Organic Superconductivity

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Brief History
A Remarkable Set of Materials!
Nature of the Superconducting State?
The Discovery of New Condensed Phases
& New Effects in High Magnetic Fields

(TMTSF)$_2$PF$_6$ the first organic superconductor

CONTROLLABLE

Coherence?
(TMTSF)$_2$PF$_6$ - Most Remarkable Electronic Material Ever Discovered

So far in one single crystal:

All the usual competitions:
Metal-Insulator, Magnetic-Superconductor,
Commensurate-Incommensurate, FermiLiquid- NonFermiLiquid,
Spin Density Wave - Charge Density Wave......

Exhibits all transport mechanisms known to man:
Metallic, Sliding Density Wave, Superconducting,
Quantum Hall

Plus somethings new :
Field Induced SDW/QHE
Giant Nernst Effect, Magic Angle Effects
Triplet Superconductivity, Field Induced Slabs
## Who’s to Blame

### Princeton
- *InJae Lee* (Chonbuk National University)
- *Weida Wu* (Rutgers)

### UCLA
- *Stuart Brown*
- Gil Clark
- David Chow

### Boston College
- Mike Naughton

With Advice from: Andrei Lebed, Victor Yakovenko, Phil Anderson, David Huse, Phuan Ong
1911 - Superconductivity Discovered by Gilles Holst

1957 - Superconductivity Explained BCS

1963 - Bill Little proposes Excitonic, Organic, Polymeric Superconductor

Schegolev, Bloch, Heeger,…. Work on “1D” metals, TCNQ’s

1970 - Fred Wudl discovers TTF

TTF-TCNQ first organic metal (not superconductor)

1973 - Alan Heeger, others

Rick Greene, (SN)$_x$, first (and only) polymeric superconductor Tc~0.3K

1975 - Bechgaard and Jerome First Organic Superconductor TMTSF$_2$ PF$_6$ Tc~1.2K

1979 - G. Saito, (ET)$_2$Cu[N(CN)$_2$Br] Tc~13K
Fig. 3. Chemical structure of the proposed superconducting organic polymer. At each point $R$ on the spine a similar side chain to the one shown is attached. These side chains are resonating hybrids of the two extreme structures shown in the inset. The positive charge resonates between the two nitrogen sites as illustrated.
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“g-ology Phase Diagram 1D electrons

Only two interactions important

backscattering

forward scattering

$g_1(q=2k_F)$

$g_2(q=0)$
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<table>
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<tr>
<th>Observed and hinted at ground states</th>
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<td><strong>BEDT-TTF family</strong></td>
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<td>Supercond – singlet</td>
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<td>- d-wave?</td>
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<td>- LOFF?</td>
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<td>Quantum Hall?</td>
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Crystal Structure of Bechgaard Salts \((TMTSF)_2X\)

- Highly anisotropic
  \[\sigma_a : \sigma_b : \sigma_c = 1 : 10^{-2} : 10^{-5}\]
  \[4t_a : 4t_b : 4t_c = 1 : 0.1 : 0.003\ (eV)\]
  \[\sigma_i \sim t_i^2\]

- Good metal
  \[\rho \sim 1\ \mu\Omega\text{cm at 4K}\]
  \[(\rho\ (Cu) \sim 1\ \mu\Omega\text{cm at 300K}).\]

- Extremely clean
  \[l \sim 10\mu\text{ at 1K},\ h/\tau \sim 0.1K\ at 1K\]

- \(\frac{1}{4}\) Filled, Slightly Dimerized
  Single chain has charge gap.

\((TMTSF)_2X,\ X = PF_6,\ ClO_4,\ ...
\]

\[\text{TMTSF = tetramethyltetraselenafulvalene}\]

Triclinic

\[\alpha = 83.39^\circ, \beta = 86.27^\circ, \gamma = 71.01^\circ\]

\[a = 7.297\ \text{Å}, b = 7.711\ \text{Å}, c = 13.522\ \text{Å}\]
Phase Diagram \((TMTSF)_{2}\text{PF}_6\)
1D metals are unstable – Fermi Surfaces Nest
Interchain hopping – warped Fermi Surface – regain metal
Pressure increases interchain hopping – more 3D
3D (P,H,T) phase diagram of (TMTSF)$_2$PF$_6$

First guess from g-ology

1D-electron gas phase diagram ("g-ology").

Insulator-Superconductor Bechgaard, Jerome 1979
Singlet or Triplet?

Radiation damage experiments

![Graph showing temperature dependence of resistivity](image)

FIGURE 7 Temperature dependence of resistivity of (TMTSF)$_2$PF$_6$ at 11 kbar pressure for various amounts of radiation induced damage. Insert shows damage dependence of resistivity at $T=1K$. Non s-wave


Resistive upper critical fields

![Graph showing anisotropic critical field](image)

$H_p = 16$ KG

Singlet (s,d-wave)?


Proton spin-lattice relaxation experiments

M. Takigawa et al.,

Non S-wave
(line node on FS)

Belin et. al.

