

Strong correlations in organic charge transfer salts: superconductors, Mott insulators, bad metals and spin liquids

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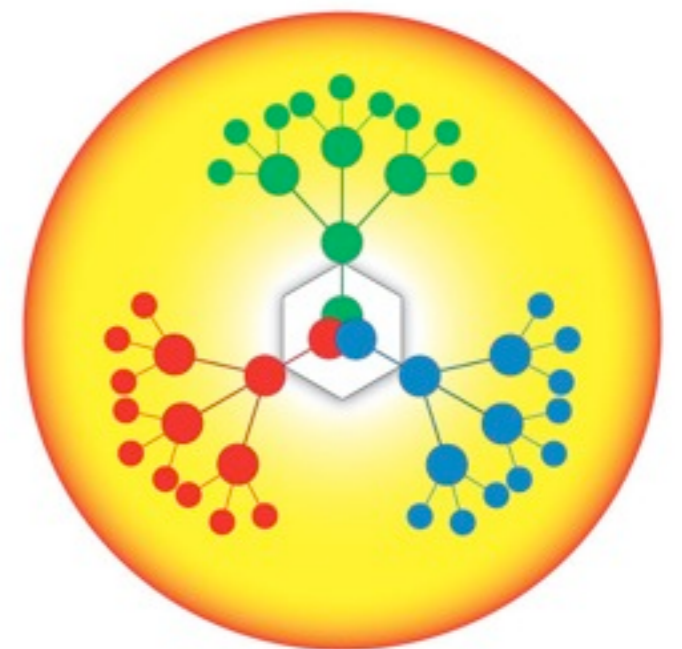
## Ben Powell

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Electronics  
University of Queensland



**Australian Government**

**Australian Research Council**



**C O P E**

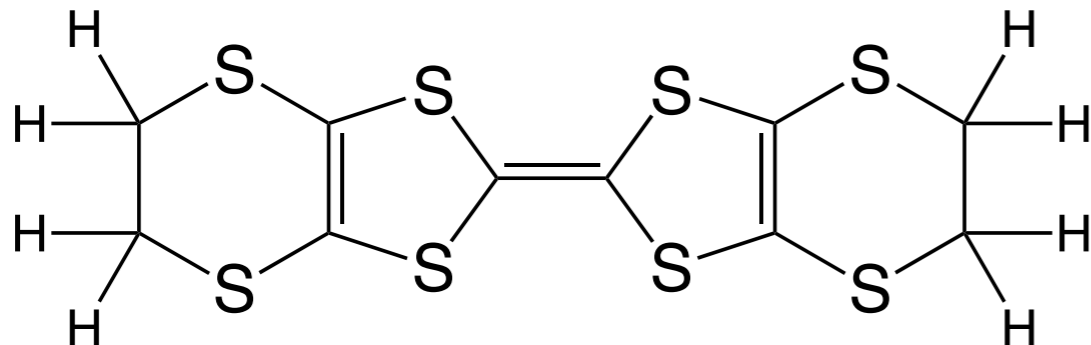
# Some reasons to study organic molecular materials

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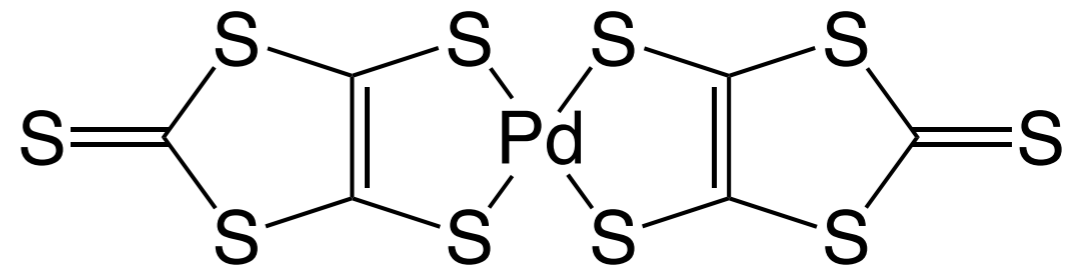
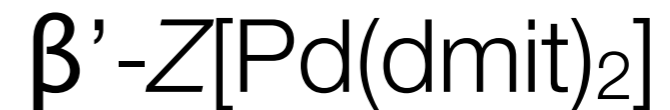
- Fascinating range of strongly correlated q2d systems - I will limit myself to half filled systems, but quarter filled and non-stoichiometric salts also exist
  - Mott transition driven by bandwidth control & wide range of associated phenomena
- Clean systems
  - Typically stoichiometric
  - Quantum oscillations are readily seen (simple, well understood Fermi surfaces)
- Low energy scales
  - $T_c$  may only be  $\sim 10$  K [bad for applications]
  - But this also means “large” fields only means  $\sim 10$  T [good for experimentalists]
- Chemical control
  - Organic chemists have can make subtle changes to the molecular structure, which allow them to tune the emergent physics

# Overview

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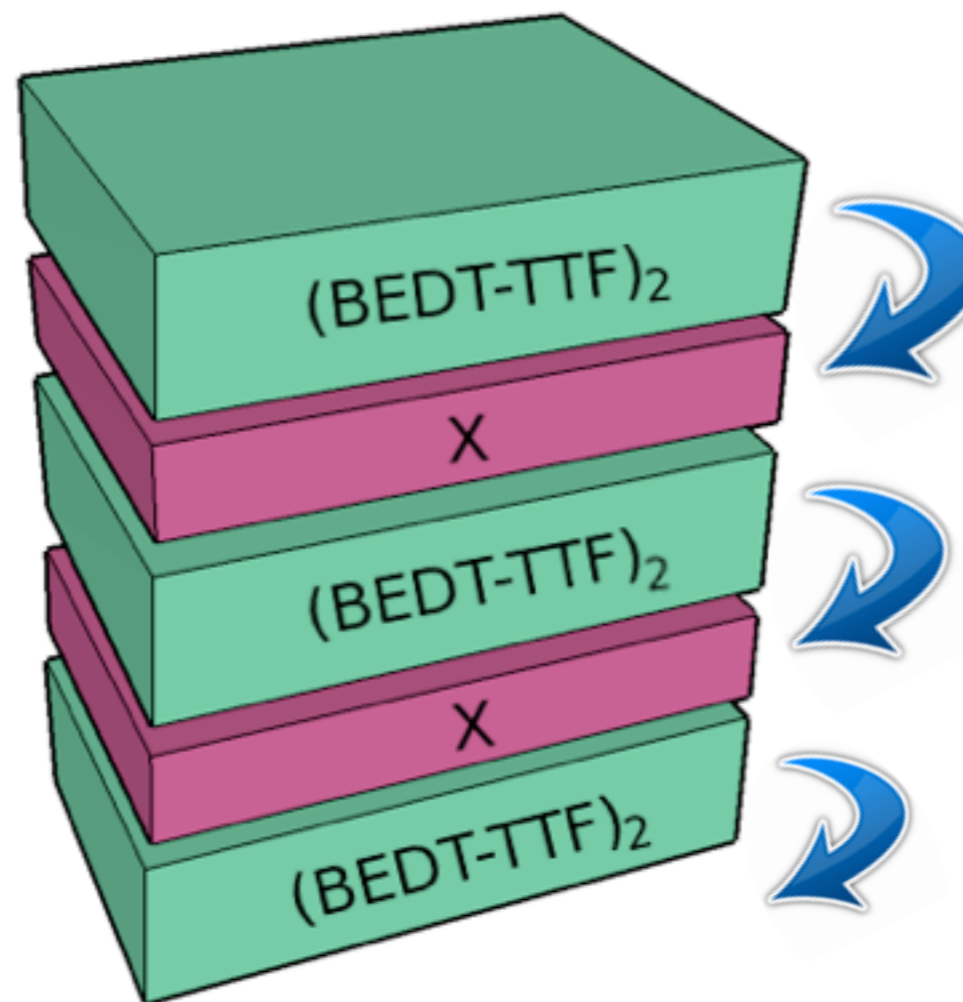
- Structure and phase diagram
- Model Hamiltonian
- Metal-insulator transition
- Spin liquid
- Strongly correlated metal
- Nernst effect
- Superconductivity
- Parameters for the model Hamiltonian



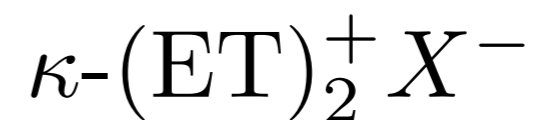
- Structure and phase diagram
- Model Hamiltonian
- Metal-insulator transition
- Spin liquid
- Valence bond solid
- Charge ordered insulator
- Superconductivity

# Structure of $\kappa$ -ET<sub>2</sub>X (ET=BEDT-TTF)

For a review see BJP and McKenzie, JPCM **18**, R827 (2006)



Charge transfer

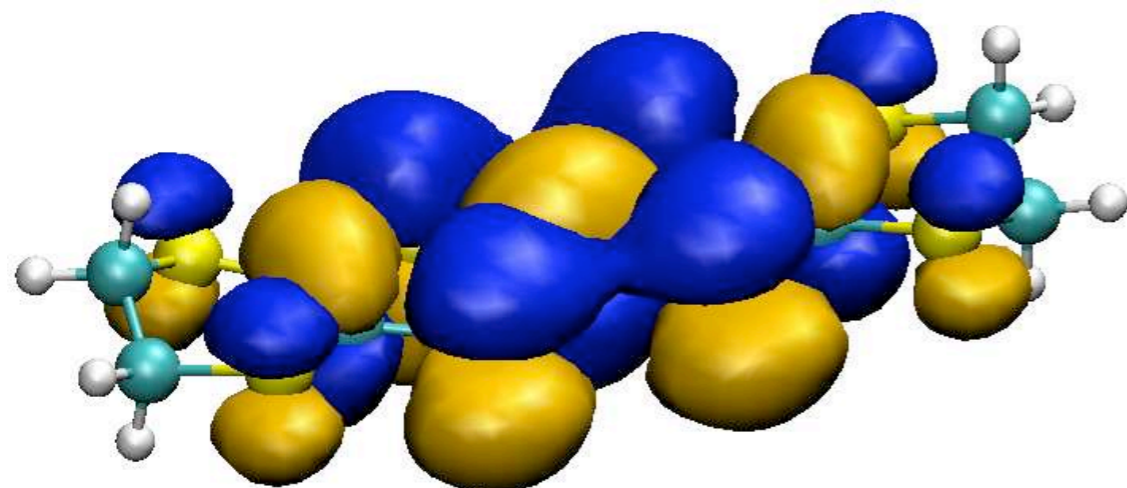


$X$  is a monovalent anion, e.g., I<sub>3</sub>, so the charge is localised in the anion layer, but the holes in the ET layer are not localised at a non-interacting level

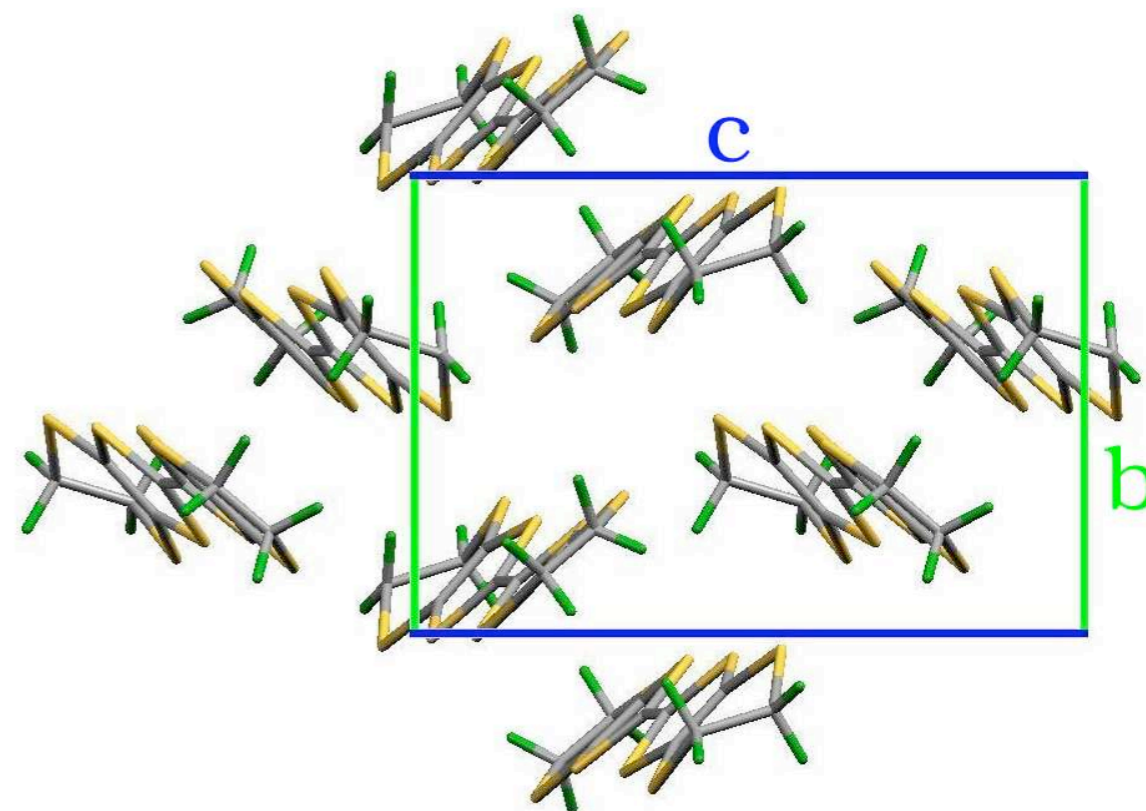


# Molecular orbitals

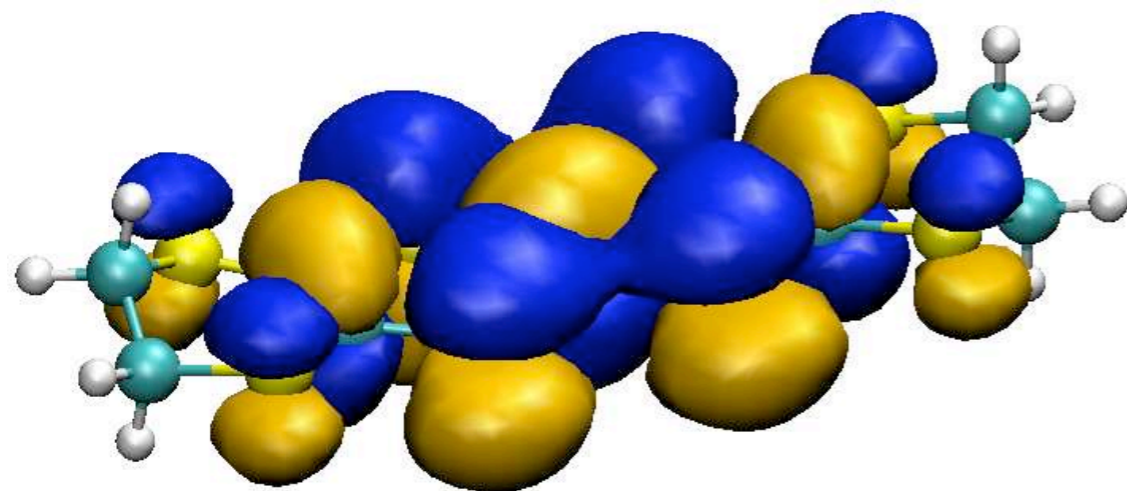
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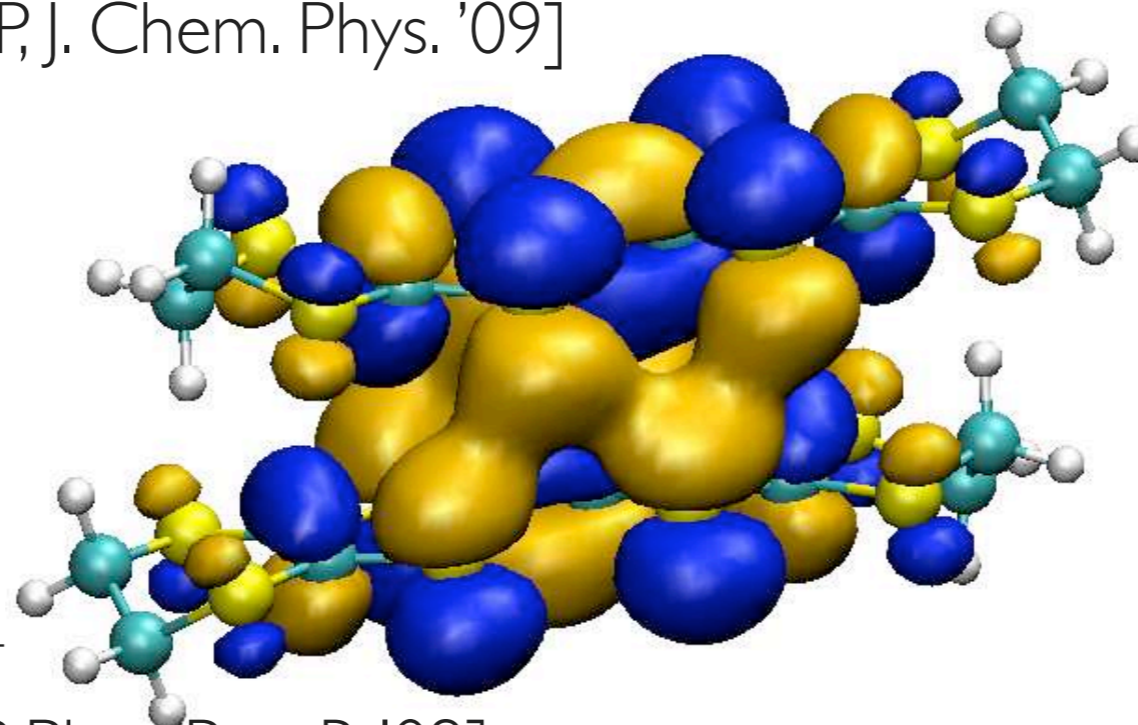
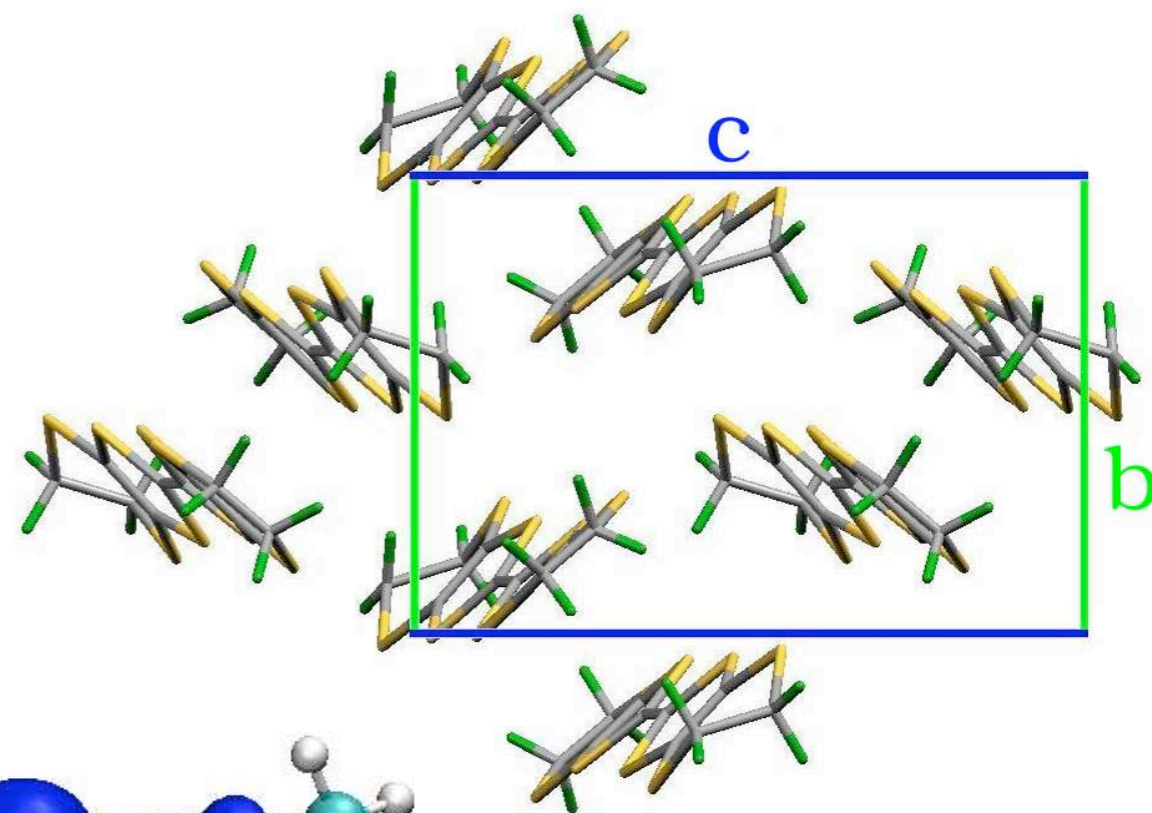
Highest occupied molecular orbital (HOMO) of a neutral monomer from DFT [Scriven and BJP, J. Chem. Phys. '09]



# Molecular orbitals



Highest occupied molecular orbital (HOMO) of a neutral monomer from DFT [Scriven and BJP, J. Chem. Phys. '09]

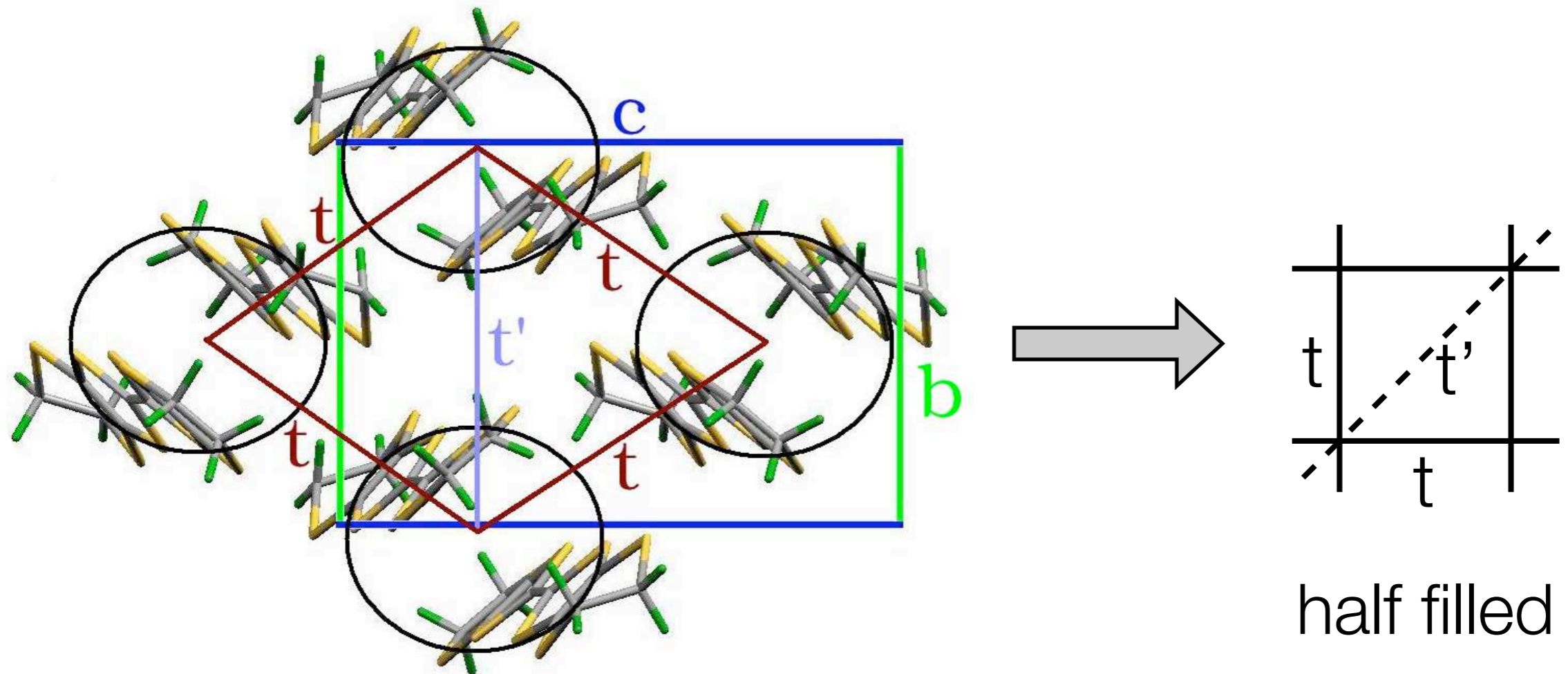


HOMO of  $ET_2^+$   
[Scriven and BJP, Phys. Rev. B '09]



# Structure of $\kappa$ -ET<sub>2</sub>X (ET=BEDT-TTF)

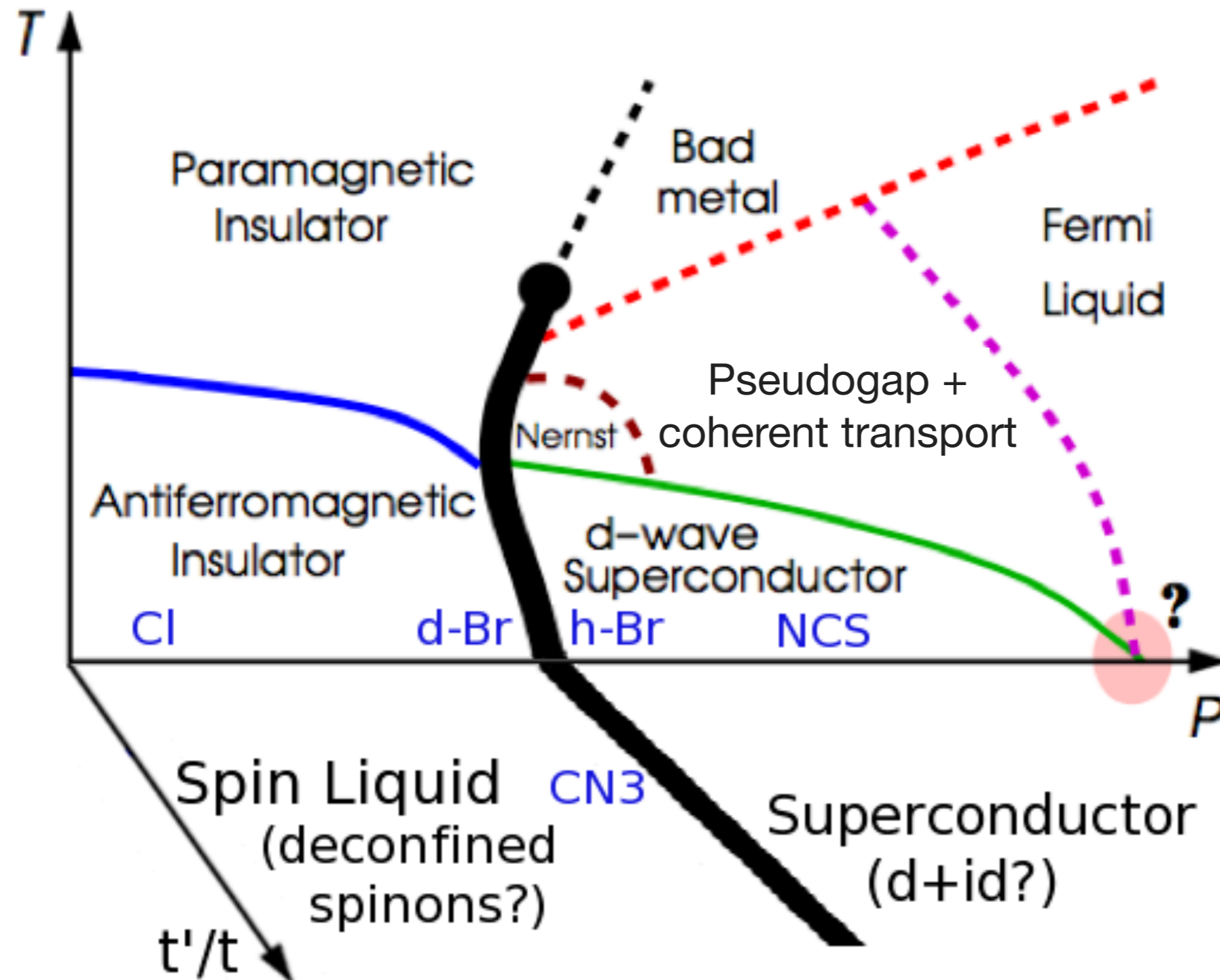
For a review see BJP and McKenzie, JPCM **18**, R827 (2006)



$$\hat{\mathcal{H}} = -t \sum_{\langle ij \rangle \sigma} \hat{c}_{i\sigma}^\dagger \hat{c}_{j\sigma} + U \sum_i \hat{n}_{i\sigma} \hat{n}_{i\sigma}$$

