

Resonating valence bond theory of organic superconductors

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Outline

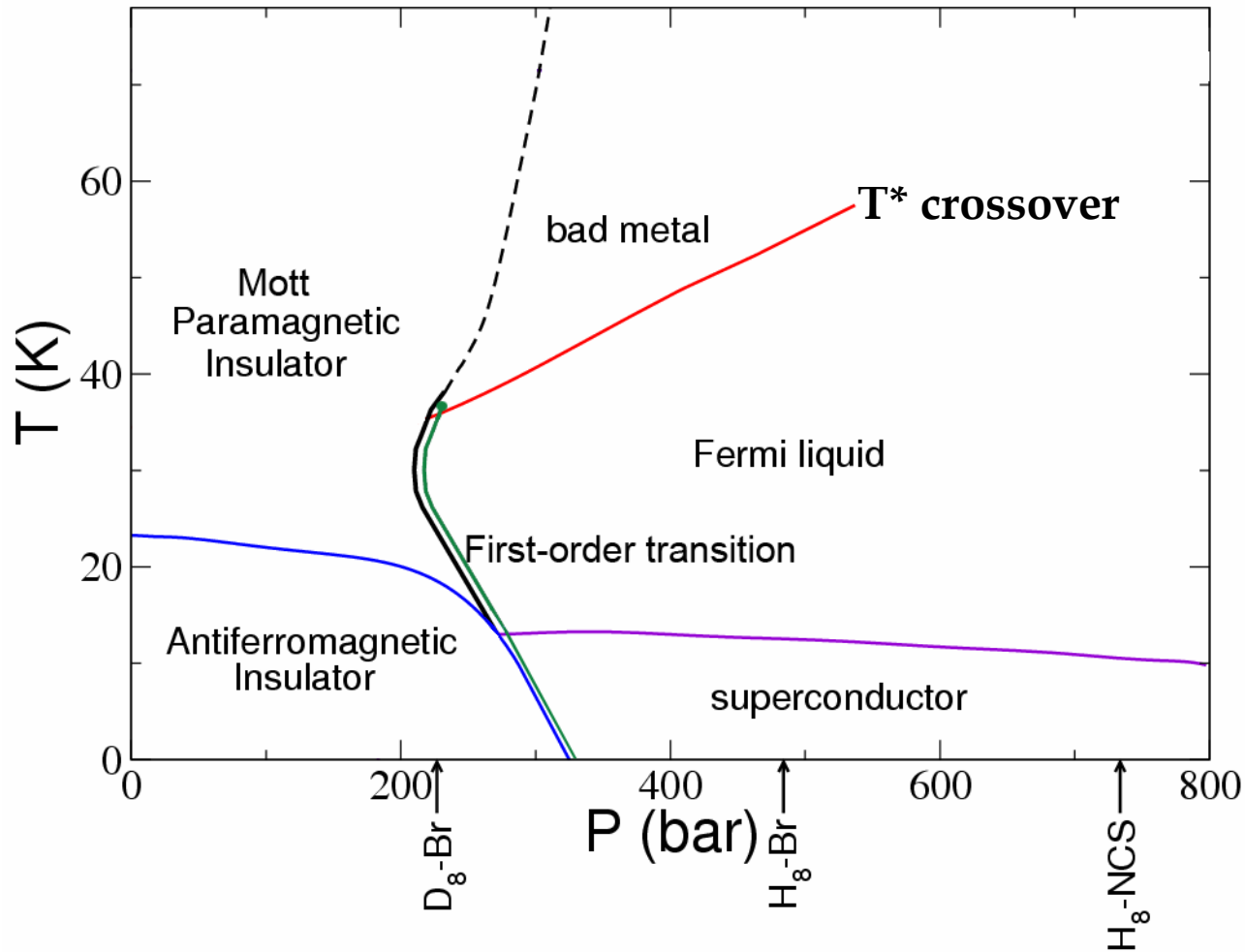
Half-filled quasi-two-dimensional charge transfer salts (e.g,

κ - (ET)₂X)

- Superconductivity is unconventional, i.e,
 - not s-wave
 - has low superfluid density (not BCS)
- Antiferromagnetic interactions (J) are frustrated.
- Minimal model is the Hubbard model on an anisotropic triangular lattice at half-filling
- RVB theory captures essential features of phase diagram. Superconductivity due to spin singlet pairing from J.
- Unique feature of the theory is the d-wave pseudogap that is present above T_c and H_{c2}
- Physics is similar to that in the high- T_c cuprates.

