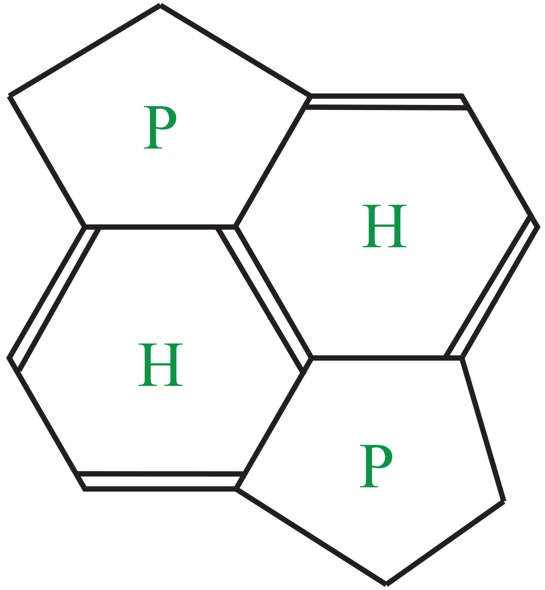
LECTURE 5. NON-CUPRATE SUPERCONDUCTIVITY

1.Alkali Fullerides

Formula:A_3C_{60}



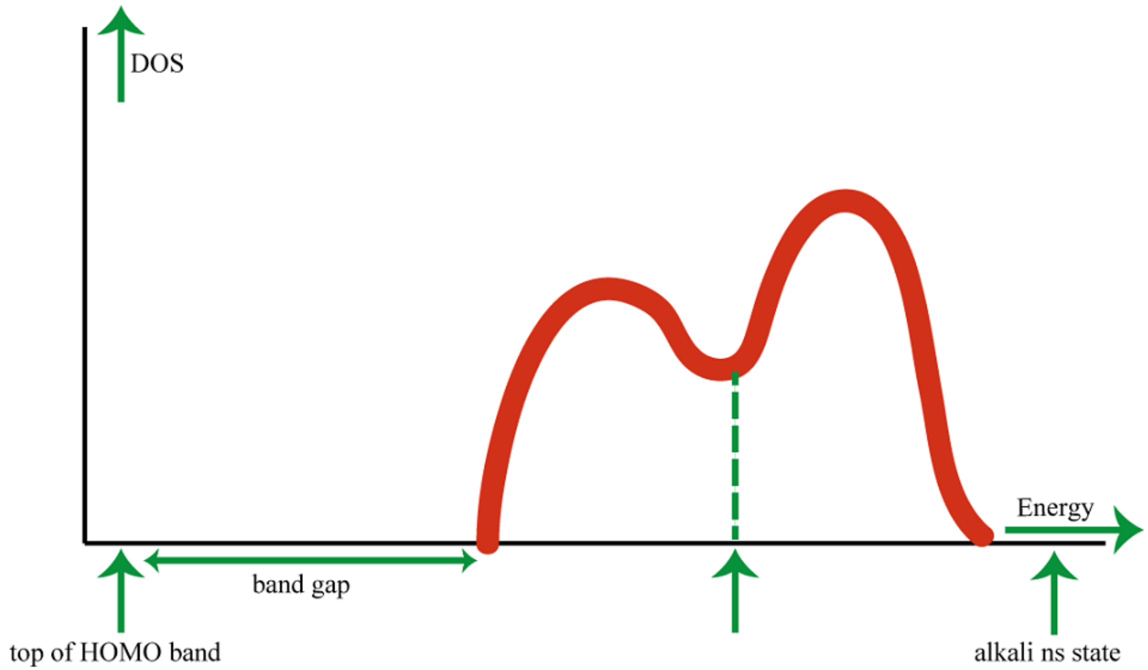
C_{60} molecule: "soccer-ball" pattern, with 20 hexagon and 12 pentagons: icosahedral symmetry.

C atom is $1s^2 2s^2 2p^4$, but in molecule or solid, $2s$ and $2p$ hybridize to form 4 sp^2 states. Of these, 3 are used up in the in-plane bonding, leaving 1 electron per C atom (= 60 per fullerene molecule) in p_z-like state (i.e. "sticking out of surface")(cf. graphene)

The $\underbrace{\text{HOMO}}_{\text{"highest occupied molecular orbital"}}$ state is 5-fold orbitally degenerate, the $\underbrace{\text{LUMO}}_{\text{"lowest unoccupied molecular orbital"}}$ state 3-fold degenerate.

In the single molecule, HOMO-LUMO splitting $\sim$ 0.6eV.

Fullerene crystals[1]: fcc, cubic lattice parameter $\sim 14.2\text{Å}$(corresponds to close-packed molecules)



Bond which evolves from LUMO state has density of states (DOS) roughly like above; Density of states in middle of band very sensitive to lattice parameter.

