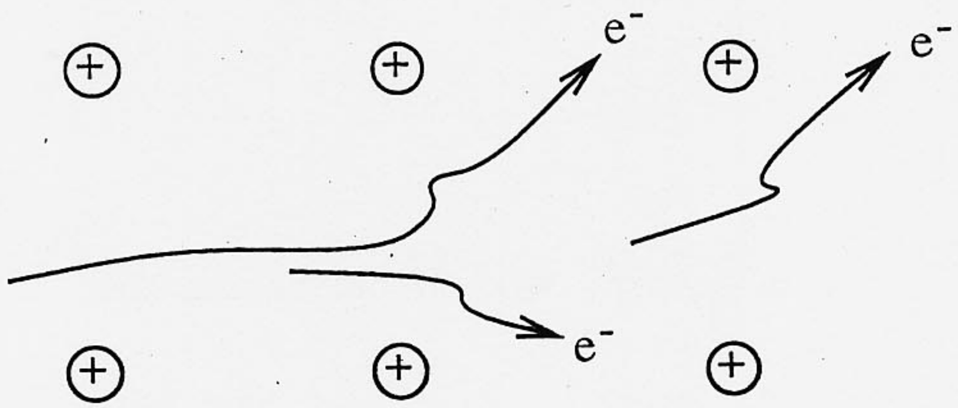
The Search for Unconventional Superconductors: A Long Story with a Happy End

T.M. Rice
Theoretische Physik
ETH Zürich

Basis of Condensed Matter Physics

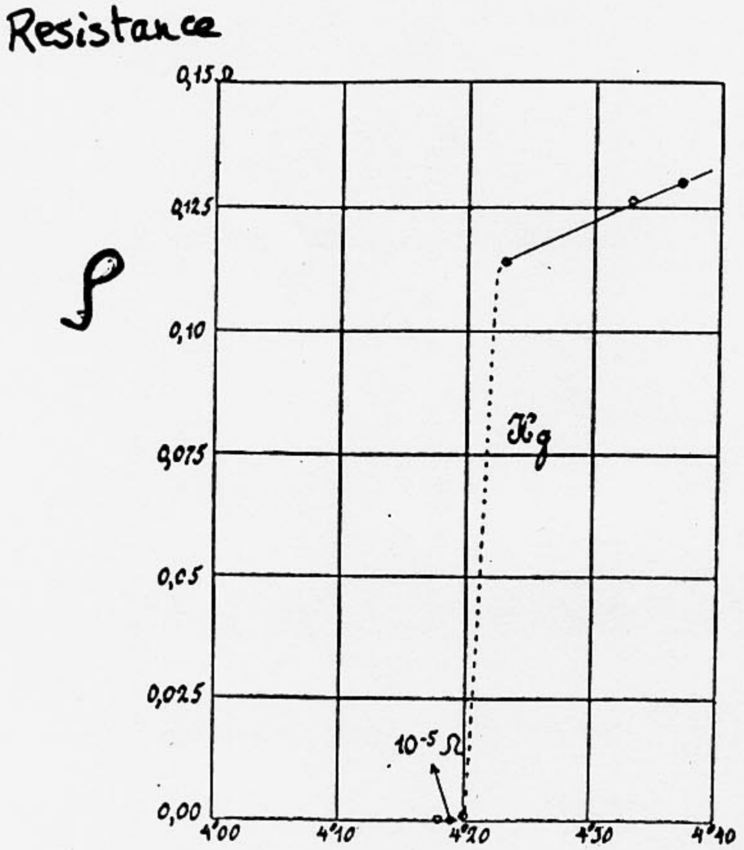
- Quantum Mechanics

- Electrons + Ions + Coulomb Interaction



- 1 cm^3 contains $\sim 10^{22}$ electrons + ions !

• Discovery of Superconductivity



• Hg.

Figure 1 Resistance in ohms of a specimen of mercury versus absolute temperature. This plot by Kamerlingh Onnes marked the discovery of superconductivity.

1911

Temperature

Wolfgang Pauli

Felix Bloch

· Zürich 1928

"Pauli thought that superconductivity was the only remaining matter of some interest in the theory of metals and that I should get on with it so as to be finally done with all these 'dirt effects'."

⋮

"Once in a while I thought that I had indeed found such states but it never took Pauli long to point to some error in the calculations. While he did not object to my approach he became rather annoyed at my continued failure to come out with the desired answer to such a simple question."

⋮

"After the fog, which so long enveloped the phenomenon, had begun to lift many years later, I could not resist reminding Pauli that the problem was not quite as easy to solve as he thought when he gave it to me. Since that time he had become more mellow - so much more, in fact, that he agreed."

F. Bloch, Proc. Roy. Soc. **A371** (1980)

- Starting point: Normal Metal with **repulsive (Coulomb)** and **attractive (electron–phonon–electron)** forces

- Low Energy Scale: **repulsive forces screened** **attractive forces enhanced**

➔ leads to formation of **bound electron pairs** in a spin singlet

➔ below a transition temperature T_c there is a macroscopic coherent occupation of pairs to form $\Psi(r)$.

✔ Explains all features of **classical superconductor**

Can Superconductivity be reached thru' electron-electron interactions ?

Yes! : Kohn-Luttinger '65

T

Landau Fermi Liquid

Sharp Fermi Surface causes attractive interactions in higher ($\ell > 0$) angular momentum channels, $\lambda_\ell < 0$ for pairing

$T_c \approx E_F e^{-1/|\lambda_\ell|}$ but $|\lambda_\ell| << 1$

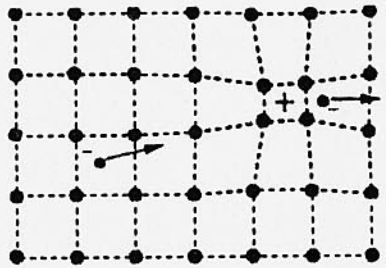
and **T_c is very small**

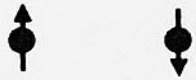
Unconventional superconductivity

Cooper Pairing, if the electrons try to avoid each other

Conventional pairing
attractive interaction by
electron-phonon interaction

BardeenCooperSchrieffer '57





angular momentum l =0
spin singlet

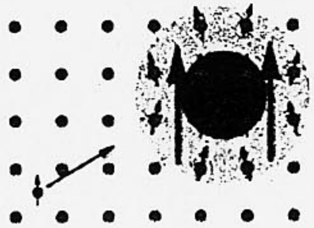
Cooper pairing from purely repulsive interactions: Kohn & Luttinger '65

l > 0 higher angular momentum; extremely small T_c

"unconventional pairing"