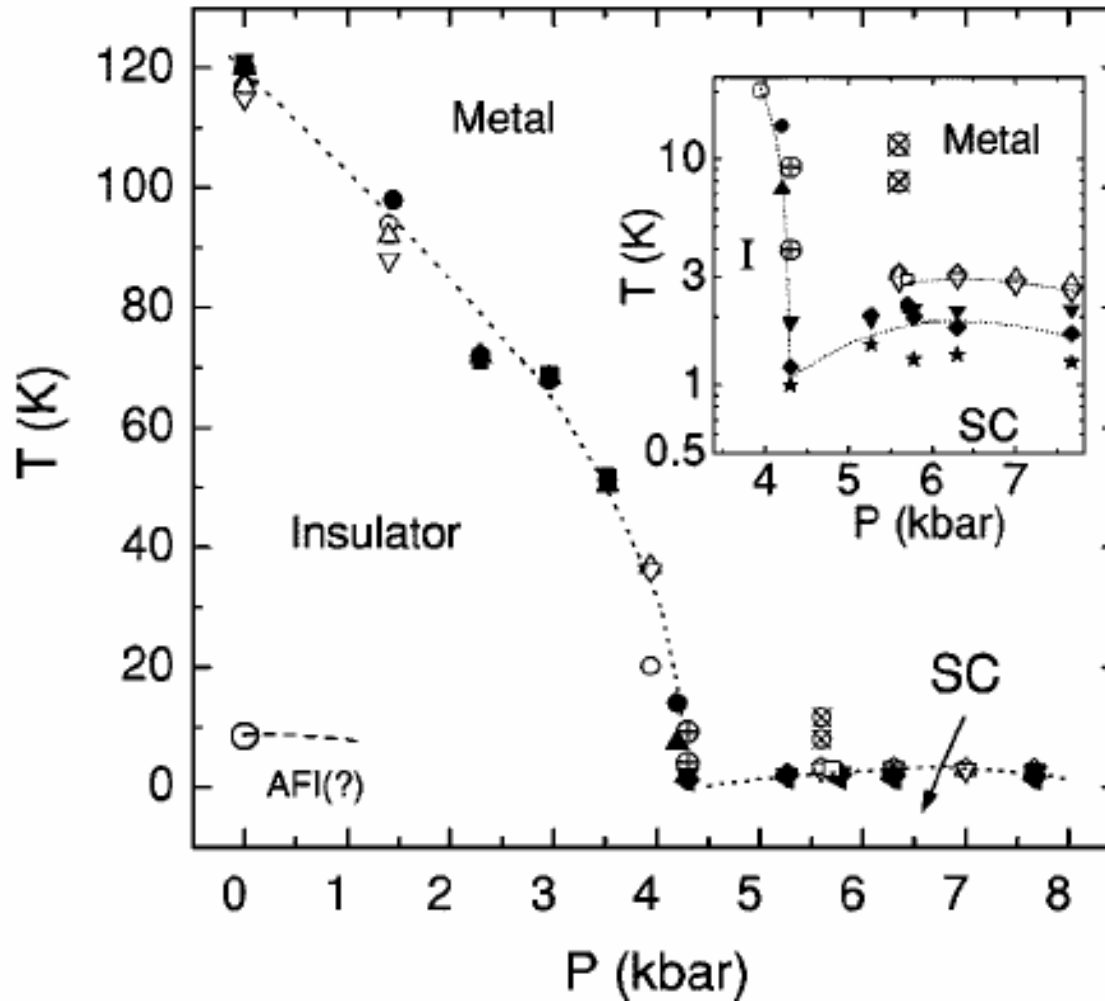


Phase diagram: temperature vs. pressure, κ -ET₂Cu[N(CN)₂]Cl



[Powell & McKenzie PRL 94, 047004 (2005)]

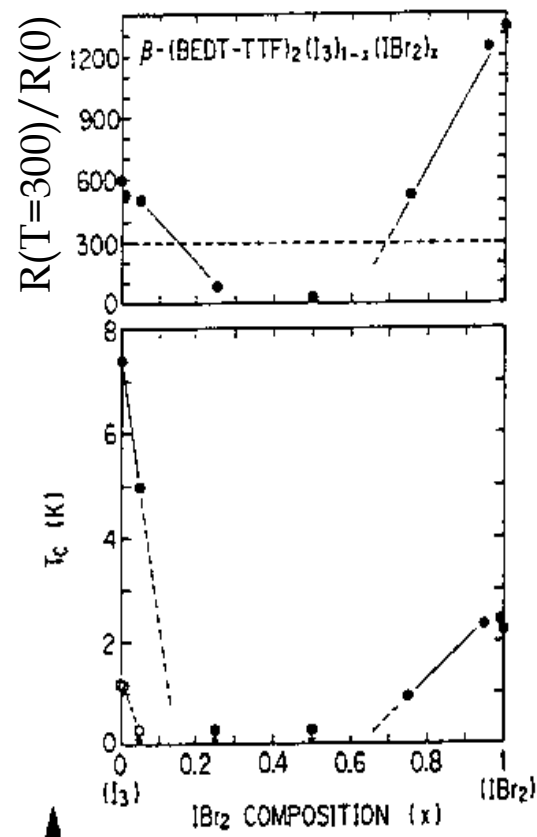
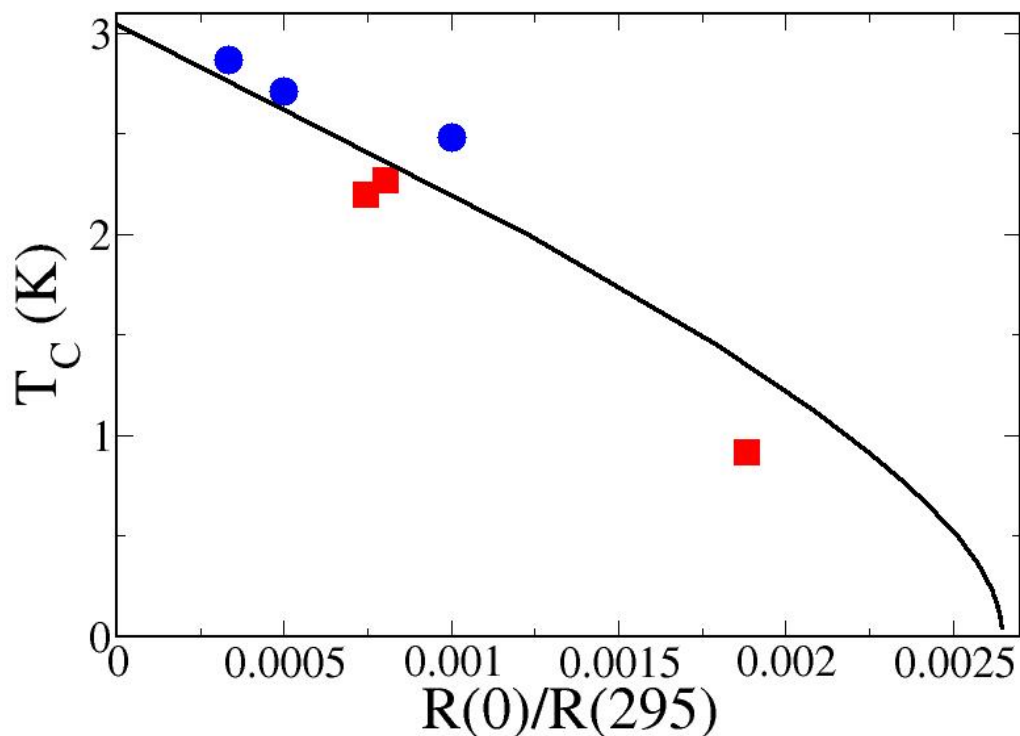
Common phase Diagram: temperature vs. pressure β -(BDA-TTP)₂ MCl₄ (M=Fe, Ga)



