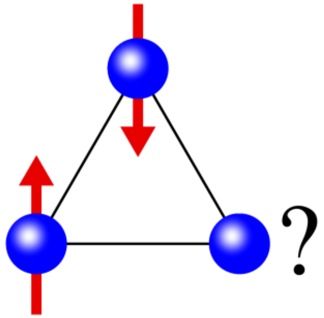
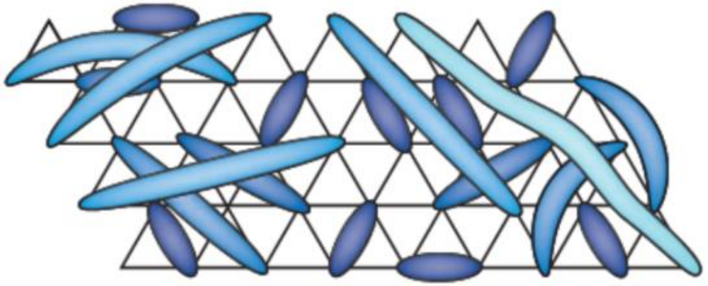
TECHNISCHE UNIVERSITÄT WIEN
Institut für Festkörperphysik

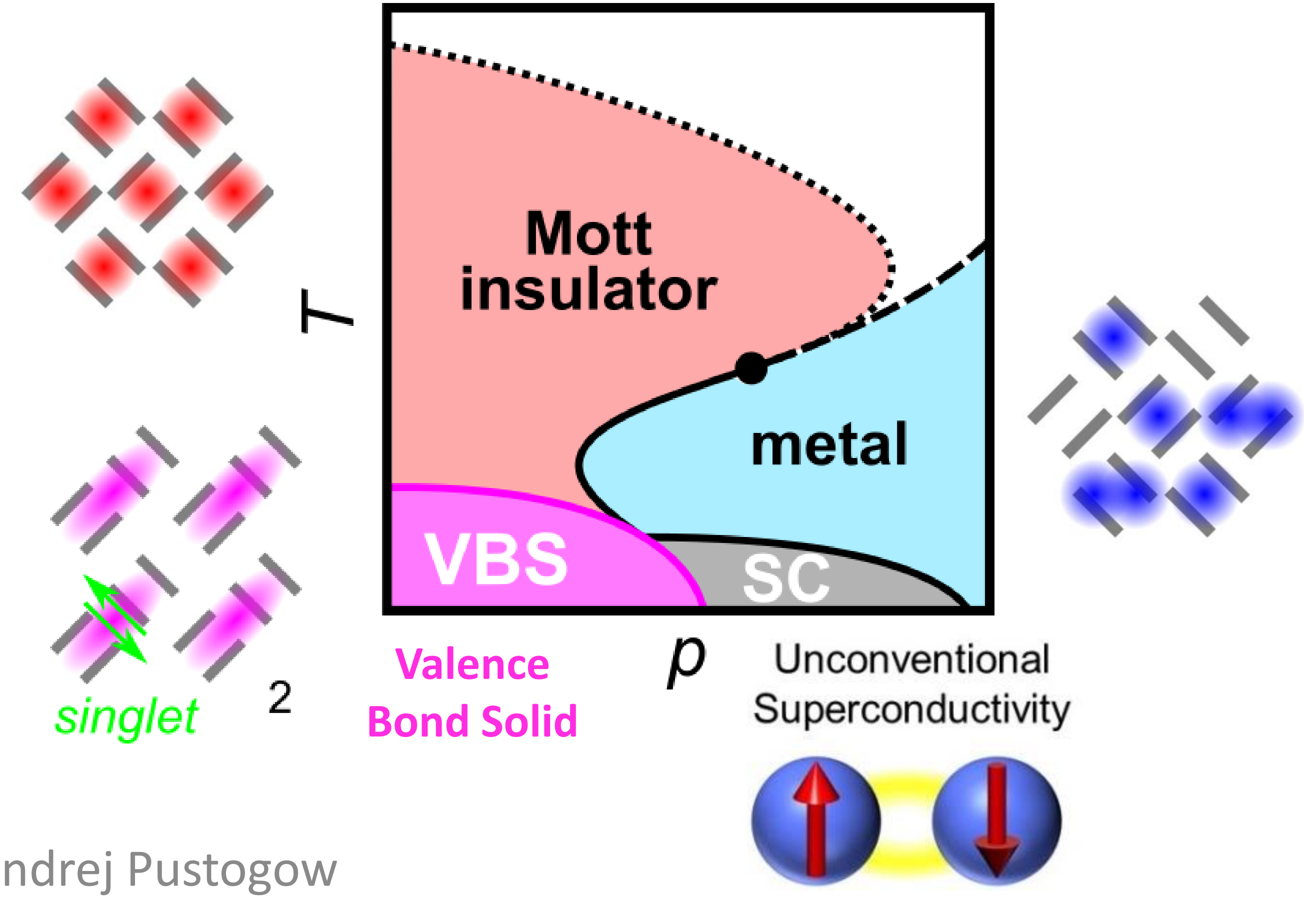
30-Year Anniversary of κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$:
Reconciling the Spin Gap in a Spin-Liquid Candidate

Pustogow, *Solids* **3**, 93–110 (2022)



Quantum Spin Liquid?





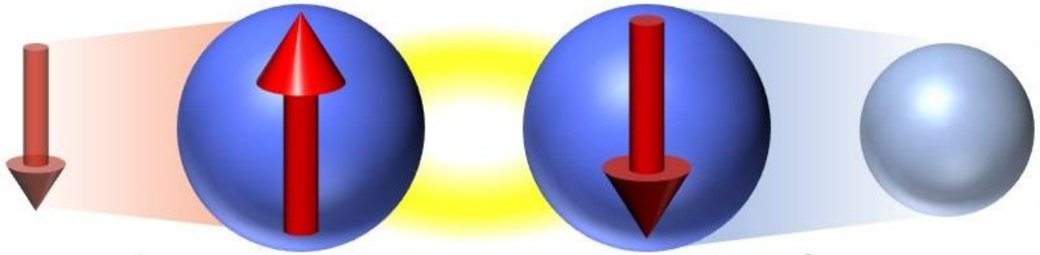
Pustogow Spectroscopy Lab

Ass. Prof. Andrej Pustogow

INSTITUT FÜR FESTKÖRPERPHYSIK
INSTITUTE OF SOLID STATE PHYSICS
Technische Universität Wien Vienna University of Technology

Alexander von Humboldt
Stiftung/Foundation

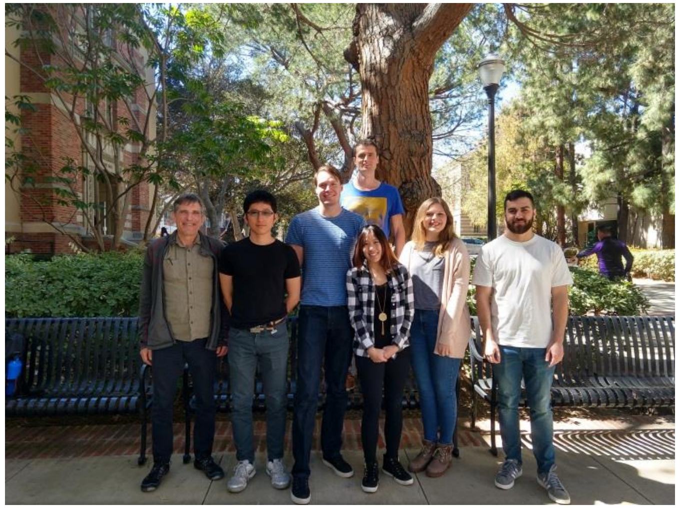
Correlated Electron Systems



spin ***charge***

Nuclear Magnetic Resonance Optical Spectroscopy

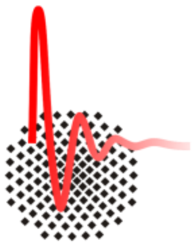
THE UNIVERSITY OF CALIFORNIA UCLA



Teresa Le
Hank Wang
Yongkang Luo

Stuart E. Brown

University of California
Los Angeles



Björn Miksch
Ralph Hübner
Marc Scheffler

Martin Dressel

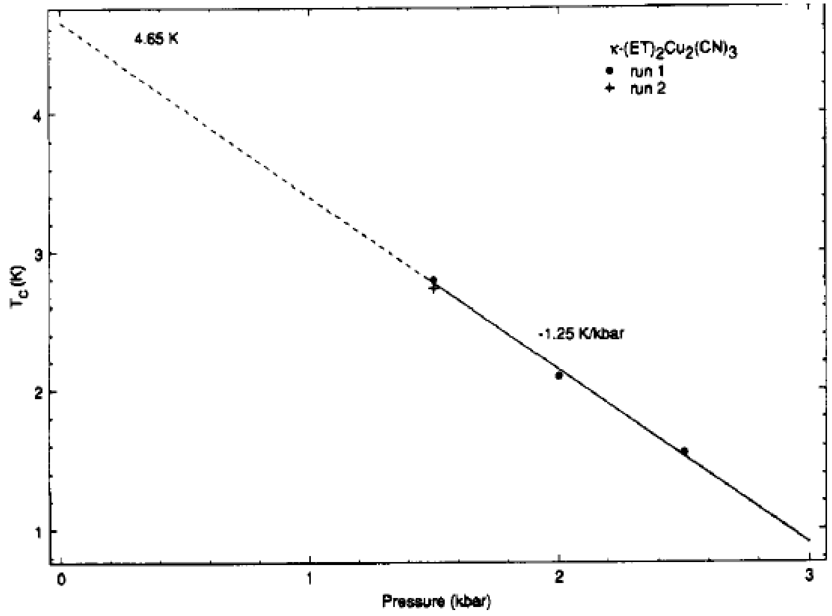
Universität Stuttgart

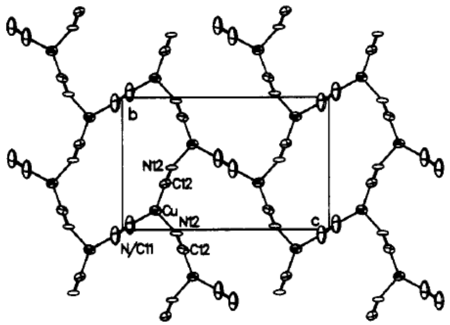
Organic Superconductor

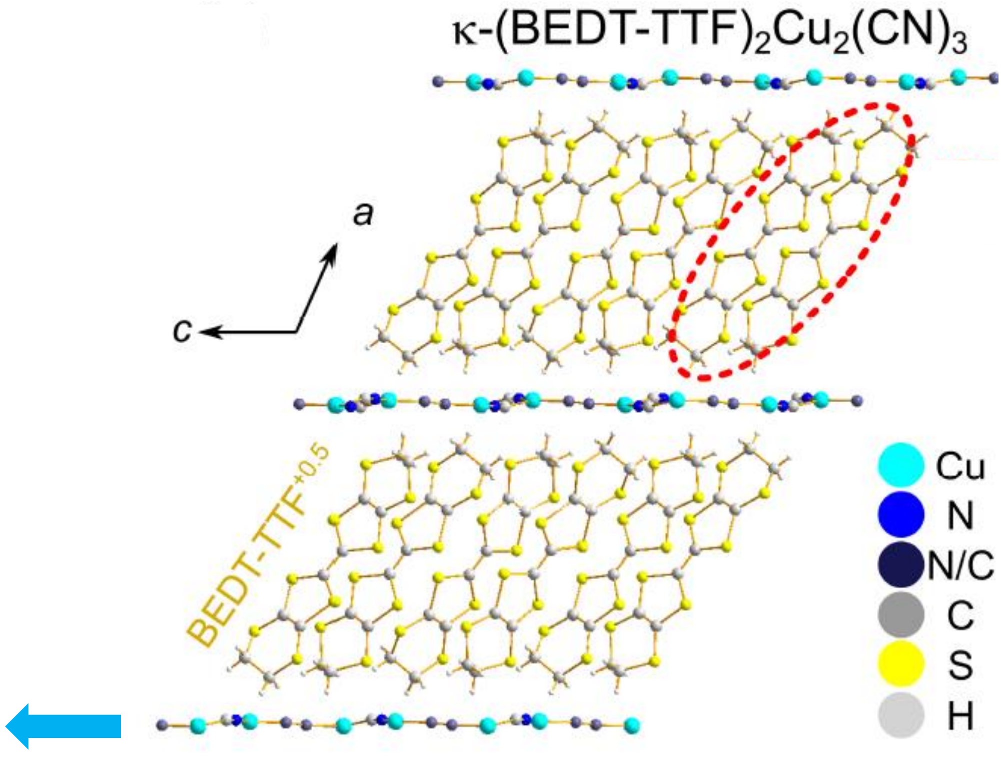
1991

Superconductivity at 2.8 K and 1.5 kbar in κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$: The First Organic Superconductor Containing a Polymeric Copper Cyanide Anion

Geiser *et al.*, *Inorg. Chem.* **30**, 2586–2588 (1991)







Quantum Spin Liquid?

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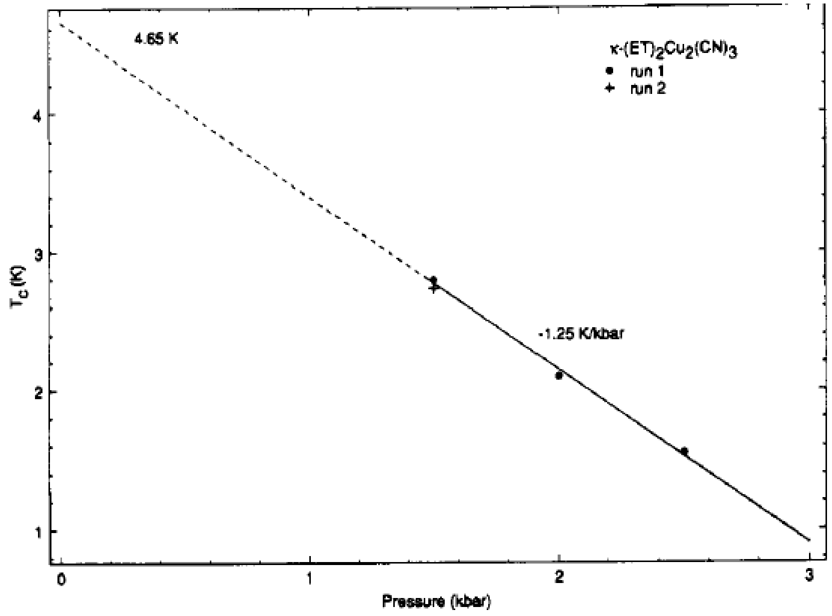
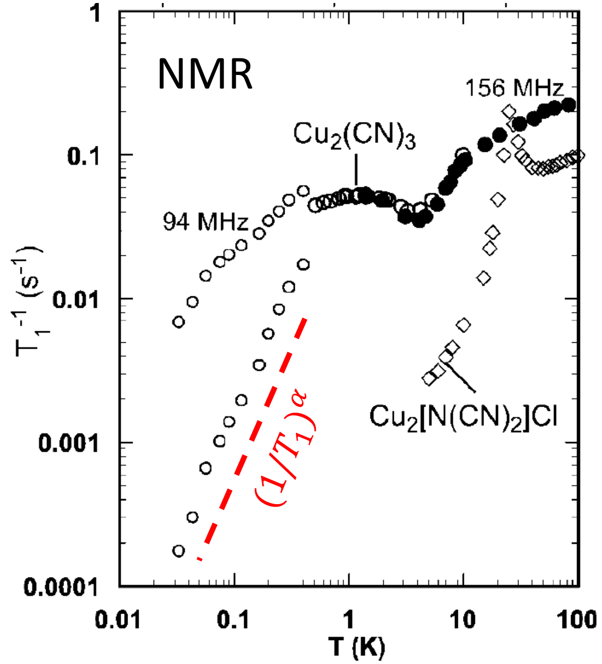
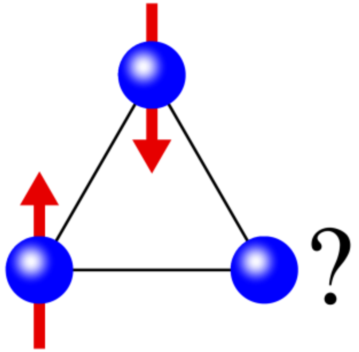


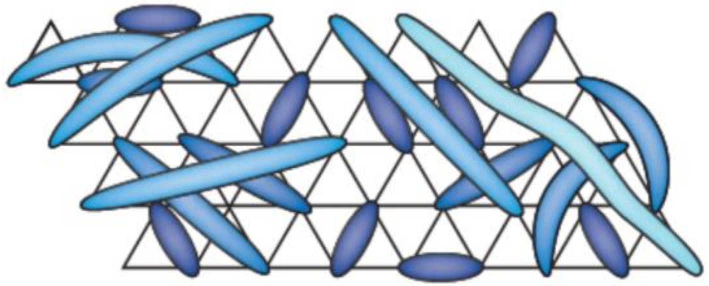
2003

- no antiferromagnetism
- quantum spin liquid?

