Exploring FeSi(Ge) as new conductive layers for iron-based superconductors

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Outline

✓ Introduction
✓ LaFeSiH
  - Crystal structure
  - Non-conventional superconductivity
  - Analogy with As SC
✓ RFeSiH (R = Ce-Tb)
  - Synthesis
  - Magnetic properties
✓ Competition between FM and SC in Fe-based germanides and silicides
  - “122” family: CaFe$_2$As$_2$ vs YFe$_2$Ge$_2$
  - “1111” family: LaFeAsO vs LaFeSiH
✓ Conclusion
Crystal structures of iron-based superconductors

FePn or FeCh conductive layers with Fe square planar lattice

As and Se are toxic

Can Fe be associated to another element than a Pn/Ch to get superconductivity?

“1111” iron-based superconductors

- Usually obtained by solid state reaction (+ high pressure)

<table>
<thead>
<tr>
<th>Year</th>
<th>Compound</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2006</td>
<td>LaFePO</td>
<td>5</td>
</tr>
<tr>
<td>2008</td>
<td>LaFeAsO$_{1-x}$F$_x$</td>
<td>26</td>
</tr>
<tr>
<td>2008</td>
<td>SmFeAsO$_{1-x}$F$_x$</td>
<td>43-56</td>
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<tr>
<td>2011</td>
<td>CeFeAsO$_{1-x}$H$_x$</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>CaFeAsF$_{1-x}$H$_x$</td>
<td>55</td>
</tr>
<tr>
<td>2014</td>
<td>Ca$_{1-x}$La$_x$FeAsH</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>CaFe$_{1-x}$Co$_x$AsH</td>
<td>23</td>
</tr>
</tbody>
</table>
LaFeSi intermetallic

Melting in arc furnace

High T° annealing
Solid gas hydrogenation of LaFeSi

LaFeSi → 1111-type hydride by solid gas hydrogenation

5-10 bars H₂
250°C

LaFeSiH

→ 1111-type hydride by solid gas hydrogenation
Crystal structure of LaFeSiH

→ Hydrogenation of LaFeSi

Single-crystal diffraction
(hk0) plane
$P4/nmm$

Powder neutron diffraction

→ H atoms in [La$_4$]

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>2c</td>
<td>1/4</td>
<td>1/4</td>
<td>0.6722(1)</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td>2a</td>
<td>3/4</td>
<td>1/4</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Si</td>
<td>2c</td>
<td>1/4</td>
<td>1/4</td>
<td>0.1500(5)</td>
<td>1</td>
</tr>
<tr>
<td>H</td>
<td>2b</td>
<td>3/4</td>
<td>1/4</td>
<td>1/2</td>
<td>1.01(2)</td>
</tr>
</tbody>
</table>
Crystal structure of LaFeSiH

Hydrogenation

- $a$: 4.098 → 4.027 Å
- $c$: 7.133 → 8.014 Å

- increase of the distances between [La$_4$] and [Si$_4$Fe$_4$] layers
- increase of the two-dimensional character of the structure

$d_{\text{Fe-Fe}}$ from 2.90 to 2.85 Å as in LaFeAsO
Electrical resistivity

- Onset of superconductivity at $T_c \approx 11$ K
- Fermi-liquid behavior between 11 and 25 K

Iron-based superconductivity extended to the novel silicide LaFeSiH
LaFeSiH: Magnetization measurement

- Diamagnetic signal $\rightarrow$ superconducting volume fraction $\sim 100$
  $\rightarrow$ Bulk superconductivity

- Strong negative slope of $M(H)$ curve
- $H_{c1} \approx 5$ Oe as lower bound value

Coll. Néel Institute
Effect of magnetic field and pressure on $T_c$

- Werthamer-Helfand-Hohenberg formula:
  \[ H_{c2} (0) = -0.69 \, T_c \, dH_{c2}(T)/dT \mid_{T_c} \]
  → upper critical field $H_{c2} (0) \approx 17 \, T$
  → correlation length
  \[ \xi(0) = \left( \frac{\Phi_0}{2\pi \, H_{c2} (0)} \right)^{1/2} = 4.3 \, \text{nm} \]

Field in the $ab$ plane

- Decrease of $T_c$ with pressure
LaFeSiH: A non conventional superconductor

- McMillan’s equation from electron-phonon coupling $\lambda$ and typical Coulomb repulsion $\mu^*=0.15$: maximum $T_c$ of 2 K (Tc=10.9 K for $\mu^*=0$)
  $\rightarrow$ Non conventional electron-phonon mediated superconductivity
- Corroborated by preliminary penetration depth measurements vs $T$