[1]ignore "merohedral" disorder.

<u>Alkali fullerides</u>: Any intercalated alkali atoms will donate their s-electrons to the LUMO bond, thereafter "spectators" (cf. "charge reservoir" atoms in cuprates).

Normal-state properties roughly consistent with "textbook" picture of half-filled band. ($C_\mathrm{v} \sim T, \chi \sim$ const., $T_1 \sim T^{-1}$etc). Note experiment confirms $N(0)(\equiv \frac{1}{2}(\frac{dn}{d\epsilon}))$ strongly dependent[2] on lattice constant a. (photoemission, plasmons)

[2] important for transport, in N and Superconducting states

Alkali fullerides: superconducting state

Superconductivity occurs, in A_xC_{60}, only very close to $x = 3$, but then has T_c up to $\sim$ 40K (Cs_3C_{60}) (contrast intercalated graphite, eg KC_8, $T_c \lesssim 1$K)

T_c increases with increasing lattice spacing a (due to pressure or substitution): typically,

$$\partial T_c/\partial a \sim 33\text{K}/\text{Å}$$

Consistent with BCS result

$$T_c \sim \omega_D \exp(-1/N(0)V_0)$$

with V_0 mainly of intramolecular origin, hence independent of a, and density of states $N(0)$ increasing with a.

A_3C_{60}'s strongly type-II, $\underbrace{\xi(0)}_{\text{pair radius}} \sim 26$Å ($<$ 2 lattice spacings), $\underbrace{\lambda(0)}_{\text{London pen. depth}} \sim$ 2400-4800Å.

Pairing state:

$$\begin{cases} T_1 + \text{infrared reflectivity} \Longrightarrow s\text{-state (densityofstates very small for } E < \Delta \approx 1.76 k_B T_c) \\ \text{HS peak seen in } \mu\text{SR and}^{13}\text{C NMR} \Longrightarrow s\text{-state (as in ``BCS'' superconductors)} \end{cases}$$

$(\star : \Delta\lambda(T) \sim T^\alpha, \alpha \sim 3)$

Mechanism:

Isotope exponent ($^{12}\mathrm{C} \to {}^{13}\mathrm{C}) \approx 0.4 \Longrightarrow$ phonon mechanism

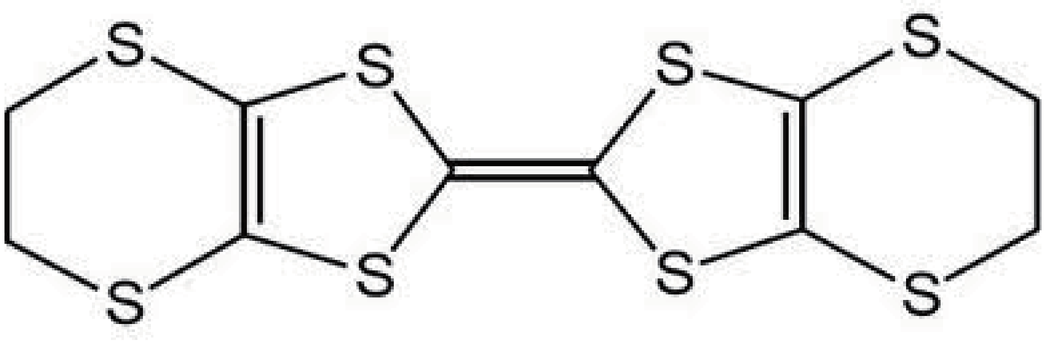
Note: $\omega_D/\epsilon_F \sim 0.3$ - 0.6 (BCS superconductors:$\sim 10^{-2}$)

so even if mechanism is phonon, details may be rather different from BCS.

Default explanation:

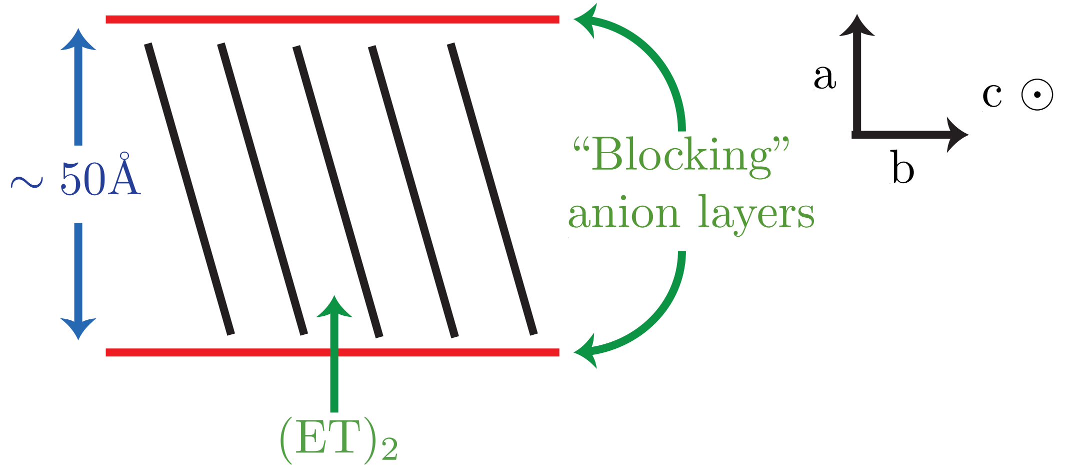
Alkali fullerides pretty well described by BCS theory, but strongly molecular structure enables them to avoid usual limit on T_{c} (cf. $\mathrm{MgB_2}$)