Shimizu *et al.*, *PRL* **91**, 107001 (2003)







Balents, *Nature* **464**, 199–208 (2010)

Mott Insulator

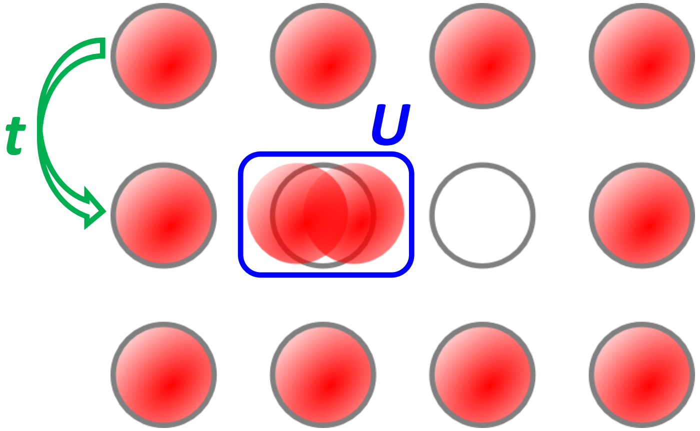
Hubbard Model $H = -t \sum_{<ij>,\sigma} (c_{i\sigma}^{\dagger} c_{j\sigma} + H.c.) + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$

repulsive interaction

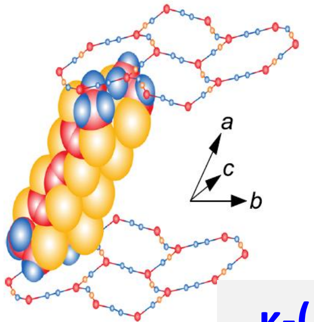
- periodic arrangement
- 1 particle per site

on-site Coulomb repulsion

½-filled band
1 electron per site

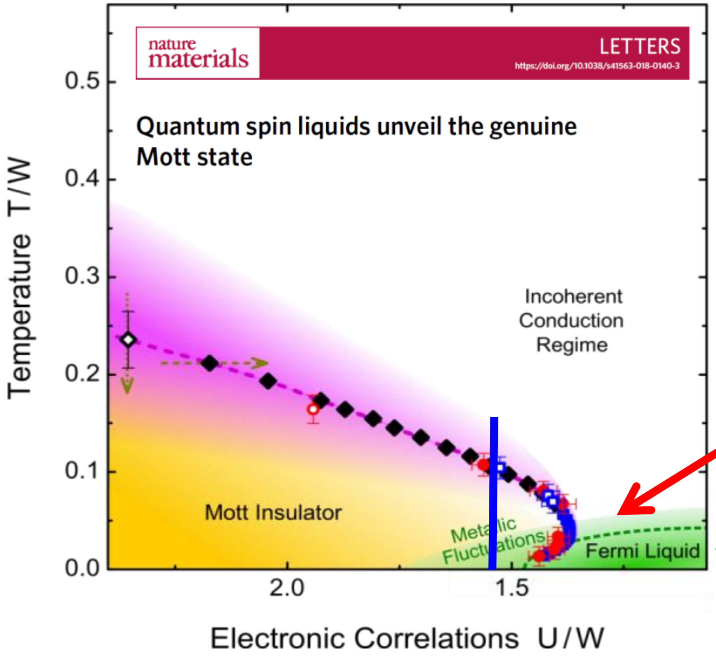


Genuine Mott Insulator



κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

Pustogow *et al., Nat. Mater*. **17**, 773-777 (2018)



Hubbard Model

$$H = -t \sum_{<ij>,\sigma} (c_{i\sigma}^{\dagger} c_{j\sigma} + H.c.) + U \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

Electronic bandwidth W ∝ t

on-site Coulomb repulsion

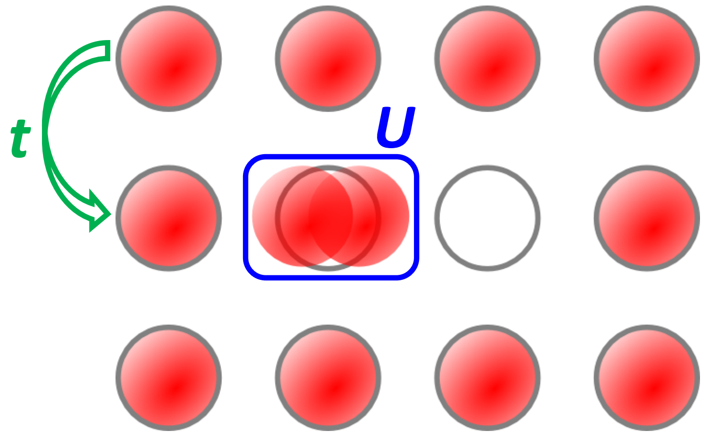
Bad Metal

Landau Fermi Liquid

('good' metal)

Pustogow *et al., Nat. Commun*. **12**, 1571 (2021)
npj Quantum Mater. **6**, 9 (2021)

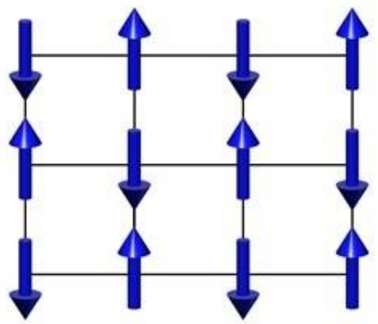
½-filled band
1 electron per site



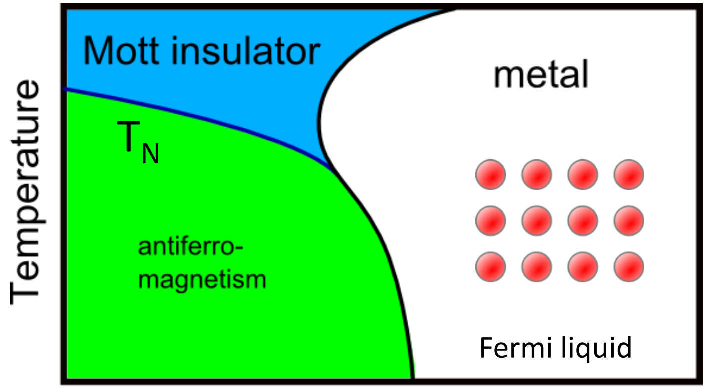
Mott Insulator - Magnetism

$$H = -\boldsymbol{t} \sum_{<ij>,\sigma} (c_{i\sigma}^{\dagger} c_{j\sigma} + H.c.) + \boldsymbol{U} \sum_{i} n_{i\uparrow} n_{i\downarrow}$$

Magnetic Order

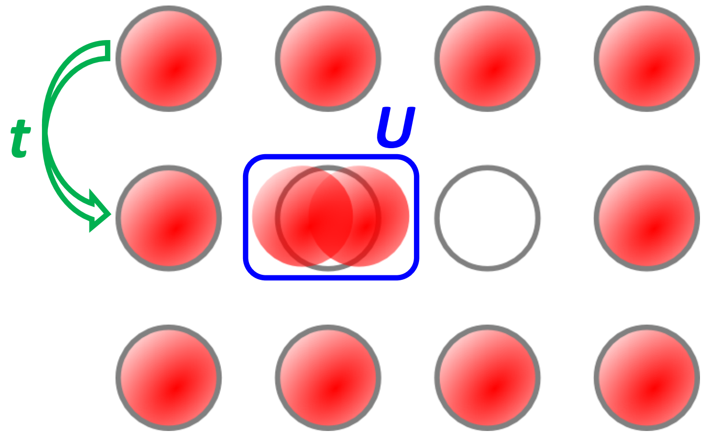


Mott-Heisenberg insulator



Pressure

½-filled band
1 electron per site

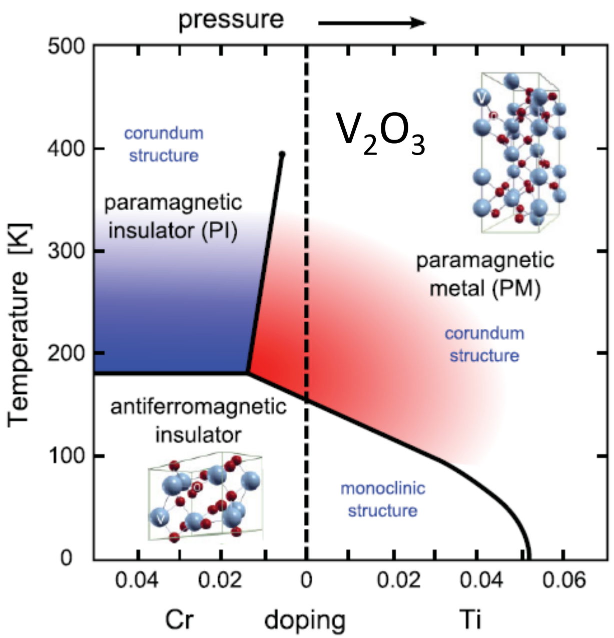


antiferromagnetic interactions

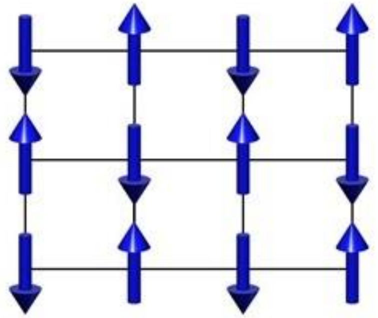
itinerant exchange mechanism $\boldsymbol{J} \propto \frac{\boldsymbol{t}^2}{\boldsymbol{U}}$

Mott Insulator - Magnetism

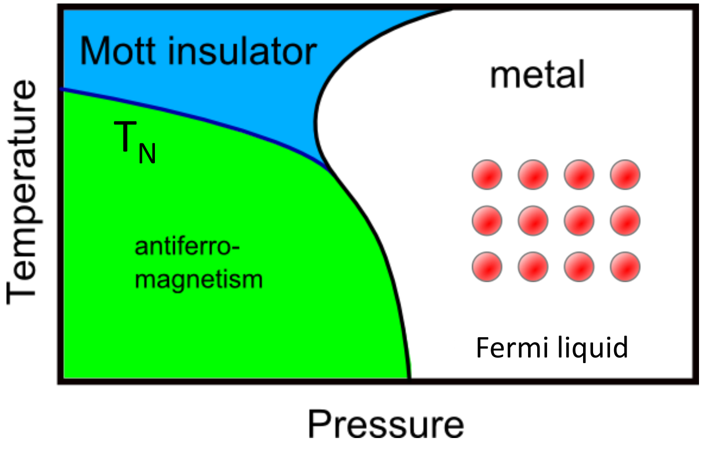
Hansmann *et al.*, *Phys. Status Solidi B* **250**, 1251–1264 (2013)

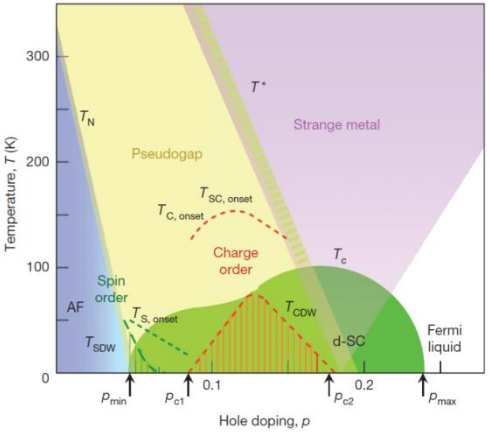


Magnetic Order



Mott-Heisenberg insulator

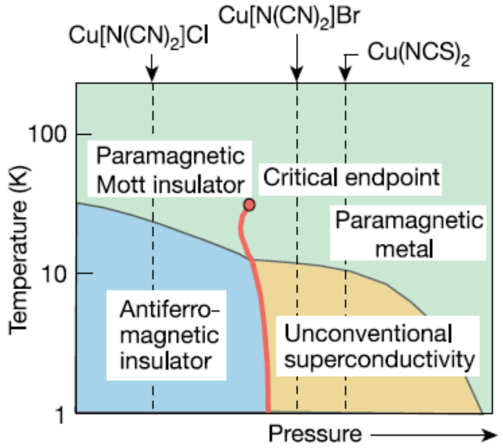




High-T_c Cuprates

Keimer *et al.*, *Nature* **518**, 179 (2015)

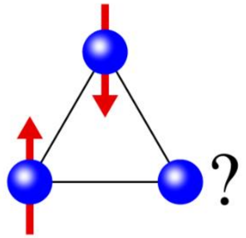
$$J \propto \frac{t^2}{U}$$



Organic Conductors

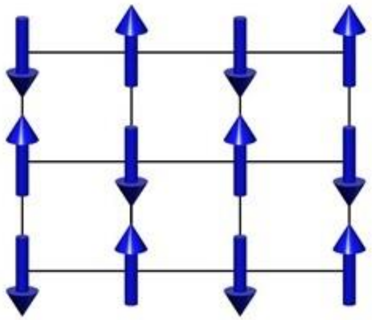
Kagawa *et al.*, *Nature* **436**, 534 (2005)

Mott Insulator - Magnetism

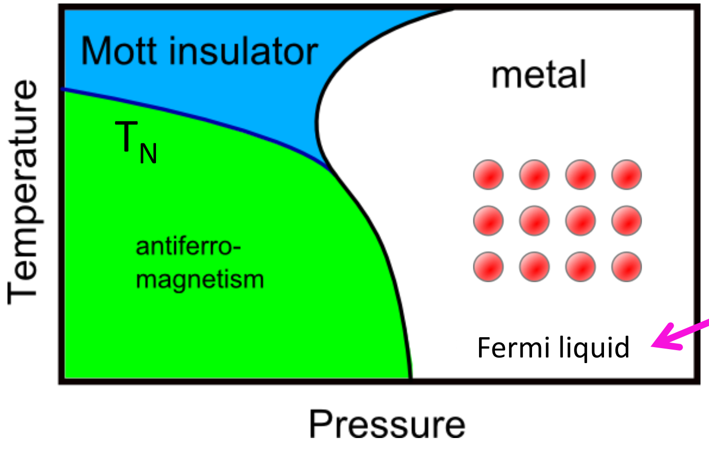


antiferromagnetic interactions

Magnetic Order

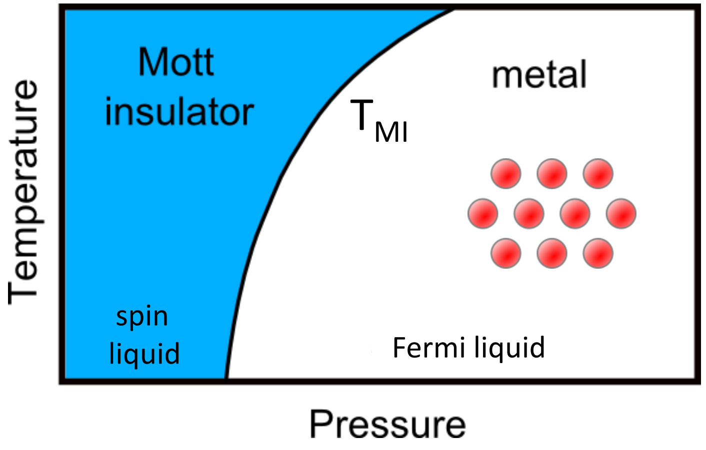


Mott-Heisenberg insulator



$S_{FL} \sim T$

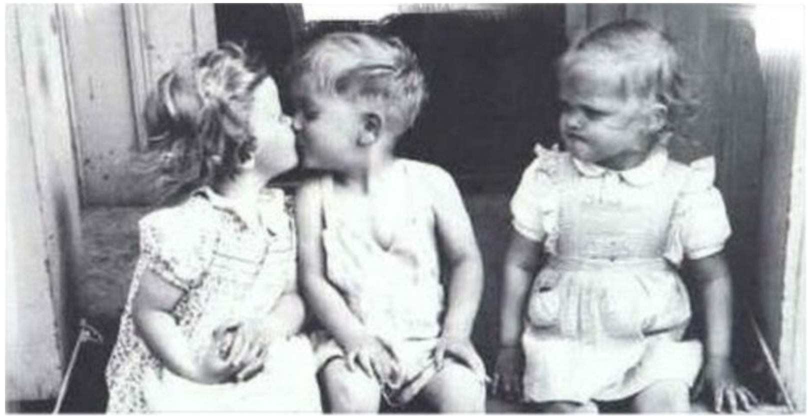
frustrated Mott insulator



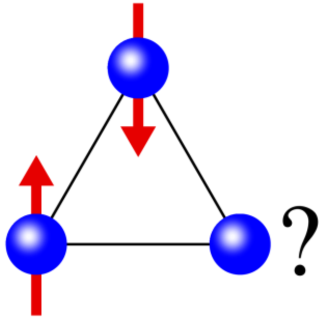
AFM order		paramagnetic
$S_{AFM} \approx 0$	low-temperature entropy	$S_{QSL} = k_B \ln 2$
$dT_N/dp < 0$	slope of phase transition	$dT_{MI}/dp > 0$

Geometrical Frustration

frustration in real life



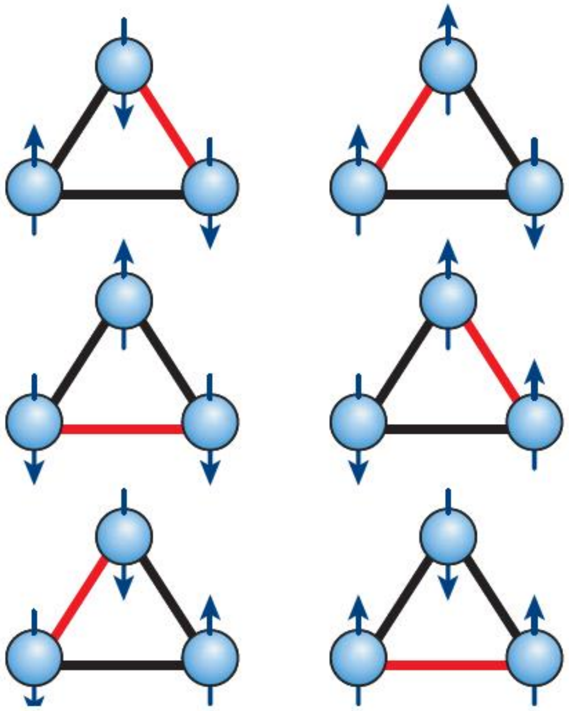
geometrical frustration in physics



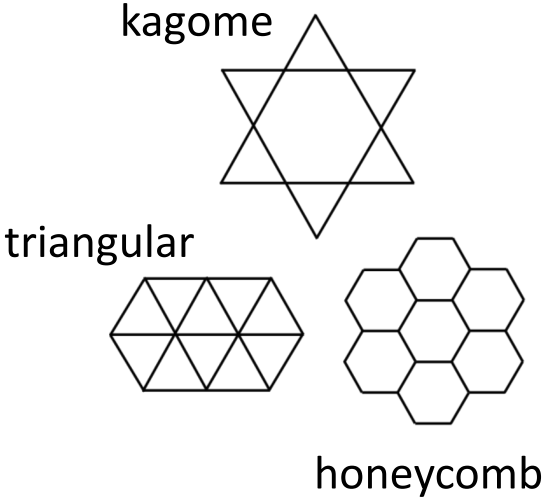
- suppression of magnetic order
- quantum spin liquid
- exotic excitations (spinons)

