Mott criticality studied by dilatometry under ^{4}He-gas pressure on the quasi-2D organic charge-transfer salts κ-(BEDT-TTF)$_2$X

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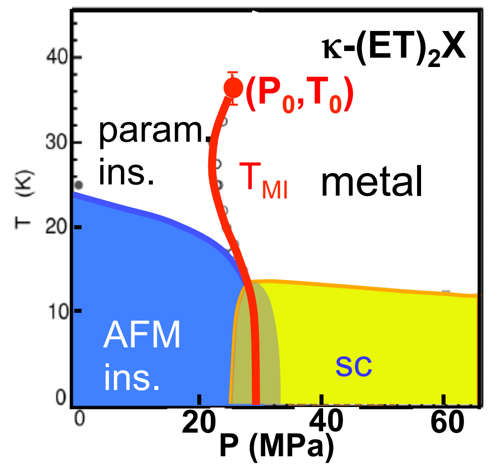

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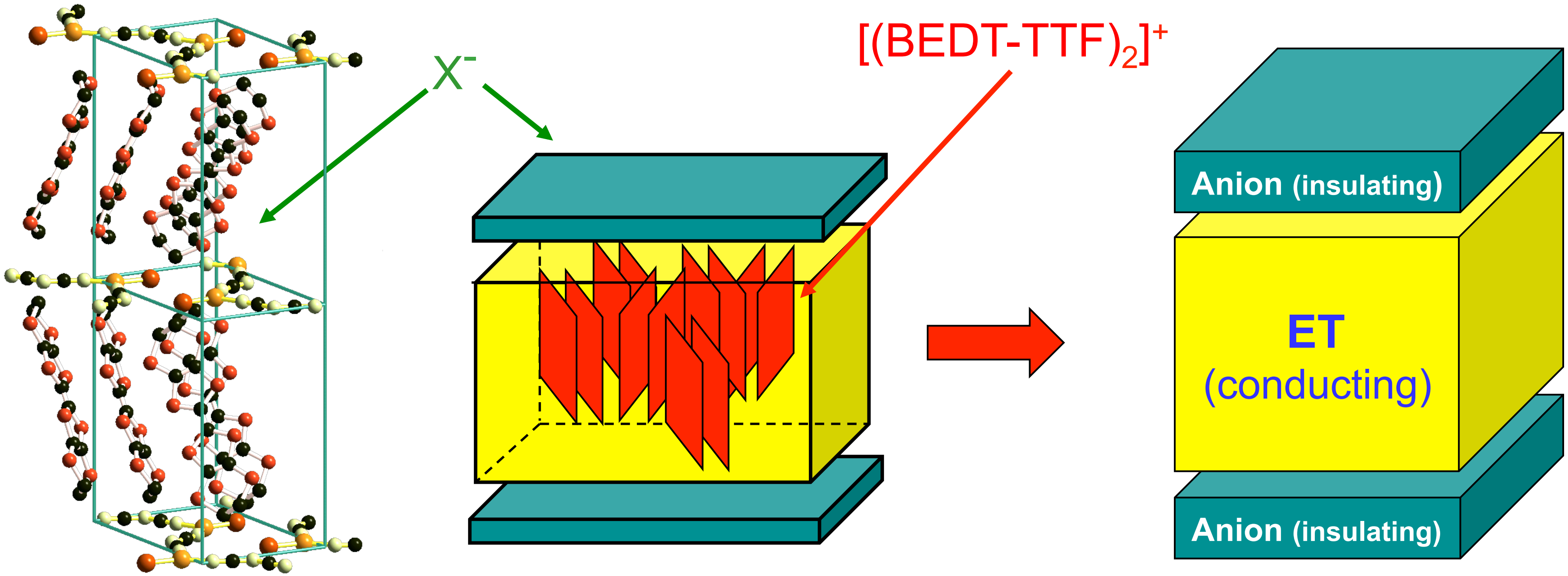
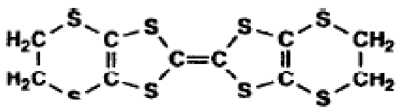
outline

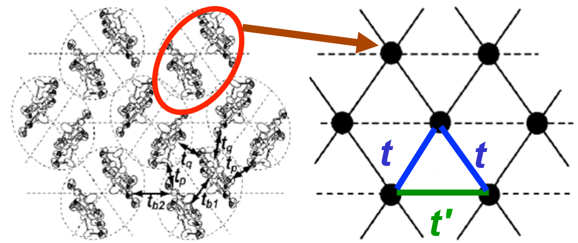
- organic charge-transfer salts
- phase diagrams
- spin-liquid: κ-$(ET)_2Cu_2(CN)_3$
- Mott criticality in κ-$(ET)_2X$
- valence-bond-solid: $EtMe_3P[Pd(dmit)_2]_2$
- summary and outlook

κ-(BEDT-TTF)$_2$X: charge-transfer salts



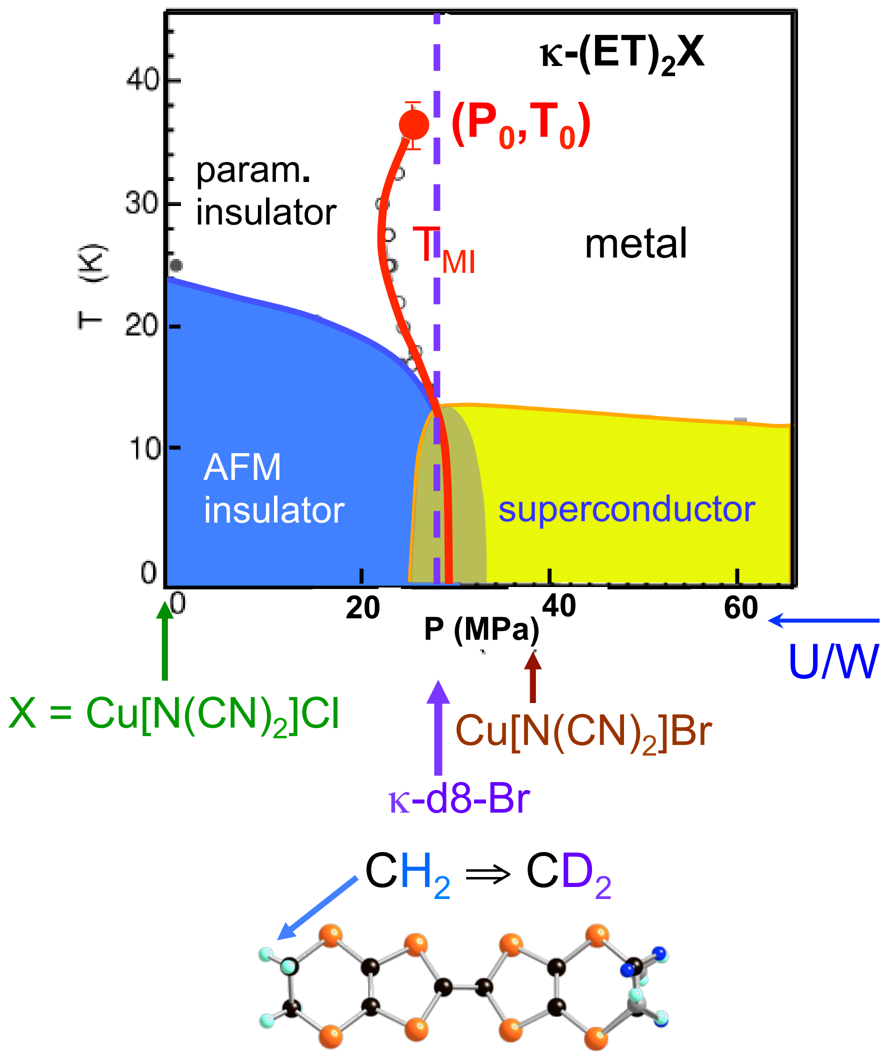


ET (BEDT-TTF)



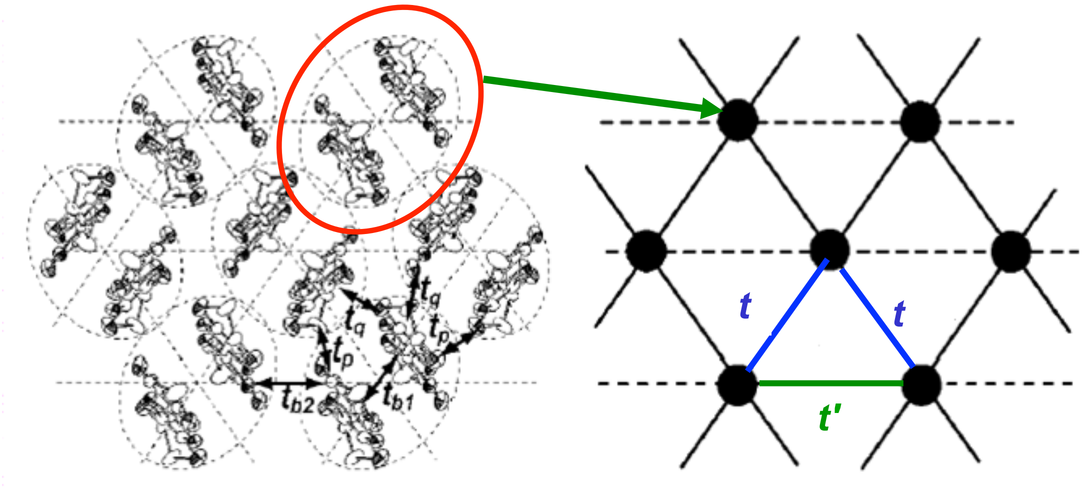
- κ-phase: “effective dimer model”: 1 hole/ dimer ⇒ half-filled conduction band
- W ~ U_{eff}: correlated π electrons

Mott criticality at the 2nd-order end-point (P_0, T_0)



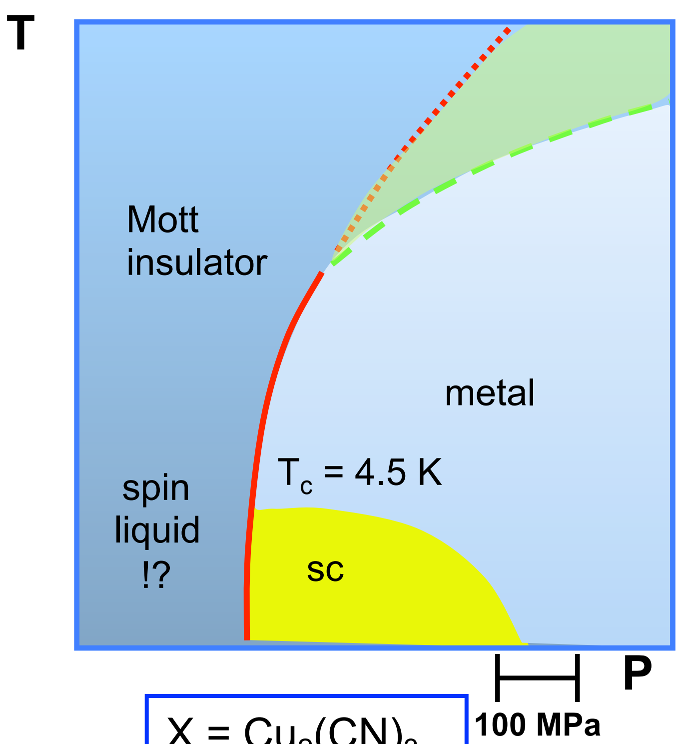
Lefebvre *et al.*, PRL **85**, 5420 (00)

effect-of-frustration



t'/t	κ-$(ET)_2Cu[N(CN)_2]Cl$	κ-$(ET)_2Cu_2(CN)_3$
ext. Hückel calc. Mori *et al.*, Chem. Soc. Jpn. **72**, 179 (99) Komatsu *et al.*, JPSJ **65**, 1340 (96)	0.72	1.06
ab initio calc. Kandpal *et al.*, PRL **103**, 067004 (09) Nakamura *et al.*, JPSJ **78**, 083710 (09)	0.44	~ 0.8

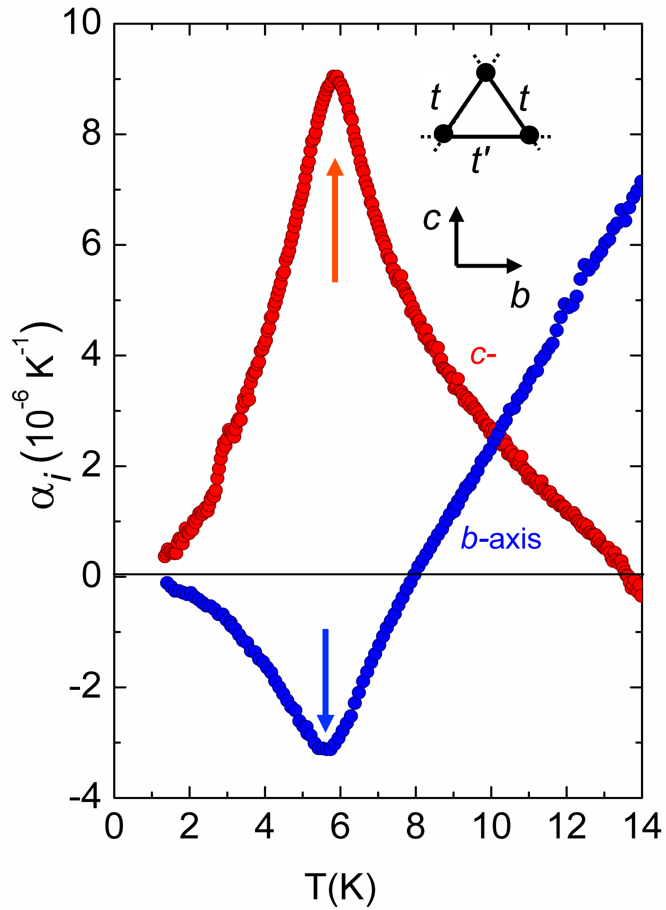
spin-liquid - κ-$(ET)_2Cu_2(CN)_3$



$X = Cu_2(CN)_3$
$t'/t \sim 0.8$

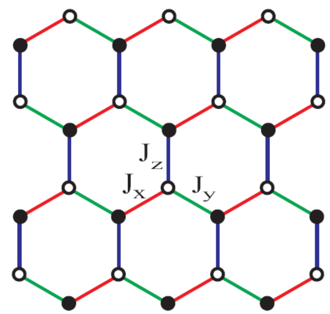
no long-range magnetic order down to 32 mK (J = 250 K)