Thermal conductivity

S-wave (a finite gap)
(No node on FS)
Singlet – Triplet Unresolved after ~ 12 years in 1980’s

But People discovered unusual things in Magnetic Fields
Electron Orbits for a Magnetic Field along $\mathbf{c}$
One-Dimensionalized by Magnetic field

\[ \nu = \frac{1}{\hbar} \frac{\partial \epsilon}{\partial k} \]
\[ \frac{dk}{dt} = \frac{e}{\hbar} (\nu \times B) \]
\[ \frac{dk}{dt} = \frac{e}{\hbar} \left( \frac{dr}{dt} \times B \right) \]

Real Space

\[ w_b = b \left( \frac{4t_b}{e v_F B_z} \right) \]

\[ \lambda = \frac{h}{e b B_z} \]

\[ \omega_b = \frac{e v_f b B_z}{\hbar} \]

Chaikin, Azbel, Holstein, ‘83
The Standard Model

Gor’kov, Lebed, Chaikin, Heritier, Montambaux, Lederer, Poinblanc, Yamaji, Maki, Virosztek, Chen, Chang, Azbel, Bak, Chaikin, Yakovenko

- Unnested Open Orbit Fermi Surface
- H makes system more 1-D
  ⇒ Unstable to density wave

But nesting at \( q = 2k_F \pm nG, \ G = 2\pi/\lambda \)

⇒ Spectrum with multiple gaps
⇒ Cascade of transitions
⇒ Quantum Hall \( \rho_{xy} = h/ne^2 \)
Cascade of Field Induced Spin Density Waves

\[ \rho_{xy}(h/e^2) \]

\[ T(K) \]

\[ H(T) \]

\[ n=0 \]

\[ n=1 \]

\[ n=2 \]

Insulator

Metal

\[ \rho_{xy} = \frac{h}{n_e e^2} \]

with Quantum Hall Effect
Integer Quantum Hall Effect in (TMTSF)$_2$PF$_6$

\[ R_{xy}(m\Omega) \]
\[ R_{xx}(m\Omega) \]

- $T = 300\text{mK}$
- $P = 10\text{kbar}$

$N = 1$, $N = 2$, $N = 3$, $N = 4$
More 1D like

More 3D like
Main lesson:

Magnetic field perpendicular to the chains reduces electronic dimension

Does this decouple chains/planes?

3D coherent Coherent planes
Two Contributions to Magnetic Critical Field - Orbital and Spin

Orbital term derives from Field Expulsion
e.g. Meisner Effect

Need currents to expel field
\[ j \sim H, \Delta F \sim K.E. \sim j^2 \sim H^2 \]

Spin derives from susceptibility
of spin paired state

\[ \Delta F \sim (1/2) \Delta \chi H^2 \]

\[
\begin{align*}
F_{\text{Normal}} & \quad \text{H}_{\text{c2orbital}} \\
F_{\text{super}} & \\
H & \quad \rightarrow
\end{align*}
\]

\[
\begin{align*}
F_{\text{Normal}} & \quad (1/2) \chi_{\text{Pauli}} H^2 \\
F_{\text{super}} & \quad \text{H}_{\text{Pauli}} \\
H & \quad \rightarrow
\end{align*}
\]

Usually \( H_{\text{c2orbital}} \ll H_{\text{Pauli}} \)
Clogston-Pauli Limit to $H_c^2$

Normal Metal
\[ \chi_{\text{spin}} = \chi_{\text{Pauli}} = \mu_0^2 N(E_F) \]

Singlet Superconductor
\[ \chi_{\text{spin}} = 0 \]

Triplet Superconductor
\[ \chi_{\text{spin}} = \chi_{\text{Pauli}} \]

Note: When
\[ \mu_0 H > \Delta \]
\[ \downarrow \uparrow \rightarrow \uparrow \uparrow \]
\[ H \]
single pairs break

\[ N(E_F) \Delta^2 / 2 = \chi_{\text{Pauli}}^2 H_p^2 / 2 = 2 N(E_F) \mu_0^2 H_p^2 / 2 \]

\[ \Delta = 3.52 k_B T_c = \sqrt{2} \mu_0 H_p \]

\[ H_p = 1.84 T_c \text{ (Tesla/K)} \]
A.G. Lebed’/DMS’s proposal. 
Field-induced dimensional crossover quenches orbital pair breaking effect


\[ H_p = \frac{\Delta}{\sqrt{2} \mu_o} = 1.84 T_c [Tesla] \]

L.I. Burlarchkov, L.P. Gor’kov and A.G. Lebed’
Critical Field with decoupling
ala Lebed, Montambaux, Dupuis, Sa de Melo

High Field
layers decoupled
Orbital $H_{c2} \to \infty$
$T_c \to T_{c0}$

Intermediate Field
coupling weakened
less screening
Higher $H_{c2}$

Low Field
layers coupled
screening currents reduce $T_c$
Conventional $H_{c2}$
$\text{(TMTSF)$_2$PF}_6$