Pairing interaction mediated by spin fluctuations: Berk & Schrieffer '66, - - -

most polarizable near
magnetic instability



l > 0: avoiding Coulomb
repulsion

Symmetry of Cooper Pairs

Pair wavefunction: $F_{ss'}(\vec{k}) = \langle \hat{c}_{\vec{k}s} \hat{c}_{-\vec{k}s'} \rangle = \underbrace{\Phi(\vec{k})}_{\text{orbital}} \underbrace{\chi(s,s')}_{\text{spin}}$

totally antisymmetric under electron exchange

$$\vec{k} \to -\vec{k} \qquad s \leftrightarrow s'$$

even parity L = 0,2,4,...	$\Phi(-\vec{k}) = \Phi(\vec{k})$	⟶	S=0 singlet
odd parity L=1,3,5,...	$\Phi(-\vec{k}) = -\Phi(\vec{k})$	⟶	S=1 triplet

Superconductivity of strongly correlated electrons

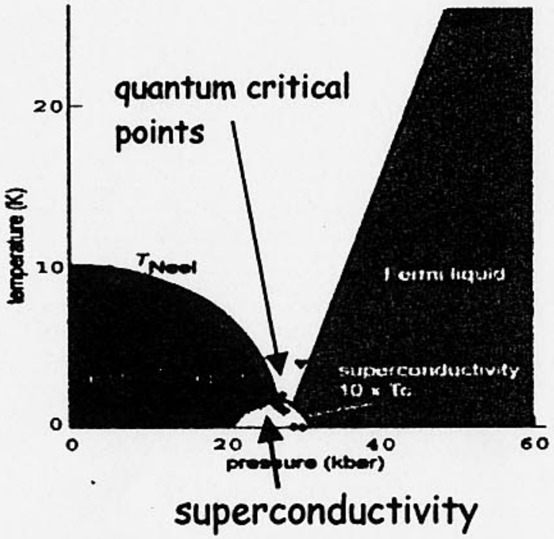
Heavy Fermion systems:

$CeCu_2Si_2$ Steglich '79

UBe_{13} Ott '83

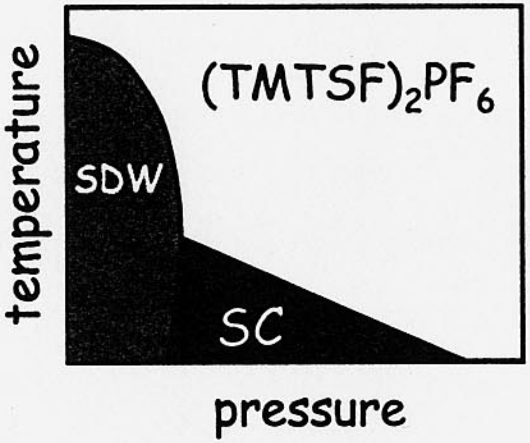
UPt_3 Stewart '84

$CeIn_3$ Mathur '98

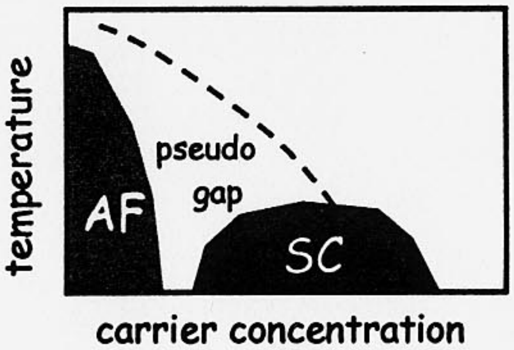


Relation to magnetism

Organic conductors: Bechgard, Jerome '80



High-T_c superconductors: Müller & Bednorz '86



cuprates

$YBa_2Cu_3O_7$

$La_{2-x}Sr_xCuO_4$

...

$T_{cmax} = 133K$

Heavy Fermion materials

Intermetallic compounds with rare earth elements (partially filled f-shells)

Electrons and Ions

↓

itinerant electrons & localized electrons

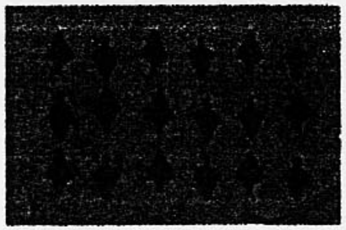
↓

↓ ↓ ↓

Magnetic order | Superconductor | Exotic order

T

T^*



Kondo lattice

T_K

Fermi liquid: itinerant and localized electron are in the coherent phase

T_c

Localized electrons behave itinerant !?

