CBPF - National Institute/MCT

Rio de Janeiro

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Magnetic and Structural Transitions in the New Fe-pnictide Superconductors

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CIAM Collaboration Program (NSF/CNPq)
Discoverer. Hideo Hosono, a materials scientist at the Tokyo Institute of Technology, cooked the first of the new superconductors that have captivated researchers the world over.

**Hideo Hosono** started with Iron-Based Layered SC: \( \text{LaOFeP} \) (\( T_c = 6 \text{K} \)) to \( \text{SmFeAsO}_{1-x} \) (\( T_c = 55 \text{K} \))
Iron-based layered compound LnOFeAs “1111 phase”

The discovery of superconductivity in fluorine doped LaFeAsO superconductor with $T_c = 26$ K* has generated enormous interests in the community of superconductivity

F-substitution
LaFeAsO$_{1-x}$F$_x$

LaOFeAs $\rightarrow$ (T$_c$ = 26 K) SC under
- doping with F$^-$
- oxygen deficiency

O-deficiency
LnFeAsO$_{1-y}$

T$_c$ = 55 K in SmFeAsO$_{1-\delta}$

Ln substitution (Gd$^{3+}$→Th$^{4+}$)

T$_c$ up to 56K for (Gd,Th)FeAsO
Cao Wang et al EPL 83 67006 (2008)

*Y. Kamihara, et al,

The crystal is composed of a stack of alternating REO or A and FeAs layers.

In 2008
More than 700 papers

Increase of $T_C$ of RE(0,F)FeAs superconductor after announcement by Hosono on Feb., 2008, made by Chinese physicists including PI Wang and LE Wen
# Catalogue of Fe-based Superconductors

## Fe-111

### LnFePO

Tc~5-6 K (Tc~8.8K at Pressure ~0.8 GPa)

### LnFeAsO\(_{1-x}\)F\(_x\)

- LaFeAsO\(_{1-x}\)F\(_x\) x=0.11, Tc~26K (Tc~43K at P~4GPa)
- CeFeAsO\(_{1-x}\)F\(_x\) x=0.16, Tc~41K
- SmFeAsO\(_{1-x}\)F\(_x\) x=0.10, Tc~43K
- NdFeAsO\(_{1-x}\)F\(_x\) x=0.11, Tc~52K
- PrFeAsO\(_{1-x}\)F\(_x\) x=0.11, Tc~52K
- TbFeAsO\(_{1-x}\)F\(_x\) Tc~46K (x=0.1, 0.2)
- DyFeAsO\(_{1-x}\)F\(_x\) Tc~45K (x=0.1, 0.2)

### LnFeAsO\(_{1-x}\)

- LaFeAsO\(_{1-x}\) 31.2
- CeFeAsO\(_{1-x}\) 46.5
- PrFeAsO\(_{1-x}\) 51.3
- NdFeAsO\(_{1-x}\) 53.5
- SmFeAsO\(_{1-x}\) 55.0
- GdFeAsO\(_{1-x}\) 53e
- TbFeAsO\(_{1-x}\) 52
- DyFeAsO\(_{1-x}\) 52

### (Ln,RE)FeAs

- (La\(_{1-x}\),Sr\(_x\))FeAsO Tc~ 25K(x=0.13), hole-doping
- Gd\(_{1-x}\),Th\(_x\))FeAsO Tc~56K (x=0.2), electron-doping

## Fe-122

### Ca(Sr)FeAsF

- Ca(Fe\(_{1-x}\),Co\(_x\))AsF Tc~22K (x=0.10) [Ni\(^{2+}\)\((3d^7)\rightarrow\)Fe\(^{2+}\)\((3d^6)\)]
- Ca(Fe\(_{1-x}\),Ni\(_x\))AsF Tc~12K (x=0.05) [Ni\(^{2+}\)\((3d^8)\rightarrow\)Fe\(^{2+}\)\((3d^6)\)]