2.Organics



Mostly quasi-2D crystal based on ET(BEDT-TTF)(bis(ethylene-dithio)-tetrathiafulvalene).

Structure:$(ET)_2X$, X=monovalent anion (I_3^-, $Cu(NCS)_2^-$ ...). Conducting layers are $(ET)_2$, "blocking" layers anions.

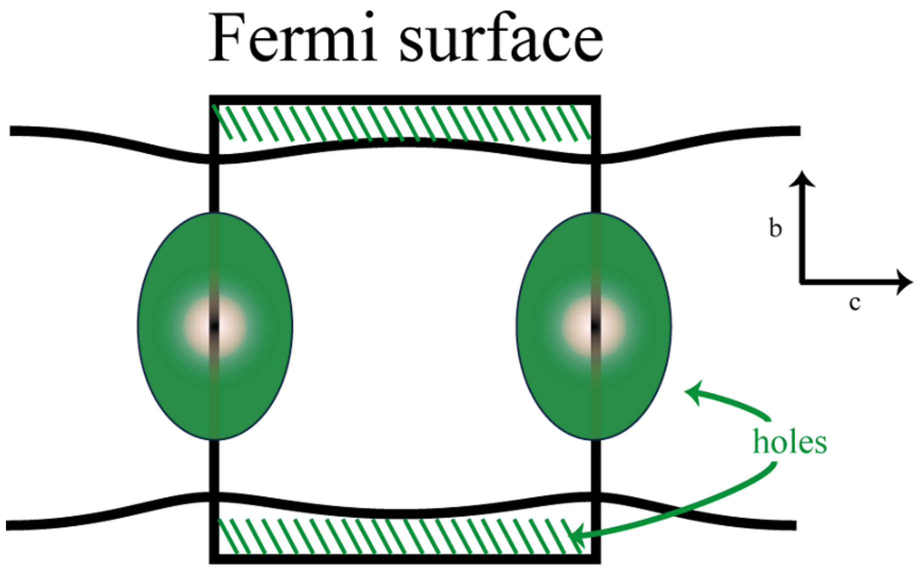


Normal State

Conduction electron density low ($\sim 10^{21}\text{cm}^{-3}$)

Very strong a-axis anisotropy[3]:$\rho_a/\rho_{bc} \sim 10^2$-$10^3$ (comparable to cuprates)

Samples can be made very clean $\Longrightarrow$ dHvA-type oscillations observable



Typical Fermi Surface Structure (K-(ET)$_2$Cu(NCs)$_2$): very strongly 2-dimensional

[3]Confusingly, the conventional notation calls the "hard" direction a (not c as in the Cuprates).

Superconducting State

T_c typically $\sim$ 10-12K (high in terms of calculated in-plane hopping matrix element)

extreme type-II ($H_{c1} \sim$ a few mT, $H_{c2} \sim$ 8-15T)

estimated $\xi_{||} \sim 50\text{Å}, \xi_{\perp} \sim 5\text{Å}$ ($\ll$ interlayer distance)

Symmetry: $c_v(T) \sim e^{-\Delta/T}$ for $T \to 0 \Longrightarrow s$-wave

$\star$: $T_1^{-1} \sim T^3$, no HS peak

Isotope effect: $^{12}\text{C} \to {}^{13}\text{C}$ has $\alpha \sim 0.1$, but $^{1}\text{H} \to {}^{2}\text{D}$ produces inverse isotope effect ($\alpha < 0$) (effect of lattice deformation?)

Default option: organics somewhat BCS-like, but electronic effects may be competitive.

3.Heavy Fermions[4]

Oldest class of exotic superconductors (1975).

Heavy-fermion systems:compounds containing rare-earth element (usually Ce) or actinide (usually U), with electronic specific heat exceeding "textbook" value by $\sim 10^2$-10^3 ($\Longrightarrow m^*/m \sim 10^2$-$10^3 \Longrightarrow$ "heavy")

(Note: large effective mass seen also in eg. dHvA.) All 3D (not layered).

