Electronic and magnetic structures of Fe Selenide SC &
First principle predication of strong electron-phonon coupled superconductors: Li_{n}B_{n+1}C_{n-1}

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Jiangping Hu Purdue University and IOP, CAS
Donglai Feng Fudan University
Electronic and Magnetic Structures of Fe Selenide Materials
Three kinds of Fe selenide superconductors

Bulk FeSe (2008)

$T_c \sim 9K$
~ $36.7 K$ at $8.9GPa$

$K_{1-x}Fe_{2-y}Se_2$ (2011)
Alkali intercalated FeSe

$T_c \sim 33K$
~ $48 K$ at $11 GPa$

FeSe monolayer (2012)
on SrTiO$_3$ substrate

$T_c > 30K$
~ $65K$ ?

decreasing dimensionality
FeAs superconductors: electronically “dirty”

- 5 orbitals
- Complicated Fermi surface topology

FeSe superconductors: relatively “clean”

- Simple Fermi surface structure: model system for identifying the origin of magnetic as well as pairing interaction
- Rich Fe vacancy orders
- Rich antiferromagnetic orders
Superconducting FeSe monolayer
- electronic Fermi surface around $M$
- no Fermi surface around $\Gamma$


Superconducting $K_{1-x}Fe_{2-y}Se_2$
- electronic Fermi surface around $M$
- 2 electronic Fermi surfaces around $\Gamma$

D Mou et al, PRL 106, 107001 (2011)
Fe vacancy order in $\text{K}_2\text{Fe}_{n}\text{Se}_{n+1}$

- **$\text{KFe}_{1.5}\text{Se}_2$**
  - rhombus-order
  - $n = 3$

- **$\text{K}_{0.8}\text{Fe}_{1.6}\text{Se}_2$**
  - $\sqrt{5} \times \sqrt{5}$ order
  - $n = 4$

- **$\text{K}_{0.5}\text{Fe}_{1.75}\text{Se}_2$**
  - $\sqrt{8} \times \sqrt{10}$ order
  - $n = 7$
Magnetic structure of the ground states

Collinear AFM order

- 2.8 $\mu_B$/Fe
- Band gap: 40 meV

Bi-collinear AFM order

- $\sim 2 \mu_B$/Fe
- Poor metal

Block AFM order

- 3.31 $\mu_B$/Fe
- Band gap: 430 meV

FeSe (films and crystal)

KFe$_{1.5}$Se$_2$

FeTe

K$_{0.8}$Fe$_{1.6}$Se$_2$

These theoretical predictions are confirmed/consistent with the experimental observation.

Ma et al PRL 102 (2009) 177003
Yan et al PRL 106, 087005 (2011)  
Liu et al PRB 85, 235123 (2012)

Yan et al PRB 84, 045502 (2011)  
Yan et al PRB 83, 233205 (2011)
Stoichiometric Fe-Se materials

- Monolayer FeSe
- Multi-layer FeSe
- Bulk FeSe / FeTe
- KFe$_2$Se$_2$
- KFe$_{1.5}$Se$_2$
- K$_{0.8}$Fe$_{1.6}$Se$_2$ (K$_2$Fe$_4$Se$_5$)
Stoichiometric Fe-Se materials

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High temperature paramagnetic phase:
Band structure similar to other Fe-based materials
Ground state of undoped FeSe films: non-superconducting

- collinear AFM ordered
- Slightly doped semiconductor

How does the mono-layer FeSe film superduct?

**Monolayer FeSe**

There are O deficiencies on the surface of STO which dope electrons to FeSe, destroy the AFM order and induce superconductivity.