### CaFe\(_2\)As\(_2\)

- Tc~27K (Pressure~3.0 GPa)
  - (Ba\(_{1-x}\),K\(_x\))Fe\(_2\)As\(_2\) Tc~38K (x=0.4)
  - (Sr\(_{1-x}\),Na\(_x\))Fe\(_2\)As\(_2\) Tc~37K (x=0.4)
  - Ba(Fe\(_{1-x}\),Co\(_x\))\(_2\)As\(_2\) Tc~22K (x=0.1)

## Fe-111

### Li\(_{1-x}\)FeAs

Tc~18K

### Sc 42622

- V 42622

### Fe-42622

### Fe-11

### FeSe

- FeSe\(_{1-x}\) Tc~8K (x=0.88), Tc~27 K (P~1.48 GPa)
- FeSe\(_{1-x}\)Te\(_x\) Tc~15K
- FeTe\(_{1-x}\)S\(_x\) Tc~10K (x=0.2), non-toxic

## Fe-1111

### RFeAsO\(_{1-x}\)F\(_x\)

### AFe2As2

### Sr\(_4\)A\(_2\)O\(_6\)Fe\(_2\)As\(_2\)
Catalogue of Fe-based Superconductors

**Fe-1111**

- **LnFePO**
  - $T_c \approx 5-6$ K ($T_c \approx 8.8$ K at Pressure $\approx 0.8$ GPa)

- **LnFeAsO$_{1-x}$F$_x$**
  - $LaFeAsO_{1-x}F_x$: $x=0.11$, $T_c \approx 26$ K ($T_c \approx 43$ K at P $\approx 4$ GPa)
  - $CeFeAsO_{1-x}F_x$: $x=0.16$, $T_c \approx 41$ K
  - $SmFeAsO_{1-x}F_x$: $x=0.10$, $T_c \approx 43$ K
  - $NdFeAsO_{1-x}F_x$: $x=0.11$, $T_c \approx 52$ K
  - $PrFeAsO_{1-x}F_x$: $x=0.11$, $T_c \approx 52$ K
  - $TbFeAsO_{1-x}F_x$: $T_c \approx 46$ K ($x=0.1$, 0.2)
  - $DyFeAsO_{1-x}F_x$: $T_c \approx 45$ K ($x=0.1$, 0.2)

- **LnFeAsO$_{1-x}$**
  - $LaFeAsO_{1-x}$: 31.2
  - $CeFeAsO_{1-x}$: 46.5
  - $PrFeAsO_{1-x}$: 51.3
  - $NdFeAsO_{1-x}$: 53.5
  - $SmFeAsO_{1-x}$: 55.0
  - $GdFeAsO_{1-x}$: 53e
  - $TbFeAsO_{1-x}$: 52
  - $DyFeAsO_{1-x}$: 52

- **(Ln,RE)FeAs**
  - $(La_{1-x}Sr_x)FeAsO$: $T_c \approx 25$ K ($x=0.13$), hole-doping
  - $(Gd_{1-x}Th_x)FeAsO$: $T_c \approx 56$ K ($x=0.2$), electron-doping

**Fe-122**

- **Ca(Sr)FeAsF**
  - $Ca(Fe_{1-x}Co_x)AsF$: $T_c \approx 22$ K ($x=0.10$)
  - $[Ni^{2+}(3d^7) \rightarrow Fe^{2+}(3d^6)]$
  - $Ca(Fe_{1-x}Ni_x)AsF$: $T_c \approx 12$ K ($x=0.05$)
  - $[Ni^{2+}(3d^8) \rightarrow Fe^{2+}(3d^6)]$

- **CaFe$_2$As$_2$**
  - $T_c \approx 27$ K (Pressure $\approx 3.0$ GPa)
  - $(Ba_{1-x}K_x)Fe_2As_2$: $T_c \approx 38$ K ($x=0.4$)
  - $(Sr_{1-x}Na_x)Fe_2As_2$: $T_c \approx 37$ K ($x=0.4$)
  - $Ba(Fe_{1-x}Co_x)_2As_2$: $T_c \approx 22$ K ($x=0.1$)