Normal-state behavior:

at $T \sim 300$K, behavior of HF systems quite different from textbook metal + not always universal in class (eg.$R(T)$ metallic for UPt_3, semiconducting for most others). However, generally

$$\begin{cases} \chi \propto 1/T \\ T_1^{-1} \propto \text{const.} \\ C_{\mathrm{V}} \propto \text{const.} \\ \text{neutron scattering simple Lorentzian peak centered at T=0} \end{cases}$$

$\Longrightarrow$ consistent with model in which f-electrons ($\mathrm{Ce}^{3+} : 4f_1, \mathrm{U}^{4+} : 5f_2$) form local moments

[4] Ref.: Y.Kuramoto, Y.Kitaoka, Dynamics of Heavy Electrons, Oxford University Press, 2000.

As T lowered, crossover to a Fermi-liquid-like regime:

$$C_{\mathrm{V}} \propto T$$

$$T_1^{-1} \propto T$$

$$\rho \propto A + BT^2 \longleftarrow \text{impurity} + \text{e - e Umklapp}$$

But coefficient γ in $C_{\mathrm{V}} = \gamma T$ is enormous, up to $\sim$ 1600mJ/mole K^2 ($\mathrm{CeCu_6}$) (contrast "textbook" metal, $C_{\mathrm{V}} \sim$ a few mJ/mole).

$\star$: are we sure this specific heat is due to mobile electrons?

Yes, since $\Delta c_{\mathrm{n-s}}/c_{\mathrm{n}}(T_{\mathrm{c}}) \sim$ BCS value (+ superconducting electrons presumably must be mobile!)

In Fermi liquid theory, $\gamma \sim m^*$, so $m^*/m \sim 10^2$-10^3: confirmed by χ (also $\sim 10^2$-$10^3\times$ textbook value), dHvA.

Naive picture of N state:

f-electrons form very narrow band, width $\sim \Delta \sim$ a few K. Then for $k_B T \ll \Delta$, can equally well represent in terms of states localized on lattice sites.

$\Longrightarrow \chi \propto 1/T, C_{\mathrm{V}}$ "small", $T_1^{-1} \propto$ const., etc. For $k_B T \lesssim \Delta$ need proper "band" picture with large $m^*(\propto \Delta^{-1})$.

$\star$: ignores conduction (s or d) electrons! better picture involves competition between Kondo effect (favors s-f singlet) and RKKY(Ruderman-Kittel-Kasuya-Yosida interaction) (favors magnetic ordering of f-electrons). In fact, many HF systems (ever some superconducting ones) show antiferromagnetism at $T \lesssim 20$K.

Heavy Fermion superconductors

4 classes of HF systems:

1) no phase transition (ex.: $CeAl_3$)

2) magnetic transition only (ex.: $CeCu_6$)

3) superconducting transition only (ex.: UPt_3, $CeCu_2Si_2$, UBe_{13}...)

4) magnetic and superconducting transitions (ex.: $UPdAl_3$, URu_2Si_2, UGe_2...). In this class, magnetic order and superconductivity coexist (contrary to established "text-book" wisdom!)

In all cases of superconductivity in a HF system, $T_c \lesssim 2K$. (In class 4, $T_N \sim$ 10-50K).

Diagnostics: most crucial observation is that

no HFS shows any appreciable isotope effect

$\Longrightarrow$ strongly suggests non-phonon ("all-electronic") mechanism.

Pairing state:

Need to discuss each HFS separately: diagnostics include low-T behavior of $C_{\mathrm{V}}, T_1^{-1}, \kappa_{\mathrm{el}}$, Knight shift, H_{c2}, sensitivity to nonmagnetic scattering, multiple phases...

Some representative HFS and their (suggested) symmetries[5]

System	Magnetic?	T_{c}(K)	Parity	Gap nodes?	Comments
UPt_3	P	0.56	$-$	✓	
$CeCu_2Si_2$	P	0.65	$+$(?)	✓	
UBe_{13}	P	0.9	$-$(?)	✓	
$UPdAl_3$	AF	2.0	$+$	✓	$T_{\mathrm{N}} = 14.5\mathrm{K}$
$CeCoIn_5$	P	2.3	$+$	✓	probably $d_{x^2-y^2}$
$UNiAl_3$	AF	1.0	$-$	?	$T_{\mathrm{N}} = 4.6\mathrm{K}$
URu_2Si_2	AF	0.8	$-$	?	$T_{\mathrm{N}} = 17.5\mathrm{K}$
UGe_2	F	0.6	$-$	?	$T_{\mathrm{Curie}} = 30\mathrm{K}^*$

* at point of maximum T_{c}.

