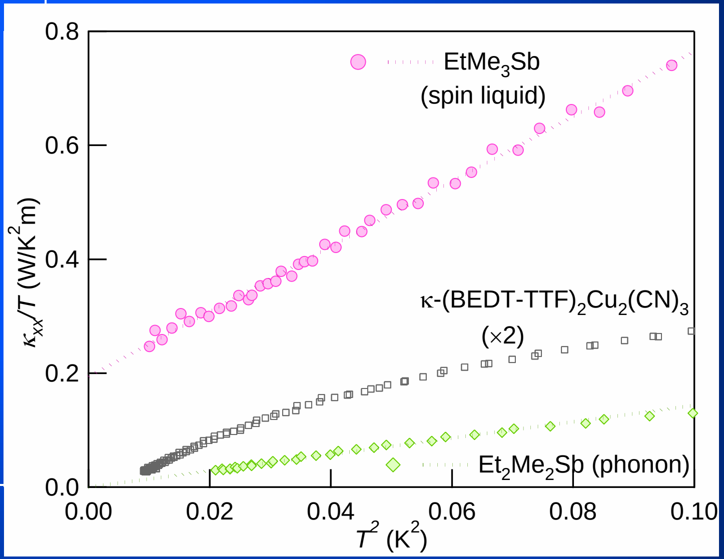
Thermal-Transport Studies of Quantum Spin Liquids in Organic Triangular Antiferromagnets

MINORU Yamashita, Riken

1. Quantum spin liquid in 2D
   - ☐ Recipe.
   - ☐ Gapless? Gapped?
2. Thermal-transport study of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$
   - ☐ Vanishing κ/T in the zero-temperature limit
     M. Y. et al., *Science*, **328**, 1246 (2010)
   - → No itinerant gapless excitation.
     Gapped? Localized gapless excitation?
3. Thermal-transport study of EtMe$_3$Sb[Pd(dmit)$_2$]$_2$
   - ☐ Finite κ/T in the zero-temperature limit
     M. Y. et al., *Science*, **328**, 1246 (2010)
   - → Gapless excitation with long mean free path

M. Y. et al., Nat. Phys. 2009
M. Y. et al., Science 2010



EXOTIC PHASES OF FRUSTRATED MAGNETS,
KITP, UCSB October 8, 2012

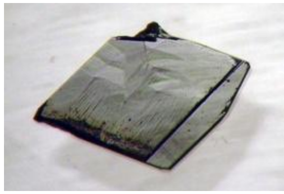
Collaborators

Kyoto University

Daiki Watanabe
Yoshinori Senshu
Sho Tonegawa
Ryuji Okazaki
Takasada Shibauchi
Yuji Matsuda

Institute for Materials Research
Tohoku University

T. Sasaki
N. Yoneyama
N. Kobayashi



κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

Riken

Yugo Oshima
Hiroshi M. Yamamoto
Reizo Kato

$EtMe_3Sb[Pd(dmit)_2]_2$

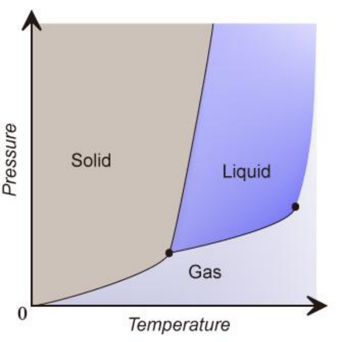
What is "exotic" phase?

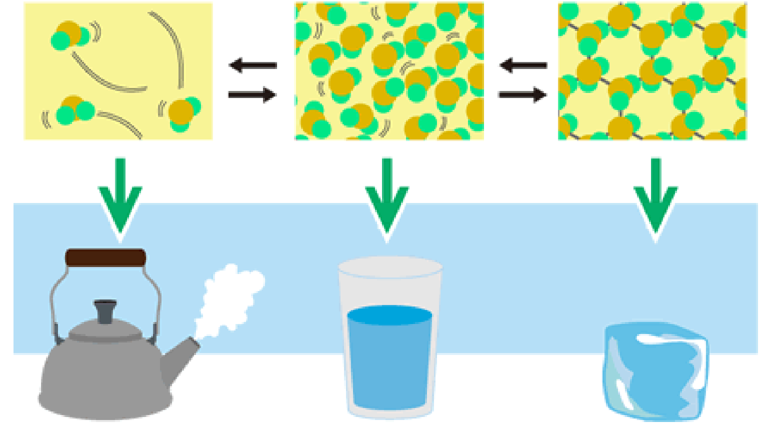
Conventional material

- ✓ Freezing in at the absolute zero temperature
- ✓ Ordering in conventional way

e.g. crystallization

Thermal fluctuation

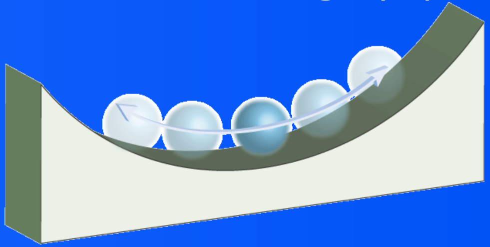




Steam Water Ice

Quantum Liquids

- No freezing by quantum fluctuation

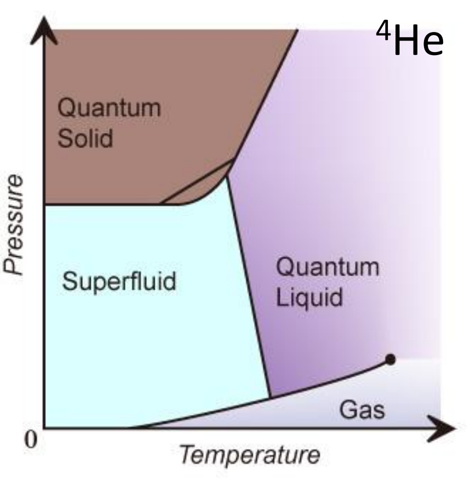


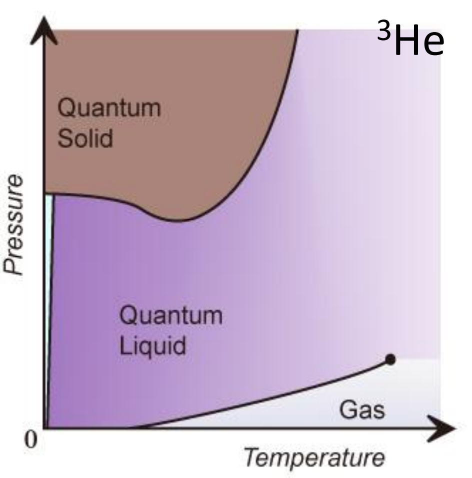
Zero point oscillation
> Interaction

Effects of quantum fluctuation explicitly emerges

Bose statics
BEC, superfluid ^{4}He

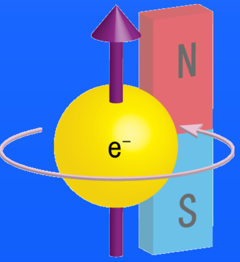
Fermi statics
Fermi liquid, Cooper pairing





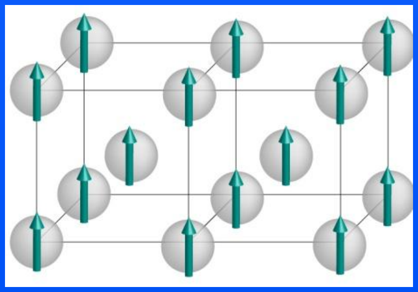
Quantum **Spin** Liquids

Spins (classical/quantum) in 3D



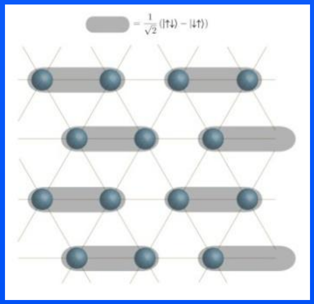
Long range order for *T* << *J*
(*J*: spin interaction)

Ferromagnetic order



Broken rotational symmetry

Valence bond solid (spin singlet)



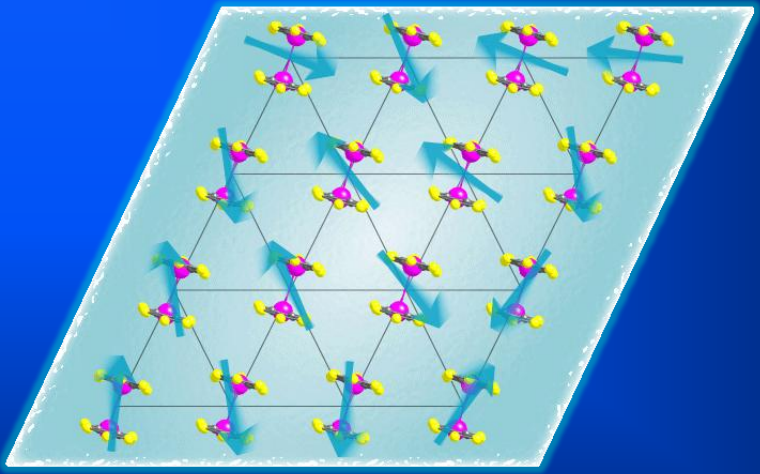
Broken translational symmetry

(exception: spin ice, 3D hyper kagomé)

Quantum Spin Liquids

1. No symmetry broken
2. Quantum fluctuation dominant
   - *T* << *J* NOT simple paramagnet
3. Long correlation of spins as liquids
   - Quantum entanglements
   - Not like paramagnet or spin glasses

Quantum **Spin** Liquid



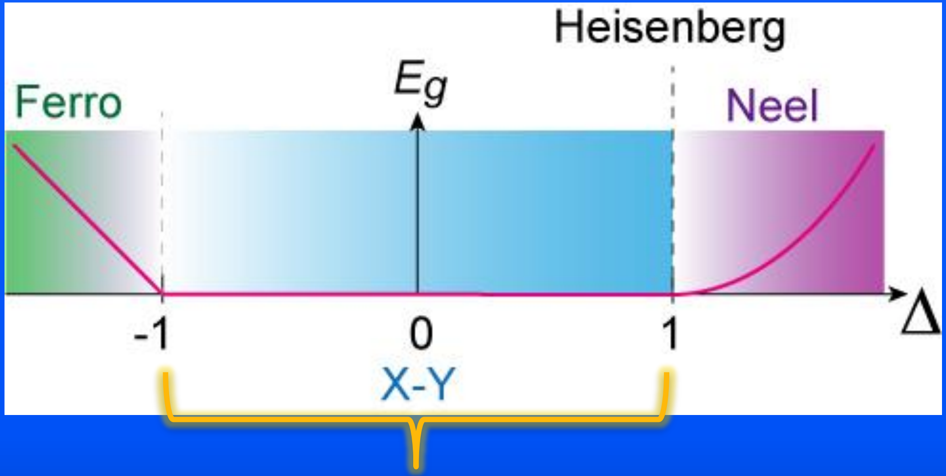
Quantum Spin Liquid in Low-dimensions

QSL in 1D

QSL state is stabilized by strong quantum fluctuation.
Exactly solvable models available (e.g. 1D XXZ chain)

1D XXZ chain (*S* = 1/2)

$$\mathcal{H} = J \sum \left(S_i^x \cdot S_j^x + S_i^y \cdot S_j^y + \Delta S_i^z \cdot S_j^z \right)$$



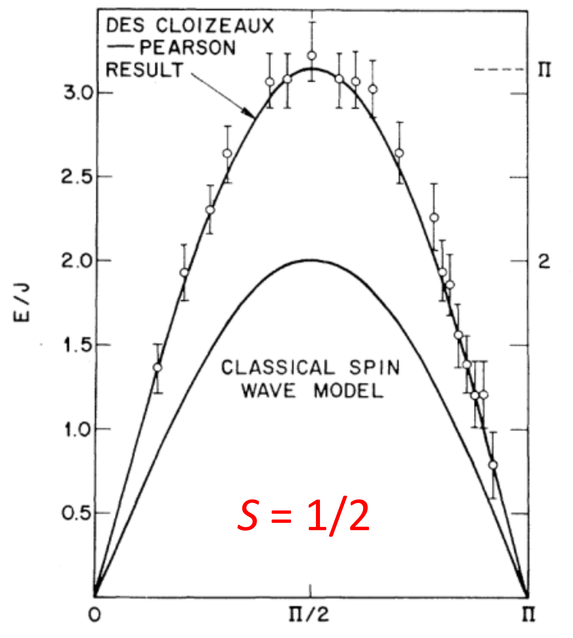
Quantum spin liquid

- ☐ No LRO
- ☐ Gapless
- ☐ Algebraic spin correlation (critical phase)

$$\langle S(r)S(0)\rangle \sim r^{-\nu}$$

Neutron scattering in $CuCl_2•2N(C_5D_5)$

Endoh, et al., (1974)



Quantum Spin Liquid in Low-dimensions

QSL in 1D

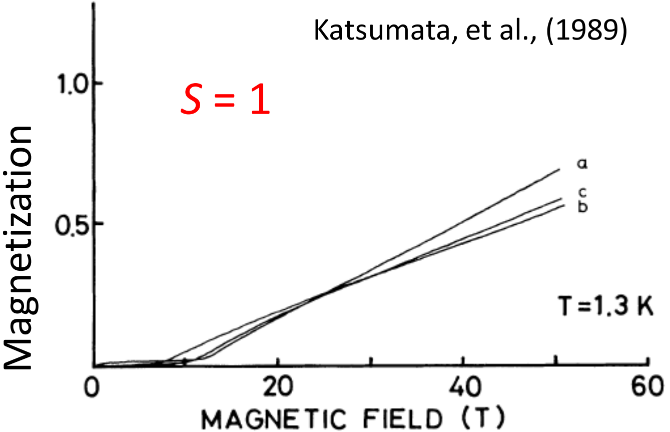
QSL state is stabilized by strong quantum fluctuation.
Exactly solvable models available (e.g. 1D XXZ chain)

Haldane gap (S = 1)

- Finite energy gap
- Exponentially decaying spin correlation

$$\langle S(r)S(0)\rangle \sim e^{-r/\xi}$$

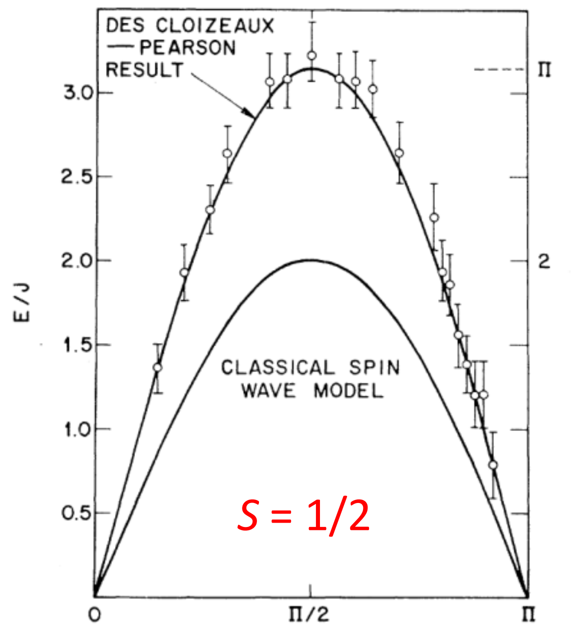
Magnetization of NENP



Katsumata, et al., (1989)

Neutron scattering in $CuCl_2 \bullet 2N(C_5D_5)$

Endoh, et al., (1974)



Quantum Spin Liquid in Low-dimensions

How about in 2D？

Order or not order?