[E.S. Choi et al., Phys. Rev B 70, 024517 (2004)]

Unconventional superconductivity

β -ET₂IBr₂: T_c decreases with increasing residual resistance



Alloying anions (red squares): Tokumoto *et al.* Japan. J. Appl. Phys. **26** 1977 ('87)

Sample variation (blue circles): Shegolev & Yagubskii Physica C **185-189** 360 ('91)

Abrikosov-Gorkov-Mineev Theory (line): Powell & McKenzie PRB **69**, 024519 (2004)

Either both types of impurity induce magnetic moments or the pairing symmetry is non-s-wave.

Unconventional superconductivity: evidence from effect of non-magnetic disorder

- (a) For s-wave (e.g., elemental) superconductors, transition temperature T_c is NOT suppressed by non-magnetic disorder. T_c is only suppressed by magnetic impurities.

- (b) For non s-wave (i.e., unconventional) superconductors T_c decreases with increasing disorder and thus increasing residual resistivity.

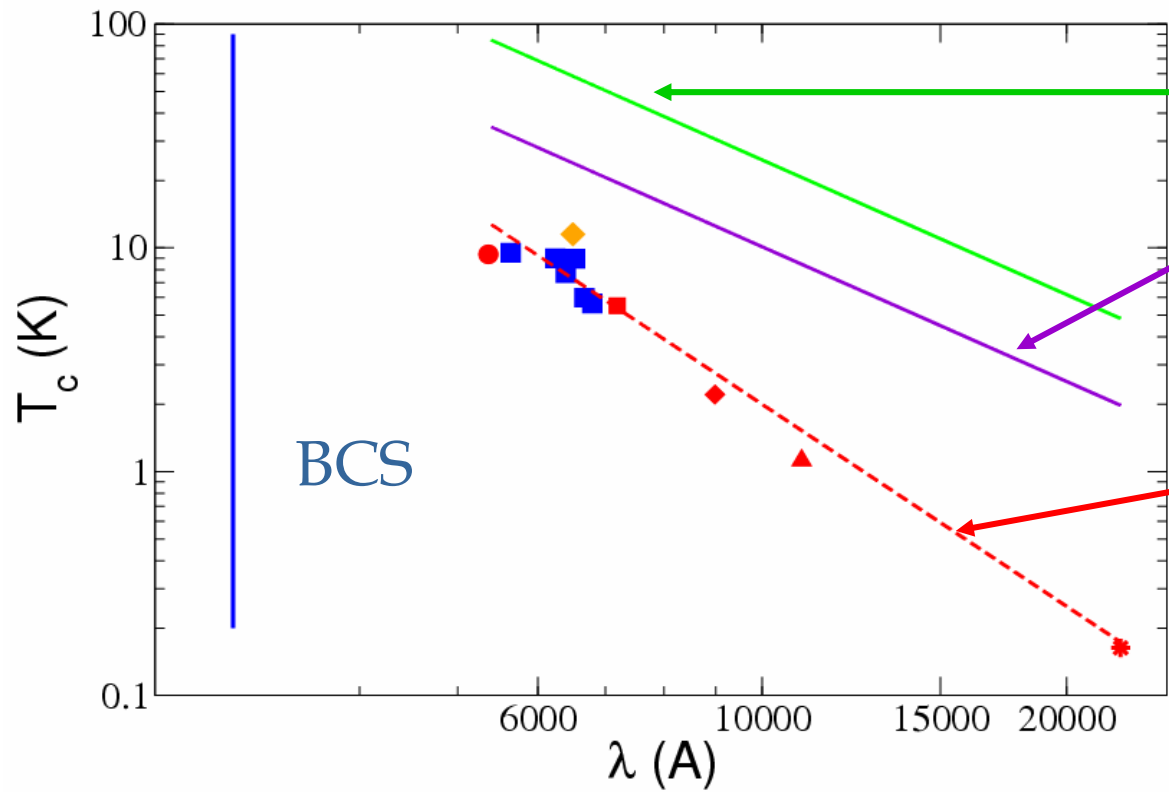
In organics disorder can be varied by alloying anions, sample variation, irradiation or cooling rate.

Powell & McKenzie, PRB 69, 024519 (2004)

Conclusion: either all these types of disorder induce magnetic moments OR the pairing symmetry is non-s-wave.



Evidence for unconventional superconductivity: small superfluid density. Critical temperature (T_c) vs. London penetration depth (λ)



3D limit of preformed pairs

2D preformed pairs (Emery & Kivelson) with T_c determined by phase fluctuations (explains Uemura plot for underdoped cuprates).

Guide to the eyes

Note this is a log-log scale

Superfluid density,
 $n_s = m^* c^2 / 4\pi e^2 \lambda^2$

BCS theory ($n_s = n$) does not describe the superconductivity.

Powell & McKenzie, J. Phys.: Condens. Matter **16** L367 (2004)
 Data from Pratt *et al.*, Polyhedron, **22**, 2307 (2003), Lang *et al.* PRB **46**, 5822 (1992) and Larkin *et al.*, *ibid.* **64**, 144514 (2001) (different shapes = different anions)



Pseudogap

- Nuclear magnetic resonance

The temperature dependence of the Knight shift and relaxation rate $1/T_1$ suggest that in the metallic phase the density of states at the Fermi energy is suppressed.

(de Soto et al., Wzietek et al., Kanoda et al)

This is similar to what is seen in underdoped cuprates.