Kurosaki *et al.*, PRL **95**, 177001 (05)
Shimizu *et al.*, PRL **91**, 107001 (03)



R. S. Manna *et al.*, PRL **104**, 016403 (10)

Kitaev spin-liquid
A_2IrO_3 (A = Na, Li)

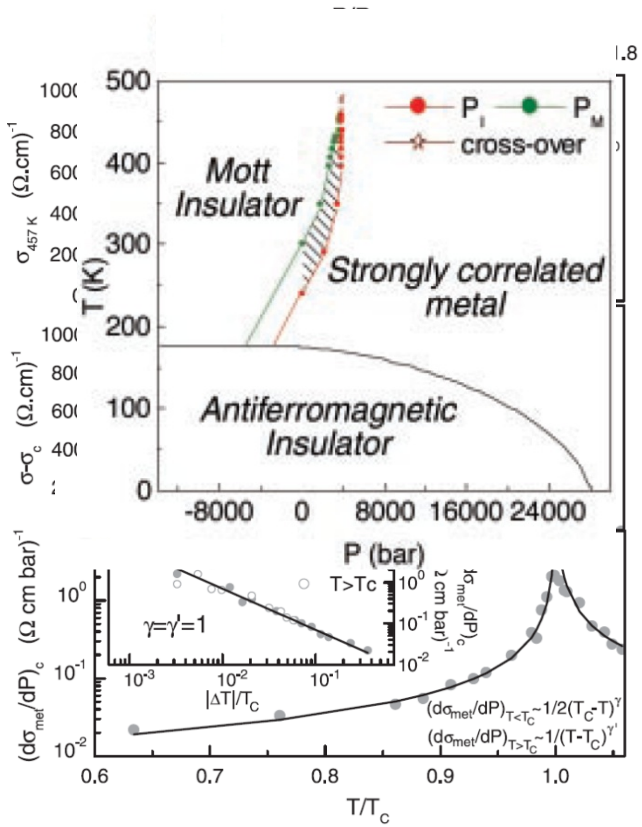


Mott universality

$(V_{1-x}Cr_x)_2O_3$
crossover: δ, β, γ = 3, 0.5, 1 (mean field values)
δ, β, γ = 4.81, 0.34, 1 (3D Ising)

$\Longrightarrow$ liquid-gas universality (3D Ising)

Limelette *et al.*, Science **302**, 89 (03)



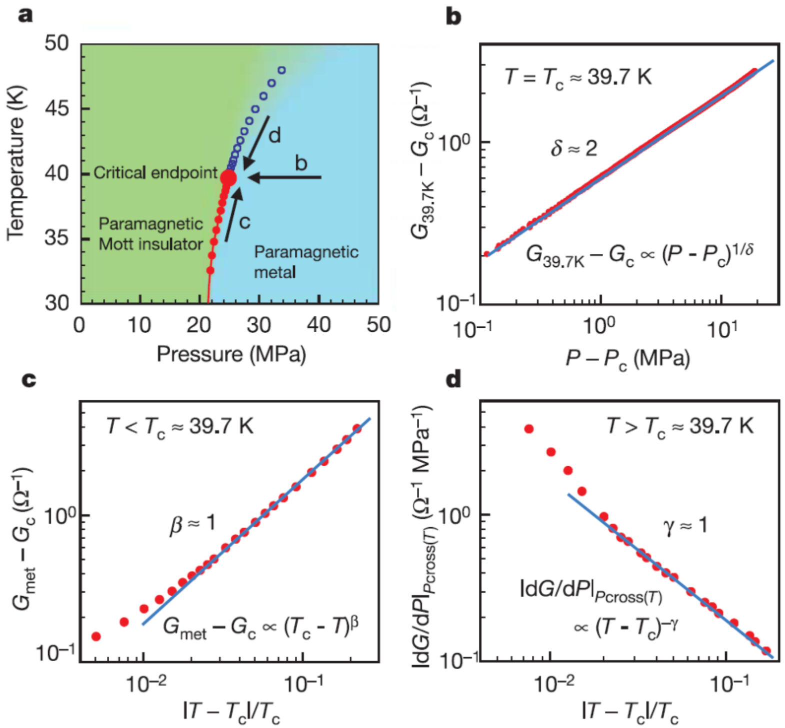
DMFT of the Hubbard model: an order parameter for the finite temperature Mott end point

$\Rightarrow$ Ising universality class, similar to the liquid-vapor transition

Castellani *et al.*, PRL **43**, 1957 (79)
Kotliar *et al.*, PRL **84**, 5180 (00)

controversy: κ-$(ET)_2Cu[N(CN)_2]Cl$

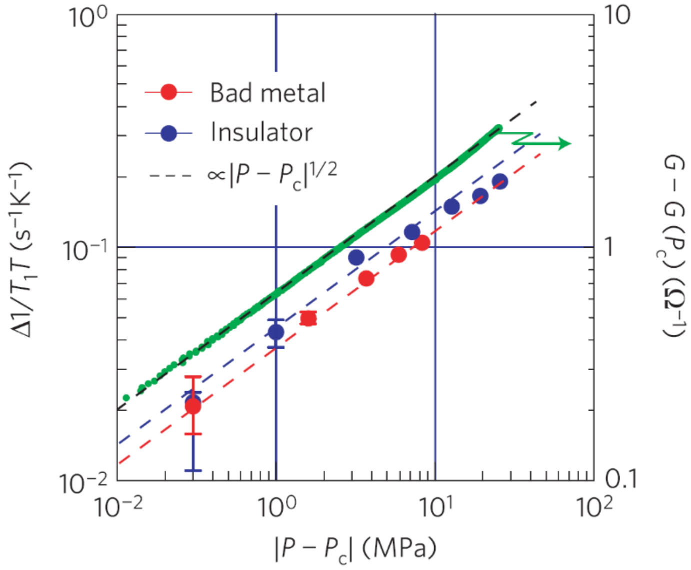
conductivity



δ, β, γ = 2, 1, 1
unconventional Mott criticality

Kagawa *et al.*, Nature **436**, 534 (05)

^{13}C-NMR



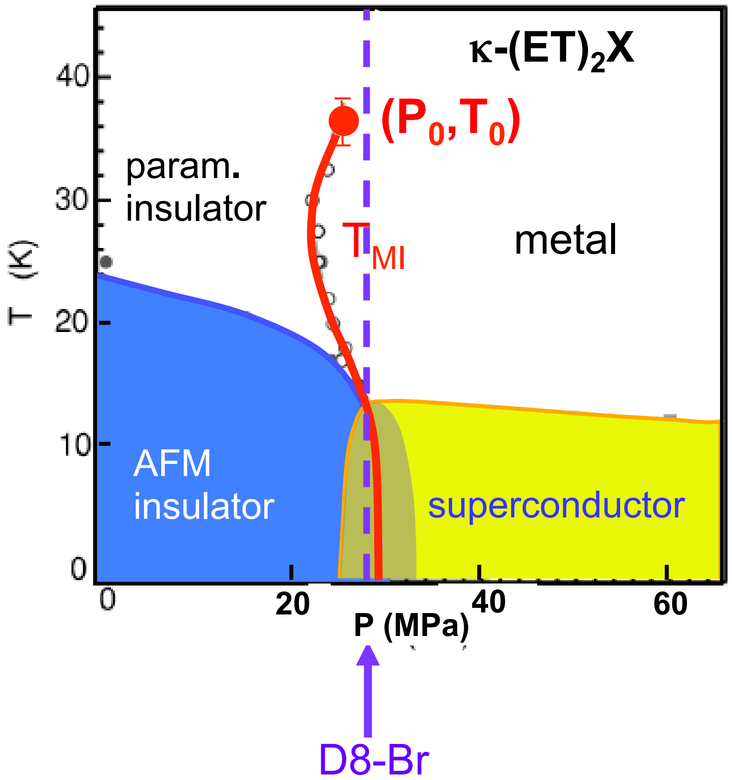
$\Delta 1/T_1T \propto |P-P_c|^{1/2} \Rightarrow \delta = 2$
unconventional

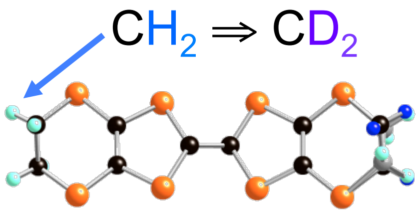
Kagawa *et al.*, Nature Physics **5**, 880 (09)

conductivity data of κ-$(ET)_2Cu[N(CN)_2]Cl$: coupling to the energy density dominates ⇒ consistent with 2D Ising universality class

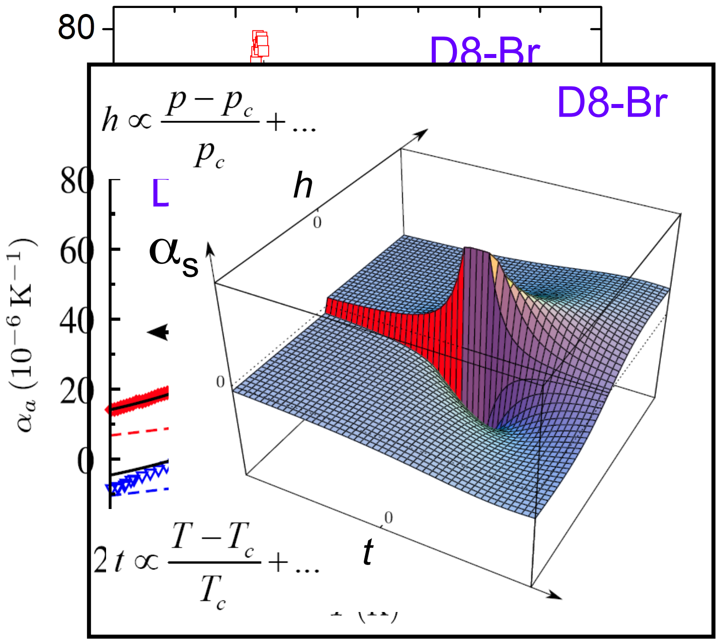
Papanikolaou *et al.*, PRL **100**, 026408 (08)

Mott criticality at the 2nd-order end-point (P_0, T_0)





Lefebvre *et al.*, PRL **85**, 5420 (00)



assumption: Grüneisen scaling

$\delta C^{sd} \propto \delta \alpha^{sd}$

critical exponent $\tilde{\alpha}$ = (0.8 ± 0.15)?!

Souza *et al.*, PRL **99**, 037003 (07)

Souza *et al.*, PRL **99**, 037003 (07)

- breakdown of Grüneisen scaling in the vicinity of a finite-temp. critical end point
- consistent with 2D Ising universality class
- large anomaly in alpha and sign change at the critical end-point (P_0, T_0)

Bartosch *et al.*, PRL **104**, 245701 (10)

thermal expansion measurements under He-gas pressure

experimental specifications

- high-resolution capacitive dilatometer (5×10^{-2} Å)

- temperature range 1.4 - 293 K

- hydrostatic pressure range 0 - 250 MPa (helium as a pressure transmitting medium)

- magnetic field range 0 - 14 T

pressure cell and dilatometer

1 dilatometer cell

2 n-InSb pressure gauge ($\Delta P = \pm\, 0.1$ MPa)