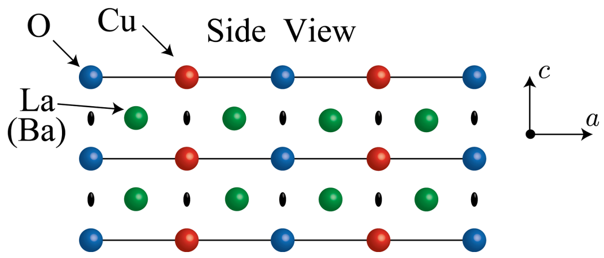
[5] Note:no evidence for T-violation in any HFS.

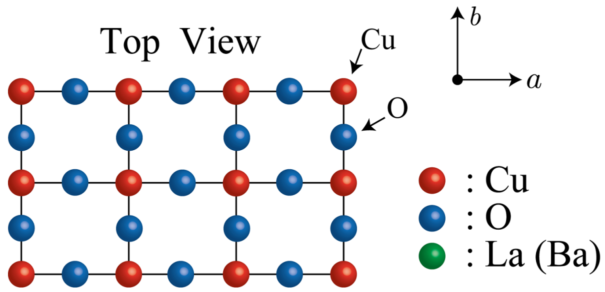
4. Strontium Ruthenate : Sr_2RuO_4

History

Superconductivity in cuprates up to $\sim$ 150 K

Typical (original) cuprate : $La_{2-x}Ba_xCuO_4$ ($T_c \sim 40K$)



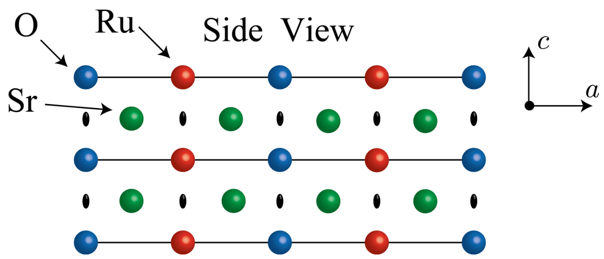


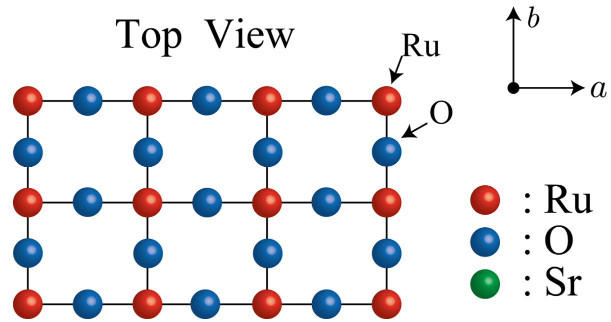
Quasi -2D CuO_2 planes appear to be essential to high-T_c superconductivity.

How essential is the Cu? Try replacing it : Ag, Au, ... doesn't work, but :

Cu (Z=29) : [Ar] + $3d^{10}4s^1 \rightarrow 3d^9$

Ru (Z=44) : [Kr] + $4d^7 5s^1 \rightarrow 4d^4$





Normal-state properties quite dissimilar

$La_{2-x}Ba_xCuO_4$ has ($T_c \sim 40$K)

Sr_2RuO_4 has T_c of ?

Experimental properties* of Sr_2RuO_4

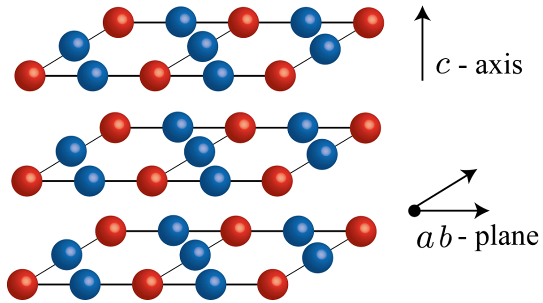
Normal Phase

Below $\sim$ 25K, appears to behave as strongly anisotropic Fermi liquid (nb : cuprates quite different)

$C_V \sim \gamma T + \beta T^3 \qquad \chi \sim$ const.

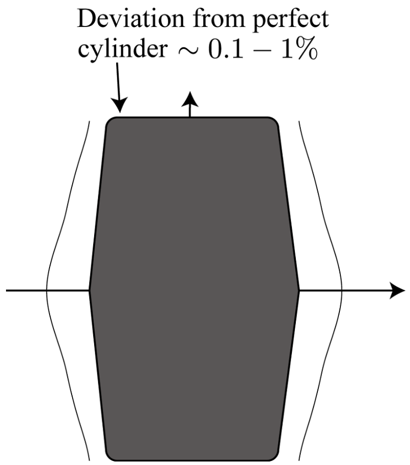
$\rho \sim A + BT^2$ both in ab-plane and along c-axis (characteristic of coherent (Bloch) wave transport limited by e^--e^- Umklapp scattering). ρ_{ab} small ($\sim 1\mu\Omega$ cm)

$\Longrightarrow$ samples very pure.