**Fe-111**

- **Li$_{1-x}$FeAs**
  - $T_c \approx 18$ K

**Fe-42622**

- **Sc 42622**
- **V 42622**

**Fe-11**

- **FeSe$_{1-x}$**
  - $T_c \approx 8$ K ($x=0.88$), $T_c \approx 27$ K (P $\approx 1.48$ GPa)

- **FeSe$_{1-x}Te_x$**
  - $T_c \approx 15$ K

- **FeTe$_{1-x}S_x$**
  - $T_c \approx 10$ K ($x=0.2$), non-toxic

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HFI-NQI 2010, 12-17 September 2010  CERN, Geneva
Ceramic polycrystalline specimens of $\text{RFeAsO}_{1-x}F_x$ (R=Nd, Ce) were synthesized by G F Cheng and N. L. Wang at Institute of Physics, Chinese Academy of Sciences, Beijing.

Single crystals of $\text{AFe}_2\text{As}_2$ (A=Ca, Ba, K) were synthesized at Ames National Lab., Ames, USA and N. L. Wang.

$\text{Sr}_4\text{A}_2\text{O}_6\text{Fe}_2\text{As}_2$ (A=Sc, V) Oxypnictides polycrystalline specimens were provided by Hai-Hu Wen, from National Lab. Superconductivity, Beijing.

µSR performed by Uemura group in TRIUMF on some samples with participation of Julian Munevar and Dalber Sanchez.

Mössbauer experiments were performed at CBPF, Rio de Janeiro with an Oxford cryostat in sinusoidal mode with transmission geometry, with $^{57}\text{Co}:\text{Rh}$ source and sample at the same T.
Previous Studies

Mössbauer Spectroscopy in $\text{RNi}_2\text{B}_2\text{C}$ and $\text{RNiBC}$ with $^{57}\text{Fe}$ at Ni site

- information about local symmetry and magnetic order
- $B_{hf}$ at the $^{57}\text{Fe}$ nucleus, due to non collinear AF spin structure of the RE moments, acts as a pair-breaking field at the Ni site

✓ Magnetism is due exclusively to R magnetic moments:
  AF, FM, WFM, and SDW determined by coupling of R layers
Reentrant behavior and incommensurate modulated magnetic structure for $4.6 \leq T \leq 6$ K.

Evidence of pair-breaking field at the Ni (Fe).

$B_{hf} = B_{thf} = \sum \alpha_i \vec{s}_i$

No $B_{hf}$ field was observed at any temperature below $T_N$ for the AFM superconductors $\text{ErNi}_2\text{B}_2\text{C}$ and $\text{DyNi}_2\text{B}_2\text{C}$
**Structures of Fe-As: RFeAO, AFe$_2$As$_2$ and Sr$_4$A$_2$O$_6$Fe$_2$As$_2**

Structure: Tetragonal $P4/nmm$  
Structural transition: $\sim 155K$  
Magnetic ordering: $\sim 140K$  
Superconductor: with F dop & O deficiency with K, Ca, Co doping   

Local structure at Fe site is similar different Fe moments and 3d Fe contribution in the density of states at $E_F$ level
LaOFeAs has structural distortion below ~150 K

LaOFeAs has long range SDW-type AF order at ~134 K with $\mu_{Fe}=0.36\mu_B$
**NdOFeAs and CeOFeAs**

<table>
<thead>
<tr>
<th></th>
<th>NdOFeAs</th>
<th>CeOFeAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_S$ (P/4nmm-Cmma)</td>
<td>~ 150K</td>
<td>~158K</td>
</tr>
<tr>
<td>$T_N$(Fe)</td>
<td>~ 141K</td>
<td>~ 140 K</td>
</tr>
<tr>
<td>$\mu_{Fe}$</td>
<td>~ 0.32 $\mu$B</td>
<td>~ 0.6 $\mu$B</td>
</tr>
<tr>
<td>$T_N$(R)</td>
<td>~ 2K</td>
<td>~ 4K</td>
</tr>
</tbody>
</table>


**NdFeAsO$_{1-x}$F$_x$ and CeFeAsO$_{1-x}$F$_x$**

Electron-doping by $F^-$ substituting for $O^{2-}$ increases $T_c$ to about 50 K.

