#### **Introduction to Iron-Based Superconductors**

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### Iron



The Iron Ring: Traditionally given to Canadian engineering graduates and worn by professional engineers.



#### **Materials**



# **A Brief Introduction to Cuprates**



Doping Level

#### Discovery of Superconductivity in Fe-As Compounds

Kamihara *et al*., JACS, 2006

LaFePO,  $T_c \sim 4$ K

Kamihara, Watanabe and Hosono, JACS, Feb. 2008

 $LaFeAsO_{1-x}F_x$   $T_c=26K$ 



#### Phase Diagram of LaFeAs(O,F)

Kamihara *et al*.



The undoped compound is now known to be an antiferromagnetic metal.

### **Fe-based Superconducting Families**



Superconductivity is robust. Occurs across a broad range of compositions, including replacement of As, and doping on the Fe site.

#### **Pressure Dependence in Fe<sub>1+x</sub>Se**





# **FeSe - The "Simplest" Fe-Superconductor**

• Simple tetragonal structure, four atoms per unit cell (Hagg and Kindstrom, Z. Phys. Chem. (1933).



### **A Word About Structure**

- Large size of As<sup>3-</sup>,Se<sup>2-</sup> relative to Fe<sup>2+</sup> leads to tetrahedral structures with anion contact (edge shared tetrahedra). Tendency to high symmetry, small unit cells without structural distortion.
- Cuprates, etc. are based on corner shared units, with resulting tendency to complex structure distortions. The interplay with properties greatly complicates the physics.



#### **A Word About Structure**



#### **Perovskite Tilt Modes**

• Corner sharing polyhedra with even numbered rings.



### **Phonons and Electron-Phonon Interaction**

- First principles calculations allow direct calculation of pairing interaction, and almost first principles calculation of  $T_{c}$ .
- Calculations show weak coupling, no superconductivity ( $\lambda_{ep} \sim 0.2$ ).



- Fe/As phonons are below 300 cm<sup>-1</sup>.
- Corresponding Ni compounds, LaNiPO, LaNiAsO, BaNi<sub>2</sub>As<sub>2</sub>... are electron-phonon superconductors!
- Fe compounds are not electron-phonon superconductors.

Boeri, et al., PRL (2008); also Mazin, et al., PRL (2008).

#### **LDA Electronic Structure of FeSe**

- A rather ionic material Fe<sup>2+</sup> and Se<sup>2-</sup> with some hybridization, as in an oxide → metallic sheets of Fe<sup>2+</sup> modified by interaction of anions.
- Pauling electronegativities: Fe = 1.83; Se = 2.55; As = 2.18.



### **Arsenide Electronic Structure: LaFeAsO**

- LaFeAsO: Rather ionic electronic structure: O<sup>2-</sup>, As<sup>3-</sup>, La<sup>3+</sup>
- Bands near  $E_F$  are derived from Fe with little As admixture



#### Density Functional Study of LaFeAsO $_{1-x}F_x$ : A Low Carrier Density Superconductor Near Itinerant Magnetism

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Band anisotropy:  $\langle v_x^2 \rangle / \langle v_z^2 \rangle \sim 15 \Rightarrow$ a modest value that is favorable for applications.

# **Normal Metallic State**

- Low carrier density semi-metal (dis-connected small Fermi surfaces).
- Less anisotropic than cuprates, even YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>.
- High  $N(E_F)$ .
  - Near itinerant magnetism in general.
  - Expect short coherence length relative to  $T_c$ .
  - Expect high superfluid density.
- Electron-Phonon interaction is weak ( $\lambda \sim 0.2$ ,  $T_c=0$ )

### **Formation of Band Structure**

- Bands from -2 eV to +2 eV are derived from Fe<sup>2+</sup> d-states.
- Fe<sup>2+</sup> has 6 *d*-electrons.