- geometrical frustration plays important rule

Many theories proposed

- Resonating-valence-bond liquid
- Chiral spin liquid
- Quantum dimer liquid
- Z_2 spin liquid
- Algebraic spin liquid
- Spin Bose Metal
- Etc.,,

New quantum condensed-state may be realized!!

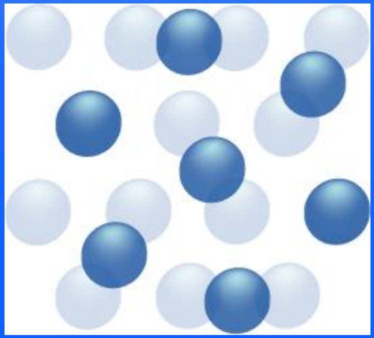
Elementary exciation not yet identified

- Spinon with Fermi surface
- Vison
- Majorana fermions

- Recent discoveries of QSL candidates
- No LRO found down to experimentally reachable low temperature

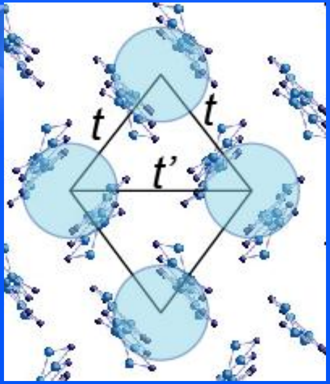
→ New frontier of condensed-matter

Some of promising candidates of 2D quantum spin liquids



^{3}He absorbed on Graphite

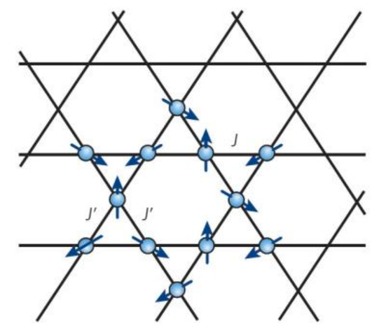
Ishida et al., PRL (1997)
Masutomi et al., PRL (2004)



Organic compounds

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$
EtMe$_3$Sb[Pd(dmit)$_2$]$_2$
κ-H$_3$(Cat-EDT-TTF)$_2$

Shimizu et al., PRL (2003)
Itou et al., PRB (2004)
Isono et al., JPSJ meeting (2012)



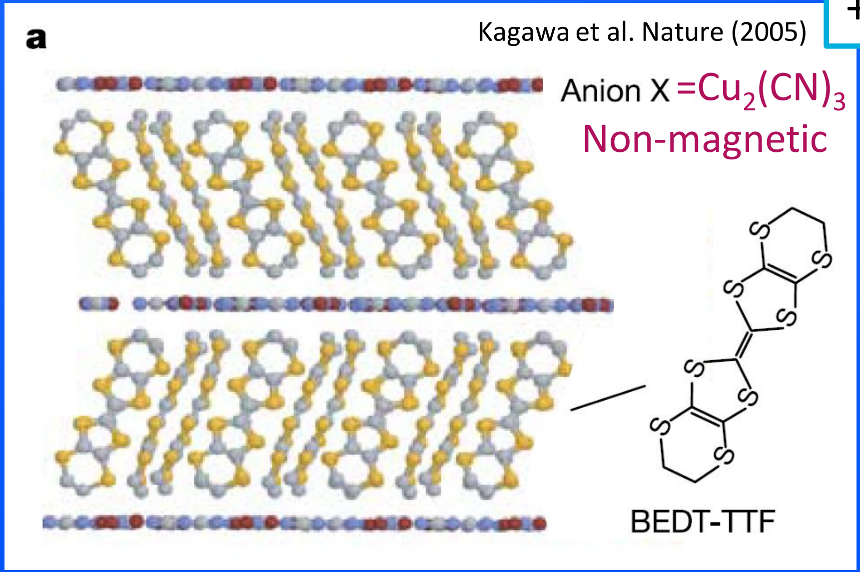
Kagomé

Herbertsmithite,
Volborthite,
Rb$_2$Cu$_3$SnF$_{12}$, Na$_3$Ir$_3$O$_8$,
etc.

Shores, JACS (2005)
Hiroi, JPSJ (2001)
Morita JPSJ (2008)
Okamoto, PRL (2007)

κ-(BEDT-TTF)$_2$X

Layer structure



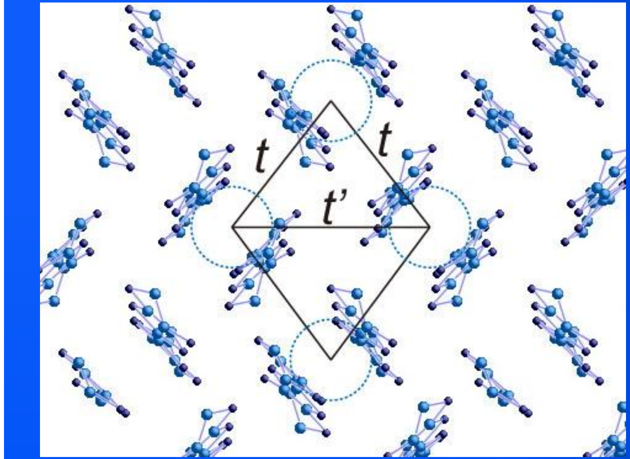
Kagawa et al. Nature (2005)

Anion X =$Cu_2(CN)_3$

Non-magnetic

Dimerization of face-to-face BEDT-TTF molecules
+0.5/molecule → 1.0/dimer

Dimer-Mott insulator



Ideal triangular lattice

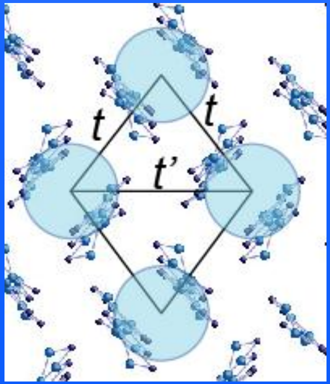
$U/t \quad \sim \quad 7$ Not strong Mott insulator

$t'/t \quad \sim \quad 1.06$ Extended Hückel

$\sim \quad 0.8$ *ab* initio

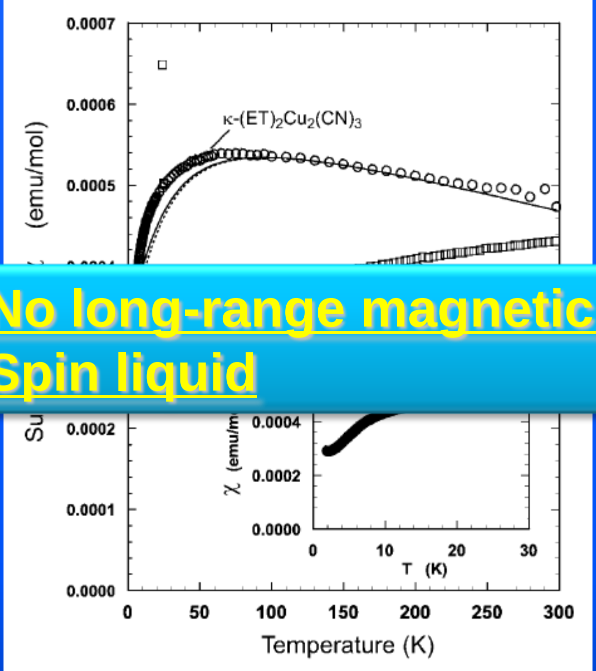
Kandpal et al. (2009)
Nakamura et al. (2010)

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

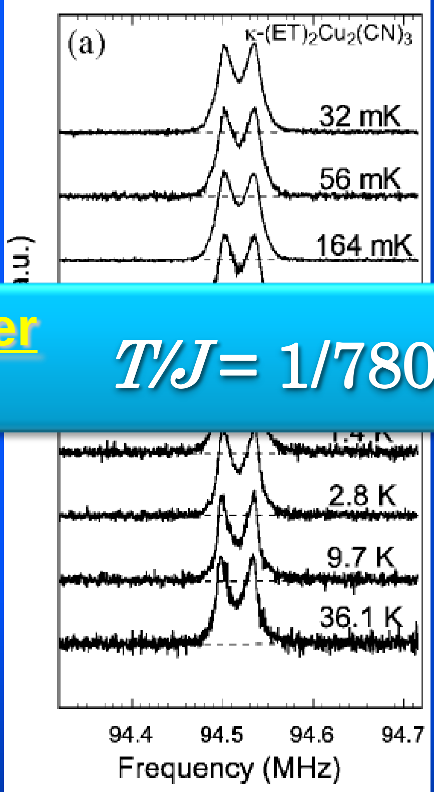


Triangular-type temperature dependence in χ

J ~ 250 K



No sign of internal magnetic field down to **32 mK**!!



No long-range magnetic order

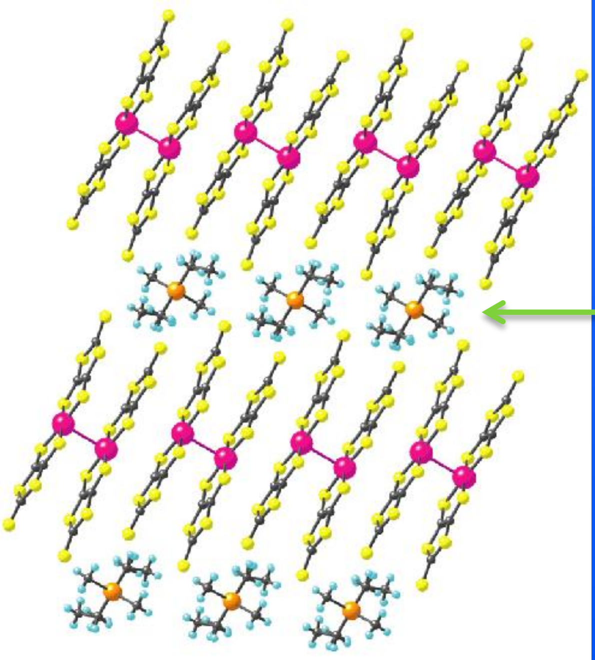
Spin liquid

$T/J = 1/7800$

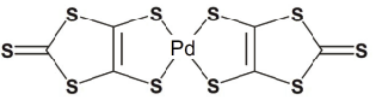
Y. Shimizu etal, PRL **91**, 107001 (2003)

β′-(Cation)[Pd(dmit)$_2$]$_2$

SIDE VIEW



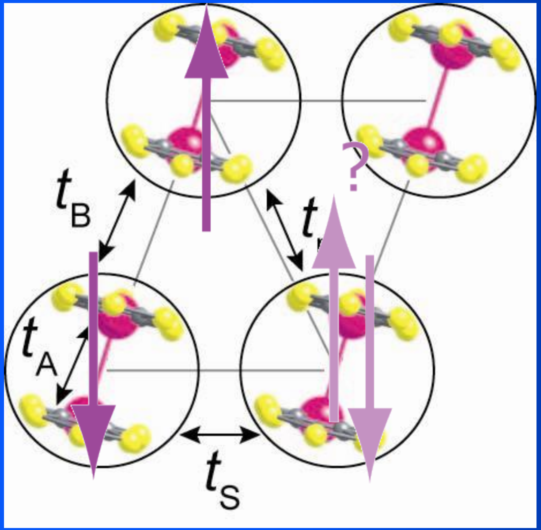
2D layer of Pd(dmit)$_2$ molecule



Cation layer
Non-magentic
X = EtMe$_3$Sb,
Et$_2$Me$_2$Sb,
etc.