*First-principle study of magnetism, lattice dynamics, and superconductivity in LaFeSiHx*
• Metallic behavior
• Multiband character
• Fe 3d orbitals dominates at the Fermi level $E_F$

Fermi surface:
• Three hole bands/ two electron bands
• Quasi two-dimensional character of the Fermi surface
• Similarity with LaFeAsO

Coll. F. Bernardini (univ. of Cagliari)
Wien2K code
Effect of pressure on crystal and magnetic structure

DFT calculation as function of pressure: AFM single stripe state as lowest energy state which is suppressed by external pressure and reemerges at higher pressure

X-ray synchrotron measurements:
Orthorhombic distortion at 15 K which is suppressed by increasing pressure and reemerges at higher pressure

→ Magnetostructural interplay

Iron-based superconductivity extended to the novel silicide LaFeSiH
Relationship between structure and $T_c$

- 3d orbitals of Fe are sensitive to change in the symmetry of FeAs$_4$ tetrahedron

$$h_{\text{Fe-Si}} = 1.20 \text{ Å} \quad \text{(ideal 1.38 Å)}$$

$$\alpha = 118.3^\circ \quad \text{(ideal 109.5°)}$$

→ **Increase** $h_{\text{Fe-Si}}$
LaFeSiH
First silicide Fe-based superconductor
\( T_c = 10 \text{ K} \)

\( R \text{FeSiH} \)
Melting + hydrogenation

LaFe(Si,Ge)H
Melting + hydrogenation & high-pressure

LaFeSi(H,O,F)
Fluorination | electrochemistry & high pressure

La(Fe,Co,Ni,Mn)SiH
Melting + hydrogenation

\( R \text{FeSiH} \)
RFeSiH
Synthesis of RFeSiH hydrides

- In RFeAsO$_{1-x}$ or RFeAsO$_{1-x}$F$_x$ Tc increases from La to Nd/Sm (pressure effect)

RFeSiH samples were prepared as LaFeSiH
Synthesis of RFeSiH hydrides

- In RFeAsO$_{1-x}$ or RFeAsO$_{1-x}$F$_x$ Tc increases from La to Nd/Sm (pressure effect)

\[
\begin{array}{ccccccccccccccc}
Y & La & Ce & Pr & Nd & Pm & Sm & Eu & Gd & Tb & Dy & Ho & Er & Tm & Yb & Lu
\end{array}
\]

Intermediate valence for Ce?
CeFeSiH

- CeFeSi: non magnetic Intermediate valence
- CeFeSiH: no diamagnetic signal on the M(T) curve
  No anomaly on the specific heat measurement
  → no magnetic order above 2K
  → no superconductivity

R. Welter, G. Venturini, B. Malaman
NdFeSi ferro at $T_C = 25 \text{ K}$

R. Welter, G. Venturini, B. Malaman

$\rightarrow$ NdFeSiH ferro at $T_C = 17 \text{ K}$
SmFeSiH: ferro at $T_C = 40\, K$

R. Welter, G. Venturini, B. Malaman

→ SmFeSiH: ferro at $T_C = 10\, K$
GdFeSiH - TbFeSiH

GdFeSi:
Ferro $T_C = 135$ K

GdFeSiH:
ferro $T_C = 20$ K

TbFeSi:
Ferro $T_C = 105$ K

TbFeSiH:
ferro $T_C = 32$ K

→ Strong reduction of the ordering temperature upon hydrogenation but no superconductivity

R. Welter, G. Venturini, B. Malaman
# Summary on RFeSiH hydrides

- Synthesis of RFeSiH hydrides from La to Tb
- Decrease of the ferromagnetic ordering temperature upon hydrogenation
- No superconductivity unlike in arsenides

→ pressure effect

→ magnetism of the rare-earth lattice with strong FM tendency
Competition between FM and SC in Fe-based germanides and silicides

Only 2 examples of SC: LaFeSiH and YFe$_2$Ge$_2$
“122” compounds: CaFe$_2$As$_2$ vs YFe$_2$Ge$_2$

- Doped-CaFe$_2$As$_2$ and YFe$_2$Ge$_2$ ($T_c \approx 1.8$ K) are superconductors

- Analyze of the relation between YFe$_2$Ge$_2$ and CaFe$_2$As$_2$ (collapse form) via
  - the new compound CaFe$_2$Ge$_2$
  - the “hypothetical” compound YFe$_2$As$_2$