#### Key is the short Fe-Fe bond length → direct Fe-Fe interactions.

# **Coulomb Correlations**

- LDA and correlated approaches give different predictions.
- So far Hubbard bands are not seen; strong Fe d character is seen at Fermi edge.
- There is however a renormalization of ~2 in band width c.f. LDA.





#### **Metallic Character**

#### Photoemission: LaFePO (D.H. Lu et al.)



Very prominent Fermi edge (not like cuprates).

Fe d bands are narrower (by ~2) compared to LDA.

# LaFeAs(O,F) Lindhard Function

• Neglecting Matrix Elements:



#### Note the pronounced peak at the zone corner.

I.I. Mazin, D.J. Singh, M.D. Johannes and M.H. Du, PRL 101, 057003 (2008)

# **Spin Fluctuations and Superconductivity**

One way to proceed (weak coupling):

- Calculate matrix elements  $V_{k,k}$ , for a set of k,k on the FS.
- Set-up gap equation -- diagonalize V.

Berk-Schrieffer-Fay-Appel weak coupling theory, 1966-1980:



In a singlet channel there is a minus sign for spin fluctuations (repulsive), which then favors opposite order parameters on the electron and hole sheets  $\rightarrow$  s +/- state.

 $V(\mathbf{q}) = - \frac{l^2(q)\chi_0(\mathbf{q})}{1 - l^2(\mathbf{q})\chi_0^2(\mathbf{q})}$ 

Singlet:

Note prior work, Aronov & Sonin (1972); Kuroki and Arita (2001)

Does not have an obvious strongly qdependent interaction for nodes in a FS.

I.I. Mazin, D.J. Singh, M.D. Johannes and M.H. Du, PRL **101**, 057003 (2008)

# **Spin Fluctuation Driven** $s_{+/-}$ **Properties**

- Two gap.
- SDW and superconductivity are driven by the same interaction and compete for the same electrons.
- Simplest form is nodeless, but this is not essential.
- Robust against low *q* scattering (Co, Ni doping)
- No corner junction shifts (*s*-wave symmetry)
- Coherence factors depend on q. Reduced Hebel-Slichter peak in NMR relaxation rate.
- Resonance peak in neutron scattering.

# **Small Fermi Surfaces in General**

• Does superconductivity arise in general if one has small Fermi surfaces with nesting driven spin fluctuations? – Answer seems to be no.



*p-wave state (triplet)*: spin-fluctuation pairing interaction has + sign  $\rightarrow$  Pair breaking for the state shown.



*s-wave state (singlet)*: spin-fluctuation pairing interaction has - sign  $\rightarrow$  Pair breaking for the state shown.

e.g. small pockets on  $Na_xCoO_2$  (Johannes et al., 2004).

In such cases, look for chemistry with strong electron phonon and low Stoner parameter, to obtain Kohn anomaly and e-p superconductivity or maybe strange states, e.g. odd frequency.

#### LETTERS

#### Unconventional superconductivity in Ba<sub>0.6</sub>K<sub>0.4</sub>Fe<sub>2</sub>As<sub>2</sub> from inelastic neutron scattering

A. D. Christianson<sup>1</sup>, E. A. Goremychkin<sup>2,3</sup>, R. Osborn<sup>2</sup>, S. Rosenkranz<sup>2</sup>, M. D. Lumsden<sup>1</sup>, C. D. Malliakas<sup>2,4</sup>, I. S. Todorov<sup>2</sup>, H. Claus<sup>2</sup>, D. Y. Chung<sup>2</sup>, M. G. Kanatzidis<sup>2,4</sup>, R. I. Bewley<sup>3</sup> & T. Guidi<sup>3</sup>



Sign changing gap with q corresponding to  $(\pi,\pi)$ 

#### **Fully Gapped**: Andreev reflection, ARPES penetration depth (oxy-arsenides), tunneling.



Microwave penetration depth, PrFeAsO<sub>1-x</sub> K. Hashimoto, et al., PRL (2009).