3 seal

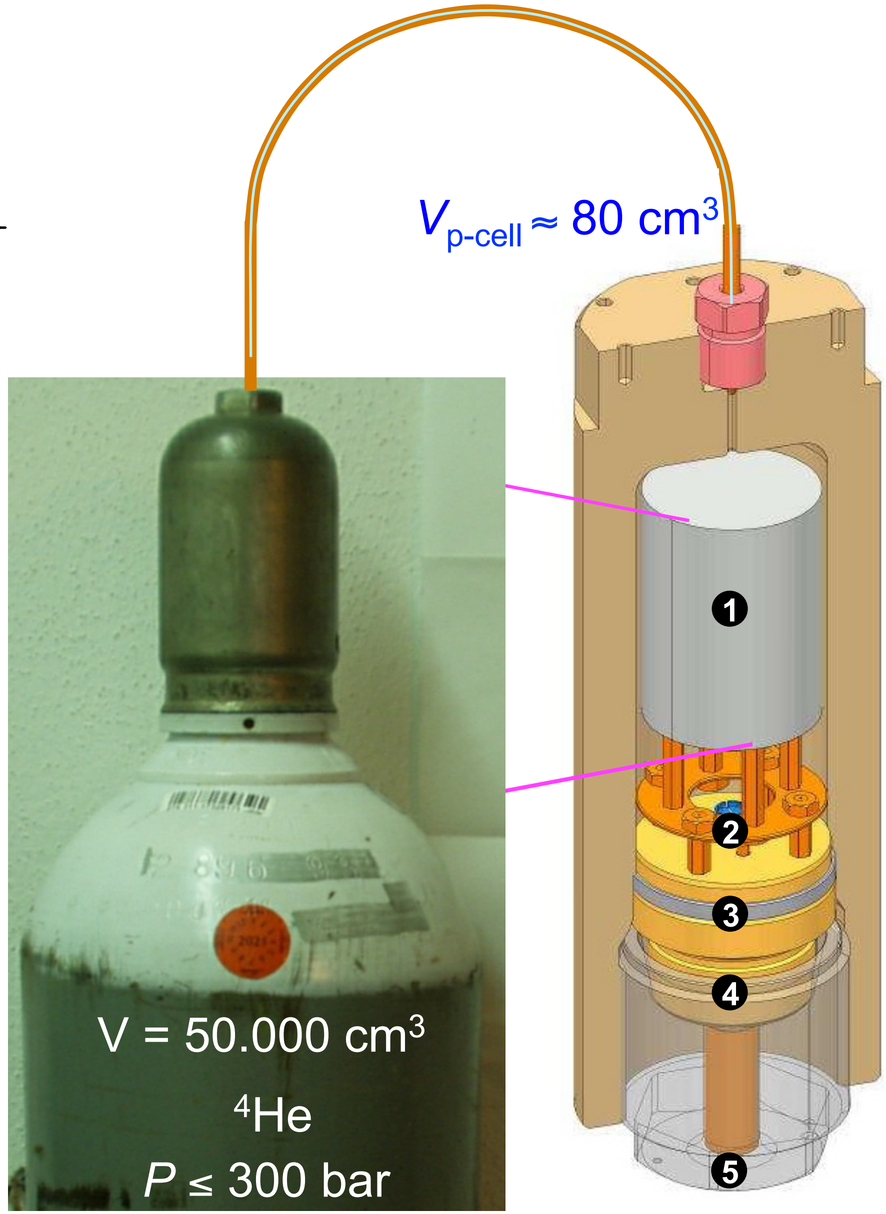
4 plug with electrical feed-throughs

5 retaining screw

Thermal expansion coefficient,

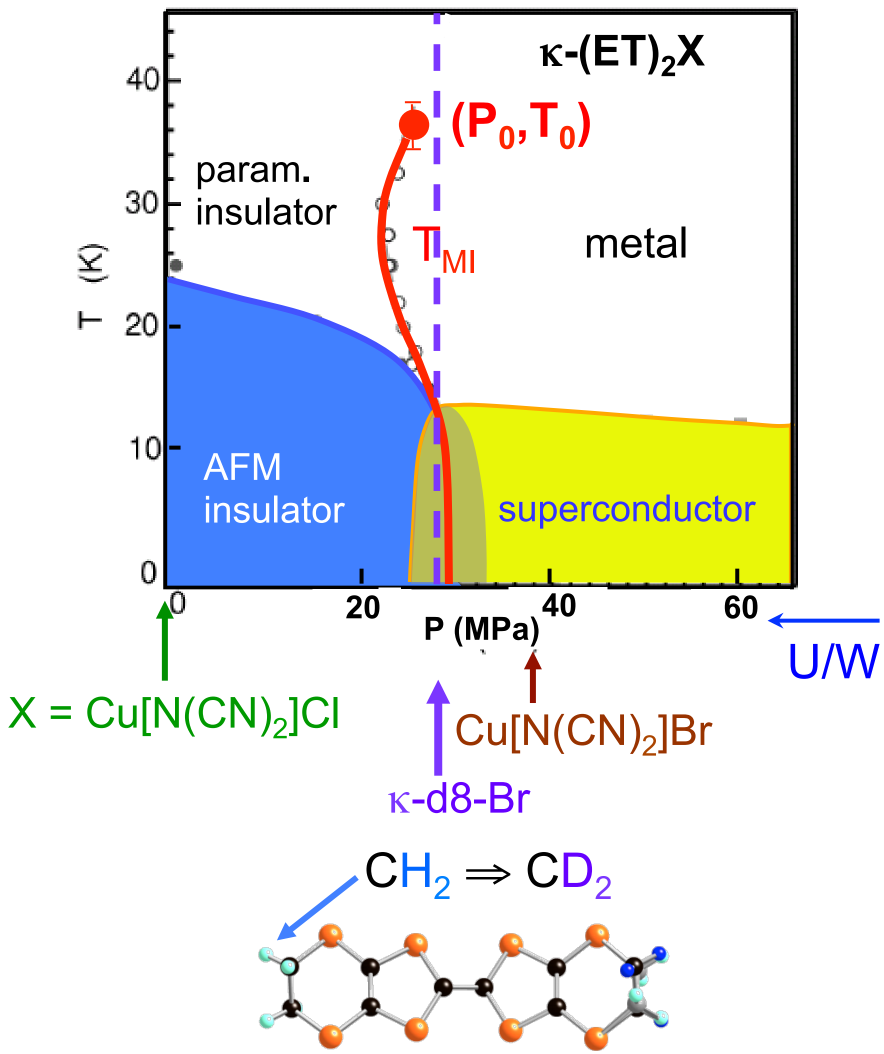
$$\alpha_i = \frac{1}{l_i}\left(\frac{\partial l_i}{\partial T}\right)_P$$

- constant-pressure condition
- ^{4}He (pressure-transmitting medium): gas/ liquid phase
- pressure reservoirs: gas bottle/ compressor with micropump



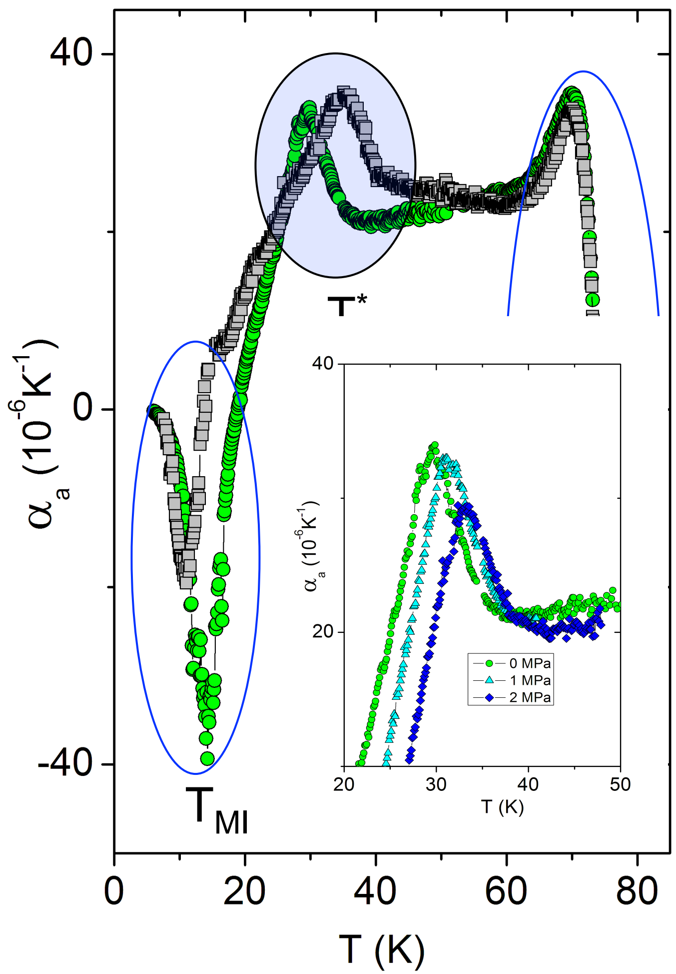
R. S. Manna, PhD thesis (12)
R. S. Manna *et al.*, Rev. Sci. Instrum. **83**, 085111 (12)

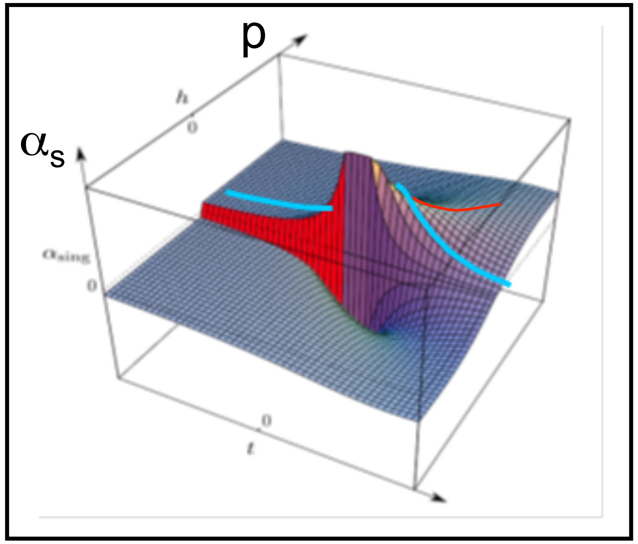
Mott criticality at the 2nd-order end-point (P_0, T_0)



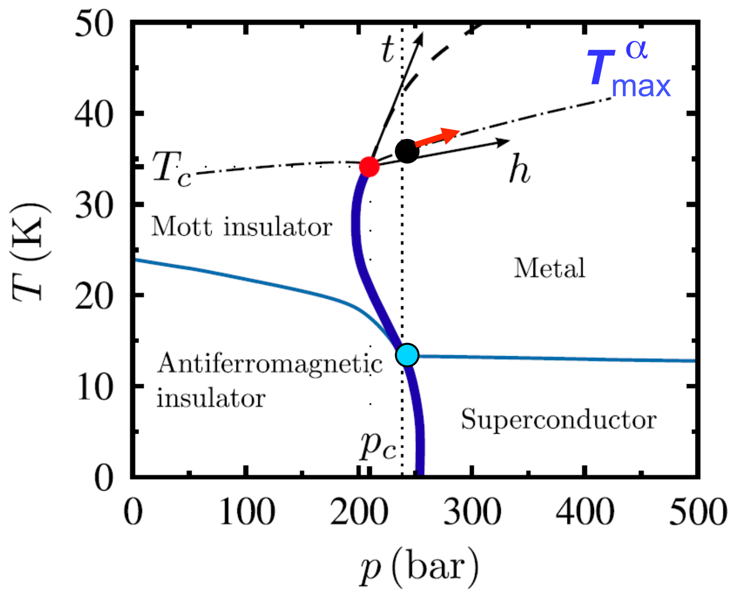
Lefebvre *et al.*, PRL **85**, 5420 (00)

κ-D8-Br at finite pressure



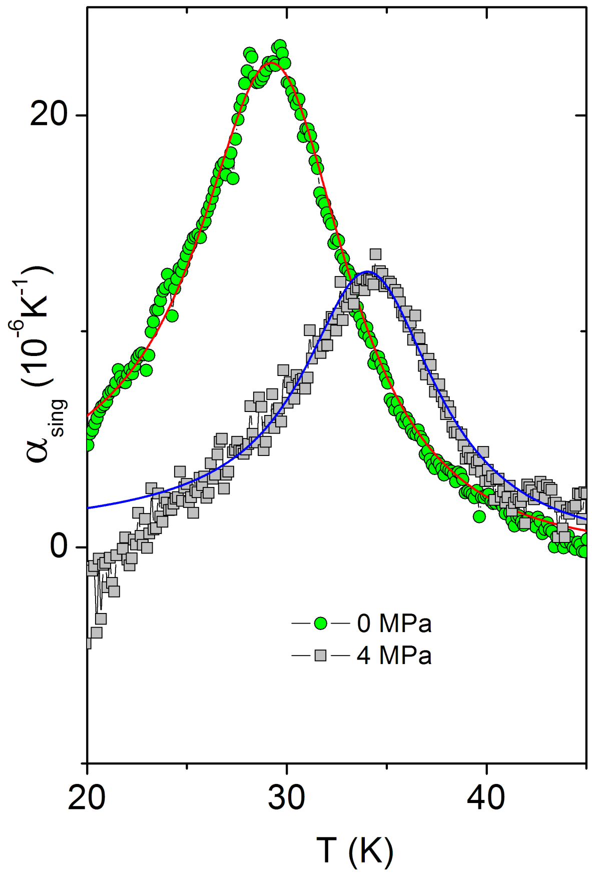


Bartosch *et al.*, PRL **104**, 245701 (10)



- T_g pressure independent, cf. Müller *et al.*, PRB (02)
- T_{MI} (1st-order) consistent with literature
- effect of pressure on T^* (2nd-order)

κ-D8-Br at finite pressure



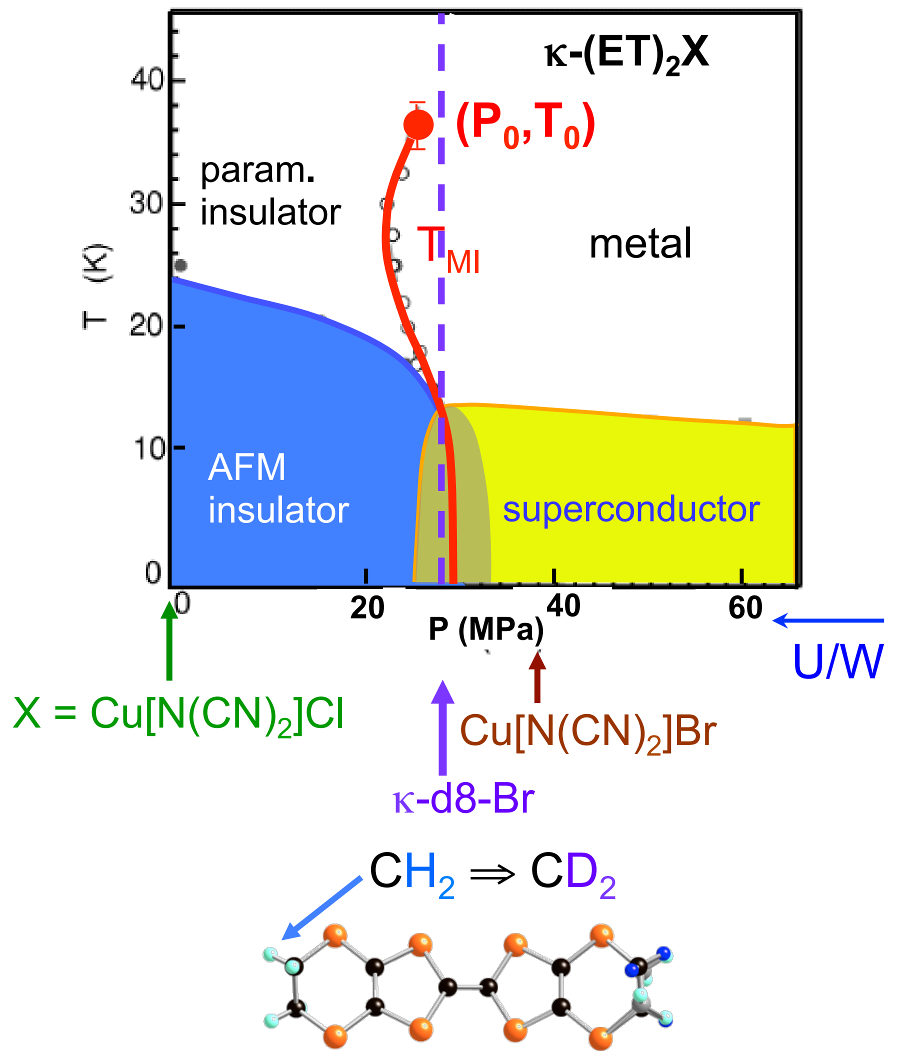
after subtracting a T-linear background

scaling theory: $\alpha_{sing} \propto \mathrm{sgn}(h)(-t)^{-1+\beta}$

$h \propto \frac{p - p_c}{p_c} + \ldots$ and $t \propto \frac{T - T_c}{T_c} + \ldots$