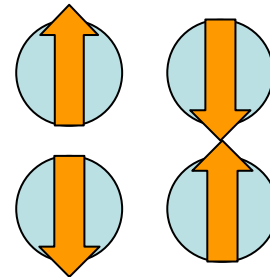
Key structural properties of $(\text{ET})_2\text{X}$

- Half hole per ET molecule
- ET molecules are dimerised in β , κ , λ , β' crystal structures
- Metallic phase has a half-filled band
- Minimal model is a Hubbard model on an anisotropic triangular lattice [McKenzie, Comm. Cond. Mat. Phys. 1998]

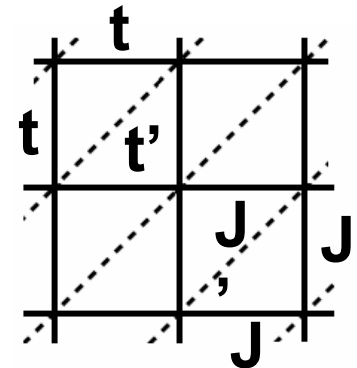
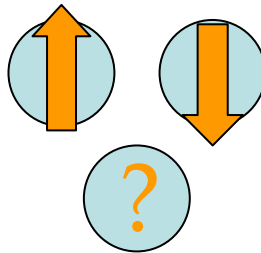


Frustrated antiferromagnetism

- To arrange spins antiferromagnetically on a square lattice it is straightforward to optimise the exchange energy



- We cannot do this on a triangular lattice – this is **FRUSTRATION**

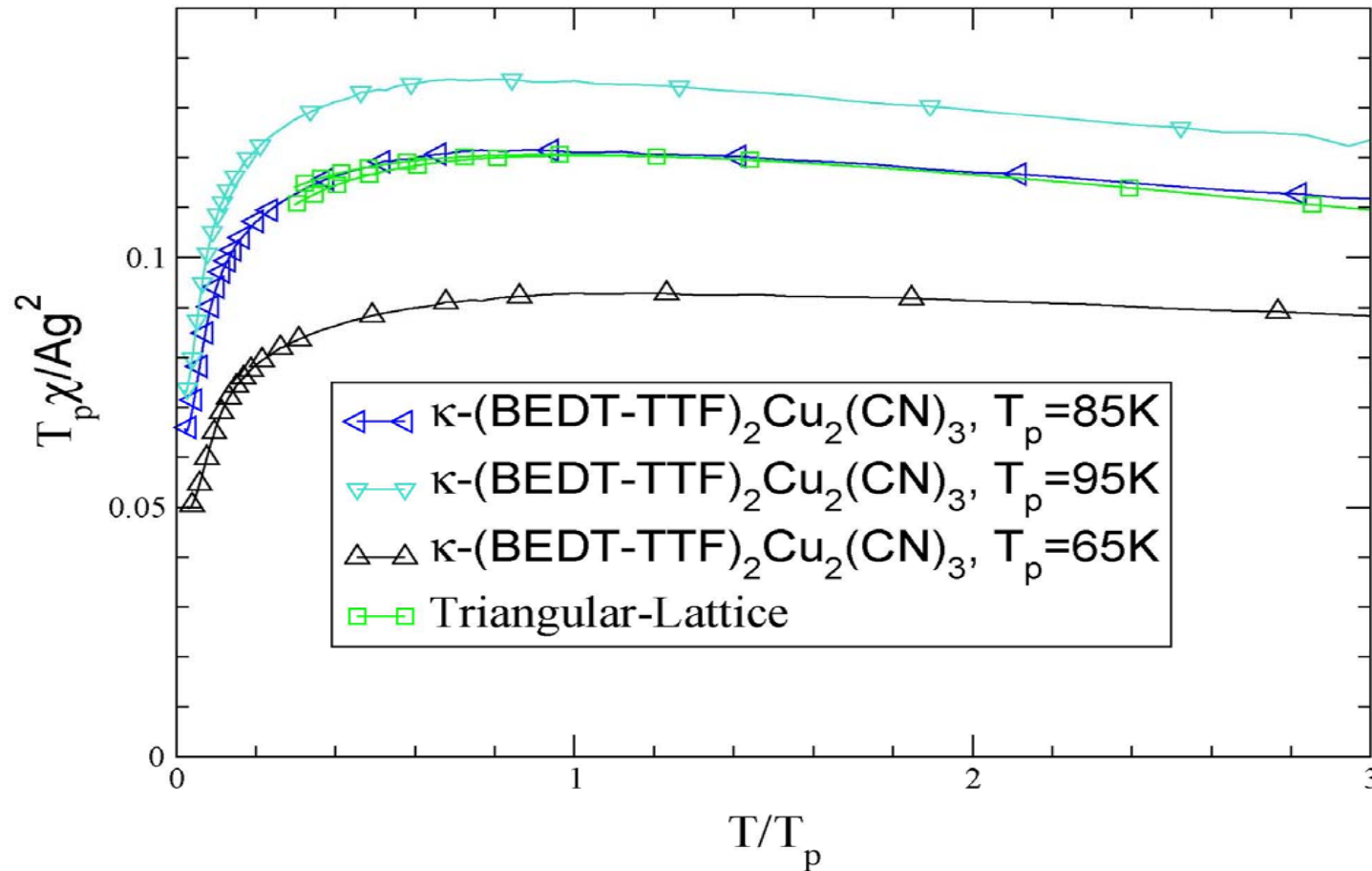


- In the Mott insulating phase spin fluctuations are described by a Heisenberg model on an anisotropic triangular lattice.



Frustrated antiferromagnetism

Magnetic susceptibility vs. temperature



Shimizu et al.,
PRL 91, 016401
(2003);
Zheng et al.,
PRB (2005)

Comparison with high-temperature series expansions.
 $\chi(T)$ is quite sensitive to amount of frustration (J'/J).

