STRONGLY CORRELATED ELECTRONS IN THE LAYERED ORGANIC SUPERCONDUCTORS κ-(BEDT-TTF)$_2$X: OPPORTUNITIES FOR DMFT

Ross H. McKenzie

University of Queensland
Brisbane, Australia

Jaime Merino

Max-Planck-Institut
Stüttgart, Germany

Comments CMP **18**, 309 (1998).
Phys. Rev. B **61**, 7996 (2000).
Phys. Rev. B **62**, 2416 (2000).
Phys. Rev. B **62**, 16442 (2000).

Supported by Australian Research Council

MAIN POINTS

(1) The metallic phase of κ-(BEDT-TTF)$_2$X is a strongly correlated metal close to a Mott insulating phase. It exhibits a crossover from a Fermi liquid to a bad metal at $T_0 \sim 30$ K.

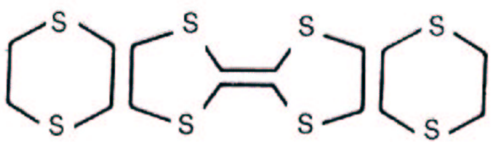
(2) The relevant theoretical model is a Hubbard model on an anisotropic triangular lattice at half-filling.

(3) The coherence temperature T_0 is described by dynamical mean-field theory.

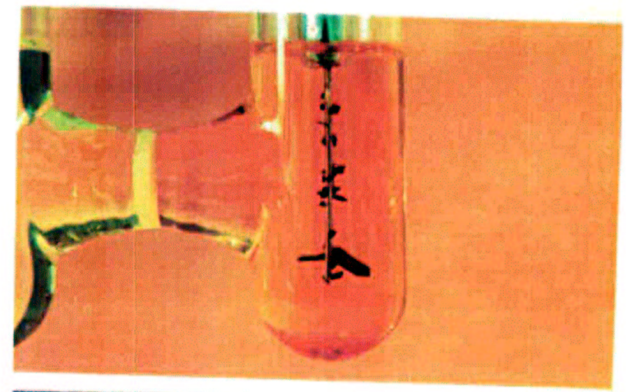
(4) Superconductivity is mediated by spin fluctuations and has $d_{x^2-y^2}$ symmetry?

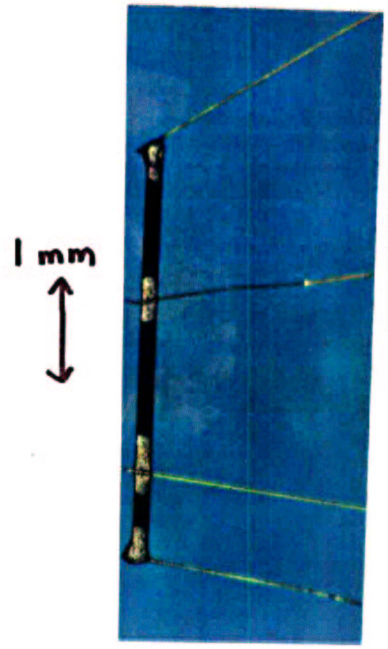
ORGANIC SUPERCONDUCTORS

- Bechgaard salts - $(TMTSF)_2X$ ($X=ClO_4, PF_6, ..$)
  Quasi-one-dimensional electronic properties
- Fullerenes - M_3C_{60}
- BEDT-TTF salts - e.g., α-$(BEDT\text{-}TTF)_2X$



Conducting layers of BEDT-TTF molecules are separated by layers of anions X.
Quasi-two-dimensional electronic properties
Greek letters α, β, κ, and θ denote the stacking pattern of the BEDT-TTF molecules in each layer.





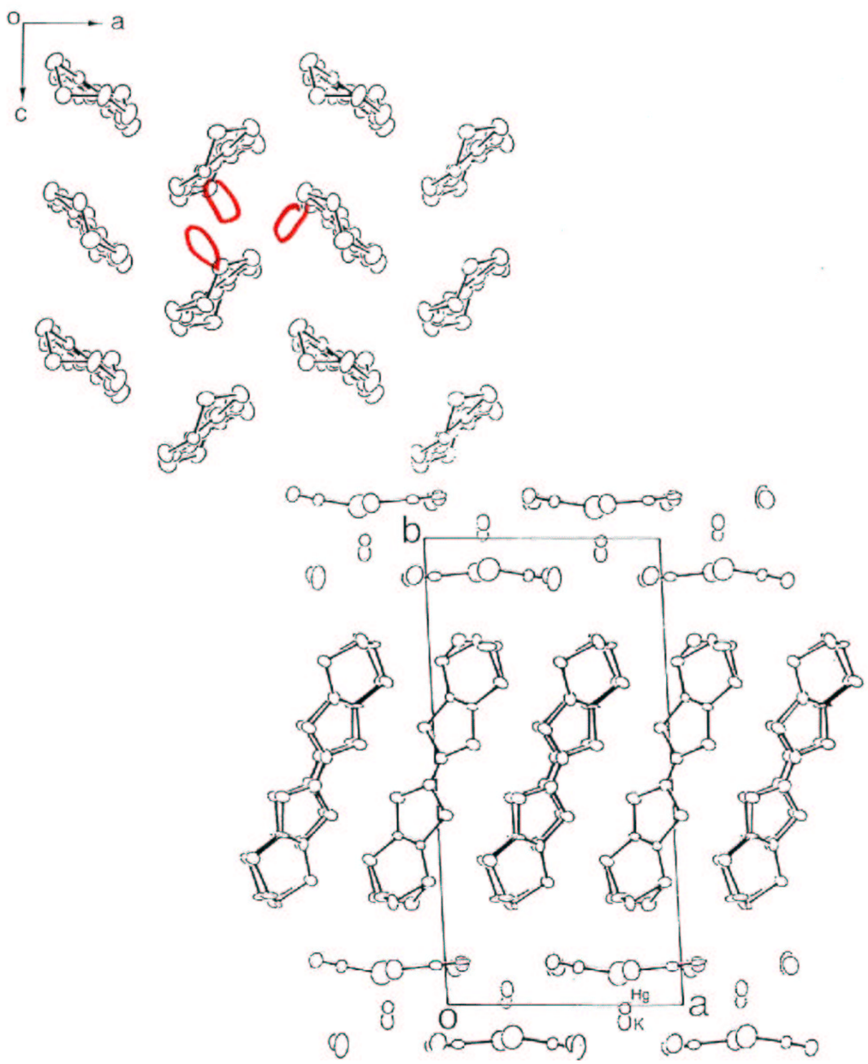
Organic metal. The dark material in the photograph at left is a single crystal of the organic metal $(TMTSF)_2ClO_4$. The four gold wires attached with gold paste are for electrical-conductivity measurements along the direction of highest conductivity. This typical crystal is 4 mm long, 0.2 mm wide and 0.05 mm thick. The crystals are prepared by electrochemical growth in solution, yielding very small single crystals that are perfect but quite brittle. The photo above shows crystals grown on a platinum electrode from a solution (highly diluted for the photo) of BEDT-TFF with triiodide anions. The largest crystal (lower right) is β-$(BEDT\text{-}TTF)_2I_3$. The black color is a result of the strong absorption of visible light in the crystalline state. (Upper photo courtesy of Jack M. Williams, Argonne National Laboratory.)