0

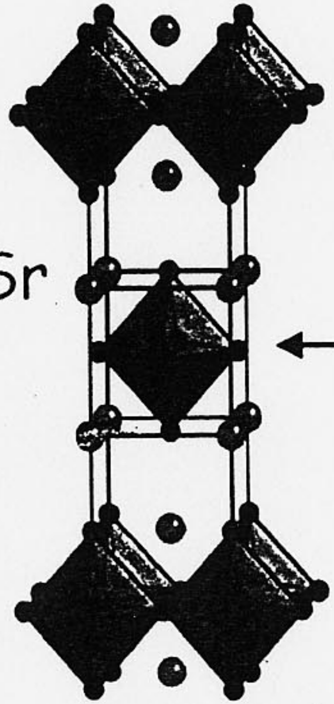
Residual interactions

➡ various orders

High-temperature superconductors

K.A. Müller & G. Bednorz 1986

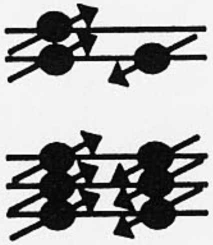
$La_{2-x}Sr_xCuO_4$



Layered perovskite structure

Electronic configuration

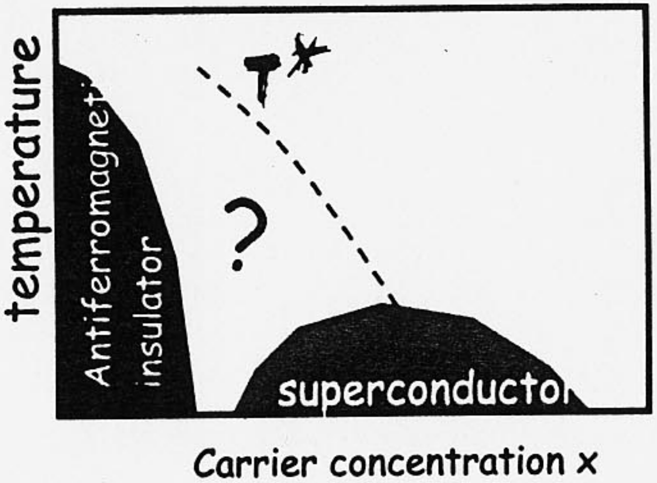
Cu^{2+}



one 3d-e_g hole

spin S = 1/2

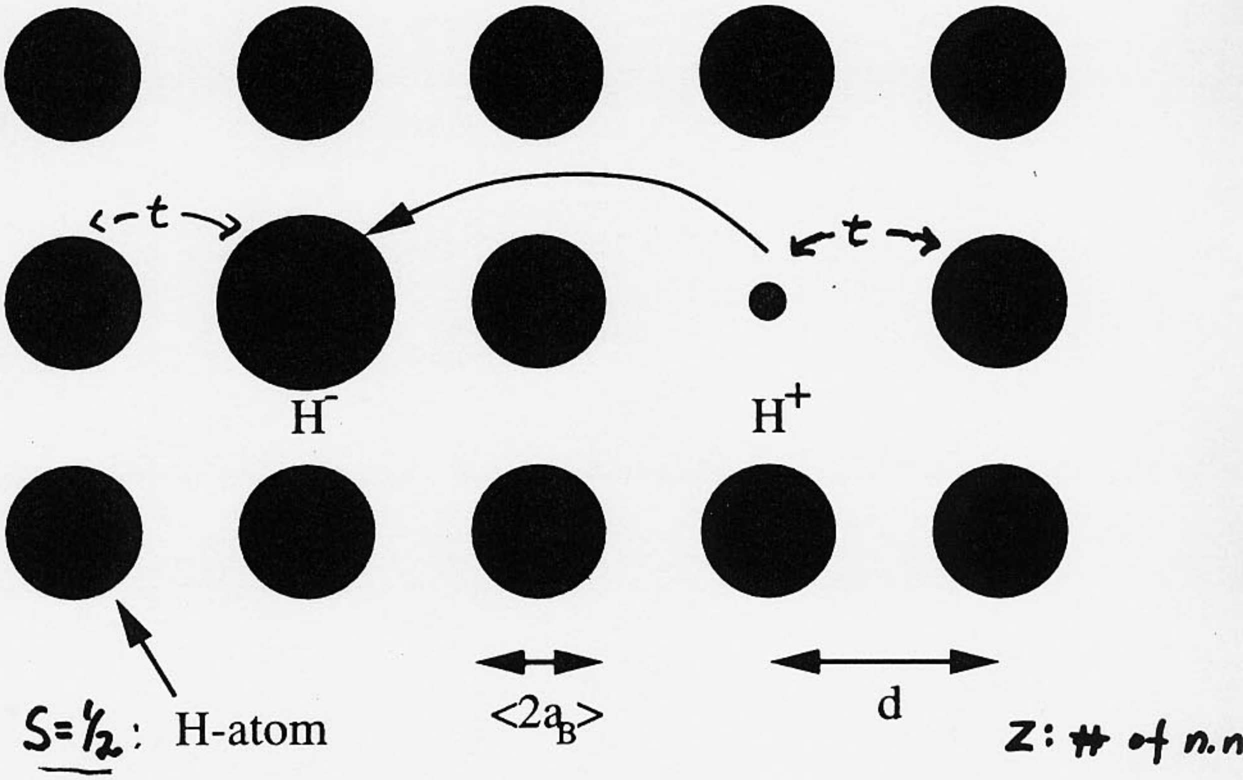
magnetic Mott insulator → superconductor



T_c up to 133K

Dilute Limit ($d >> a_B$)

$\Rightarrow$ Localized H-atoms.



- ➡ Charge Excit. Energy: $U - 2zt > 0$.
  $[U \rightarrow E(H^- - H^+) \sim 0.95\text{Ry}, d \rightarrow \infty]$.

- ➡ Mott Insulator with gap for charge excitations.

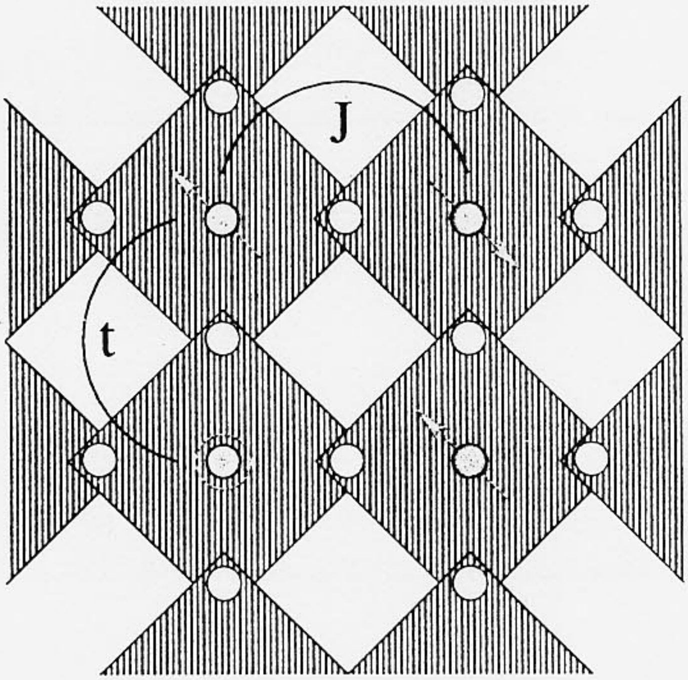
- ➡ Low Energy Sector purely spin, $H_{Heis} = J \sum_{<ij>} \mathbf{S}_i \cdot \mathbf{S}_j \Rightarrow$ AF order.