Geometrical Frustration

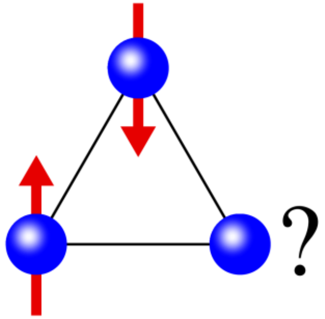
suppression of long-range order



Balents, *Nature* **464**, 199–208 (2010)

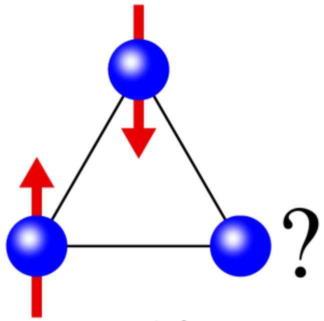


geometrical frustration in physics



- suppression of magnetic order
- quantum spin liquid
- exotic excitations (spinons)

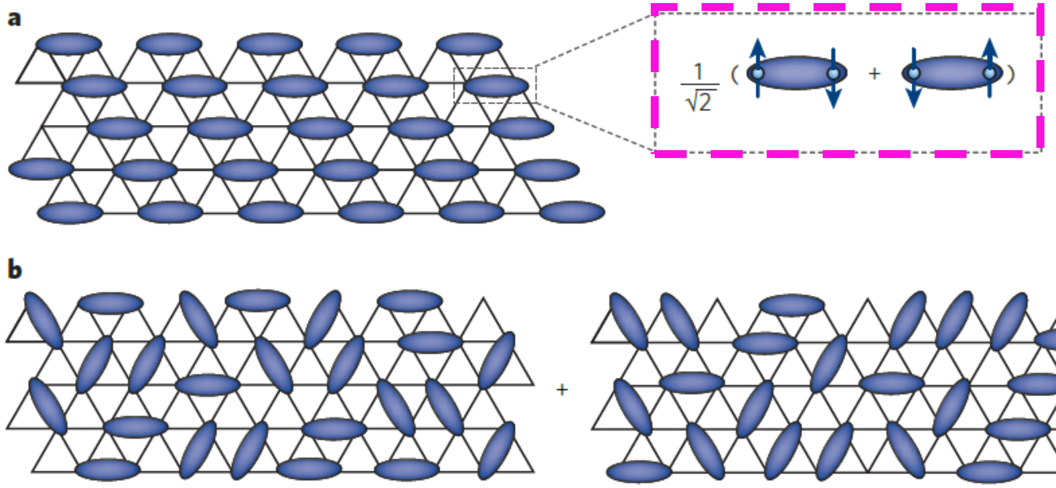
Frustrated Magnetism



geometrical frustration

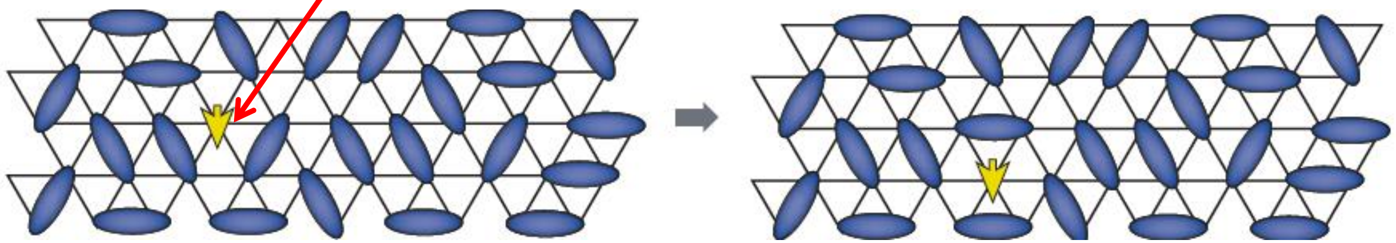
Valence Bond Solid
(e.g. Spin-Peierls in 1D)

Resonating Valence Bond (RVB) State



valence bond

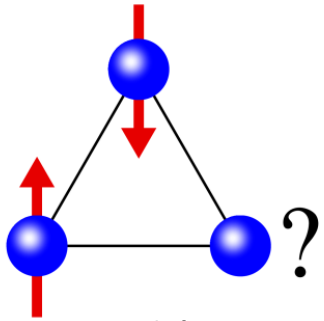
spinon: neutral $S = ½$ excitation



Balents, *Nature* **464**, 199–208 (2010)

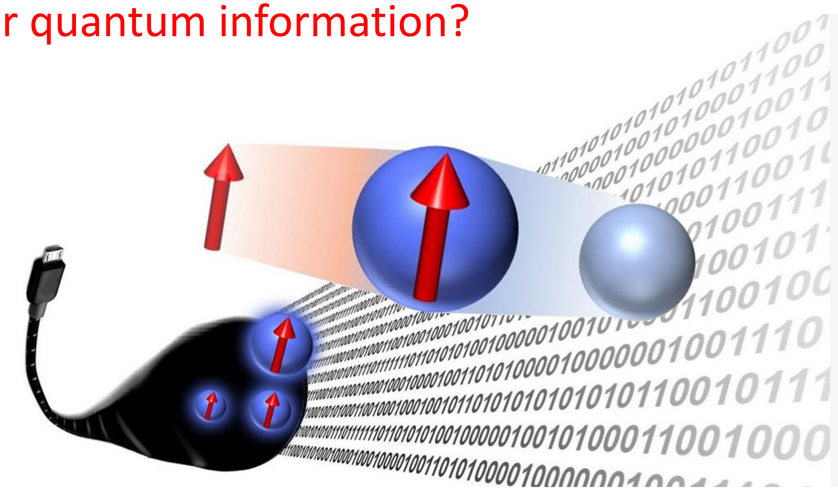
mobile spinons (‘gapless’)
similar to electrons in a metal, but without charge

Frustrated Magnetism



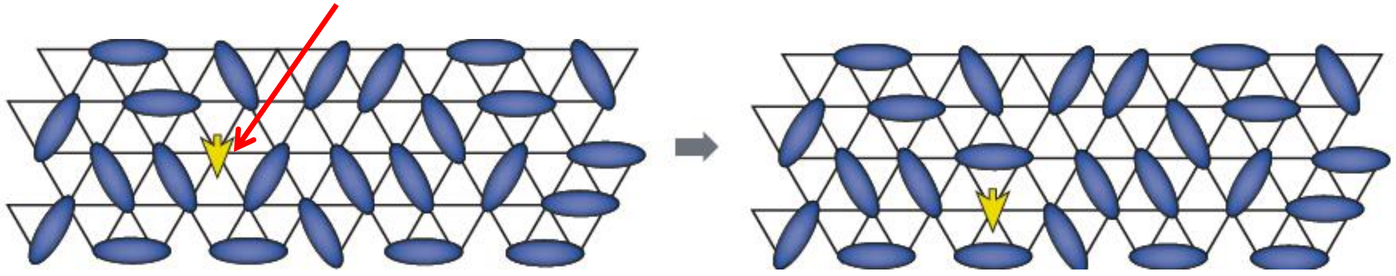
geometrical frustration

Useful for quantum information?



https://www.tuwien.at/en/tu-wien/news/news/neue-messungen-stellen-spin-fluessigkeiten-in-frage

spinon: neutral $S = ½$ excitation

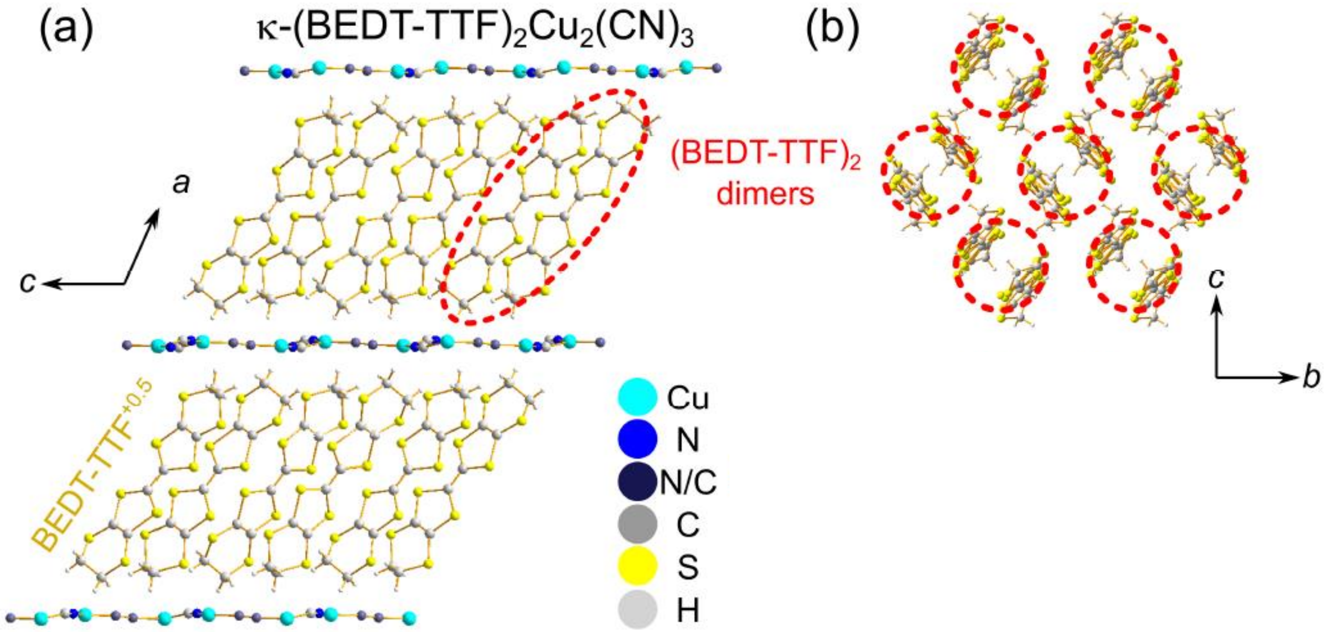


Balents, *Nature* **464**, 199–208 (2010)

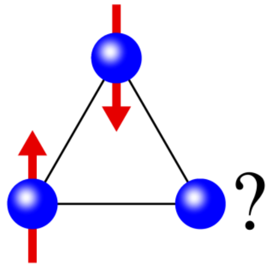
mobile spinons ('gapless')
similar to electrons in a metal,
but without charge

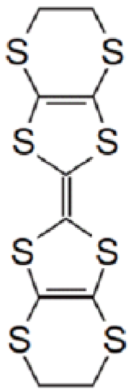
κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

triangular lattice

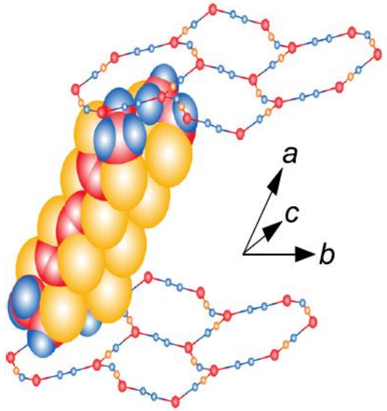


Pustogow, *Solids* **3**, 93–110 (2022)





BEDT-TTF



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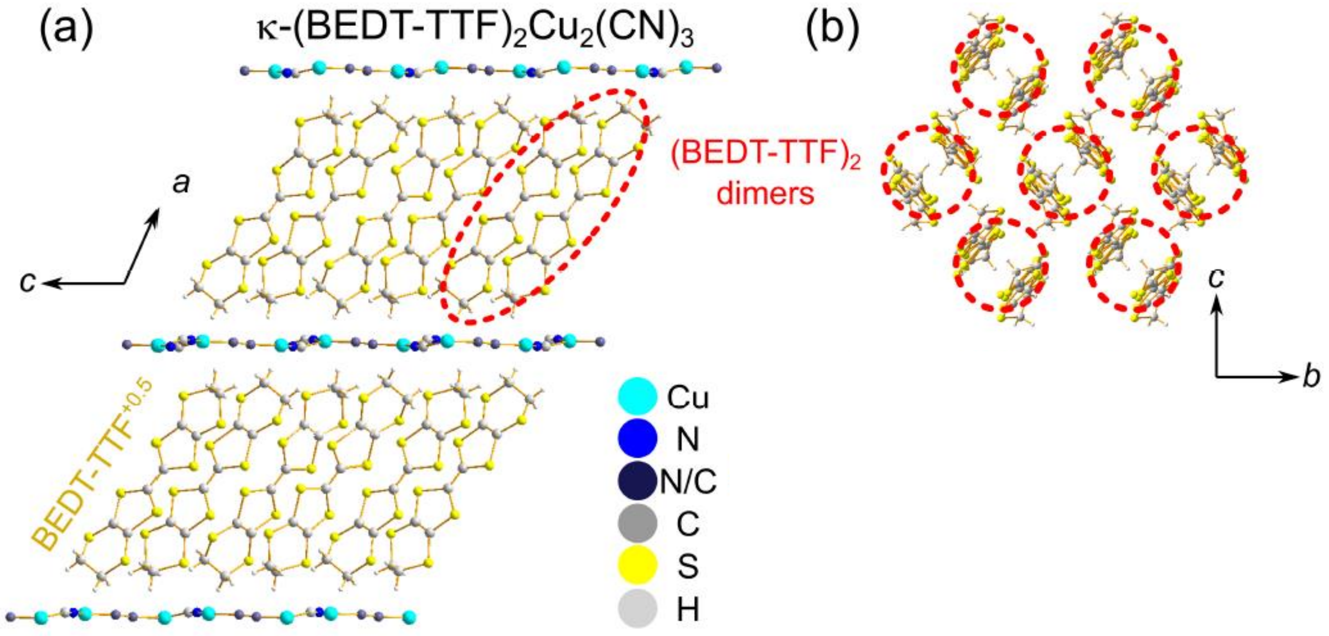

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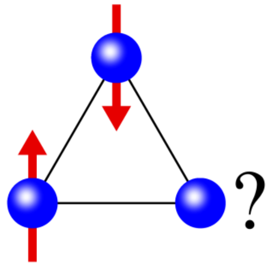
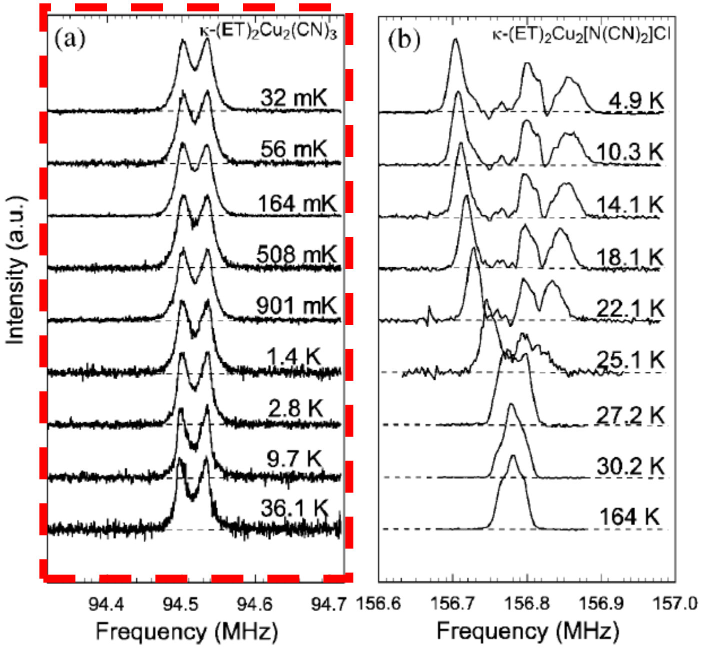


Pustogow, *Solids* **3**, 93–110 (2022)

- **no antiferromagnetism**

nonmagnetic
no splitting

antiferromagnet
splitting of NMR lines



Shimizu *et al.*, *PRL* **91**, 107001 (2003)

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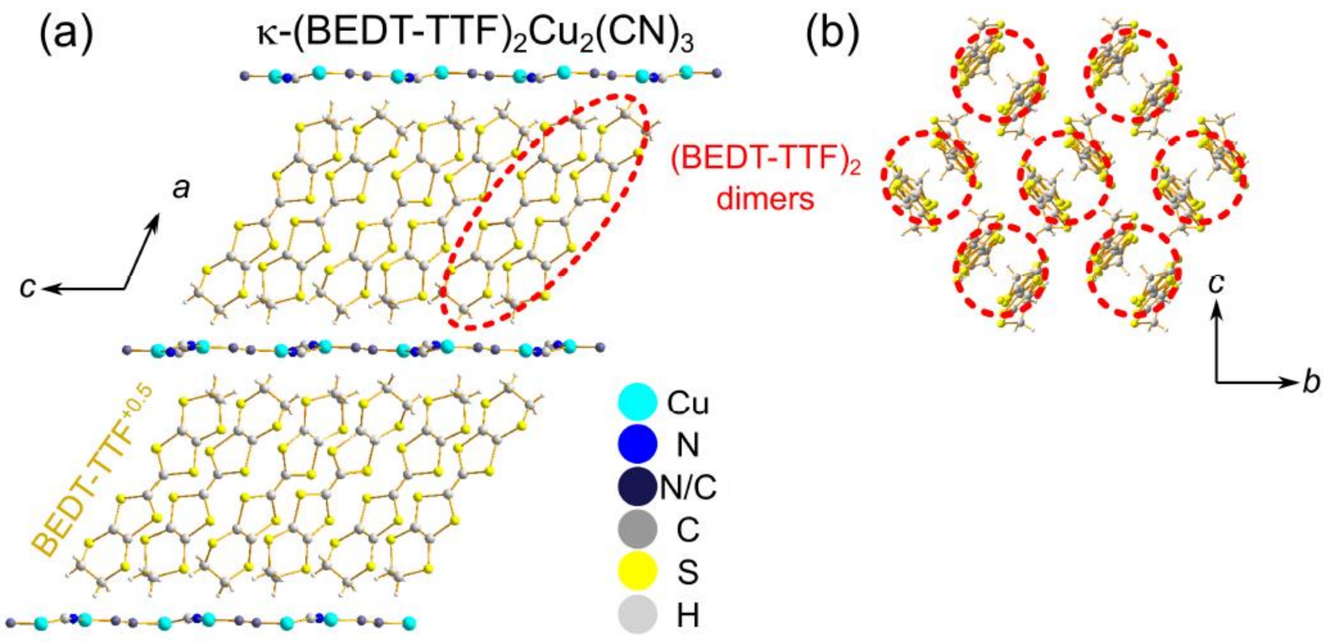