Figure 1

ORIGIN OF ANISOTROPIC ELECTRONIC PROPERTIES

Crystal structure of α-(BEDT-TTF)$_2$MHg(SCN)$_4$

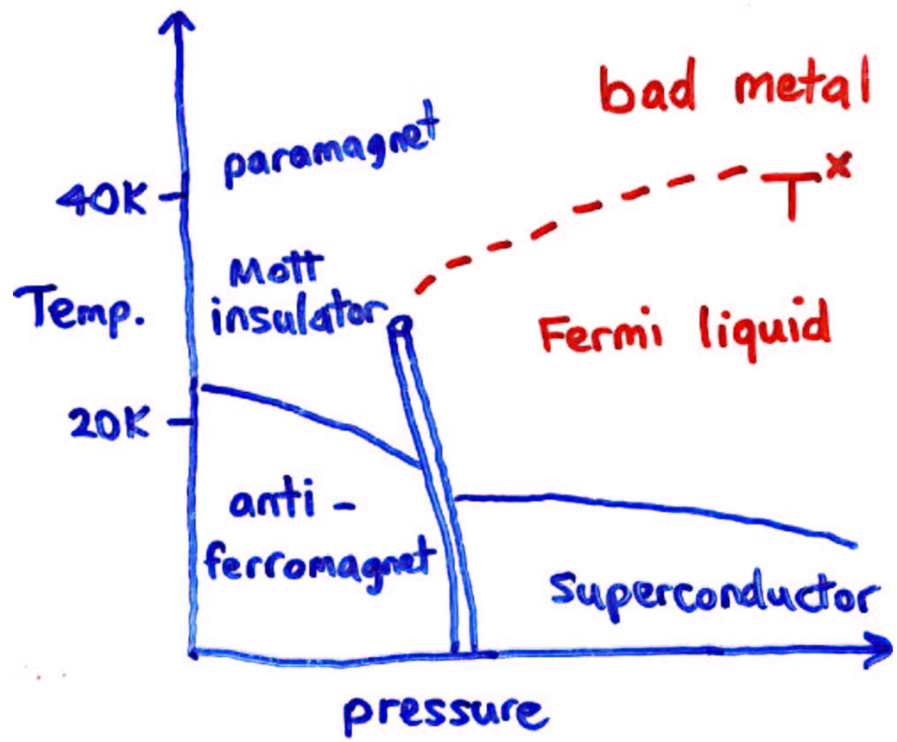
Highly conducting directions are due to large overlap of sulfur orbitals in the BEDT-TTF molecules.



PHASE DIAGRAM

κ-(BEDT-TTF)$_2$X

TEMPERATURE vs. PRESSURE



Lefebreve, Lang, ...
Kanoda, Sasaki, ...
Kino + Fukuyama

PHASE DIAGRAM

TEMPERATURE vs. PRESSURE

κ-$(ET)_2Cu[N(CN)_2]Cl$

Lefebvre et al., cond-mat/0004455
PRL 85, 5420 (2000)