$*$ Mackenzie, and Maeno, RMP **75**, 1 (2003)

However, $\rho_{\mathrm{c}}/\rho_{\mathrm{ab}} \sim 10^3$ (comparable to cuprates)
Band structure:



Etranxperiment (dHvA, Shubnikov-De Haas) and theory (LDA) agree:
Fermi surface consists of 3 strongly 2D sheets: α (hole-like), β, γ (electron-like)

	α	β	γ
$k_F(\mathring{A}^{-1})$	0.3	0.6	0.75
m^*/m_e	3.3	7.0	16.0
m^*/m_{band}	3.0	3.5	5.5

indecation of
strong correlations

$\chi \sim$ const. in superconducting state $\Rightarrow$ triplet equal-spin-pairing

Suppose order parameter of Sr_2RuO_4 is indeed of equal-spin-pairing form: then

$$F(\boldsymbol{k};\sigma_1,\sigma_2) = F(\boldsymbol{k};\sigma_1,\sigma_2) = f(\boldsymbol{k})(\uparrow\uparrow + \downarrow\downarrow)$$

Then the crucial question is :

What is $f(\boldsymbol{k})$? $\leftarrow$ orbital wave function of pairs

$f(\boldsymbol{k})$ odd parity (consistent with Josephson experiments)

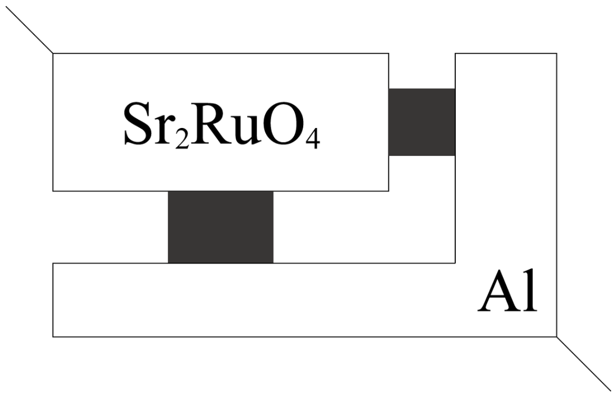
In particular, is it real (e.g. $f(\boldsymbol{k}) \sim k_x$) or complex (e.g. $f(\boldsymbol{k}) = k_x + ik_y$)?

$\uparrow$

breaks T-invariance

In BCS theory, want $|\mathrm{OP}|^2$ to be as uniform as possible over Fermi surface $\rightarrow k_x + ik_y$ always favored. But in more general theory, need not be so. Experiments favoring violation of T-symmetry:

a) Muon spin rotation extra "internal" magnetic field in superconductor state ($\uparrow$: apparently H has ab-plane component!)
b) Magnetic field dependence and telegraph noise in I_c of Josephson junctions interpreted in terms of switching of domains ($p_x + ip_y \leftrightarrows p_x - ip_y$)
c) Kerr effect in zero magnetic field.
$\star$: "ideal" $p_x + ip_y$ state ($\Delta \sim F \sim$ const.$(k_x + ik_y)$ has no nodes)
$\Longrightarrow$ exponentially small no. of quasiparticles for $T \ll T_c$
$\Longrightarrow$ no appreciable specific heat, thermal conductivity.....
In fact, experimental evidence for power law contribution of many of these quantities $\rightarrow$ gap has nodes?
In principle, critical test I_c max. at $\Phi = \frac{1}{4}$ or $\frac{3}{4}\phi_0$



5.Ferropnictides

⋆: only 3 years old, so much experimental data may not be definitive.

Composition: two major atoms, each containing a transition metal (usually Fe) and a pnictide (element in N column of periodic table), usually As.

2 main classes of parent compounds:

1111: $\underbrace{(\mathrm{RE})}_{\text{rare earth}}\ \underbrace{(\mathrm{TM})}_{\text{transition metal}}\ \underbrace{(\mathrm{PN})}_{\text{pnictide}}$ O:example, $\mathrm{LaFeAsO}(_{1-x}\mathrm{F}_x)$

122: $\underbrace{(\mathrm{AE})}_{\text{alkaline earth}}(\mathrm{TM})_2(\mathrm{PN})_2$: example, $BaFe_2As_2$

third class: LiFeAs, FeSe... ← "11"

most work on (1111), will mostly refer to this.