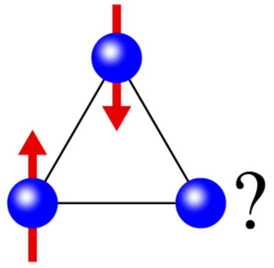

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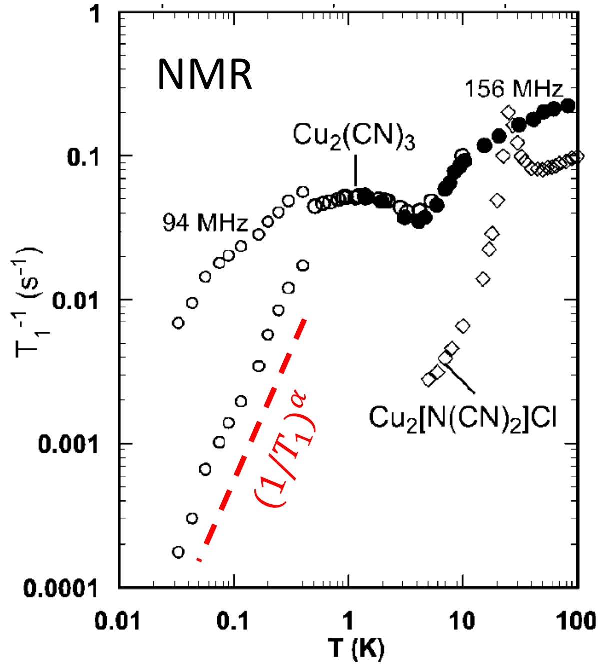
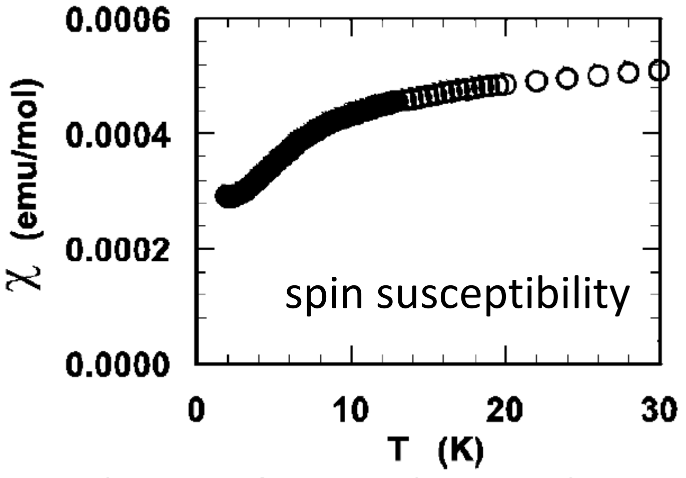


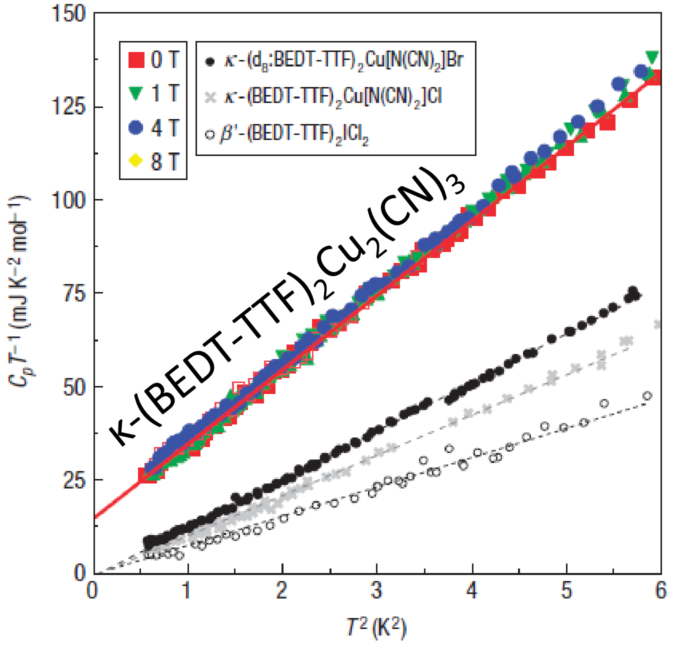
Shimizu *et al.*, *PRL* **91**, 107001 (2003)

- **no antiferromagnetism**
- **χ does not drop to zero towards $T \rightarrow 0$**

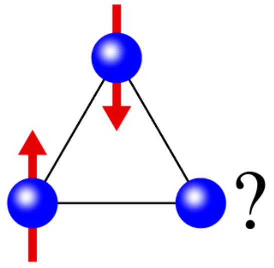


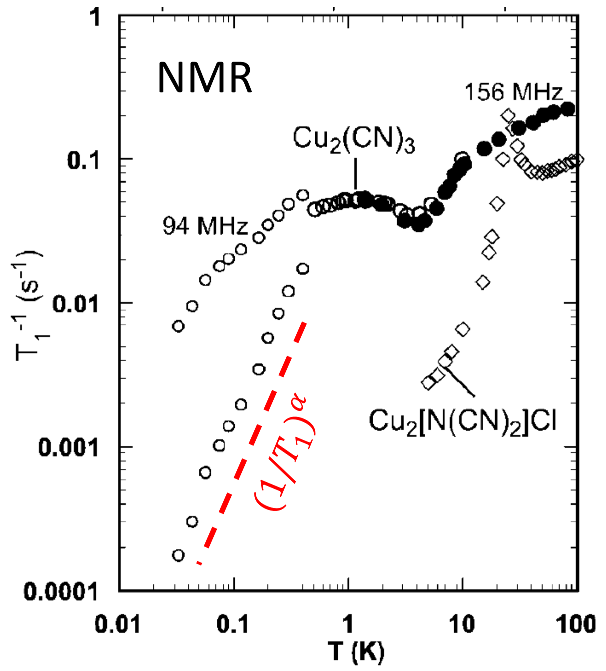
κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

specific heat: gapless



Yamashita *et al.*, *Nat. Phys.* **4**, 459–462 (2008)





Shimizu *et al.*, *PRL* **91**, 107001 (2003)

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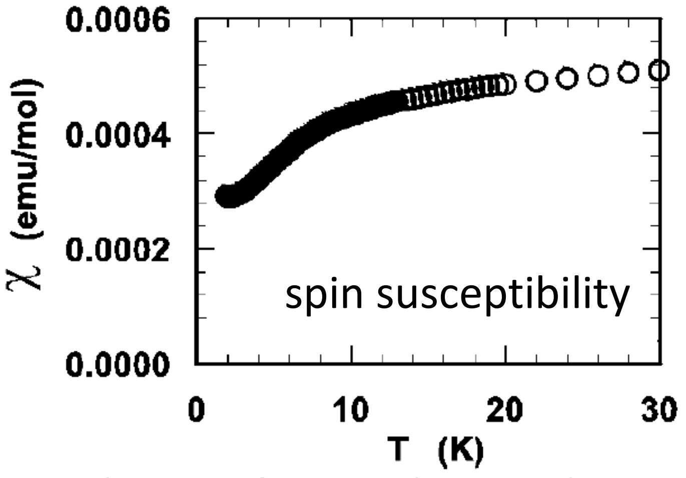
- **linear term of specific heat $C \propto \gamma T$**
- **gapless spinons?**



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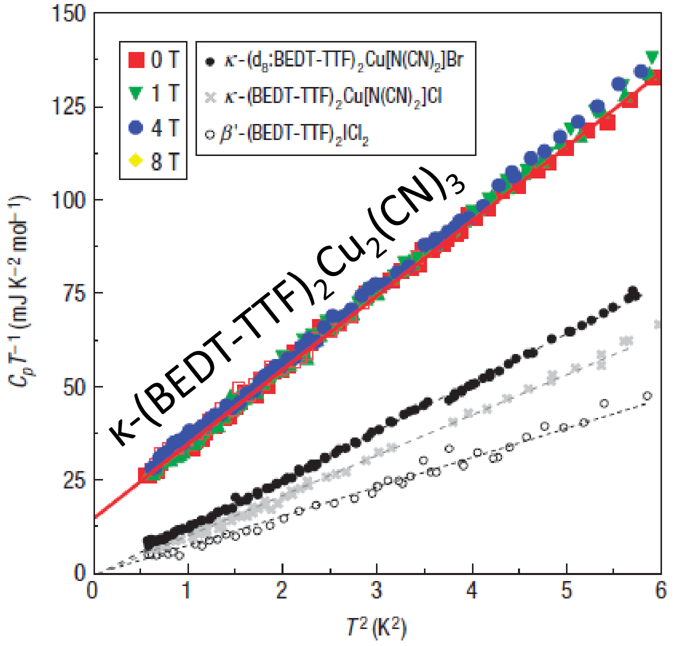
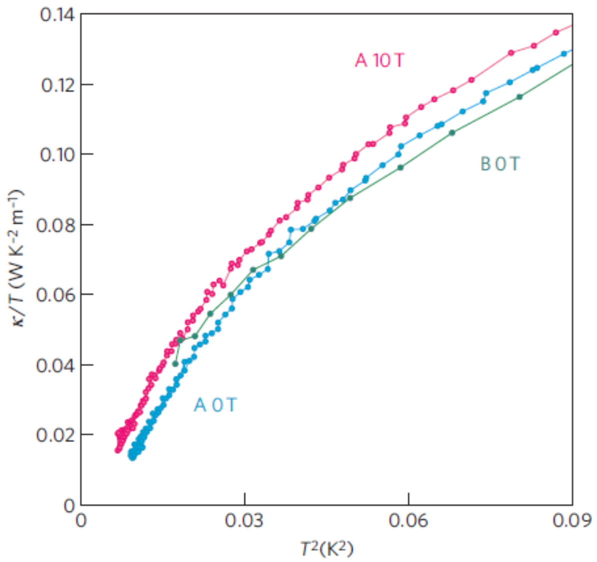
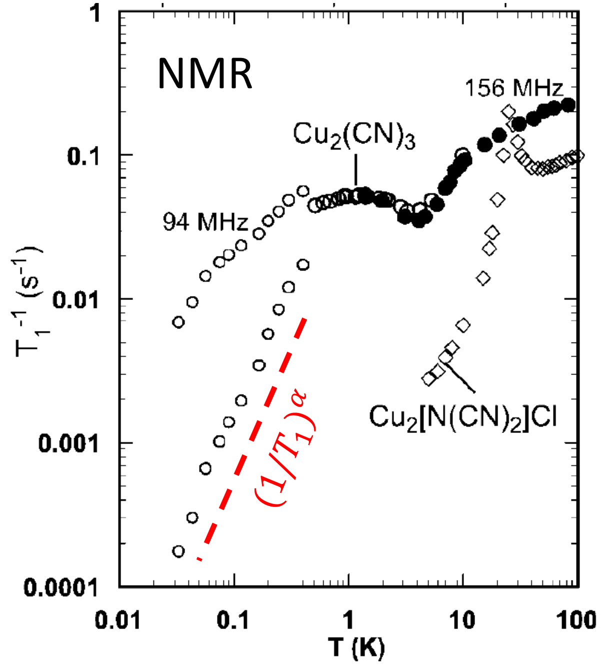


Yamashita *et al.*, *Nat. Phys.* **4**, 459–462 (2008)

thermal transport: gapped



Yamashita *et al.*, *Nat. Phys.* **5**, 44–47 (2009)



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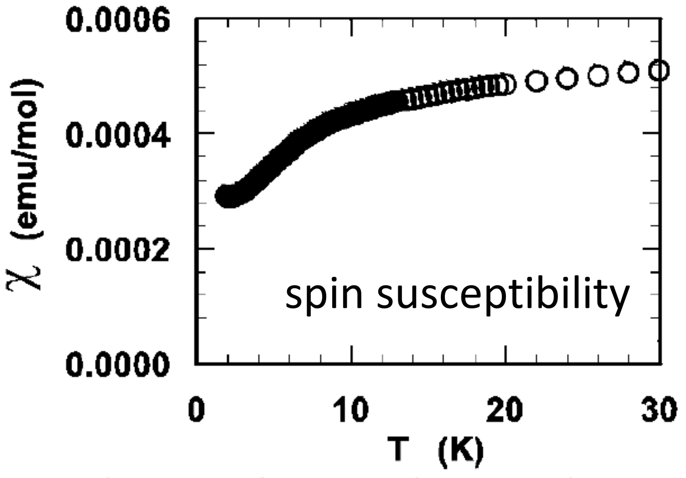
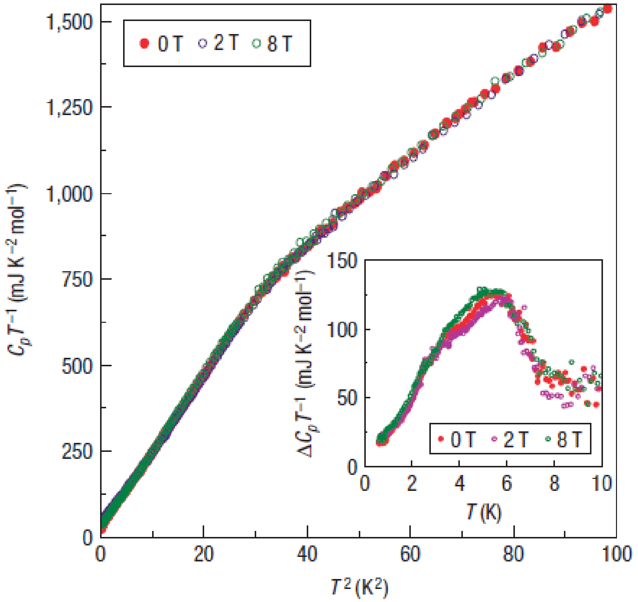
- **linear term of specific heat $C \propto \gamma T$**
- **gapless spinons?**



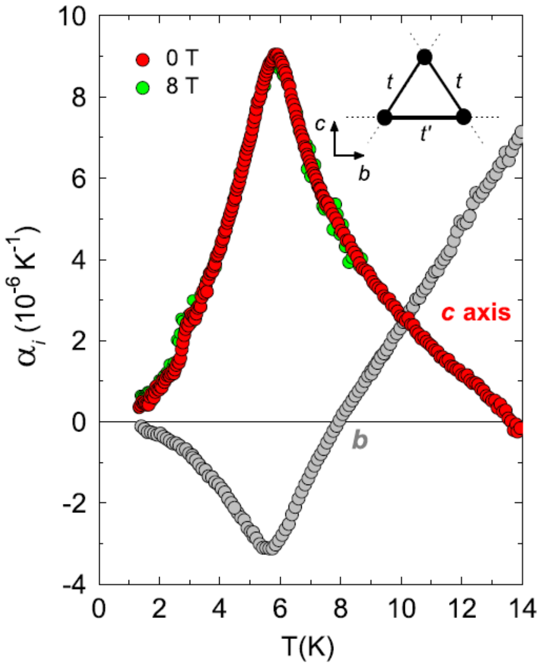
κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$: "6 K Anomaly"

specific heat
entropy release at 6 K
$\Delta S \approx 0.17\, k_B ln(2)$



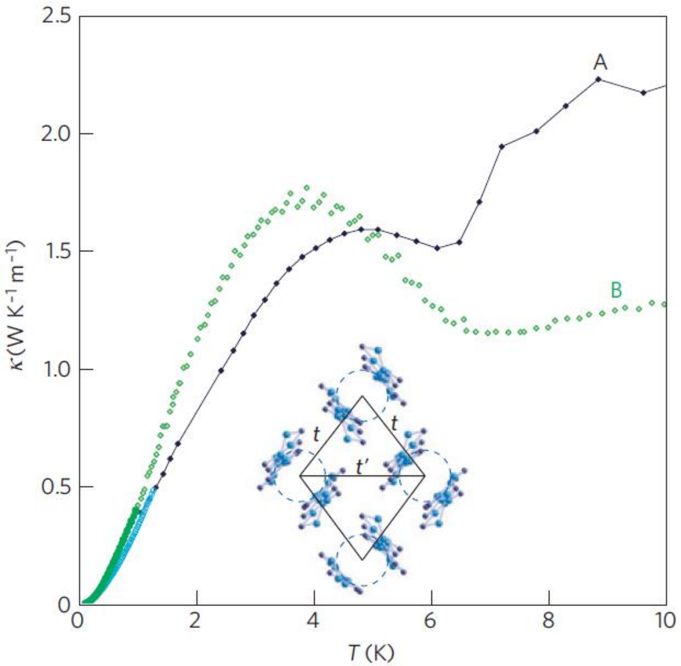
Yamashita *et al.*, *Nat. Phys.* **4**, 459–462 (2008)

thermal expansion



Manna et al., *PRL* **104**, 016403 (2010)

thermal transport



Yamashita *et al.*, *Nat. Phys.* **5**, 44–47 (2009)