#### **Power Law (e.g. Line Nodes):**



NMR, LaFeAs(O,F) Y. Nakai, et al., JPSJ (2008).

If some compounds have a clean gap and others have nodes, does this mean that there are two competing (different) superconducting states, such as s+/- and something else?



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s+/-



# Fermi Surface Structure

Fermi surface shaded by d xz/yz character

FeSe

LaFeAsO



Lobes of the electron sheets are not as nested as the inner parts due to matrix element

A. Subedi

# Neutron Scattering – Magnetism & Structure

#### LaFeAsO:

Ordered  $m(Fe) = 0.36 \mu_B$ (other compounds so far are between 0.3 and 1  $\mu_B$ )



#### **In-plane SDW structure**



# 1 D Chains of parallel spin Fe atoms.

# **Nesting, Doping and the Lindhard Function**



Could we realize disorder induced superconductivity?

### **Metallic SDW State**

#### SrFe<sub>2</sub>As<sub>2</sub> (Sebastian *et al.*)



Shubnikov – de Hass measured by tunnel diode method.

SDW state has quantum oscillations reflecting a Fermi surface and is therefore a metal.

#### **NMR: Connection of SDW and SC States**

 $1/T_1T$  shows strong spin fluctuations (constant for ordinary F.L.)



Ning, et al., JPSJ **78**, 013711 (2009) – Ba(Fe,Co)<sub>2</sub>As<sub>2</sub>.

### **Implications for Models**

- Models reduce the degrees of freedom in order to extract and understand the important physics. They must retain fidelity to the important aspects of the physical system to be relevant.
- The FeSC are NOT near Mott insulators in any normal sense – a Mott insulating state is not produced by doping, alloying, pressure, magnetic field or other small or even large experimentally realizable perturbations.
- Models "near" a Mott insulator (small parameter changes produce a Mott state) need improvement.

# **Resistivity in LaFeAsO**

McGuire et al. (cond-mat):

Hall:



# **Strong Spin Fluctuations in Normal State**

- Transport data.
- Susceptibility  $\chi(T)$ .
- Spectroscopy.
- Scattering.
- Overly magnetic in LDA.
- Precursor structural transition.





# **Superconductivity in Metal Doped Materials**

- Superconductivity requires destruction of SDW by doping.
- Remarkably, doping with Co or Ni works (*c.f.* cuprates).



Calculations show that alloy behaves very much in a rigid band sense.

Fe-Co-Ni behave very similarly apart from electron count.

Mn and Cr show strong spin dependent hybridization (different).

Is iron essential?

# The ThCr<sub>2</sub>Si<sub>2</sub> Structure Type

#### The Most Populous of All Crystal Structure Types—the Tetragonal BaAl<sub>4</sub> Structure

W. B. PEARSON Pearson data-base now has 2,000+ ThCr<sub>2</sub>Si<sub>2</sub> entries Departments of Physics and of Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1

Received April 9, 1984; in revised form August 3, 1984

The BaAl<sub>4</sub> (ThCr<sub>2</sub>Si<sub>2</sub>) t/10 structure,  $MN_2X_2$ , is not only the most populous of all known structure types, being adopted by some 400 phases, but is representative of a new group of metallurgically

**Examples**:  $BaZn_2P_2$ ,  $BaFe_2As_2$ ,  $BiN_2Th_2$ ,  $CaAl_2Ga_2$ ,  $SrCd_2Ga_2$ ...

# The ThCr<sub>2</sub>Si<sub>2</sub> Structure Type



Stabilized by different types of bonding: ionic, M-X bonding, M-M bonding, X-X bonding, A-X --- can tune to crossovers.

Interplay between magnetism and bonding in Fe compounds, e.g. collapsed phase of  $CaFe_2As_2$ (Yildirim)

# ThCr<sub>2</sub>Si<sub>2</sub> Structure DT<sub>2</sub>As<sub>2</sub>

Mn Fe

Strong spin dependent *T*-As hybridization, G-type AF with high  $T_{N.}$ BaCr<sub>2</sub>As<sub>2</sub> is itinerant metal. BaMn<sub>2</sub>As<sub>2</sub> is a semiconductor.