NdFeAsO$_{0.88}$F$_{0.12}$ and NdFeAsO

**Room temperature MS**

RT NdFeAsO$_{0.88}$F$_{0.12}$ spectrum: unique phase, similar to that found for LaOFeAs*

$\Delta E_Q=0.02(2)$ mm/s

IS=$0.437(1)$ mm/s,

RT NdFeAsO: small impurities, FeAs ($\sim 8\%$) and FeAs$_2$ ($\sim 5\%$).

The main component (doublet) is attributed to Fe in NdFeAsO phase and their hyperfine parameters are almost the same as for NdFeAsO$_{0.88}$F$_{0.12}$

The magnetic transition at ~140K is due to the magnetic ordering of Fe moments. Below ~2K an additional increase of $B_{hf}$ at Fe due to collinear AF order of Nd moments.

\[ \Delta E_Q \rightarrow \text{measure of the As Tetrahedra} \]

**CM1:** $\theta(I) = 90 \pm 5^\circ$, commensurate AF structure with the Fe spins lying in the $(a,b)$ plane.

**CM2:** $\theta(II) \approx 55^\circ$, all angles in the range $0 \leq \theta \leq 90^\circ$ occur with equal probability.

$\mu$SR results* support our model used to analyze our Mössbauer spectra.
No hyperfine magnetic field was observed at $^{57}$Fe nucleus [$B_{hf}(1.5K) \leq 0.1T$] of Fe in superconducting NdFeAsO$_{0.88}$F$_{0.12}$ at any temperature (down to 1.5K)
Results for in CeFeAsO$_{1-x}$F$_x$

All spectra were fitted with single lines.

The Bhf field at Fe nucleus decreases with F content and disappears for $x=0.16$. Magnetism suppressed by F doping.
Mössbauer results shown a region of coexistence of superconductivity and magnetism (phase separation).

For CeOFeAs $\mu_{Fe} \approx 0.39 \mu_B$

Neutron studies
Results for CeFeAsO

Fe spins ordering at ~145K lying in the (a,b) plane

MS support the AFM ordering of Fe spins

A fraction of Fe spins tend to align parallel ($B_{\text{eff}} \sim 12\ T$) and the remaining ones antiparallel ($B_{\text{eff}} \sim 3\ T$) to the external field

$B_{\text{eff}} = B_{\text{ext}} + B_{\text{hf}}$

HFI-NQI 2010, 12-17 September 2010  CERN, Geneva
The Bhf in NdFeAsO and CeFeAsO can be associated to SDW AFM order of Fe spins below ~140 and ~145K, as seen by neutrons.

The AFM ordering of Nd and Ce spins seen by neutrons at ~2K and ~5K generate additional Bhf.

No Bhf was observed at $^{57}$Fe nucleus in NdFeAsO$_{0.88}$F$_{0.12}$ and CeFeAsO$_{0.84}$F$_{0.16}$ down 2K.

Doping with F suppresses both the magnetic order and structural distortion in favor of superconductivity.

Fe magnetic moment estimated to be ~0.35 $\mu_B$ in NdFeAsO and ~0.39 $\mu_B$ in CeFeAsO. Similar to neutron data.

Coexistence (phase separation) of SC and magnetism has been observed in CeFeAsO$_{1-x}$F$_x$ for 0.05 $\leq x \leq$ 0.11.
- Structural transition (Tetr to orthorhombic) at ~ 170K
- Order of the Fe moments, in a commensurate AF structure.

*Pressure Induced Superconductivity in CaFe$_2$As$_2$.