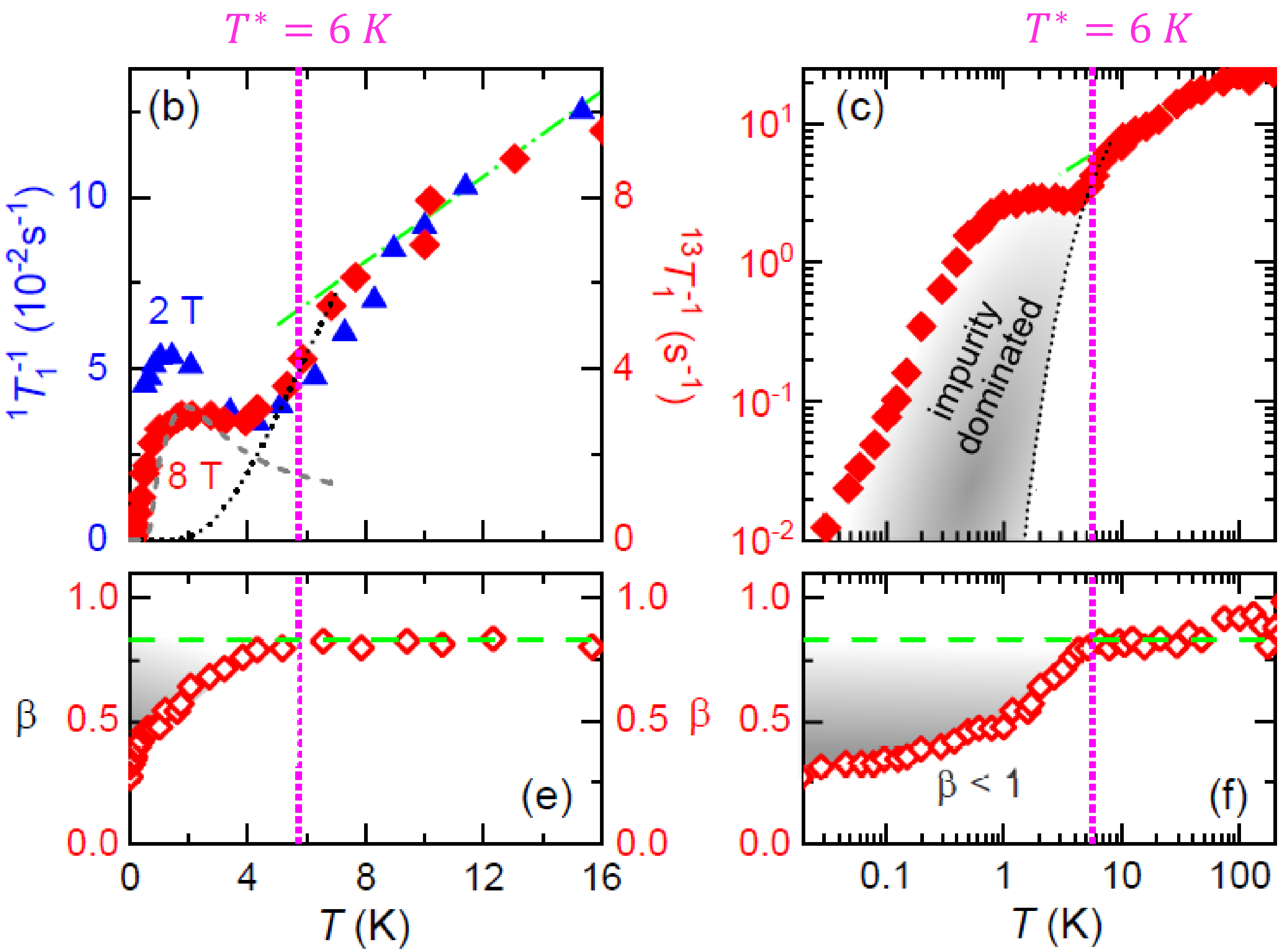
κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$: Impurity Spins

NMR properties $T < T^*$

- field-dependent peak in $1/T_1$
- stretched exponential relaxation

magnetic response at $T < T^*$ dominated by impurity spins

Pustogow *et al.*, *PRB* **101**, 140401(R) (2020)
Solids **3**, 93–110 (2022)



[data from: Shimizu *et al.*, *PRL* **91**, 107001 (2003)]

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$: Impurity Spins

ESR properties $T < T^*$
- additional satellite peak appears
- strong angle dependence (dipole-dipole coupling)

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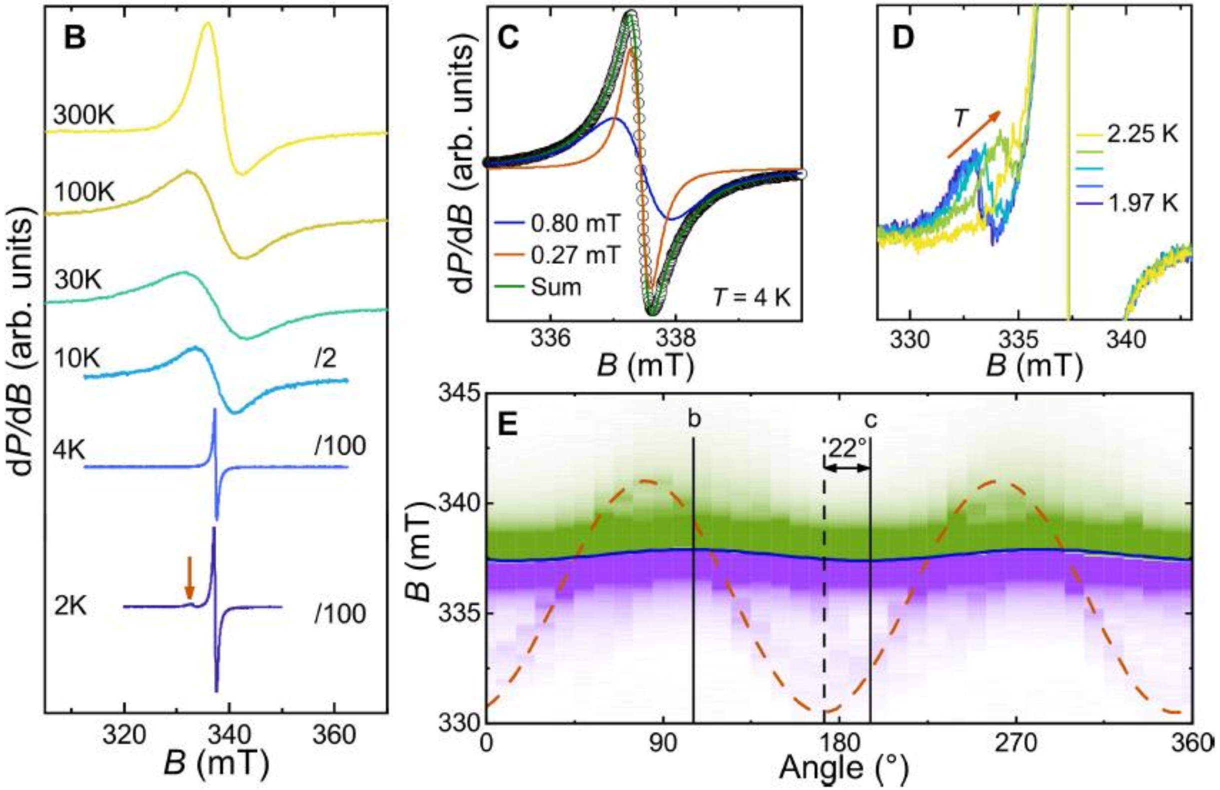

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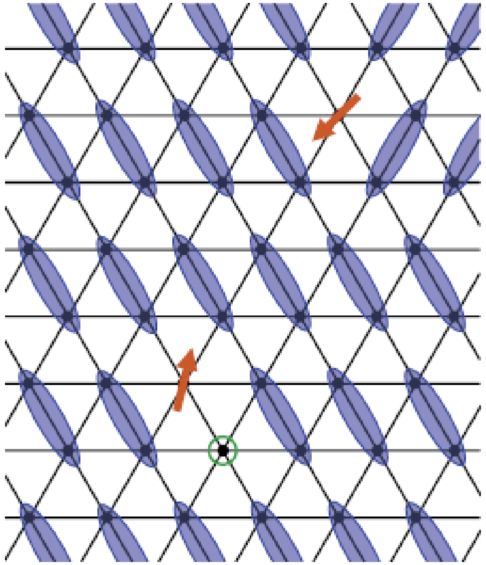

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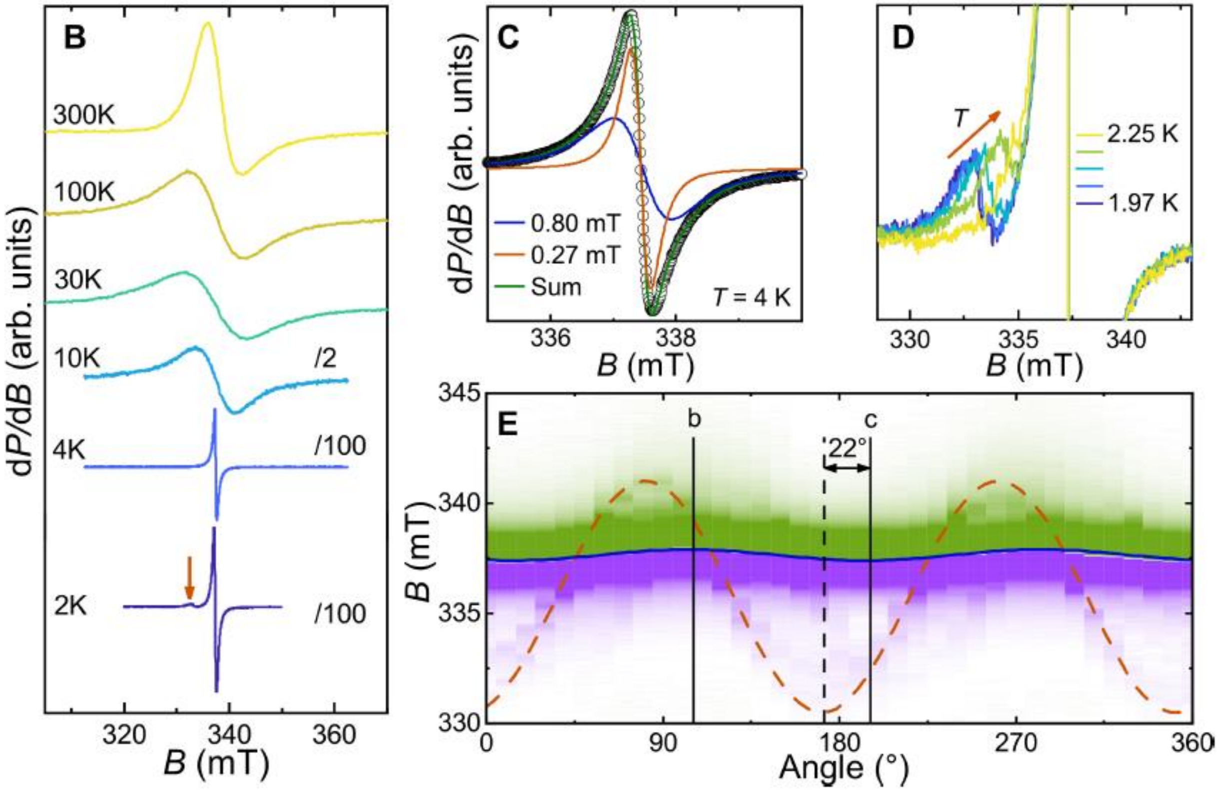

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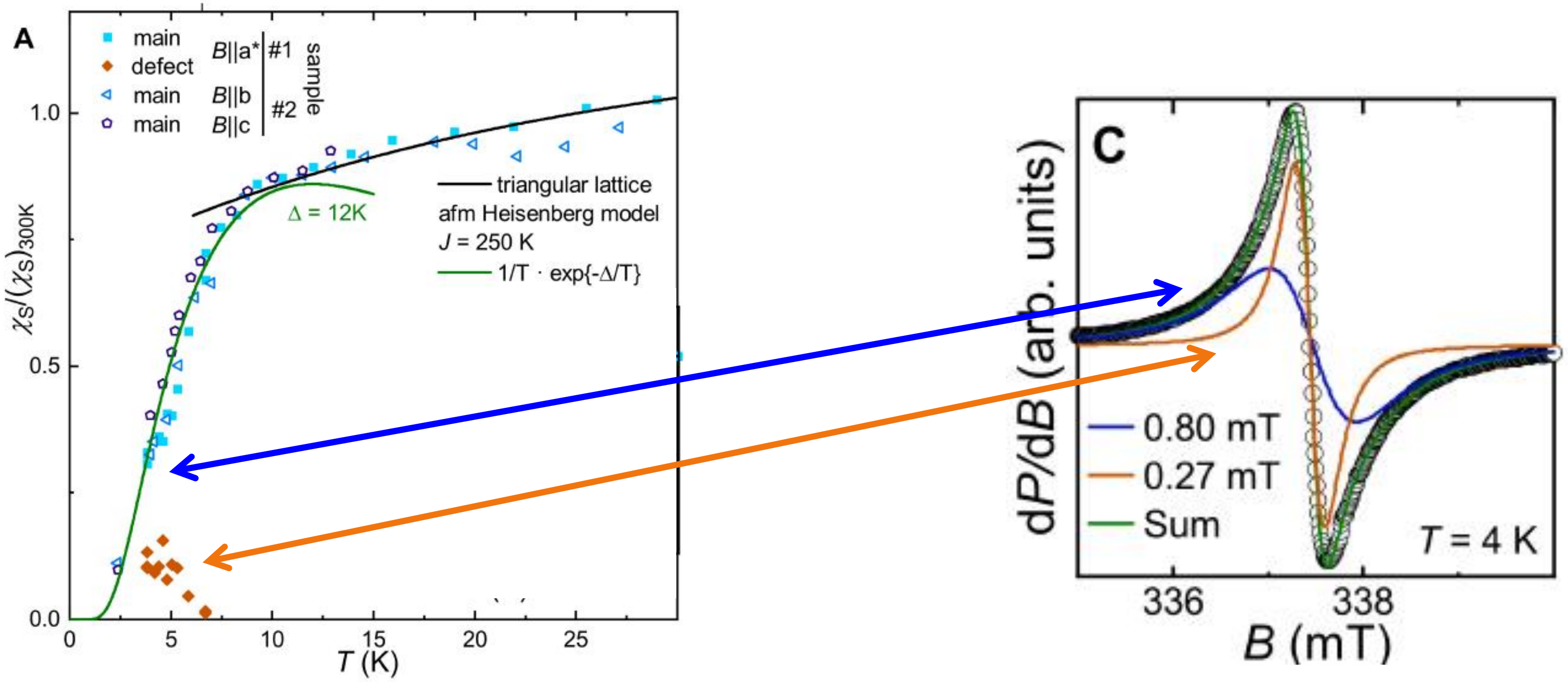


Miksch *et al.*, *Science* **372**, 276-279 (2021)

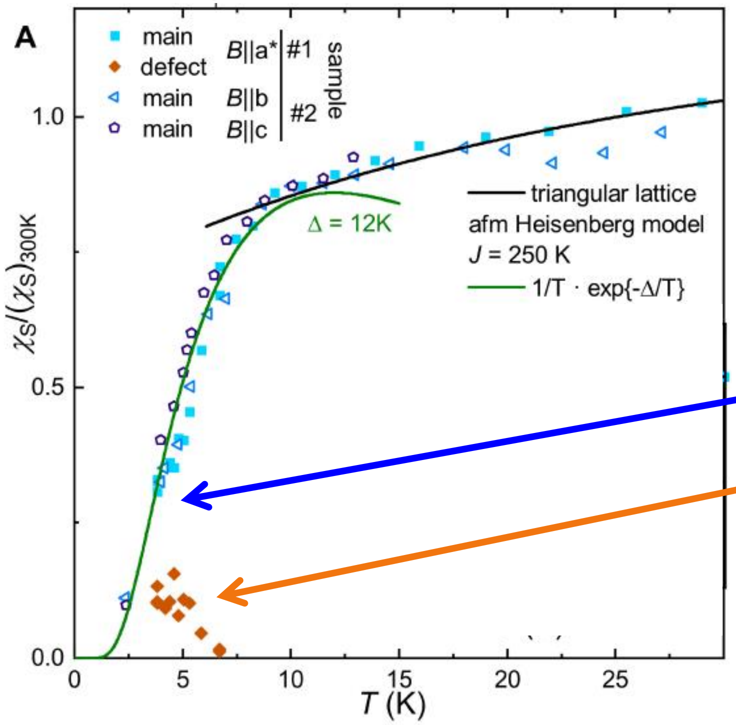
κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$: Spin Gap

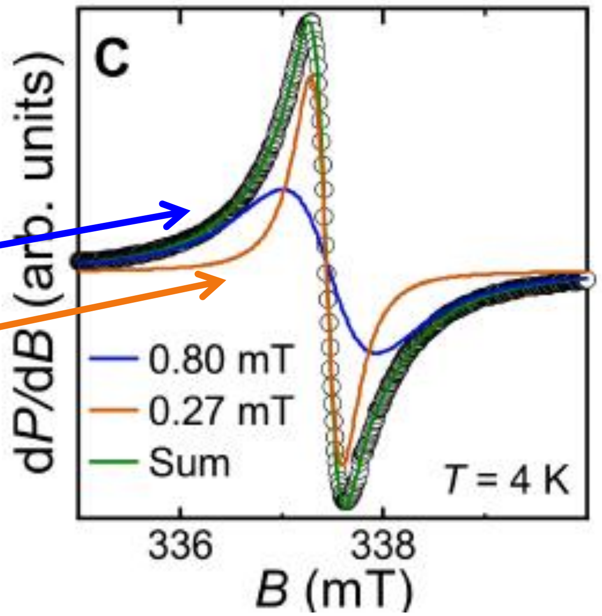
REPORT

MAGNETISM

Gapped magnetic ground state in quantum spin liquid candidate κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