- ➡ Local Gauge Invariance in Real Space (Kohn '64):
  $\Phi_L = \prod_i c^\dagger_{i,\sigma_i} |\text{vac}\rangle, \qquad c^\dagger_{i,\sigma_i} \rightarrow e^{i\phi_i} c^\dagger_{i,\sigma_i}$.

Hole Doping introduces Cu^{3+}

t-J Model

- restrict Hilbert space to Cu^{2+} and Cu^{3+} oxidation states.



o O

- overlapping CuO_4-squares lead to processes:

$Cu^{2+} \leftrightarrow Cu^{2+}$, AF Heisenberg coupling, $J\vec{S}_i.\vec{S}_j$

$Cu^{3+} \leftrightarrow Cu^{2+}$, hopping of electrons, t. $\frac{J}{t} \sim \frac{1}{3}$

Cu^{2+}: $S = 1/2$ [$3d^9$] Cu^{3+}: $S = 0$ [$3d^8$: Zhang-Rice singlet]

Numerical Simulation of the t–J Model

severely limits Quantum Monte Carlo method

Results:

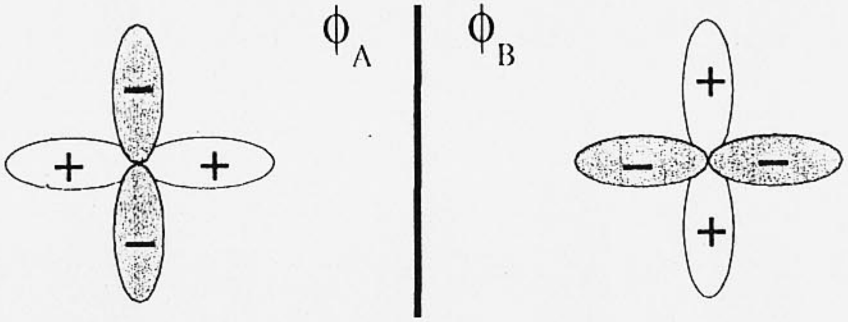
- Superconducting state must have $d_{x^2-y^2}$ pairing
- Competing ground states upon doping
  - ➔ $d_{x^2-y^2}$ superconductivity
  - ➔ stripe–phase with charge and spin order
  - ➔ orbital antiferromagnetism or flux phase

Questions:

- which is the ground state of the *t–J* model ?
- which additional terms will favor which ground state ?

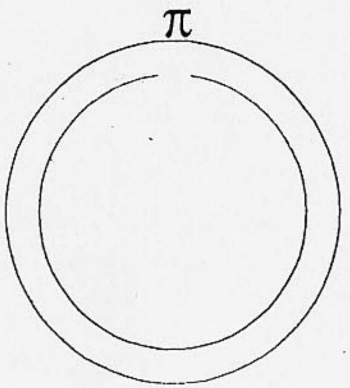
Internal Symmetry of Cooper Pairs

Possible sign changes in pairing amplitude around the Fermi surface tested by π–junctions



Energy in barrier: $\Delta F \propto -\cos(\phi_A - \phi_B + \pi)$

ΔF causes a phase slip of π across the barrier



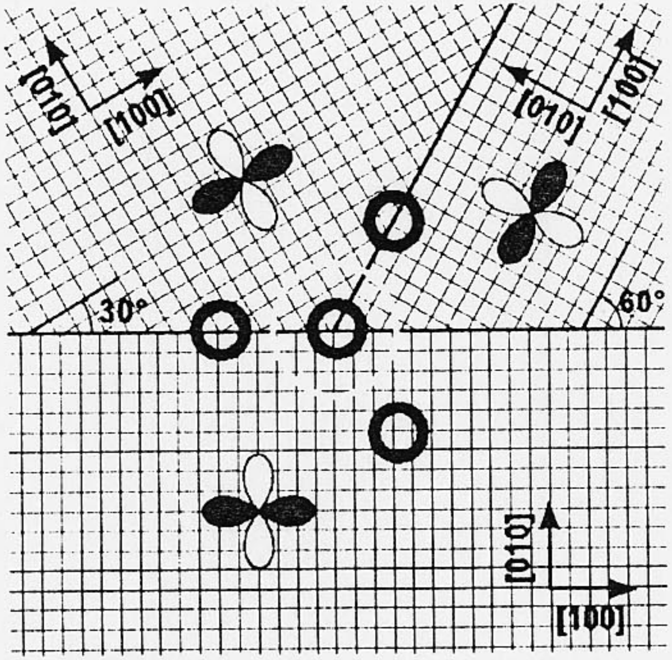
magnetic flux
$|\Phi| = (n + \quad) \, \Phi_0$

➔ Frustration in a loop with an odd number of π–junctions (Geshkenbein, Larkin, Barone '87)

➔ First signs in random ceramic samples, paramagnetic Meissner effect (Braunisch et al '92), $d_{x^2-y^2}$ symmetry (Sigrist, Rice '92).

➔ Controlled geometries (Wollmann et al. '93, Brawner, Ott '94, Mathai et al. '95, Tsuei, Kirtley '95)

Tri-crystal-configuration

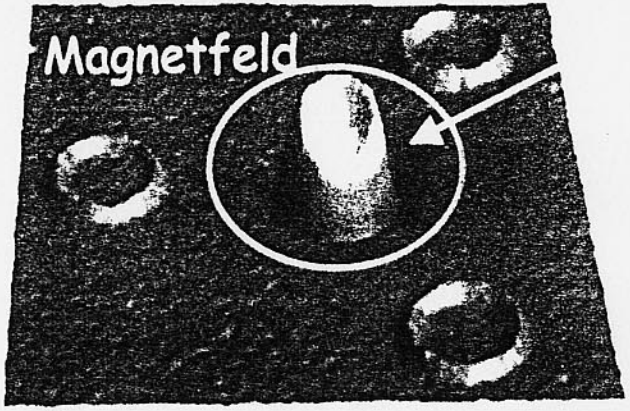


Tsuei, Kirtley et al. (IBM)