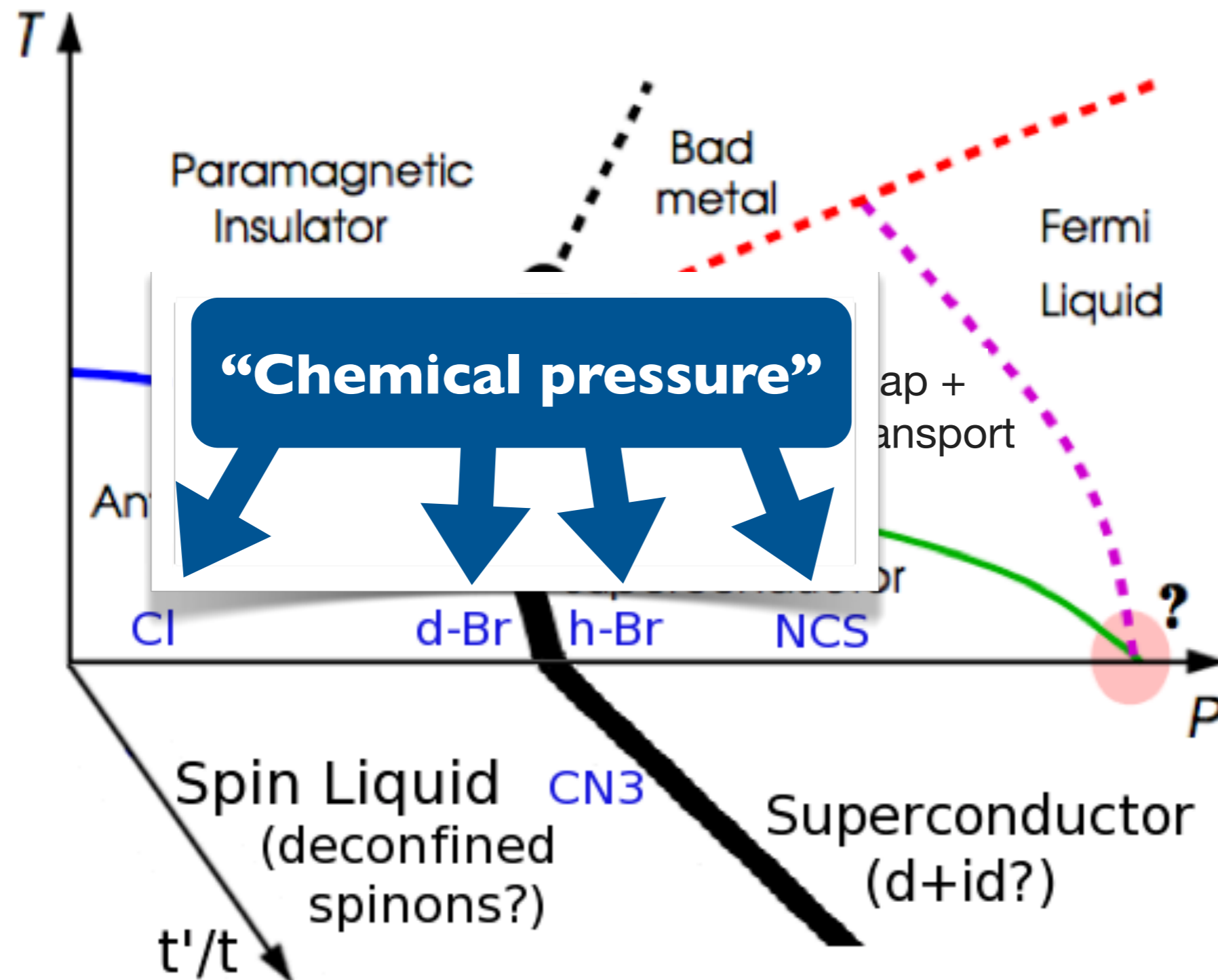
# Experimental phase diagram

For a review see BJP and McKenzie, JPCM 18, R827 (2006)



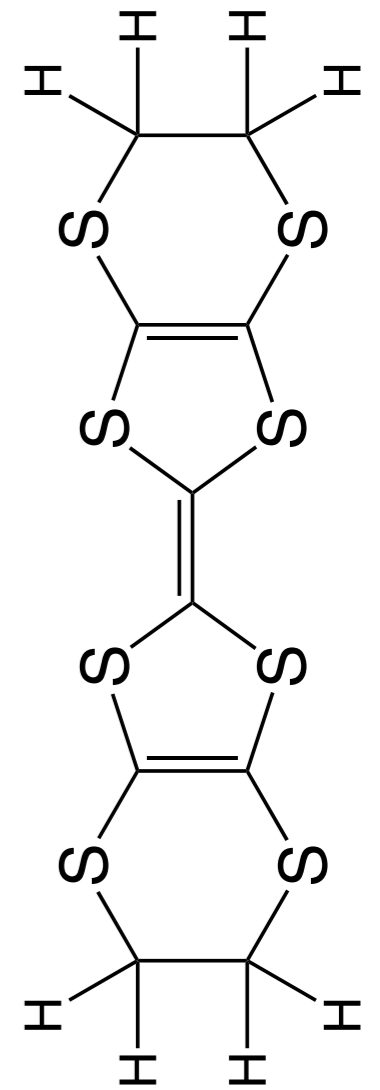
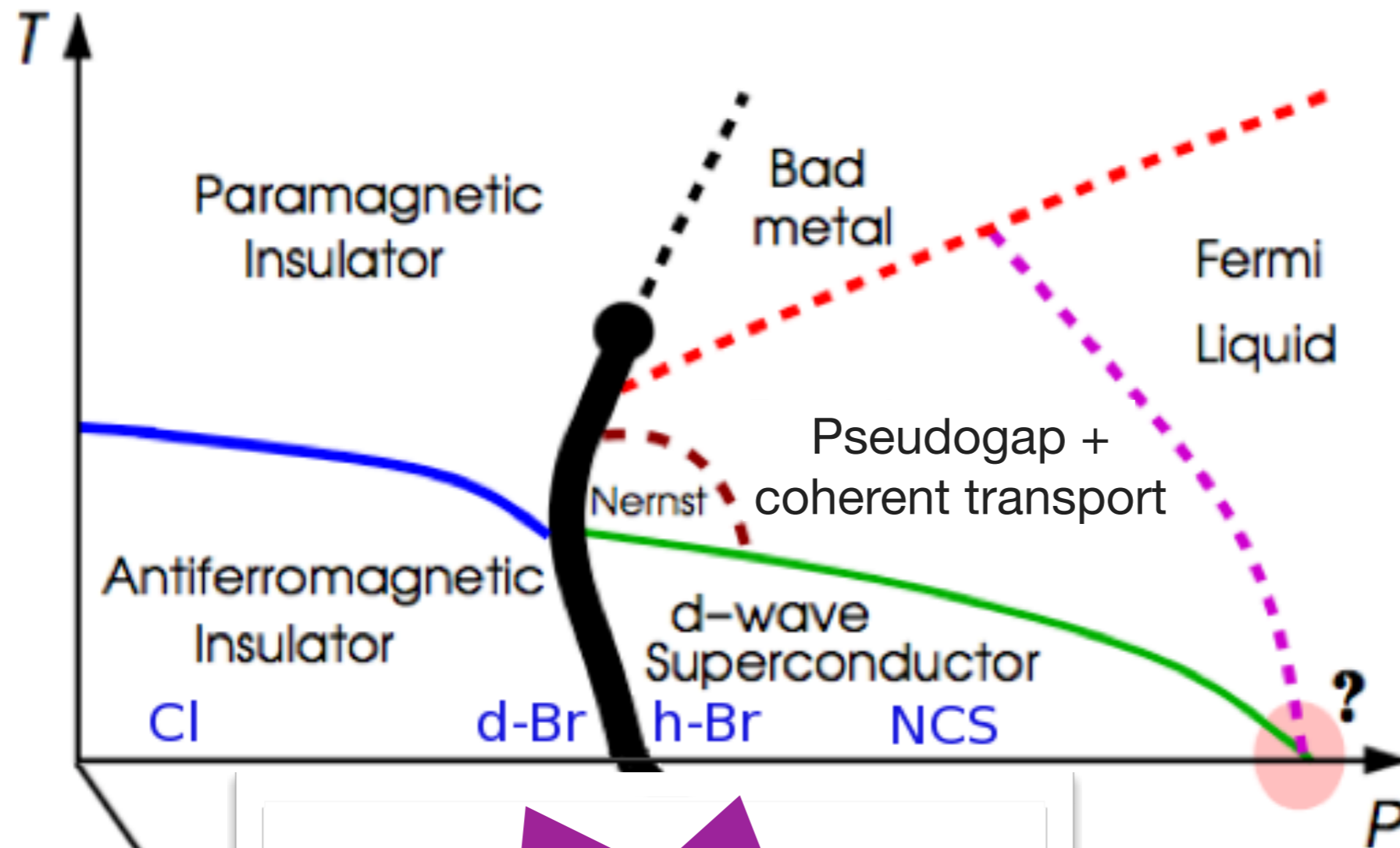
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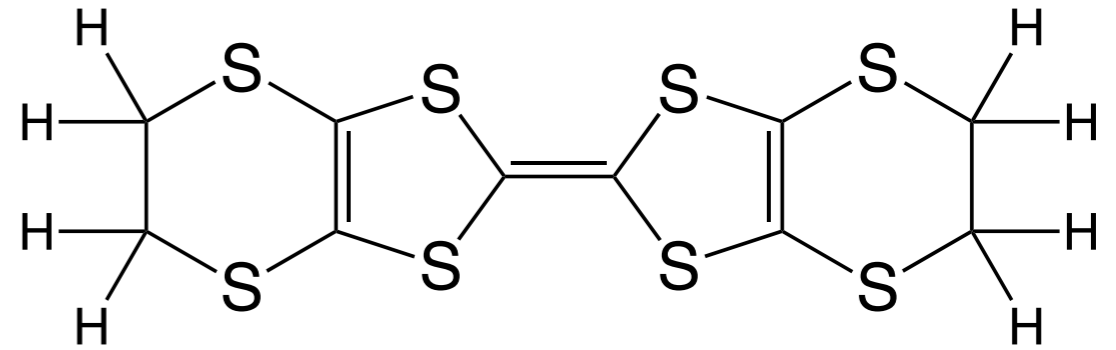
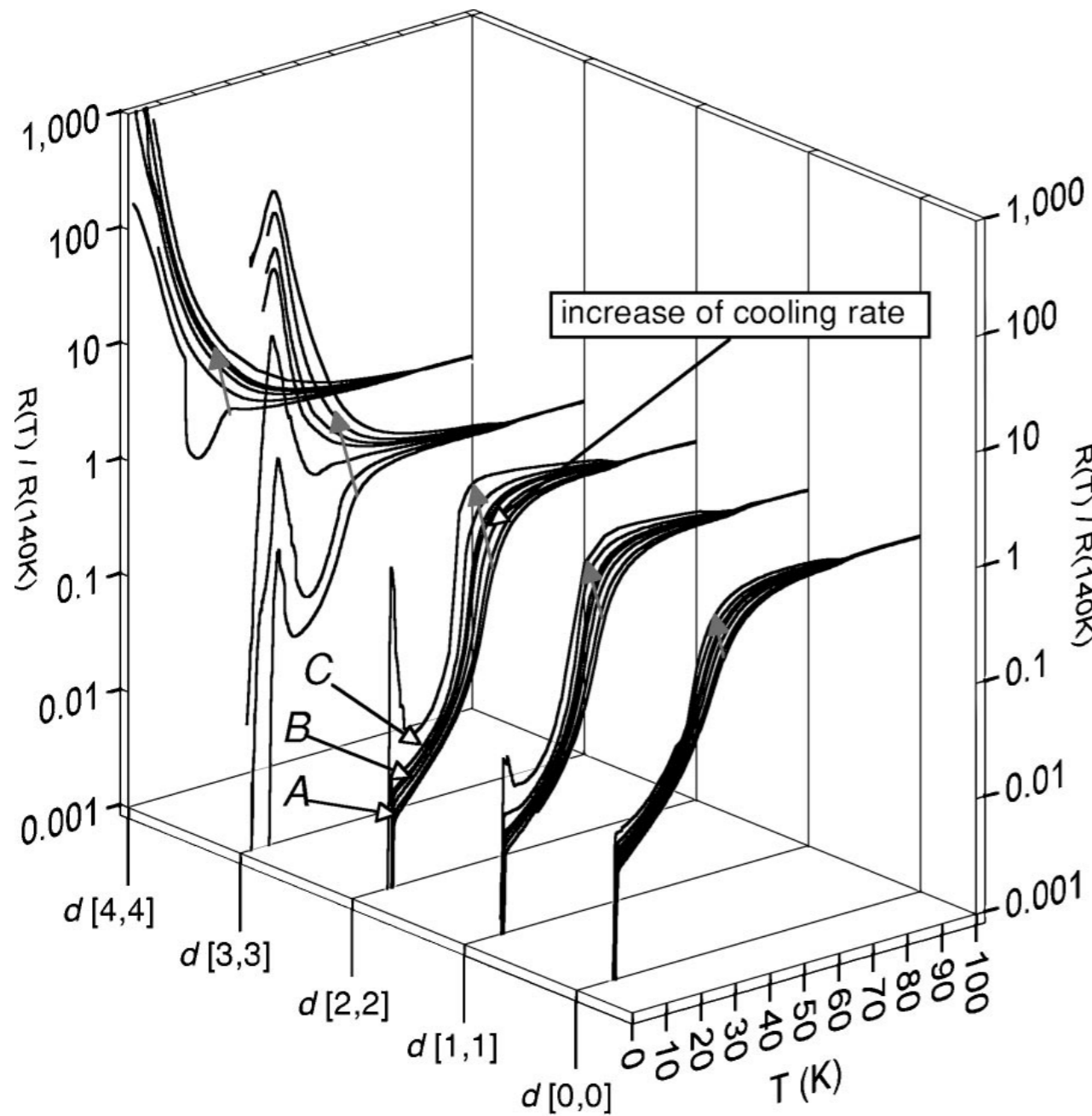
**Mott transition driven by deuteration**

conductor  
(id?)



# Metal insulator transition driven by deuteration!

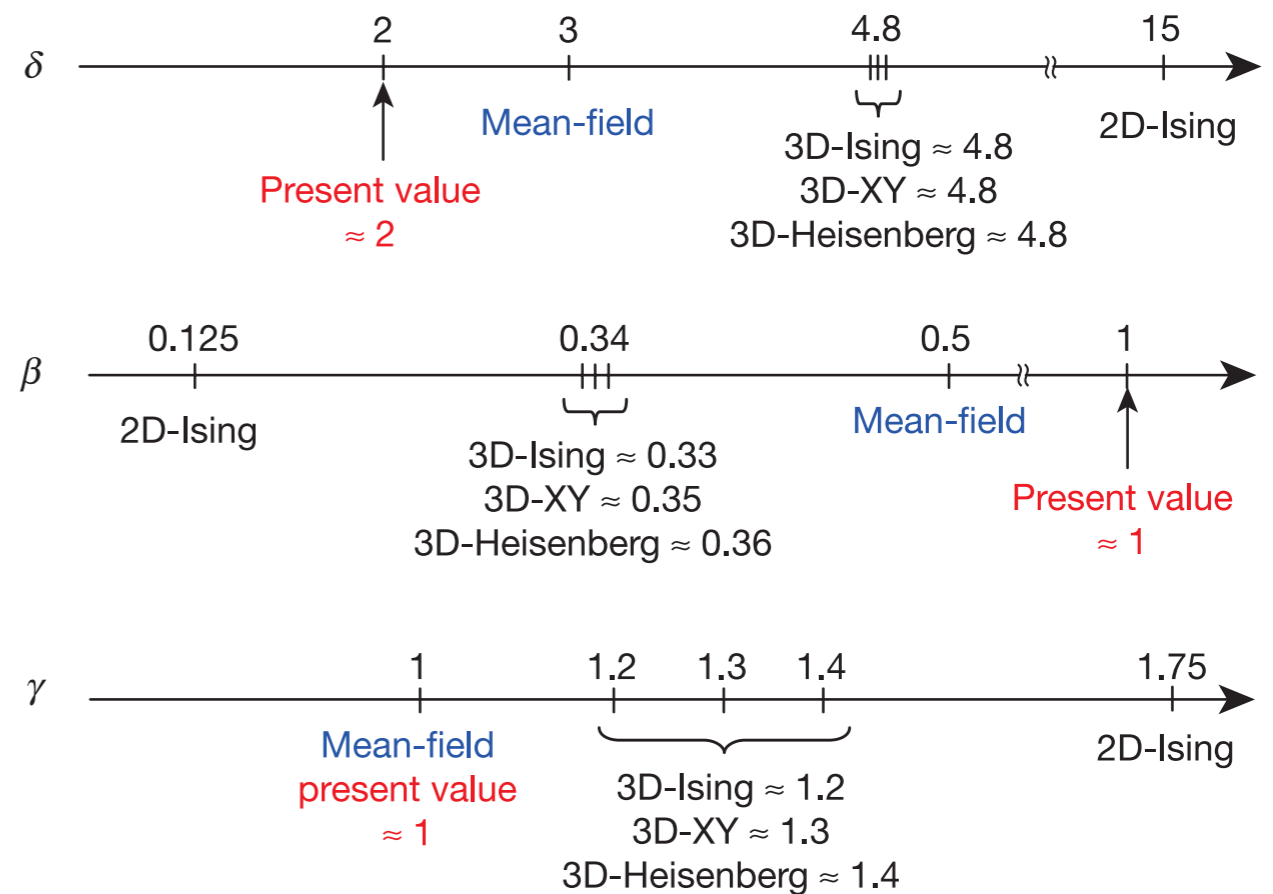
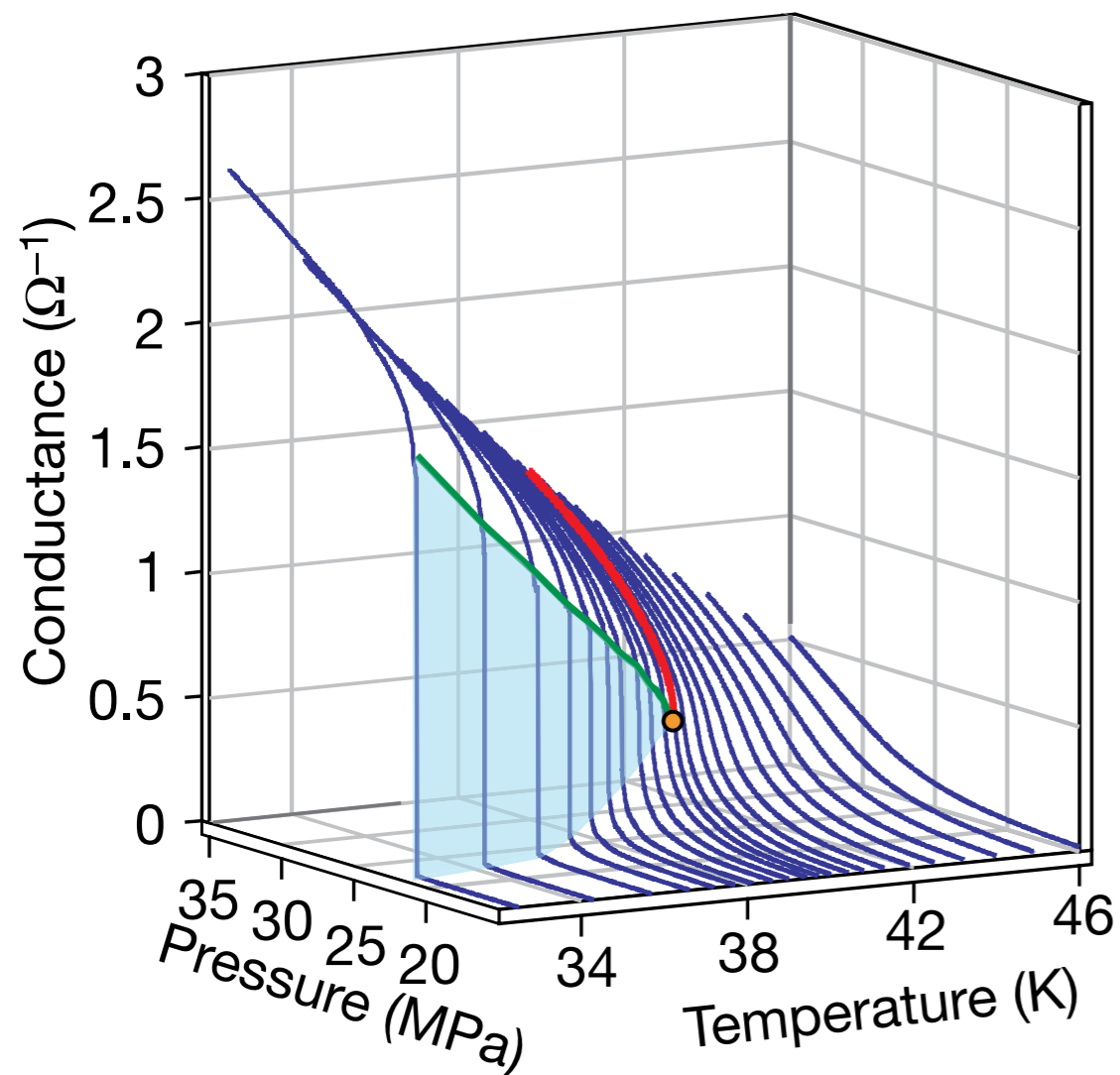
Taniguchi et al. PRB '03



- This shows that molecular crystals can be controlled by subtle changes in the molecular chemistry
- This gives experimentalists an extra “dial”

# Metal insulator transition driven by pressure

Kagawa et al. Nature '05; Nature Phys. '09

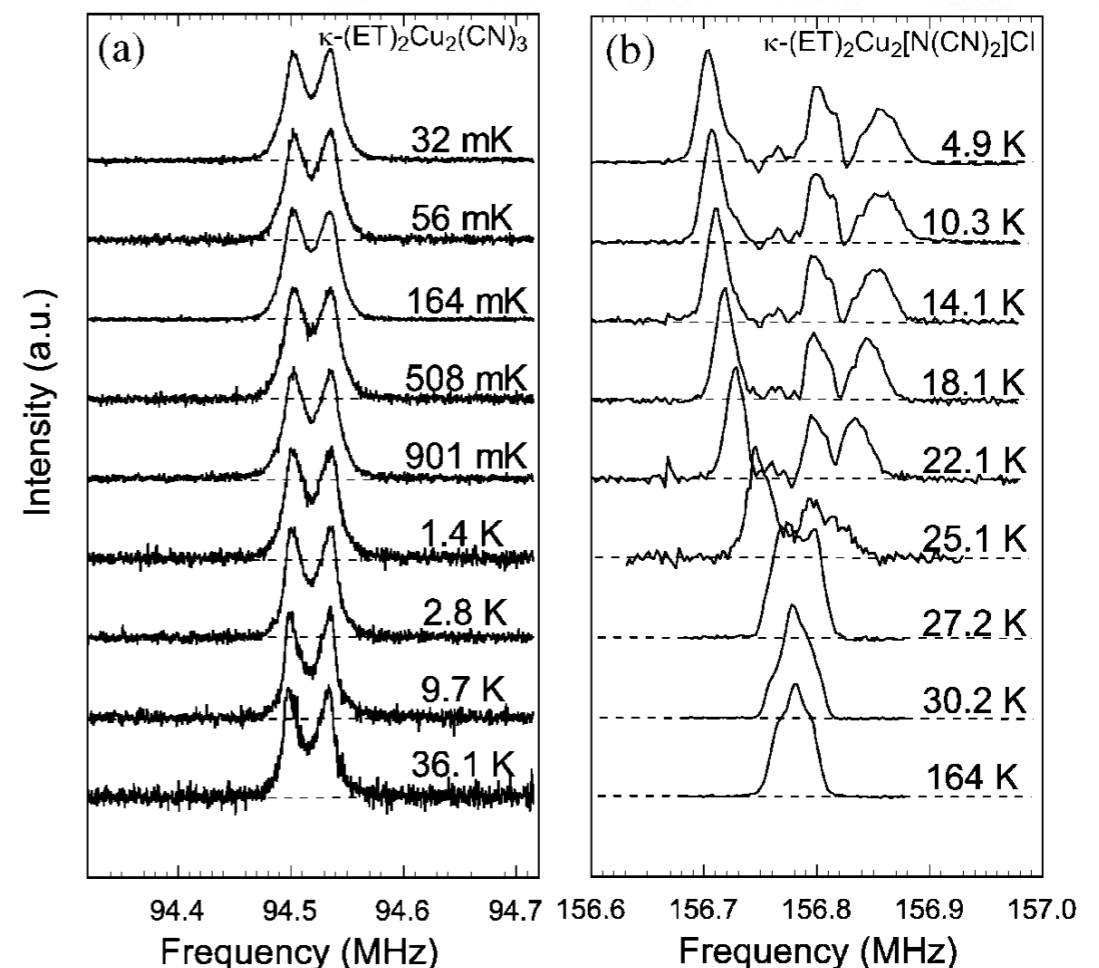
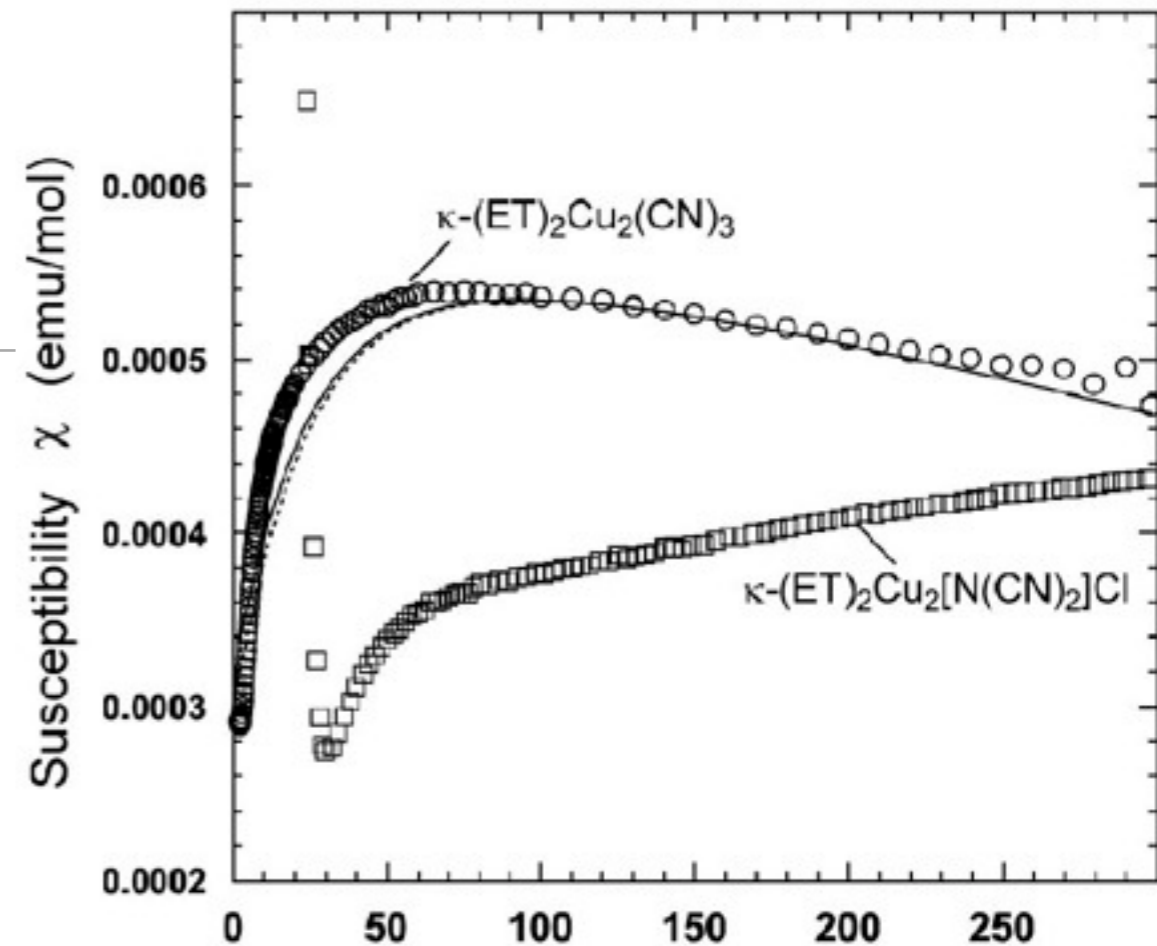


**Figure 3 | Comparison of the critical exponents ( $\delta, \beta, \gamma$ ) of the present case with those of the known universality classes (mean-field, Ising model, XY model and Heisenberg model). The examples of phase transitions**

- The observed critical exponents are not Ising like as in  $V_2O_3$  and DMFT [cf. Limelette et al. Science '03]
- Various theoretical proposals [e.g., Misawa et al. JPSJ '06 - proximity to QCP; Papanikolaou et al. PRL '08 - not deep enough into critical region]
- Same  $\delta$  exponent seen in NMR experiments [Kagawa et al. Nature Phys. '09]