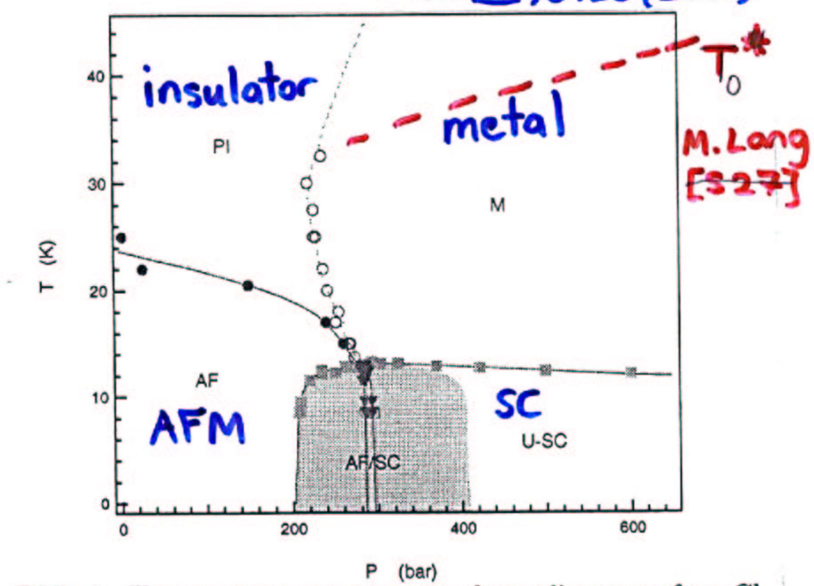
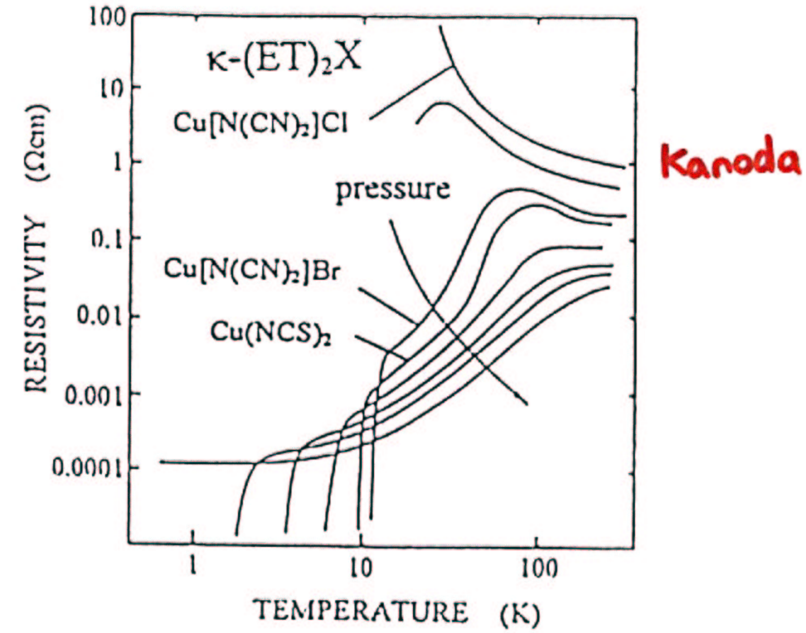


FIG. 1. Temperature *vs* pressure phase diagram of κ−Cl. The antiferromagnetic (AF) critical line $T_N(P)$ (dark circles) was determined from NMR relaxation rate while $T_c(P)$ for unconventional superconductivity (U-SC: squares) and the metal-insulator $T_{MI}(P)$ (MI: open circles) lines were obtained from the AC susceptibility. The AF-SC boundary (double dashed line) is determined from the inflexion point of χ'(P) and, for 8.5K, from sublattice magnetization. This boundary line separates two regions of inhomogeneous phase coexistence

UNCONVENTIONAL METALLIC PROPERTIES

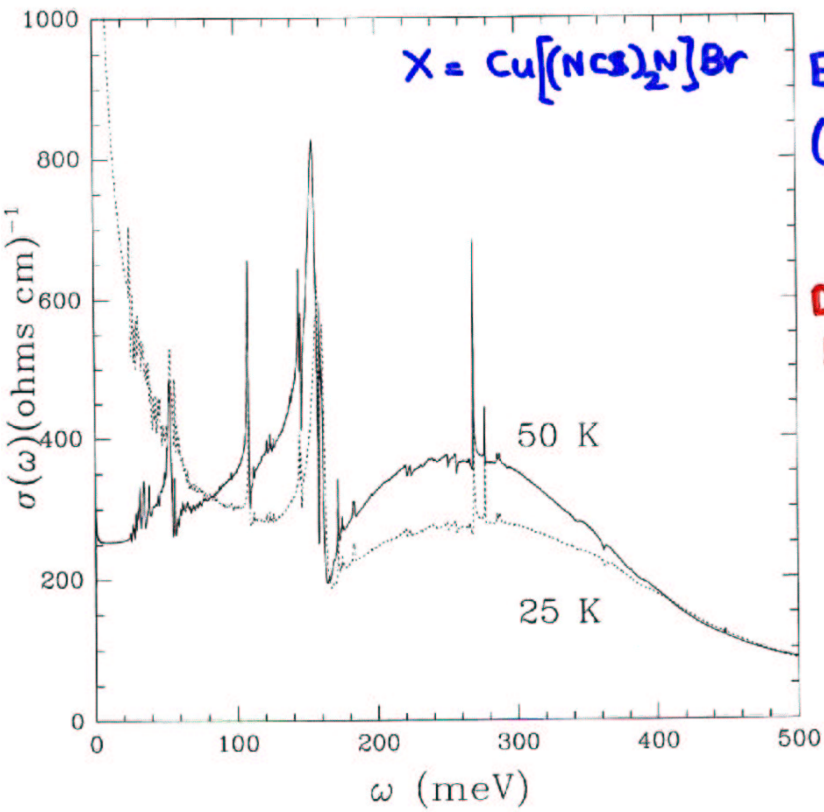
Temperature dependence of resistivity



- A low temperatures, $\rho \sim AT^2$ at low T, suggesting a Fermi liquid.
- At high temperatures, $\rho > \hbar a/e^2$ ('bad metal') so the "mean-free path" is less than a lattice constant.
- Non-monotonic temperature dependence

UNCONVENTIONAL METALLIC PROPERTIES

Temperature dependence of optical conductivity



Eldridge (UBC)

Drozdova B4

- No Drude ($\omega = 0$) peak above 50 K
- Broad peak around 300 meV.