Structure (1111 compounds) (schematic)

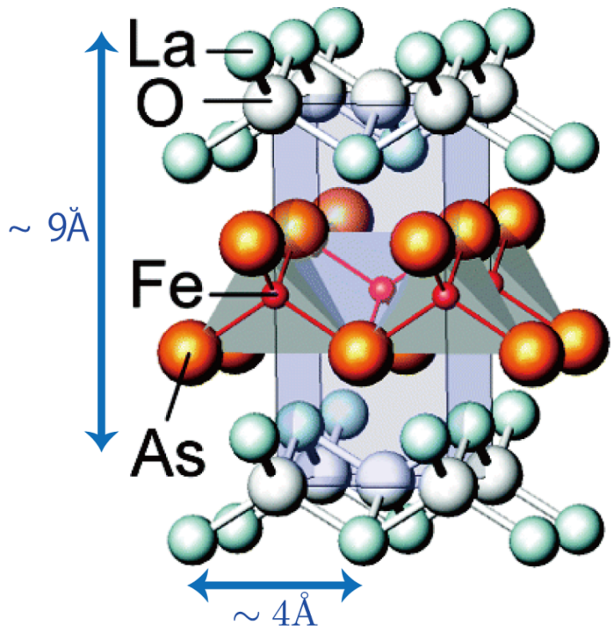


Figure 1: Kamihara et al., J.Am.Chem.Soc., 2008, 130 (11)

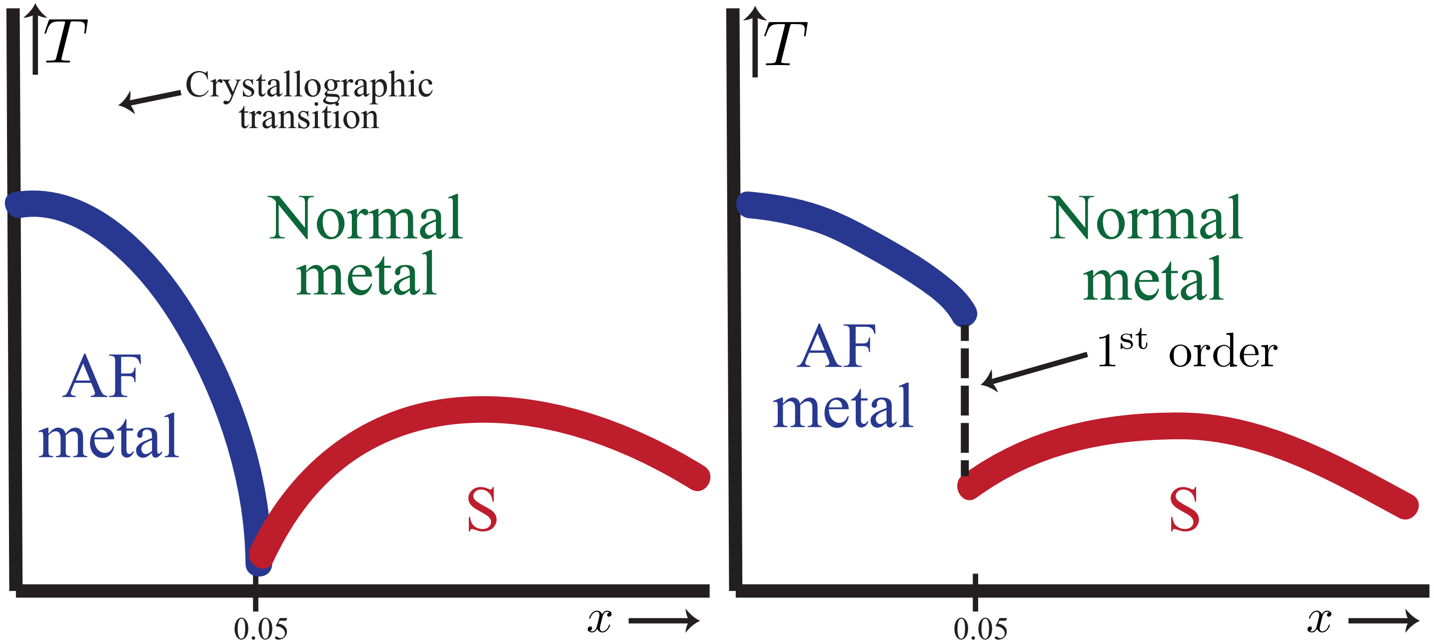
in parent compound, valence state probably $(La^{3+}O^{2-})^{+}(Fe^{2+}As^{3-})^{-}$ (+ some Fe $3d$-As $4p$ hybridization)

(doubly) closed shell ↑ ↑ $3d^6$ ↑ closed shell

If F substituted for O, extra electron → FeAs layer: for $O_{1-x}F_x$, $x \sim 0.1$, carrier density $\sim 10^{21}$ cm^{-3} (comparable to cuprates)

Note that as in cuprates, "charge reservoir" (F's in LaO layer) well separated from metallic (FeAs) layer. Note: 1111's are electron-doped (but 122's hole-doped)

Phase diagram



Note max. in $T_c(x)$ at $x \sim 0.12$-0.15 is very “shallow” compared to cuprates

Experimental properties (N state)