Björn Miksch[1], Andrej Pustogow[1,2], Mojtaba Javaheri Rahim[1], Andrey A. Bardin[3], Kazushi Kanoda[4], John A. Schlueter[5,6], Ralph Hübner[1], Marc Scheffler[1], Martin Dressel[1]*





Miksch *et al.*, *Science* **372**, 276-279 (2021)

Spin Gap – Susceptibility

REPORT

MAGNETISM

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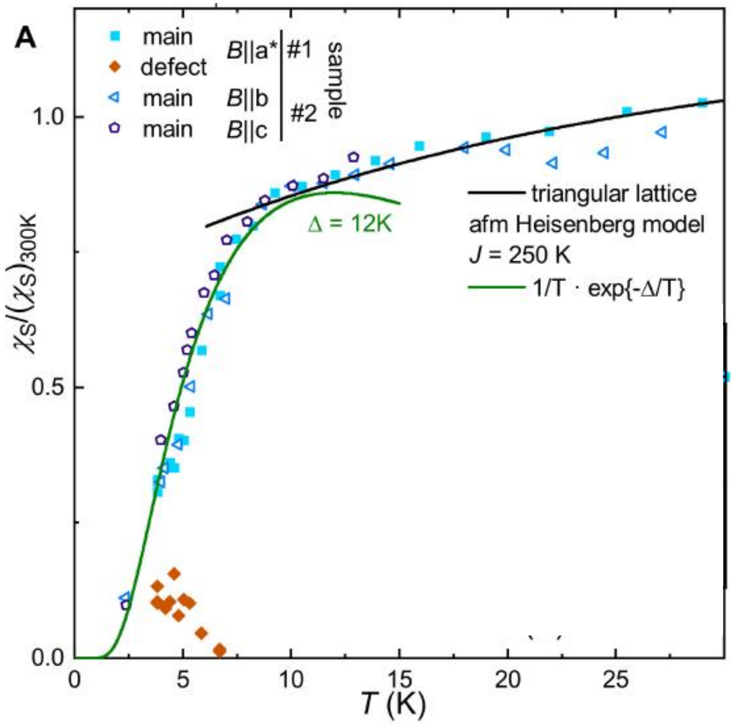
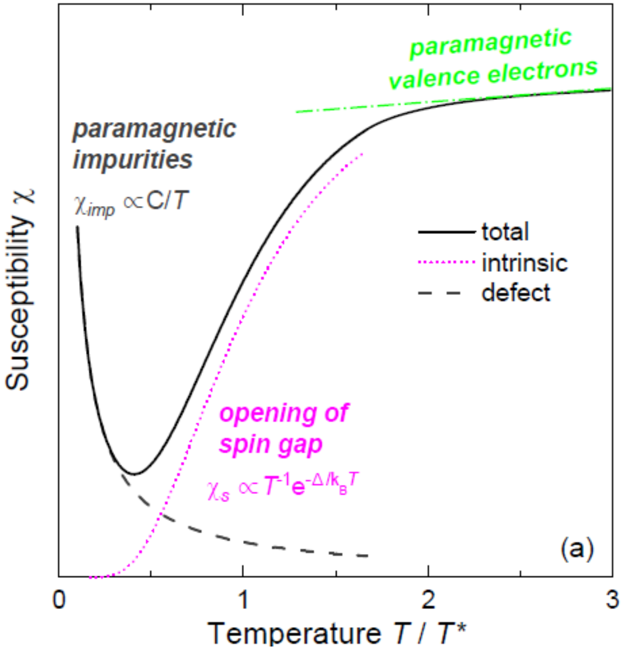
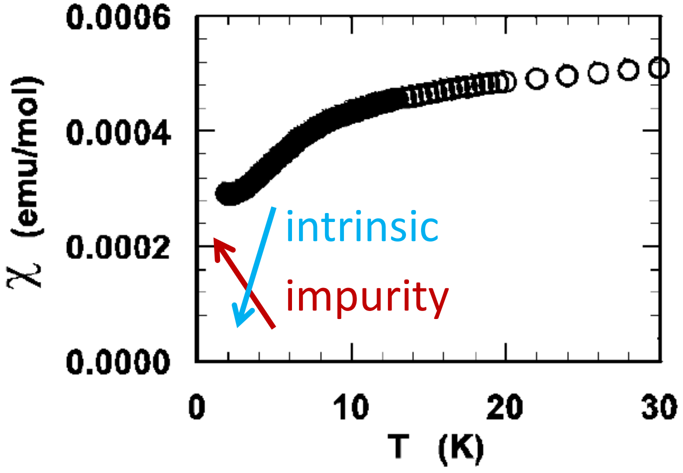


Miksch *et al.*, *Science* **372**, 276-279 (2021)

$$\chi_{bulk} = \chi_s + \chi_{impurity}$$



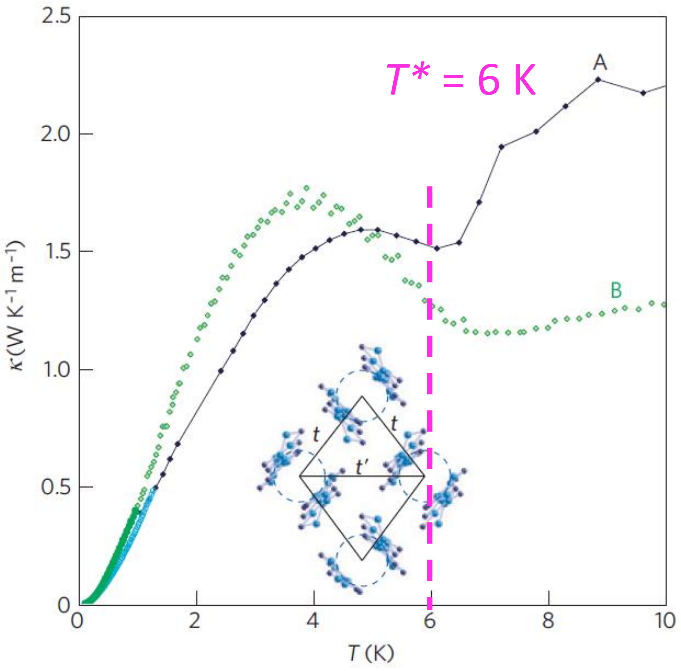
Pustogow, *Solids* **3**, 93–110 (2022)



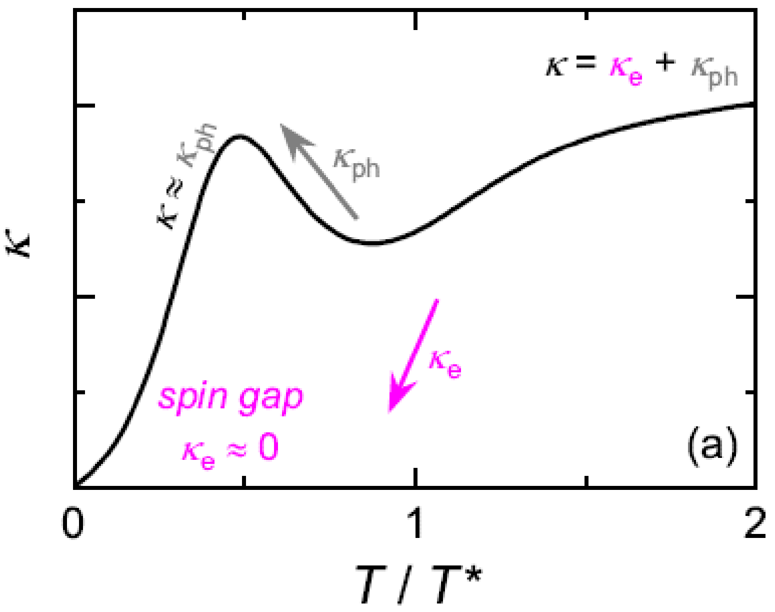
Shimizu *et al.*, *PRL* **91**, 107001 (2003)

Spin Gap – Thermal Transport

κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$



Yamashita *et al.*, *Nat. Phys.* **5**, 44–47 (2009)



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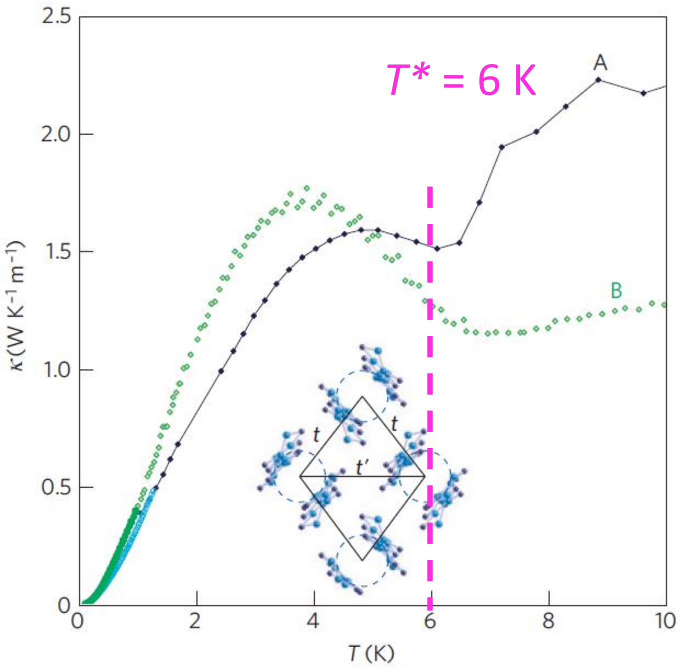

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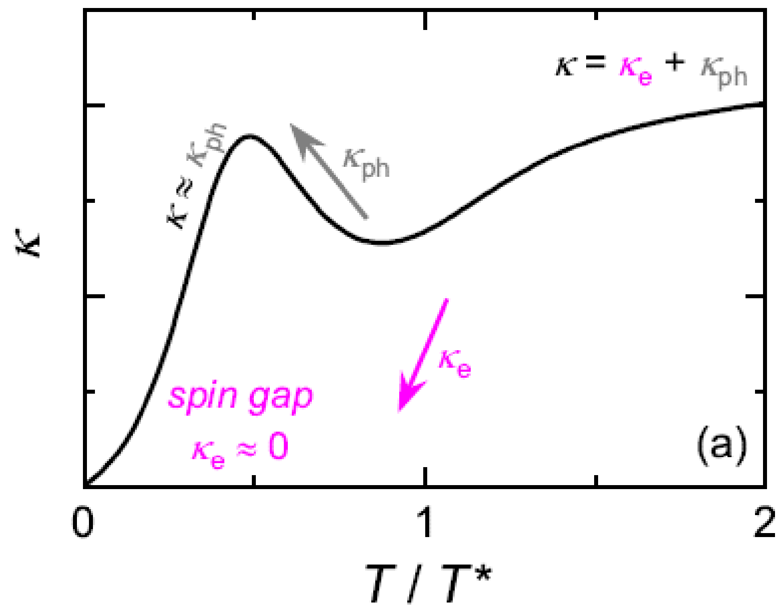
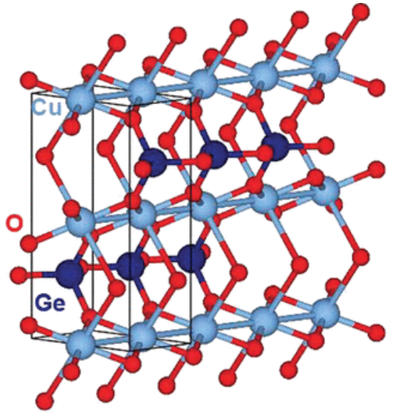
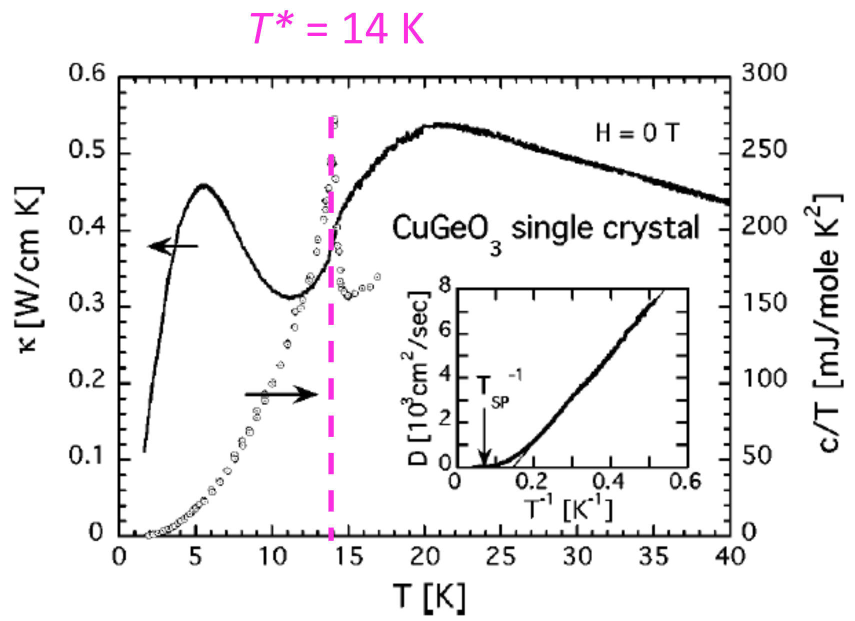


Pustogow, *Solids* **3**, 93–110 (2022)



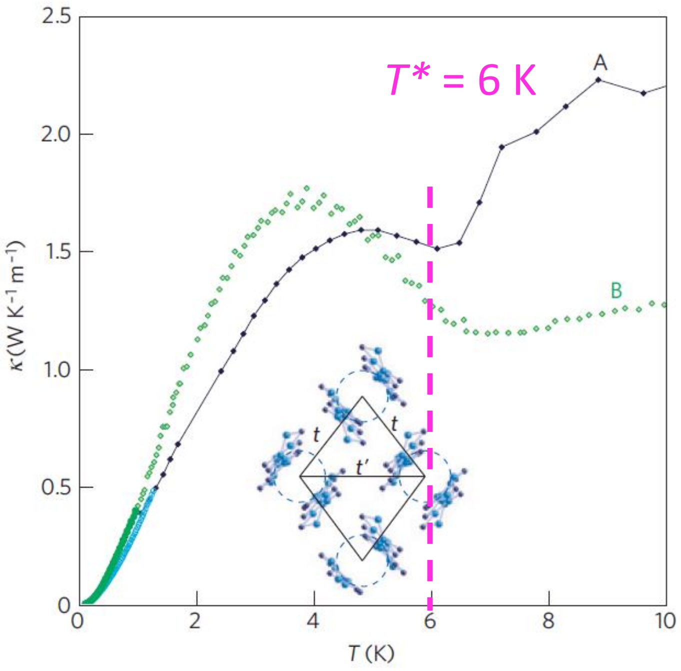
Spin-Peierls transition in $CuGeO_3$



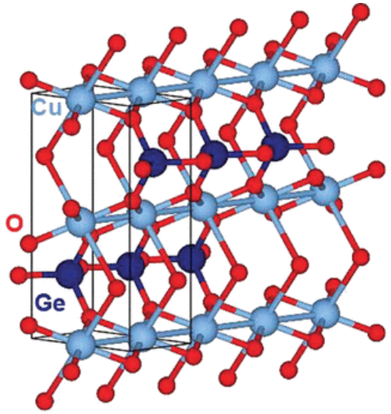
Ando *et al.*, *PRB* **58**, R2913 (1998)

Spin Gap – Thermal Transport

κ-$(BEDT\text{-}TTF)_2Cu_2(CN)_3$

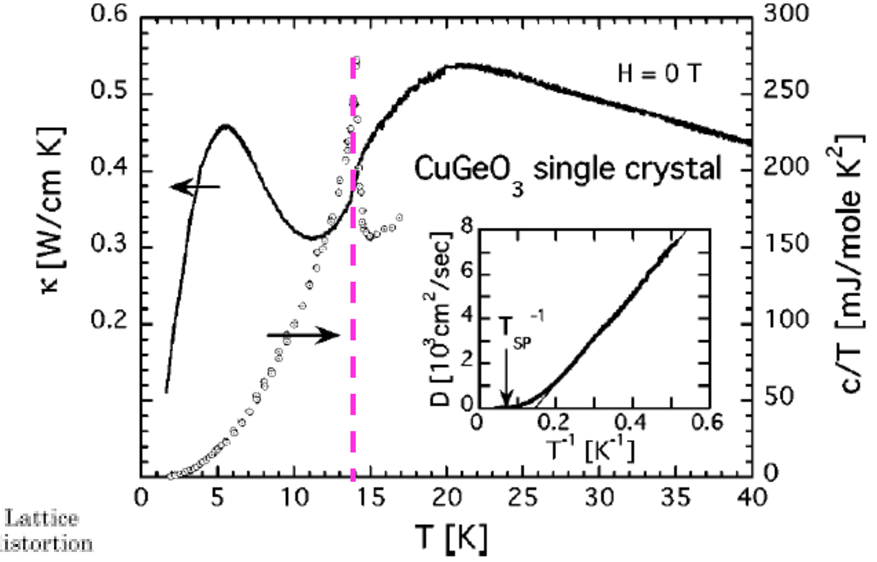


Yamashita *et al.*, *Nat. Phys.* **5**, 44–47 (2009)



