Electronic structure and magnetic properties of LaFeAsO- and FeSe- based superconductors

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Crystal structures of Fe-based superconductors

LaFeAsO(F)  
Ba(K)Fe$_2$As$_2$

LiFeAs  
FeSe(Te)
Phase diagram of LaFeAsO(F) system

Block diagram of *ab-initio* Full-Potential LMTO calculations within LSDA-DFT theory

\[
[T + V(r) + \int \frac{2\rho(r')}{|r-r'|} dr' + \mu_{xc}(\rho)]\psi_i = \epsilon_i \psi_i
\]

\[
\rho(r) = \sum_i |\psi_i(r)|^2
\]

\[
E_{tot} = \sum_i^{occ} \epsilon_i - F[\rho]
\]

Converged \(E_{tot}\)?

\(E_{tot},\ DOS(E),\ magnetic\ moment,\ susceptibility\)
Density of states of LaFeAsO(F)
Volume dependence of magnetic moment of LaFeAsO
Phase diagram 1 of FeTe(Se) system

Phase diagram 2 of FeTe(Se) system

Concentration dependence of $T_C$ and magnetic susceptibility of the normal state
Temperature dependence of magnetic susceptibility of FeSe(Te) compounds

\[
\chi (10^{-3} \text{ emu/mol})
\]

- **FeTe (S)**
- **FeTe_{0.95} (P)**

\[
H=30 \text{ kOe (}||\text{ab)}
\]

- **FeSe_{0.2} Te_{0.8}**
- **FeSe_{0.5} Te_{0.05}**

\[
T (K)
\]
Temperature dependence of the magnetic susceptibility of FeSe
Pressure dependence of the magnetic susceptibility of FeTe
Pressure dependence of the magnetic susceptibility of FeSe
Pressure derivative of the magnetic susceptibility $d \ln \chi / dP \ (10^{-2} \text{ GPa}^{-1})$ for FeSe and FeTe compounds at different temperatures.

<table>
<thead>
<tr>
<th>$T$(K)</th>
<th>$d \ln \chi / dP$ FeSe</th>
<th>$d \ln \chi / dP$ FeTe $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>experiment:</td>
<td>300</td>
<td>$-6.5 \pm 1$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sim -7 \ ^a$</td>
</tr>
<tr>
<td></td>
<td>78</td>
<td>$10 \pm 3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\sim 6.5 \ ^a$</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>theory:</td>
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<td>$\sim 8$</td>
</tr>
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</table>
Band structure of FeSe compound
Density of states of FeSe compound
Dependence of density of states at Fermi energy for FeTe on volume and parameter $Z$.

Diagram (a) shows the variation of DOS (Ry$^{-1}$·cell$^{-1}$) with volume $V$ (Å$^3$) for $Z_x = 0.25$. Diagram (b) displays the DOS variation with $Z_X$ for $V_{cell} = 90.9$ Å$^3$. The diagrams illustrate the linear relationship between DOS and the respective parameters.
Pressure dependence of the internal chalcogen structural parameter $Z$ for FeSe
Calculated pressure dependencies of the density of states at the Fermi level for FeSe. (The solid lines are guides for the eye).
Pressure dependence of the superconducting transition temperature of FeSe

![Graph showing the pressure dependence of the superconducting transition temperature of FeSe. The graph plots $T_c$ (K) against P (GPa) with data points and a trend line.](a)
Calculated temperature dependence of the paramagnetic susceptibility of FeSe
Paramagnetic susceptibility of FeSe vs. unit cell volume. Arrows indicate theoretical (1) and experimental (2) volumes.

Paramagnetic susceptibility of FeSe vs. parameter $Z$ for the experimental volume. Arrow indicates the experimental $Z$. 
Main mechanisms for pressure effect on the magnetic susceptibility of FeSe

\[
\frac{d \ln \chi}{dP} = \frac{\partial \ln \chi}{\partial \ln V} \times \frac{\partial \ln V}{\partial P} + \frac{\partial \ln \chi}{\partial Z_X} \times \frac{d Z_X}{dP}
\]

\[
\frac{\partial \ln \chi}{\partial \ln V} \approx 8 \text{ (theory)}, \quad \frac{\partial \ln V}{\partial P} \approx -3 \cdot 10^{-2} \text{ GPa}^{-1} \text{ (exp)}
\]

\[
\frac{\partial \ln \chi}{\partial Z_X} \approx 65 \text{ (theory)}, \quad \frac{d Z_X}{dP} \approx 0.55 \cdot 10^{-2} \text{ GPa}^{-1} \text{ (fit)}
\]

\[
\frac{\partial \ln \chi}{\partial \ln V} \times \frac{\partial \ln V}{\partial P} \approx -24 \cdot 10^{-2} \text{ GPa}^{-1}, \quad \frac{\partial \ln \chi}{\partial Z_X} \times \frac{d Z_X}{dP} \approx 36 \cdot 10^{-2} \text{ GPa}^{-1}
\]

\[
\frac{d \ln \chi}{dP} \approx 12 \cdot 10^{-2} \text{ GPa}^{-1} \text{ (theory)}
\]

\[
\frac{d \ln \chi}{dP} = 8 \cdot 10^{-2} \text{ GPa}^{-1} \text{ (exp)}
\]
Band structure of FeTe compound
Density of states of FeTe compound
Magnetovolume effect in FeTe

$$\frac{\Delta V}{V} \equiv \omega_m (T) = \frac{C}{B} M^2 (T)$$

$$\frac{C}{B} = - \frac{1}{2 \chi V} \frac{d \ln \chi}{dP}$$

$$M(0) \sim 2 \mu_B / \text{Fe}$$

$$\omega_m (0) \sim -0.02$$
Calculated total energy vs. volume for FeTe in the **monoclinic** (solid line) and **tetragonal** (dashed line) structures. The lattice parameters are fixed to experimental ambient pressure values at the phase transition point.
Paramagnetic susceptibility of FeTe versus unit cell volume. The arrows indicate the theoretical (1) and experimental (2) volumes.

