Magnetic and Orbital Orderings in Iron Chalcogenides

Wei-Guo Yin

Brookhaven National Laboratory

Collaborators:
Theory: Wei Ku, Chi-Cheng Lee, Chia-Hui Lin, Limin Wang, Wei Kang
Experiment: Q. Li, C. Petrovic, G. Gu, G. Xu, J. Tranquada
Outline

1. Magnetism
   - E-type AF in FeTe
   - Unified picture in a toy model
   - Hund’s metal and insulator

2. Orbital ordering
   - Review OO in pnictides
   - FeTe

3. FeTe under pressure
Why FeTe?

- The parent compound of the 11 family
- Its magnetism is one of the main unresolved issues in the field of FeSC. Its resolution is relevant to many other puzzles.
- FeTe for high Tc?

N. Katayama et al., JPSJ (2010)
FeTe for high Tc?

A. Subedi et al., PRB 78, 134514 (2008)

“In a scenario where superconductivity is mediated by spin fluctuations at the SDW nesting vector, the strongest superconductor in this series would be doped FeTe.”

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>z_X</th>
<th>N(E_F)</th>
<th>m_{SDW}(μ_B)</th>
<th>E_{SDW}</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS</td>
<td>3.6735</td>
<td>5.0328</td>
<td>0.2243</td>
<td>1.35</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>FeSe</td>
<td>3.765</td>
<td>5.518</td>
<td>0.2343</td>
<td>0.95</td>
<td>0.65</td>
<td>5</td>
</tr>
<tr>
<td>FeTe</td>
<td>3.8215</td>
<td>6.2695</td>
<td>0.2496</td>
<td>1.83</td>
<td>1.28</td>
<td>47</td>
</tr>
</tbody>
</table>
arsenides
(1111, 122, 111, etc.)

• Rule out the FS nesting mechanism
  FS nesting vector is $(\pi, 0)$ in 1-Fe u.c.

• Heisenberg models?
  F. Ma et al., PRL (09) DFT $\rightarrow$ J1-J2-J3
  J. Hu et al., t-J1-J2-J3 $\rightarrow$ SC
E-type: Not compatible with SC

FeTe$_{1-x}$Se$_x$

Xu et al., PRB 82, 104525 (2010)
- FeTe is a politically incorrect parent
- It knows some dirty tricks in FeSC
More about Heisenberg model fits

5-orbital Hubbard model: HF


- E*-type is stabilized only for large U and $J_H$
- Heisenberg: better for FeTe than for LaOFeAs?
**J from linear response: Arsenides**

**DFT:** M. J. Han et al., PRL 102, 107003 (2009)

<table>
<thead>
<tr>
<th>System</th>
<th>Moment</th>
<th>$J_{1a}$</th>
<th>$J_2$</th>
<th>$J_{1b}$</th>
<th>$J_{1a}/2J_2$</th>
<th>$J_{1a} + 2J_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaFeAsO</td>
<td>1.69</td>
<td>47.4</td>
<td>22.4</td>
<td>-6.9</td>
<td>1.06</td>
<td>92.2</td>
</tr>
<tr>
<td>CeFeAsO</td>
<td>1.79</td>
<td>31.6</td>
<td>15.4</td>
<td>2.0</td>
<td>1.03</td>
<td>62.4</td>
</tr>
<tr>
<td>PrFeAsO</td>
<td>1.76</td>
<td>57.2</td>
<td>18.2</td>
<td>3.4</td>
<td>1.57</td>
<td>93.6</td>
</tr>
<tr>
<td>NdFeAsO</td>
<td>1.49</td>
<td>42.1</td>
<td>15.2</td>
<td>-1.7</td>
<td>1.38</td>
<td>72.5</td>
</tr>
<tr>
<td>CaFe$_2$As$_2$</td>
<td>1.51</td>
<td>36.6</td>
<td>19.4</td>
<td>-2.8</td>
<td>0.95</td>
<td>75.4</td>
</tr>
<tr>
<td>SrFe$_2$As$_2$</td>
<td>1.69</td>
<td>42.0</td>
<td>16.0</td>
<td>2.6</td>
<td>1.31</td>
<td>74.0</td>
</tr>
<tr>
<td>BaFe$_2$As$_2$</td>
<td>1.68</td>
<td>43.0</td>
<td>14.3</td>
<td>-3.1</td>
<td>1.51</td>
<td>71.5</td>
</tr>
<tr>
<td>KFe$_2$As$_2$</td>
<td>1.58</td>
<td>42.5</td>
<td>15.0</td>
<td>-2.9</td>
<td>1.42</td>
<td>72.5</td>
</tr>
<tr>
<td>LiFeAs</td>
<td>1.69</td>
<td>43.4</td>
<td>22.9</td>
<td>-2.5</td>
<td>0.95</td>
<td>89.2</td>
</tr>
</tbody>
</table>