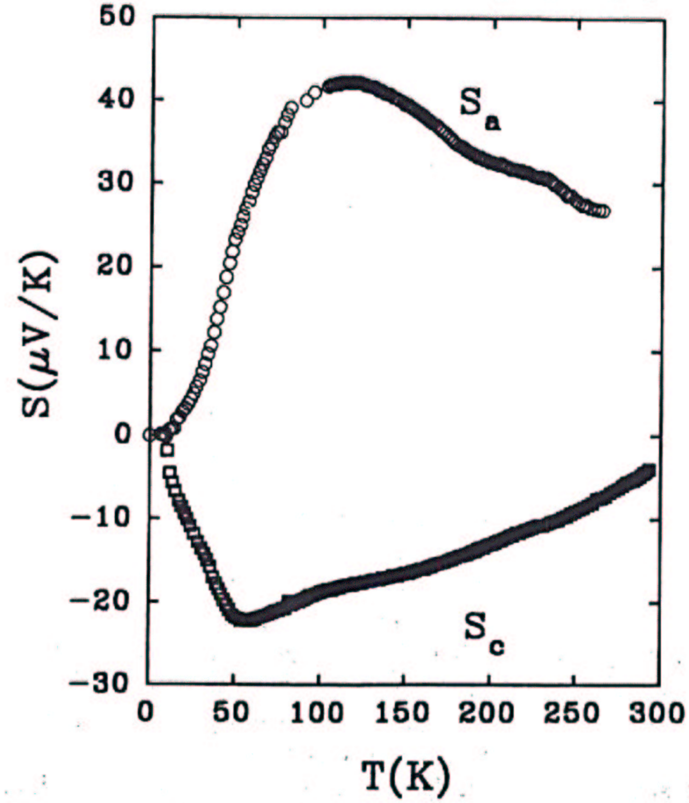
Is only a "conventional" metal below $T_0 \sim 50$K << Fermi energy E_F

Band structure gives $E_F \sim 1000$K .

UNCONVENTIONAL METALLIC PROPERTIES

Temperature dependence of thermopower

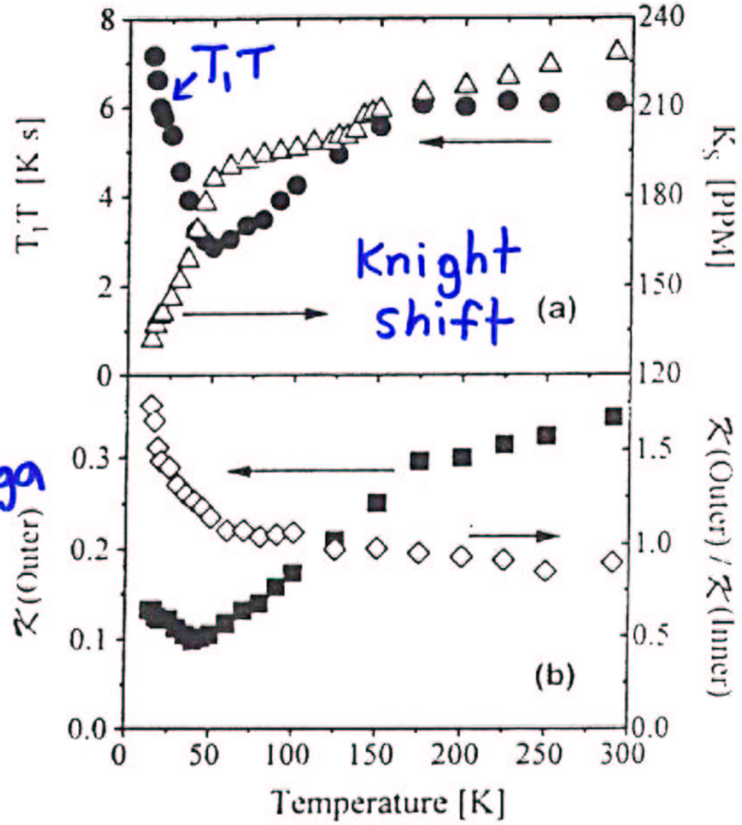
κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br



- Values of the order of k_B/e.
- Non-monotonic temperature dependence

TEMPERATURE DEPENDENCE OF NMR

κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br

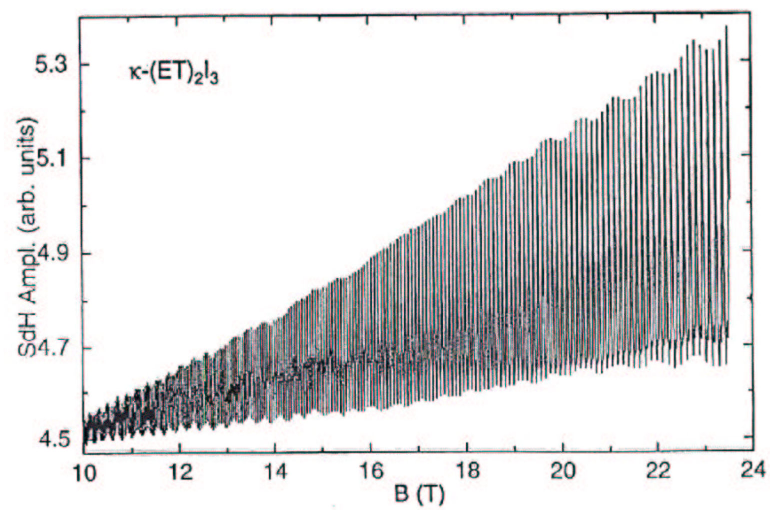


MAGNETIC OSCILLATIONS

J. Wosnitza, *Fermi surfaces of low dimensional organic metals and superconductors* (Springer, 1996)

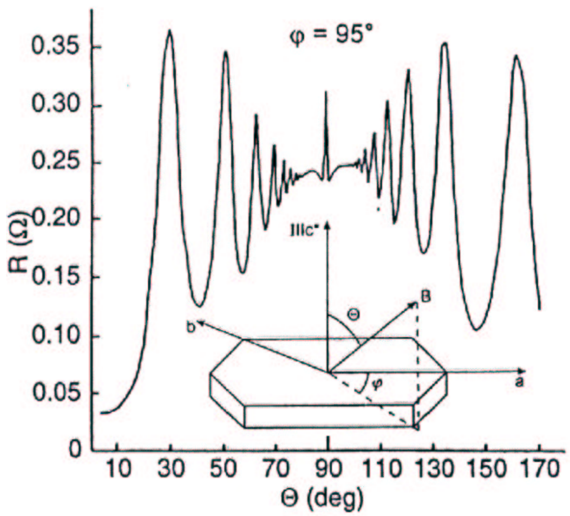
The temperature and magnetic field dependence of SdH and dHvA oscillations is consistent with a 2d or quasi-2d Fermi liquid at low temperatures ($T < 3$ K).