Key properties of half-filled organic superconductors to explain

- First order transition from Mott insulator to unconventional superconductor
- Bad metal near Mott transition
- Low superfluid density
- Frustrated antiferromagnetism
- Pseudogap in metallic state



RVB theory of superconductivity

In 1987 Anderson proposed that:

- the Hubbard model is the relevant model to understand the high- T_c cuprate superconductors.
- the ground state of the two-dimensional Heisenberg model and the doped Hubbard model may be a **RVB (resonating valence bond) state**.
- a good variational wave function:
 - a BCS superconducting state with the **double occupation of all sites projected out (Gutzwiller projection)**.
- RVB states were most favourable for low dimensions, spin-1/2, and in the presence of **frustration**.



The Hubbard-Heisenberg model

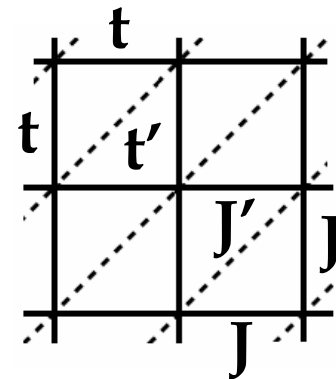
$$\hat{H} = \hat{H}_t + \hat{H}_J + \hat{H}_U$$

Can be derived from the Hubbard model in the limit of **large** but **finite** U [Y. Yu, cond-mat/0303501]

$$\hat{H}_t = t \sum_{\langle ij \rangle \sigma} \hat{c}_{i\sigma}^+ \hat{c}_{j\sigma} + t' \sum_{\{ij\} \sigma} \hat{c}_{i\sigma}^+ \hat{c}_{j\sigma} - \mu \sum_{i\sigma} \hat{c}_{i\sigma}^+ \hat{c}_{i\sigma}$$

$$\hat{H}_J = J \sum_{\langle ij \rangle} \hat{S}_i \cdot \hat{S}_j + J' \sum_{\{ij\}} \hat{S}_i \cdot \hat{S}_j$$

$$\hat{H}_U = U \sum_i \hat{c}_{i\uparrow}^+ \hat{c}_{i\uparrow} \hat{c}_{i\downarrow}^+ \hat{c}_{i\downarrow}$$



RVB variational wave function

At half filling we allow for partial double occupancy, $d > 0$.

This is similar to Laughlin and Zhang's ``Gossamer'' superconductor.

As U/t or t/t' increases there is a first-order phase transition from a d-wave superconductor to a Mott insulator (which can be a spin liquid or have Neel antiferromagnetic order).

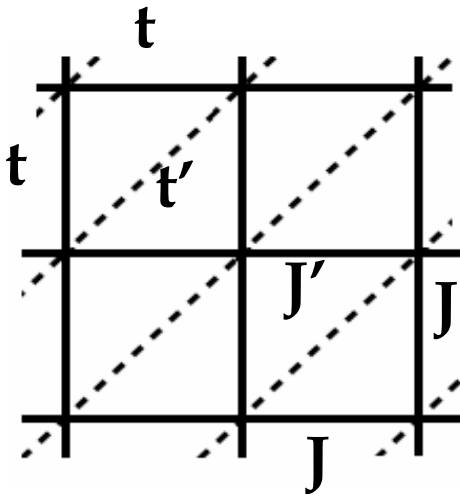
The Cooper pairing is due to the fluctuating spin singlets present in the Mott insulator due to the antiferromagnetic interactions J and J'

For a similar approach and results compare:

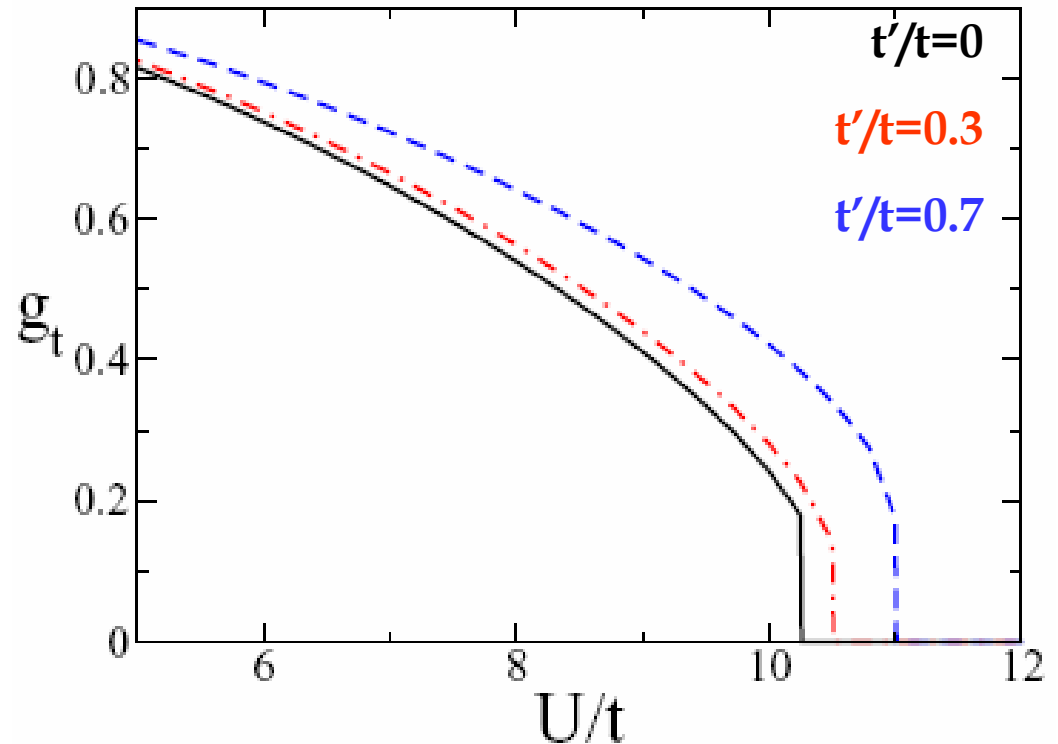
Gan et al., Phys. Rev. Lett. 94, 067005 (2005); Liu et al., *ibid.* 94, 127003 (2005)