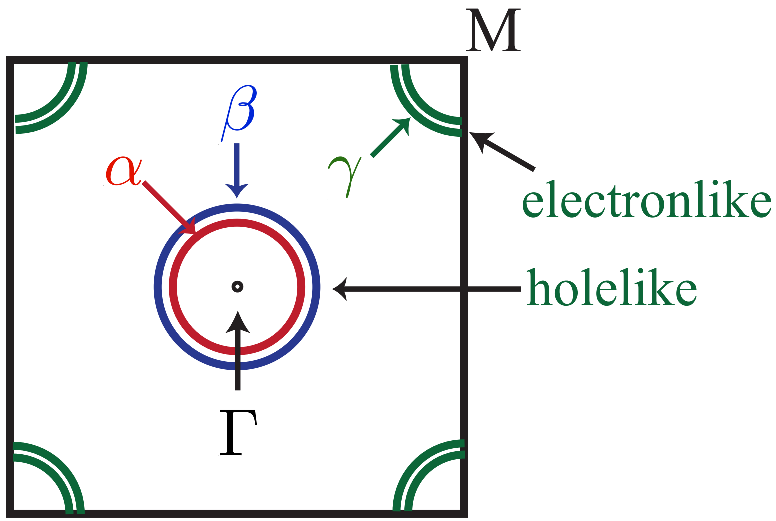
$$\begin{cases} C_{\mathrm{V}} & \sim \alpha T + \beta T^3 \\ \chi & \sim A + BT \\ \rho \text{ (dc conductivity)} & \sim A + BT^2, \sim 3\mathrm{m}\Omega \text{ at RT } (\sim \text{cuprates}) \\ \text{Hall coefficient} & \sim A + BT \end{cases}$$

$\star$: so far, anisotropy not measured (?)

overall fairly "textbook"

Band structure:

$$\begin{cases} \text{ARPES} \\ \text{quantum oscillation} \\ \text{LDA calculations} \end{cases} \Longrightarrow$$



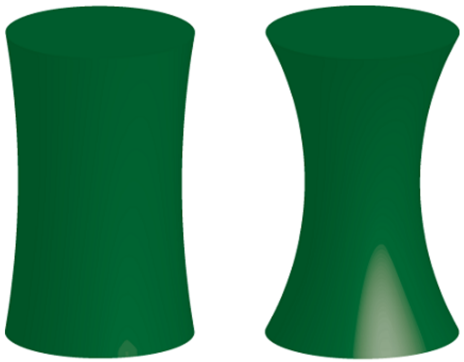
($\star$ beware notation!)

Note:

in 1111 Fermi surface very 2D. ("barrel-like")

in 122 much more 3D.

also, magnetism much stronger in 122.



2D
(1111)

3D
(122)

Superconductivity

T_c up to $\sim$ 56K in (doped) 1111, 38K in 122, 20K in 11. : weakly x-dependent (e.g. $\mathrm{LaFeAsO}_{1-x}\mathrm{F}_x$): a surprise, because Fe ions have magnetic moments $\sim \mu_B$ (neutron scattering).

Experimental properties (Superconducing state)

All ferropnictides strongly type-II, with (extrapolated) $H_{c2}(0) \sim$ 55T:

(exceeds Chandrasekhar Clogston limit)$\Uparrow$

anisotropy relatively small ($\sim$ 2-3). $\lambda_{ab}(0) \sim$ 1600-2400Å, $\xi_{ab}(0) \sim$ 20Å

ARPES: on all sheets, gap only weakly $\boldsymbol{k}$-dependent.

NMR, penetration depth: at low T data mutually inconsistent, but favor power law.

very importantly: Knight shift $\to 0$ for $T \to 0$ for all directions of magnetic field.

Isotope effect: experiments mutually inconsistent, but most recent give small value of α

$\Longrightarrow$ suggests mechanism mostly non-phonon.(consistent with firm theoretical prediction that phonon mechanism cannot give 55K)

The pairing state

Knight shift $\Longrightarrow$ spin state singlet (fairly firm conclusion)

For (approximate) tetragonal symmetry, main candidates are s (presumably nodeless) and $d_{x^2-y^2}$ (nodes at (π, π)).

ARPES data suggest nodeless $\Longrightarrow$ s. but $T \to 0$ T_1, λ rather favor nodes

$\star$: However, extra complication:

gap need not have same sign on all sheets of Fermi surface!

Theory based on spin-fluctuation mechanism (most "obvious" non-phononic mechanism) predicts gap changes sign between electronlike and holelike sheets ("$s^{\pm}$")

Experimental evidence claimed in favor of this assignment:

"Josephson-like" experiment on polycrystalline sample[6] (shows half flux quanta)

STM[7]

No "true" Josephson experiments yet...

[6] Chen et al., Nature Physics **6**, 260 (2010)
[7] Hanaguri et al., Science **327**, 474 (2010)