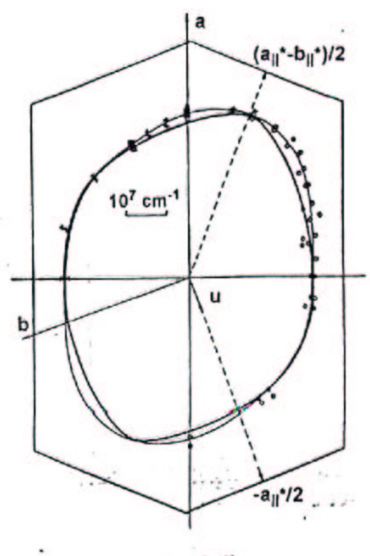
$$\frac{m^*}{m_e} \sim 1 - 7 \qquad \frac{\hbar}{\tau\, k_B} \sim 0.1 - 2 \text{ K}$$



ANGLE-DEPENDENT MAGNETORESISTANCE OSCILLATIONS

The angle dependence is consistent with a 2d or quasi-2d Fermi liquid with semi-classical dynamics and can be used to map out the Fermi surface.





UNCONVENTIONAL SUPERCONDUCTIVITY

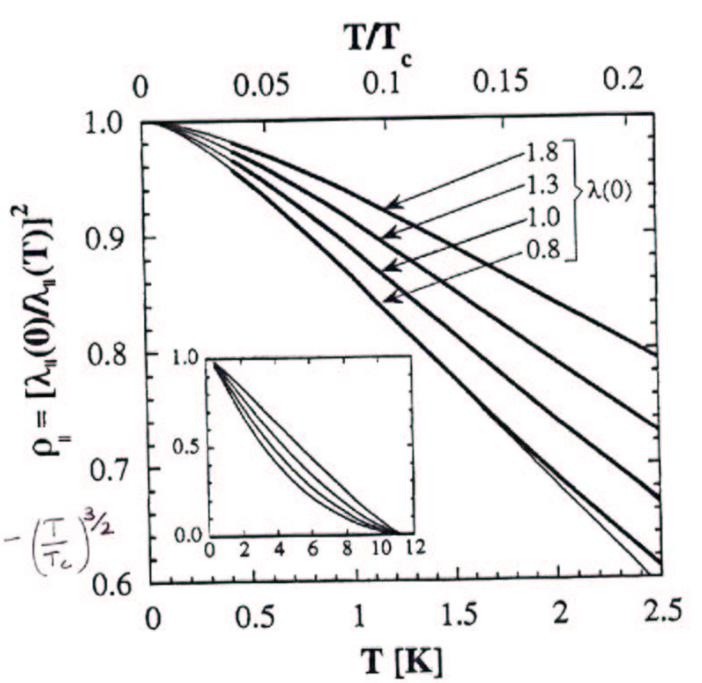
Evidence for *gapless excitations* or nodes in the gap is that some properties are not exponentially activated but have a power law dependence on temperature.

- nmr relaxation rate
  - $1/T_1 \sim T^3$
  - no Hebel-Slichter peak
- Thermal conductivity $\kappa \sim T$ magnetic field dependence (controversial)
- specific heat (controversial)
- penetration depth (controversial)
- magneto-optical (controversial)

Evidence for *singlet pairing*
The nmr Knight shift $K(T) \to 0$ as $T \to 0$.
The upper critical field B_{c_2} for the field in the layers is comparable to the Pauli paramagnetic (Clogston) limit at which the Zeeman splitting destroys singlets.

SUPERFLUID DENSITY VERSUS TEMPERATURE

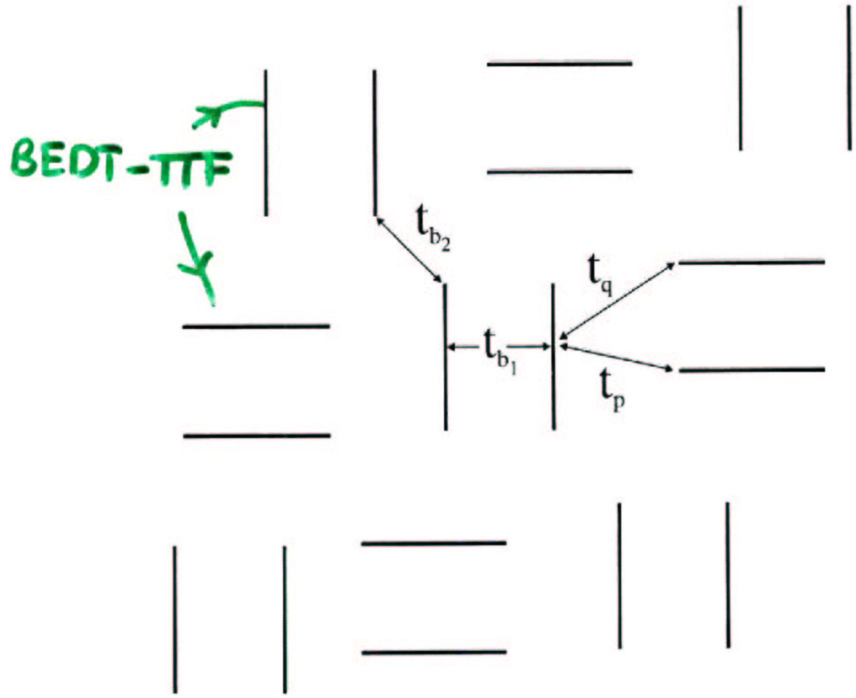
Carrington et al., PRL **83**, 4172 (1999)