2D spin system

TOP VIEW



$$t_A \sim 0.5\ \mathrm{eV} \gg t_B, t_S, t_r \sim 30\ \mathrm{mV}$$

Dimerization → Half-filled Mott insulator

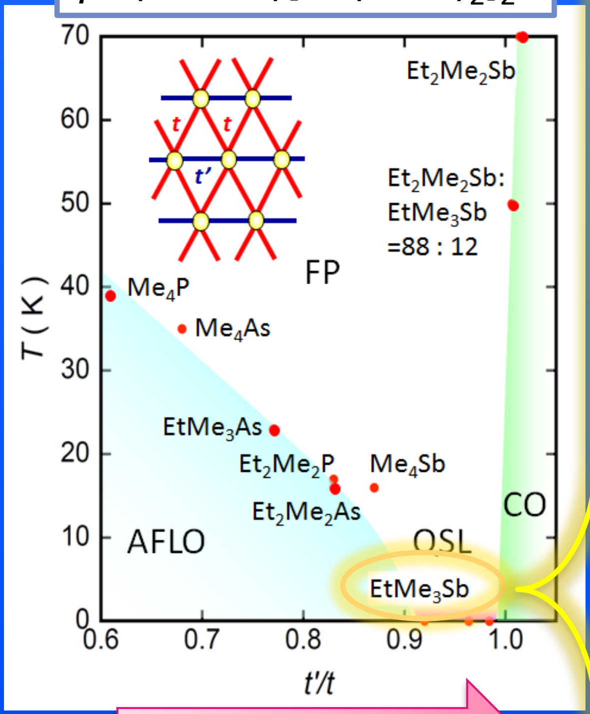
Insulator with *S* = 1/2
Triangular lattice

✓Very clean single crystal available
✓“Weak” Mott insulator (small *U*/*t*)
✓Variety of material syntheses available

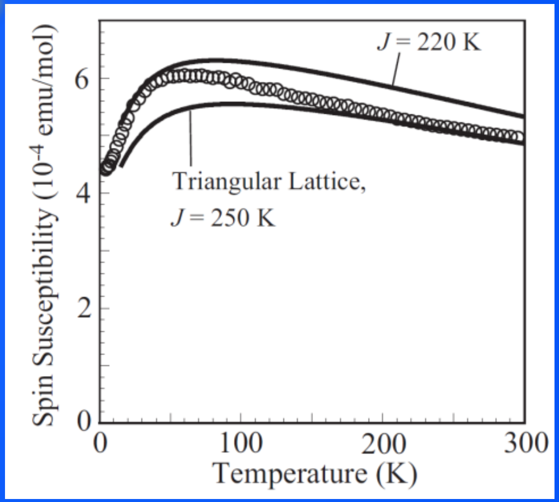
QSL in $EtMe_3Sb[Pd(dmit)_2]_2$

K. Kanoda and R. Kato
Annu. Rev. Condens. Matter Phys. (2011)

β'-(Cation)$[Pd(dmit)_2]_2$



Frustration

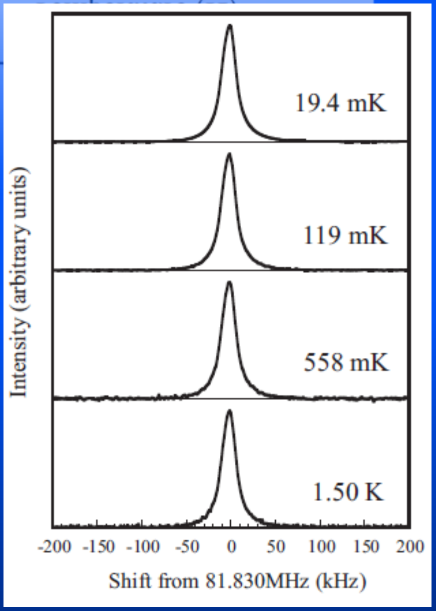


① $\chi(T)$: 2D triangular

J = 220 ~ 250 K

~ *J*/10,000 at 20 mK

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



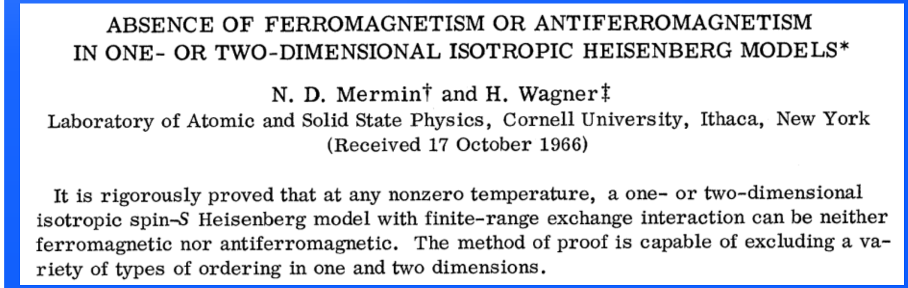
② No LRO down to
~*J*/10,000

Quantum spin liquid!!

Itou et al., J. Phys. Conf.
Ser. **145**, 012039 (2009)

QSL in EtMe$_3$Sb[Pd(dmit)$_2$]$_2$

Mermin-Wagner PRL (1966)



ABSENCE OF FERROMAGNETISM OR ANTIFERROMAGNETISM
IN ONE- OR TWO-DIMENSIONAL ISOTROPIC HEISENBERG MODELS*

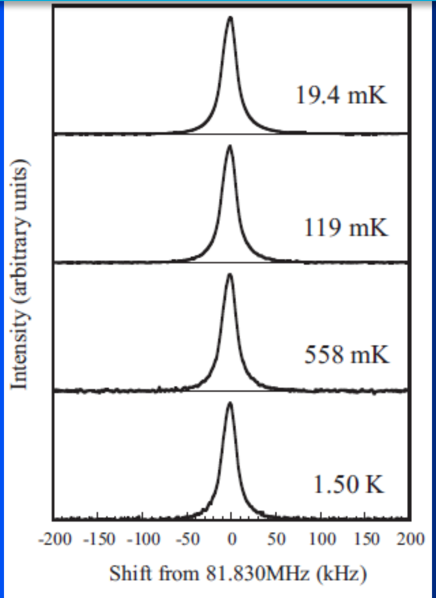
N. D. Mermin† and H. Wagner‡
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York
(Received 17 October 1966)

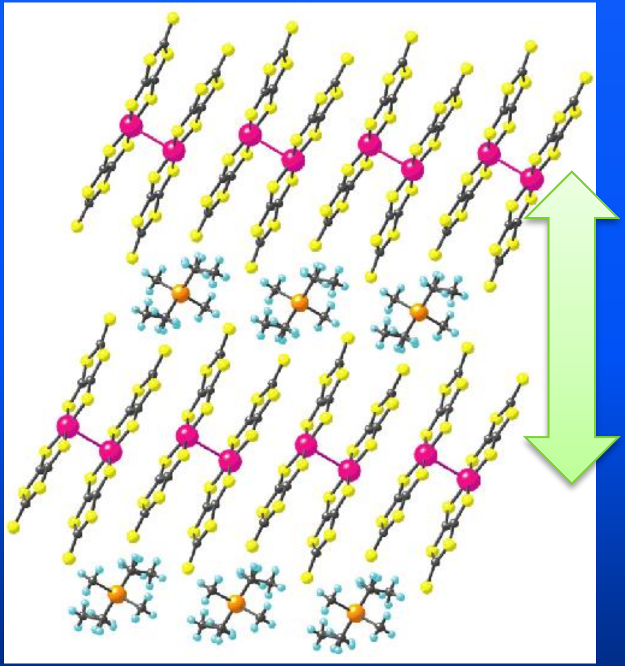
It is rigorously proved that at any nonzero temperature, a one- or two-dimensional isotropic spin-S Heisenberg model with finite-range exchange interaction can be neither ferromagnetic nor antiferromagnetic. The method of proof is capable of excluding a variety of types of ordering in one and two dimensions.

No LRO at finite T in ***ideal*** 2D system.

No LRO down to J/10,000

Itou et al., J. Phys. Conf. Ser. **145**, 012039 (2009)





Finite inter-layer coupling

$$t_{\text{inter layer}} \sim t/100$$

$$T_N/T \sim \sqrt{J'/J} \sim 1/100$$

Spins choose quantum spin liquid state as a stable ground state

(c.f. LRO in 1D chain material (e.g. Sr$_2$CuO$_4$) due to inter-chain coupling)

You got new material. Now what?

New material on Mars?

Sol 46th, NASA/JPL-Caltech

Metal?

- Good metal?
- Non-Fermi liquid?
- New superconductor?

$\boxed{\Delta = 0}$

Conductive spin liquid

Insulator?

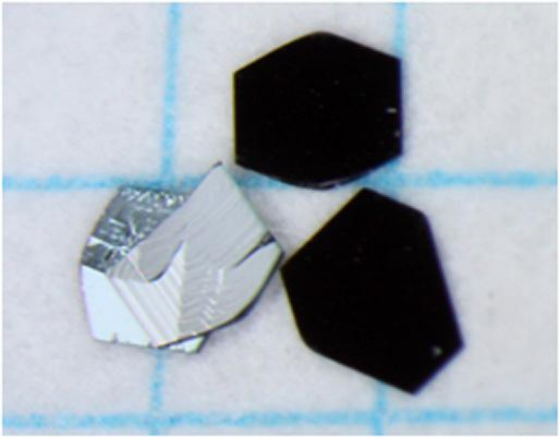
Band insulator?
Mott insulator?
Topological insulator?

$\boxed{\Delta > 0}$

Non-conductive spin liquid

You got new material. Now what?

$EtMe_3Sb[Pd(dmit)_2]_2$



κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

Metal?

- Good metal?
- Non-Fermi liquid?
- New superconductor?

$\boxed{\Delta = 0}$

Conductive spin liquid
$EtMe_3Sb[Pd(dmit)_2]_2$

Insulator?

Band insulator?
Mott insulator?
Topological insulator?

$\boxed{\Delta > 0}$

Non-conductive spin liquid
κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

Gapless or gapped QSL

Gapless or Gapped?

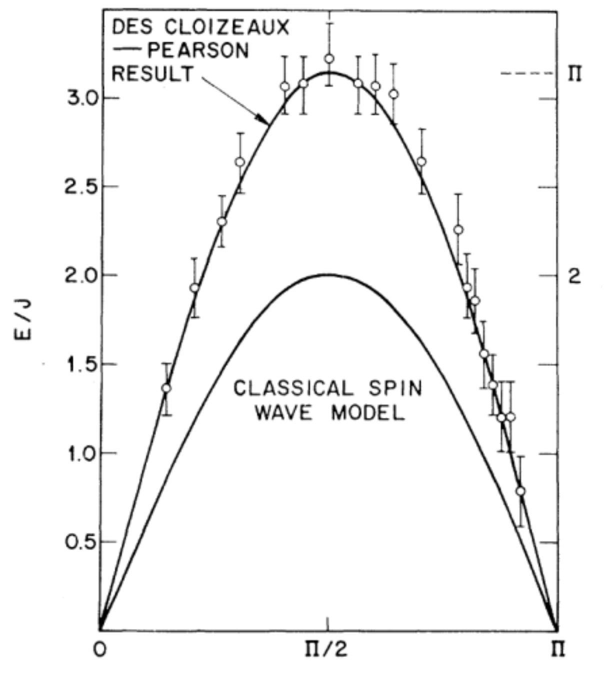
Neutron scattering:

Not available for organic compound

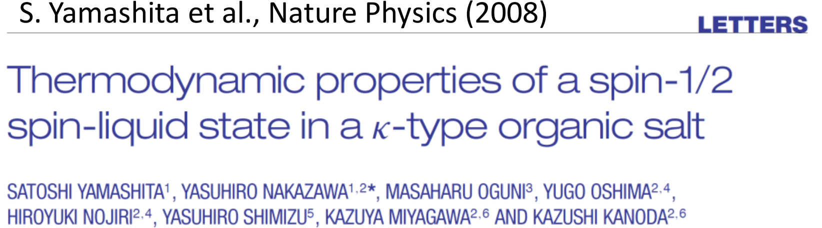
Thermodynamic measurements

Heat capacity, magnetization, etc.

Endoh, et al., (1974)



C measurement of κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

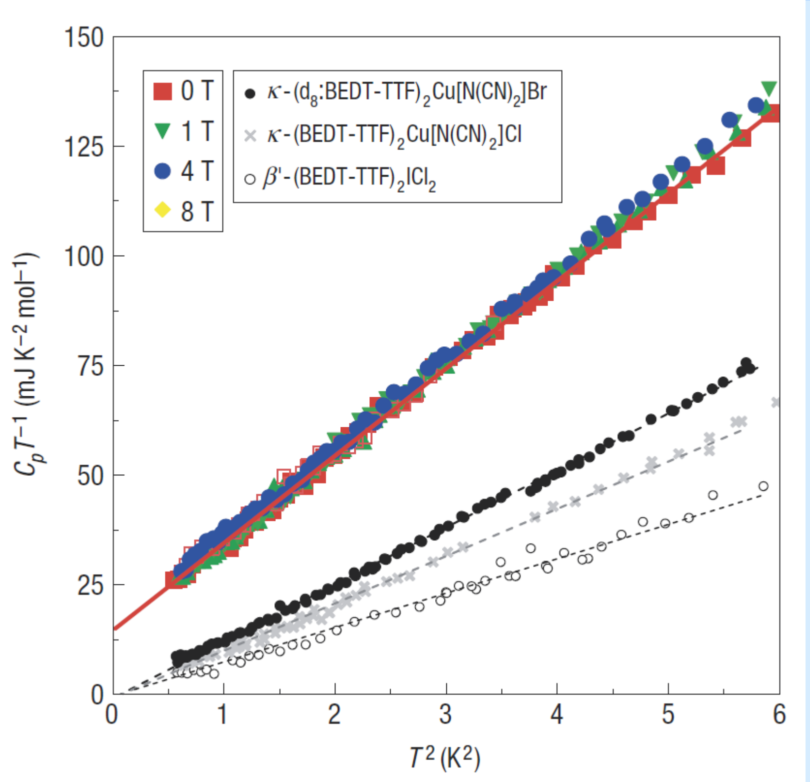


S. Yamashita et al., Nature Physics (2008)

LETTERS

Thermodynamic properties of a spin-1/2 spin-liquid state in a κ-type organic salt

SATOSHI YAMASHITA[1], YASUHIRO NAKAZAWA[1,2]*, MASAHARU OGUNI[3], YUGO OSHIMA[2,4], HIROYUKI NOJIRI[2,4], YASUHIRO SHIMIZU[5], KAZUYA MIYAGAWA[2,6] AND KAZUSHI KANODA[2,6]



