsuperscript{3+} and each excess Fe atom has donates approximately one electron to the Fe\textsubscript{1} layer. It may noted that Fe\textsuperscript{3+} is a somewhat unusual valence state for stable Fe compounds. Here this state is stabilized because of a balance between the two Fe sites. Specifically, in stoichiometric FeTe, Fe is already di-valent, and so the more rapid electron doping that would result if the excess Fe were di-valent would lead to a more rapid conversion of the plane Fe towards Fe\textsuperscript{3+}. This balance between low valence states for Fe in the plane and excess positions may be responsible for the fact that the structure does not form at higher excess Fe concentrations.

For undoped FeTe, the Fermi level is located somewhat below the bottom of the pseudogap as shown in Ref.\textsuperscript{19}. The presence of the excess Fe atoms in Fe\textsubscript{1.125}Te moves the E\textsubscript{F} up, reducing the total DOS at E\textsubscript{F}. However, despite the electron doping, the total DOS at E\textsubscript{F} remains relatively high (1.8 states/eV/Fe), which would still put the Fe\textsubscript{1.125}Te close to magnetic instabilities. Our calculations show that stripe antiferromagnetic ordering (the SDW type) is most stable compared to the nonmagnetic, ferromagnetic, and the checkerboard antiferromagnetic phases (see Table I) assuming the fixed structure for the nonmagnetic phase in all these calculations. Relaxing the structure for the SDW antiferromagnetic state further lowers the total energy by nearly 70 meV.

\begin{table}[h]
\centering
\caption{Calculated energy difference (in meV/Fe\textsubscript{1.125}Te, relative to the non-magnetic state for all of Fe) between different types of magnetic arrangements for Fe\textsubscript{1} in layers and excess Fe\textsubscript{2}.}
\begin{tabular}{lcc}
\hline
  & Fe\textsubscript{2}(non-magnetic) & Fe\textsubscript{2}(magnetic) \\
\hline
Fe\textsubscript{1}(non-magnetic) & -84.9 & -104.9\textsuperscript{a} \\
Fe\textsubscript{1}(ferromagnetic) & -72.0 & -93.1 \\
Fe\textsubscript{1}(checkerboard antiferromagnetic) & -151.0 & -131.0 (\textsuperscript{256.6}\textsuperscript{a}) \\
Fe\textsubscript{1}(SDW antiferromagnetic) & -186.7 & -186.7 (\textsuperscript{256.6}\textsuperscript{a}) \\
\hline
\end{tabular}
\textsuperscript{a}Actually, this type of arrangement always converges to an “anti-ferromagnetic” order with Fe\textsubscript{1} and Fe\textsubscript{2} having opposite spin directions.
\textsuperscript{b}The calculated value with relaxed structure when fully considering magnetic orders.
\end{table}
FIG. 3: (Color online) Calculated electronic DOS for Fe$_{1.25}$Te with the moment formation on the excess Fe$_2$ (non-magnetic order for Fe$_1$ layers).

The magnetic moment of the Fe$_2$ is calculated to be 2.4 $\mu_B$, much higher than that for the Fe$_1$ layers (1.6-1.8 uB). The excess Fe’s strong magnetism is supported by the recent neutron scattering experiment.\textsuperscript{18} The large local magnetic moment of the excess Fe is expected to persist even if the SDW antiferromagnetic ordering of the Fe layers is suppressed by the doping or pressure, thus causing pair breaking in the superconducting phase.

As we have found in our early work, FeTe has the strongest SDW state in the iron chalcogenide family.\textsuperscript{19} This is consistent with experimental observations that the SDW state is maintained up to high excess Fe contents, which as discussed correspond to high doping levels (with $x$ up to 0.125 in the Fe$_{1+x}$Te systems).\textsuperscript{3,18} It should also be noted that the heavy doping corresponds to a large size mismatch between the approximately cylindrical electron and hole Fermi surfaces. The driving force for an itinerant spin density wave is Fermi surface nesting. As noted,\textsuperscript{12} for a large size mismatch the structure in the susceptibility around $(1/2,1/2)$ will develop a dip at the center, with the maximum therefore moving off center. If the SDW stays stable the ordering vector will then become incommensurate. This apparently is the case in Fe$_{1+x}$Te, and may explain the incommensurate SDW observed in neutron scattering.\textsuperscript{18} We note that an itinerant SDW can arise simply within this itinerant framework, but would require a complex frustration within a local moment picture.

Turning to the trends, as noted FeTe has a stronger tendency towards magnetism than FeSe and the arsenides, but also still shows signatures of spin fluctuations.\textsuperscript{19} As such, within a scenario where superconductivity arises from pairing due to spin fluctuations associated with the Fermi surface nesting, FeTe may have particularly high temperature superconductivity if the SDW can be suppressed. However, the SDW persists up to high doping levels.\textsuperscript{18} A particularly interesting experiment would be then to destroy the SDW by pressure and search for superconductivity in the resulting paramagnetic phase. Furthermore, the fact that the excess Fe in this compound, and presumably the Fe$_{1+x}$Se and Fe$_{1+x}$(Se,Te) superconductors, has a local moment in proximity to the Fe layers offers an interesting opportunity for experimental investigation of the interplay between superconductivity and presumably pair breaking magnetic scattering in the Fe superconductors.

In summary, we find that the excess Fe in Fe$_{1+x}$Te is strongly magnetic and is also an electron donor, with each excess Fe atom donating approximately one electron to the Fe layer.

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