Superconducting loops $\emptyset$ = 60 μm

$YBa_2Cu_3O_7$ T_c = 92 K

spontaneous currents and magnetic field

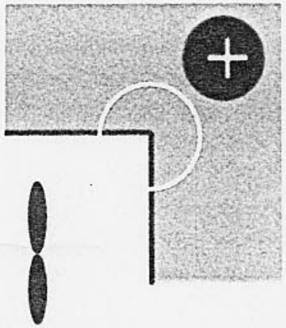


π

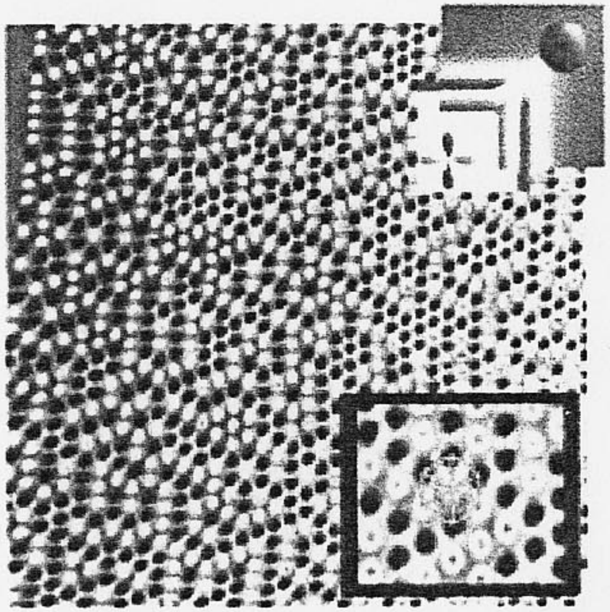
SQUID scanning microscope

…strated s-d loops

Basic unit



flux at the corner junction



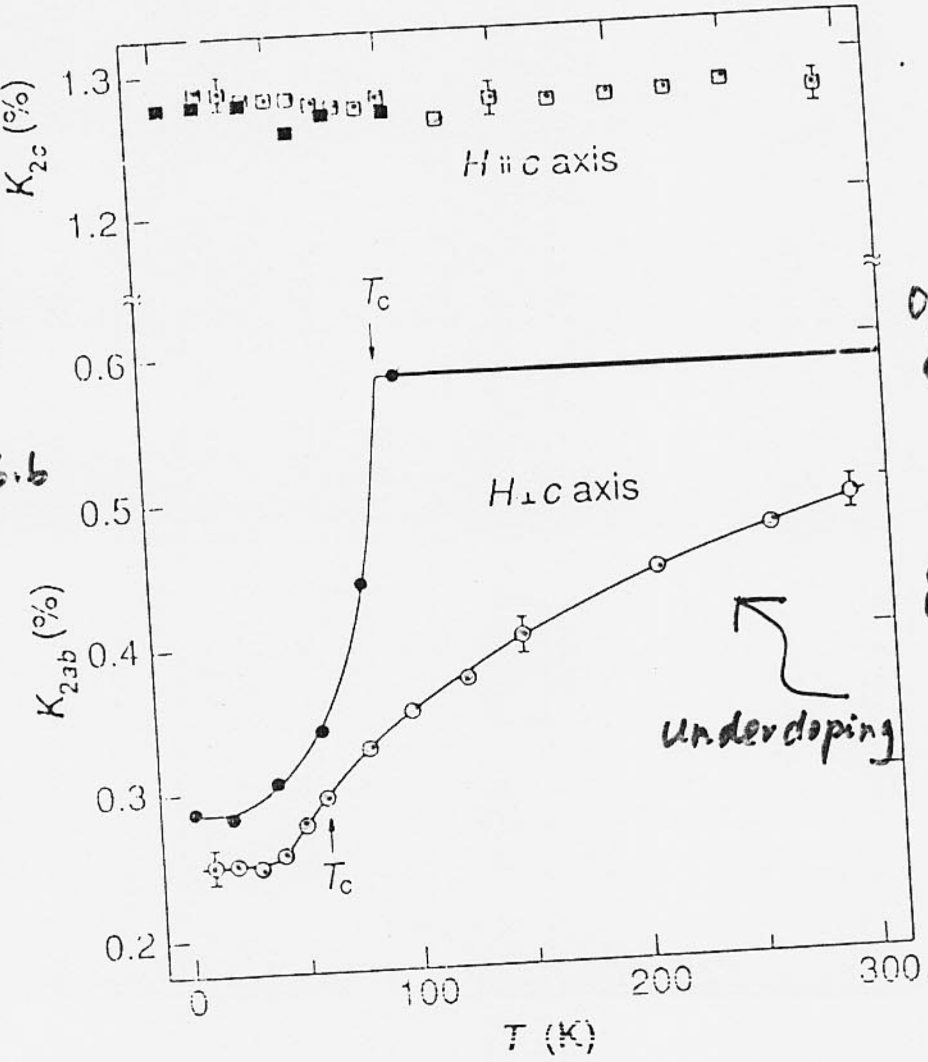
H. Hilgenkamp et al., Nature 422, 50 (2003)

^{63}Cu - Knight Shifts $K \propto \chi_s(T)$: spin susceptibility

• $YBa_2Cu_3O_7$

$YBa_2Cu_3O_{6.6}$

Walstedt - Warren Science ('90)



optimal doping

Evidence of spin-gap

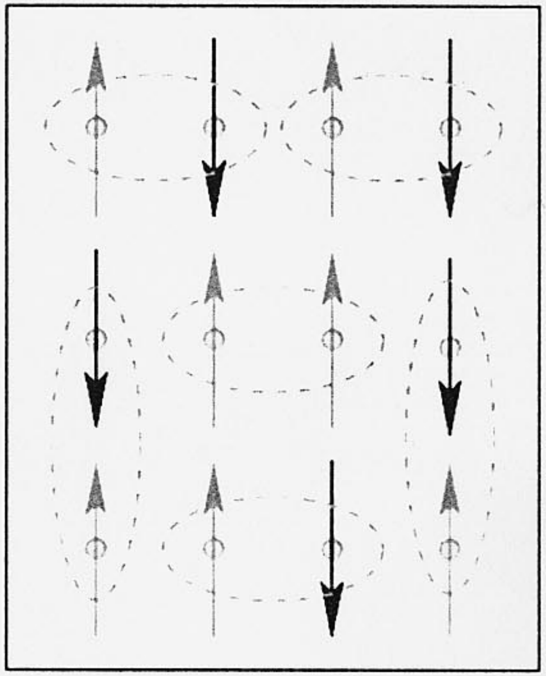
underdoping

Continuous onset of pairing of Cu^{2+}-spins at $T \gg T_c$ in the underdoped regime

Resonant Valence Bond State

Anderson '87

Quantum Fluctuations can lead to a Spin Liquid of Singlet pairs



- Energy of a Singlet: $-\frac{3}{4}J$

very favorable

(But AF order has a lower energy at ½-filling in 2-Dimensions)

Will hole doping stabilize RVB and make singlet pairs mobile leading to superconductivity?