**INS:** J. Zhao et al., Nature Phys. 5, 555 (2009)

$SJ_{1a} = 49.9$, $SJ_{1b} = -5.7$, $SJ_2 = 18.9$

- DFT agrees with INS
- The J’s agree with the C type
J from linear response: FeTe

DFT:
M. J. Han et al., PRL 103, 067001 (2009)

<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$_{1.068}$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>...</td>
</tr>
<tr>
<td>LaFeAsO$_a$</td>
<td>1.69 (0.36)</td>
<td>47.4</td>
<td>-6.9</td>
<td>22.4</td>
<td>...</td>
</tr>
</tbody>
</table>

INS:
O. J. Lipscombe et al., PRL 106, 057004 (2011)

$J_{1a}$=-17.5; $J_{1b}$=-51.0; $J_{2a}$=$J_{2b}$=21.7; $J_{3}$=6.8

- DFT disagrees with INS
- All sets of J’s disagree with the E type
- J’s from different orders are different
Both set of J’s disagree with the E type GS
Fluctuations and ordering appear at different wave vectors in Fe$_{1.08}$Te.

D. Parshall et al., PRB 85, 140515(R) (2012)
For more strange T-dependent spin dynamics in Fe$_{1+y}$Te, come to Igor Zaliznyak’s talk tomorrow.
What’s weird?

- More correlated FeTe is much worse described by one Heisenberg model.
- Needs different J’s for different spin orders and T.
- E-type is incompatible with SC; its physics is not J1-J2-J3.

The magnetism in FeTe is one of the main unresolved issues in the field of FeSC.

Hints:

- Correlation in FeTe is governed not by U but by Hund’s rule coupling K.
- Explicit orbital degree of freedom to self-adjust to different spin orders, T, and vacancy order.
# Fe-vacancy order

<table>
<thead>
<tr>
<th>Material</th>
<th>Fe vacancy</th>
<th>Spin pattern</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeTe</td>
<td>0</td>
<td>E / Block</td>
<td>Xiang / Yin</td>
</tr>
<tr>
<td>FeSe</td>
<td>0</td>
<td>C</td>
<td>Singh</td>
</tr>
<tr>
<td>K$_2$Fe$_7$Se$_8$</td>
<td>12.5%</td>
<td>C</td>
<td>Cao</td>
</tr>
<tr>
<td>K$_2$Fe$_4$Se$_5$</td>
<td>20%</td>
<td>Block</td>
<td>Cao/Xiang/Yin</td>
</tr>
<tr>
<td>K$_2$Fe$_3$Se$_4$</td>
<td>25%</td>
<td>C</td>
<td>Xiang</td>
</tr>
<tr>
<td>BaFe$_2$Se$_3$</td>
<td>33% ladder</td>
<td>Block</td>
<td>Hu</td>
</tr>
<tr>
<td>KFe$_2$Se$_3$</td>
<td>33% ladder</td>
<td>C</td>
<td>Yin</td>
</tr>
<tr>
<td>Ce$_2$O$_2$FeSe$_2$</td>
<td>50% chain</td>
<td>F-intra</td>
<td>Hu</td>
</tr>
<tr>
<td>KFeAgTe$_2$</td>
<td>50%</td>
<td>???</td>
<td>Lei</td>
</tr>
<tr>
<td>TaFeTe$_3$</td>
<td>ladder?</td>
<td>A</td>
<td>Feng</td>
</tr>
<tr>
<td>KFe$_2$Se$_2$</td>
<td>0</td>
<td>Block</td>
<td>Hu</td>
</tr>
<tr>
<td>CuFeSb</td>
<td>0</td>
<td>F</td>
<td>Mao</td>
</tr>
</tbody>
</table>
Spin-Fermion Model

\[ H = - \sum_{ij\gamma\sigma} \left( t_{ij}^{\gamma\sigma} d_{i\gamma\sigma}^\dagger d_{j\gamma\sigma} + h.c. \right) - K \sum_i \vec{S}_i \cdot \vec{S}_i + \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j \]

W.-G. Yin et al., PRL (2010); W. Lv et al., PRB (2010); S. Liang et al., PRL (2012).