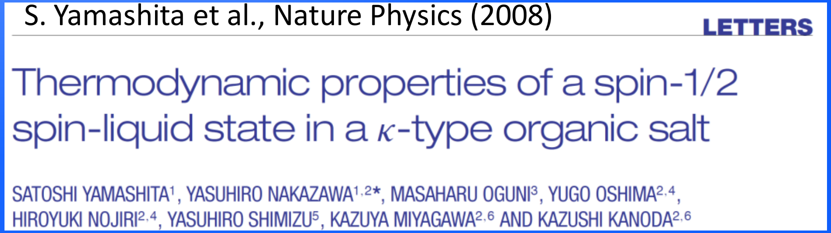
Finite residual in the zero-temperature limit of *C*/*T*

$$C/T = \gamma + \beta T^2$$

$$\gamma = 15\ \frac{\text{mJ}}{\text{K}^2\text{mol}}$$

Evidence for gapless excitation

C measurement of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

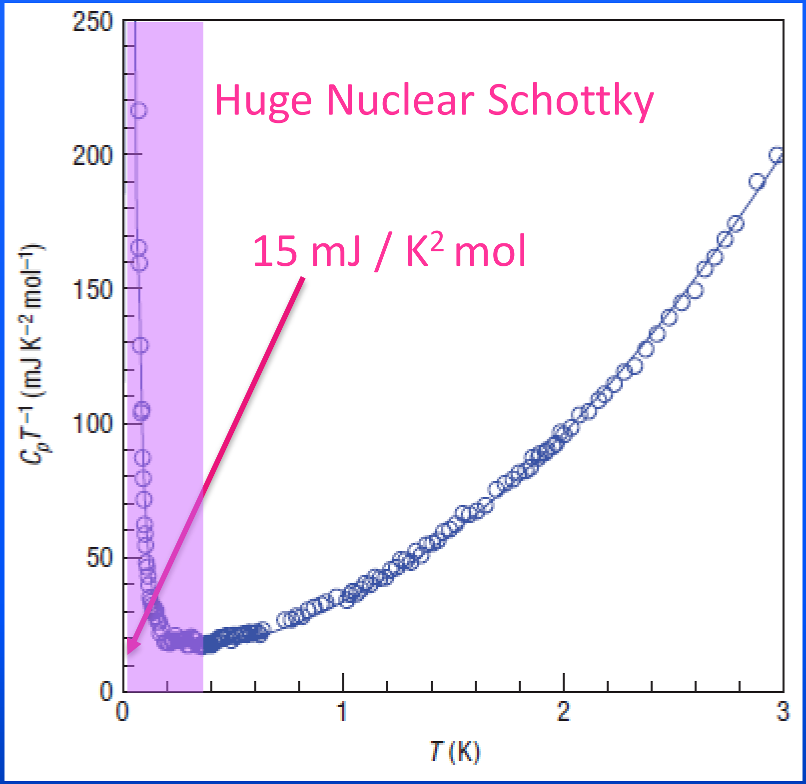


S. Yamashita et al., Nature Physics (2008)

LETTERS

Thermodynamic properties of a spin-1/2 spin-liquid state in a κ-type organic salt

SATOSHI YAMASHITA[1], YASUHIRO NAKAZAWA[1,2*], MASAHARU OGUNI[3], YUGO OSHIMA[2,4], HIROYUKI NOJIRI[2,4], YASUHIRO SHIMIZU[5], KAZUYA MIYAGAWA[2,6] AND KAZUSHI KANODA[2,6]



Finite residual in the zero-temperature limit of *C*/*T*

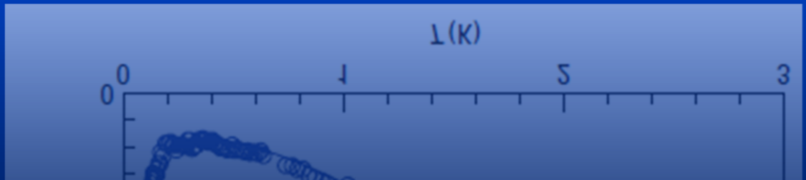
$$C/T = \gamma + \beta T^2$$

$$\gamma = 15\ \frac{\mathrm{mJ}}{\mathrm{K^2 mol}}$$

Evidence for gapless excitation

Huge nuclear Schottky below ~ 300 mK

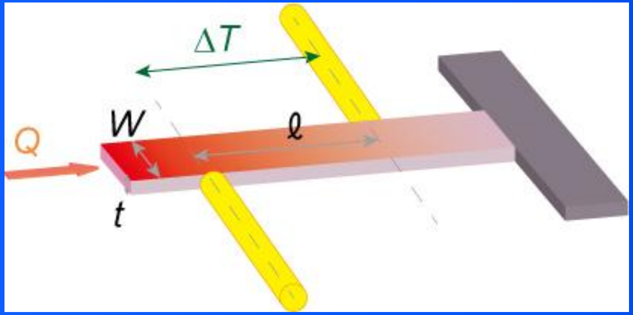
→ Measurements reliable in lower temperature (T < 300 mK) required.

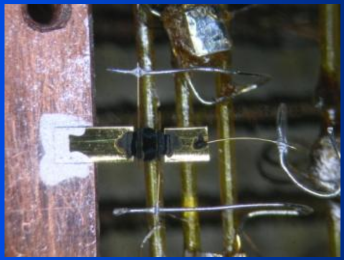


Thermal-transport & Magnetic torque

☐ Thermal conductivity

$$\frac{1}{wt}Q = \kappa\frac{\Delta T}{\ell}$$





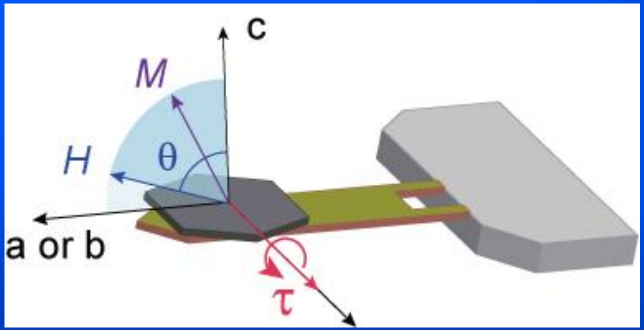
κ_{xx} Measurement

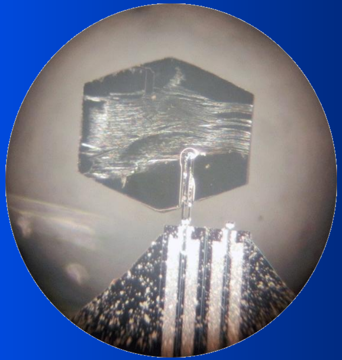
Selectively sensitive to itinerant excitations.
Not affected by localized impurity (Schottky anomaly).

☐ Magnetic torque measurement

$$\tau = \frac{1}{2}\mu_0 H^2 V \Delta\chi \sin 2\theta$$

- Only anisotropic susceptibility detected.
- Isotropic impurity (free spins) cancelled.
- High sensitivity. ONE single crystal measurement available.

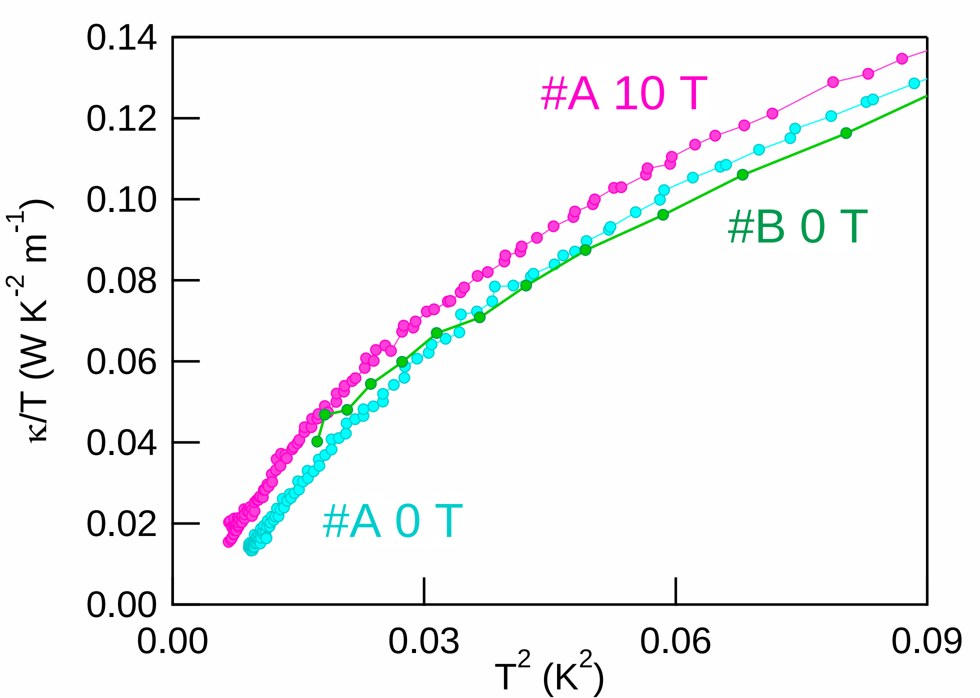




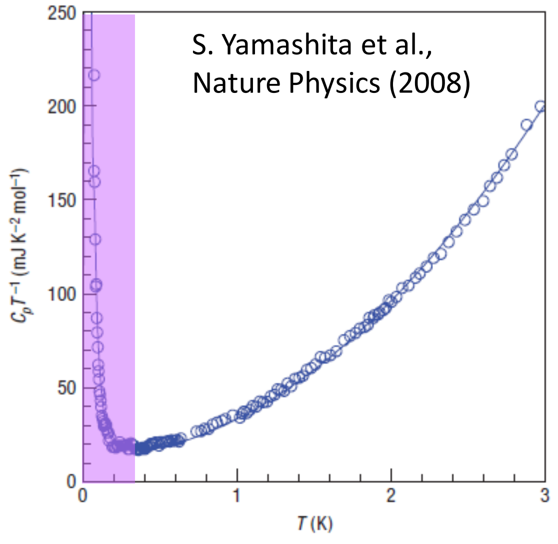
Thermal conductivity of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

κ of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ below 300 mK

M. Y., Nature Physics (2009)



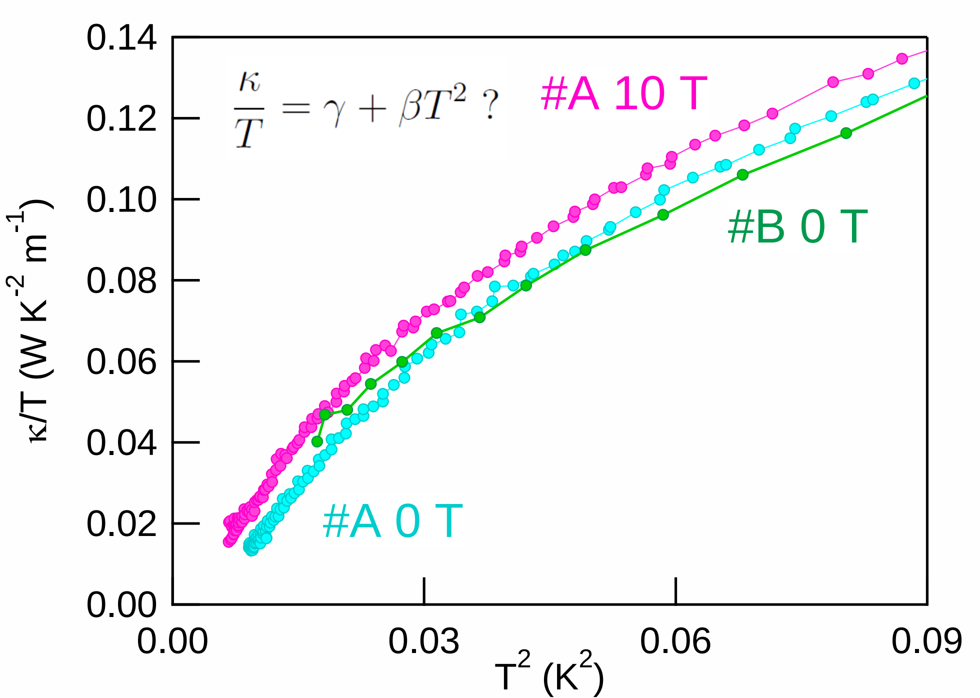
- No Schottky anomaly



S. Yamashita et al., Nature Physics (2008)

κ of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$ below 300 mK

M. Y., Nature Physics (2009)



- No Schottky anomaly
- Convex, non-T^3 dependence in κ
- Magnetic fields enhance κ

$$\kappa = \kappa_{phonon} + \kappa_{spin}$$

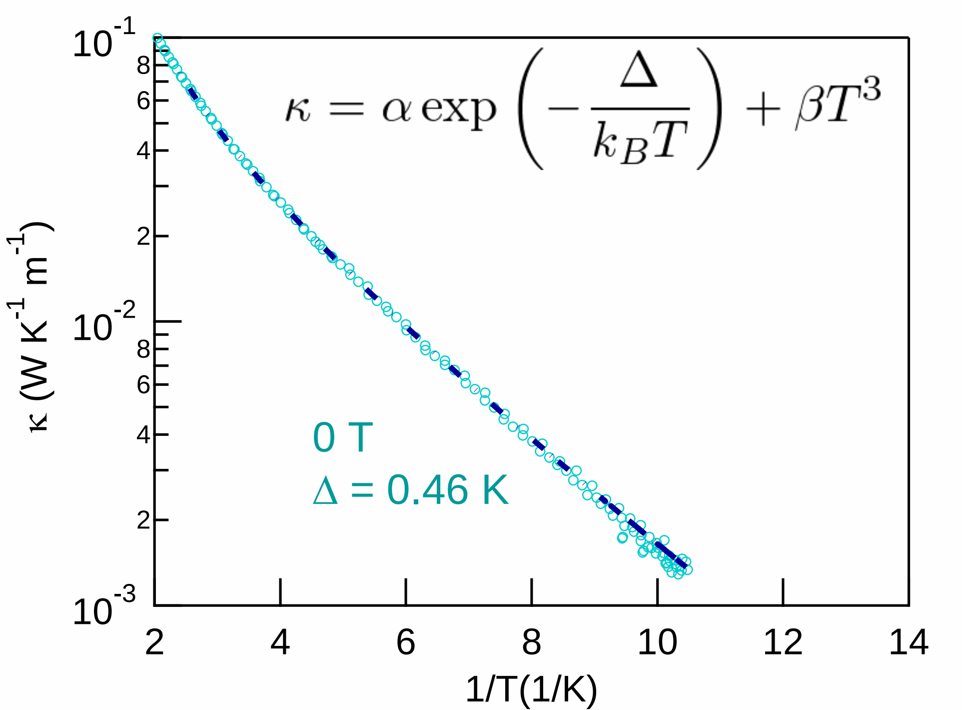
$$\left(\kappa_{phonon} \propto T^3 \text{ in low T}\right)$$

$$\underline{\gamma = 0}$$

No conductive spin excitation.