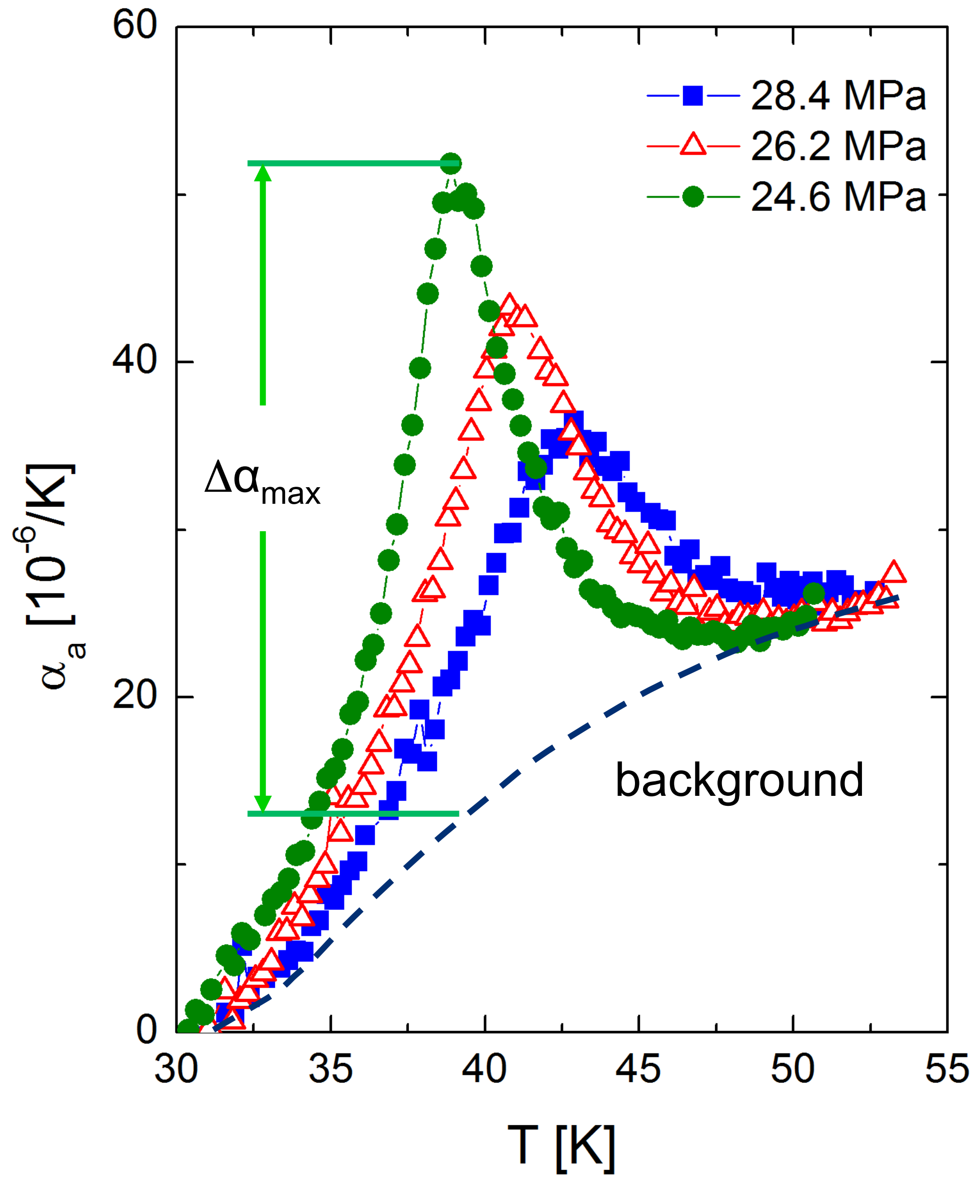
consistent with 2D Ising universality class

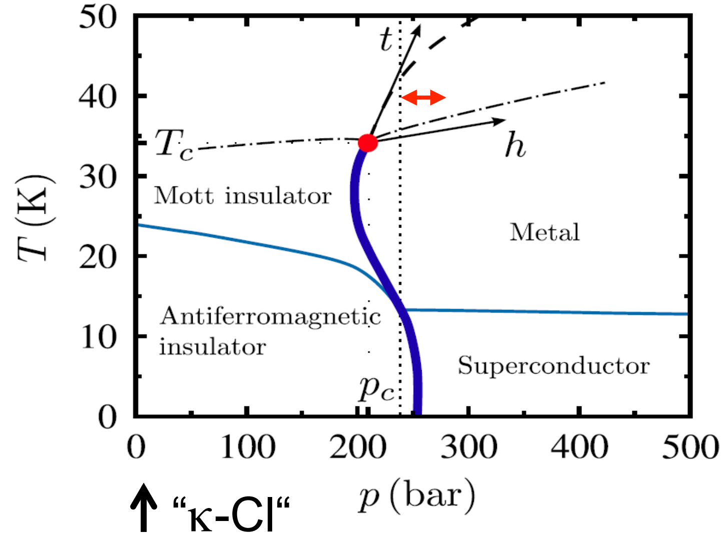
Mott criticality at the 2^{nd}-order end-point (P_0, T_0)



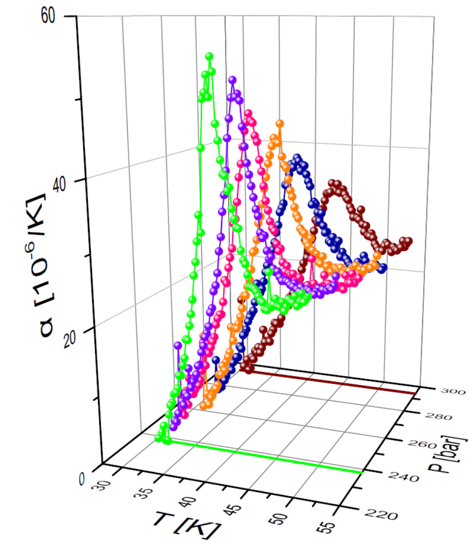
Lefebvre *et al.*, PRL **85**, 5420 (00)

κ-Cl at finite pressure





↑ "κ-Cl"

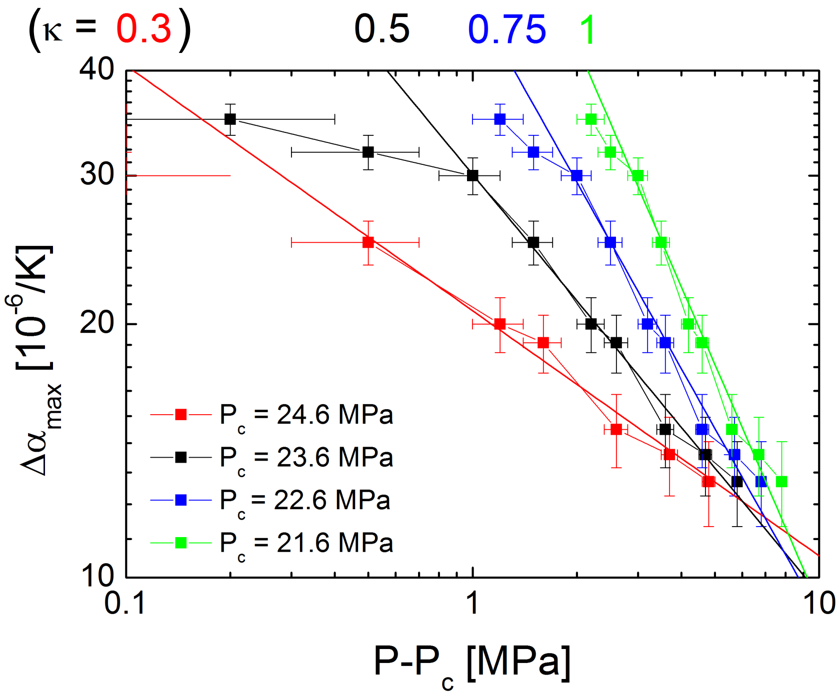


κ-Cl at finite pressure

Scaling theory: $\Delta\alpha_{max} \propto (P - P_c)^{-\kappa}$

Bartosch *et al.*, PRL **104**, 245701 (10)

$$\kappa = \frac{1 - \beta}{\beta + \gamma} = \begin{cases} 0 & \text{for "unconventional criticality" } (\beta = 1)\text{ ?!} \\ 7/15 & \text{for 2D Ising} \end{cases}$$



determination of κ requires precise knowledge of P_c !

crossover from 2D Ising (κ ≈ 0.5) to mean-field (κ ≈ 0.3) criticality?

Zacharias *et al.*, PRL **109**, 176401 (12)

summary

• Thermal expansion measurements under ^{4}He-gas pressure have been performed on κ-$(ET)_2X$ for probing critical fluctuations.

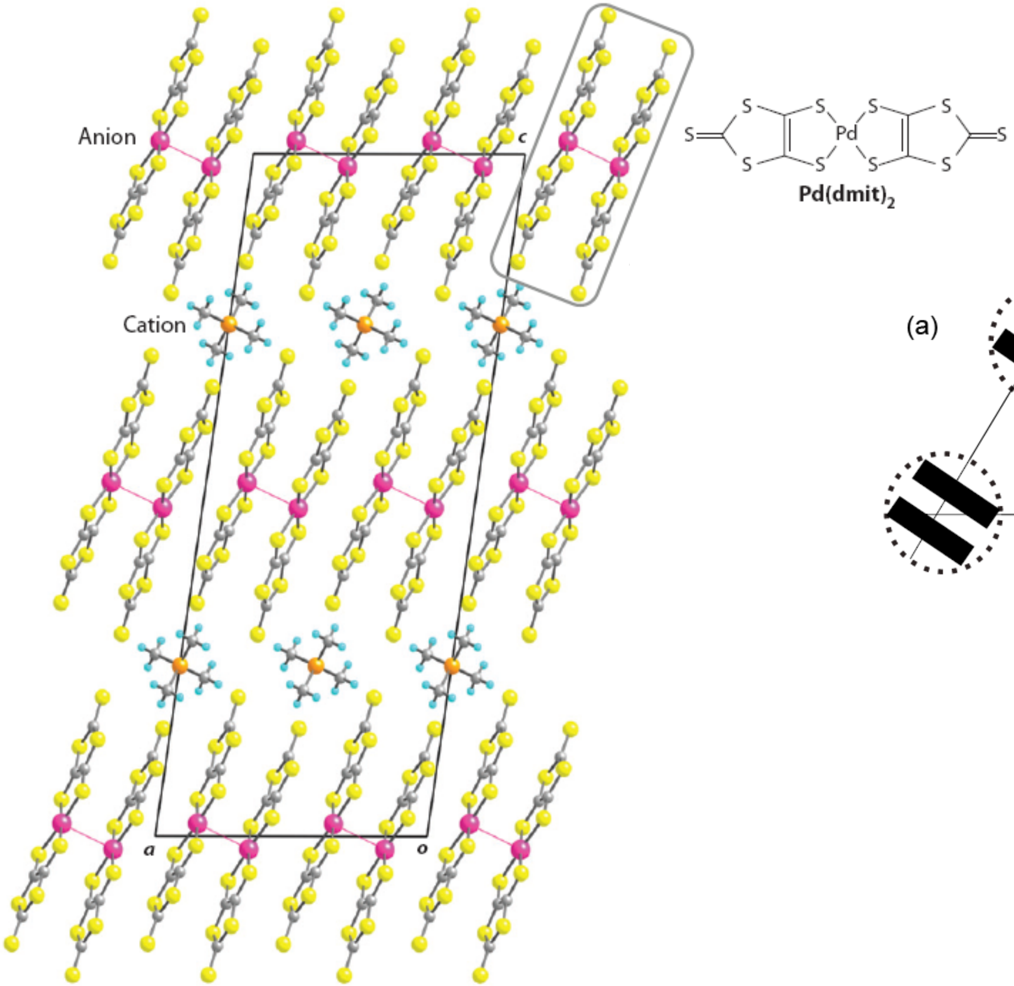
• data of κ-D8-Br and κ-Cl:

- Mott critical end point is consistent with 2D Ising universality class.