V

Cr

Metallic  $M^{2+}$  sheets. As is anionic. M can be alloyed. Fe: SDW and superconductivity. Co: Near FM Ni: electron-phonon superconductor.

Co

Ni

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BaCu<sub>2</sub>As<sub>2</sub> has Cu  $d^{10}$  with As-As and Cu-As sp bonding.

Chemistry of chalcogenides may be expected to differ.

# Is Iron Essential for Iron-Based Superconductivity?

KRu<sub>2</sub>As<sub>2</sub>; KFe<sub>2</sub>As<sub>2</sub>; KCo<sub>2</sub>As<sub>2</sub>: Can we do something with the alloys? KFeCoAs<sub>2</sub>  $\approx$  BaFe<sub>2</sub>As<sub>2</sub>



Coherent alloy: Look for superconductivity in KFe<sub>1-x</sub>Co<sub>1+x</sub>As<sub>2</sub> (Fe-poor)

Also, similar results, but less magnetic for  $KRu_{1-x}Co_{1+x}As_2$ , but significantly less magnetic (Fe-free).

### Fermi Surface of Ordered KRuCoAs<sub>2</sub>



Ru lowers average Stoner parameter  $I(\mathbf{q})$  both because it is 4d and because of Ru d – As p hybridization.

# **Neutron Scattering – Structure Details**

#### LaFeAsO (Tetragonal → Orth/Mono):

#### Table 2 | Properties of LaOFeAs at 4 K

a, Refined st Atom	ructure param Site	eters x	у	z	В (Ų)
La	2e	1/4	1/4	0.1426(3)	0.54(6)
Fe	2†	3/4	1/4	0.5006(12)	0.16(4)
As	2e	1/4	1/4	0.6499(4)	0.23(7)
0	2f	3/4	1/4	-0.0057(17)	0.69(7)

 $z_{As}(4K) = 1.308 \text{ Å}$  $z_{As}(175K)=1.317 \text{ Å}$ 

#### LaFeAsO<sub>0.92</sub>F<sub>0.08</sub> (Tetragonal):

Table 3 | Properties of  $LaO_{0.92}F_{0.08}FeAs$  at 10 K (first line), 35 K (second line) and 175 K (third line)

a, Refined structure parameters					
Atom	Site	x	у	Z	B (Å <sup>2</sup> )
La	2c	1/4	1/4	0.1448(3)	0.40(5)
		1/4	1/4	0.1458(3)	0.50(5)
		1/4	1/4	0.1446(3)	0.73(5)
Fe	2b	3/4	1/4	1/2	0.32(4)
		3/4	1/4	1/2	0.41(4)
		3/4	1/4	1/2	0.65(4)
As	2c	1/4	1/4	0.6521(4)	0.41(7)
		1/4	1/4	0.6515(4)	0.40(6)
		1/4	1/4	0.6527(4)	0.69(7)
O/F	2a	3/4	1/4	0	0.53(6)
		3/4	1/4	0	0.62(6)
		3/4	1/4	0	0.71(6)

C. de la Cruz et al., Nature 453, 899 (2008)

 $z_{As}(10K) = 1.323 \text{ Å}$  $z_{As}(175K)=1.331 \text{ Å}$ 

Non-magnetic LDA calc. (LaFeAsO – Tetragonal)  $z_{As}(LDA) = 1.159 \text{ Å}$ 

A huge difference!

# **Structure and Magnetism**

- As height is too low by ~0.1 Å in non-magnetic LSDA calculations.
- SDW is too robust compared to experiment.
- Using GGA and including magnetism one can obtain much better As height. In that case magnetism is extremely robust  $(m\sim 2\mu_B)$  contrary to experiment.
- Discrepancy in As height persists in the paramagnetic (superconducting) doped phases.
- There is a strong isotope effect both on  $T_c$  and on  $T_{SDW}$  (Liu *et al.*, condmat, 2008).
- We take this as an indication of very strong non-trivial spin-fluctuations.