$\rho_\parallel(T) \simeq 1 - \left(\frac{T}{T_c}\right)^{3/2}$

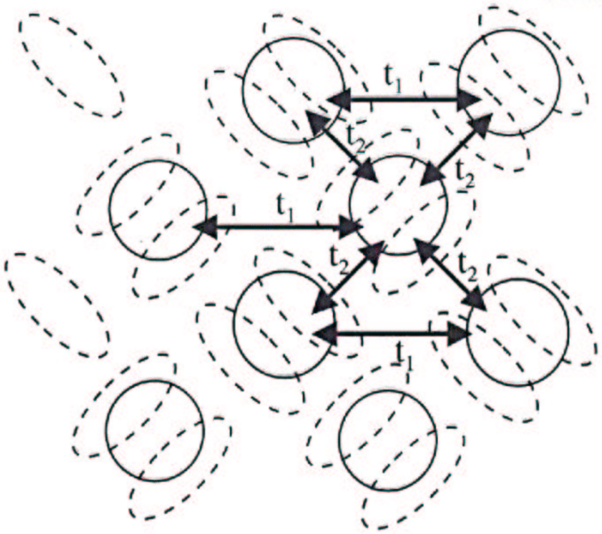
FIG. 2. In-plane superfluid density $\rho_\parallel = \lambda_\parallel^2(0)/\lambda_\parallel(T)^2$ calculated from the $\Delta\lambda_\parallel(T)$ data in Fig. 1, for several values of $\lambda_\parallel(0)$. The thin lines are fits to the data with Eq. (1). The

DIMER STRUCTURE OF κ-(BEDT-TTF)$_2$X



Hopping parameters between neighbouring BEDT-TTF molecules within each layer. The bonding and anti-bonding orbitals on each dimer are split by $2t_{b_1} \gg t_{b_2}, t_p, t_q$. Thus, the inter-dimer hopping can be viewed as a perturbation.

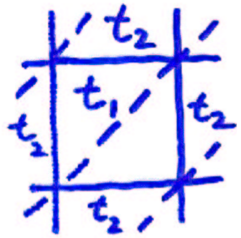
DIMER MODEL (Kino and Fukuyama)



There is one hole per dimer.
The dimers form an *anisotropic triangular lattice* with different hopping in the horizontal (t_1) and slanted directions (t_2).
U is the Coulomb repulsion between two holes on a dimer. From quantum chemistry U is larger than the band width.
This is a strongly correlated system.
Magnetic frustration results from competition between t_1 and t_2.

Kino + Fukuyama

THE RELEVANT HUBBARD MODEL



$$H = -t_1 \sum_{<\mathbf{ij}>,\sigma} (c^\dagger_{\mathbf{i},\sigma} c_{\mathbf{j},\sigma} + h.c.)$$
$$-t_2 \sum_{<\mathbf{in}>,\sigma} (c^\dagger_{\mathbf{i},\sigma} c_{\mathbf{n},\sigma} + h.c.)$$
$$+U \sum_{\mathbf{i}} (n_{\mathbf{i}\uparrow} - \frac{1}{2})(n_{\mathbf{i}\downarrow} - \frac{1}{2}) + \mu \sum_{\mathbf{i},\sigma} n_{\mathbf{i}\sigma}$$

one site = ET dimer

At half filling (one electron per site) ground state is an *insulator* for $U \gg t_1, t_2$.

Insight can be obtained by considering limits for which there are known results.

$t_1 = 0$ square lattice

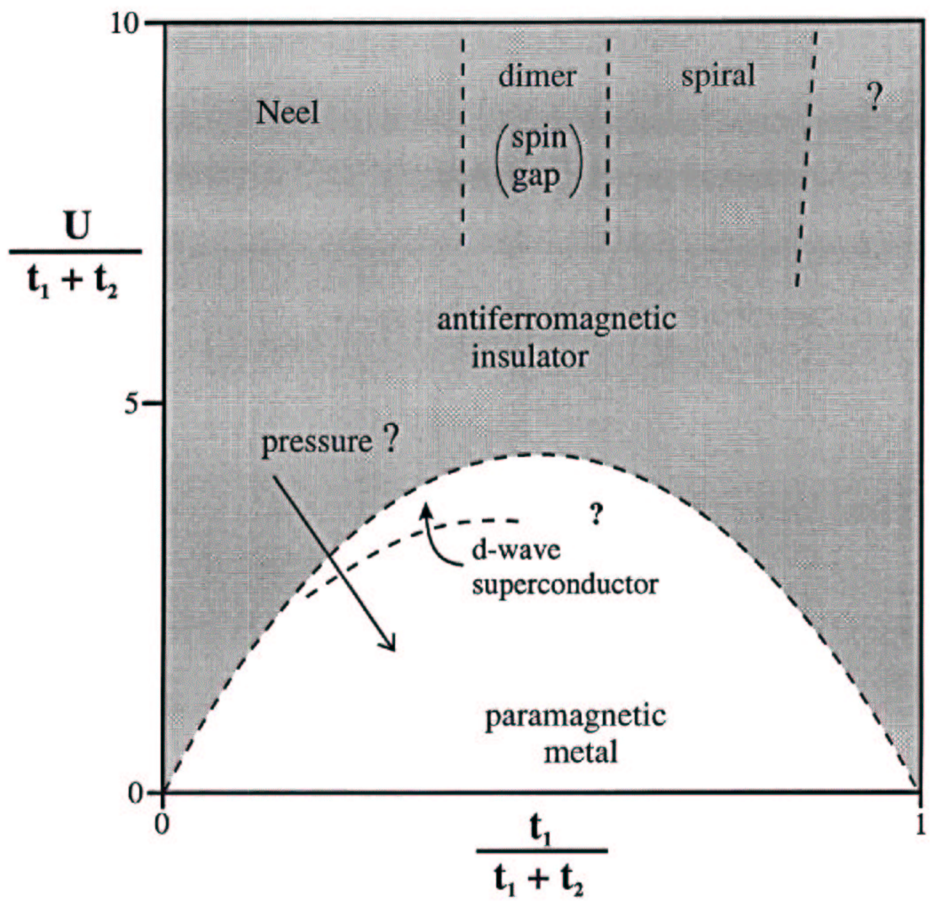
$t_1 = t_2$ triangular lattice

$t_2 = 0$ decoupled chains

If t_1 and t_2 are both non-zero then due to imperfect nesting of the Fermi surface there is a Mott-Hubbard *metal-insulator transition* at a finite value of U.