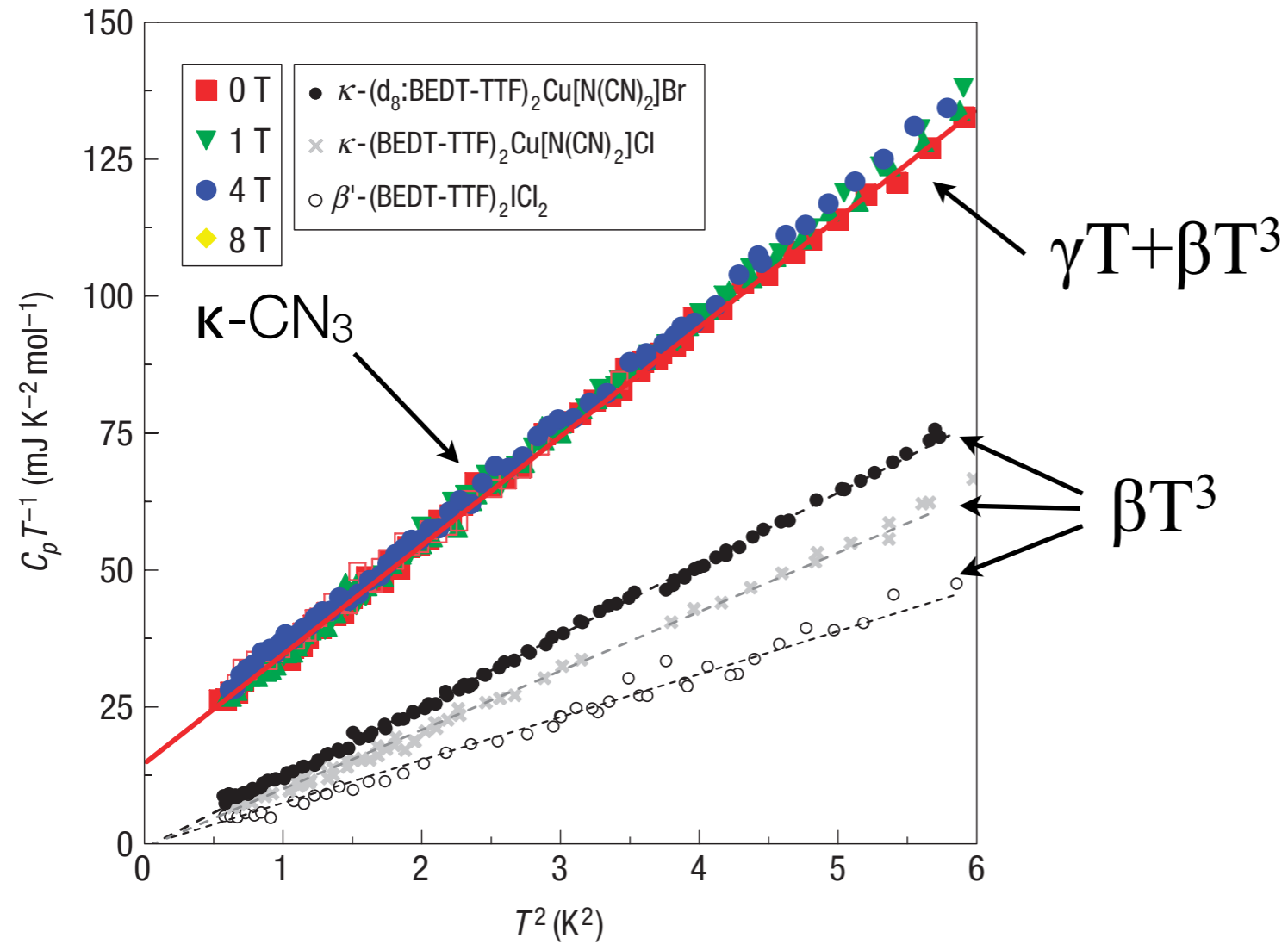
# Spin liquid

- $\kappa$ -(ET)<sub>2</sub>Cu[N(CN)<sub>2</sub>]Cl (henceforth  $\kappa$ -Cl) has an antiferromagnetic ground state - there is a slight canting of the moments leading to a large effect in the static susceptibility
- $\kappa$ -(ET)<sub>2</sub>Cu(CN)<sub>3</sub> (henceforth  $\kappa$ -CN<sub>3</sub>) has a spin-liquid ground state [Shimizu et al. PRL '03] - no long range order in magnetic ground state
- A splitting is observed in the NMR below  $T_N$  in  $\kappa$ -Cl - no such splitting is seen in  $\kappa$ -CN<sub>3</sub>.
- [The line in the figure is a fit to high-T series expansions for the isotropic ( $J=J'$ ) triangular lattice Heisenberg model, which give  $J \sim 250$  K]



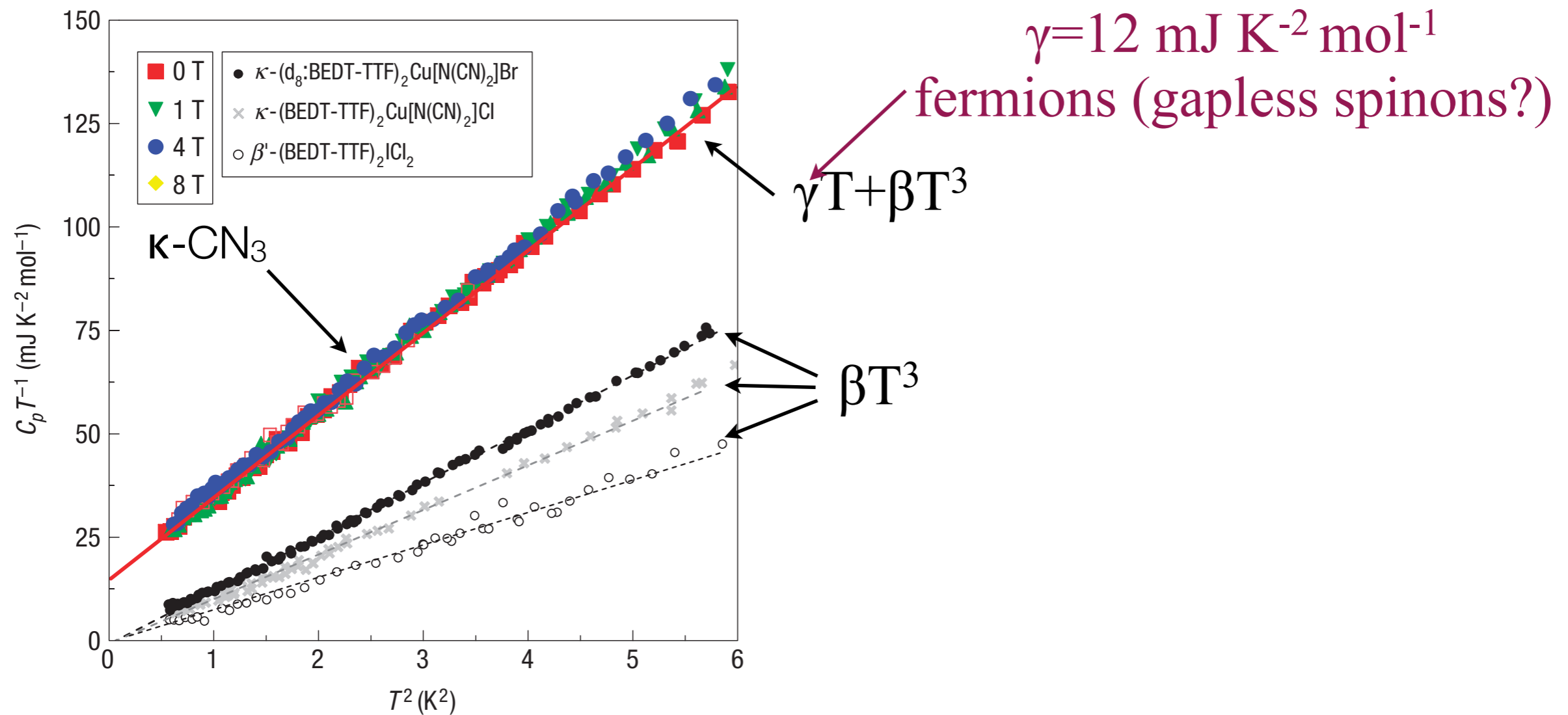
# Gapped or gapless spin liquid?

S. Yamashita et al. Nature Phys. '08; M. Yamashita et al. Nature Phys. '09



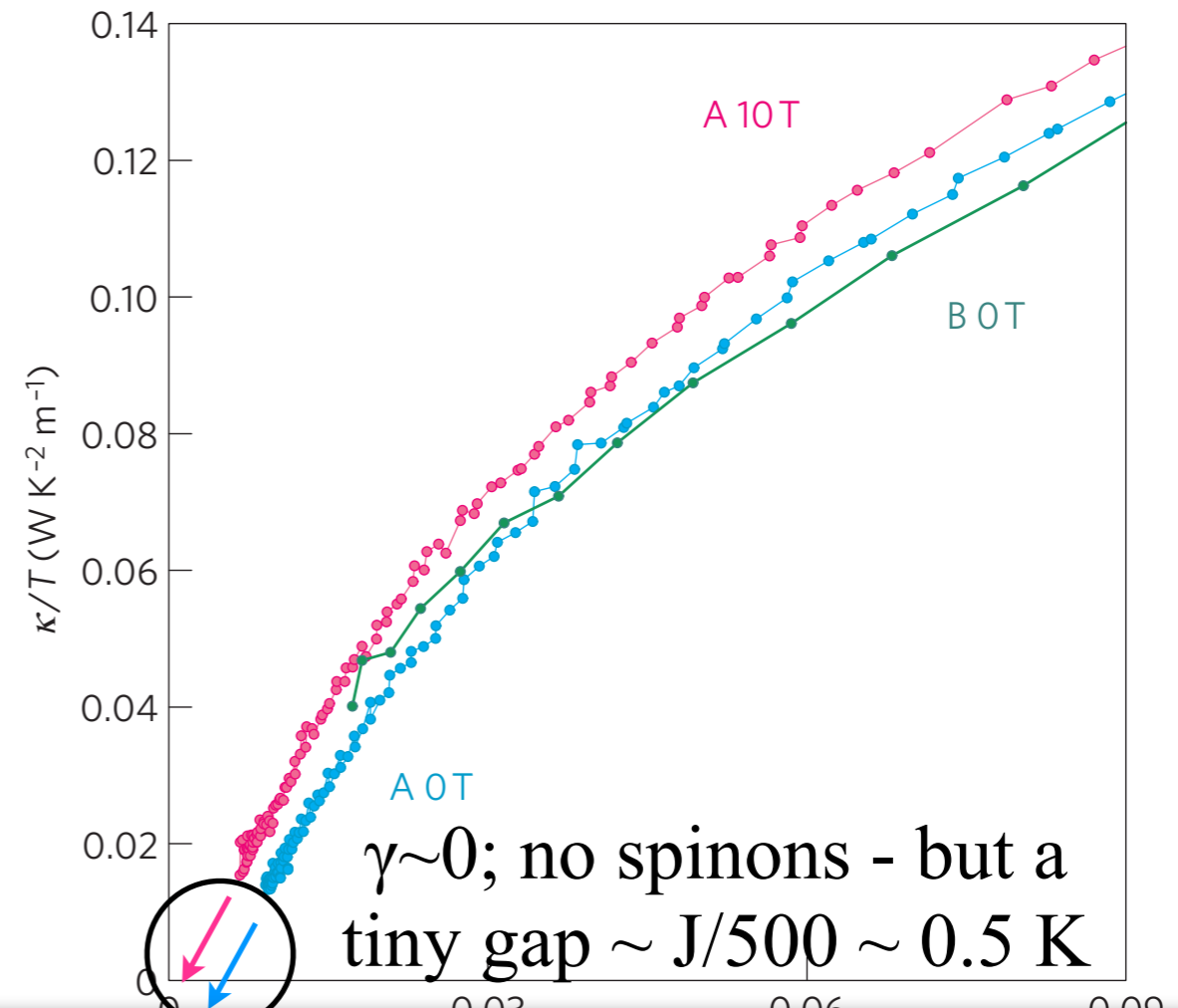
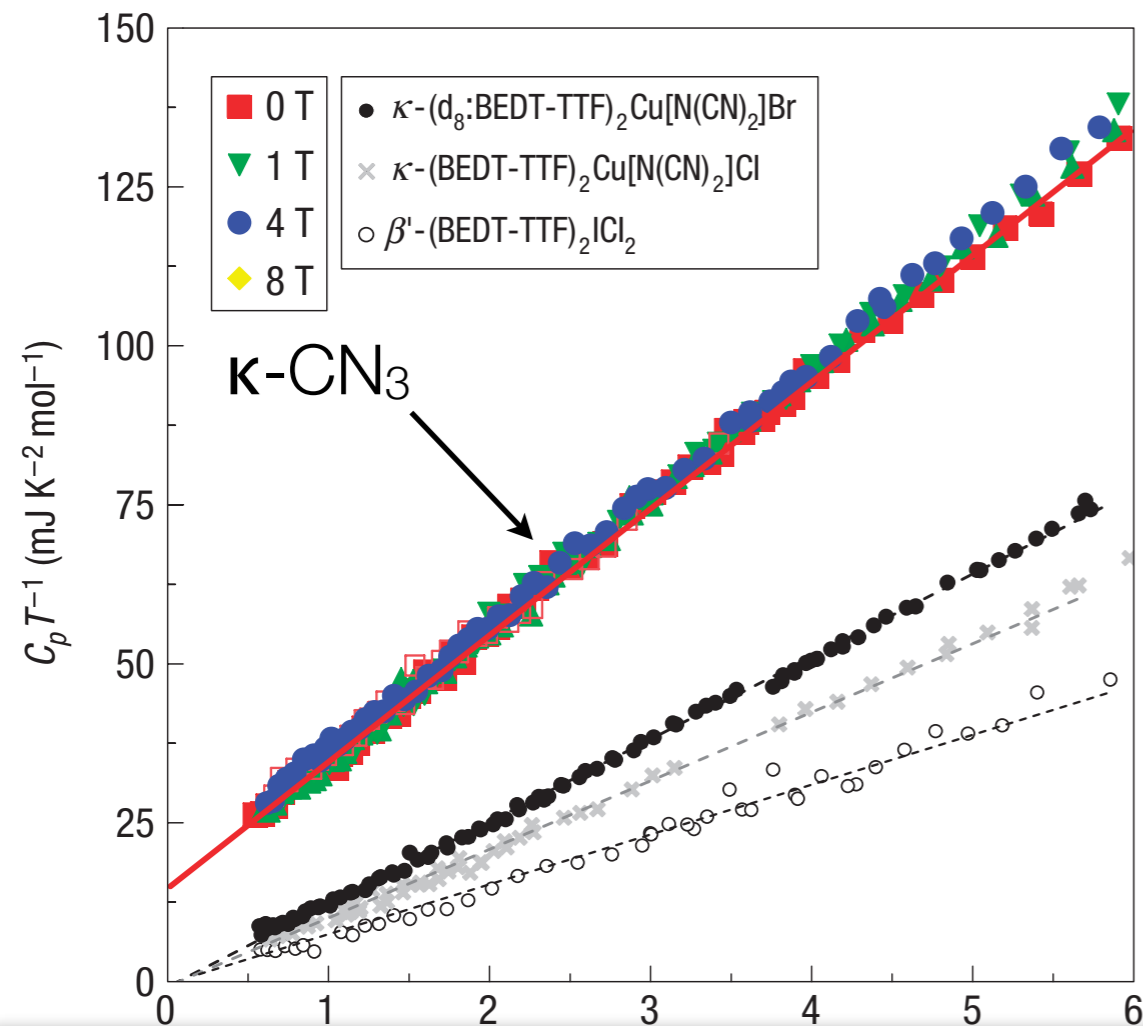
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# Gapped or gapless spin liquid?

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☪ Why the difference?

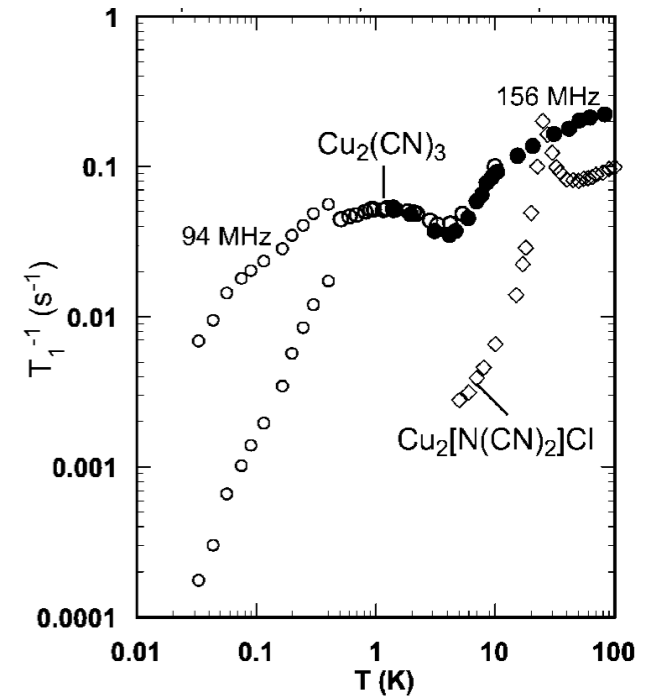
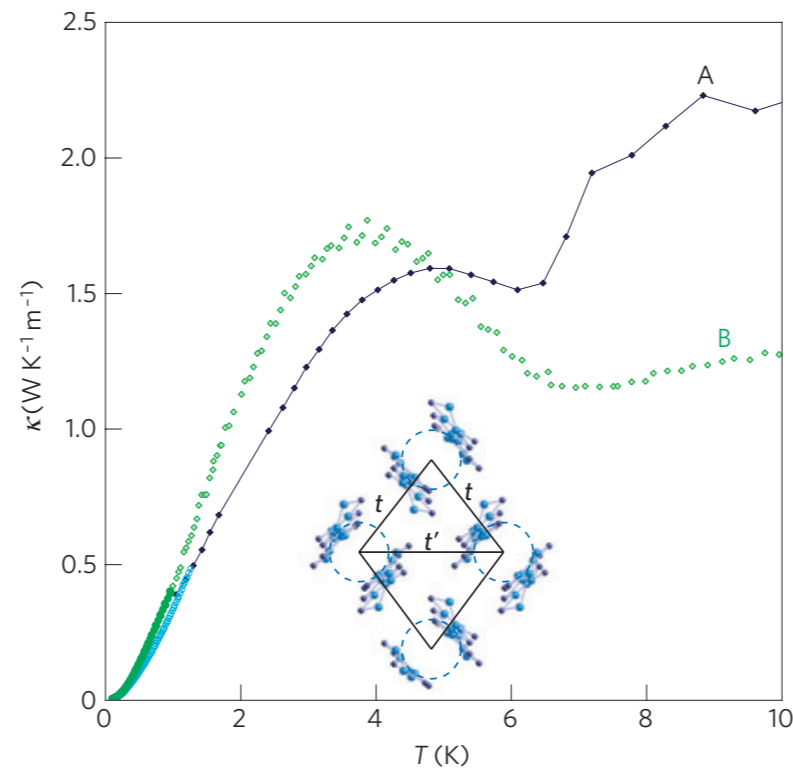
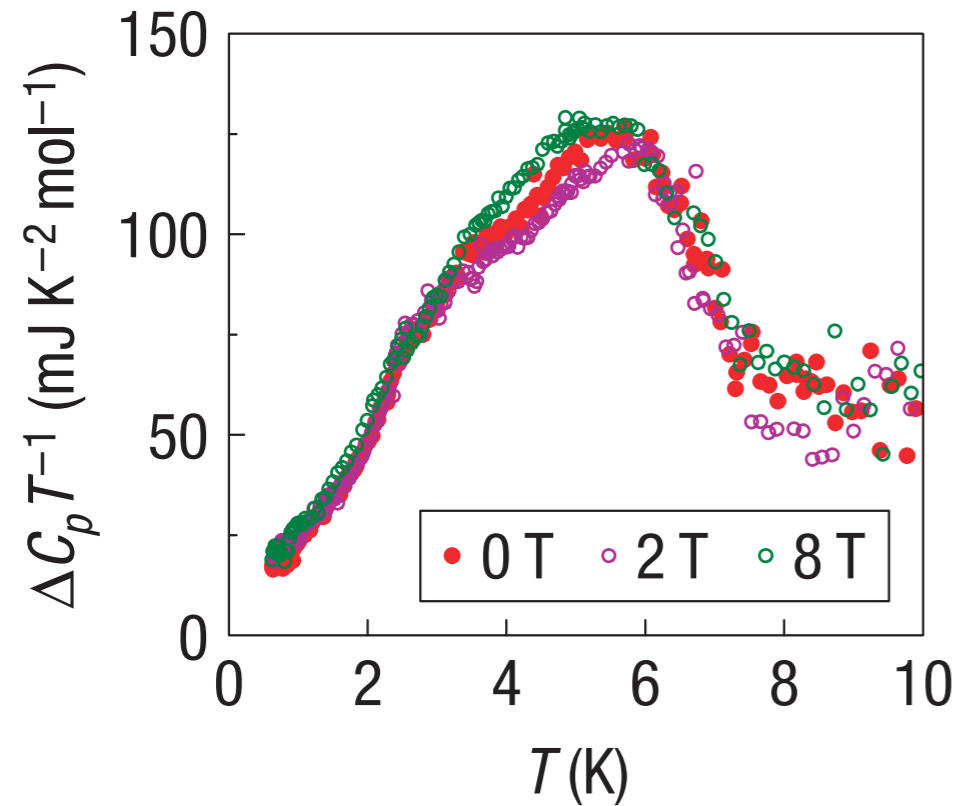
☪ M. Yamashita et al. argue it is because of the Schottky anomaly (from the Cu spins in the anion) in the anion affecting  $C_p$

☪ Also see discussion (particularly the comments) at

<http://condensedconcepts.blogspot.com/2009/08/can-we-see-visons.html>



# 6 K anomaly

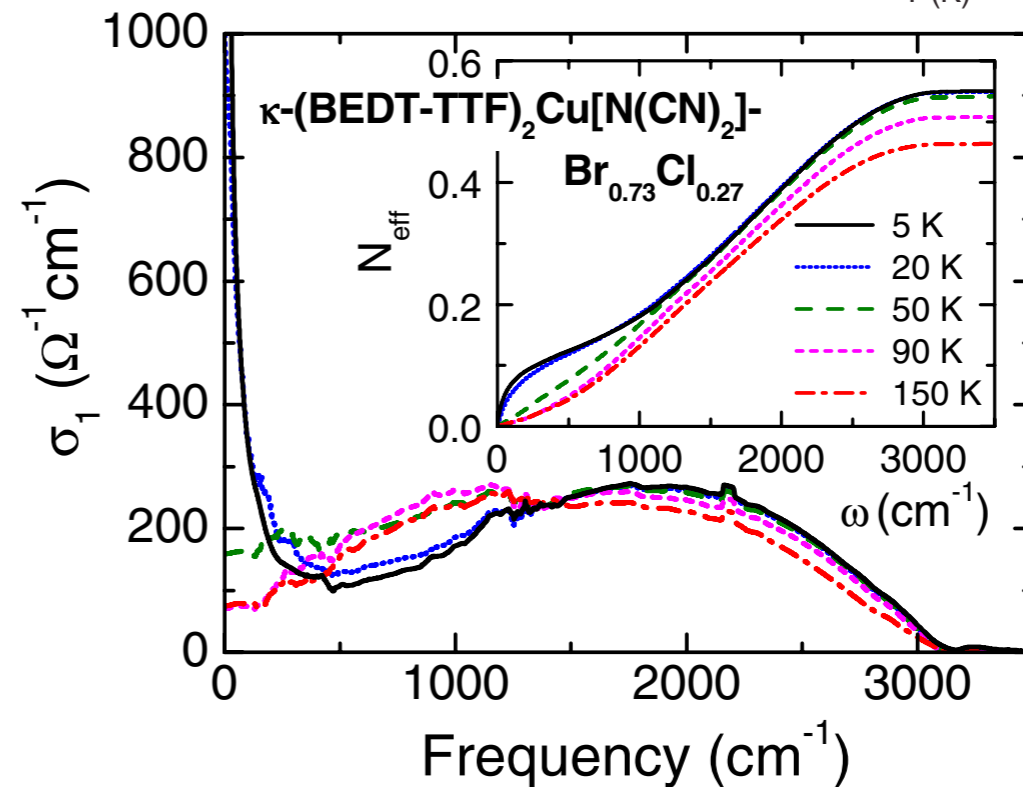
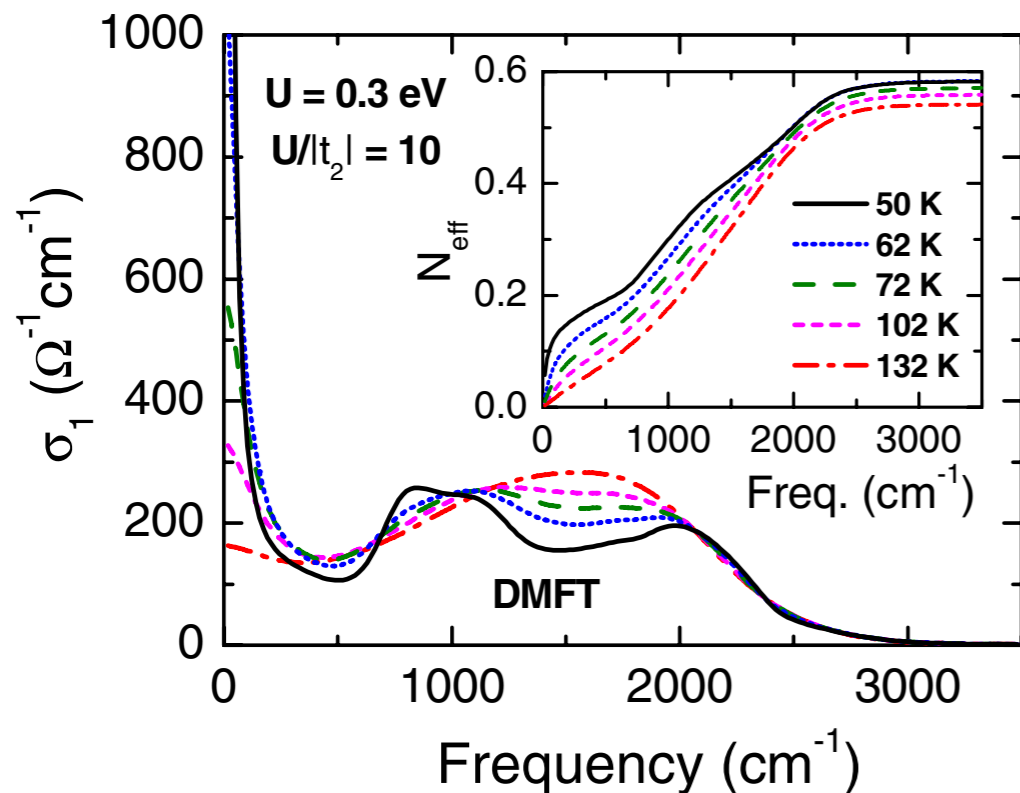
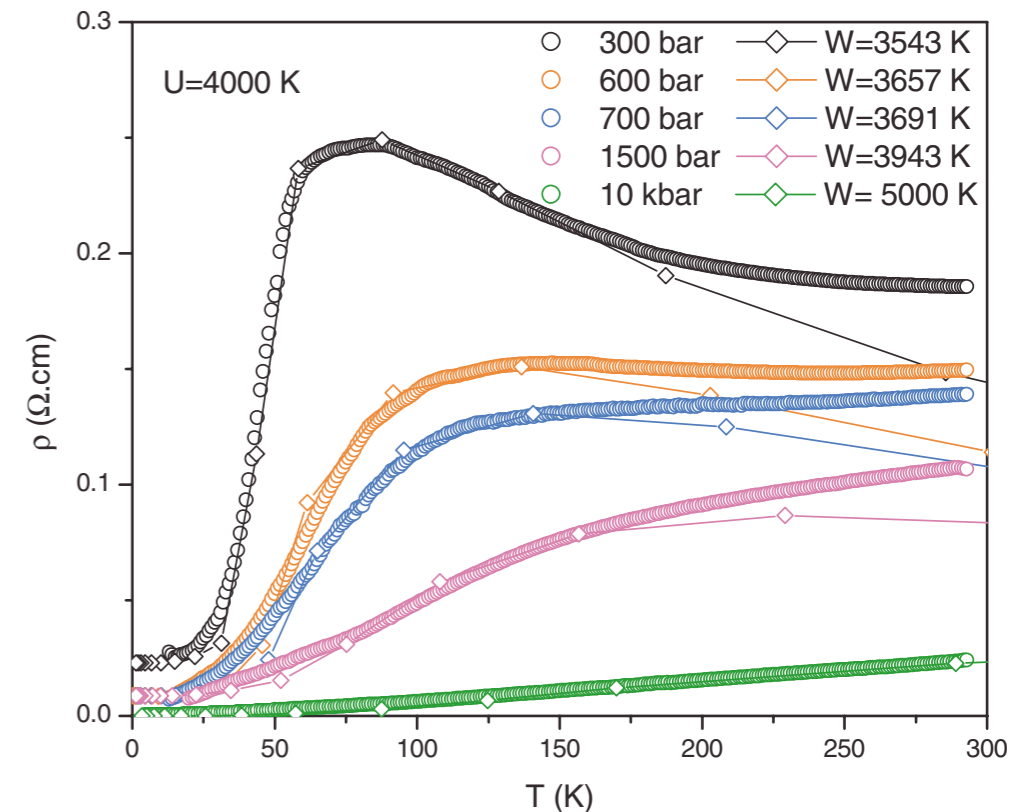


- A “bump” is seen below  $\sim 6$  K in the heat capacity, thermal conductivity, and spin-lattice relaxation rate
- Many possible explanations have been proposed including: visons (vortices in a  $Z_2$  spin liquid) [Qi et al. PRL ‘09], crossover to spin liquid [Yamashita et al. NP ‘08], “Amperean pairing of spinons [Lee et al. PRL ‘07], spin-chirality ordering [Baskaran PRL ‘89], excitation condensation [Qi & Sachdev PRB ‘08],...