Spin-Peierls transition in $CuGeO_3$

T* = 14 K



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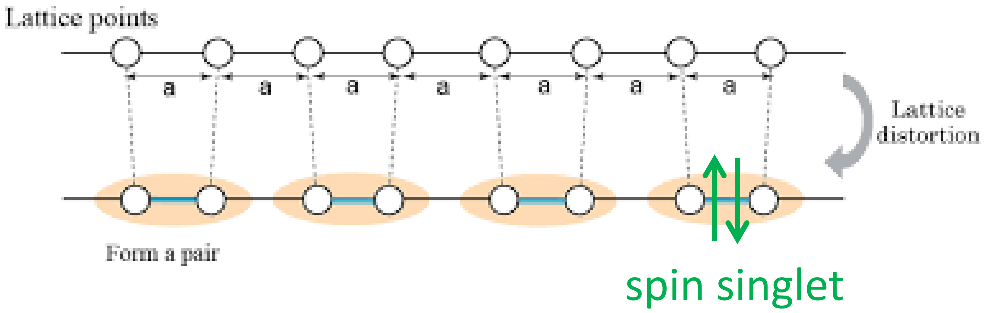
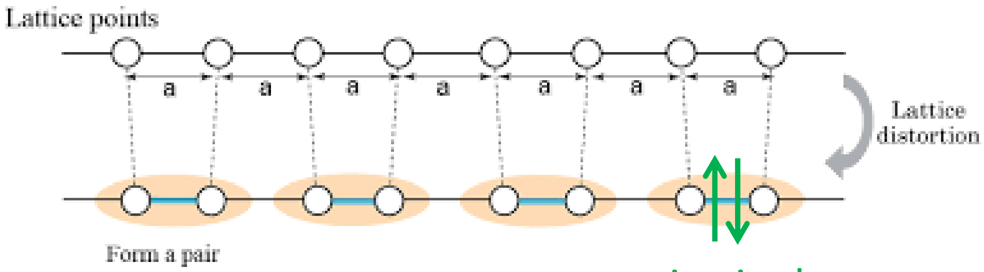
Spin-Peierls transition in 1D



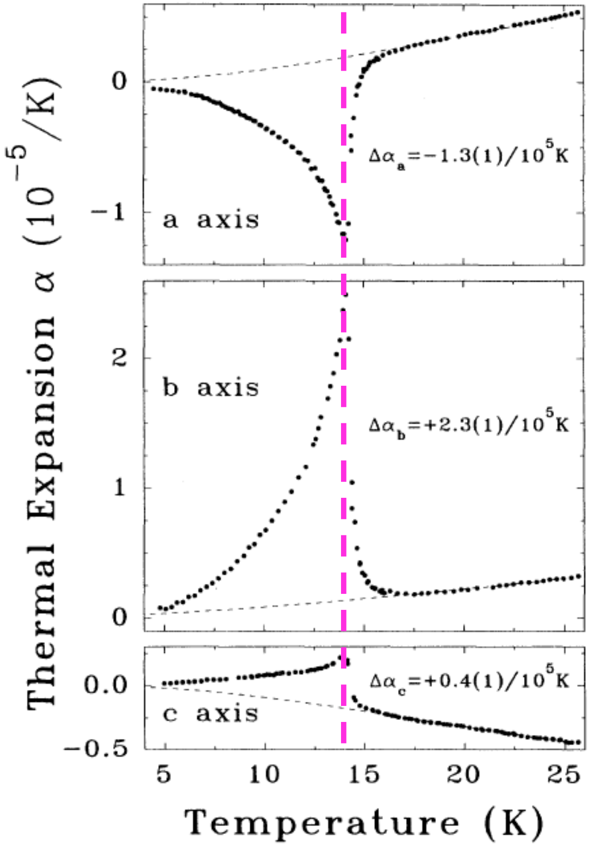
Spin Gap – Thermal Expansion

Spin-Peierls transition in 1D



$CuGeO_3$

T^* = 14 K



Winkelmann *et al.*, *PRB* **51**, 12884 (1995)

Spin Gap – Thermal Expansion

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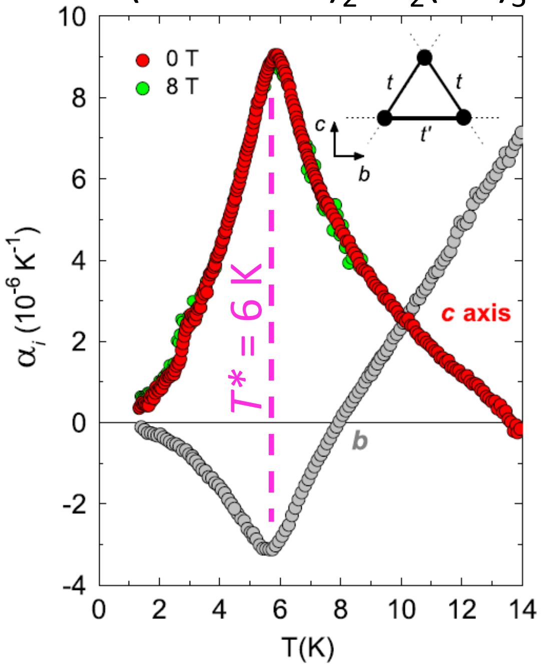
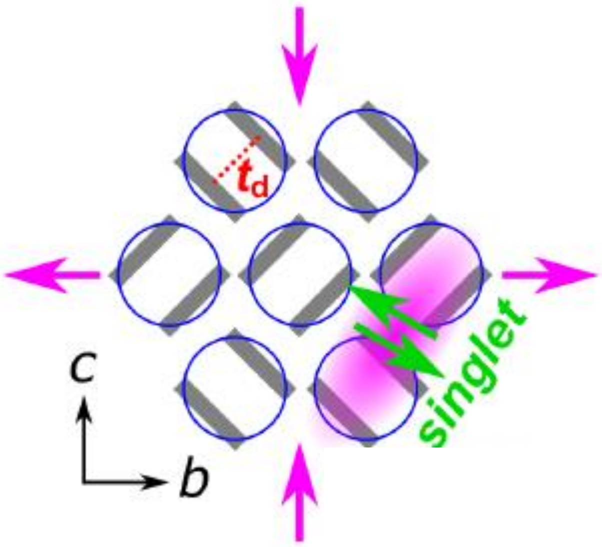


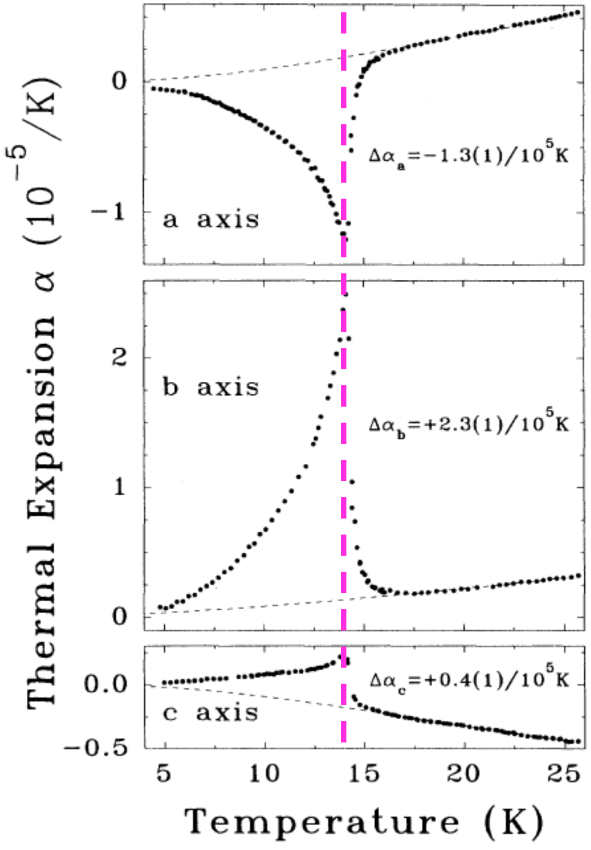
Manna et al., *PRL* **104**, 016403 (2010)



Pustogow, *Solids* **3**, 93–110 (2022)

$CuGeO_3$

*T** = 14 K



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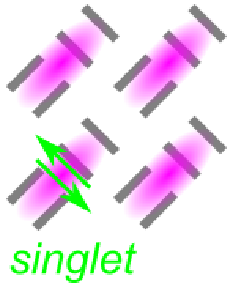
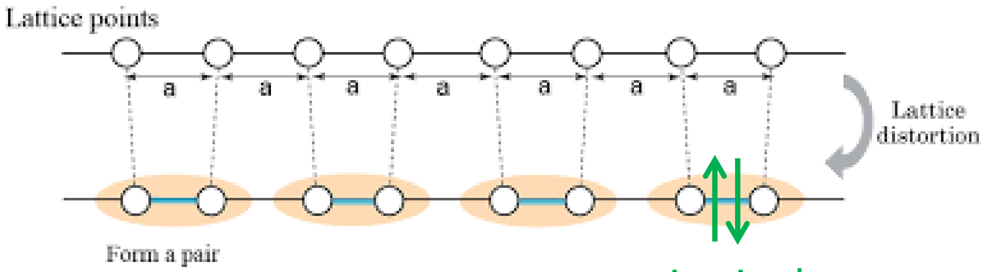


Valence Bond Solid in 2D

Spin-Peierls transition in 1D

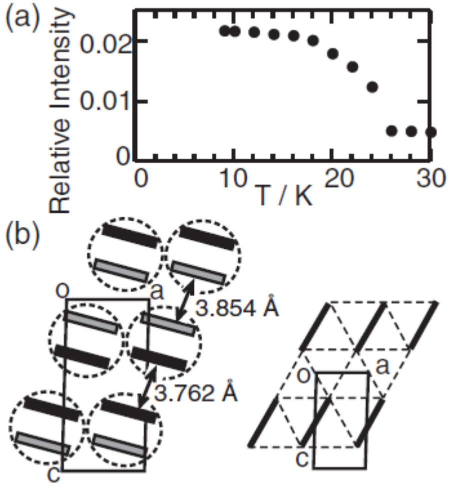


spin singlet

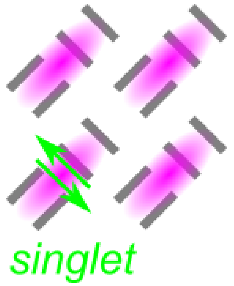
Spin Gap – Thermal Expansion

Chasing the spin gap through the phase diagram of a frustrated Mott insulator

A. Pustogow,[1] Y. Kawasugi,[2,3] H. Sakurakoji,[2] and N. Tajima[2,3] *under review* (2022)



Tamura *et al.*, *JPSJ* **75**, 93701 (2006)
Manna et al., *PRB* **89**, 045113 (2014)



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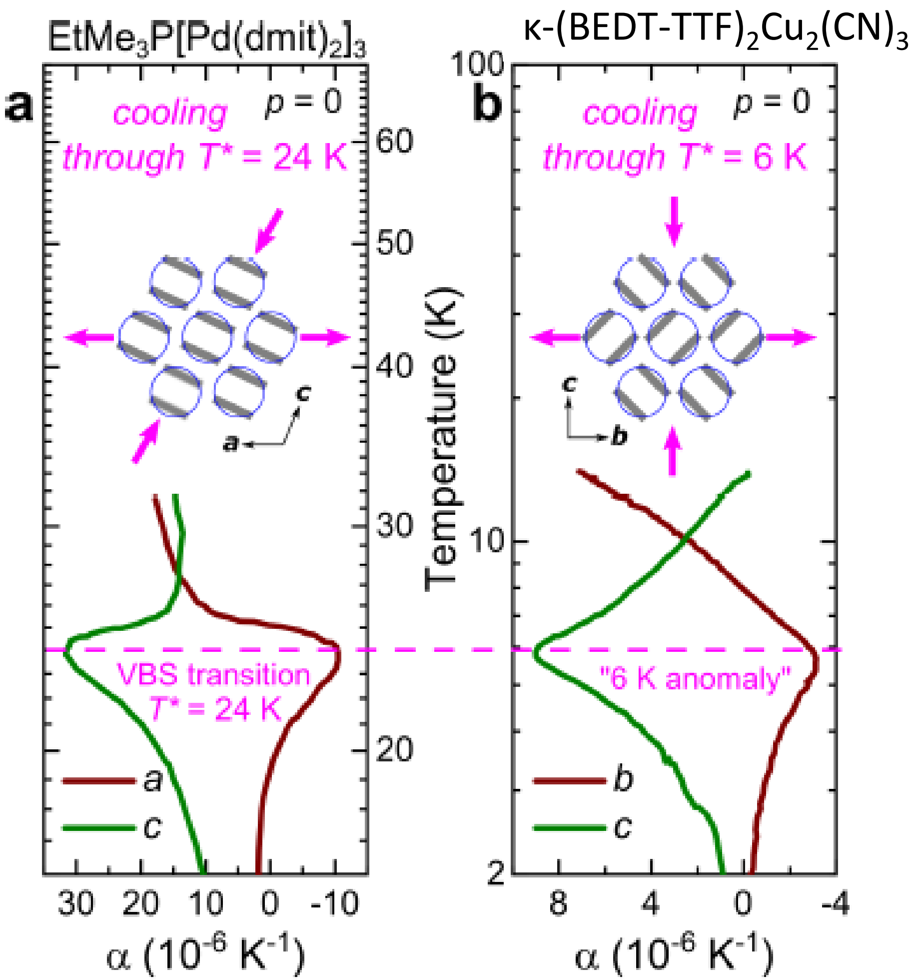

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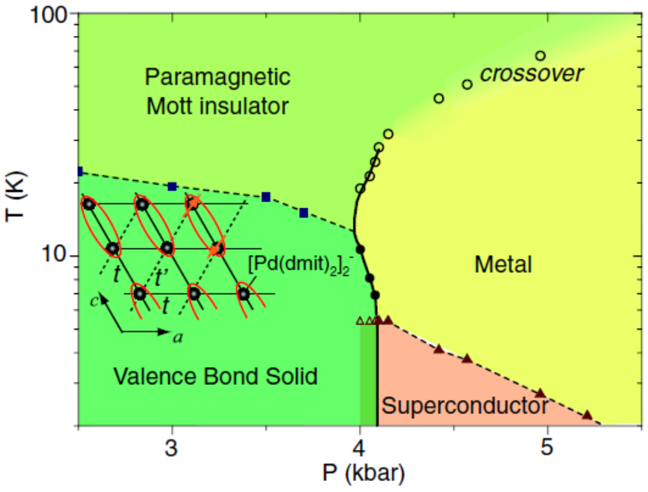
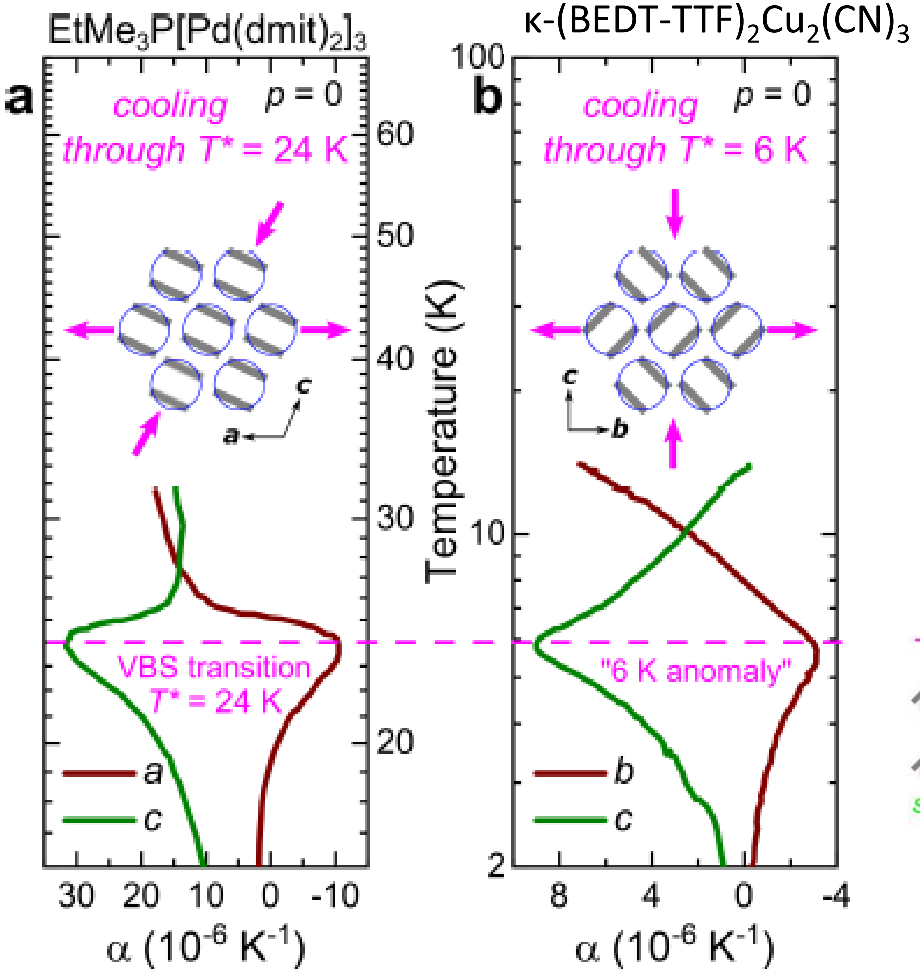
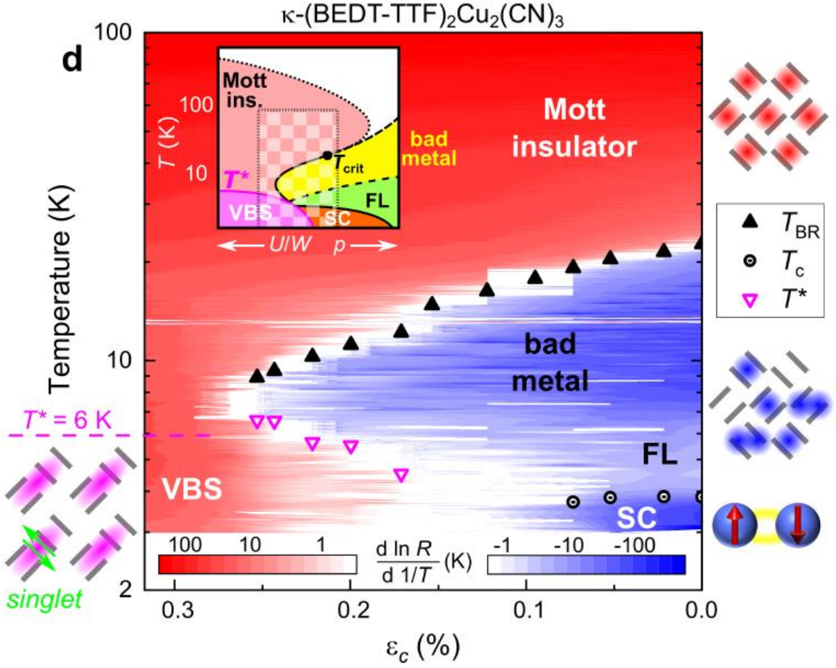