TENTATIVE PHASE DIAGRAM FOR THE HUBBARD MODEL ON AN ANISOTROPIC TRIANGULAR LATTICE

Zero temperature



UNCONVENTIONAL SUPERCONDUCTIVITY

Is there superconductivity in the model?

Yes. According to Quantum Monte Carlo calculations and the random-phase approximation (RPA) and the fluctuation-exchange approximation (FLEX). It is mediated by spin fluctuations.

What is the relationship between the magnetic ground state of the insulating phase and the symmetry of Cooper pairs in the superconducting phase?

Neel (π, π) order leads to d-wave singlet superconductivity, as in the cuprates.

The 120 degree spiral order of the isotropic triangular lattice leads to Cooper pairing in the s-wave triplet odd-frequency channel.

M. Votja and E. Dagotto, PRB, 1999; J. Schmalian, PRL **81**, 4232 (1998); H. Kino and H. Kontani, cond-mat/9807147; H. Kondo and T. Moriya, cond-mat/980732 K. Kuroki and H. Aoki, cond-mat/9812026.

Kondo + Moriya, cond-mat/9909024

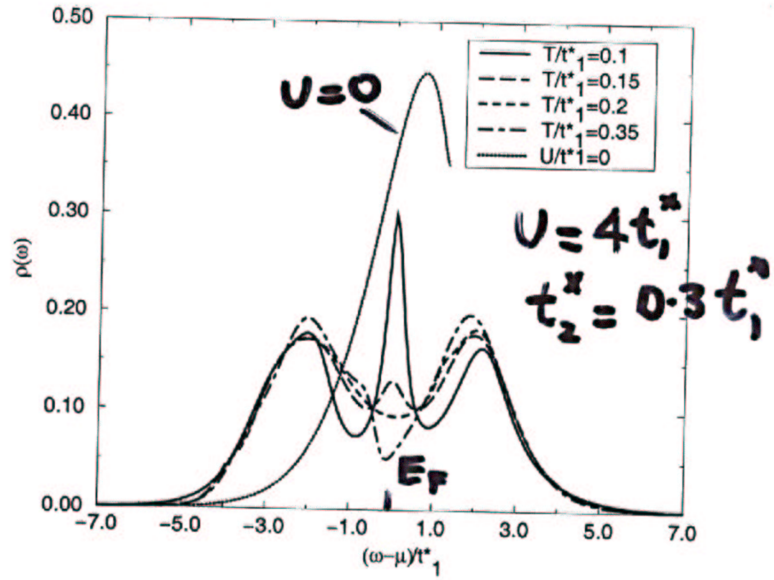
Metal - insulator transition

Morita, Watanabe, Imada, cond-mat/0203020
Onada + Imada, cond-mat/0206531

DYNAMICAL MEAN-FIELD THEORY

Georges et al. Rev. Mod. Phys. 68, 13 (1996)

Spectral density



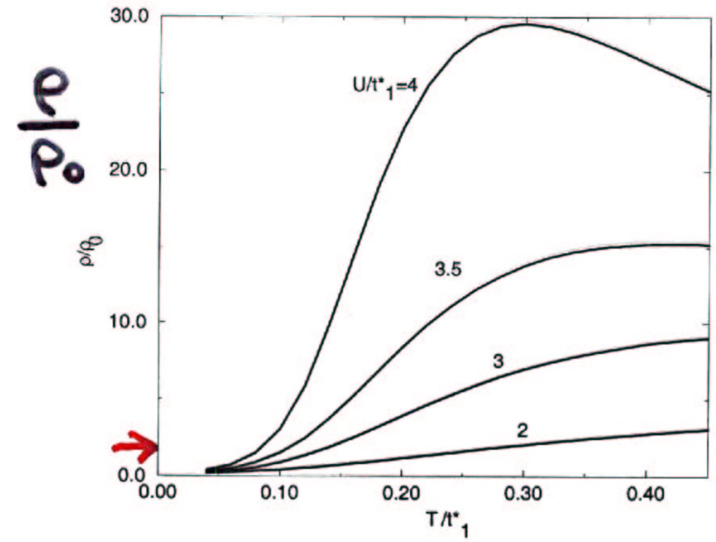
- Low energy scale given by T_0, analogue of the "Kondo" temperature.
- Crossover from coherent Fermi liquid excitations for $T \ll T_0$ to incoherent excitations at $T > T_0$. This gives the strong temperature dependence of transport quantities.