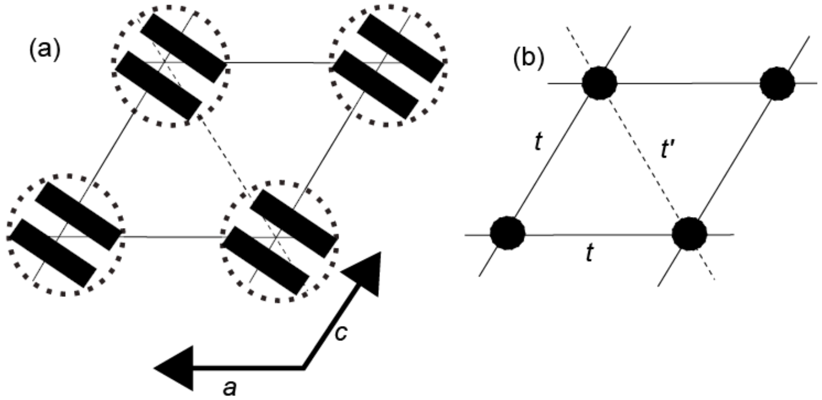
outlook

• sample-to-sample variations
• determination of $P_c \Rightarrow \kappa = (1 - \beta)/(\beta + \gamma)$
• measurement in the insulating (low-P) regime ⇒ sign change in α !
• role of lattice degrees of freedom

$EtMe_3X[Pd(dmit)_2]_2$ (X = P/Sb)



X = P



uniform stacking
(one type of $[Pd(dmit)_2]$ layer)

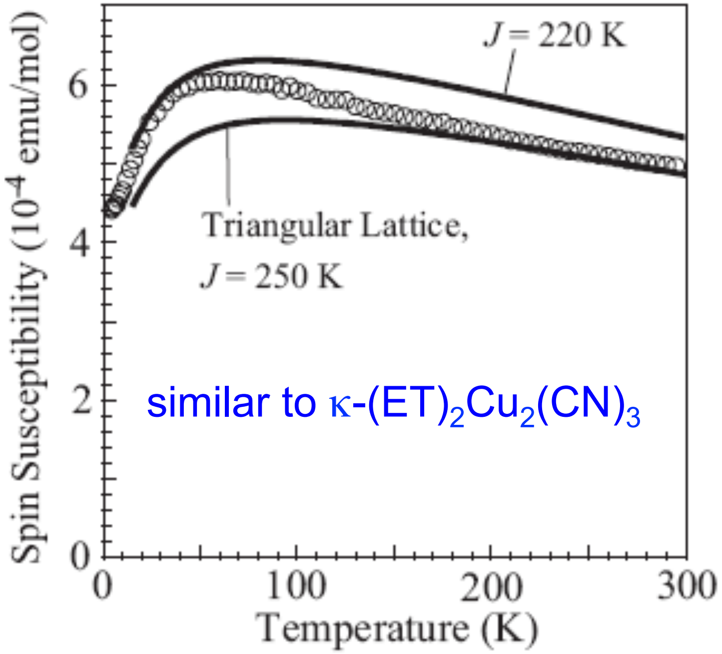
Tamura *et al.*, JPSJ **75**, 093701 (06)

Itou *et al.*, Nat. Phys. **6**, 673 (10)

K. Kanoda and R. Kato, Annu. Rev. Condens. Matter Phys. **2**, 167 (11)

$EtMe_3X[Pd(dmit)_2]_2$ – ground state properties

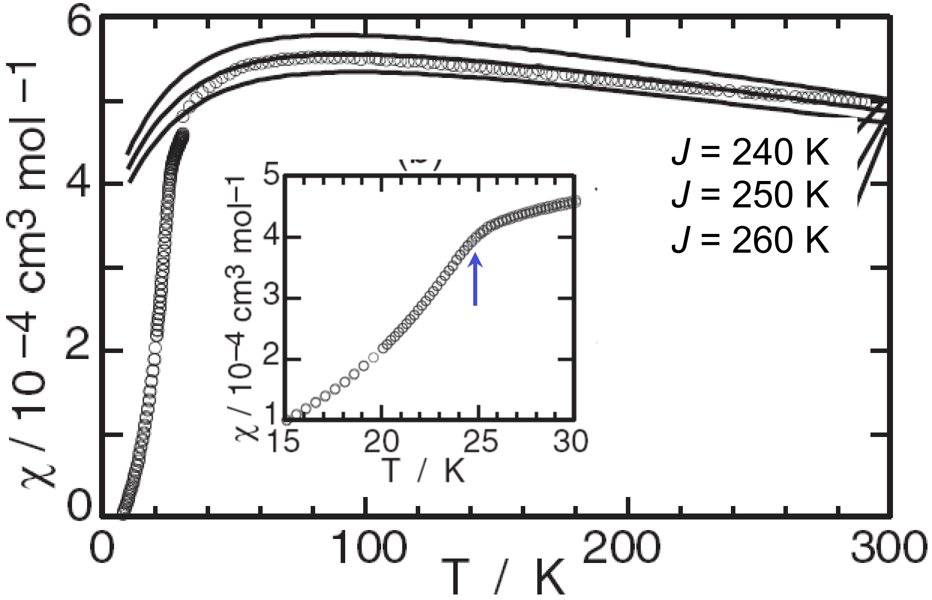
X = Sb ⇒ spin-liquid



similar to κ-$(ET)_2Cu_2(CN)_3$

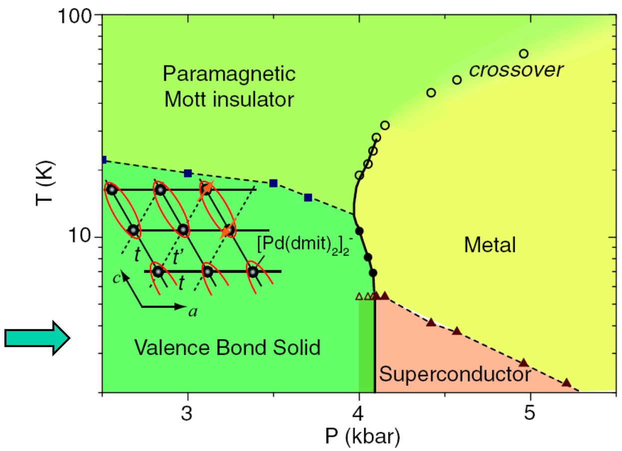
Itou *et al.*, PRB **77**, 104413 (08)

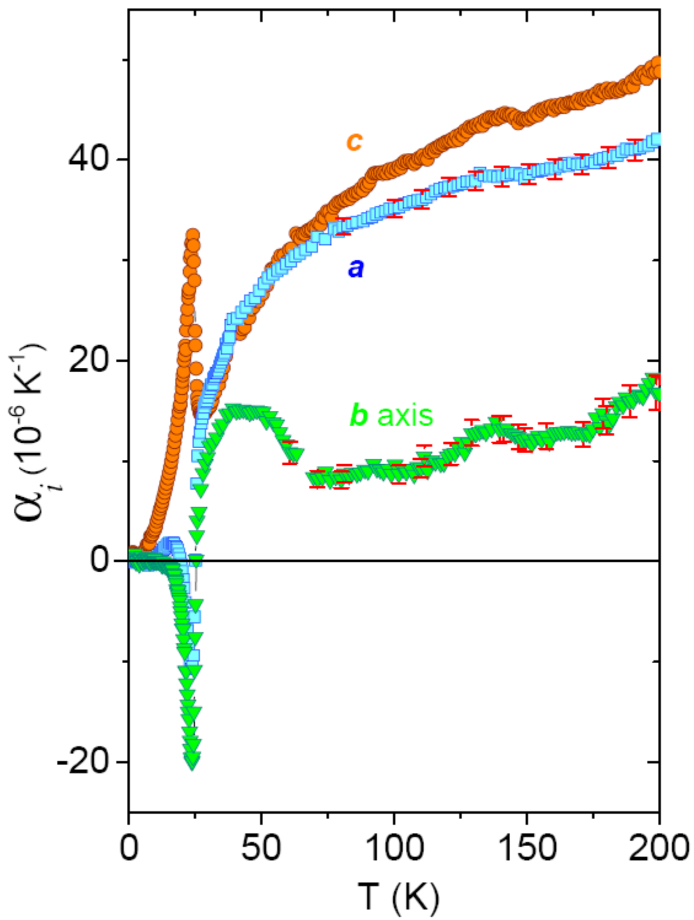
X = P ⇒ valence-bond-solid

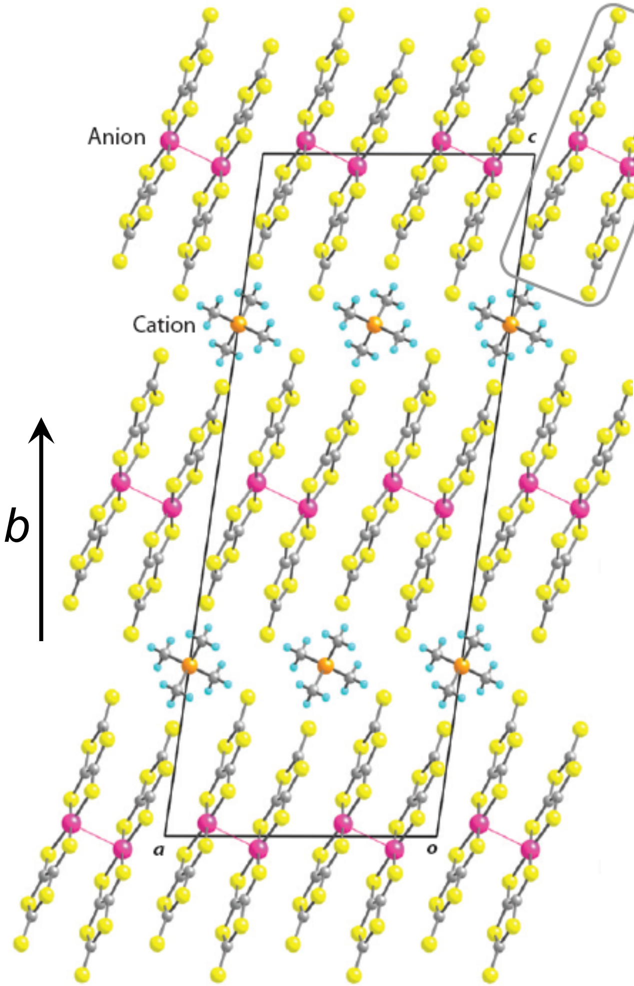


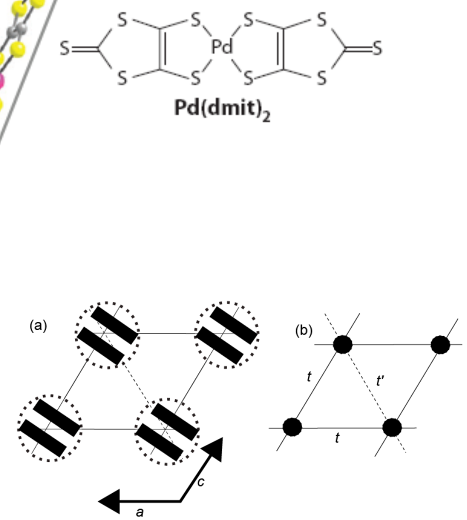
Tamura *et al.*, JPSJ **75**, 093701 (06)

Shimizu *et al.*, PRL **99**, 256403 (07)





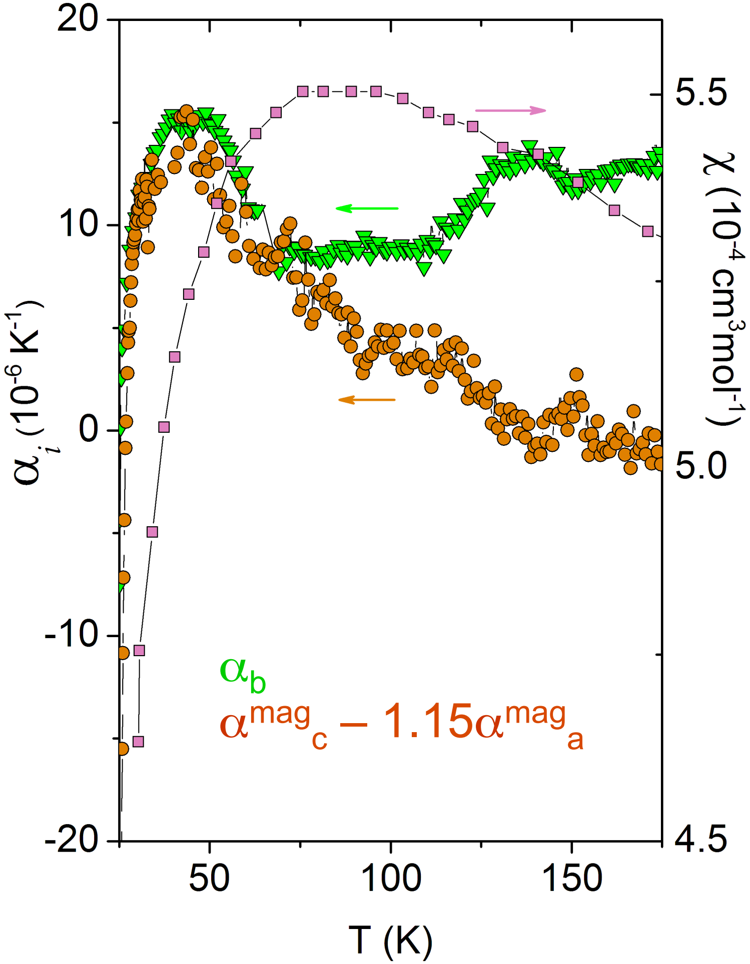




- strongly anisotropic lattice distortions accompanying the formation of VBS
- weak in-plane α_a vs α_c anisotropy for T > T_{VBS} suggests dominant contribution from $EtMe_3P$ cations

R. S. Manna *et al.*, PRB 89, 045113 (14)

anomalous thermal expansion in the paramagnetic region



Assumptions:

$\alpha_a = \alpha^{lat}_a + \alpha^{mag}_a$

$\alpha_c = \alpha^{lat}_c + \alpha^{mag}_c$

$\alpha^{lat}_c = A\alpha^{lat}_a$

$\alpha^{mag}_c = B\alpha^{mag}_a$

anomalous contribution at $T^{\alpha}_{max} \approx 40$ K due to the short-range afm correlation, cf. $T^{\chi}_{max} = 70$ K

χ-data: Tamura *et al.*, JPSJ **75**, 093701 (06)