- dRVB Variational State: $P_0|\mathrm{dBCS}\rangle$

  Gutzwiller Projector — no double occupancy (P_0)

  d-wave SC ($|\mathrm{dBCS}\rangle$)

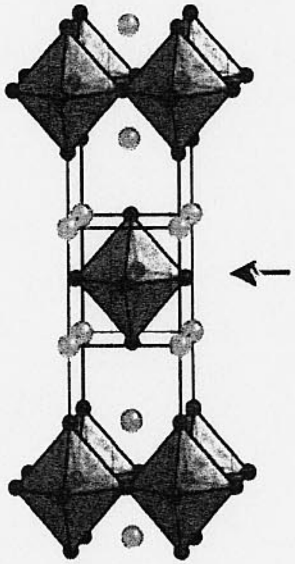
- Low Energy States of t-J model
  - $d_{x^2-y^2}$ pairing symmetry
- Density of superconducting carrier $\sim x$: hole density
  - $T_c \sim x$ for x small due to nodal quasiparticles
- Spin pairing at higher temperatures $T^* > T$
- Explains main features of ARPES experiments

See: P.W. Anderson, P.A. Lee, M. Randeria,
T.M. Rice, N. Trivedi and F.C. Zhang, to be published.

Sr_2RuO_4 - a spin triplet superconductor

There is no better characterized unconventional superconductor - except may be high-T_c superconductors.

Transition metal oxide



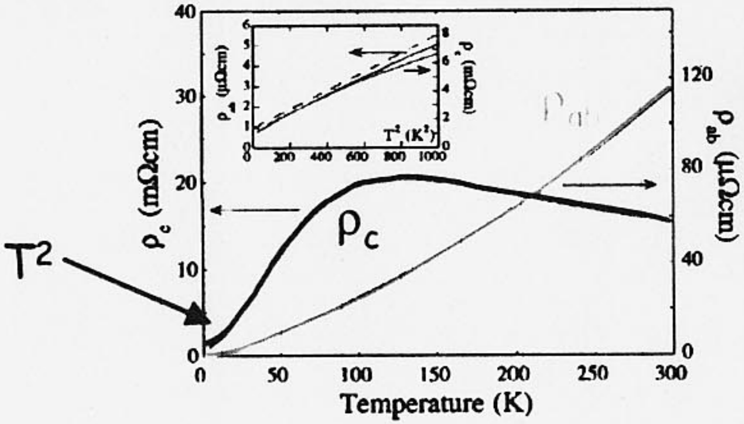
← RuO_2 plane

Maeno, Bednorz et al. ('94)

Superconductor with $T_c \approx 1.5$ K

Quasi-two-dimensional Fermi liquid

Strong correlation effects



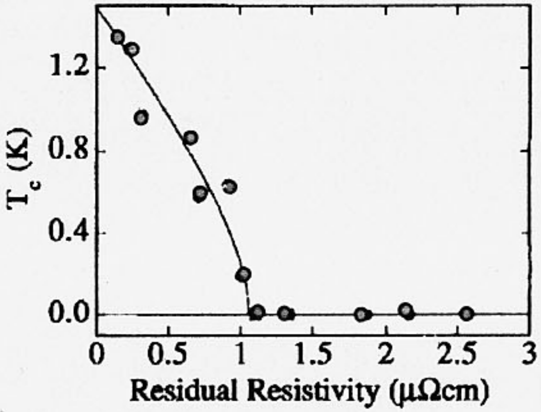
Analogy to Fermi liquid ^3He

Spin triplet superconductivity

Superconductivity in Sr_2RuO_4

- strongly correlated 2D Fermi liquid
- superconducting with T_c = 1.5 K   Maeno et al., Nature 372, 532 (1994)

T_c highly sensitive to non-magnetic impurities



Mackenzie et al.,
Phys. Rev. Lett. 80, 161 (1998)

⇓

unconventional superconductivity
pairing in higher-angular momentum channel

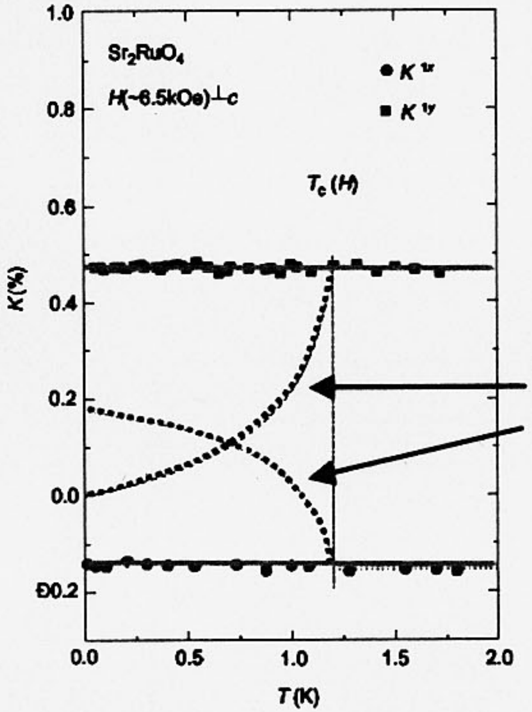
⇓

electronic analog to ^{3}He?   Rice - Sigrist '9
pairing in the p-wave spin-triplet   Baskaran '9
channel (A- or B-phase ?)