Enhancement of effective mass & reduction of quasi-particle weight, Z , near Mott transition

$$g_t \sim Z \sim 1/m^*$$



We take $J=t/3$ and $J'=t'^2/3t$



Compare exact diagonalisation for $t'=t$ (Capone et al., PRB 2001)

Superfluid stiffness & Drude weight is **reduced** by a factor of order g_t

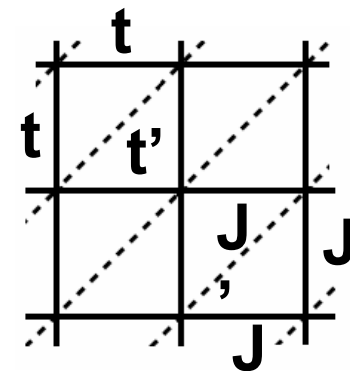
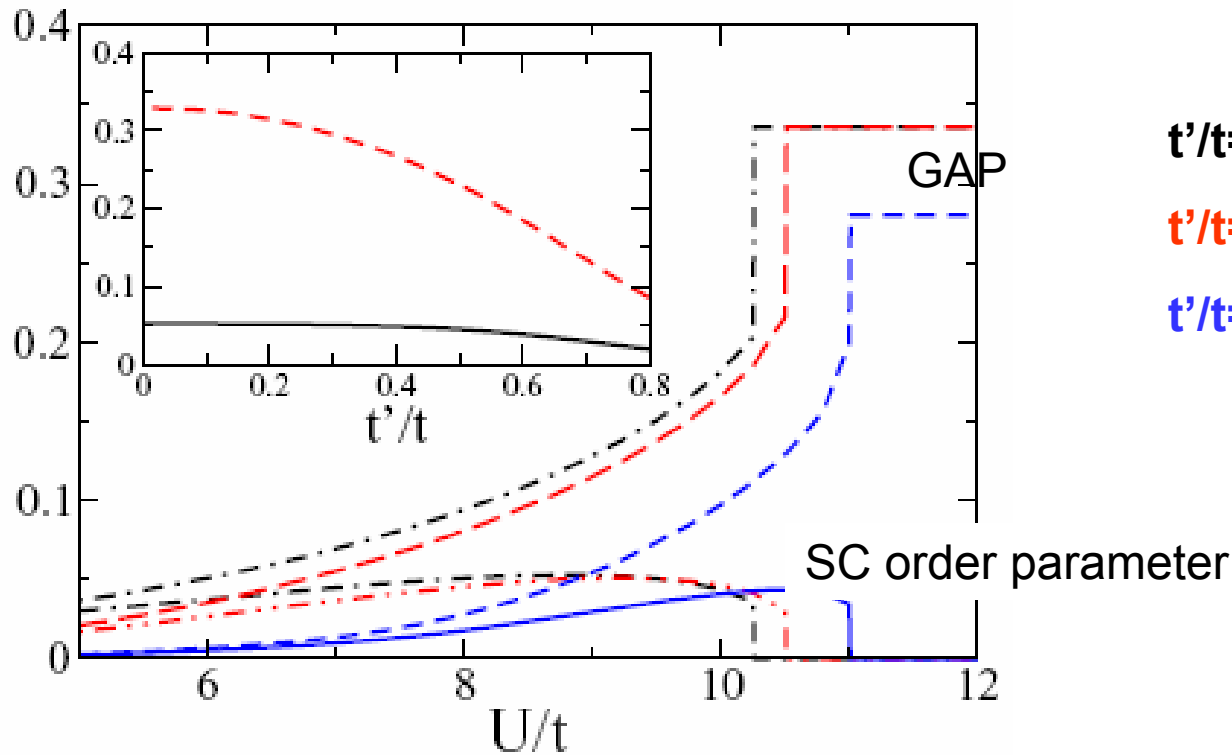
Powell and McKenzie, PRL 94, 047004 (2005).



RVB superconductivity

Superconducting order parameter (spin-singlet pairing amplitude) is **not** the same as the d-wave gap

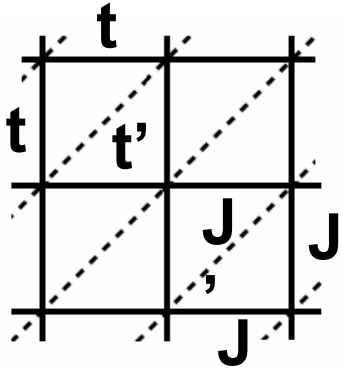
$$\tilde{\Delta}_k = g_t \Delta_k$$



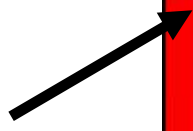
Note: first-order transition from Mott insulator to superconductor at U/t decreases as t'/t increases

d-wave superconductivity

Phase of the order parameter over the Brillouin zone for $t'/t=0.81$

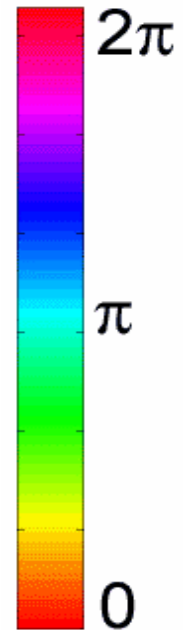
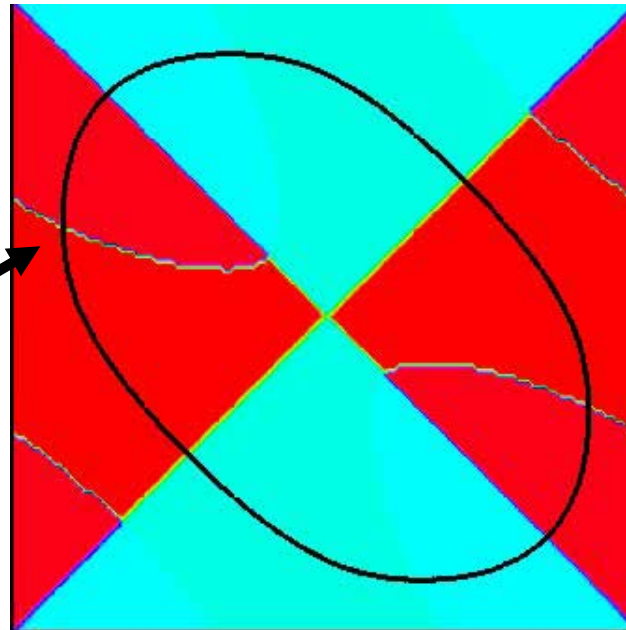