“122” compounds: CaFe$_2$As$_2$ vs YFe$_2$Ge$_2$

→ Changing first the Fe ligand

DOS($E_F$)=2.7 eV$^{-1}$

DOS($E_F$)=10.2 eV$^{-1}$

→ Stoner instability

DOS($E_F$)=7.2 eV$^{-1}$

Coll. F. Bernardini (univ. of Cagliari)
WIEN2K code
Magnetic state of CaFe$_2$Ge$_2$

Spin-polarized calculations

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E$ (meV/Fe) $\mu_{Fe}$ ($\mu_B$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>checkerboard</td>
<td>-99.2</td>
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<tr>
<td>single-stripe</td>
<td>-112.5</td>
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<tr>
<td>double-stripe</td>
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<tr>
<td>A-AFM</td>
<td>-116.5</td>
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<tr>
<td>FM</td>
<td>-132.6</td>
</tr>
</tbody>
</table>

→ Substitution of As by Ge enhances the FM tendency

→ Substitution of Ca by Y reduces the FM tendency and favors the competition between magnetic orders

Magnetization measurements

H = 1 kOe
“122” compounds: CaFe$_2$As$_2$ vs YFe$_2$Ge$_2$

→ Changing first the spacer ion

Close to QCP

AFM
CaFe$_2^{2+}$As$_2$ ↔ YFe$_2^{2.5+}$Ge$_2$

Non mag.

Spin-polarized calculations

<table>
<thead>
<tr>
<th>YFe$_2$As$_2$</th>
<th>ΔE (meV/Fe)</th>
<th>μ$_{Fe}$ (μ$_B$)</th>
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</thead>
<tbody>
<tr>
<td>checkerboard</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>single-stripe</td>
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</tr>
<tr>
<td>double-stripe</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>A-AFM</td>
<td>133.8</td>
<td>1.64</td>
</tr>
<tr>
<td>FM</td>
<td>106.5</td>
<td>1.64</td>
</tr>
</tbody>
</table>

→ Non-magnetic ground state

DOS(E$_F$)=5.0 eV$^{-1}$ → Weakening of the FM instability

DOS(E$_F$)=7.2 eV$^{-1}$
"122" compounds: CaFe$_2$As$_2$ vs YFe$_2$Ge$_2$

→ Substitution of As by Ge enhances the FM tendency

→ Substitution of Ca by Y reduces the FM tendency, the non-magnetic YFe$_2$Ge$_2$ can be SC
“1111” compounds: LaFeAsO vs LaFeSiH

- Doped-LaFeAsO and LaFeSiH are superconductors
- Analyze of the relation between LaFeAsO and LaFeSiH *via*
  - the “hypothetical” compound LaFeSiO
"1111" compounds: LaFeAsO vs LaFeSiO

LaFeAsO:
Single striped AFM state with no FM solution

→ Substitution of As by Si introduces a FM tendency
→ FS unfavorable for SC

→ Shift upwards of the band structure
→ Modification of the FS
→ Similar DOS(E_F)

Coll. F. Bernardini (univ. of Cagliari)
WIEN2K code
“1111” compounds: LaFeSiO vs LaFeSiH

LaFeAsO:
Single striped AFM state with no FM solution

LaFeSiH:
<table>
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<tr>
<th></th>
<th>$\Delta E$ (meV/Fe)</th>
<th>$\mu_{Fe}$ ($\mu_B$)</th>
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<tbody>
<tr>
<td>checkerboard</td>
<td>-5.71</td>
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<tr>
<td>FM</td>
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<tr>
<td>single-stripe</td>
<td>-44.56</td>
<td>1.16</td>
</tr>
</tbody>
</table>

→ Substitution of O by H restores a single-stripe AFM state

→ FS favorable for SC

→ Shift back of the band structure
→ FS is restored
“1111” compounds: LaFeAsO vs LaFeSiH

LaFe$^{2+}$AsO $\rightarrow$ LaFe$^{3+}$SiO $\rightarrow$ LaFe$^{2+}$SiH

$\rightarrow$ Substitution of As by Si enhances the FM tendency

$\rightarrow$ Substitution of O by H reduces the FM tendency

For the 122 and 1111 compounds the ion in the spacer layer can be used to counterbalance the FM tendencies induced by Si/Ge ligands.

Conclusion

- Novel iron based superconductor LaFeSiH/new original way of synthesis

- Superconductor free of toxic pnictogen/chalcogen element → FeSi as new superconducting layer in the family of Fe-based SC
  - Coexistence between magnetic order/superconductivity?
  - Superconducting gap symmetry?

- Novel RFeSiH (R= Ce-Tb) silicides with ferromagnetism

- The substitution of As by Si(Ge) induces FM tendencies that can be counterbalanced by ion substitution in the spacer layer
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Thanks for your attention!