- Itinerant electrons: \( xz, yz \)
- Localized spins: the other Fe 3d orbitals
  - \( J_1 \) & \( J_2 \): AF superexchange (\( J_2 \approx J_1 \) → stripy AF)
- \( K \): Hund’s rule coupling
- “Double-Exchange” FM to gain kinetic energy, sensitive to band filling
- “DE” FM vs. “SE” AF
  - different length scales
Inspired by

- Orbital-selective Mott transition
  - L. de’ Medici et al., PRL (09).

- Electron correlation controlled by Hund’s coupling $K$
  - Johannes & Mazin, PRB (09).
  - Solvation of $U$ by highly polarizable anions but not $K$.
    Sawatzky et al., EPL 86, 17006 (2009).

- Spin-dependent QP dispersion (SI-STM)
  - Chuang et al., Science 327, 181 (2010) “the delocalized electronic states detectable by quasiparticle interference imaging are dispersive along the b axis [FM direction] only.”
E-type vs. A-type AF in $\text{RMnO}_3$

- **Degenerate orbitals with anisotropic hoppings**
- **Double-exchange (DE) mechanism**

- **Electronic softness:** Small change in parameters

---

Zhou & Goodenough, PRL (1996)  
Hotta et al., PRL (1996)
Model Parameters: \( n \)

\[
H = - \sum_{i\gamma\gamma'} (t_{ij}^{\gamma\gamma'} d_{i\gamma}^\dagger d_{i\gamma'} + h.c.) - K \sum_i \vec{s}_i \cdot \vec{S}_i + \sum_{ij} J_{ij} \vec{s}_i \cdot \vec{S}_j
\]

\( n=1 \): one electron (intermediate spin)

\( n=3 \): one hole (high spin)

\( t_{2g} \)

\( e_g \)

Kruger et al., PRB (2009)

Lee, Yin, Ku, PRL (2009)

OSMT
Material Dependence

\[ H = - \sum_{i \gamma \gamma' \sigma} (t_{ij}^{\gamma \gamma'} d_{i \gamma \sigma}^{\dagger} d_{i' \gamma' \sigma} + h.c.) - K \sum_{i} \mathbf{s}_i \cdot \mathbf{S}_i + \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \]

- \( t \): strong anisotropy
- \( t' \): comparable to \( t \)
- \( J, J' \): comparable and isotropic
- \( KS \): leading material dependence

\( JS^2, J'S^2 \approx 10 \text{ meV} \)
\( KS \approx 0.8 \text{ eV} \)

LaOFeAs:
- 1.31 Å
- 0.36 \( \mu_B \)

FeTe:
- 1.73 Å
- 1.70 \( \mu_B \)

\( z_{\text{anion}} \) (up) \( \rightarrow \) \( S \) (up), \( J \) (down) \( \rightarrow \) \( JS^2 \) less sensitive; \( KS (z_{\text{anion}}) \).
\( Z_{\text{anion}} \) induced quantum PT

\( BaFe_2As_2 \)

Large $z_{\text{anion}} \rightarrow$ FM

CuFeSb

W. Kang et al., unpublished

B. Qian et al., PRB 85, 144427 (2012)
then, a critical question is why the $E$-type AF order of FeTe is metallic. The answer is that the iron-based superconductors have a considerably large NNN intraorbital hopping parameter $t'$. Comparable NN and NNN parameters are suggested by the crystal structure—the anions sit above or below the center of the Fe plaque. Besides, that the observed Fermi surface has a hole pocket around $(0, 0)$ and an electron pocket around $(\pi, 0)$ implies that $-2t' > t_{||}$. This condition is found to warrant the overlap of the split subbands and the metallicity of the system. We verified that had $t' = 0$, the $E$ type would be insulating.

\begin{itemize}
  \item Gap: bonding-antibonding splitting
\end{itemize}
In the absence of Fe vacancy, X-type* and E-type are nearly degenerate.

- Each Fe atom is linked to one xz bond and one yz bond.
- Likewise, X-type is metallic, but insulating for $t' = 0$.