Fermi surface



We take $J=t/3$ and $J'=t'^2/3t$ which ensures $J'/J=(t'/t)^2$

$\text{Arg}|\Delta(k)|$



Conclusions

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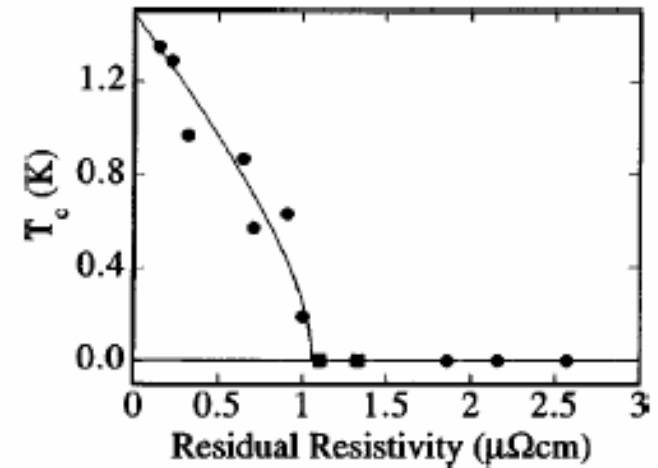
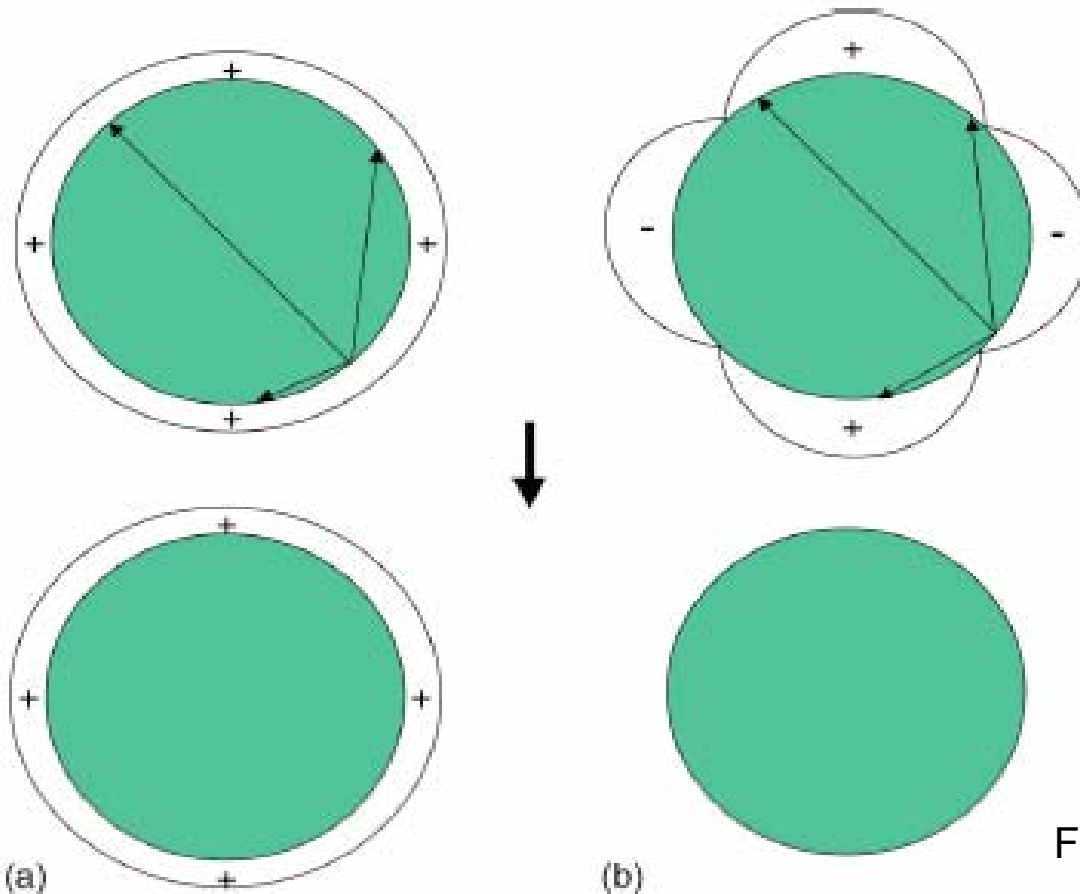


Collaborators

- UQ: Ben Powell & John Fjaerestad
- UC Davis: Rajiv Singh
- UNSW: Weihong Zheng
- NRL: Mark Pederson & Tunna Baruah
- Oxford: Radu Coldea
- Madrid: Jaime Merino

Support from the Australian Research Council.

Non-magnetic disorder in superconductors



Sr_2RuO_4 - A.P. Mackenzie *et al.* PRL (1998)

From Mackenzie & Maeno RMP (2003)

- (a) T_c is NOT suppressed for s-wave.
- (b) T_c IS suppressed for d-wave.