**Bilayer FeSe**

semiconducting
the top layer is undoped and non-superconducting

Electronic structure of bulk FeSe

Ground state
✓ collinear AFM ordered
✓ Semi-metal

The Fermi surface in the non-magnetic phase (high temperature)
Only the interface layer superconducting
The difference suggests that the ground state of bulk FeSe is in an antiferromagnetic ordered phase.
Comparison with the ARPES data of FeSe films

SY Tan et al, arXiv:1301.2748
Origin of the Collinear AFM Order

weak coupling: Fermi surface nesting
strong coupling: Local spin $J_1$-$J_2$-like interaction

Difficult to distinguish these two scenarios in Fe pnictides

AFM ordering vector = Fermi surface nesting vector

LaOFeAs

AFM vector $q = (0, \pi)$

nesting vector $q = (0, \pi)$
Favor the strong coupling scenario

AFM ordering vector ≠ Fermi surface nesting vector

FeTe

AFM vector

\[ q = (\pi/2, \pi/2) \]

nesting vector

\[ q = (0, \pi) \]
Stoichiometric Fe-Se materials

- Monolayer FeSe
- Multi-layer FeSe
- Bulk FeSe
- $\text{KFe}_2\text{Se}_2$
- $\text{KFe}_{1.5}\text{Se}_2$
- $\text{K}_{0.8}\text{Fe}_{1.6}\text{Se}_2 \ (\text{K}_2\text{Fe}_4\text{Se}_5)$
Electronic structure of non-magnetic KFe$_2$Se$_2$

XW Yan et al, PRB 84, 045502 (2011)  
D Mou et al, PRL 106, 107001 (2011)
KFe$_{1.5}$Se$_2$ is a collinear AFM semiconductor

Yan, Gao, Lu, Xiang, PRL 106, 087005 (2011)
Comparison with experiments

KFe$_{1.5}$Se$_2$ is a collinear AFM semiconductor:

no Fermi surface nesting

**ARPES**

Band gap: $>40$ meV

**Neutron scattering**

Ordering moment: $2.8 \mu_B$/Fe

F Chen et al, PRX 1, 021020 (2011)

J. Zhao et al, PRL 109, 267003 (2012)
$K_{0.8}Fe_{1.6}Se_2 : \sqrt{5} \times \sqrt{5}$ cluster AFM ordered semiconductor

Ordering moment:

- **DFT**: $m = 3.37 \mu_B / Fe$
- **Neutron**: $m = 3.31 \mu_B / Fe$

Yan, Gao, Lu, Xiang, PRB 83, 233205 (2011)
### Stoichiometric Fe-Se materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Ground State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolayer FeSe</td>
<td>Collinear AFM</td>
</tr>
<tr>
<td></td>
<td>semiconductor</td>
</tr>
<tr>
<td>Bilayer FeSe</td>
<td>Collinear AFM</td>
</tr>
<tr>
<td></td>
<td>semiconductor</td>
</tr>
<tr>
<td>Bulk FeSe</td>
<td>Collinear AFM</td>
</tr>
<tr>
<td></td>
<td>semi-metal</td>
</tr>
<tr>
<td>KFe\textsubscript{2}Se\textsubscript{2}</td>
<td>Collinear AFM</td>
</tr>
<tr>
<td></td>
<td>metal</td>
</tr>
<tr>
<td>KFe\textsubscript{1.5}Se\textsubscript{2}</td>
<td>Collinear AFM</td>
</tr>
<tr>
<td></td>
<td>semiconductor</td>
</tr>
<tr>
<td>K\textsubscript{0.8}Fe\textsubscript{1.6}Se\textsubscript{2}</td>
<td>Block AFM</td>
</tr>
<tr>
<td></td>
<td>semiconductor</td>
</tr>
</tbody>
</table>

AFM correlations are strong in all these materials.
<table>
<thead>
<tr>
<th>Material</th>
<th>Ground State</th>
<th>Superconducting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monolayer FeSe</td>
<td>Collinear AFM semiconductor</td>
<td>Yes upon electron doping</td>
</tr>
<tr>
<td>Bilayer FeSe</td>
<td>Collinear AFM semiconductor</td>
<td>Yes? upon doping?</td>
</tr>
<tr>
<td>Bulk FeSe</td>
<td>Collinear AFM semi-metal</td>
<td>Yes suppress AFM order</td>
</tr>
<tr>
<td>KFe$_2$Se$_2$</td>
<td>Collinear AFM metal</td>
<td>Yes by proximity to K$<em>{0.8}$Fe$</em>{1.6}$Se$_2$</td>
</tr>
<tr>
<td>KFe$_{1.5}$Se$_2$</td>
<td>Collinear AFM semiconductor</td>
<td>No</td>
</tr>
<tr>
<td>K$<em>{0.8}$Fe$</em>{1.6}$Se$_2$</td>
<td>Block AFM semiconductor</td>
<td>No</td>
</tr>
</tbody>
</table>
Summary of Part I