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$: Arrhenius plot

M. Y., Nature Physics (2009)



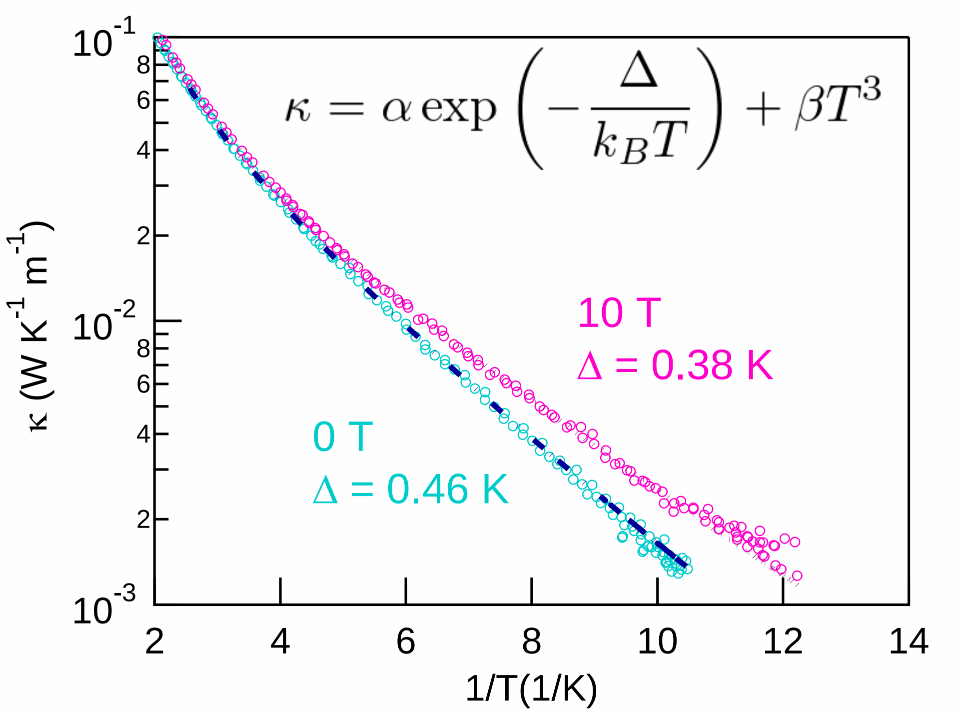
- Arrhenius behavior for T < Δ !

- Tiny gap
  - Δ = 0.46 K ~ *J*/500

M. Y., Nature Physics (2009)

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$: Arrhenius plot

M. Y., Nature Physics (2009)



- Arrhenius behavior for T < Δ !

- Tiny gap
  - ➢ **Δ = 0.46 K ~ *J*/500**

- Insensitive to magnetic field
  0T 0.46 K → 10T 0.38 K

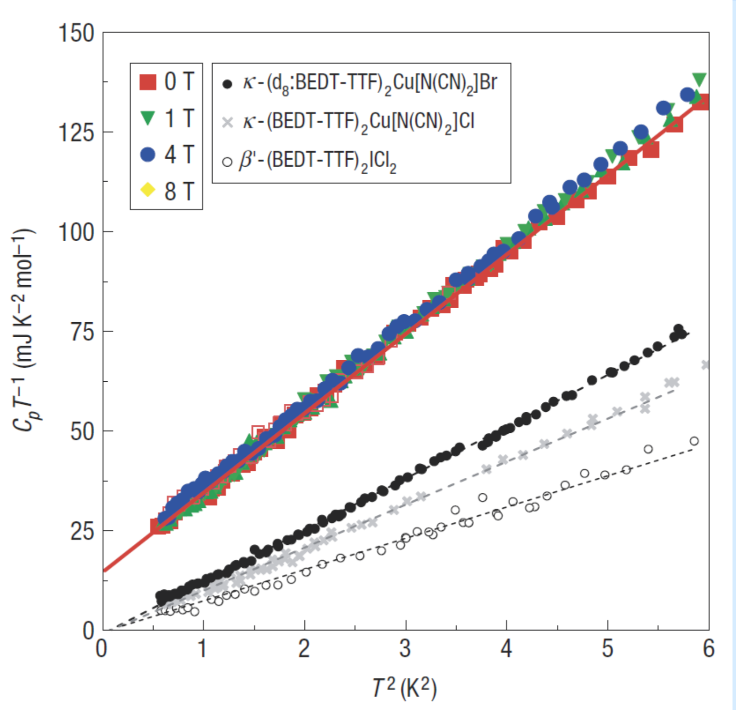
Discrepancy C & κ in κ-(BET-TTF)$_2$Cu$_2$(CN)$_3$

Yamashita-Yamashita Conflict

Small Δ ~ 0.46 K, resolved only in low temperature.
Bad contact in thermal conductivity?

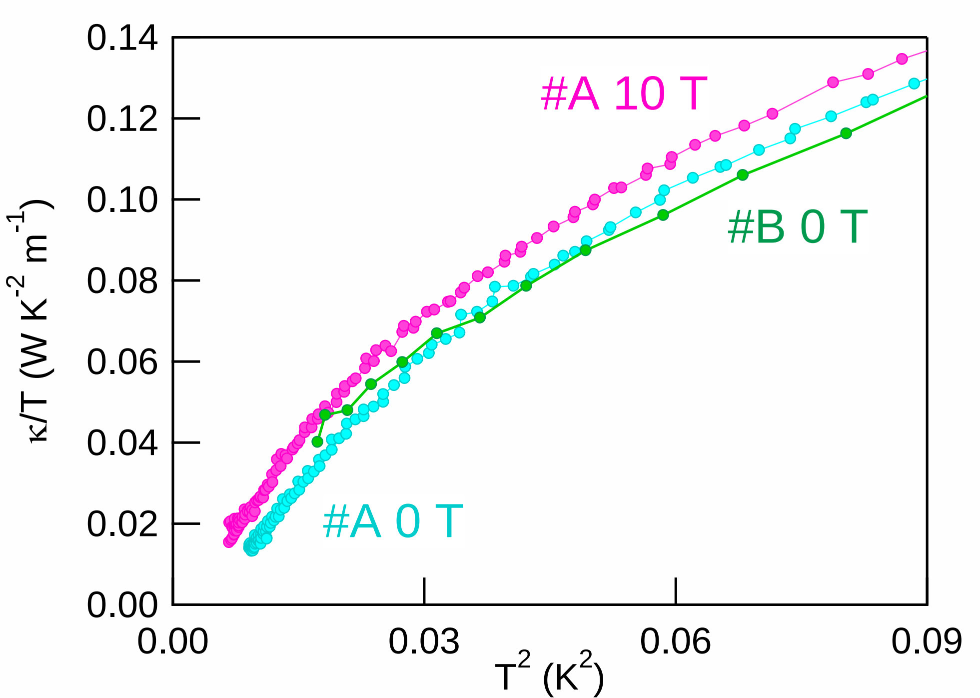
Heat capacity $\Delta = 0$

S. Yamashita et al., Nature Physics (2008)



Thermal conductivity $\Delta > 0$

M. Yamashita et al., Nature Physics (2009)



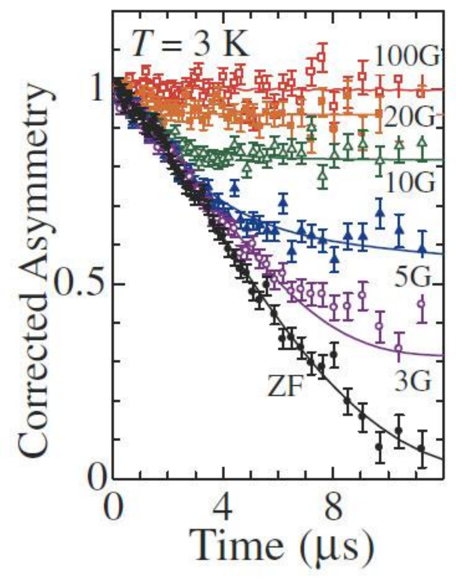
Discrepancy C & κ in κ-(BET-TTF)$_2$Cu$_2$(CN)$_3$

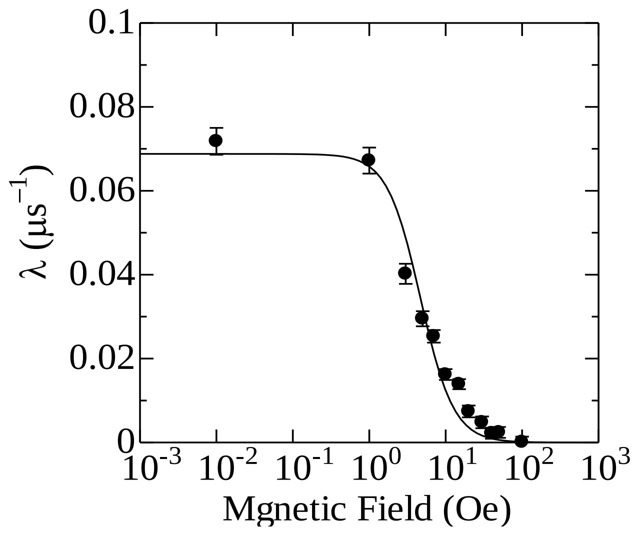
μSR measurements

Two components

Nakajima et al., JPSJ-81-063706 (2012)

High temperature T = 3 K





Single component fitting

$$G_{\mathrm{KT}}(\Delta, t; H_{\mathrm{LF}})\mathrm{e}^{-\lambda t}$$

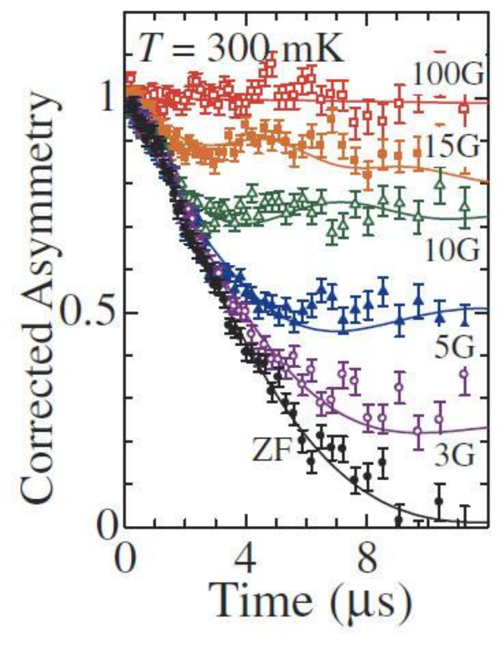
Discrepancy C & κ in κ-(BET-TTF)$_2$Cu$_2$(CN)$_3$

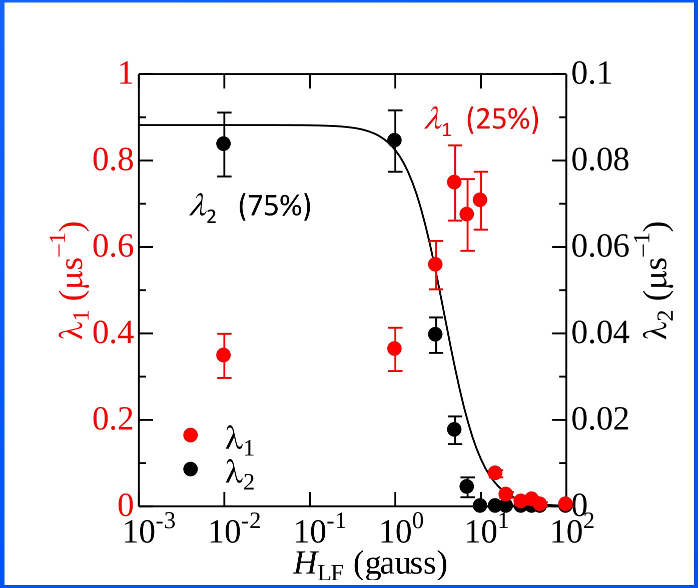
μSR measurements

Two components

Nakajima et al., JPSJ-81-063706 (2012)

Low temperature T = 0.3 K





Two component fitting

$$G_{KT}(t)(A_1 e^{-\lambda_1 t} + A_2 e^{-\lambda_2 t})$$

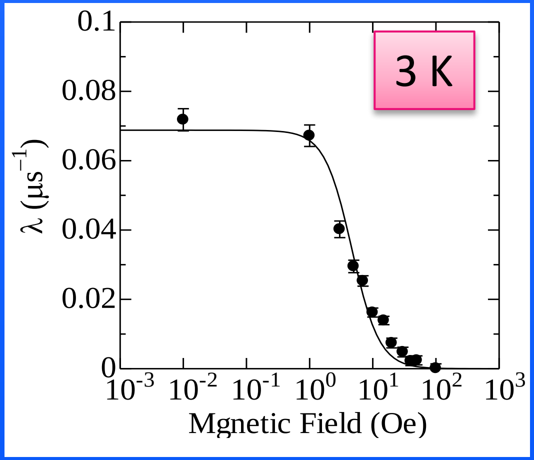
λ_1: singlet components appears in low T.