R. S. Manna *et al.*, PRB 89, 045113 (14)

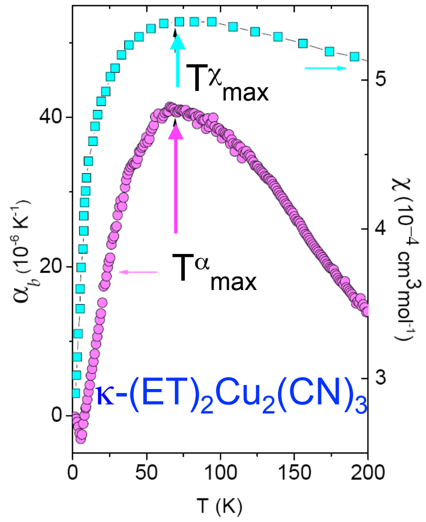
variation of $T^{\chi}_{max}/ T^{\alpha}_{max} = T^{\chi}_{max}/T^{C}_{max}$ for low-D quantum magnets with different degree of frustration

- for 2D triangular lattice S = ½ Heisenberg afm ~ 1

- for Cs_2CuBr_4: $J'/J = 0.74$

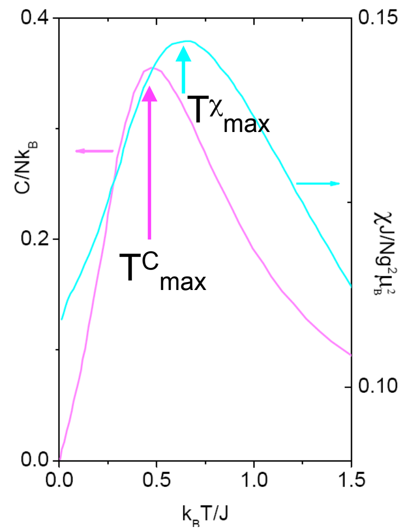
- for κ-$(ET)_2Cu_2(CN)_3$: $J'/J = 0.64 - 0.74$

Shimizu *et al.*, PRL **91**, 107001 (03)
R. S. Manna *et al.*, PRL **104**, 016403 (10)

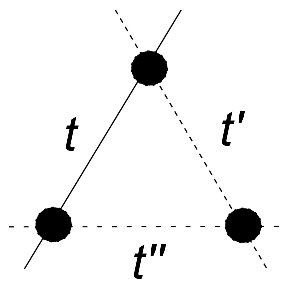


- for 1D uniform S = ½ Heisenberg chain ~ 1.34,
  for alternating exchange variant ~ 3 and
  including next-nearest-neighbor interactions ~ 3.6

Klümper, Eur. Phys. J. B **5**, 677 (98)
Bühler *et al.*, PRB **64**, 024428 (01)

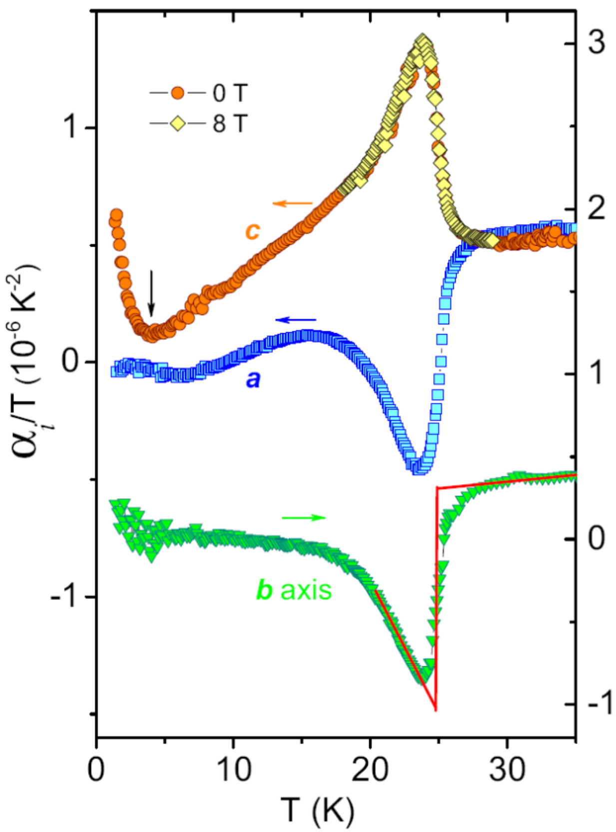


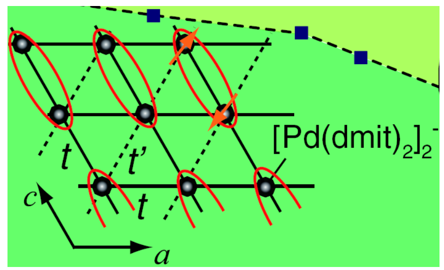
present case: $T^{\chi}_{max}/ T^{\alpha}_{max} \approx 1.7 - 2.3$
$\Rightarrow$ suggests a more anisotropic (quasi-1D) scenario



R. S. Manna *et al.*, PRB 89, 045113 (14)

lattice distortion at VBS transition





R. S. Manna *et al.*, PRB 89, 045113 (14)

- distinct and strongly anisotropic second-order phase transition into the low-T VBS phase at 25 K

- upon cooling *c*-axis (in-plane) contracts, *a*-axis (in-plane) expands while the dominant effect is along the *b*-axis (out-of-plane) which expands

⇒ pressure dependency comes from the out-of-plane component as the in-plane pressure effects cancel each other out (- 4.2 K/100 MPa)

summary

- valence-bond-solid, $EtMe_3P[Pd(dmit)_2]_2$

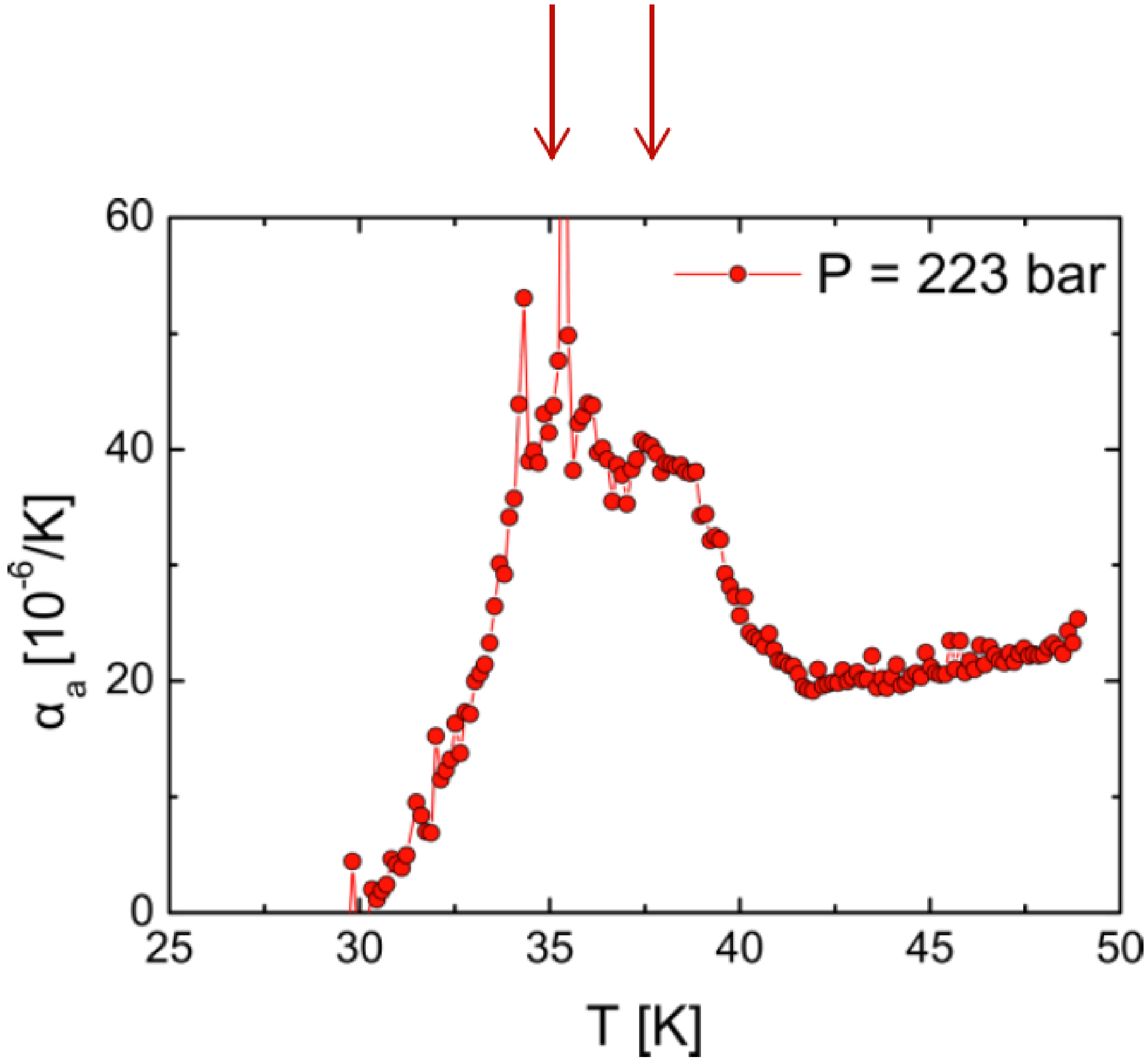
  - An anomalous contribution at $T^{\alpha}_{max} \approx 40$ K is found and assigned to the short-range afm correlations.

  - $T^{\chi}_{max}/ T^{\alpha}_{max} \approx 1.7 - 2.3$ seems incompatible with quasi-2D triangular lattice (~ 1), rather compatible with a quasi-1D more anisotropic scenario.

outlook

- perform similar experiments for the spin-liquid (dmit-Sb) compound
- study the Mott criticality in dmit-salts vs ET-based compounds ?!

Thank you for your attention !

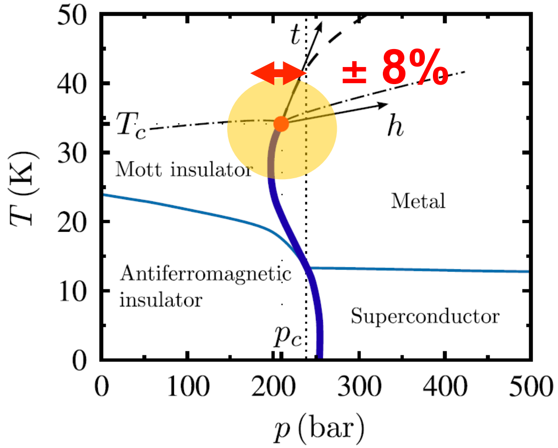


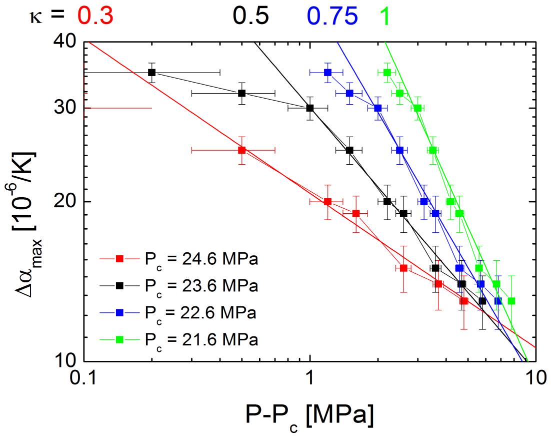
closer to P_0: occurrence of double-peak structure, interference of another phase transition (intrinsic) or bicrystal (extrinsic)?

coupling to the lattice degrees of freedom

Zacharias *et al.*, PRL **109**, 176401 (12)

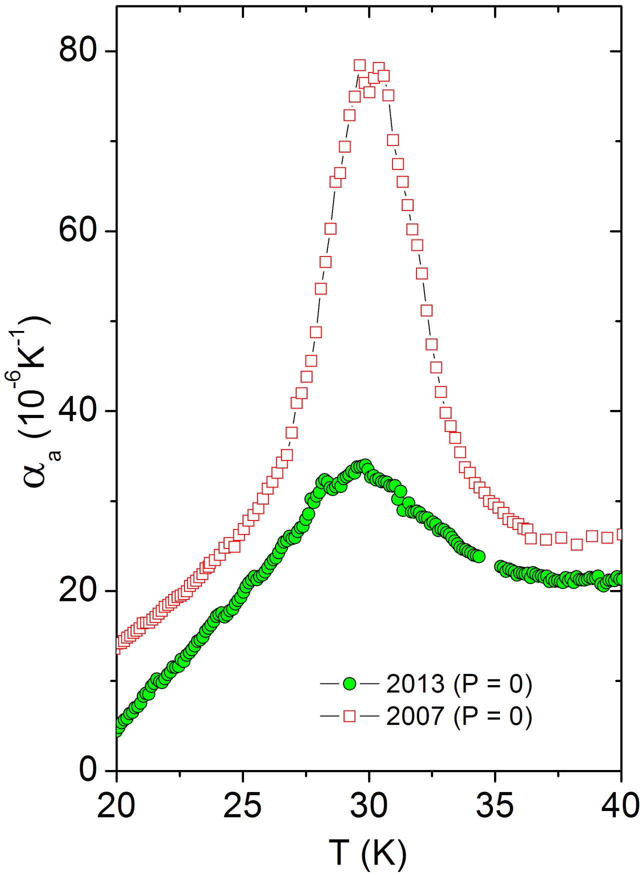
Approaching (P_0,T_0): crossover to mean-field criticality (κ_{MF} = 0.33)