Fe vacancy blockade

- Fe vacancies interfere with bonding except in X
- $t'$ effects between FM blocks is suppressed $\rightarrow$ insulating
245 is not a Mott insulator

- High-energy “gap” scales with $U$.
- Low-energy gap is not a Mott gap
  - insensitive to $U$,
  - sensitive to the magnetic pattern.
- scales with tetramer distortion $\Rightarrow$ bonding-antibonding splitting

W.-G. Yin et al., PRB 86, 081106(R) (2012)

“Hund’s metal”
### Two-leg Spin Ladder $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{Se}_3$

<table>
<thead>
<tr>
<th>$x$</th>
<th>Fe valence</th>
<th>AF type</th>
<th>Pattern</th>
<th>$T_N$ (K)</th>
<th>$m$ ($\mu_B$)</th>
<th>Insulating</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2+ ($d^6$)</td>
<td>Block</td>
<td></td>
<td>260</td>
<td>3</td>
<td>Yes</td>
</tr>
<tr>
<td>1</td>
<td>2.5+ ($d^{5.5}$)</td>
<td>Stripy</td>
<td></td>
<td>200</td>
<td>2</td>
<td>Yes</td>
</tr>
<tr>
<td>$x$</td>
<td>2 – 2.5</td>
<td>Glass</td>
<td></td>
<td>-</td>
<td>2 - 3</td>
<td>Yes</td>
</tr>
</tbody>
</table>

J. M. Caron et al., PRB 85, 180405(R) (2012).
Block vs. Stripy AF

Large K limit: **No** hopping between opposite spins

Kinetic energy gain from bonding-antibonding splitting

- $xz, yz \rightarrow$ strong anisotropy: $t_\sigma \gg t_\pi$
- High-spin configuration: 1 hole/Fe in $xz$ & $yz$ orbitals for Fe$^{2+}$ (Ba123)

<table>
<thead>
<tr>
<th>per 4 Fe</th>
<th>Contributor</th>
<th>Block (X)</th>
<th>Stripy (C)</th>
<th>E(X) – E(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 spins</td>
<td>“SE” AF</td>
<td>$2J_1S^2$</td>
<td>$-(2J_1 + 4J_2)S^2$</td>
<td>$4(J_1 + J_2)S^2 &gt; 0$</td>
</tr>
<tr>
<td>Ba123</td>
<td>4 holes</td>
<td>“DE” FM</td>
<td>$-4t_\sigma$</td>
<td>$-2t_\sigma - 2t_\pi$</td>
</tr>
<tr>
<td>K123</td>
<td>6 holes</td>
<td>“DE” FM</td>
<td>$-2(t_\sigma - t_\pi - t')$</td>
<td>$-2t_\sigma$</td>
</tr>
</tbody>
</table>

$t_\sigma = 0.4 \text{ eV}, \ t_\pi = 0.13 \text{ eV}, \ t' = -0.25 \text{ eV} \rightarrow 0.06 \text{ eV} < (J_1 + J_2)S^2 < 0.135 \text{ eV}$

- **AF favors C-type**
- **FM favors X strongly for Ba123, but weakly for K123**
Spin Glass in $\text{Ba}_{1-x}\text{K}_x\text{Fe}_2\text{Se}_3$

- Kinetic energy gain from bonding-antibonding splitting
- High degeneracy in the deployment of block and “dimer” bonds
  \[1-x : 2x\]
- Monte Carlo simulation is desirable
  like Shuhua Liang et al., PRL 109, 047001 (2012).
Implication: Unified Picture

- **AF & FM play at different length scales.**
  - “SE” AF: local, favoring C-type
  - “DE” FM: extended and sensitive to spatial changes.

- **1D → 2D (the spin-fermion model with the same t’s)**
  - C: K123, LaOFeAs (1111), BaFe$_2$As$_2$ (122), KFe$_{1.5}$Se$_2$ (234), K$_{0.5}$Fe$_{1.75}$Se$_2$ (278)
  - E: FeTe (11)
  - X: Ba123, FeTe$_{1-x}$Se$_x$ (11), K$_{0.8}$Fe$_{1.6}$Se$_2$ (245)
  - F/A: Ce$_2$O$_2$FeSe$_2$ (2212), TaFeSe$_3$ (113), CuFeSb (111)

W.-G. Yin et al., PRL 105, 107004 (2010); PRB 86, 081106(R) (2012)
2. Orbital Ordering
Resistivity Anisotropy

For NaFeAs, $R$ along the AF direction is smaller than along the FM direction.

For FeTe, the opposite is true $\rightarrow$ DE physics.

Ferro-site-orbital order

\[ U = n_{xz} - n_{yz} \]

- AF-induced FM direction
- Not inconsistent with resistivity anisotropy

<table>
<thead>
<tr>
<th>U</th>
<th>P = n_{xz} - n_{yz}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.15</td>
</tr>
<tr>
<td>2 eV</td>
<td>0.40</td>
</tr>
</tbody>
</table>

C.-C. Lee et al., PRL 103, 267001 (2009)
Ferro-site-OO in FeTe?