1. Correlation effect is strong in Fe selenide SC.

2. Theoretical results obtained with the density functional calculations agree well with experimental observations.
First principle predication of strong phonon mediated superconductors: $\text{Li}_n\text{B}_{n+1}\text{C}_{n-1}$
Physical motivation:
Creating high-Tc SC by lifting $\sigma$-bonds to the Fermi Level

- $\sigma$-bond is a strong chemical bond of singlet electron pair with strong electron-phonon interaction
- $\sigma$-electrons generally fall below the Fermi level and have no contribution to conductivity
Example: 39 K superconductivity in MgB$_2$

J. M. An et al., PRL 86, 4366 (2001)
J. Kortus et al., PRL 86, 4656 (2001)
Electron-Phonon Coupling in MgB$_2$

$\lambda = 0.87$, $\mu^* = 0.14$, $T_c = 39$ K
LiBC : insulator

Li$_{0.5}$BC: $\lambda = 1.5, \mu^* = 0.09, T_c = 100$ K

MgB$_2$: $\lambda = 0.82, \mu^* = 0.09, T_c = 39$ K

H. Rosner et al., PRL 88, 127001(2002)
A. M. Fogg et al., JACS 128, 10043(2006)
Doping LiBC by Partially Substituting C with B: $\text{Li}_n\text{B}_{n+1}\text{C}_{n-1}$

$n = 2 \quad \text{Li}_2\text{B}_3\text{C}$

Strong Electron-phonon Coupling in Li$_2$B$_3$C

<table>
<thead>
<tr>
<th></th>
<th>MgB$_2$</th>
<th>Li$_{0.5}$BC</th>
<th>Li$_2$B$_3$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>0.85</td>
<td>1.5</td>
<td>1.51</td>
</tr>
<tr>
<td>$\omega_{\text{log}}$ (meV)</td>
<td>61.85</td>
<td>68</td>
<td>45.13</td>
</tr>
<tr>
<td>$T_c$ (K)</td>
<td>39.2</td>
<td>100</td>
<td>61.4</td>
</tr>
</tbody>
</table>

![Graph showing band structure and $T_c$ as a function of $\mu^*$](image)

![Structural diagrams](image)
Electron-phonon coupling in Li$_n$B$_{n+1}$C$_{n-1}$ with $n=3$

$n = 3 \quad \text{Li}_3\text{B}_4\text{C}_2$

$\lambda = 1.055$

$\omega_{\text{log}} = 58.8 \text{ meV}$,

$T_c \sim 51 \text{ K}$
Unlike LiBC, $\text{Li}_n\text{B}_{n+1}\text{C}_{n-1}$ ($n=2, 3$) do not exist in nature. There might exist certain lattice instability in these materials. To grow bulk $\text{Li}_n\text{B}_{n+1}\text{C}_{n-1}$ ($n=2, 3$) might be difficult.

But the lattice mismatch between LiBC and these materials is very small, to grow high quality $\text{Li}_n\text{B}_{n+1}\text{C}_{n-1}$ ($n=2, 3$) films on LiBC substrate by the molecular beam epitaxial is feasible.

<table>
<thead>
<tr>
<th></th>
<th>LiBC</th>
<th>$\text{Li}_2\text{B}_3\text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$ (Å)</td>
<td>2.746</td>
<td>2.843</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>7.018</td>
<td>7.124</td>
</tr>
<tr>
<td>$c/a$ (Å)</td>
<td>2.556</td>
<td>2.506</td>
</tr>
<tr>
<td>$z_{\text{Li}}$</td>
<td>0.25/0.75</td>
<td>0.2547/0.7453</td>
</tr>
</tbody>
</table>
To lift the strong $\sigma$-bonding bands to the Fermi level is a good way to produce high-$T_c$ superconductors.

Li$_2$B$_3$C and Li$_3$B$_4$C$_2$ are two such candidates.