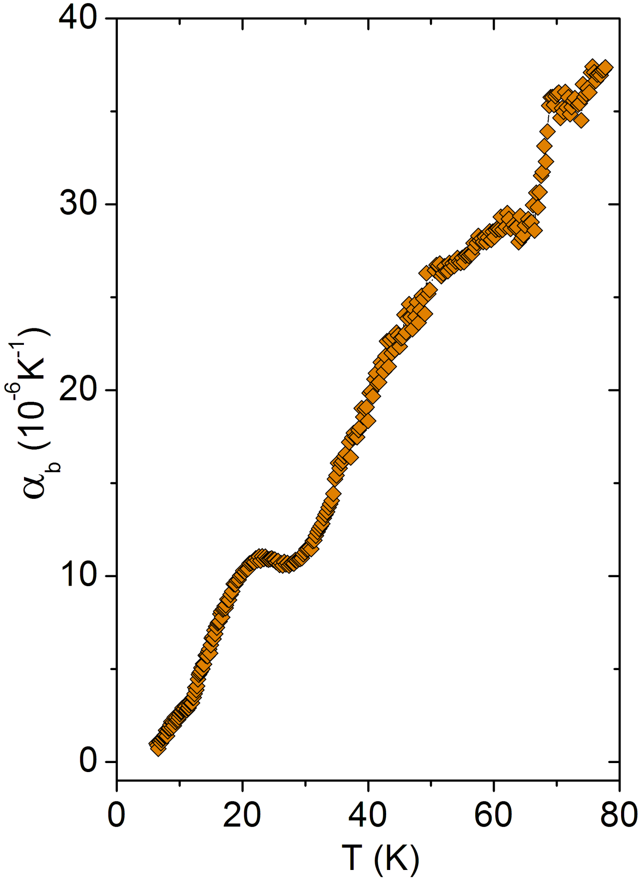


κ-$(d8\text{-}ET)_2Cu[N(CN)_2]Br$

sample-to-sample dependency

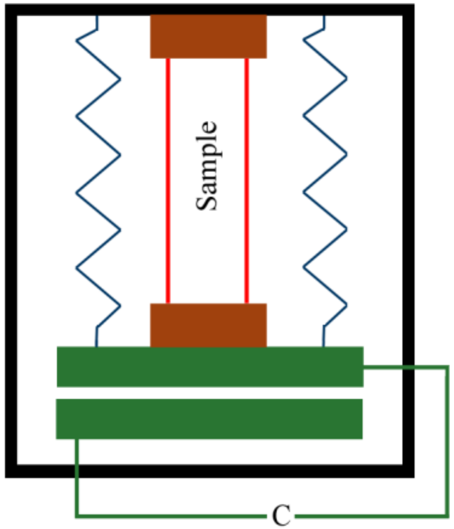


κ-$(d8\text{-}ET)_2Cu[N(CN)_2]Cl$



high-resolution dilatometry

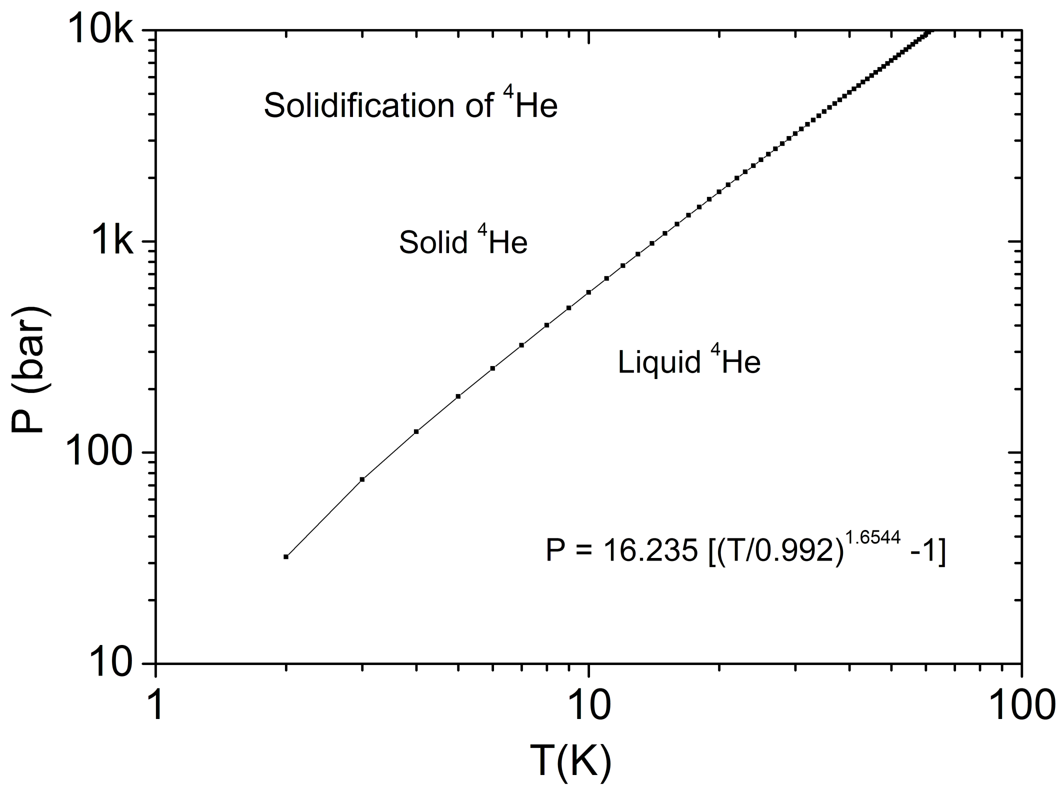
30 mm



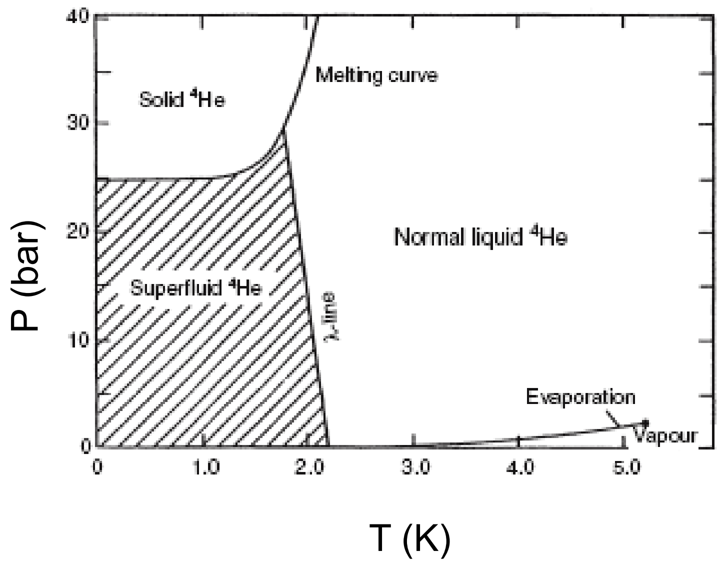
resolution: $\Delta l / l \sim 10^{-10}$ (for l = 10 mm)

Thermal expansion coefficient, $\alpha_i = \frac{1}{l_i}\left(\frac{\partial l_i}{\partial T}\right)_p$

experimental limitation



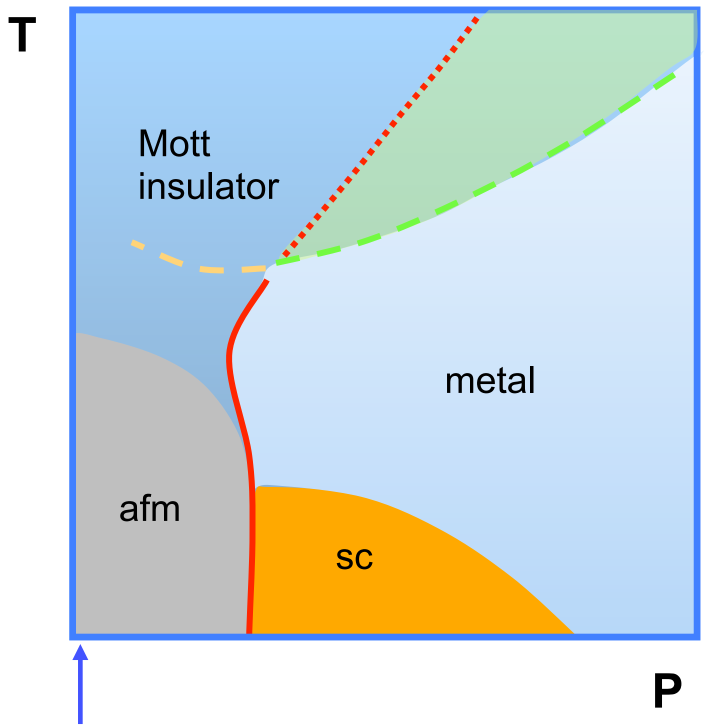
Langer, J. Phys. Chem. Solids **21**, 122 (61)



F. Pobell, *Matter and Methods at Low Temperatures*, Springer

Phase diagrams

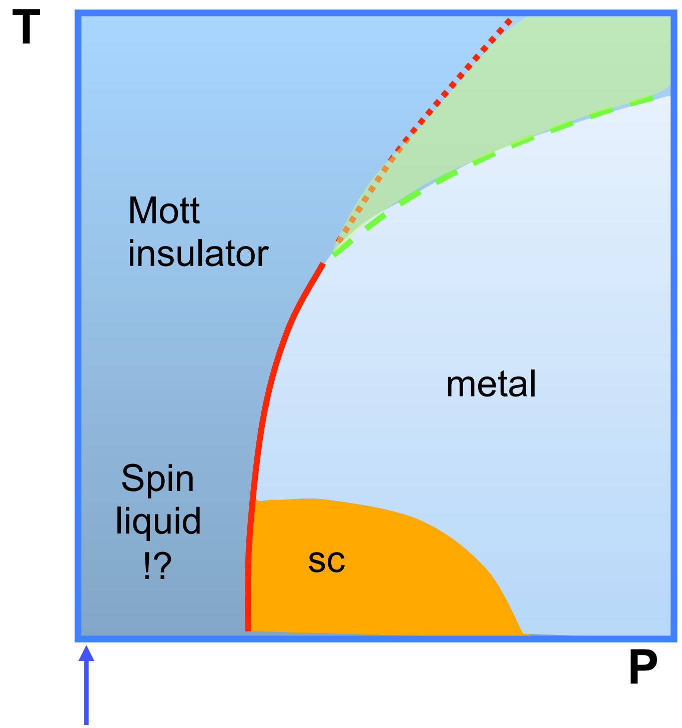
κ-$(ET)_2Cu[N(CN)_2]Cl$



T_N ~ 27 K, long-range magnetic order

Lefebvre *et al.*, PRL **85**, 5420 (00)

κ-$(ET)_2Cu_2(CN)_3$



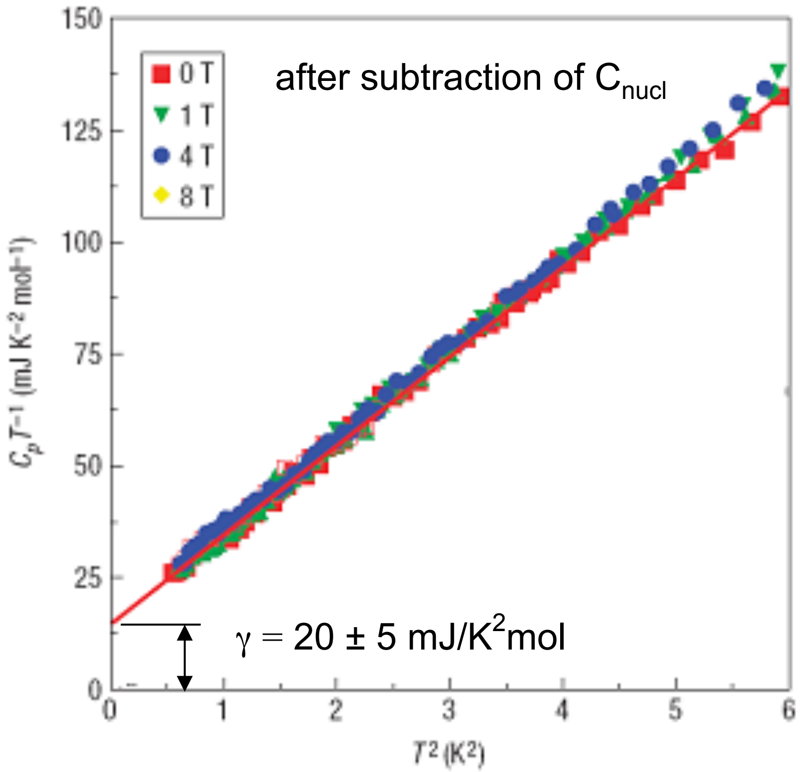
no long-range magnetic order down to 32 mK

Kurosaki *et al.*, PRL **95**, 177001 (05)

Shimizu *et al.*, PRL **91**, 107001 (03)

low-energy excitations

Specific heat

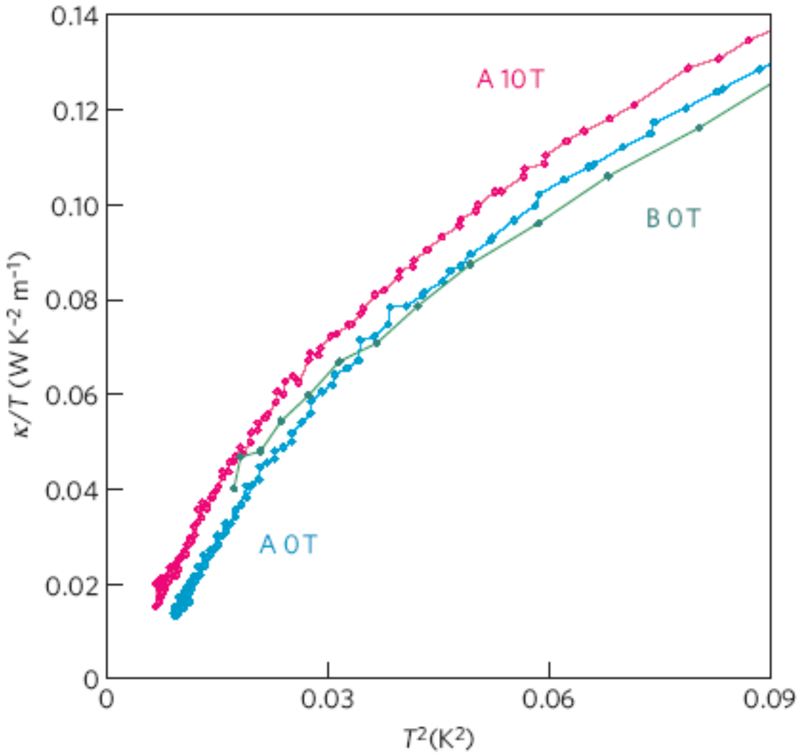


$$(C_P / T)_{T \to 0} = \gamma_0$$

'gapless spinons with a Fermi surface'