# Bad metal

Merino & McKenzie, PRB 00, Limelette et al. PRL 03, Merino et al. PRL 08

- Many of the experiments on the normal state are quantitatively consistent with the “bad metal” phase predicted by DMFT
- Non-monotonic temperature dependence of thermopower, resistivity [top fig.: Limelette et al. PRL 03] and Hall coefficient
- Resistivity values above the Mott-Ioffe-Regal limit
- Absence of Drude peak in the high-T optical conductivity [lower figs.: Merino et al. PRL 08]



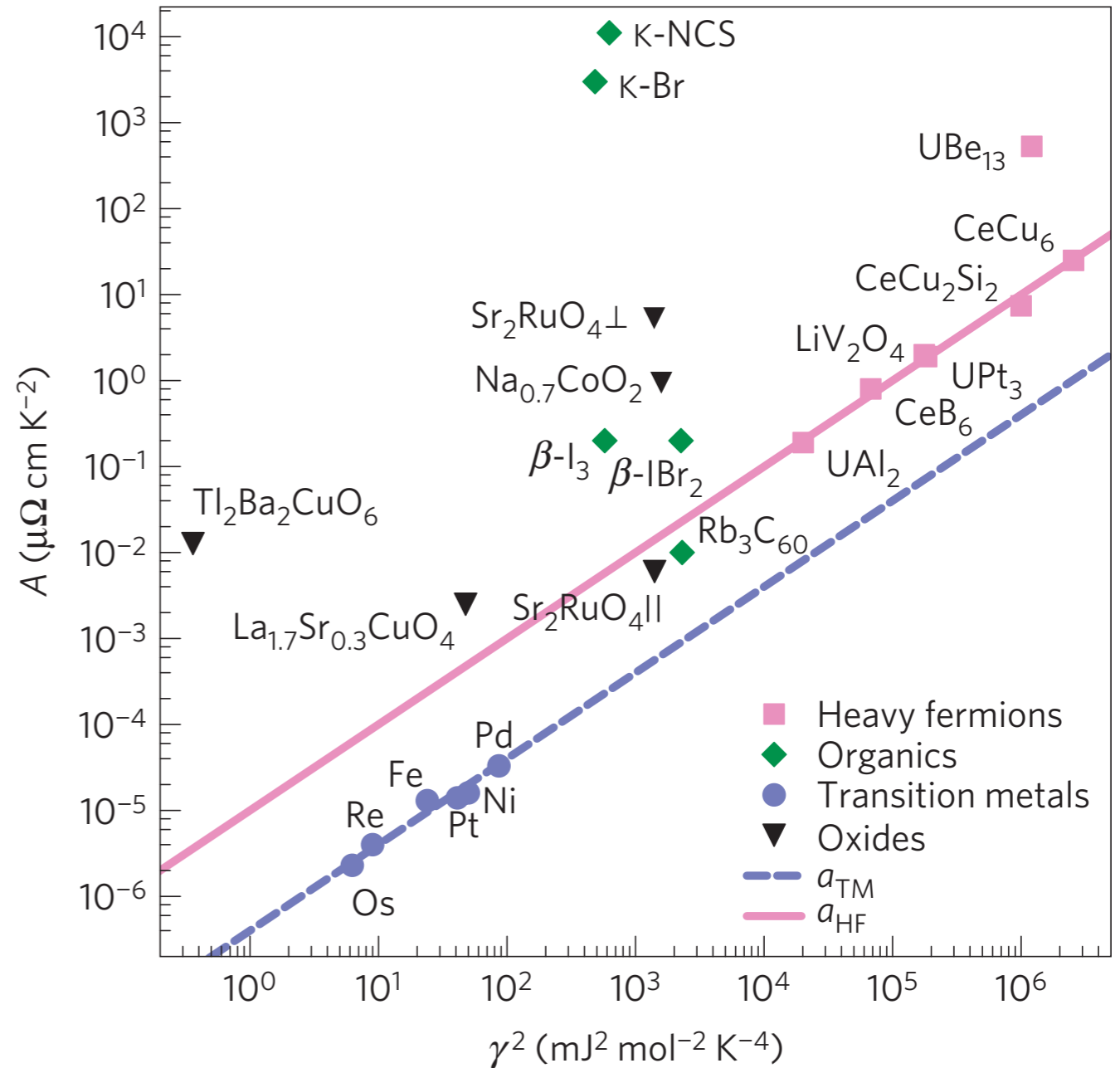
# Kadowaki-Woods ratio ( $A/\gamma^2$ )

Jacko, Fjaerestad, and BJP, Nature Phys. **5**, 422 (2009)

$$\rho(T) = \rho(0) + AT^2$$

$$C_v = \gamma T + \beta T^3$$

- Dressel, Wosnitza and others have noted that  $A/\gamma^2$  is very large in the organics
- Miyake et al. [SSC 71, 1149 ('89)] argued that the heavy fermion materials have a large KWR because  $\partial\Sigma/\partial\omega$  is large (strongly correlated) and that the KWR is much smaller in the transition metals because  $\partial\Sigma/\partial\omega$  is much smaller.
- Hussey [JPSJ 74, 1107 ('05)] proposed plotting  $\gamma$  in volumetric units for oxides etc.
- Does the same physics give rise to the mass enhancement ( $\gamma$ ) and  $A$ ?



# Kadowaki-Woods ratio ( $A/\gamma^2$ )

Jacko, Fjaerestad, and BJP, Nature Phys. **5**, 422 (2009)

- Following Miyake, Matsuura, and Varma, [Solid State Commun. **71**, 1149 ('89)], we study a phenomenological local Fermi liquid theory where the imaginary part of the self energy is given by

$$\begin{aligned}\Sigma''(\omega, T) &= -\frac{\hbar}{2\tau_0} - \frac{2n}{3\pi D_0} \frac{\omega^2 + (\pi k_B T)^2}{\omega^{*2}} && \text{for } |\omega^2 + (\pi T)^2| < \omega^{*2} \\ &= -\left(\frac{\hbar}{2\tau_0} + \frac{2n}{3\pi D_0}\right) F\left(\sqrt{\frac{\omega^2 + (\pi k_B T)^2}{\omega^{*2}}}\right) && \text{for } |\omega^2 + (\pi T)^2| > \omega^{*2}\end{aligned}$$

- $F(1)=1$ ,  $F(\infty)=0$ ,  $F(y)$  is an unspecified monotonic function.

- Relate  $A$  to  $\gamma$  via the Kramers-Kronig transform for the self energy

$$A = \frac{16nk_B^2}{\pi\hbar e^2 \langle v_{0x}^2 \rangle D_0^2 \omega^{*2}}; \quad \gamma = \gamma_0 \left(1 - \frac{\partial \Sigma'}{\partial \omega}\right) \simeq \frac{8nk_B^2 \xi}{9\omega^*}$$

$$\frac{A}{\gamma} = \frac{81}{4\pi\hbar k_B^2 e^2} \frac{1}{f_{dx}(n)}$$

where  $f_{dx}(n) \equiv nD_0^2 \langle v_{0x}^2 \rangle \xi^2$

# Modified Kadowaki-Woods ratio

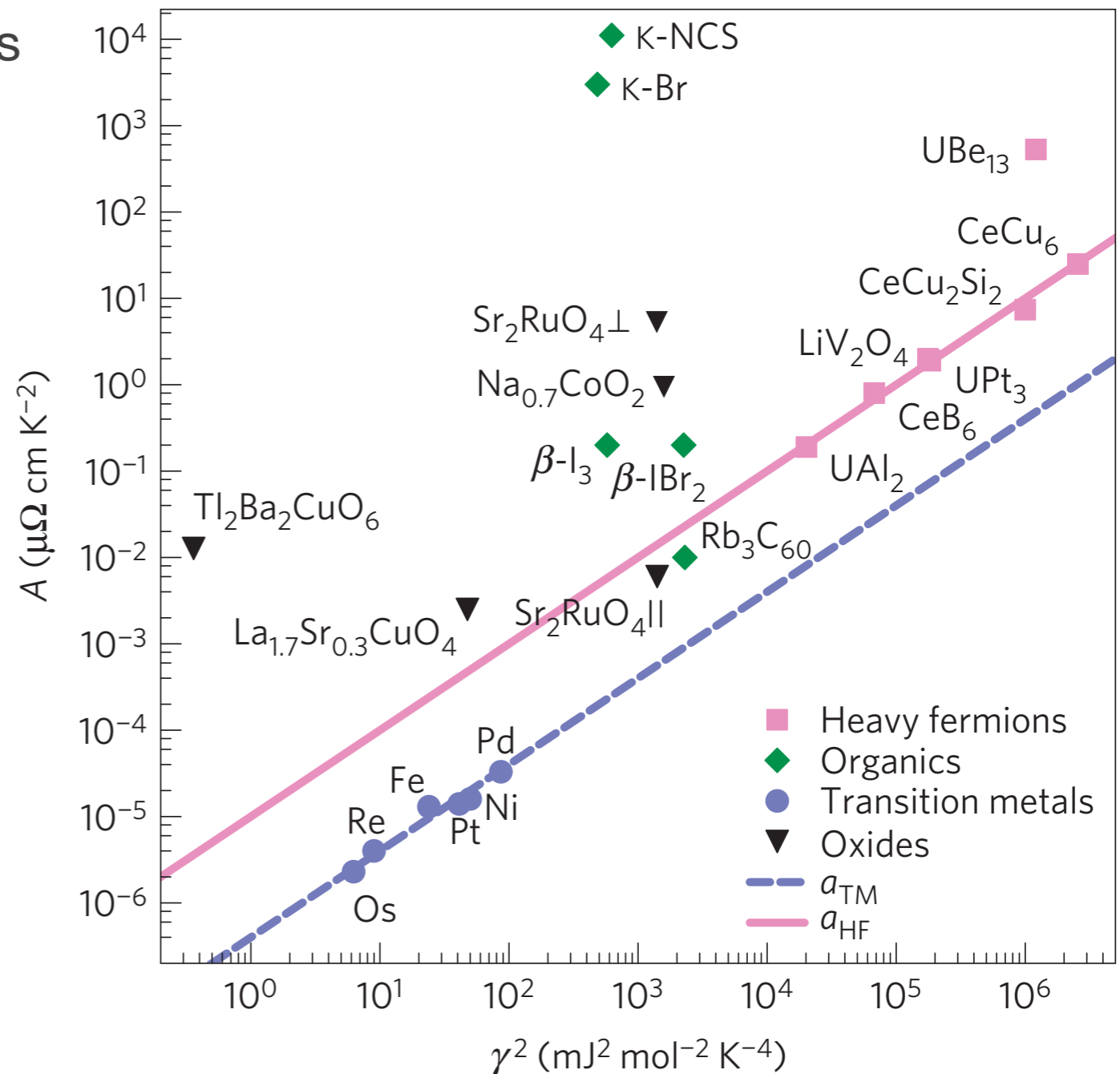
Jacko, Fjaerestad, and BJP, Nature Phys. **5**, 422 (2009)

- This suggests that a more natural ratio is

$$\frac{A f_{dx}(n)}{\gamma^2} = \frac{81}{4\pi \hbar k_B^2 e^2}$$

- Assume simple model band structures to calculate  $f_{dx} \equiv n D_0^2 \langle v_{0x}^2 \rangle \xi^2$

- Spherical Fermi surfaces for 3D materials
- Cylindrical Fermi surfaces for quasi-2D materials



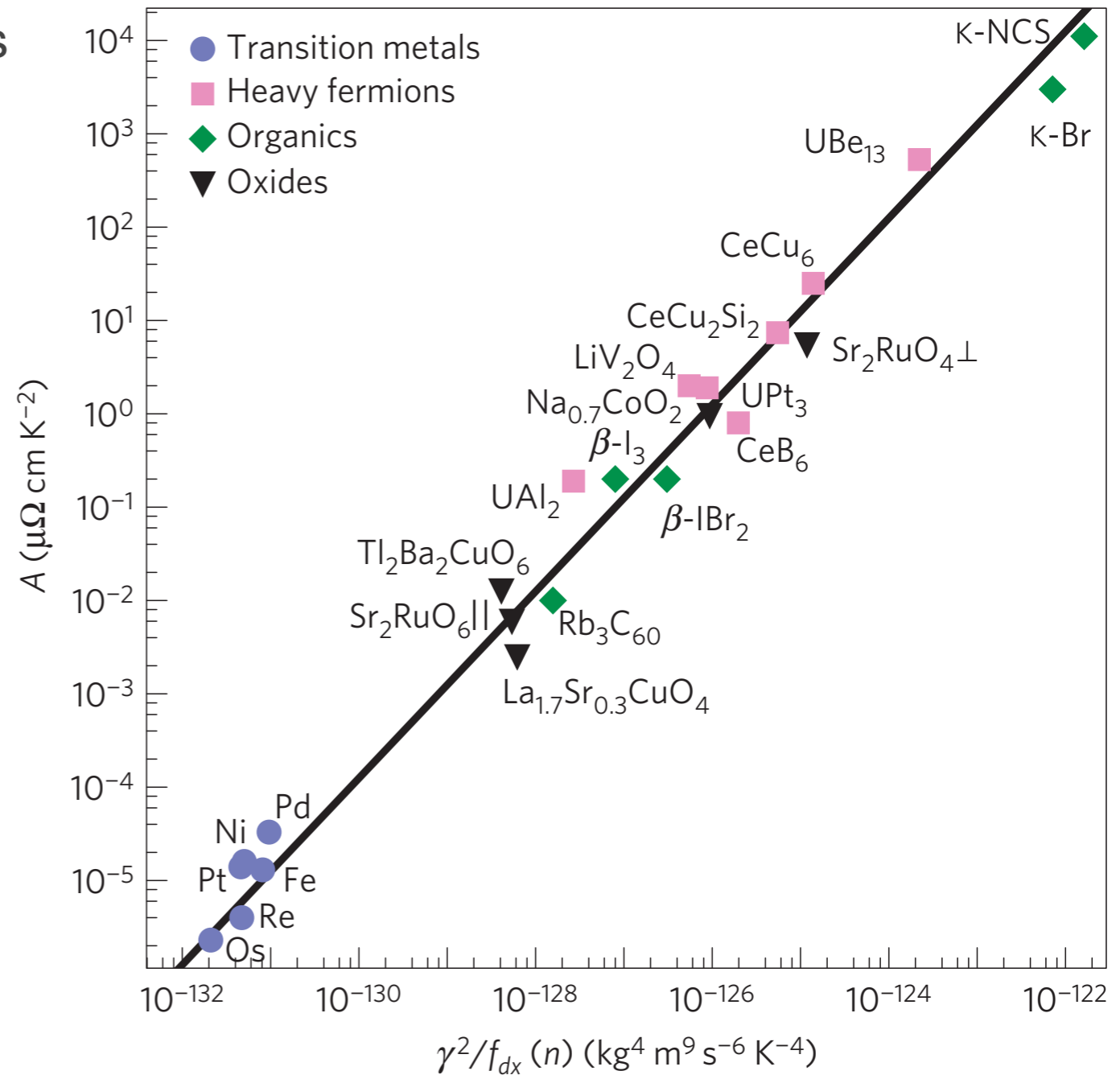
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- Assume simple model band structures to calculate  $f_{dx} \equiv n D_0^2 \langle v_{0x}^2 \rangle \xi^2$ 
  - Spherical Fermi surfaces for 3D materials
  - Cylindrical Fermi surfaces for quasi-2D materials
- We find excellent agreement with data from a broad range of strongly correlated materials.
- This shows that the main difference between the heavy fermions and the transition metals are due to band structure [ $f_{dx}(n)$ ], rather than correlations.
- The same correlations cause  $A$  and  $\gamma$  in the organics





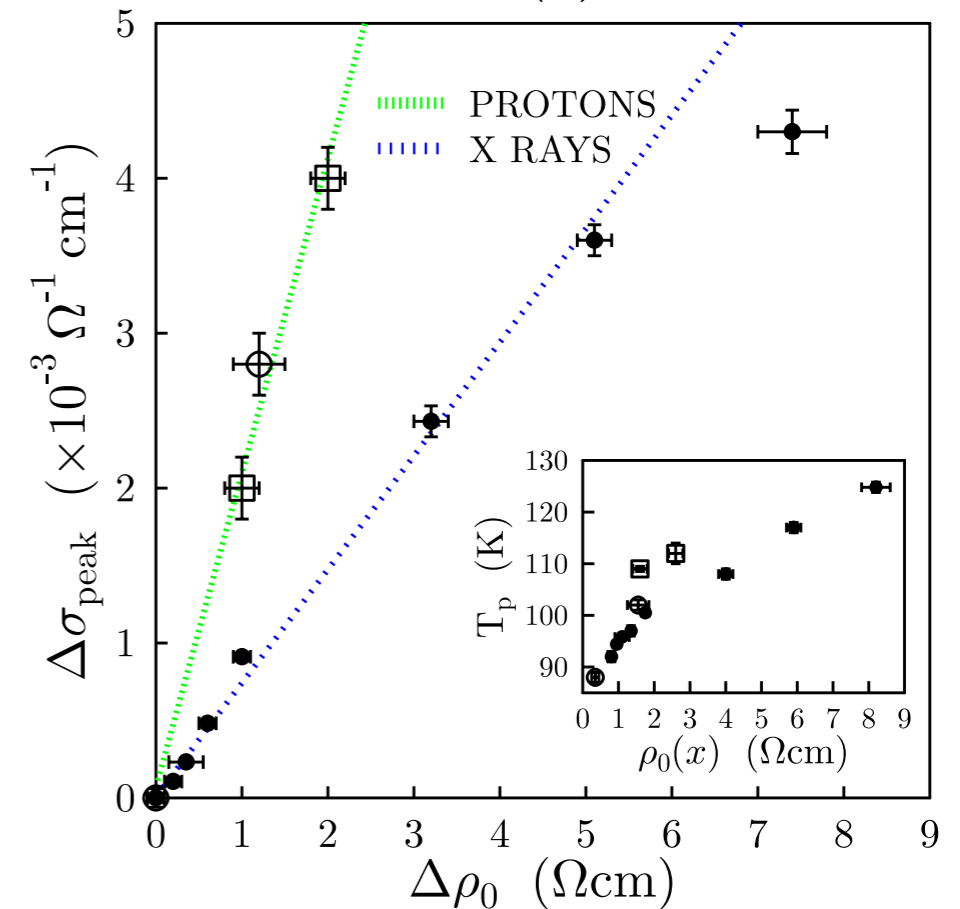
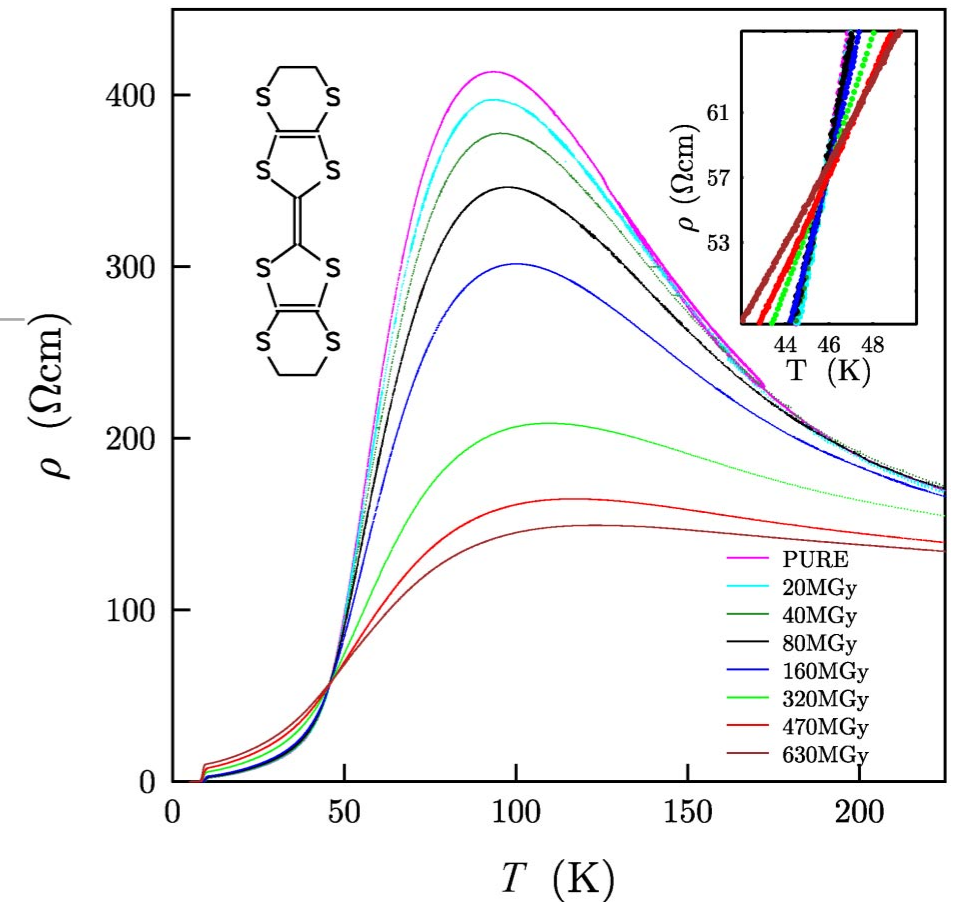
# Disorder and transport

Analytis, BJP et al., PRL **96**, 177002 (2006)

- ☛ Defects induced into samples by x-ray and proton irradiation
- ☛ Matthiessen's rule obey at low T, but strongly violated at high T
- ☛ Resistivity independent of disorder at  $T = T_{\text{cross}} \sim 46$  K
- ☛ Can be explained if we assume that the impurities have two effects
  1. Scattering in the usual way
  2. Act to assist interlayer tunnelling [Graf et al., PRB 93; Rojo et al., PRB 93, etc.]

$$\sigma(x, T) = \frac{1}{\rho_{\text{clean}} + x\rho_{\text{imp}}} + x\sigma_{\perp}$$

- ☛ This leads to the prediction that the residual resistivity is proportional to the peak conductivity, which is observed



# Disorder and transport

Analytis, BJP et al., PRL **96**, 177002 (2006)

Defects induced into samples by x-ray and

pro

Ma

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Res

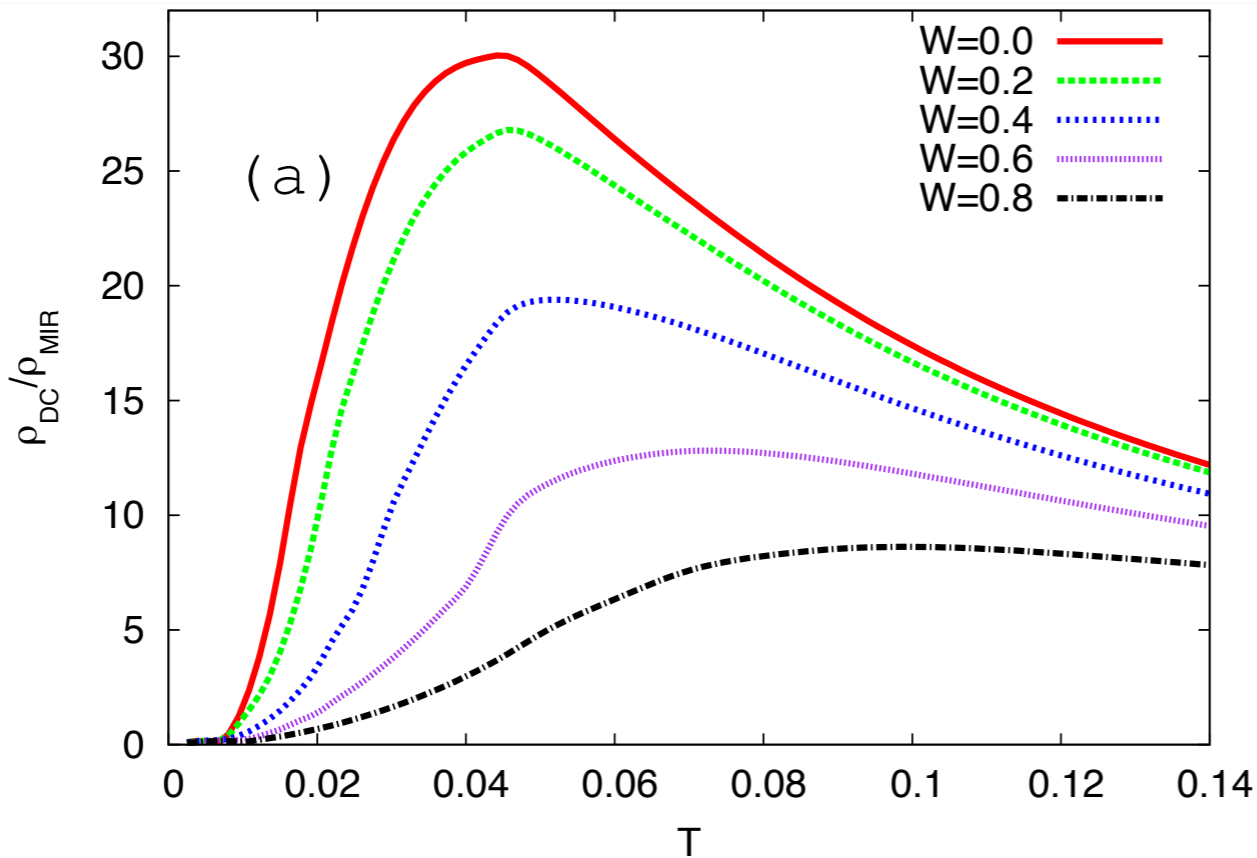
T=

Ca

imp

1.

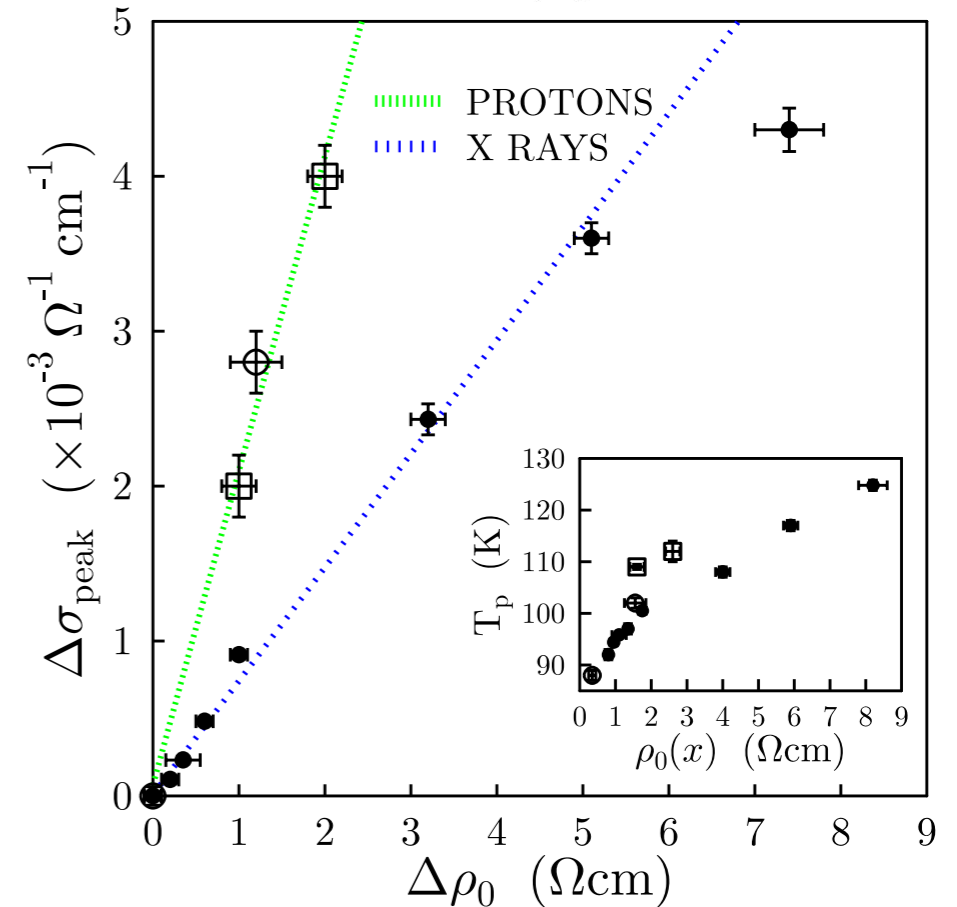
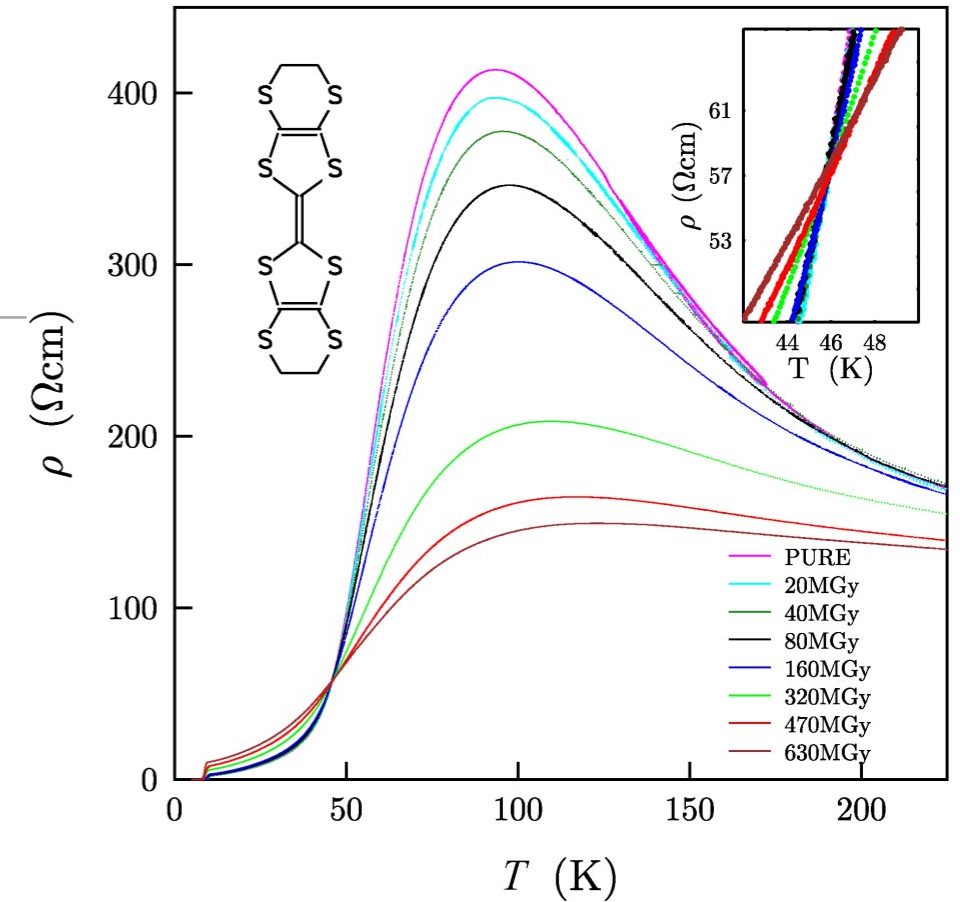
2.