RVB needs frustration

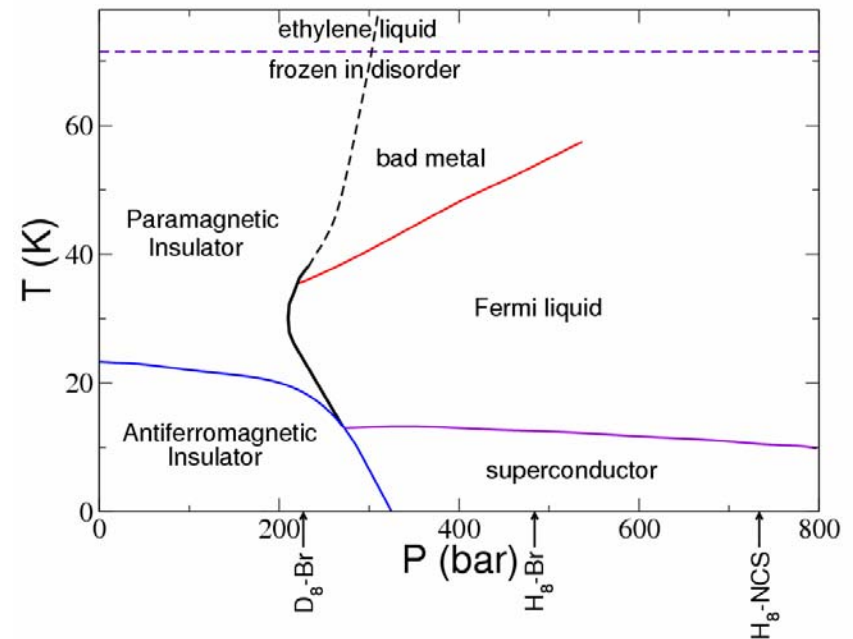
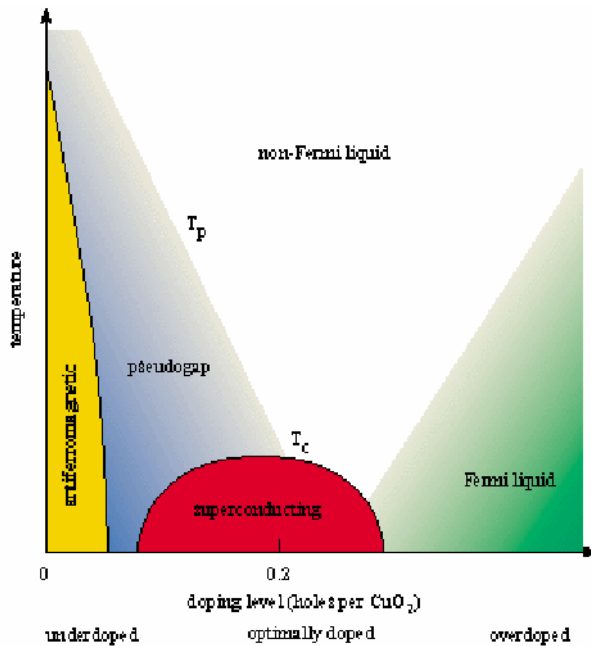
A RVB wavefunction turns out to be a poor approximation for the Heisenberg model on the square lattice.

However, it is a **good trial wavefunction** for some **frustrated models**, e.g., square with next nearest neighbour couplings or the anisotropic triangular lattice

[Cappriotti *et al.*, PRL **87** 097201 (2001); Yunoki and Sorella, PRL **92**, 157003 (2004).]



Similarities between cuprates & organics



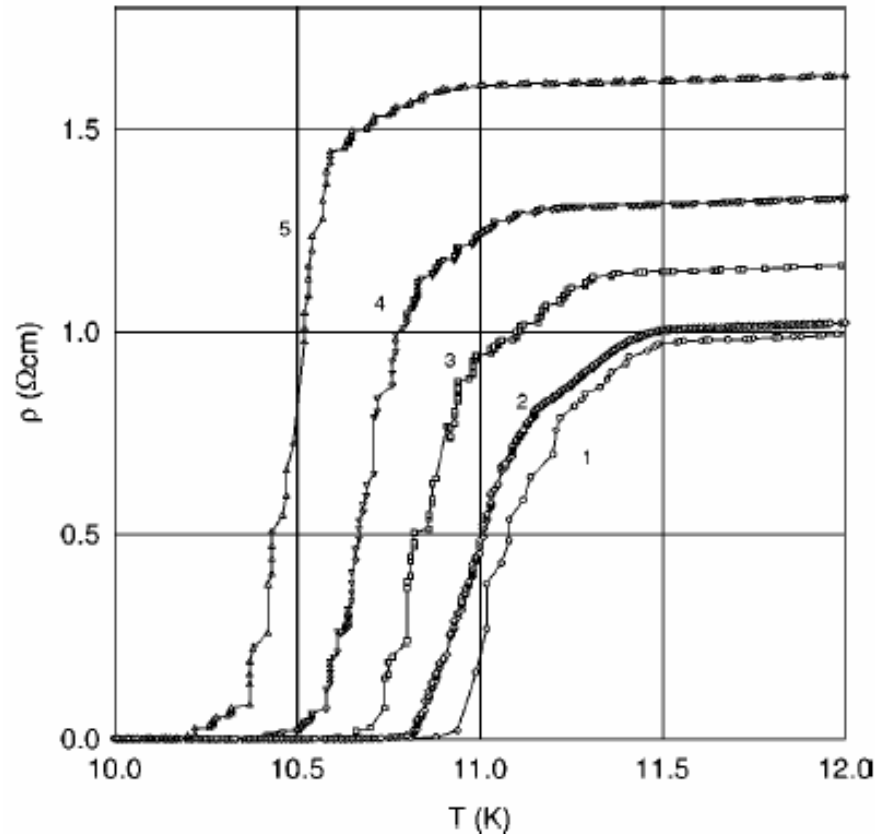
Changing the doping in the cuprates changes the filling (the average number of electrons per site) but leaves $U \gg t$.

Changing the pressure on the organics may change the ratio U/t [McKenzie, CCMP, 98] but it maintains half filling [Powell & McKenzie, JPCM, 04]

Note that although T_C is ten times larger in the cuprates than the organics, so are t and J . So T_C/t is comparable in both systems

Cooling rate disorder suppresses T_c

Resistivity vs. Temperature



Su *et al.* [Phys. Rev. B **57**, 14056 ('99)]

[Powell & McKenzie PRB **69**, 024519 (2004)] Implies either there are magnetic moments formed or d-wave pairing