A. M. Turner et al., PRB 80, 224504 (2009).

\[ P = n_{XZ} - n_{YZ} = 1 \]

- Large \( J_2 \) and weak \( J_1 \)

**INS:** \( J_{1a} = -17.5; \ J_{1b} = -51.0; \ J_{2a} = J_{2b} = 21.7; \ J_3 = 6.8 \)
Weak site-OO in FeTe

\[
\begin{pmatrix}
3z^2 - r^2 & x^2 - y^2 & yz & xz & xy \\
3z^2 - r^2 & 1.44 & 0.00 & -0.04 & -0.04 & 0.03 \\
x^2 - y^2 & 0.00 & 1.31 & 0.04 & -0.04 & 0.00 \\
yz & -0.04 & 0.04 & 1.05 & 0.01 & 0.05 \\
xz & -0.04 & -0.04 & 0.01 & 1.05 & 0.05 \\
xy & 0.03 & 0.00 & 0.05 & 0.05 & 1.13 \\
\end{pmatrix}
\]

<table>
<thead>
<tr>
<th>U</th>
<th>P = n_{xz} - n_{yz}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.02</td>
</tr>
<tr>
<td>2 eV</td>
<td>0.06</td>
</tr>
</tbody>
</table>
Bond-OO in FeTe

(spin-up channel)

(Hopping in parenthesis)

\[\langle yz | DM | yz \rangle = 0.121873 (-0.274038)\]

\[\langle xz | DM | xz \rangle = -0.10607 (0.0574313)\]
Site-OO is considerably weak in chalcogenides.

Effect of U on site-OO is large in LaOFeAs but weak in FeTe.

Consistent with large effective $J_H$ in FeTe

\[ U_{eff} = U' - J_H \]
Take home messages

- Orbital order is tied to the C-type spin order
- Is C-type spin fluctuation also accompanied by orbital fluctuation?
Part 3  FeTe under pressure
Motivation

A. Subedi et al., PRB 78, 134514 (2008)

“In a scenario where superconductivity is mediated by spin fluctuations at the SDW nesting vector, the strongest superconductor in this series would be doped FeTe.”

<table>
<thead>
<tr>
<th></th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>$z_X$</th>
<th>$N(E_F)$</th>
<th>$m_{SDW}(\mu_B)$</th>
<th>$E_{SDW}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeS</td>
<td>3.6735</td>
<td>5.0328</td>
<td>0.2243</td>
<td>1.35</td>
<td>0.00</td>
<td>0</td>
</tr>
<tr>
<td>FeSe</td>
<td>3.765</td>
<td>5.518</td>
<td>0.2343</td>
<td>0.95</td>
<td>0.65</td>
<td>5</td>
</tr>
<tr>
<td>FeTe</td>
<td>3.8215</td>
<td>6.2695</td>
<td>0.2496</td>
<td>1.83</td>
<td>1.28</td>
<td>47</td>
</tr>
</tbody>
</table>

• Pressure can dramatically enhanced Tc in 1111, 122, FeSe.
• FeTe? Failed → Why?
C. Zhang et al, PRB 80, 144519 (2009)

• c axis collapse reminiscent of pressurized CaFe2As2
P decreases the Fe-Te-Fe angle $\Rightarrow$ rigid Fe-Anion bond length

Opposite to what happens in pressurized CaFe$_2$As$_2$

W. Kang et al., unpublished
Pressure driven FM

W. Kang et al., unpublished
M. Bendele et al., PRB 87, 060409(R) (2013).
Tensile strain to increase the Fe-Te-Fe angle

Y. Han et al., PRL 104, 017003 (2010).


60-150 nm thick films
FeTe film can be superconducting

W. Si et al., PRB 81, 092506 (2010) → Oxygen
Are ultrathin FeTe films under sufficient tensile strain superconductive?
Conclusion

- Iron chalcogenides are strongly correlated systems
  - kind of similar to CMR manganites, where Hund’s rule coupling and orbital degeneracy play central roles.
  - kind of similar to cuprates, where AF superexchange between localized moments is also important
  - E-type or block AF results from the above competition
  - Hund’s metal and insulator
  - Orbital order is tied to the C-type spin order
  - The DE physics is correlated with the anion height
  - SC appears when the system is away from the DE limit.

Outlook

- High-Tc FeTe
- Calculate spin dynamics in FeTe, etc., a nonperturbative problem
- C-type spin fluctuation + orbital fluctuation
- Role of Fe-anion interaction