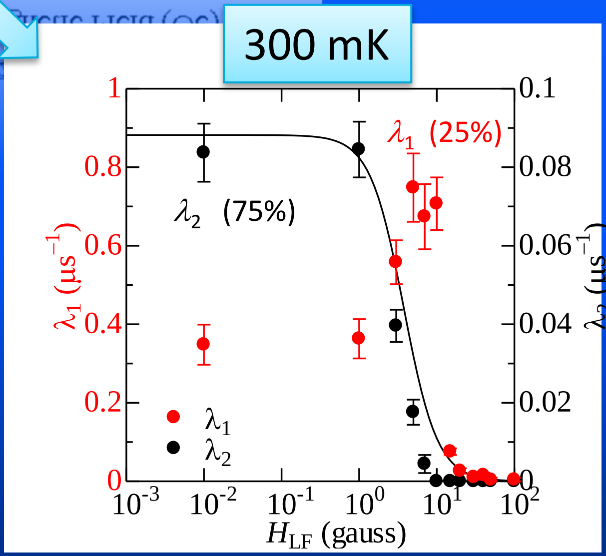
λ_2: paramagnetic component existing from high T.

Discrepancy C & κ in κ-(BET-TTF)$_2$Cu$_2$(CN)$_3$

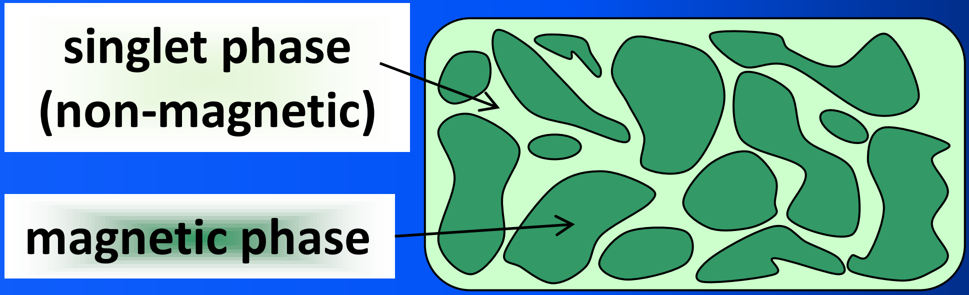
Two components in μSR

Nakajima et al., JPSJ-81-063706 (2012)





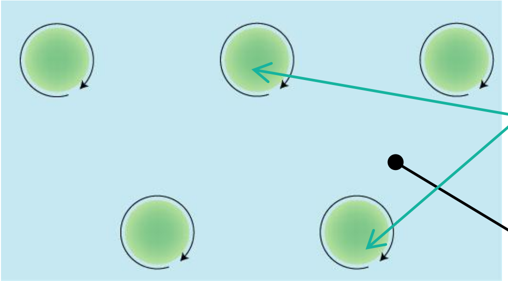
T. Goto (private cmmunication)



singlet phase (non-magnetic)

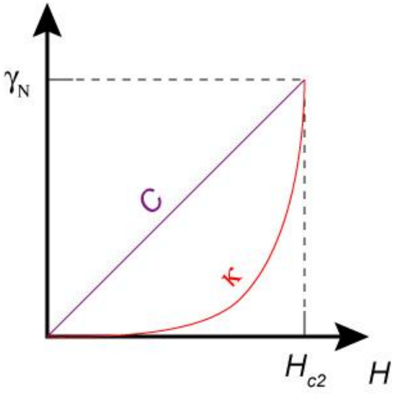
magnetic phase

Different field dependence in SC



Gapless excitation
Localized in vortices

Gapped
(s-wave SC)



- Heat capacity probes all excitations.
- Thermal conductivity sees itinerant ones only

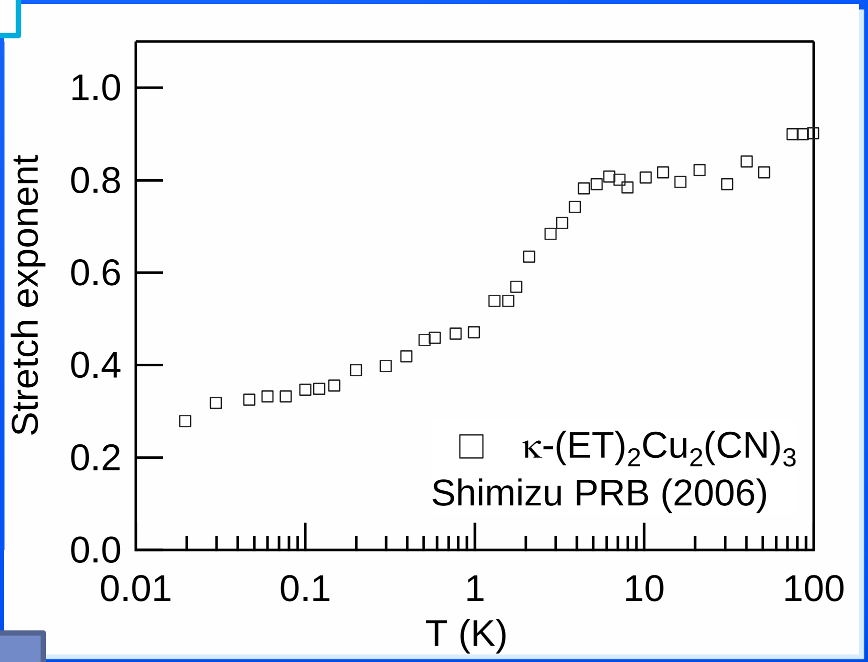
6 K anomaly

Stretch exponent in NMR relaxation

$$\frac{M(\infty)-M(t)}{M(\infty)} = \exp\left[-(t/T_1)^{\beta}\right]$$

Homogeneous

Inhomogeneous



Stretched exponent β

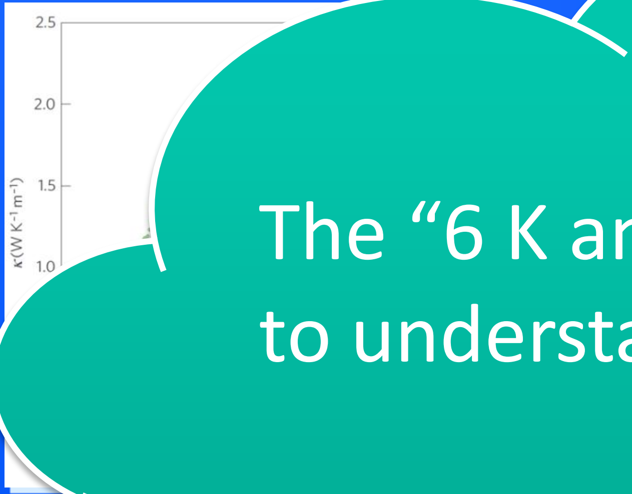
$\beta = 1$: homogeneous

$\beta < 1$: inhomogeneous

6 K anomaly

Thermal conductivity

M. Y., Nature Physics (2009)

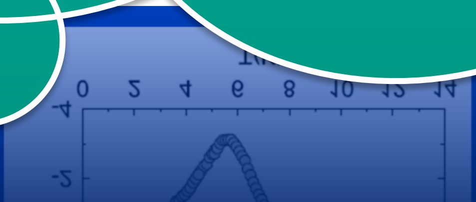


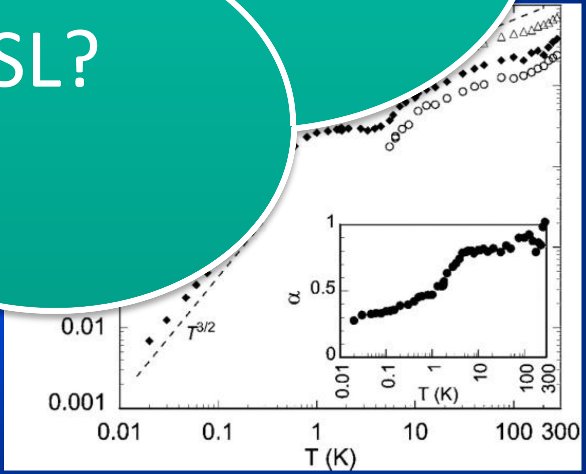
Heat capacity

hita, Natur 08)

The “6 K anomaly” is likely a key to understand the discrepancy.

How about homogeneous QSL?





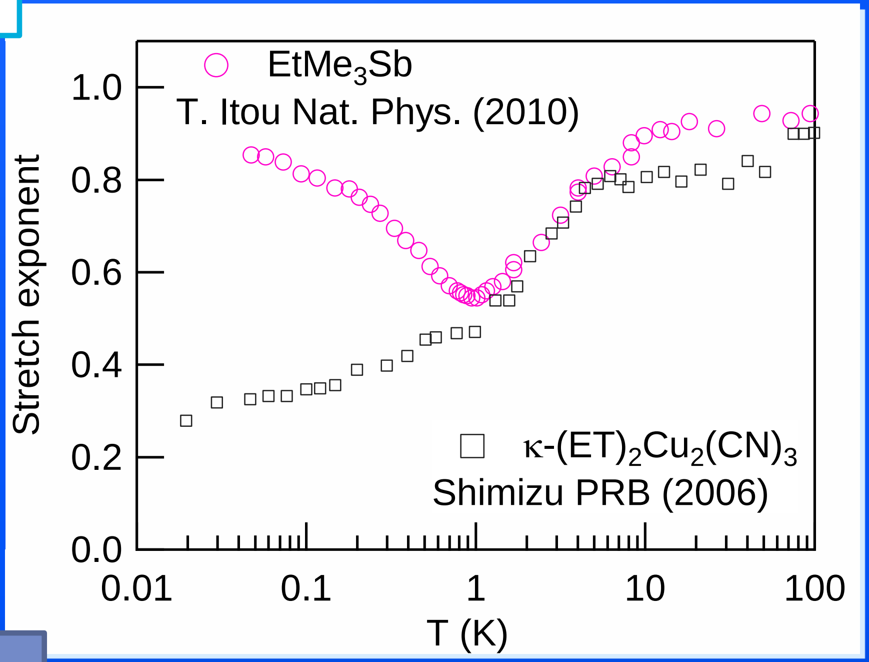
κ-(BEDT-TTF)$Cu_2(CN)_3$ and $EtMe_3Sb[Pd(dmit)_2]_2$

Stretch exponent in NMR relaxation

$$\frac{M(\infty)-M(t)}{M(\infty)}=\exp\left[-(t/T_1)^{\beta}\right]$$

Homogeneous

Inhomogeneous



Stretched exponent β

$\beta = 1$: homogeneous

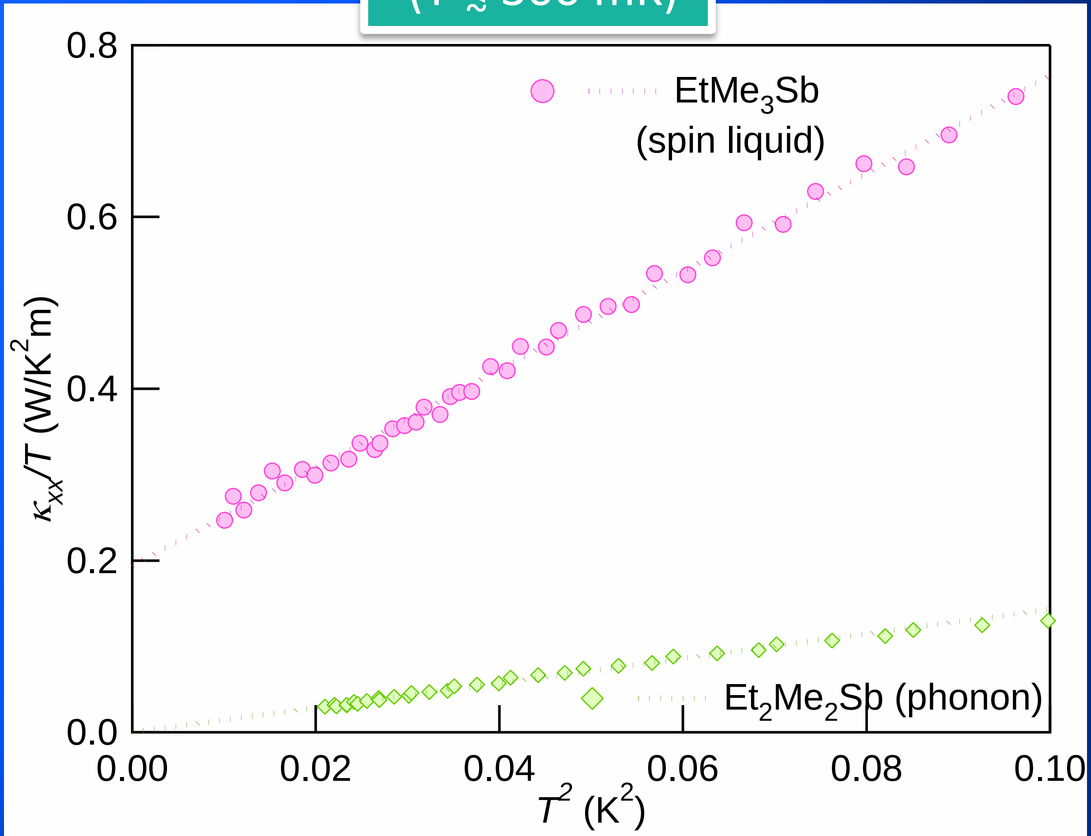
$\beta < 1$: inhomogeneous

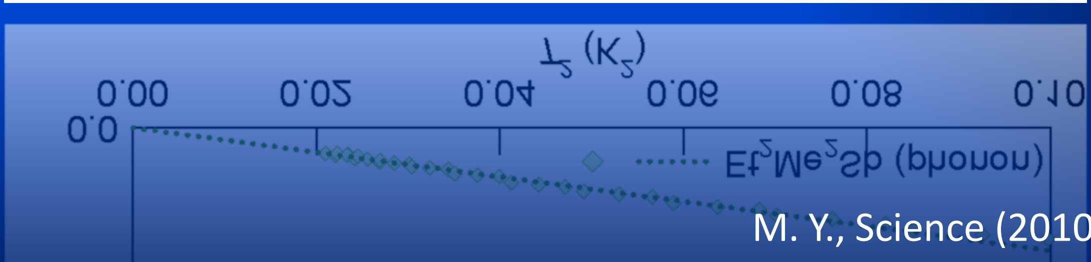
Homogeneity of spin liquid makes difference?