Disordered Hubbard model (DMFT)

Radonjić et al. arXiv:0910.5100

This leads to the prediction that the residual resistivity is proportional to the peak conductivity, which is observed



# Pseudogap?

BJP, Yusuf & McKenzie, PRB 80, 054505 (2009)

## Pseudogap + coherent transport

$$\rho(T) \sim T^2$$

SdH and dHvA oscillations

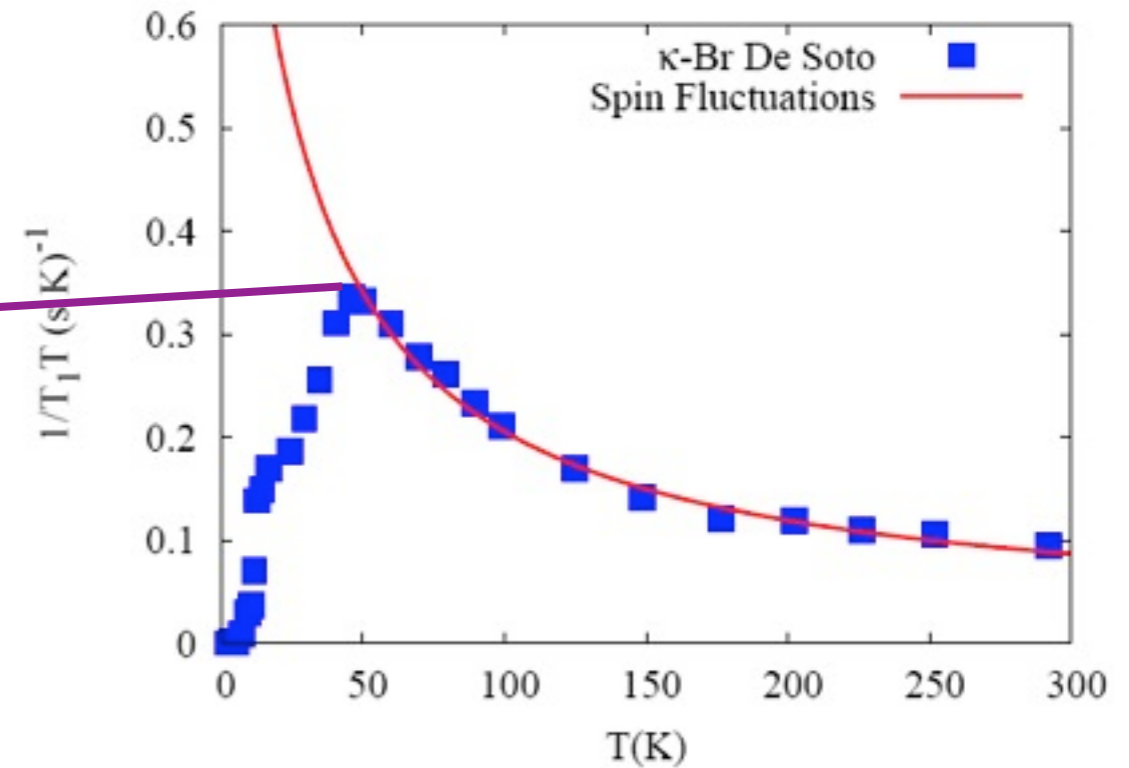
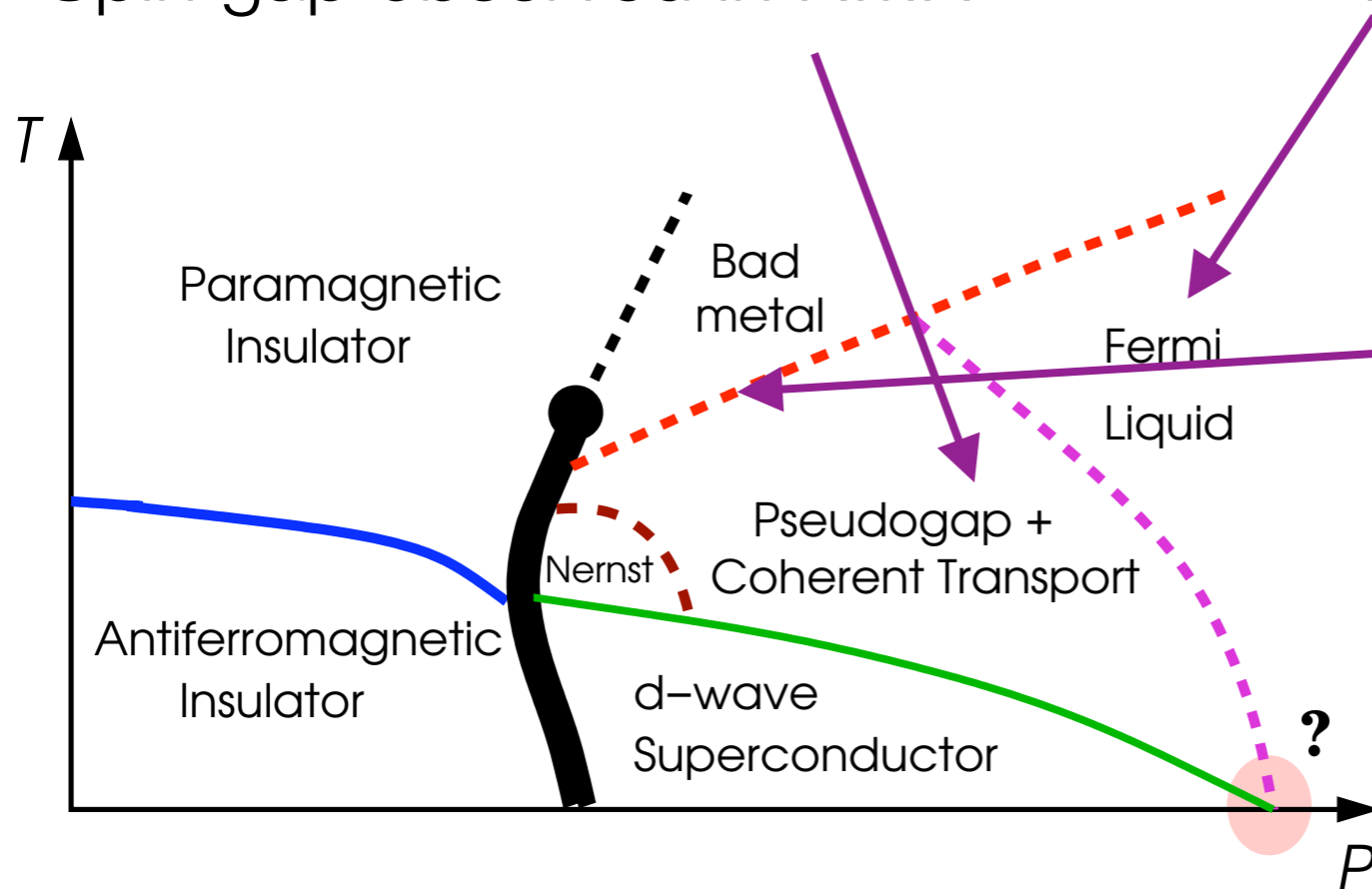
Spin gap observed in NMR

## Fermi Liquid

$$\rho(T) \sim T^2$$

SdH and dHvA oscillations

No gap observed in NMR

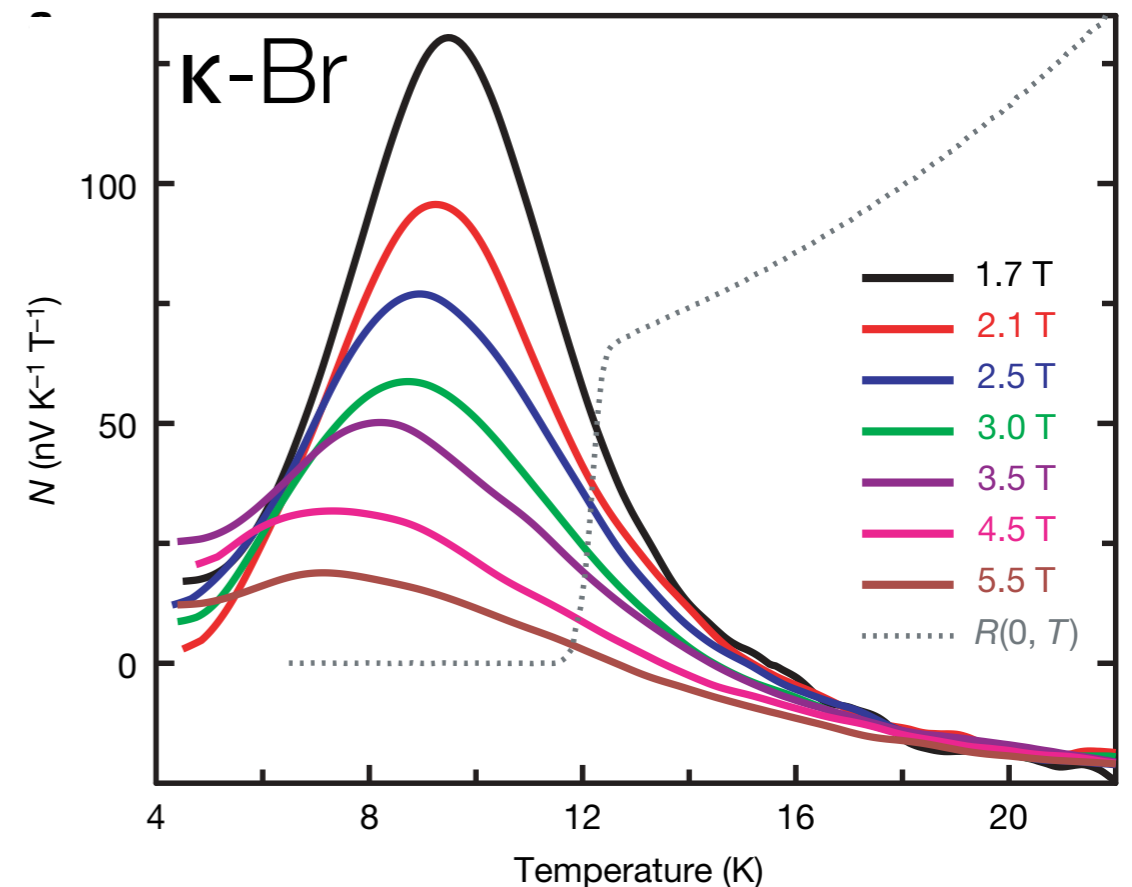
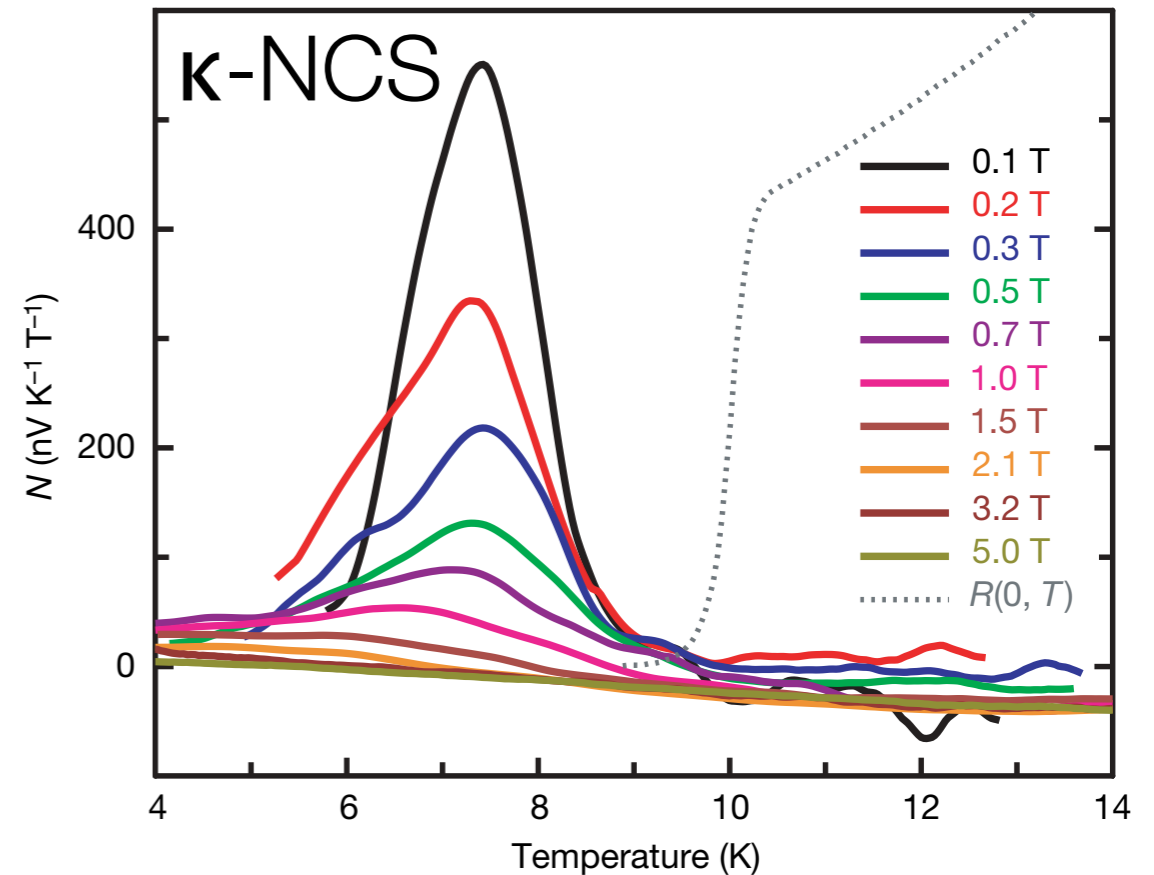
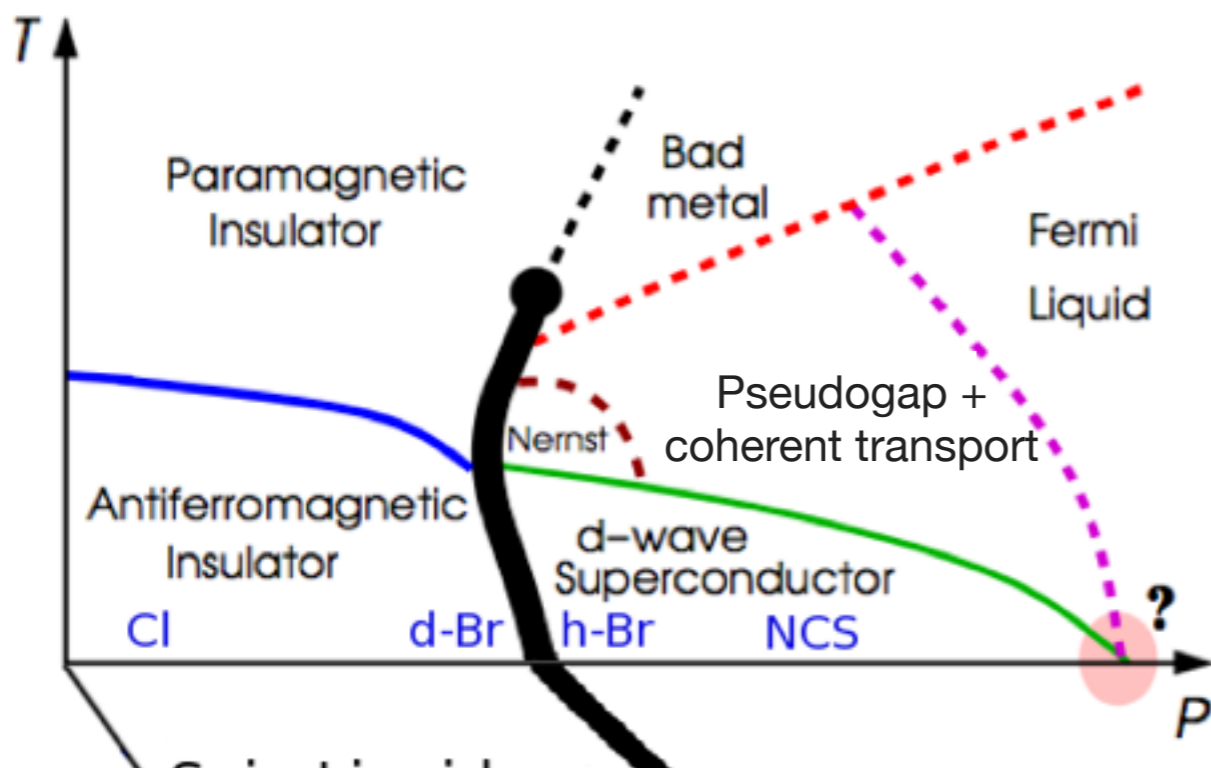


De Soto et. al., Phys. Rev. B 52, 10364 (1995); Mayaffre, et al., EPL, 25, 208 (1994); etc.

# Nernst effect near the Mott insulator

[Nam et al. Nature 07]

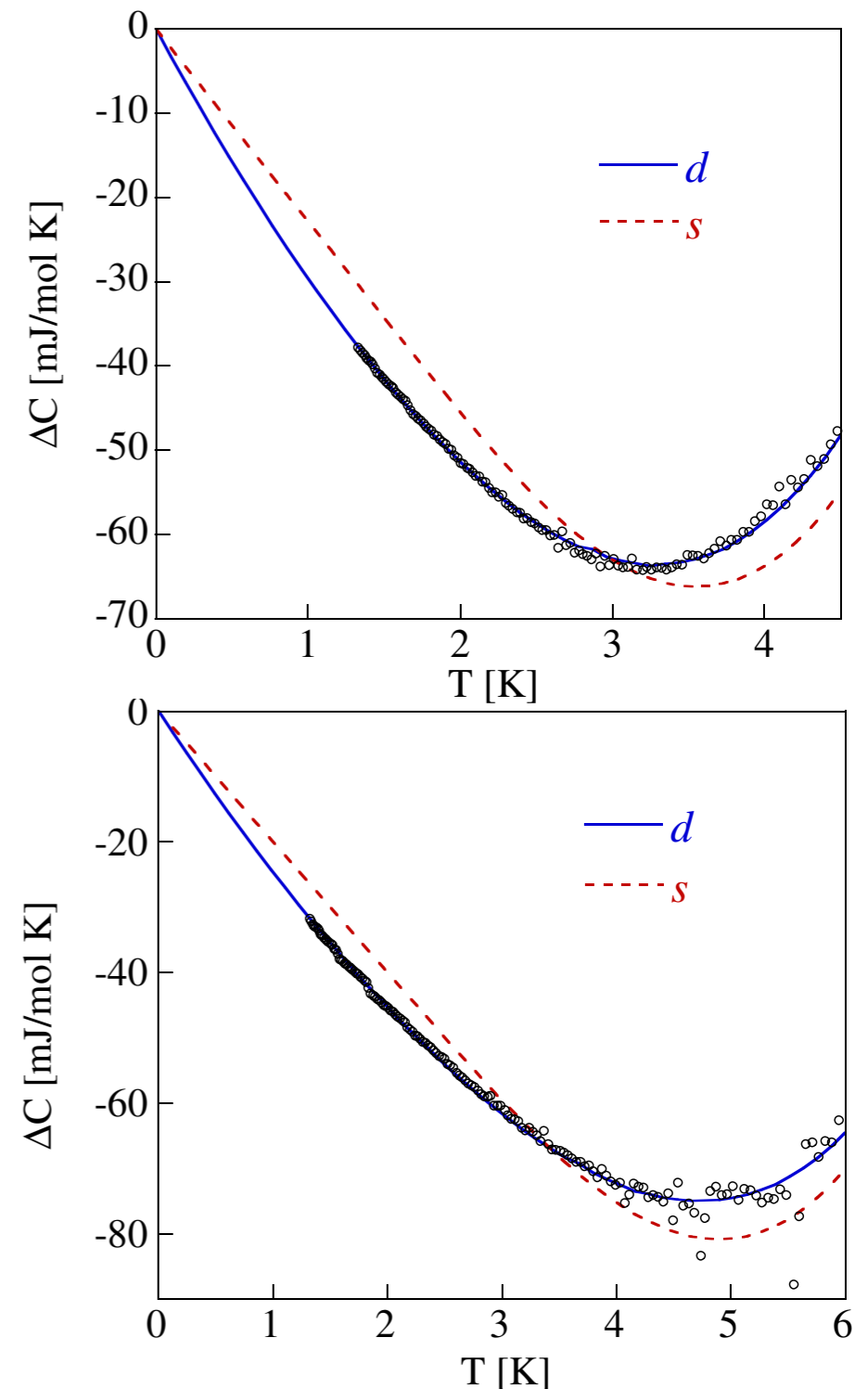
- In  $\kappa$ -NCS one sees a small Nernst effect in the normal state, and a large vortex Nernst below  $T_c$
- In  $\kappa$ -Br Nernst signal is large in a significant region about  $T_c$
- $\kappa$ -Br is very close to being a Mott insulator, whereas  $\kappa$ -NCS is at a higher “chemical pressure”
- This is reminiscent of what is seen in the underdoped cuprates



# d-wave superconductivity in $\kappa$ -Br and $\kappa$ -NCS

For a review see BJP and McKenzie, JPCM **18**, R827 (2006)

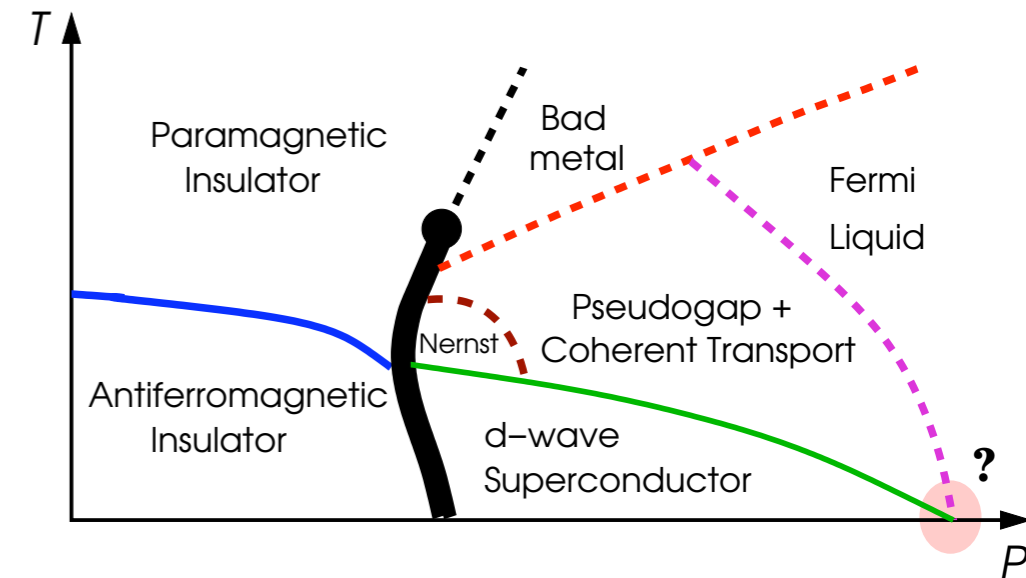
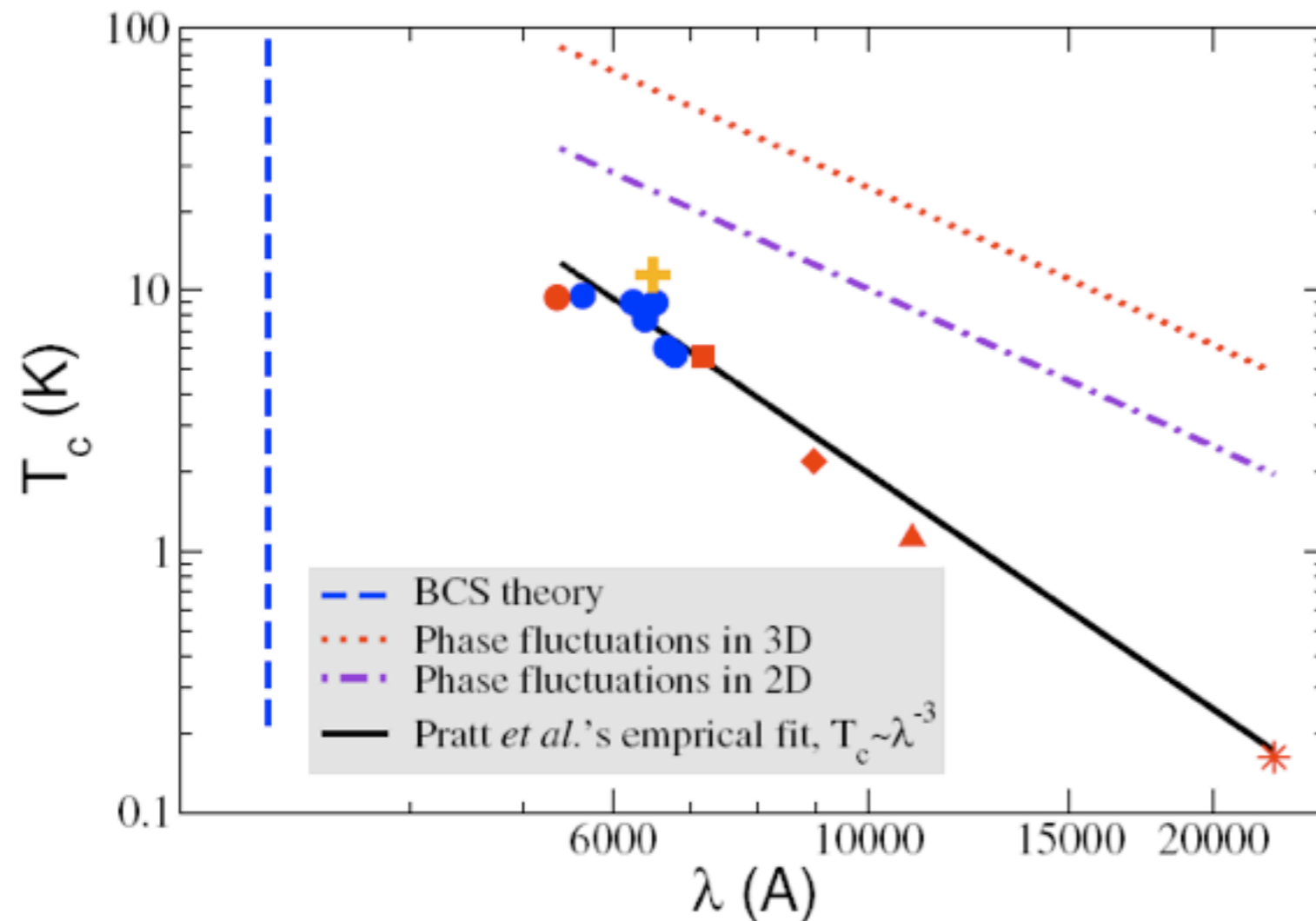
- There has been a long debate about the pairing symmetry
- My view is that the most likely answer is d-wave but others would still argue for s-wave (everyone agrees it is singlet)
- Disorder suppresses  $T_c$  [BJP & McKenzie, PRB 04] - but story is more complicated than it appeared at first sight [Analytis, BJP et al. PRL 06]
- Power laws in low temperature heat capacity [left: Taylor et al. PRL 07] and NMR [Kanoda et al. PRB 96]
- Absence of Hebel-Slichter peak in NMR





# Small superfluid stiffness

BJP & McKenzie, JPCM 16, 367 ('04)



$$D_s \propto \frac{1}{\lambda^2}$$

Data from Pratt et al., Polyhedron ('03), Lang et al. PRB ('92) and Larkin et al. PRB ('01) for a variety of organic superconductors (different shapes denote different anions). Also see Pratt & Blundell PRL ('05).