Two crucial experiments for Sr_2RuO_4

Spin susceptibility

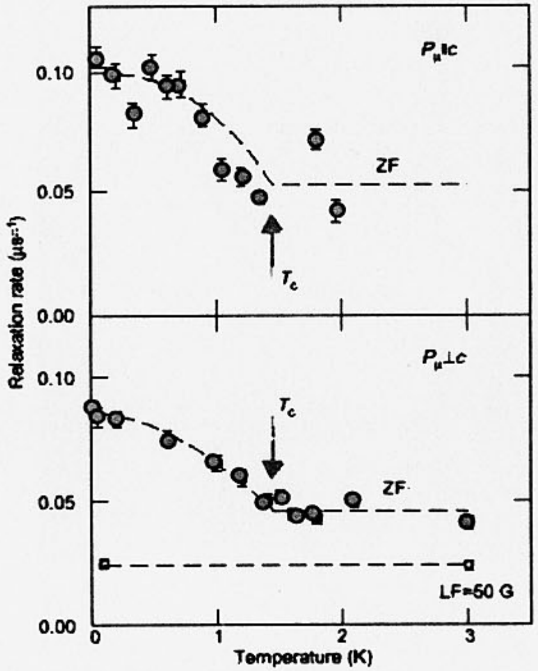
^{17}O-NMR Knight shift



Ishida et al., Nature 396, 242 (1998)

inplane equal-spin pairing

Muon-spin relaxation



Luke et al., Nature 394, 558 (1998)

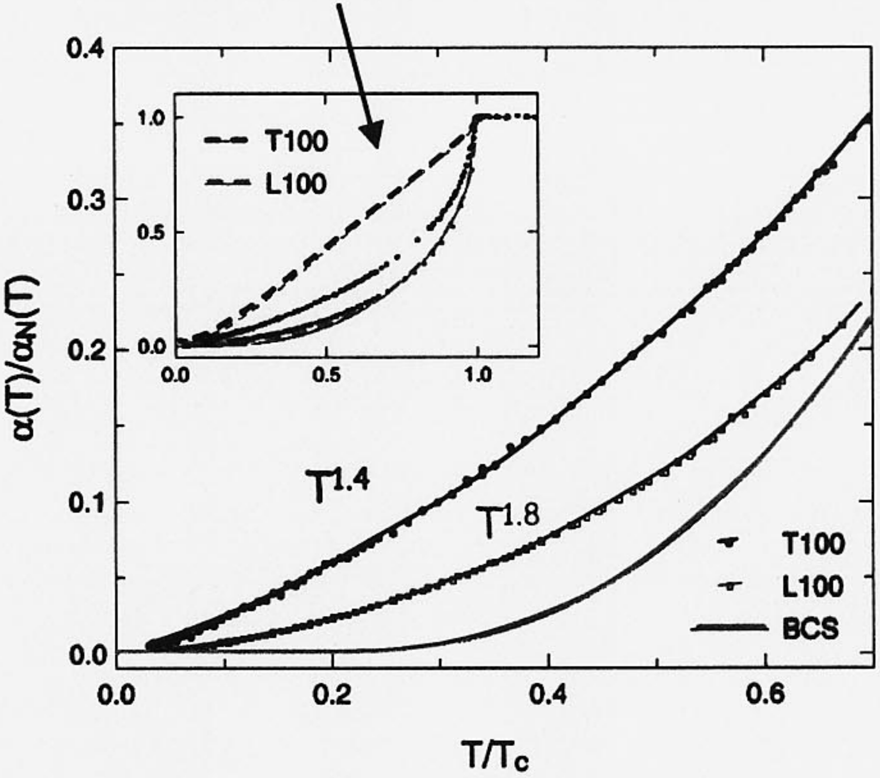
intrinsic magnetism

T-violation

$\Rightarrow$ triplet <u>A-phase</u>: $\Delta_{\alpha\beta}(\vec{k}) = (i\sigma^y\sigma^z)_{\alpha\beta} \cdot d_z(\vec{k})$ with $\vec{d} = \hat{z}(k_x \pm i k_y)$

Ultrasound absorption

vertical line nodes



Lupien, Taillefer et al.

Real powerlaw or multi-band effect?

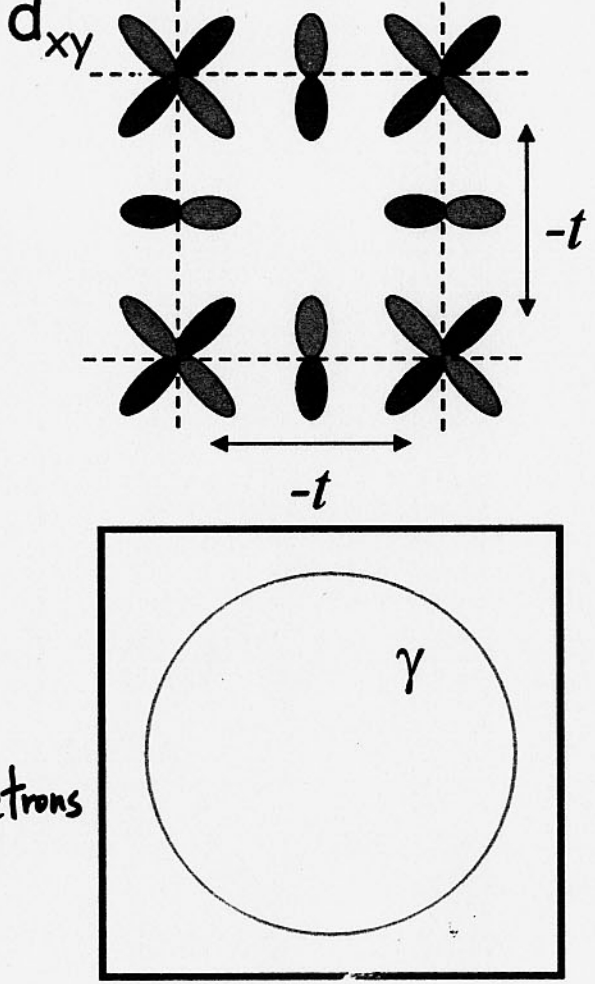
Propagation direction and polarization of ultrasound is important!