Thermal conductivity of $EtMe_3Sb[Pd(dmit)_2]_2$

Thermal conductivity of $EtMe_3Sb[Pd(dmit)_2]_2$

κ/T vs T^2 plot
($T \lesssim 300$ mK)





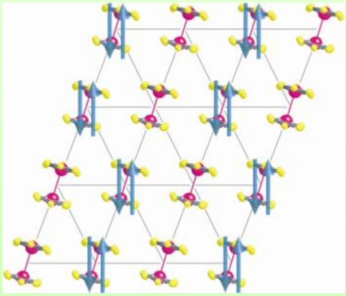
M. Y., Science (2010)

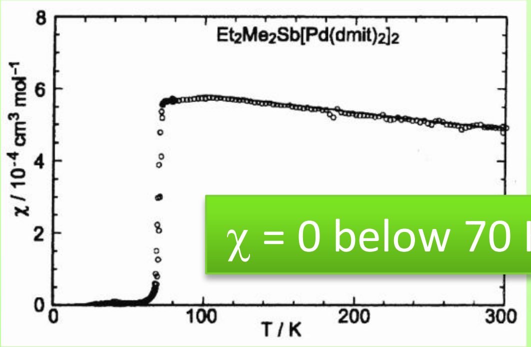
Thermal conductivity of $EtMe_3Sb[Pd(dmit)_2]_2$

$Et_2Me_2Sb[Pd(dmit)_2]_2$

- Similar lattice structure (*C*2/*c*)
- Charge order
- Spin singlet

$\kappa = \kappa_{phonon}$

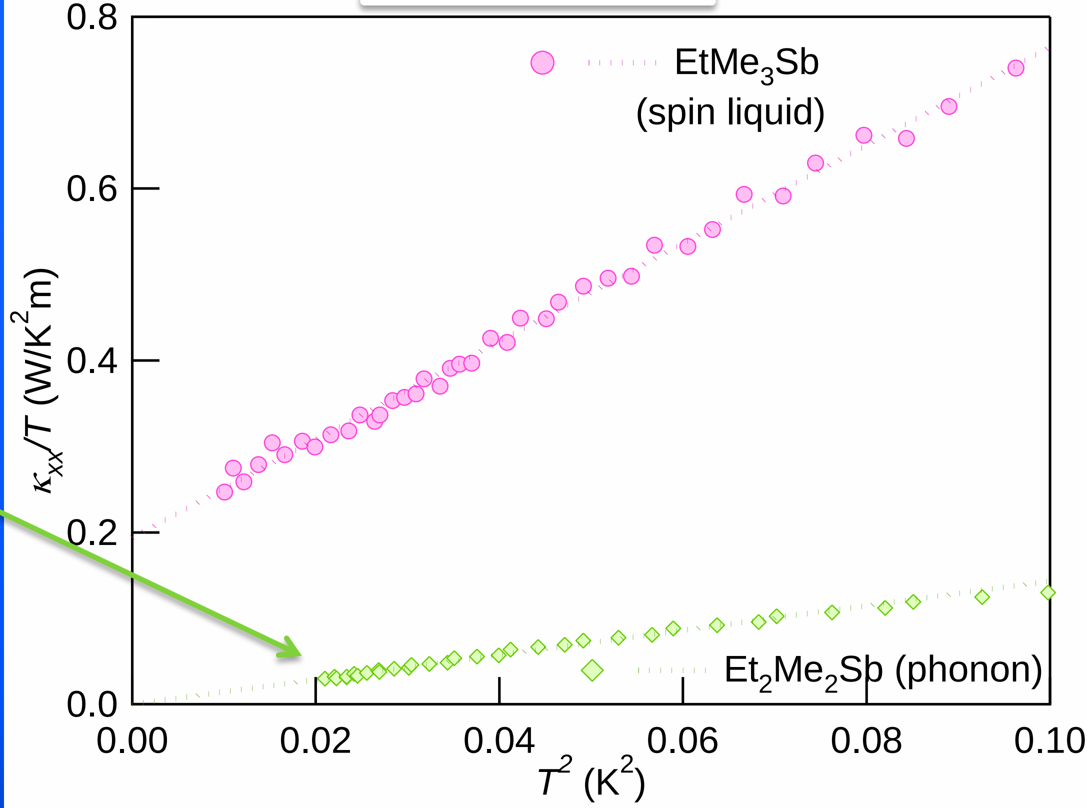




χ = 0 below 70 K

Tamura (2005) Synth Met 152, 397

κ/T vs T^2 plot
(T ≲ 300 mK)



M. Y., Science (2010)

Thermal conductivity of EtMe$_3$Sb[Pd(dmit)$_2$]$_2$

- Enhancement of κ in spin liquid state

$$\kappa = \underline{\boldsymbol{\kappa_{spin}}} + \kappa_{phonon}$$

- Clear residual of *κ*/*T* !

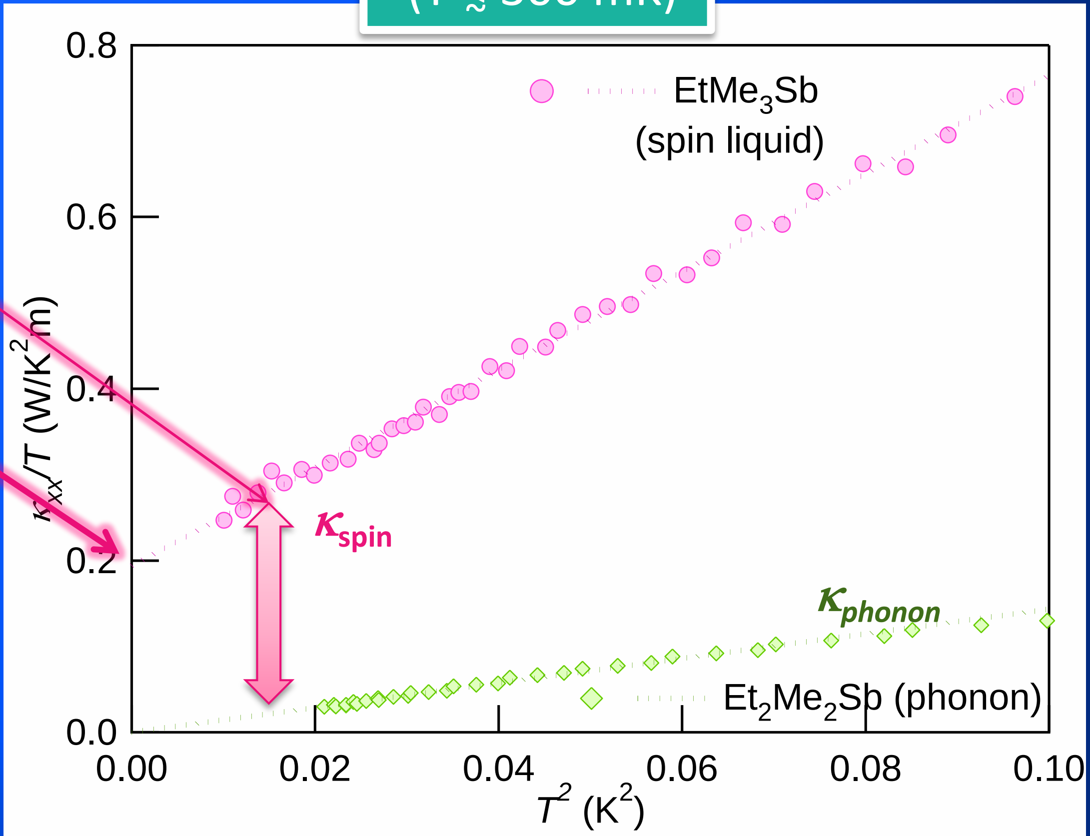
$$\frac{\boldsymbol{\kappa_{spin}}}{\boldsymbol{T}} \longrightarrow \mathbf{0.19\ W/K^2m}$$

Normally property of metals.
(comparable to κ of Brass
WF raw → ρ_0 = 13 μΩ•cm)
But, this is INSULATOR!!

Conductive spin liquid.

Gapless spin excitation behaving like electrons in normal metals.

κ/T vs T^2 plot
(T ≲ 300 mK)

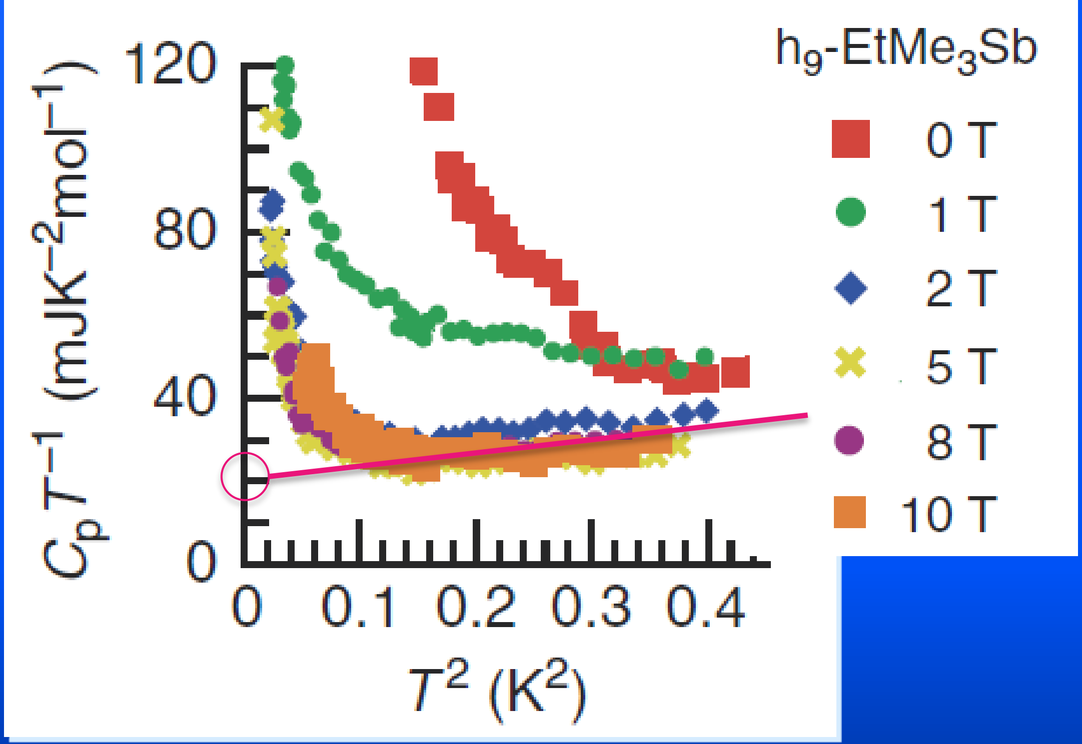


M. Y., Science (2010)

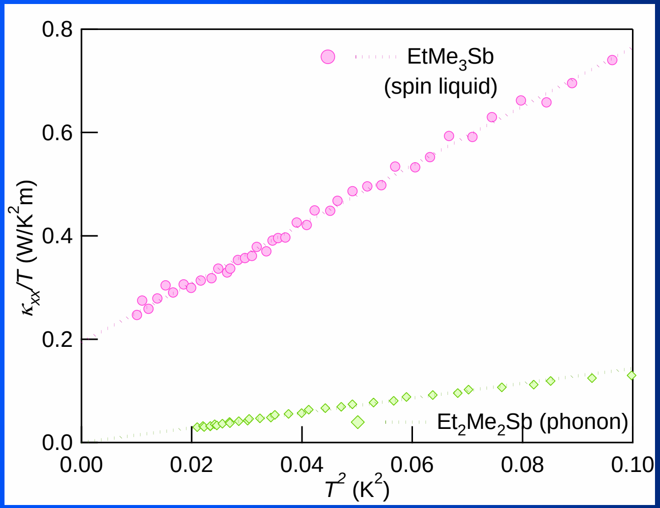
Heat Capacity Measurement

Presence of γ-term also confirmed by heat capacity measurements.

$$\frac{C_0}{T} \sim 20 \ \frac{\mathrm{mJ}}{\mathrm{K} \cdot \mathrm{mol}}$$



M.Y. et al., Science (2010)