Yamashita *et al.*, Nat. Phys. **4**, 459 (08)

Thermal conductivity



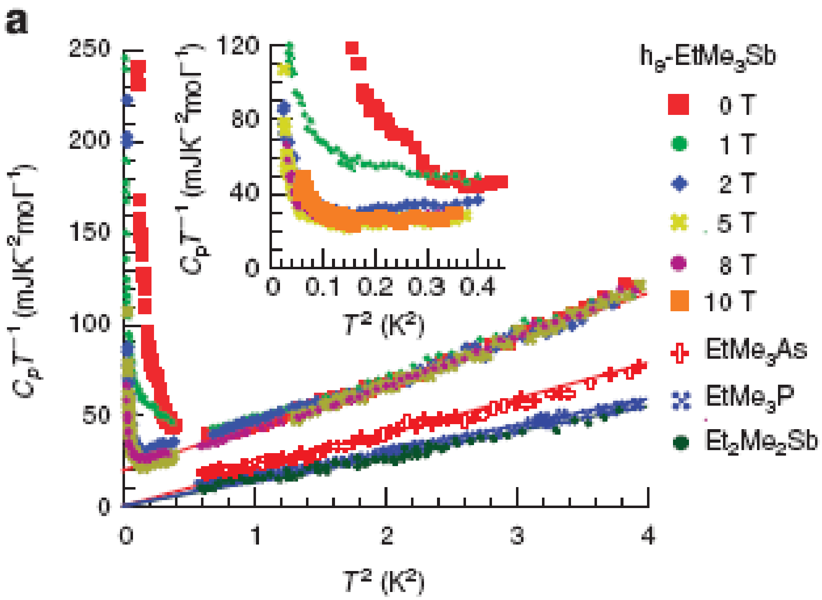
$$(\kappa / T)_{T \to 0} = 0$$

'spin gap of Δ = 0.46 K ~ *J*/500'

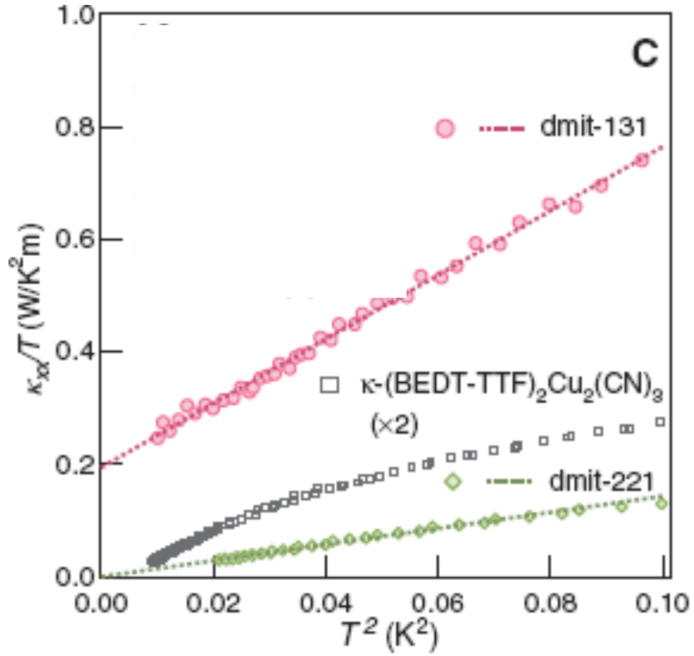
Yamashita *et al.*, Nat. Phys. **5**, 44 (09)

low-energy excitations: $EtMe_3Sb[Pd(dmit)_2]_2$

Specific heat



Thermal conductivity



'gapless spinons with a Fermi surface'

Yamashita *et al.*, Nat. Commun. **2**, 275 (11)

Yamashita *et al.*, Science **328**, 1246 (10)

Exponent	$Ising_2$	$Ising_3$	XY_3	$Heisenberg_3$
α	0(log)	0.110(1)	-0.015	-0.10
β	1/8	0.3265(3)	0.35	0.36
γ	7/4	1.2372(5)	1.32	1.39
δ	15	4.789(2)	4.78	5.11

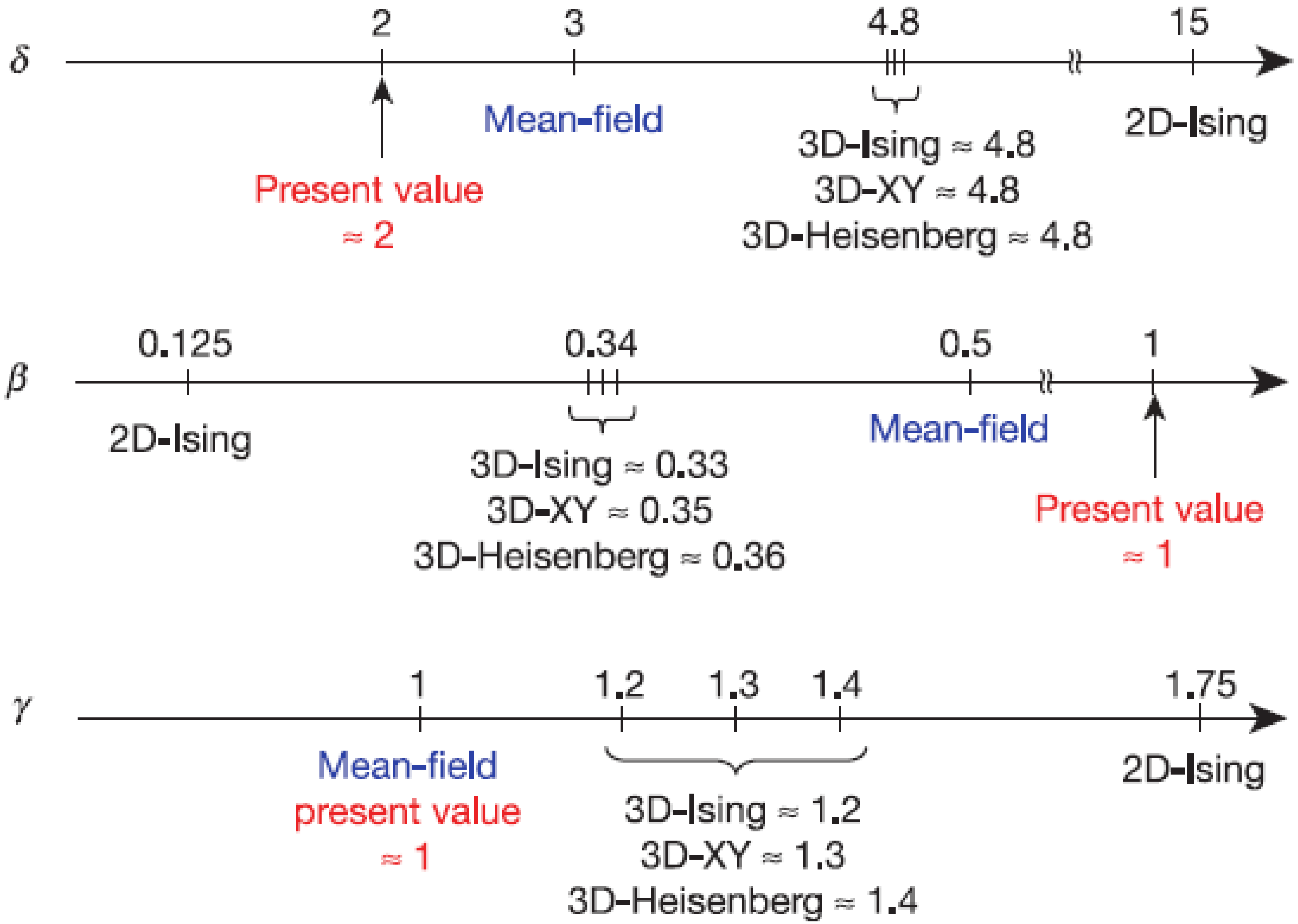
$$C(t) \propto |t|^{-\alpha}$$

$$m(t) \propto (-t)^{\beta}, t \leq 0$$

$$\chi(t) \propto |t|^{-\gamma}$$

$$m(h) \propto |h|^{1/\delta} sgn(h), t = 0$$

C (t) = sp. Heat
m (t) = spontaneous magnetization
χ*(t)* = mag. Susceptibility
m (h) = critical isotherm



Kagawa *et al*., Nature **436**, 534 (05)

- Lattice coupling changes the critical properties of the electronic system drastically so that eventually Landau mean-field behavior (corresponding to m_f = 0.33) prevails close to the Mott critical end point.

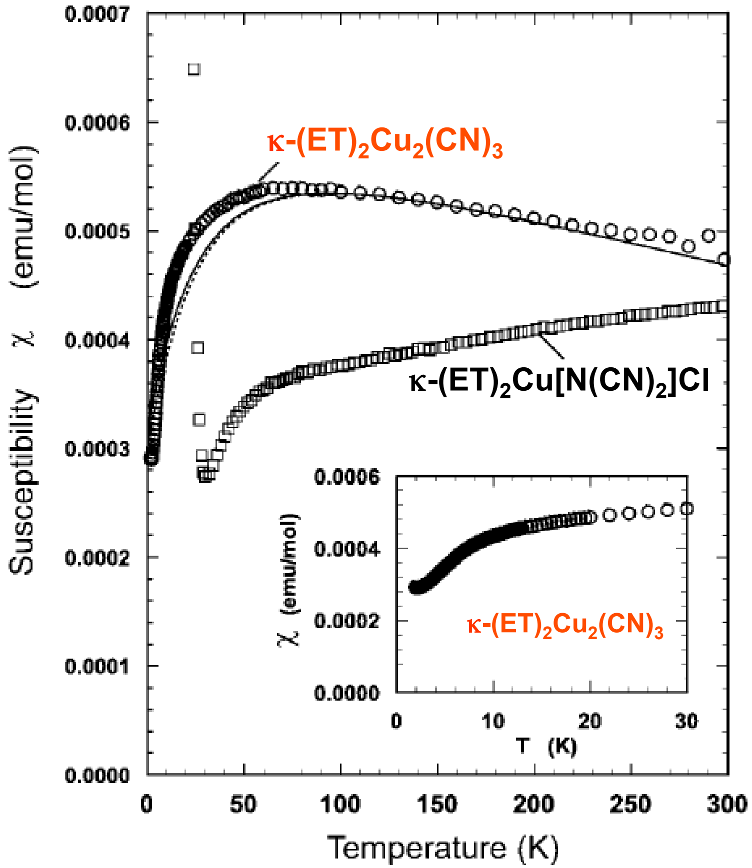
- κ-(BEDT-TTF)$_2$X systems yields a width of the Landau critical regime $\Delta T_0/T_0$ of about 8%, which is experimentally accessible the flattening of the preliminary α_{max} vs $(p - p_0)$ data might indicate such a crossover behavior.

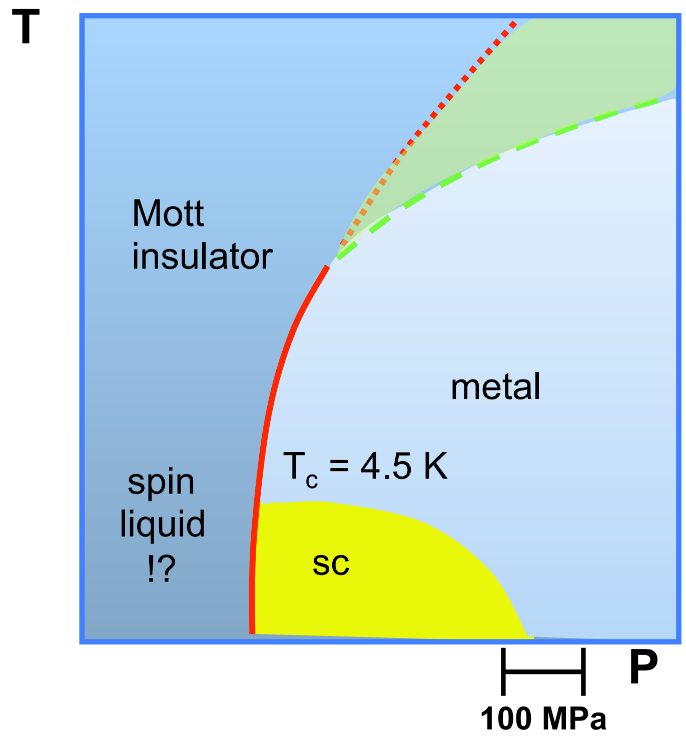
Zacharias *et al.*, PRL **109**, 176401 (12)

Crossover from 2D Ising (κ ≈ 0.5) to mean-field (κ ≈ 0.3) criticality?

Zacharias *et al.*, PRL **109**, 176401 (12)

spin-liquid - κ-$(ET)_2Cu_2(CN)_3$

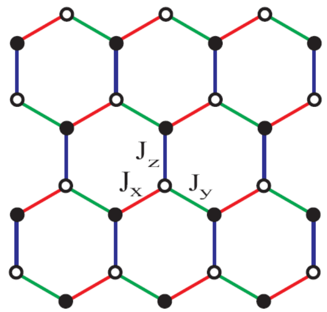




X = $Cu_2(CN)_3$
$t'/t \sim 0.8$

Kitaev spin-liquid
A_2IrO_3 (A = Na, Li)

no long-range magnetic order down to 32 mK (J = 250 K)



R. S. Manna *et al.*, PRL **104**, 016403 (10)
Kurosaki *et al.*, PRL **95**, 177001 (05)
Shimizu *et al.*, PRL **91**, 107001 (03)