Line nodes:

$$\alpha(T) \rightarrow \begin{cases} T^{1.5} & \text{active nodes} \\ T^{3.5} & \text{inactive nodes} \end{cases}$$

Moreno & Coleman

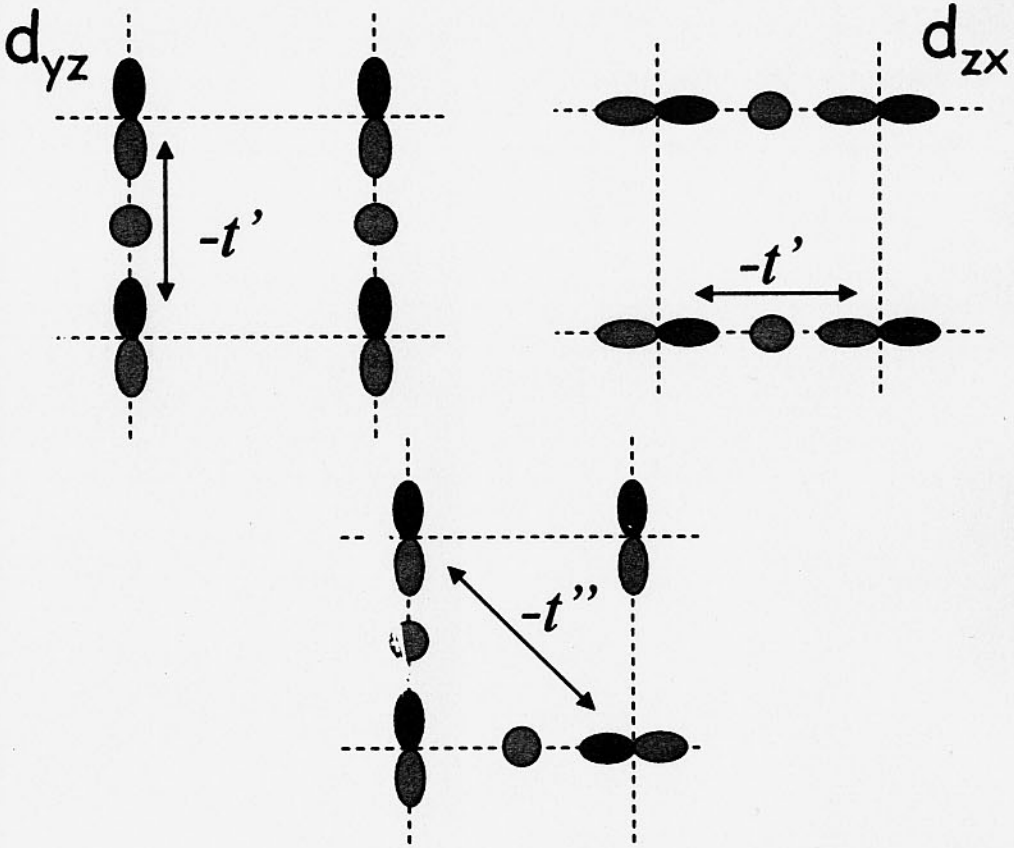
Electronic structure



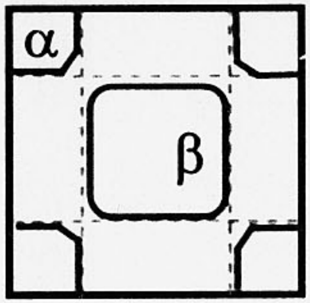
4/3 electrons

electron-like

even parity



z → -z



hole-like

electron-like

odd parity

Microscopic Model for $Sr_2 Ru O_4$

- γ-band active band
- α-β bands passive bands

- Agterberg, Rice Sigrist for superconductivity
- Zhitomirsky-Rice

γ-band: - 2-Dim. (xy-orbital) and 4/3 el./Ru

- Fermi Surface very close to saddle-pts. (van Hove singalarities)

Functional RG Treatment of $\underset{nn}{t}$ - $\underset{nnn}{t'}$ - U Hubbard mod

predicts enhanced T_c for triplet pairing when Fermi Surface is near to saddle-points

- proximity to a Stoner ferromagnetism

Honerkamp-Salmhofer

The Superconductor that stood on the shelf.

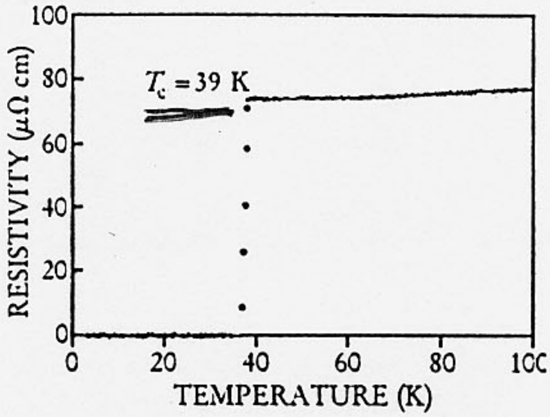


FIGURE 2. SUPERCONDUCTIVITY in magnesium diboride appears at a temperature of 39 K. (Adapted from ref. 1).

- Nagamatsu
  ⋮
  Akimitsu
  Nature Mar. '01

MgB_2

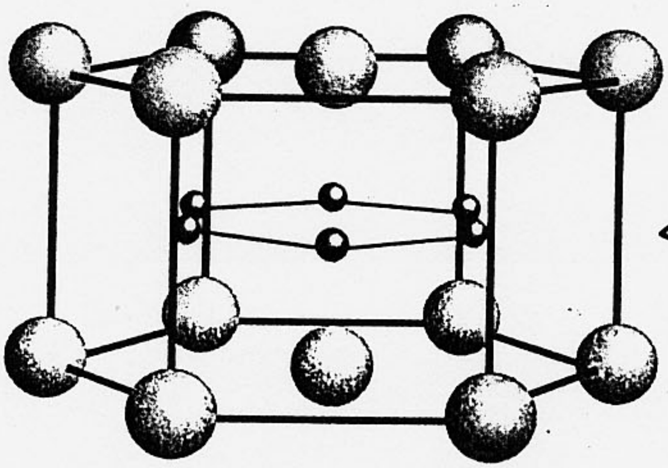


FIGURE 1. MAGNESIUM DIBORIDE belongs to the AlB_2 family of structures. The magnesium atoms, shown here in gray, form a hexagonal layer, while the boron atoms, shown in brown, from a graphite-like honeycomb layer.

- Fermi Surface in π- and σ- Bands

- A BCS electron-phonon superconductor ✓

Endless search for ever more exotic species