Note that the superfluid stiffness is smallest far from the Mott transition



# Gossamer-RVB and organics

BJP & McKenzie; Gan et al.; Liu et al. [all PRL '05]

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- First theory of organics to be able to study the competition between the superconducting and insulating phases
- We take a partially Gutzwiller projected BCS wavefunction – solve for the fraction of doubly occupied sites as a variational parameter simultaneously with the BCS variational problem.

$$|\text{Gossamer-RVB}\rangle = \prod_i (1 - \alpha \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}) |\text{BCS}\rangle$$

- cf. the “plain vanilla” RVB theory where

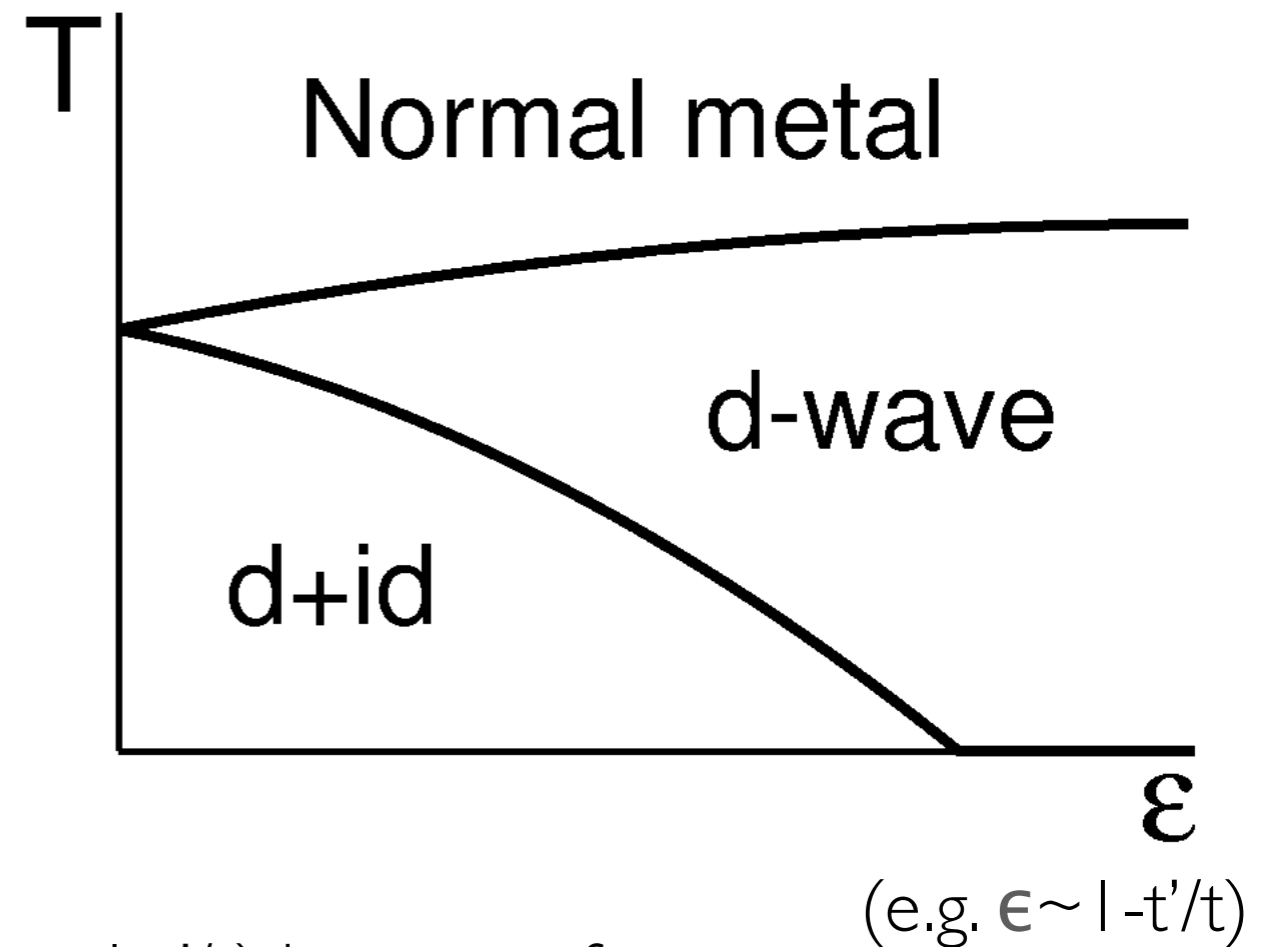
$$|\text{RVB}\rangle = \prod_i (1 - \hat{n}_{i\uparrow} \hat{n}_{i\downarrow}) |\text{BCS}\rangle$$

- In qualitative agreement with many experiments [BJP & McKenzie, PRL '05] and CDMFT [Kyung & Tremblay, PRL '06], variational cluster perturbation theory calculations [Sahebsara & D. Sénéchal, PRL '06] and VMC [Watanabe et al. JPSJ '06]
- But does not explain the vanishing superfluid stiffness at high pressures (yet)

# Double superconducting phase transition

BJP, JPCM **18**, L575 (2006)

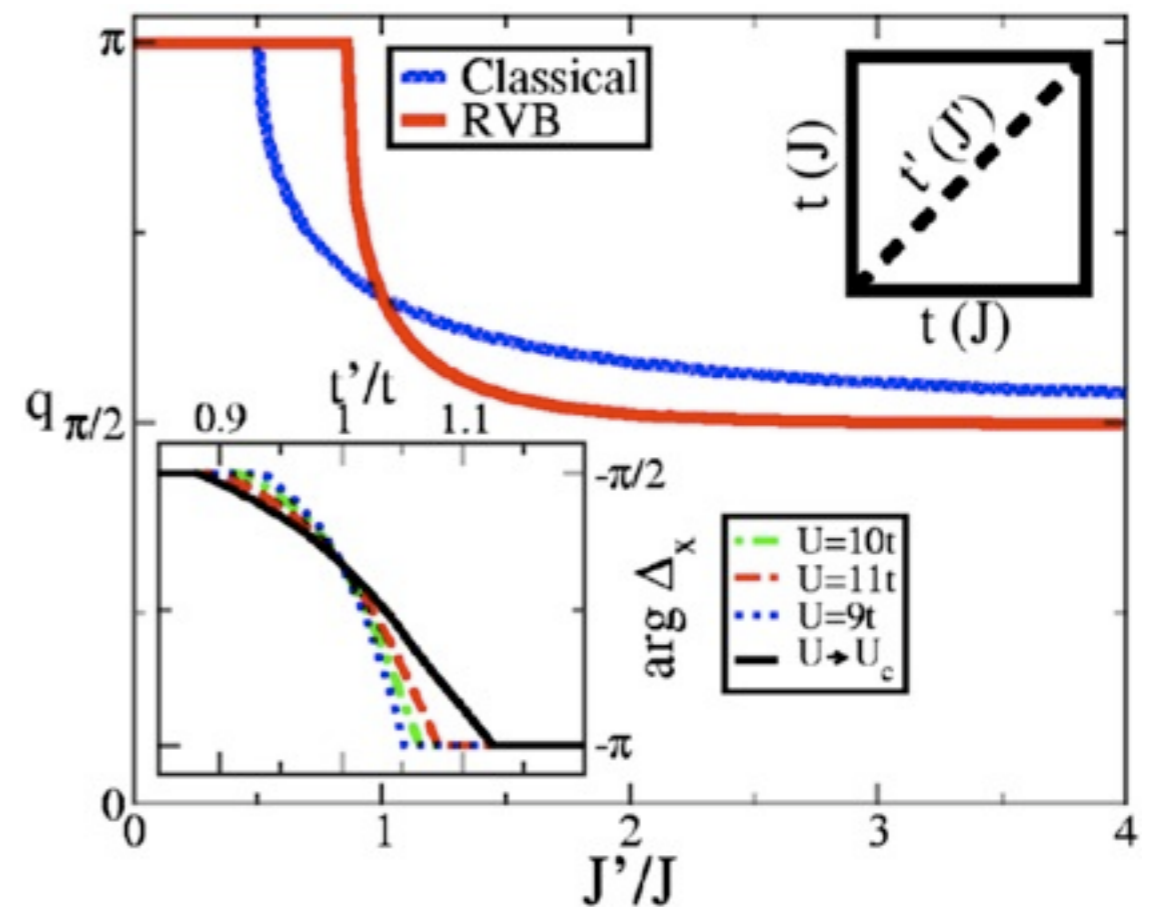
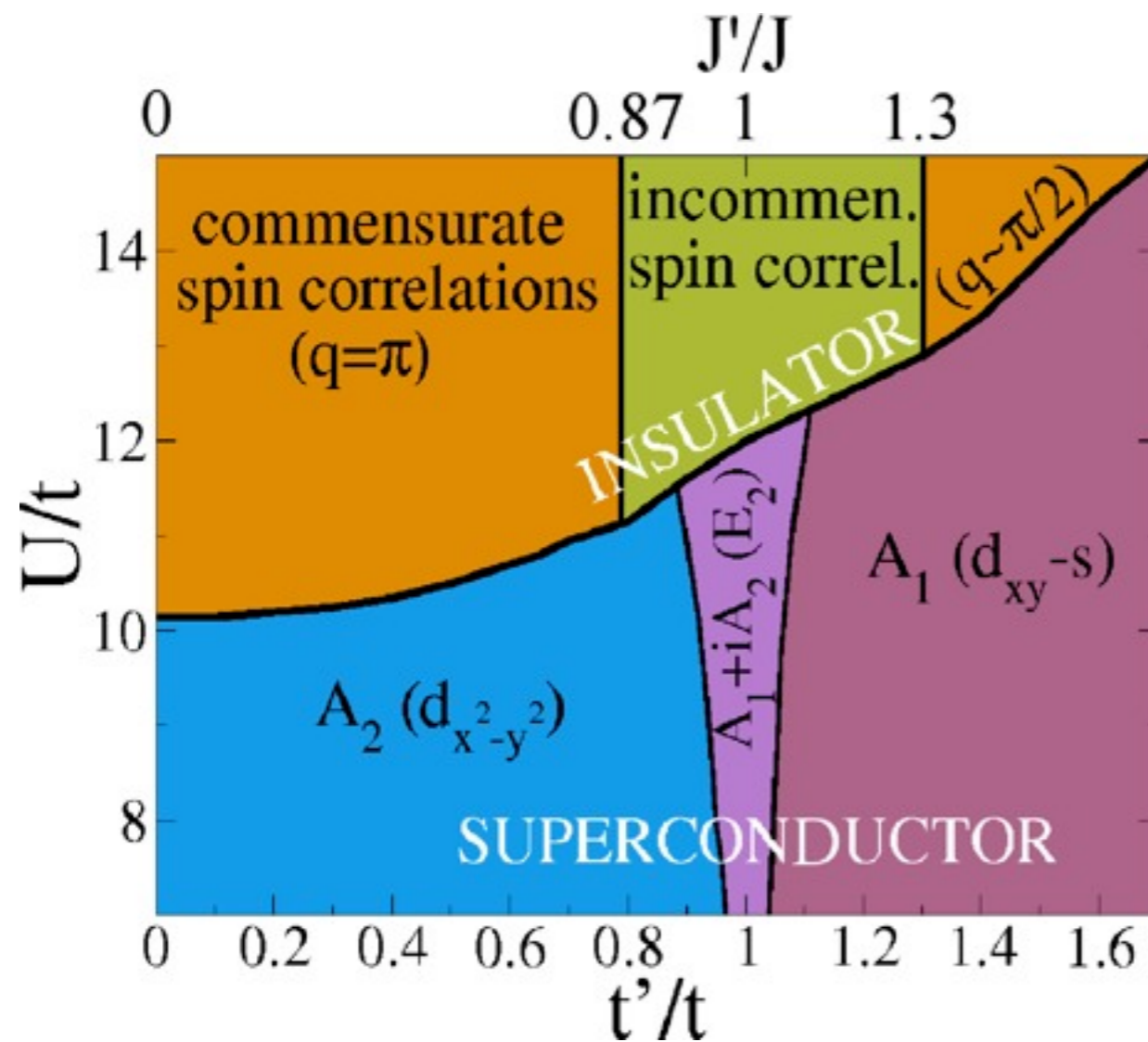
- On the isotropic triangular lattice a group theoretical analysis suggests that it is natural for  $d_{x^2-y^2}+id_{xy}$  superconductivity to be realised.
- This occurs because they transform according to the different bases of a 2d irrep.
- But as we break the symmetry we regain either  $d_{x^2-y^2}$  or  $d_{xy}$  superconductivity
- $\epsilon$  is a symmetry breaking parameter (e.g.  $\epsilon \sim |t'/t|$ ) because of the low crystal symmetry we always have  $\epsilon \neq 0$ .
- $\beta'$ - $PnMe_{4-n}Et_n[Pd(dmit)_2]_2$  seem a particularly promising class of systems to look for this double transition in.



# Broken time reversal symmetry

BJP & McKenzie, PRL **98**, 027005 (2007)

- As the spin correlations change this drives changes in the superconducting state.
- The  $d+id$  state breaks time reversal symmetry.
- This could be directly detected in, for example, muon spin relaxation experiments.

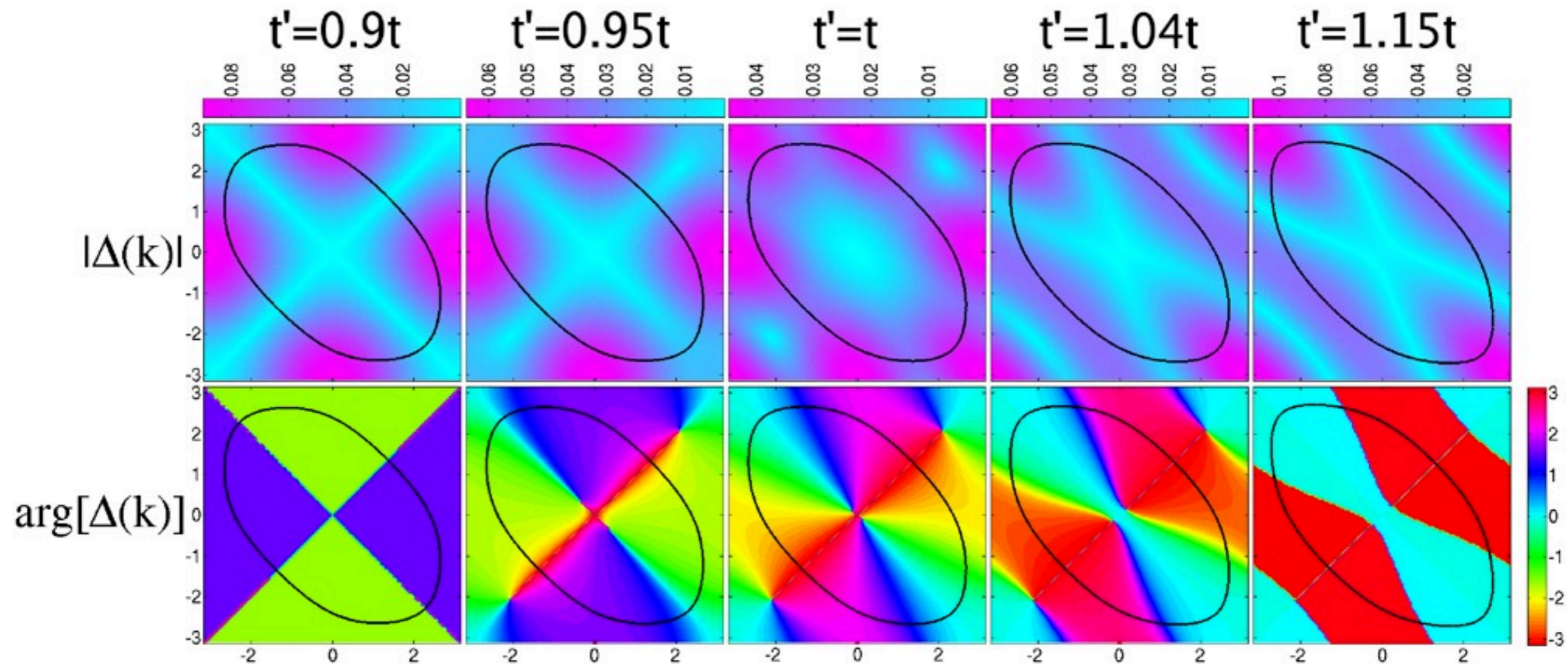




# What is the structure of the order parameter?

BJP & McKenzie, PRL **98**, 027005 (2007)

- The  $d+id$  state breaks time reversal symmetry.
- This could be directly detected in, for example, muon spin relaxation experiments.



# Parameterisation of Hubbard models: band-structure

Nakamura et al., JPSJ '09; Kandpal et al., PRL '09

- Most band structure calculations for BEDT-TTF and Pd(dmit)<sub>2</sub> salts have historically been based on the Huckel approximation (a parameterised tight-binding method)
- More recent DFT calculations seem to confirm one's fears that these are not accurate
- For example for  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(CN)<sub>3</sub> Huckel gives  $t'/t \sim 1$ , i.e. an (nearly) isotropic triangular lattice - but the triangular lattice Heisenberg model has 120° order (ring exchange [Motrunich PRB '05, '06]?)



Phase diagram of the Heisenberg model on an anisotropic triangular lattice after Weihong *et al.*, PRB 59, 14367 (1999).

- But two recent tight-binding parameterisations of DFT band-structures [Nakamura *et al.*, JPSJ '09; Kandpal *et al.*, PRL '09] find that  $t'/t=0.8$  for  $\kappa$ -(BEDT-TTF)<sub>2</sub>Cu(CN)<sub>3</sub>
- Does this resolve the conflict with the 120°-state?
- But, high-T series expansions for the isotropic triangular lattice Heisenberg model seem to fit well with the magnetic susceptibility data [Zheng *et al.* PRB '05]



# Parameterisation of Hubbard models: Hubbard $U$

Scriven & BJP, JCP **130**, 105408 ('09); PRB **80**, 205107 (2009).

$$U_d = E_d(0) + E_d(+2) - 2E_d(+1)$$

where  $E_d(q)$  is the energy of a (BEDT-TTF)<sub>2</sub> dimer of charge  $q$

- Previous approach has been to treat that dimer as a two site Hubbard model, where each site is a monomer

$$\mathcal{H} = t_m \sum_{\sigma} \hat{c}_{1\sigma}^{\dagger} \hat{c}_{2\sigma} + \text{h.c.} + U_m \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} + V_m \hat{n}_1 \hat{n}_2$$

- For  $V_m=0$  and  $U_m \gg t_m$  one finds that  $U_d = |2t_m|$  - therefore  $U_d = 0.2-2$  eV (variation both between groups and between materials) estimated from Huckel calculations
- DFT calculations of  $E_d(q)$  give  **$U_d = 3.2$  eV** - for a wide range of  $\kappa$  and  $\beta$  phase BEDT-TTF salts
- Further we find that  $U_m \sim V_m \gg t_m$ , which leads to  $U_d = \frac{1}{2}(U_m + V_m) \gg |2t_m|$
- Thus we expect a  $U_d$  to be reduced by the polarisability of the crystalline environment, hence

$$U_d^{\text{eff}} = U_d - \delta U_d$$

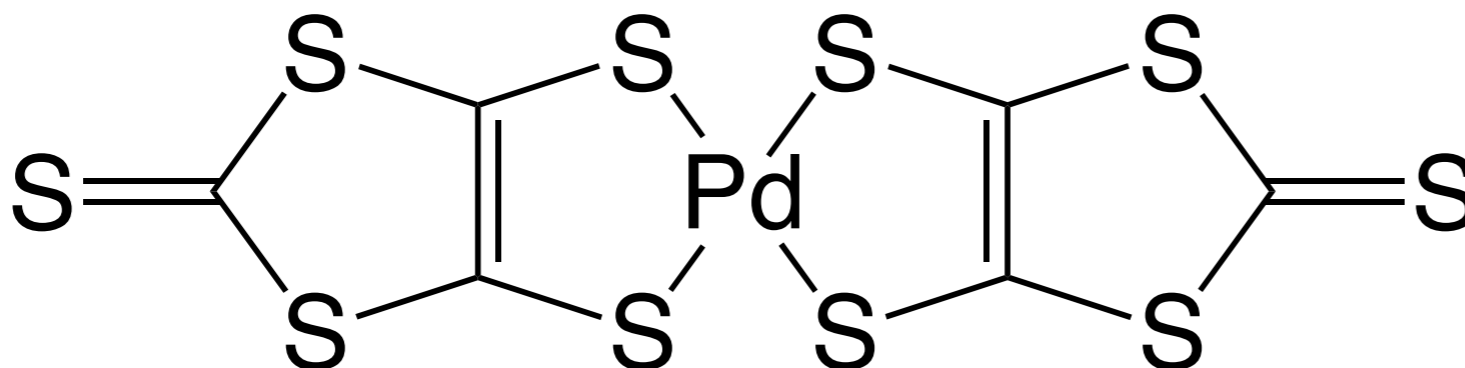
- $\delta U$  calculated in other molecular crystals ( $A_3C_{60}$ , TTF-TCNQ, oligoacene, thiopenes, etc.), but it is complicated in the BEDT-TTF salts by the polymeric anions, geometry, etc. [Merino et al.]
- However,  $\delta U_d$  may well be quite sensitive to hydrostatic and chemical pressure, and may, therefore, be important for properly explaining the pressure dependence of these materials
- $U_d^{\text{eff}} = 0.8$  eV** from DFT + constrained-RPA [Nakamura et al., JPSJ '09]
- $U_d^{\text{eff}} = 0.3$  eV** from comparison of DFMT to optical conductivity [Merino et al., PRL '08]

# $\beta'$ -Z[Pd(dmit)<sub>2</sub>]

Review: BJP & McKenzie - in preparation



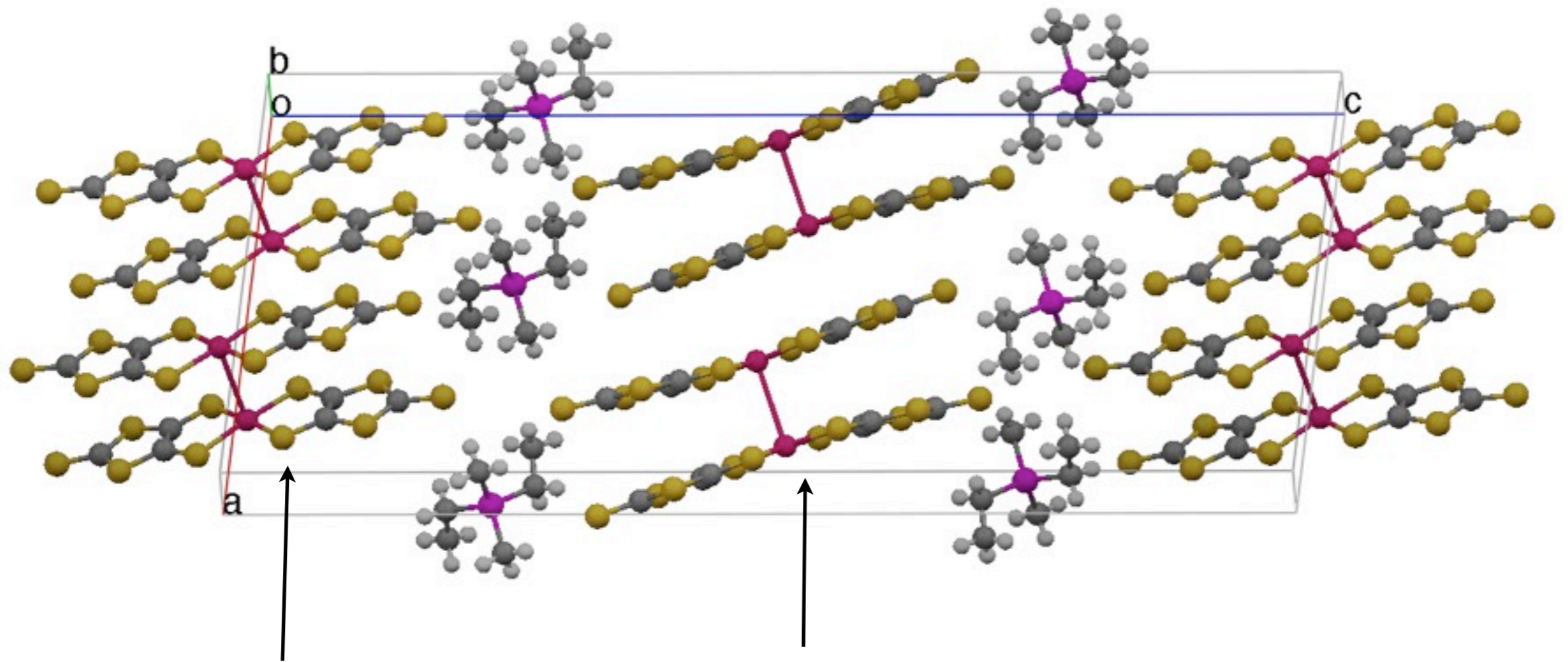
Reizo Kato



- dmit = 1,3-dithiol-2-thione-4,5-dithiolate
- Pd(dmit)<sub>2</sub> is a member of a larger class of molecules  $M(\text{dmit})_2$ , where  $M$  is a transition metal
- Another interesting molecule is Ni(dmit)<sub>2</sub>, which forms a similar set of charge transfer salts.
  - The Ni salts seem to be quite one-dimensional, but I will not discuss them much today

28 Ni 58.69
46 Pd 106.42
78 Pt 195.08

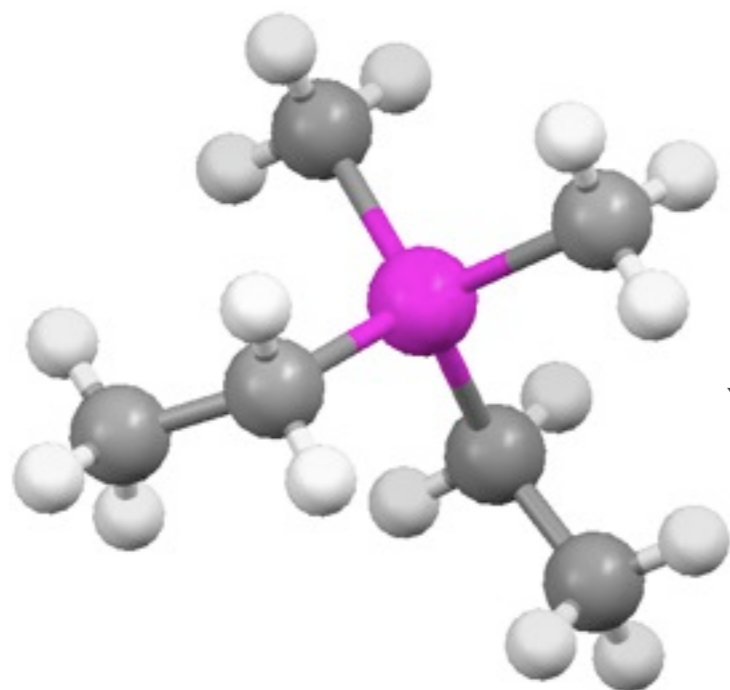
# Structure of $\beta'$ -Et<sub>2</sub>Me<sub>2</sub>As[Pd(dmit)<sub>2</sub>]<sub>2</sub>



In alternating layers the dimers stack along different directions ( $a+b$  and  $a-b$ ) this is known as the “solid crossing” structure

# Cations

- We will focus on cations of the form  $\text{Et}_n\text{Me}_{(4-n)}\text{V}$ , where  $\text{V}$  is a pnictogen (group V element) and  $n$  is an integer.
- We will introduce a shorthand notation to  $\text{V}-n$  to represent  $\beta'$ - $\text{Et}_n\text{Me}_{(4-n)}\text{V}[\text{Pd}(\text{dmit})_2]_2$ .
  - e.g.,  $\text{As}-3 = \text{Et}_3\text{MeAs}[\text{Pd}(\text{dmit})_2]_2$
- The pnictogen has to give up one electron in order to form the four bonds - this bond is donated to