incoherent = no Bloch states
no Fermi surface

Merino and McKenzie, cond-mat/9909011 Phys. Rev B 61, 7996

CROSSOVER TO INCOHERENT EXCITATIONS

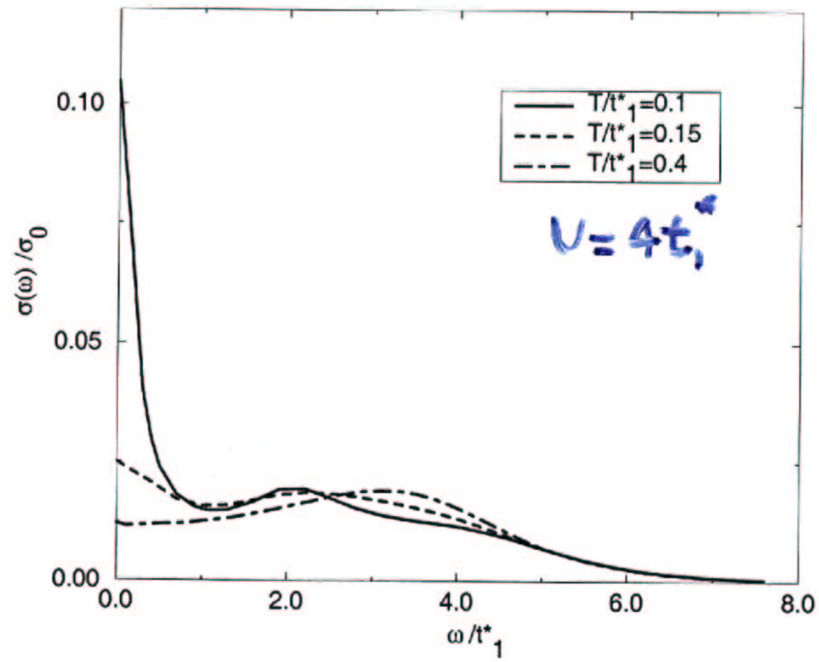
Temperature dependence of resistivity



- $\rho_0 = \hbar a/e^2 \sim m\Omega$cm, Mott limit
- For "mean-free path" smaller than the lattice parameter, the resistivity continues to increase.
- Crossover from T^2 Fermi liquid behaviour to a bad metal.

OPTICAL CONDUCTIVITY

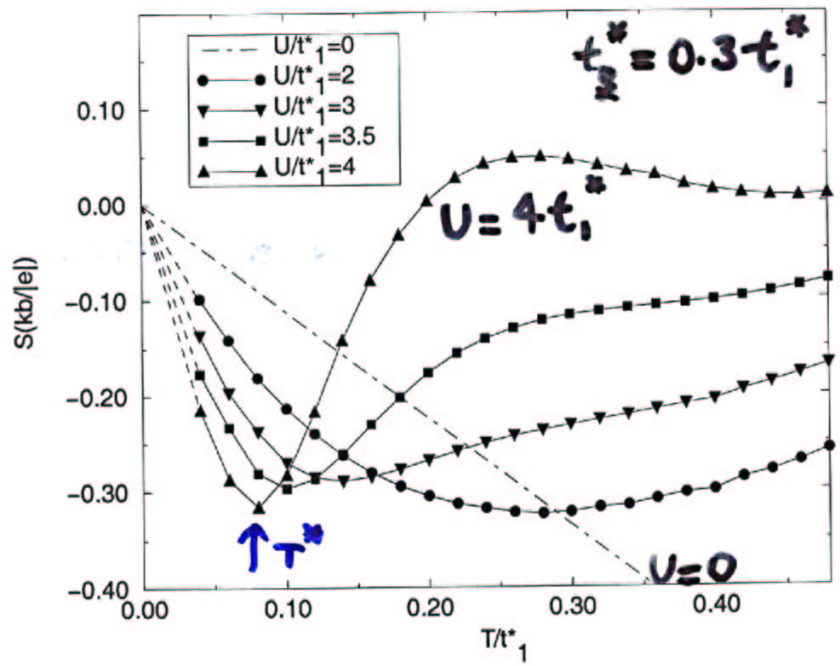
Frequency-dependence of conductivity



- The Drude peak only appears for temperatures of the order of T_0 or lower.
- Broad peak at $\omega \sim U = 4t_1^*$ is due to transitions from the lower to the upper Hubbard band.

CROSSOVER TO INCOHERENT EXCITATIONS

Temperature dependence of thermopower

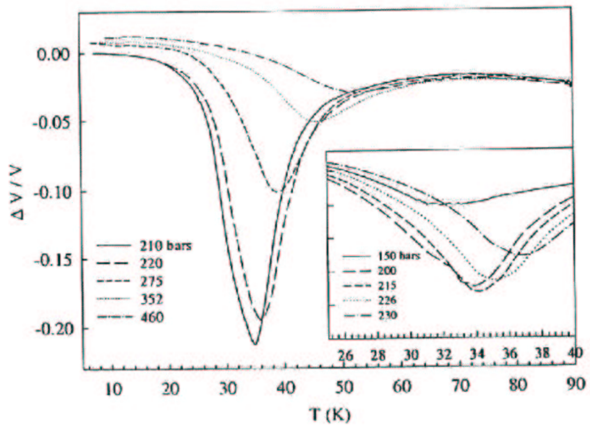


- Minimum associated with "Kondo" temperature and loss of coherence.
- Values of order $S \sim k_B/e$

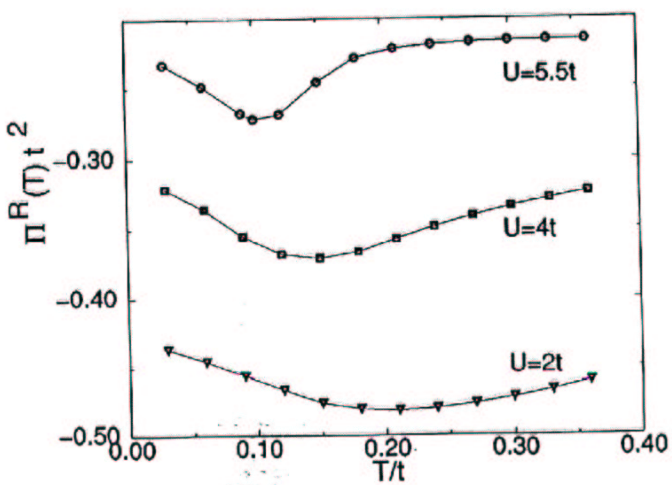
ACOUSTIC ANOMALIES AT T_0

D. Fournier *et al.*, cond-mat/0209536

Sound velocity versus temperature



Phonon self energy is related to electronic density-density correlation function.
DMFT calculation



BIG QUESTIONS?

What is the origin of

– the superconductivity?

– the pressure and anion dependence of the phase diagram?

– the incoherent-coherent crossover in inter-layer transport?

Is the metal really a 2d Fermi liquid as the Mott transition is approached?

OPPORTUNITIES FOR DMFT

- tight binding plus DMFT
- LDA plus DMFT
- Can extended DMFT give the whole phase diagram including d-wave superconductivity?
- Other materials: e.g., β-(BEDT-TTF)$_2$X and λ-(BETS)$_2$X.