# **Quantum Critical Points and the LDA**

**Density Functional Theory**: LDA & GGA are widely used for first principles calculations but have problems:

- •Mott-Hubbard: Well known poor treatment of on-site Coulomb correlations.
- •Based on uniform electron gas. Give mean field treatment of magnetism: Fluctuations missing.



LDA overestimate of ferromagnetic tendency is a signature of quantum critical fluctuations – neglected fluctuations suppress magnetism

# Some Metals Where the LSDA Overestimates Ferromagnetism

**Class 1**: Ferromagnets where the LDA overestimates the magnetization.

 $\begin{array}{ccc} m \; (LDA, \; \mu_B / f.u.) & m \; (expt., \; \mu_B / f.u.) \\ ZrZn_2 & 0.72 & 0.17 \\ Ni_3 Al & 0.71 & 0.23 \end{array}$ 

**Class 2**: Paramagnets where the LDA predicts ferromagnetism

Sc<sub>3</sub>In 1.05 0.20

	m (LDA, μ <sub>B</sub> /f.u.)	m (expt., μ <sub>B</sub> /f.u.
FeAl	0.80	0.0
Ni₃Ga	0.79	0.0
Sr <sub>3</sub> Ru <sub>2</sub>	O <sub>7</sub> 0.9	0.0
Na <sub>x</sub> Co	$D_2 0.50$	0.0

**Class 3**: Paramagnets where the LDA overestimates the susceptibility.

 $\chi$  (LDA, 10<sup>-4</sup> emu/mol)  $\chi$  (expt., 10<sup>-4</sup> emu/mol) Pd 11.6 6.8

# **Properties of the Over-Doped Side: TIFe<sub>2</sub>Se<sub>2</sub>**

#### Haggstrom, 1986



Antiferromagnetic with  $T_N \sim 450$  K. Unknown order.

First Principles Results (GGA):

- Electronic structure is very similar to FeSC, but with higher electron count (0.5 e/Fe).
- Strong instability against nearest neighbor AFM (78 meV/Fe) and weaker instability against FM (44 meV/Fe). No instability for SDW type chain order → itinerant n.n. AFM





Non spin polarized Fermi surface

# **Competing Magnetic States**

Competition between different magnetic states provides phase space for fluctuations and works against ordering.



#### **Possible Electron Doped Phase Diagram**



# **Hund's Coupling**

- Hund's coupling in 3d ions is strong (Stoner *I*~0.8 eV)
- Spin-fluctuations are then expected to couple to electronic states in the *d*-band going up to high energy (i.e. the *d*-band width) may be observable in spectroscopy. Drude weight seems reduced in optics.



Fig. 3. The temperature dependent reflectivity of chromium normalized to T=400 K.

# **Comparison with Cuprates**

	Cuprates	Fe-As
Magnetic & superconducting phases	Yes, magnetic phase insulating above & below $T_{N.}$ (Mott insulator)	Yes. Magnetic phase is metallic. Above $T_N$ is is similar to the metal in the superconducting phase.
Electronic structure	Moderate $N(E_F)$ , large FS at least for optimal doped	High $N(E_F)$ , small disconnected FS
Doping	Essential.	Destruction of SDW is enough.
Magnetic character	Local moment	Strong coupled, apparently itinerant.
Correlations	Strong. Mott-Hubbard type (e.g. p.e. satellites)	Possibly substantial but different e.g. spin fluctuations. Not Mott- Hubbard type.
Superconductivity	<i>d</i> -wave. Nodes. One band. Highly anisotropic	Nodeless ( <i>s</i> +/- ?). Two band. Less anisotropic (material dependent).
Structure	Oxides, corner shared octahedra complex	Simpler – tetragonal / orthorhombic, small unit cells.