S. Yamashita et al.
Nat. Commun. (2011)

Thermal conductivity of EtMe$_3$Sb[Pd(dmit)$_2$]$_2$

$$\boxed{\frac{\kappa_0}{T} = 0.19\ \mathrm{W/K^2m}}$$

☐Estimation of mean free path

$$\frac{\kappa_0}{T} \sim \frac{C_0}{T} \cdot v \cdot \ell$$

1. $\frac{C_0}{T} \sim 20\ \frac{\mathrm{mJ}}{\mathrm{K \cdot mol}}$

S. Yamashita et al.
Nat. Commun. (2011)

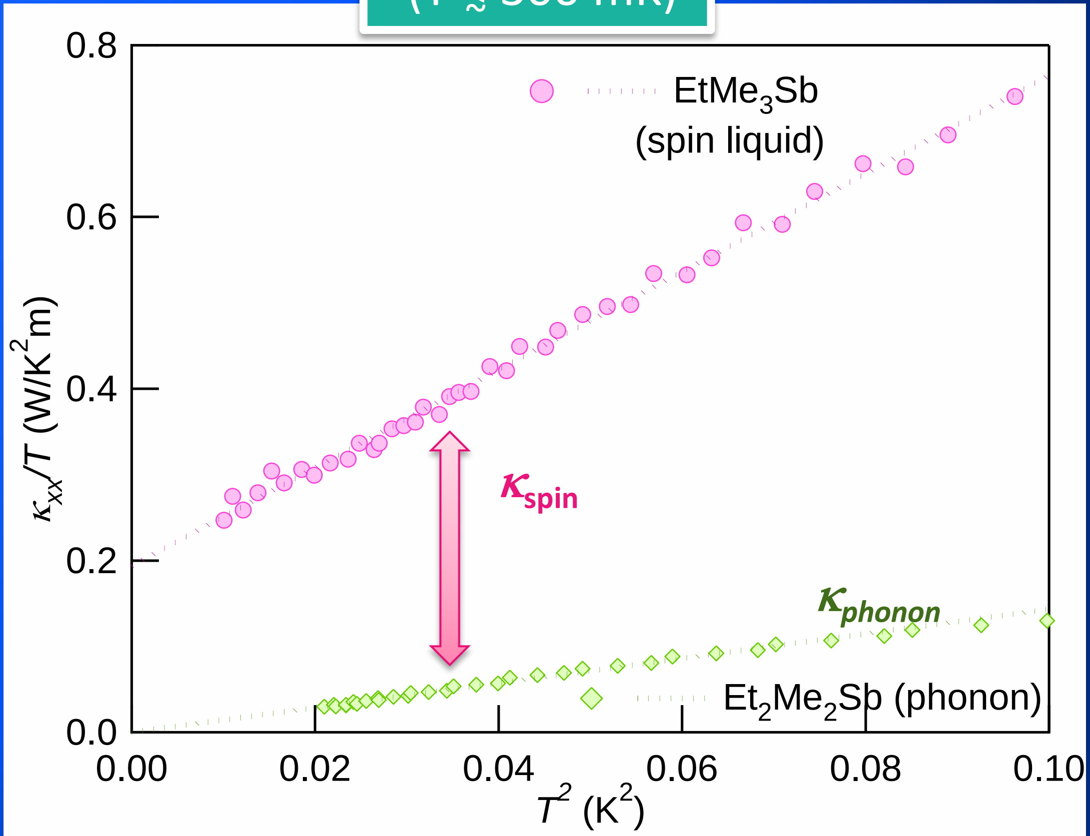
2. $\varepsilon(k) = \hbar \cdot v \cdot k$

$$\rightarrow v = Ja/\hbar$$

$$\ell \sim 1\ \mu\mathrm{m} \gg a \sim 1\ \mathrm{nm}$$

Nearly ballistic transport

κ/T vs T² plot
(T ≲ 300 mK)



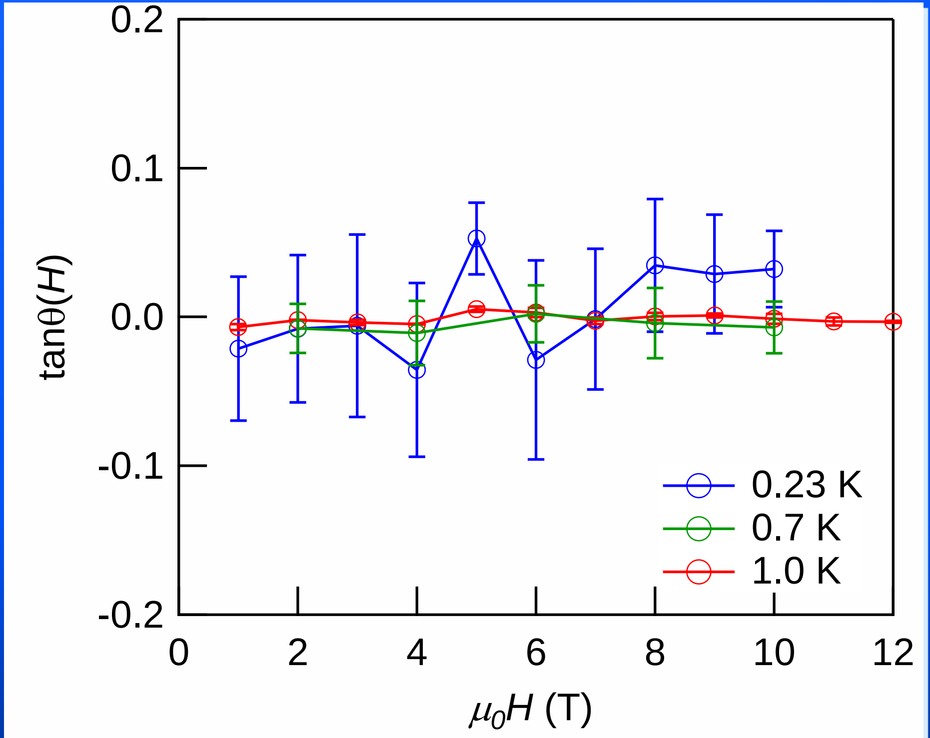
M. Y., Science (2010)

Thermal-Hall of EtMe$_3$Sb[Pd(dmit)$_2$]$_2$

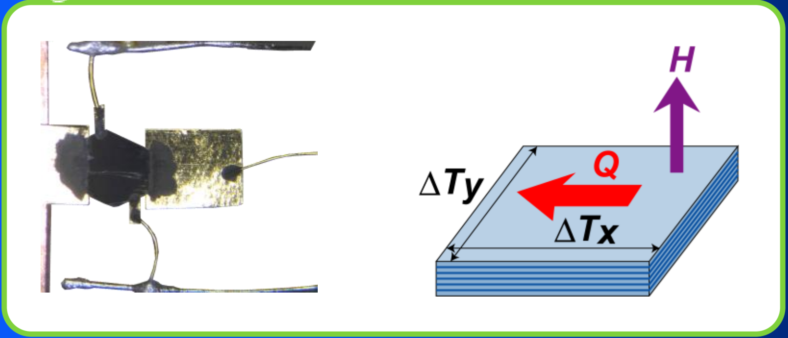
☐Thermal-Hall effect in QSL

H. Katsura, N. Nagaosa, P.A. Lee, PRL (2010)

$$\tan\ \theta = \frac{\kappa_{xy}}{\kappa_{xx}} \sim eB\frac{\tau_{spinon}}{m_{spinon}}$$



κ_{xy} measurement



Estimated upper limit

tanθ(B) < 0.03 (10 T, 0.23 K)

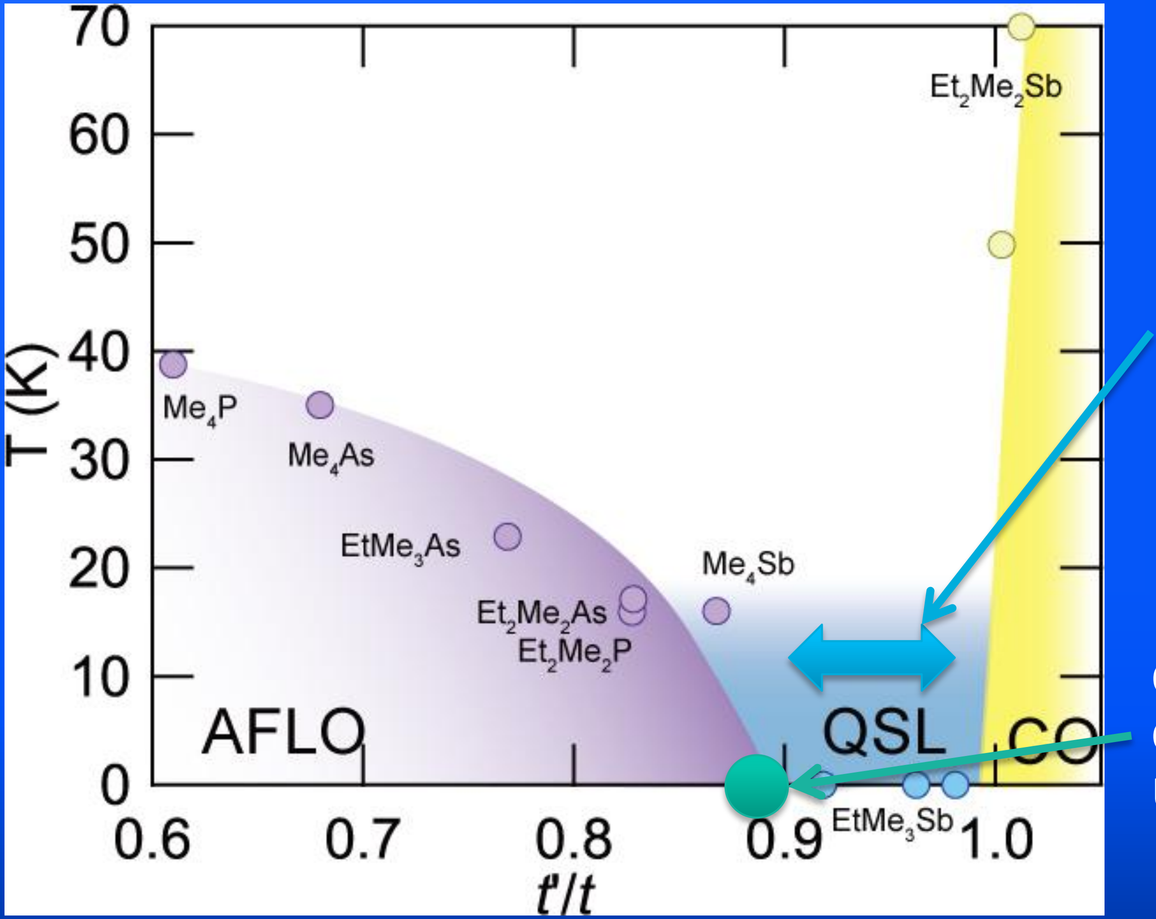
tanθ(B) < 0.001 (12 T, 1.0 K)

No thermal-Hall confirmed so far.

Phase diagram: QSL a stable phase?

Frustration control in β’-(Cation)[Pd(dmit)$_2$]$_2$

Kanoda&Kato, Annu. Rev. Condens. Matter Phys. 2 167 (2011)

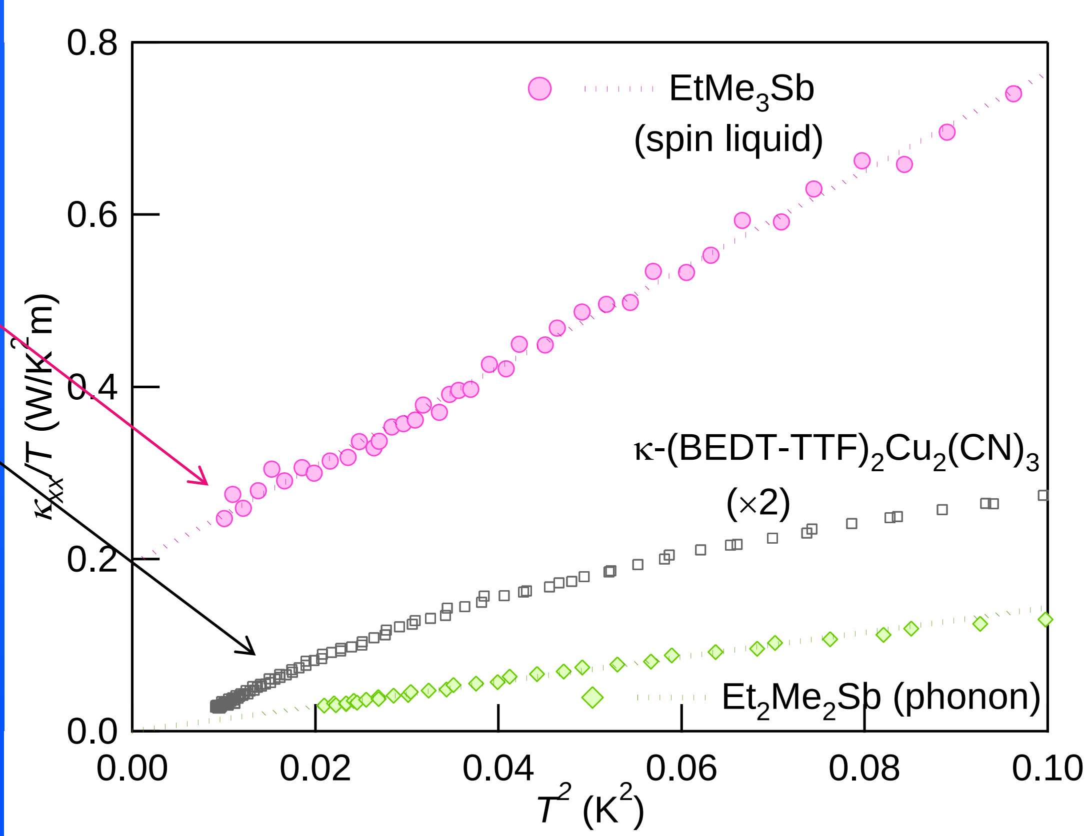


Stable phase?
Marginal parameter?

Quantum critical behavior?
Critical exponent?
Universality class?

Summary

Presence of γ	κ/T	C/T
$EtMe_3Sb[Pd(dmit)_2]_2$	○	○
κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$	✕	○



- κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

  Non-conductive spin liquid

  Δ = 0.46K

  Inhomogeneity triggered by 6K anomaly.

  Two components?

- $EtMe_3Sb[Pd(dmit)_2]_2$

  Conductive spin liquid

  Long mean free path

Future experiment

Frustration-tune Quantum criticality.

Impurity effect. Localization? Kondo effect?

New material, new QSL?