Milton S. Torikachvili et al., PRL 101, 057006 (2008)
CaFe$_2$As$_2$ single crystal

$\Delta E_Q = 0.207$ mm/s
$\Delta E_Q = 0.339$ mm/s
IS = 0.44 mm/s
$\Gamma = 0.26$ mm/s
$\varphi \approx 10^\circ$

Only one site at low T

$\mu_{Fe} \approx 0.66 \mu_B$ and lie in a-b plane
(agrees with neutron results)
CaFe$_2$As$_2$ (T)

Jump in $B_{hf}(T)$ at ~180K, typical for a first-order transition

Structural transition

commensurate AFM ordering with Fe spins lying in the (a,b) plane
V_{zz} in CaFe$_2$As$_2$ was found to be parallel to c.

Only one Fe site showing a first order transition at ~140K with the Fe spin lying in the (a,b) plane.

Hole doped AFe$_2$As$_2$ (with K or Na) shows a phase separation at low temperature with a fraction of Fe ions in a paramagnetic state while remaining ones have a magnetic moment reduced related to undoped, order magnetically \( T_O > T_c \).

This two phases are indistinguishable at room temperature.

Same behavior is observed for Co doped BaFe$_2$As$_2$ with the difference that in this case the doping is being performed at the Fe site.

In all the cases the doping distribution seems not to be homogeneous.
Sr₄A₂O₆Fe₂As₂ Iron Pnictides

- (so-called 42622), with a perovskite layer between FeAs layers,
  - No SDW ordering
  - No structural transition
  - Large Fe-Fe interlayer distances (~15 Å)
  - \( T_c = 37 \text{ K for } \text{SrVOFeAs} \)
  - 0.1 T transferred field to Fe in SrVOFeAs
  - No SDW in SrScOFeAs

\( \delta = 0.297(2) \text{ mm/s} \quad \Delta E_Q = -0.256(2) \text{ mm/s} \)

\( \text{Sr}_4\text{V}_2\text{O}_6\text{Fe}_2\text{As}_2 \)

\( \mu\text{SR} \) show strong static magnetism below 100 K, increasing volume fraction for low temperature
• Possible coexistence of magnetic ordering in V atoms and superconductivity in FeAs layers in SrVOFeAs

• Magnetic ordering found for SrScOFeAs does not correspond to SDW or incommensurate-commensurate magnetic ordering
Perspectives for Mössbauer in the studies of Unconventional SC

Follow details at local level of magnetic transitions

Determine the structural phase transition and any special related feature
Thank you

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CLAF-CNPq  
CLAF-CNPq / CNPq  
PNPD CNPq  
FAPERJ  
FAPERJ/PCI-CNPq  
FAPEAM  
CNPq  
BID  
CNPq-TWAS  
CLAF-CNPq  
CNPq
We are looking for Pos docs to work in:
Mossbauer, PAC, magnetization and transport under pressure
Magnetic Multilayer, SC, Oxides, Heavy Fermions!

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$T_c$ versus $c/a$ for $\text{RNi}_n\text{B}_n\text{C}$ and for $\text{CeMIn}_5$


The structural distortion from the ideal FeAs tetrahedron is critical to the superconducting transition temperature.

Fe is a Mössbauer probe.
NdFeAsO$_{0.88}$F$_{0.12}$
$\Delta E_Q = 0.02(2)$ mm/s
IS = 0.437(1) mm/s,

<table>
<thead>
<tr>
<th>Compound</th>
<th>IS (mm/s)</th>
<th>EQ (mm/s)</th>
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</thead>
<tbody>
<tr>
<td>Ba$<em>{0.5}$K$</em>{0.5}$Fe$_2$As$_2$</td>
<td>0.37</td>
<td>0.18</td>
</tr>
<tr>
<td>CaFe$_2$As$_2$</td>
<td>0.44</td>
<td>0.256(2)</td>
</tr>
</tbody>
</table>

Sr$_4$Sc$_2$O$_6$Fe$_2$As$_2$
IS = 0.465(3) mm/s
EQ = 0.186(2) mm/s

Sr$_4$V$_2$O$_6$Fe$_2$As$_2$
IS = 0.411(3) mm/s
EQ = 0.256(2) mm/s