Paramagnetic susceptibility of FeTe as function of $Z_X$ for the optimized unit cell volume.
Main mechanisms for pressure effect on the magnetic susceptibility of FeTe

\[
\frac{d \ln \chi}{dP} = \frac{\partial \ln \chi}{\partial \ln V} \times \frac{\partial \ln V}{\partial P} + \frac{\partial \ln \chi}{\partial Z_X} \times \frac{d Z_X}{dP}
\]

\[
\frac{\partial \ln \chi}{\partial \ln V} \sim 40 \text{ (theory)}, \quad \frac{\partial \ln V}{\partial P} \approx 3.0 \text{ Mbar}^{-1} \text{ (exp)}
\]

\[
\frac{\partial \ln \chi}{\partial Z_X} \sim 350 \text{ (theory)}, \quad \frac{d Z_X}{dP} \approx 0.40 \text{ Mbar}^{-1} \text{ (fit)}
\]

\[
\frac{\partial \ln \chi}{\partial \ln V} \times \frac{\partial \ln V}{\partial P} \sim -120 \text{ Mbar}^{-1}, \quad \frac{\partial \ln \chi}{\partial Z_X} \times \frac{d Z_X}{dP} \sim 140 \text{ Mbar}^{-1}
\]

\[
\frac{d \ln \chi}{dP} \sim 20 \text{ Mbar}^{-1} \text{ (theory)}
\]

\[
\frac{d \ln \chi}{dP} = 20 \div 25 \text{ Mbar}^{-1} \text{ (exp)}
\]
Conclusions

• V-shaped minimum and local maximum in DOS(E) in vicinity of $E_F$ can govern magnetic properties of LaFeAsO under fluorine doping and/or oxygen deficiency.
• A substantial and puzzling growth of susceptibility with temperature is revealed in FeSe up to 300 K.
• The observed anisotropy of susceptibility is very large in FeSe, and comparable with the averaged susceptibility at low temperatures.
• Magnetic susceptibility in FeSe(Te) is found to increase gradually with Te content in about ten times.
• Ab initio calculations of paramagnetic susceptibility of LaFeAsO, FeSe and FeTe have revealed that these systems are in close proximity to quantum critical point.
• The strong positive pressure effect on $\chi$ is observed in FeSe and FeTe at low temperatures. At room temperature this effect is also strong, but negative in FeSe. The established large positive pressure effect on $\chi$ at low temperatures is related to the strong sensitivity of susceptibility to the height of Se (Te) species from the Fe plane, determining the dominant positive contribution to $\text{dln} \chi / \text{dP}$.
• Behavior of the superconducting transition temperature of FeSe with pressure correlates with density of electronic states at Fermi level.
Phase diagram of FeSe system

Magnetization of FeSe(Te)

(a) FeSe$_{0.963}$ (P)

- $H \parallel c$
  - $5\,K$ (circles)
  - $110\,K$ (green squares)
  - $270\,K$ (red triangles)

(b) FeTe$_{0.5}$Se$_{0.5}$ (S)

- $H \parallel c$
  - $20\,K$ (circles)
  - $110\,K$ (green squares)
  - $200\,K$ (red triangles)

(c) FeTe (S)

- $H \parallel c$
  - $4.2\,K$ (circles)
  - $110\,K$ (green squares)
  - $200\,K$ (red triangles)

(d) FeTe$_{0.95}$ (P)

- $H \parallel c$
  - $5\,K$ (circles)
  - $110\,K$ (green squares)
  - $250\,K$ (red triangles)
Magnetization of FeSe and FeTe

$M$ (emu/mol) vs. $H$ (kOe)

$T=5$ K, $H \parallel c$

FeSe

FeTe
Concentration dependence of the magnetic susceptibility in FeSe(\(Te\)) at \(T=0\) K and 300 K
Temperature dependencies of the NMR Knight shift $K$ in FeSe measured at ambient pressure (solid line) and at $P=1.4$ GPa (dashed line). The inset shows dependence of $K$ on the averaged magnetic susceptibility for FeSe.
Magnetic susceptibility $\chi$ (in $10^{-3}$ emu/mol) and its pressure derivative $d \ln \chi / dP$ (Mbar$^{-1}$) at different temperatures for polycrystalline FeTe$_{0.95}$ and single-crystalline FeTe compounds.

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<tr>
<th></th>
<th>FeTe$_{0.95}$</th>
<th>FeTe</th>
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<tbody>
<tr>
<td>$\chi$</td>
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</tr>
<tr>
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<tr>
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<td>$30 \pm 1.5$</td>
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