Temperature (K)

Magnetic Field (T)

$H \parallel b'$

$H \parallel a$

$H \parallel c^*$

Junction

Injae Lee
\[ \Delta = H \mu^2 \]

\( (\text{TMTSF})_2\text{PF}_6, \) peak(onset) point

\( H//b' \)

- 6 kbar
- 5.7 kbar
- 5.8 kbar

\[ \sqrt{2}\mu H = \Lambda \]

Paramagnetic limit for singlet
$H_{C2} > 4 \times H_{\text{Pauli}}$ proves triplet (equal spin paired)

$\uparrow \uparrow \text{ or } \downarrow \downarrow$

But people are more used to seeing NMR Knight Shift
Setup for $^{77}\text{Se}$ NMR Knight Shift experiments

- Dilution temperature (0.03 K)
- High pressure (7 kbar)
- Precise angular alignment (resolution: 0.0025°)
- Simultaneous NMR and transport measurements

Miniature pressure cell mounted on the bottom of mixing chamber
Spin susceptibility in \((\text{TMTSF})_2\text{PF}_6\)

\[
\frac{\chi}{\chi_n} = \frac{\langle \omega \rangle - \langle \omega \rangle_n}{K_s}
\]

Spin triplet superconductivity?


I.J. Lee et al., PRL, 88, 17004 (2002)

\((H=2.38T)/(H_{c2}(0)=5T) \sim 0.5\) for \(H \parallel b\)

\((H=1.43T)/(H_{c2}(0)=3.4T) \sim 0.4\) for \(H \parallel a\)
On the superconducting state of the organic conductor (TMTSF)$_2$ClO$_4$

J. Shinagawa,1 Y. Kurosaki,1,2 F. Zhang,1 C. Parker,1,3 S. E. Brown,1 D. J’erome,4 J. B. Christensen,5 and K. Bechgaard5

(Dated: April 9, 2007)

(TMTSF)$_2$ClO$_4$ is a quasi-one dimensional organic conductor and superconductor with $T_c = 1.4$K, and one of at least two Bechgaard salts observed to have upper critical fields far exceeding the paramagnetic limit. Nevertheless, the 77Se NMR Knight shift at low fields reveals a decrease in spin susceptibility $s$ consistent with singlet spin pairing. The field dependence of the spin-lattice relaxation rate at 100mK exhibits a sharp crossover (or phase transition) at a field $H_s \sim 15kOe$, to a regime where $s$ is close to the normal state value, even though $H_{c2} \gg H_s$.

But at low field there is a Knight Shift shift?
Back to Magnetic Field Induced Decoupling/Decoherence
Lebed’s magic Angles

Something happens when
\( \omega_b/\omega_c = p/q \) rational

\( \omega_c = e v_F H b \sin(\theta)/h \)

\( \omega_b = e v_F H b \cos(\theta)/h \)
Lebed Magic Angle Effects

Commensurate Orbits correspond to field directed between real space chains

**Magic Angles → Lattice Vectors**

\[
\frac{dk}{dt} = \frac{e}{\hbar}(v \times B)
\]

Recip space \(\perp\) Real space
Quasi-particle coherence

Basic Idea: Coherent-Incoherent Transition above Threshold $H_{\text{perp}}$ field

Strong, Clark, Anderson
PRL 73, 1007 (1994)
At magic angles metallic
dR/dT > 0

At nonmagic angles
Nonmetallic dR/dT < 0

These differ by 6°

Similar effect along a, b, c axes
Look at Conductivity instead of resistivity

Insulating when decoupled
Conducting when field allows interchain tunneling
Angular dependent Nernst
Drude, Boltzmann:

\[ e_N \propto T \cdot B \sin \theta \]

\[ \sim \frac{k_B}{e} \frac{T}{T_F} \omega_c \tau \]

\[ \approx 1 \text{nV} / K \]

\((\text{TMTSF})_2\text{PF}_6: e_N \sim 10 \mu\text{V} / K\)
Field induced inter-chain decoupling
Transport: Only coherent at planes // H

What is the coherence?
SC Phase coherence at Magic Angle Planes

Vortex Nernst enhanced Near Mott Insulator

$X = \text{Cu}[\text{N(CN)}_2]\text{Cl}$

$X = \text{Cu}[\text{N(CN)}_2]\text{Br}$

$X = \text{Cu(NCS)}_2$

Paramagnetic insulator

Fermi liquid

Mott insulator

Superconductor

Pressure (kbar)

Increasing $t/U$

$\kappa-(\text{BEDT-TTF})_2X$
Summary

- 2D organics - S and D wave Superconductors,
- 1D organics - Singlet and Triplet superconductors,
- Strong fields control dimensionality and coherence.

- Organic Superconductors remain an exciting testing ground for low dimensional strongly interacting electrons with characteristic energies $\text{HTc}/10$

\[(\text{TMTSF})_2\text{PF}_6\]
STILL MOST REMARKABLE ELECTRONIC MATERIAL?