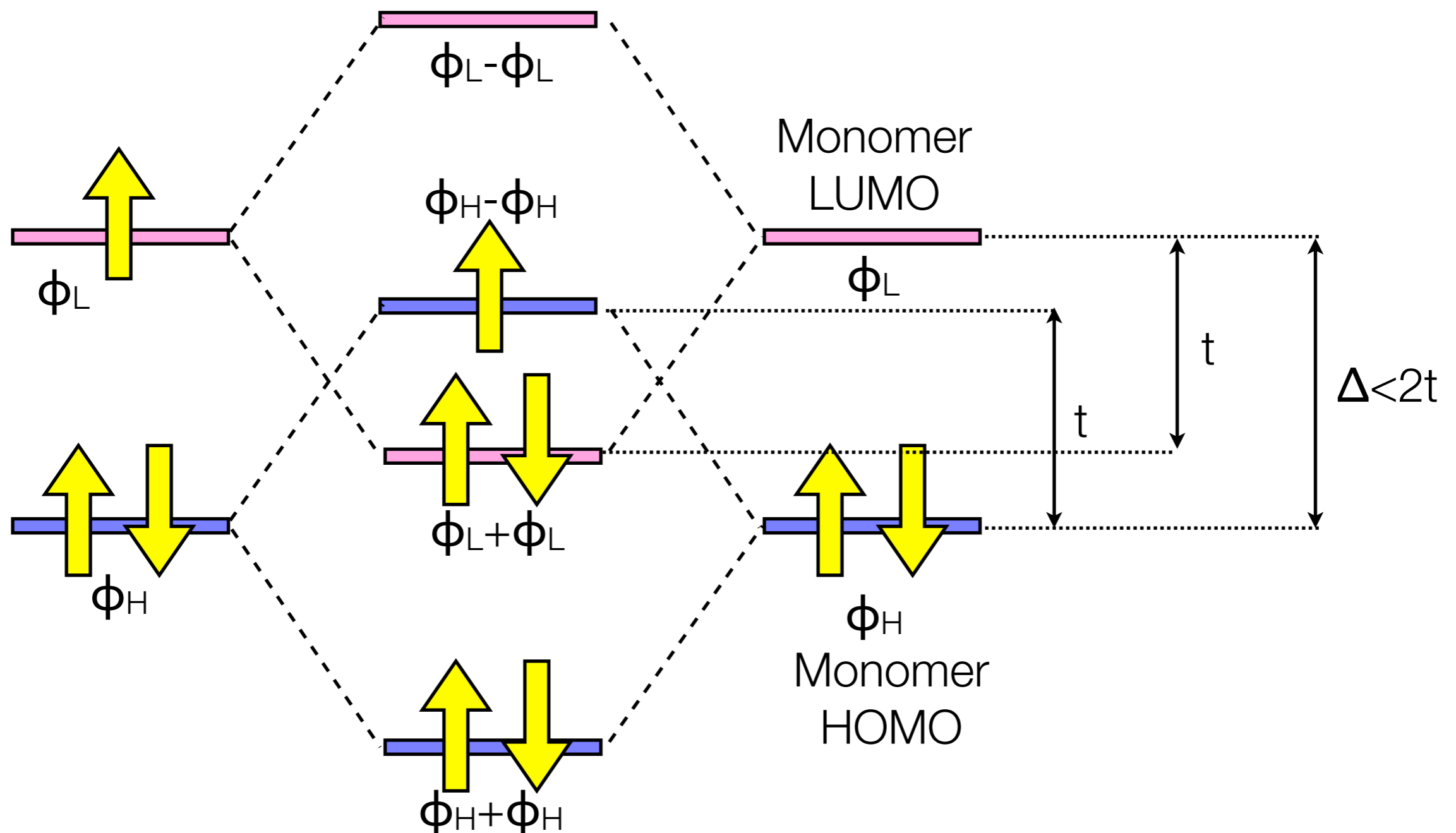


$\text{Et}_2\text{Me}_2\text{As}$  - the cation in  $\text{As}-2$

7	N	14.01
15	P	30.97
33	As	74.92
51	Sb	121.75
83	Bi	208.98

# (Non-interacting) electronic structure of the $[\text{Pd}(\text{dmit})_2]_2^-$ dimer

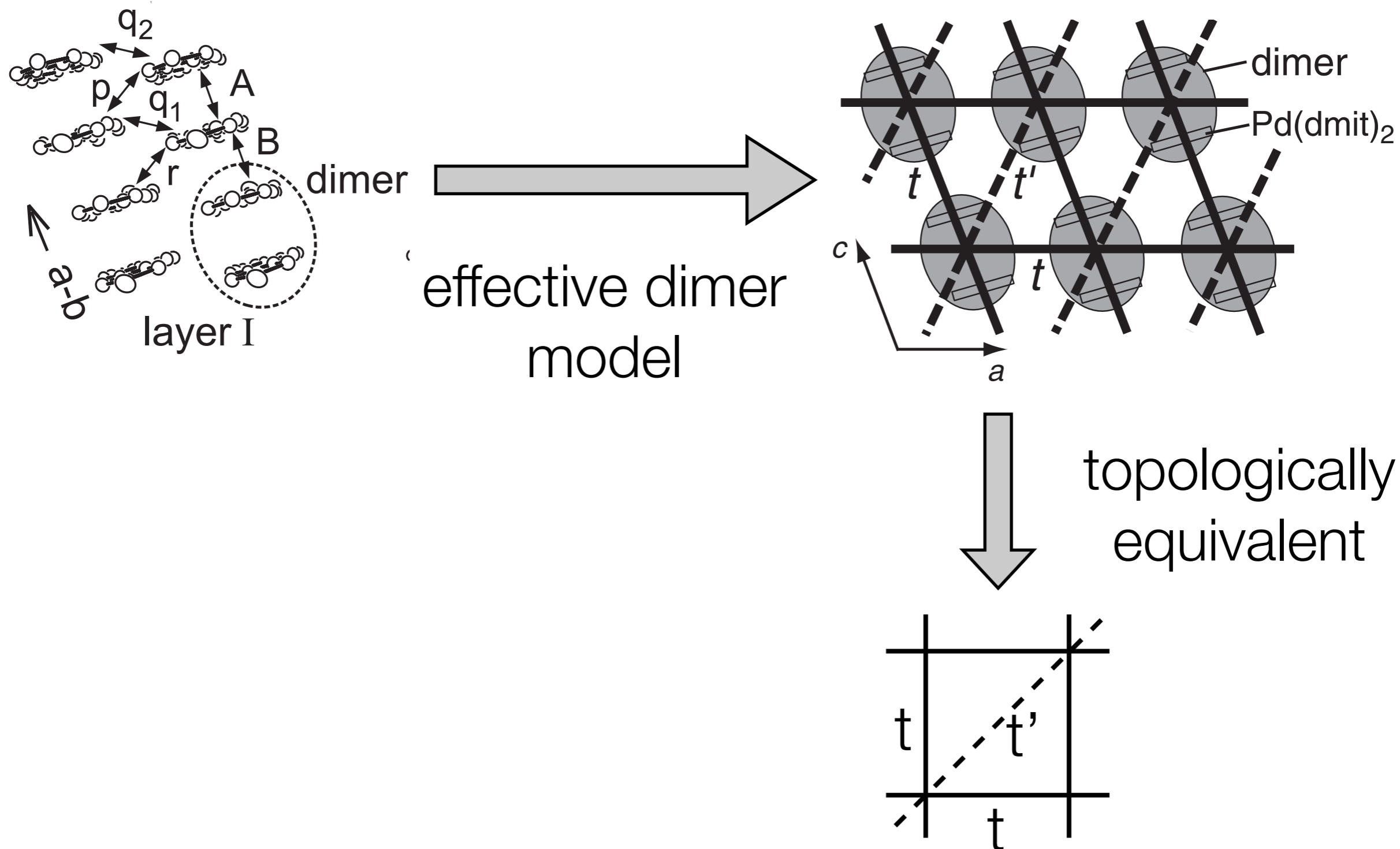
- Picture from Huckel (confirmed by DFT [Miyazaki & Ohno, PRB '99])
- The HOMO-LUMO splitting,  $\Delta < 2t$  (or, more accurately,  $t_H + t_L$ )





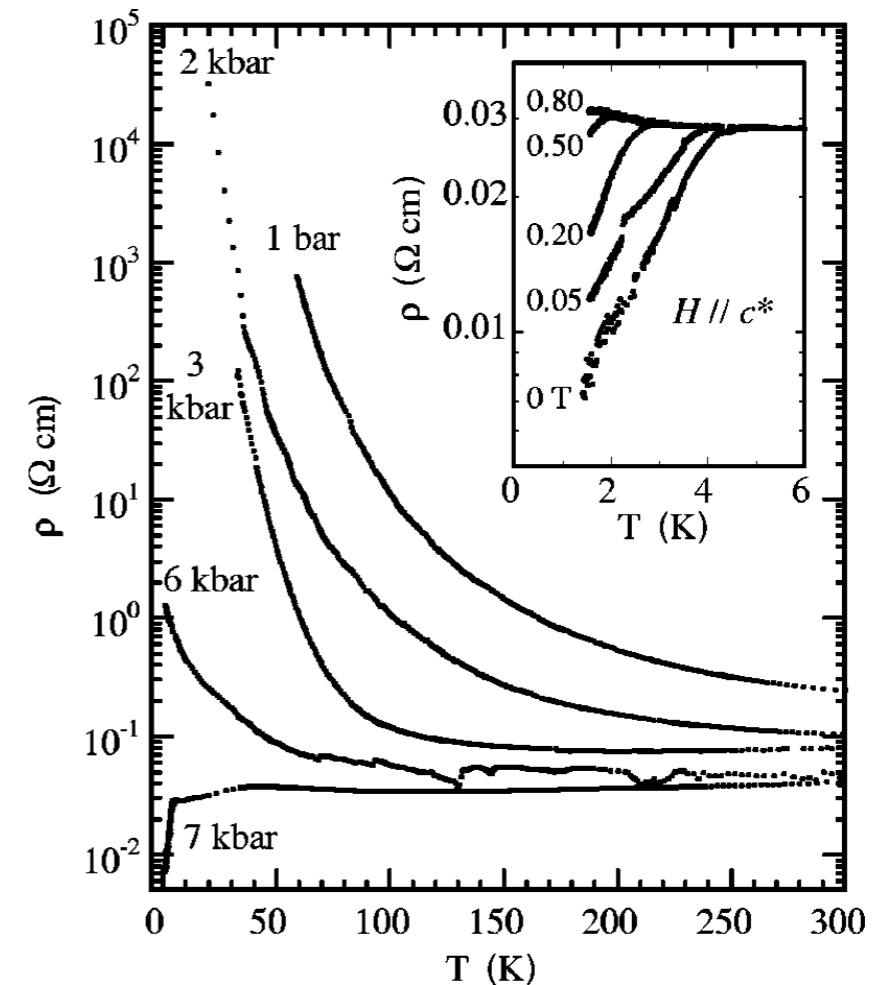
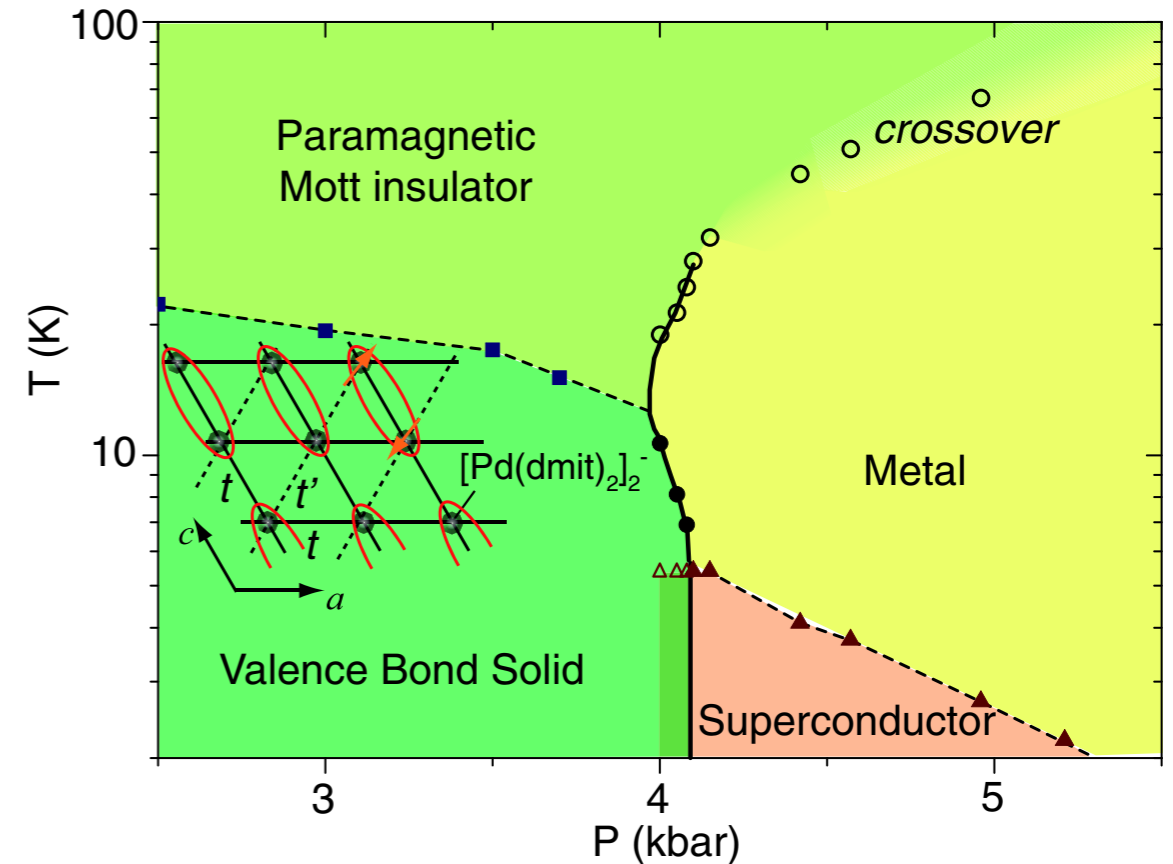
# Band structure (extended Huckel-tight binding)

Miyazaki & Ohno, PRB **59**, R5269 (1999)



# Metal-insulator transition

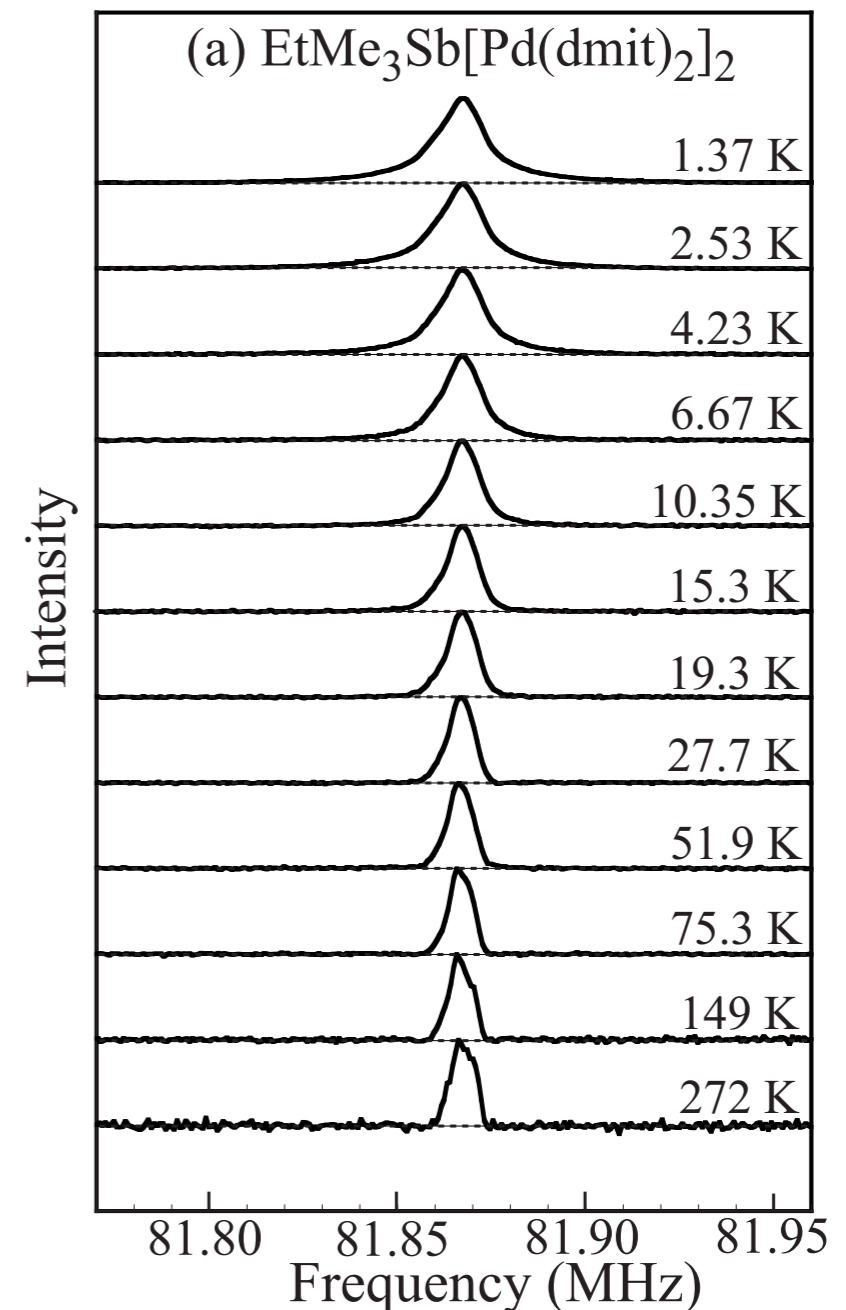
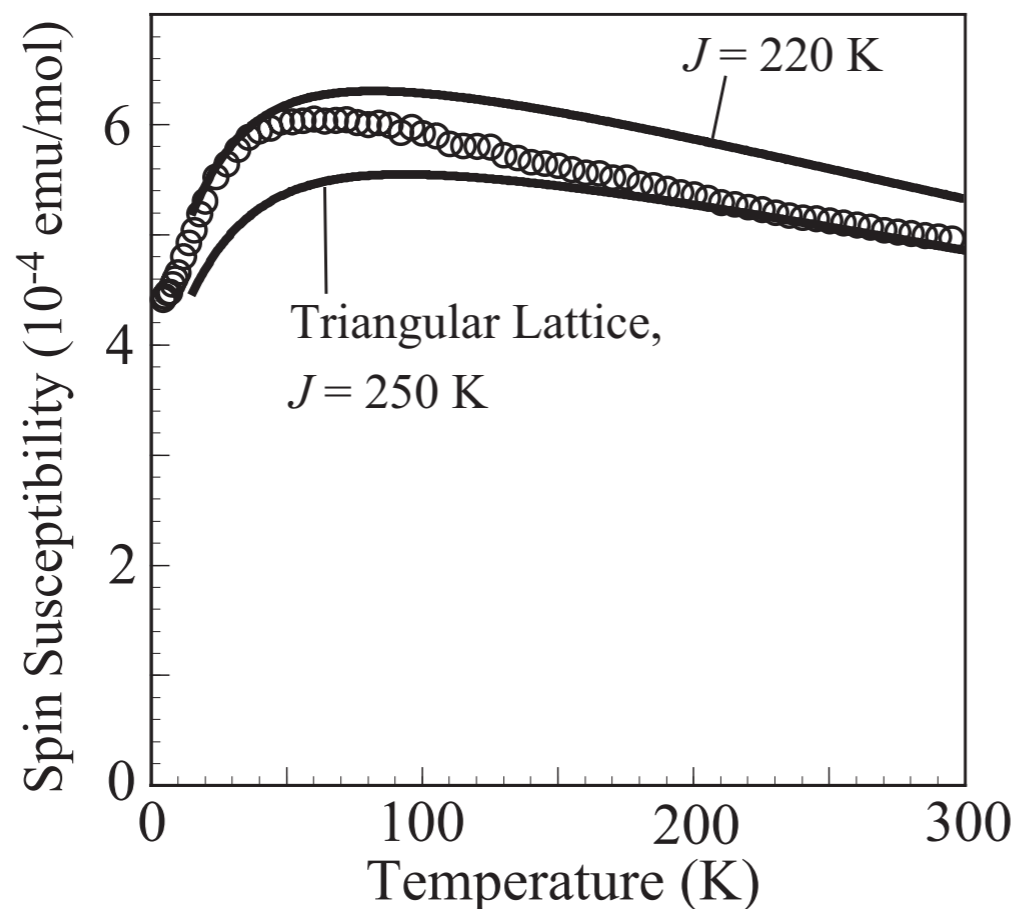
- Note that both of the DFT and the Huckel calculations predict that the  $Z^+$   $[\text{Pd}(\text{dmit})_2]_2^-$  salts are metals - as they have half filled bands
- Experimentally they are insulators
- This suggests that they are Mott insulators
- A Mott metal insulator transition can be driven in *some materials* by hydrostatic pressure [Shimizu et al. PRL 07; P-1, upper Fig.] or uniaxial stress [e.g. Kato et al. PRB '02; As-0; lower Fig.] (but not by chemical pressure)



# Spin liquid in Sb-1

Itou et al., PRB 77, 104413 (2008)

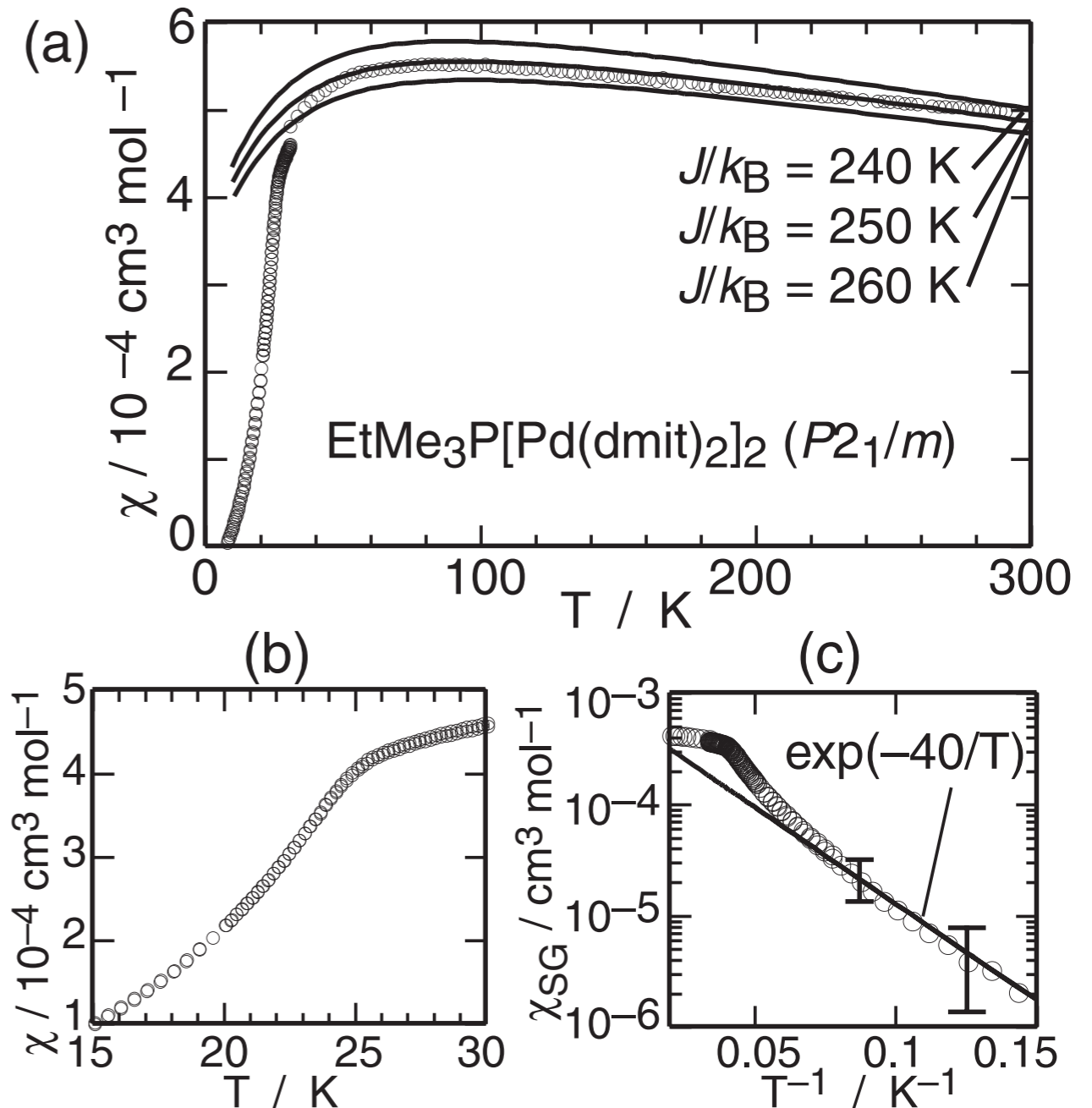
- No magnetic phase transition observed down to the lowest temperature studied
- $J \sim 240$  K from fits to high temperature series expansions
- Very reminiscent of  $\kappa\text{-CN}_3$



# Valence bond solid in P-1?

Tamura et al. JPSJ 75, 093701 (2006)

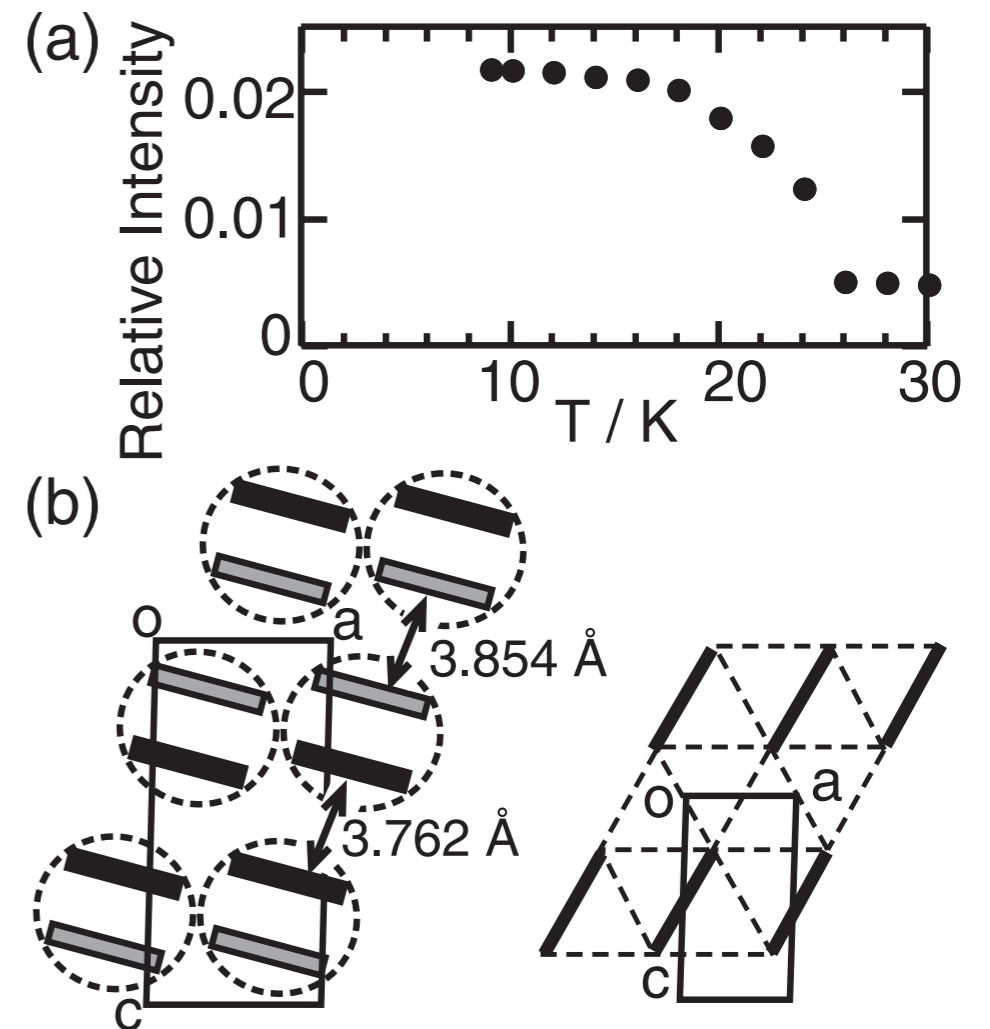
- Sudden drop in the magnetic susceptibility,  $\chi$ , at 25 K.
- The transition is hysteric (first order)
- Below the transition there susceptibility displays an Arrhenius behaviour (i.e., a gap opens between the ground state and the lowest lying triplet excitation - there is no such gap in the high temperature phase)
- The VBS phase has a gap between the ground state and the lowest lying triplet excitation



# Valence bond solid in P-1?

Tamura et al. JPSJ 75, 093701 (2006)

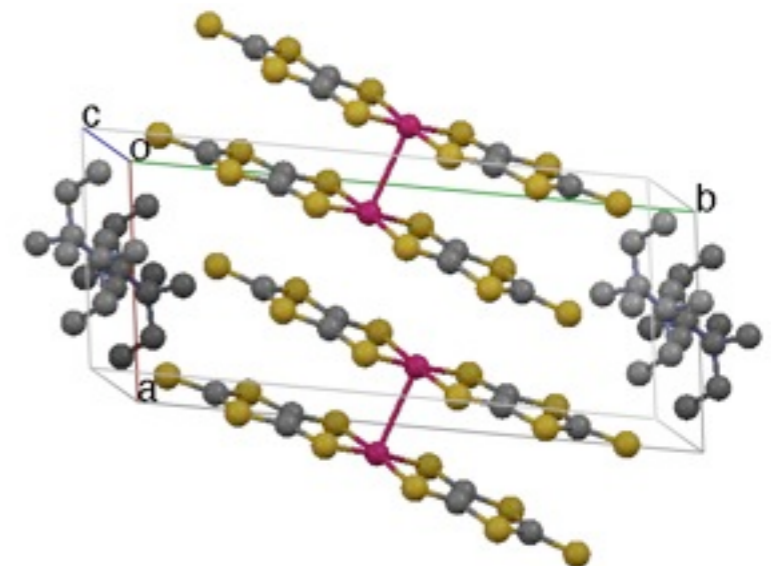
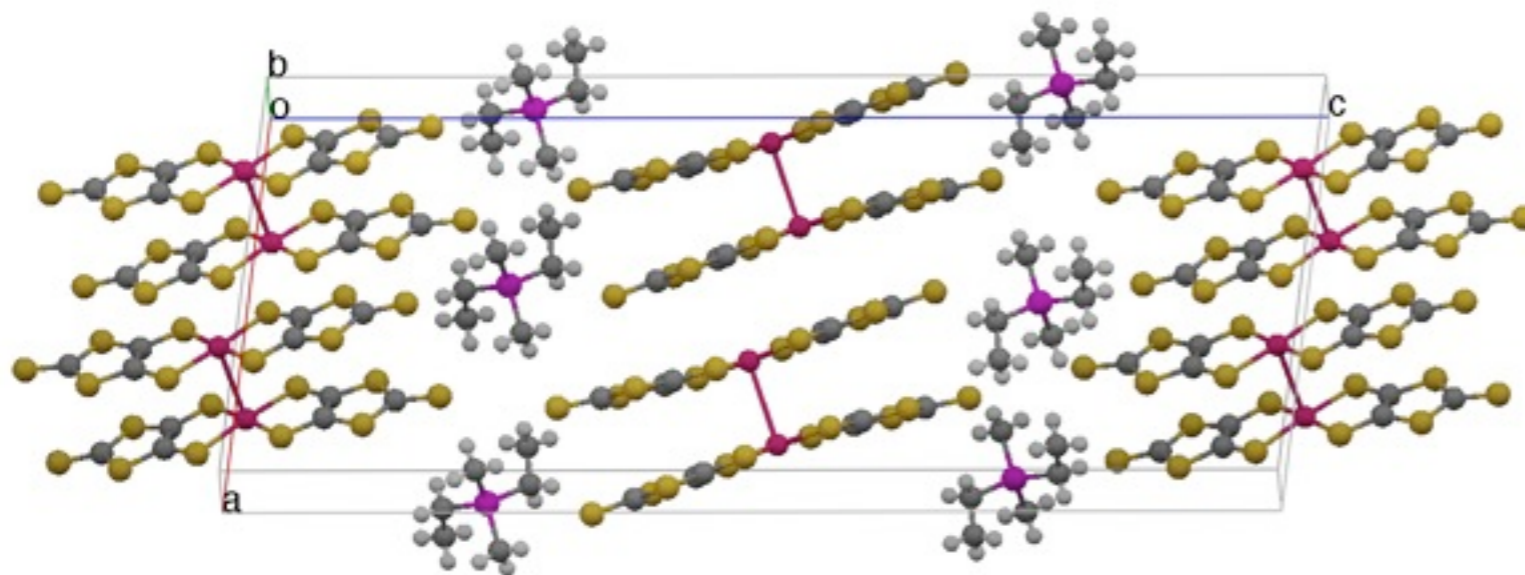
- Satellite reflections are also seen in the x-ray diffraction pattern below 25 K
- These correspond to a loss of periodicity in the crystal
- In the low temperature phase the distances between (the planes of S atoms neighbouring the Pd atom in) neighbouring dimers is either 3.85 or 3.76 Å, whereas in the high temperature phase the all dimers are separated by 3.82 Å
- This is what one would expect in the VBS phase as the spin-phonon coupling would favour exactly this type of disorder in the VBS phase





# What is special about P-1?

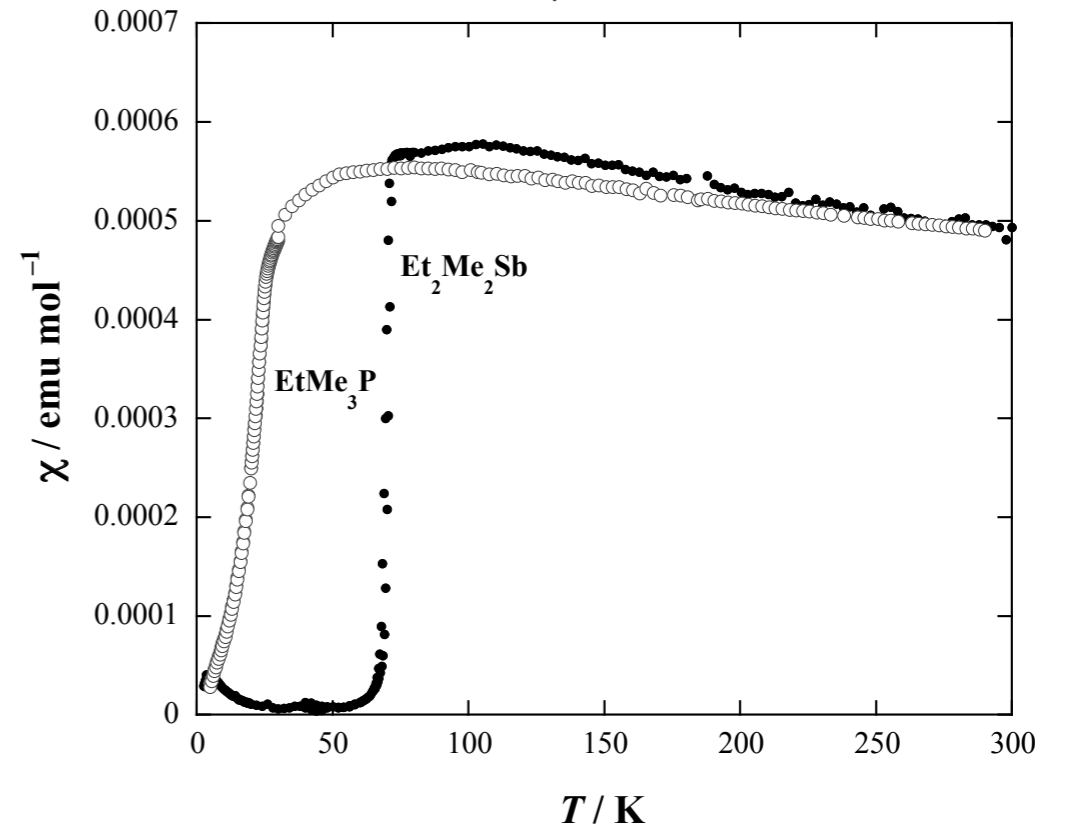
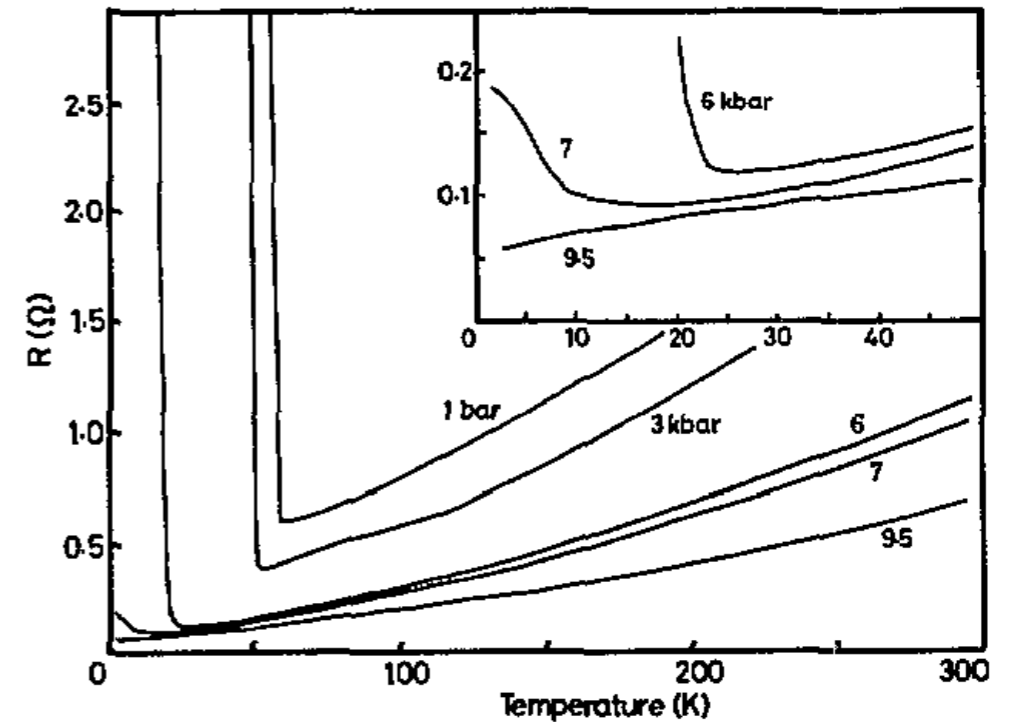
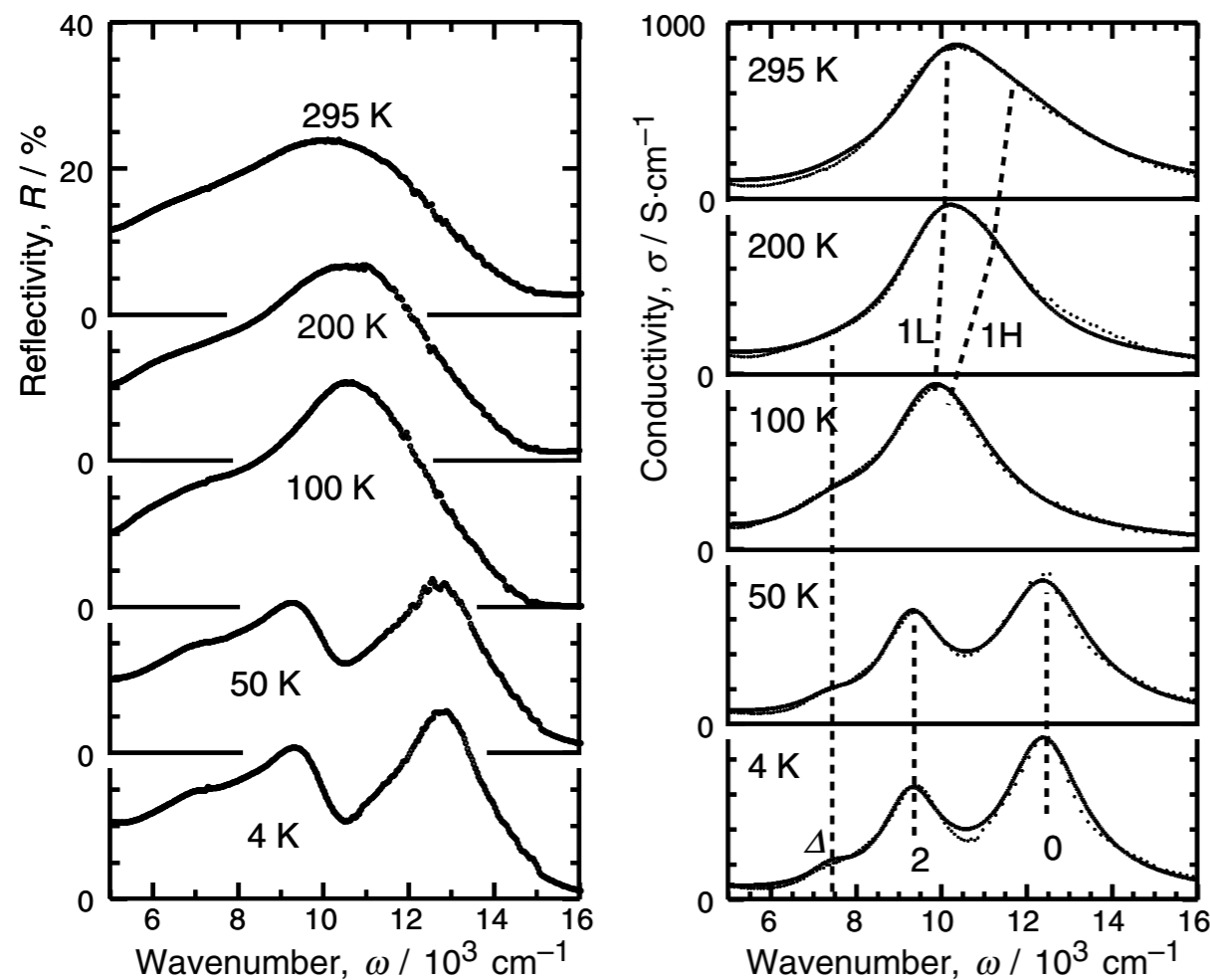
- None of the other  $V-n$  salts show a VBS phase so we would like to understand what is special about P-1.
- P-1 has a  $P2_1/m$  crystal whereas most of the others have a  $C2/c$  crystals
- The loss of the glide plane ( $\dots/m$  instead of  $\dots/c$ ) in P-1 corresponds to absence of the “solid crossing” crystal packing (shown, right)
- In P-1 all the organic layers are equivalent
- Tamura *et al.* argued that the in the  $C2/c$  crystals the lattice distortion in different layers would be in different directions, and so would cause a large strain making the VBS phase unfavourable



# Charge ordered insulator in Sb-2 and Cs-00?

Tamura et al. CPL **411**, 133 (2005)

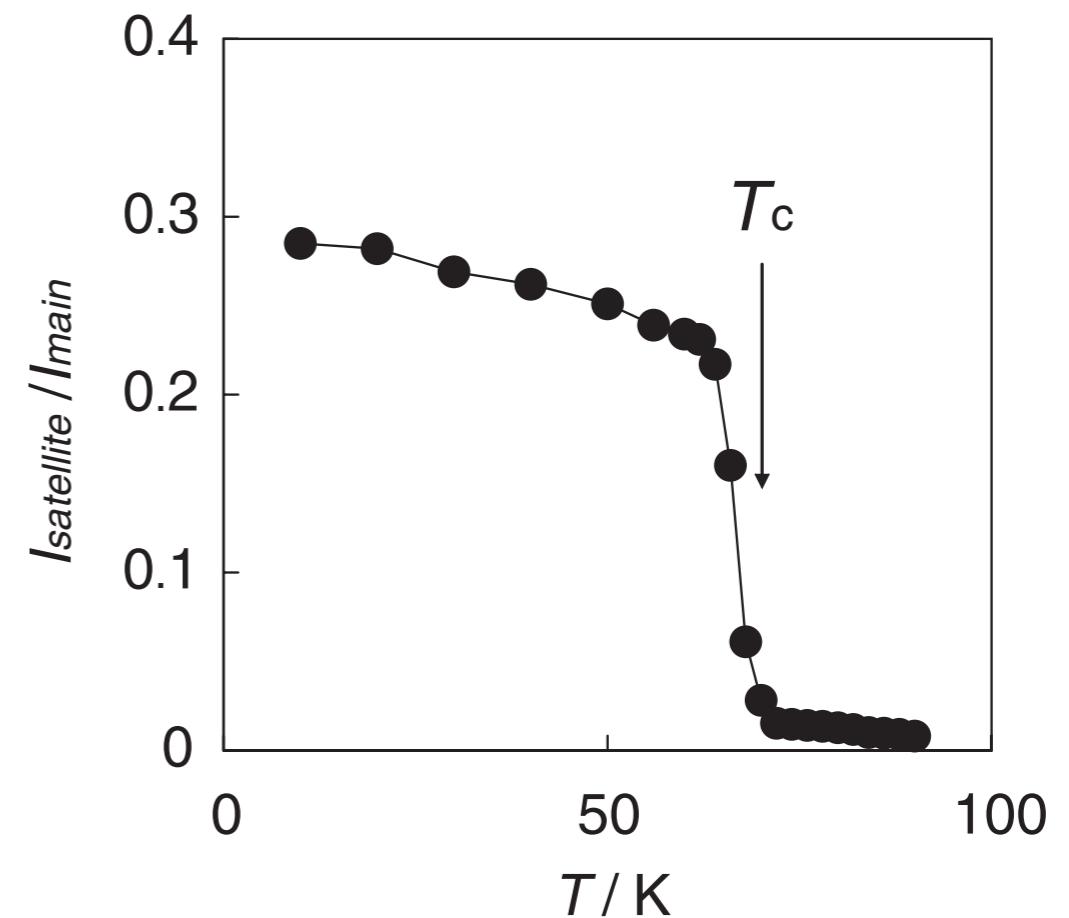
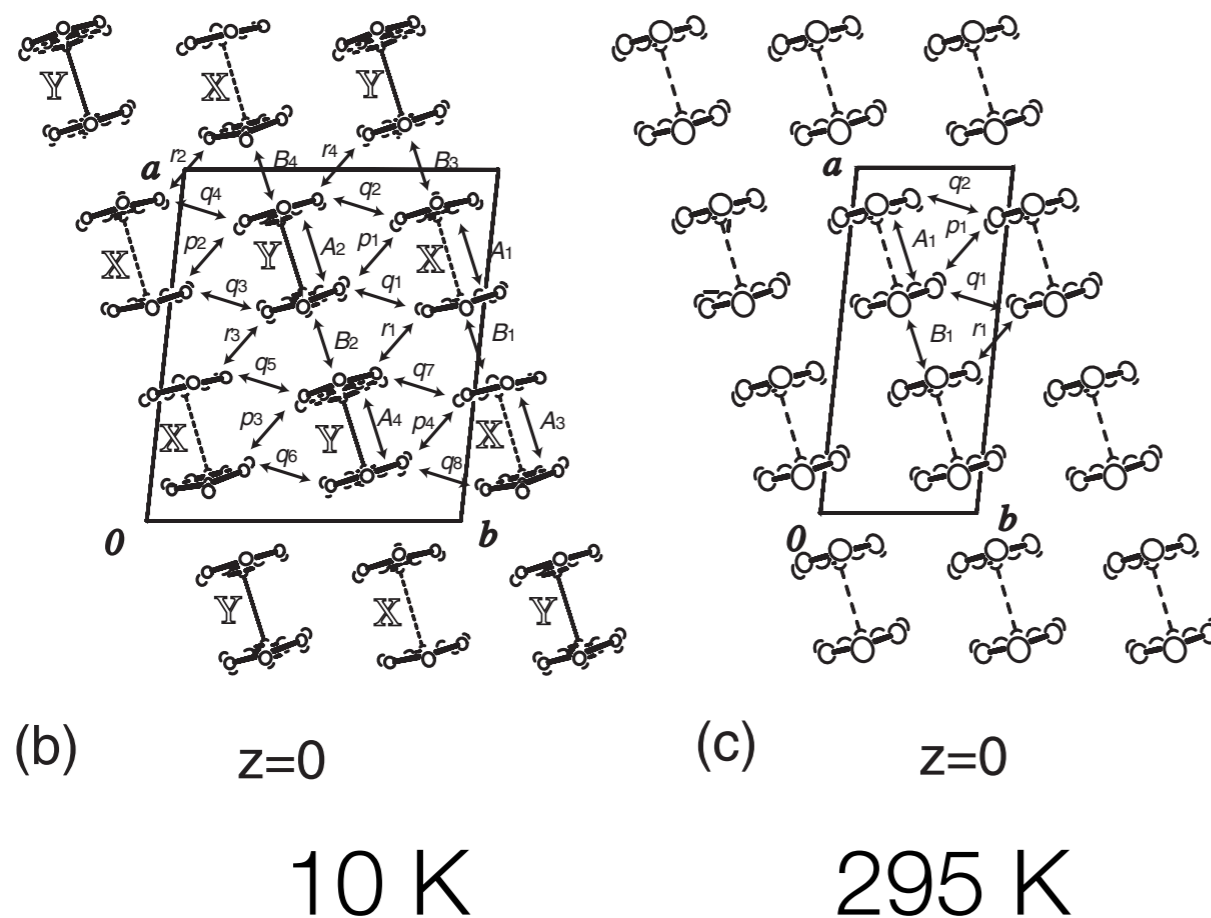
- P-2 and Cs-00 show very similar phase transitions are 70 & 65 K respectively
- The susceptibility vanishes rapidly in both materials, suggest all the spins pair up
- Cs-00 undergoes a metal-insulator transition at the same temperature (I am not aware of equivalent data for Sb-2)



# Structural phase transition in Sb-2 and Cs-00?

Nakao & Kato, JPSJ **74**, 2754 (2005)

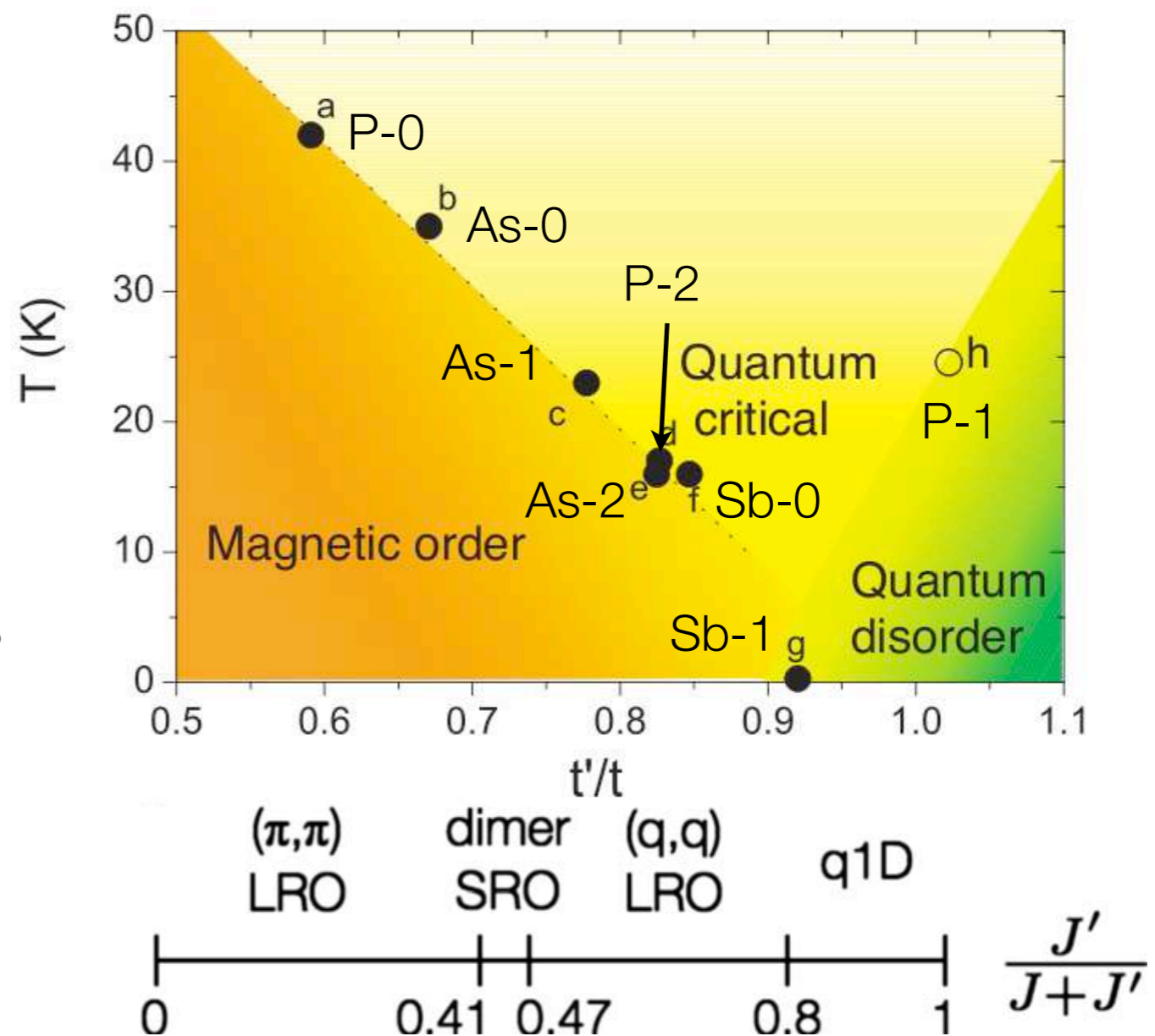
- Nakao *et al.* [JPSJ **74**, 2754 (2005)] found that this phase transition is associated with a crystallographic phase transition  $C2/c \rightarrow P2_1/m$
- This basically corresponds to a doubling of the unit cell
- The phase transition appears to be first order



# Phase diagram

Shimizu *et al.* JPCM **19** 145240 (2007)

- Shimizu *et al.* [JPCM '07] have argued that controlling the frustration drives the system into the spin liquid state
- However their phase diagram does not match what is known theoretically about the model
- Their  $t$  values come from Huckel - is this the problem?
- It is known the Huckel overestimates  $t'/t$  in the BEDT-TTF salts
- Another trend in the data is that systems near the Mott transition have lower  $T_{NS}$  (i.e., become antiferromagnetic at lower temperatures)
- A simple trend is that salts with larger cations have lower  $T_{NS}$



7	N	14.01
15	P	30.97
33	As	74.92
51	Sb	121.75
83	Bi	208.98

Weihong *et al.*, PRB **59**, 14367 (1999).

# Superconductivity

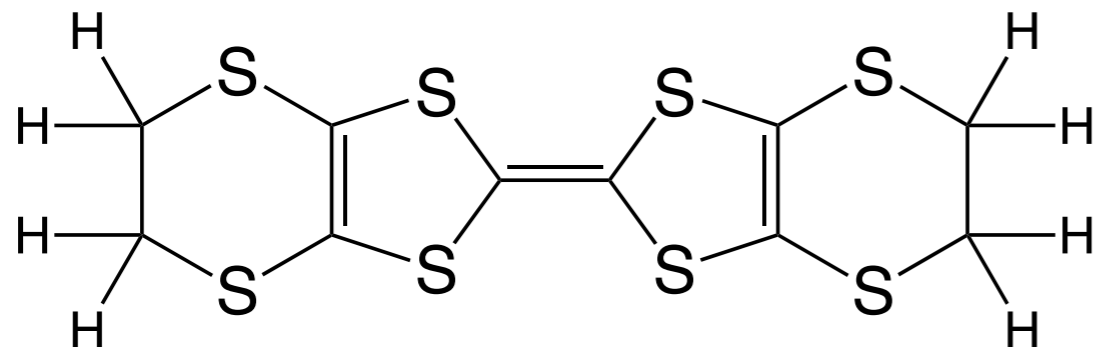
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- Very little is known about the superconducting state.
- Zero resistance has been observed under pressure or uniaxial stress in several  $\text{Pd}(\text{dmit})_2$  salts - this tells us that they superconduct, but not much more ( $T_c$  is typically a few K)
- The Meisner state has been observed in P-1 [Ishii *et al.*, JPSJ '07], which confirms that it's bulk superconductivity
- As far as I'm aware we don't know any more about the superconducting state

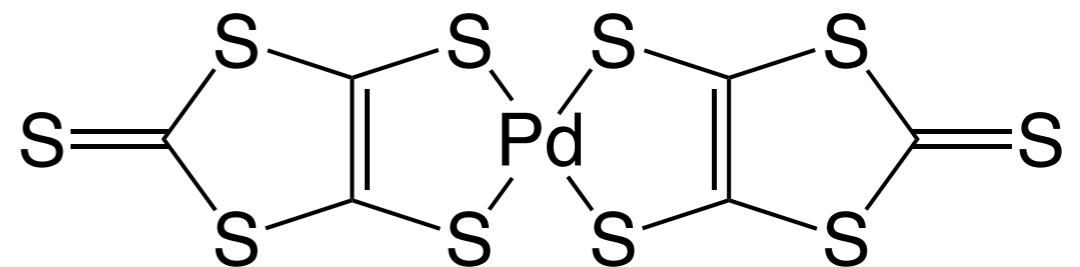
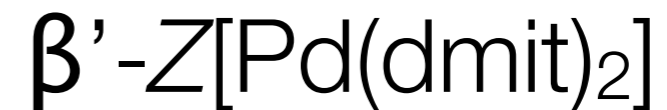


# Overview

For a review see BJP and McKenzie, JPCM **18**, R827 (2006)



- Structure and phase diagram
- Model Hamiltonian
- Metal-insulator transition
- Spin liquid
- Strongly correlated metal
- Nernst effect
- Superconductivity
- Parameters for the model Hamiltonian



- Structure and phase diagram
- Model Hamiltonian
- Metal-insulator transition
- Spin liquid
- Valence bond solid
- Charge ordered insulator
- Superconductivity
- **White space for theorists!**