Shimizu *et al.*, *PRL* **99**, 256403 (2007)
Manna et al., *PRB* **89**, 045113 (2014)





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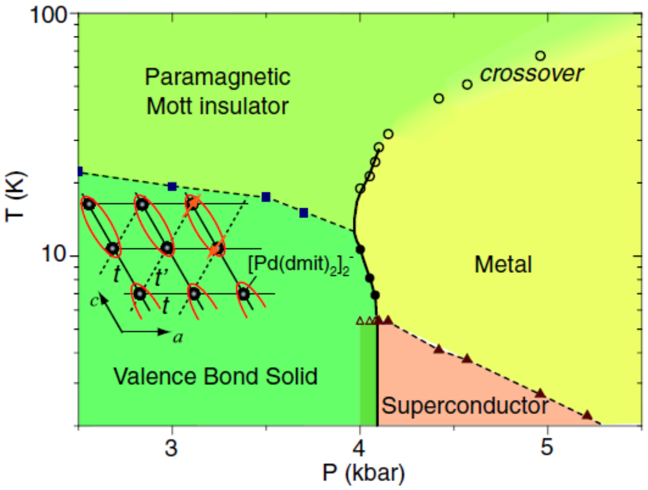

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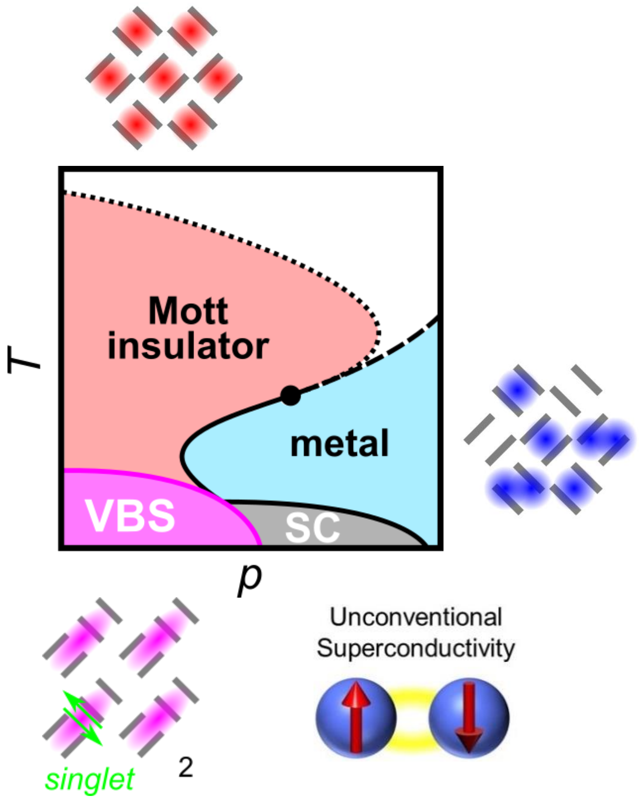

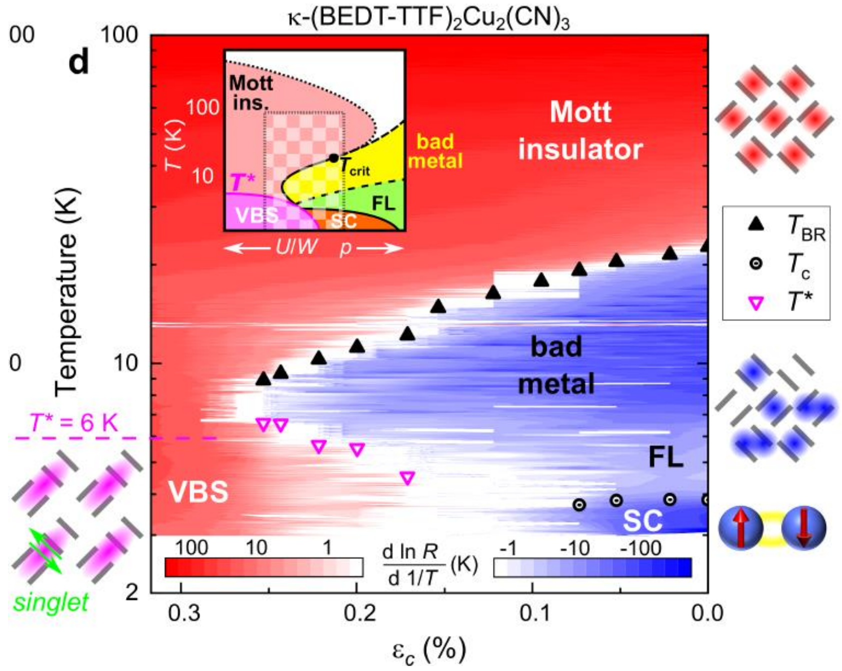

Ground State – Valence Bond Solid

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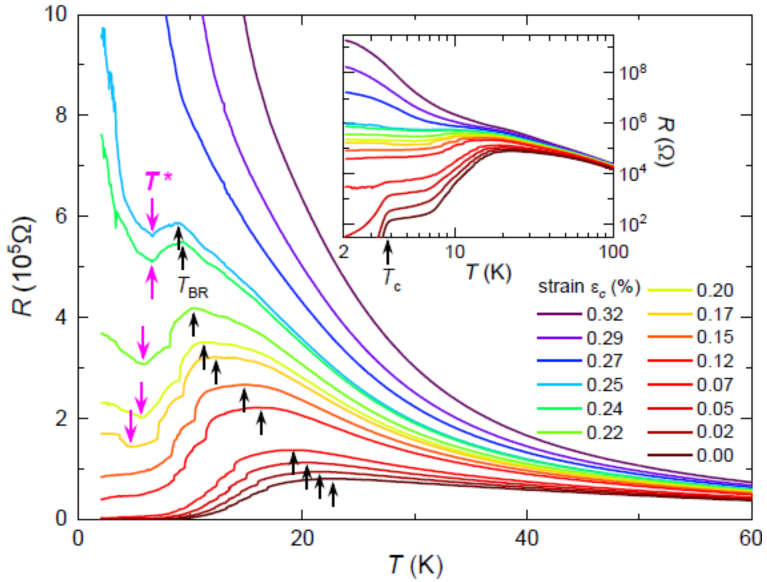
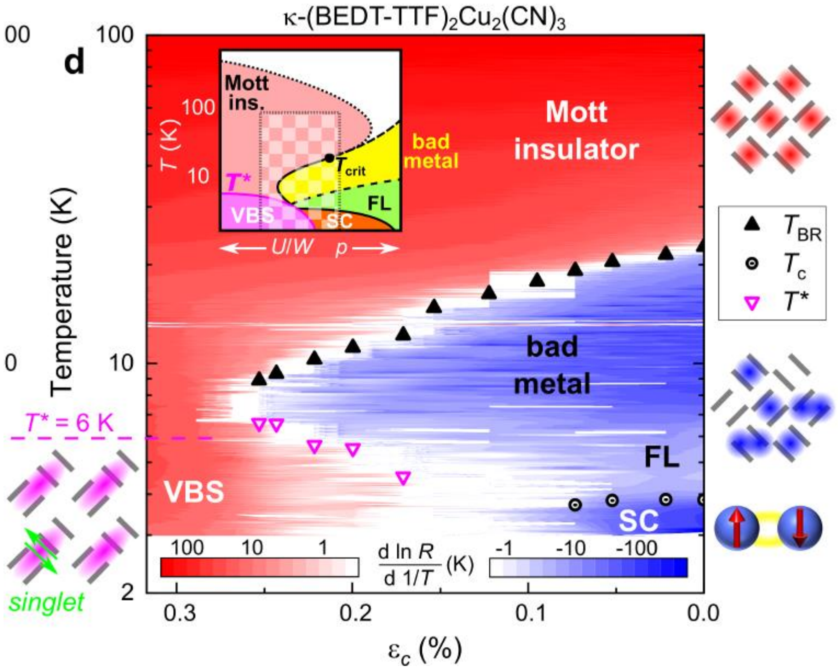


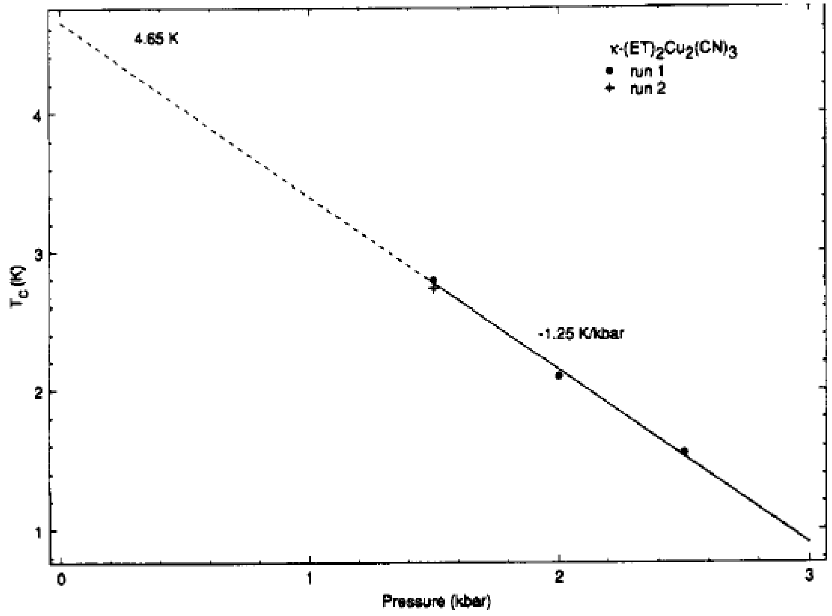


Quantum Spin Liquid?

1991

Superconductivity at 2.8 K and 1.5 kbar in κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$: The First Organic Superconductor Containing a Polymeric Copper Cyanide Anion

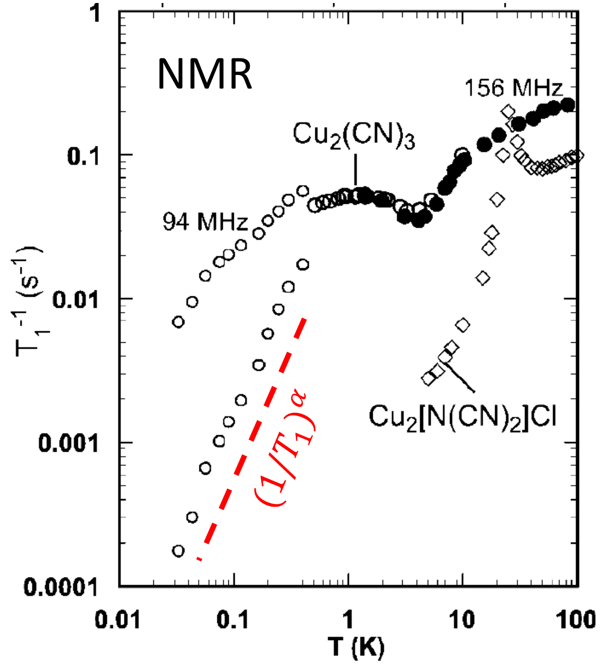
Geiser *et al.*, *Inorg. Chem.* **30**, 2586–2588 (1991)

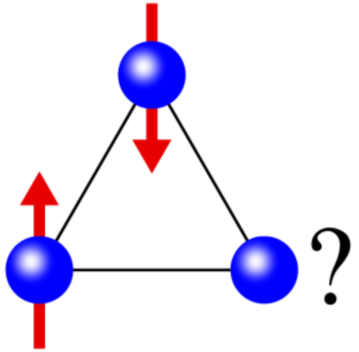


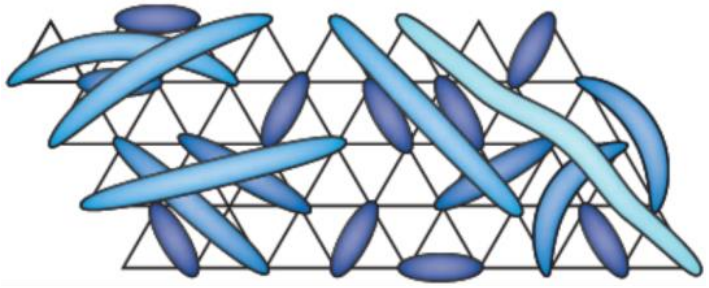
2003

- no antiferromagnetism
- quantum spin liquid?

Shimizu *et al.*, *PRL* **91**, 107001 (2003)







Balents, *Nature* **464**, 199–208 (2010)

Quantum Spin Liquid? ⟷ Spin Gap!

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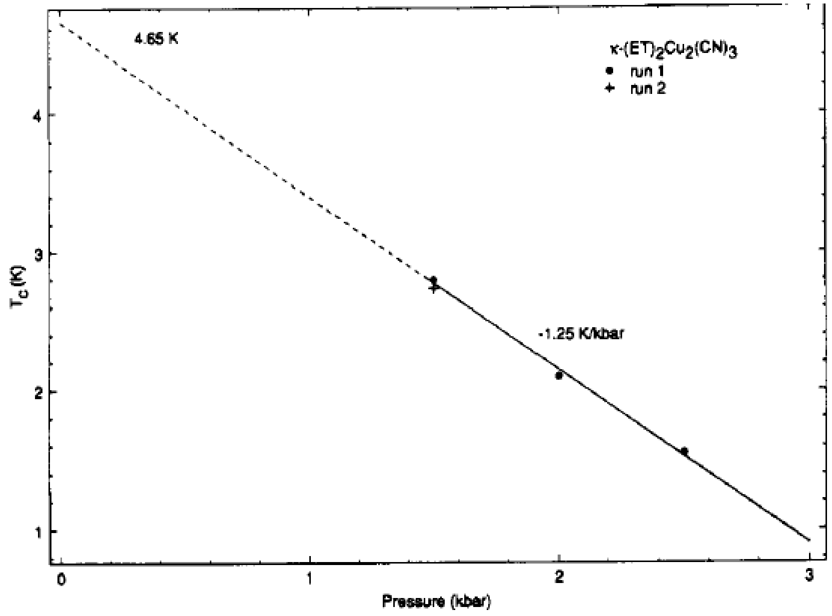

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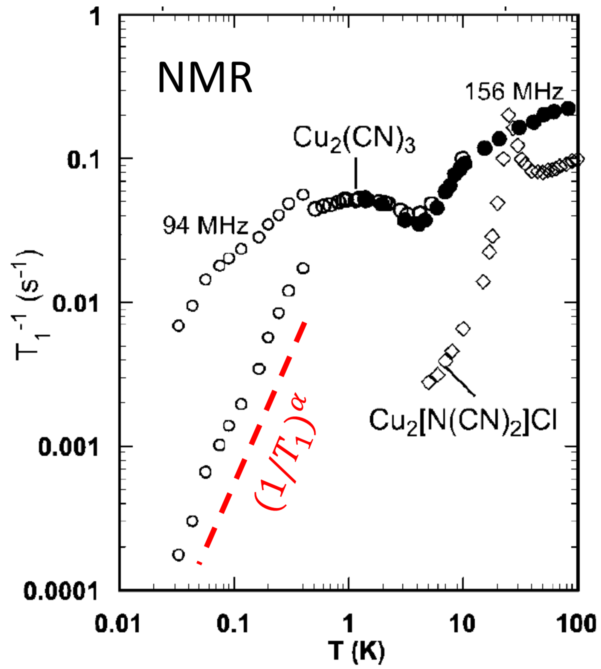

2021

REPORT

Science

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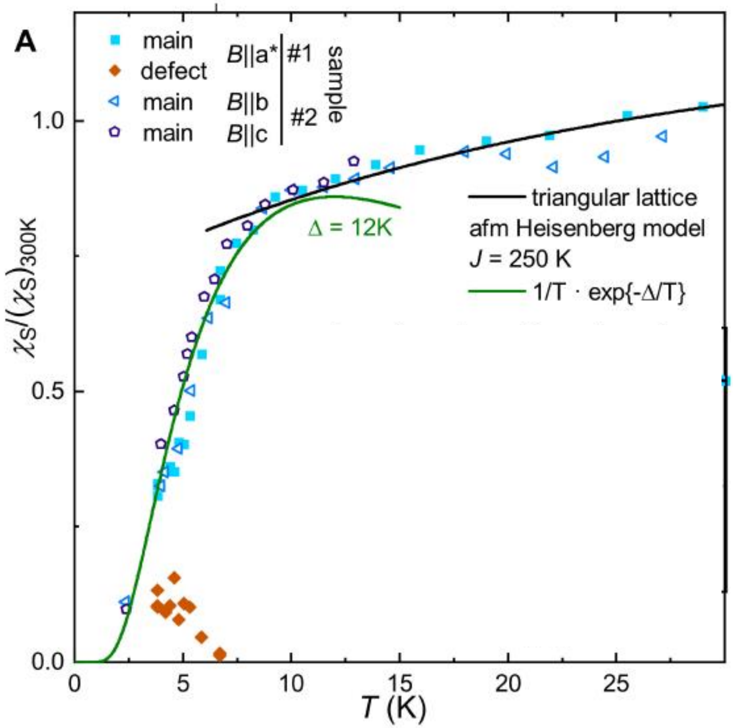


Pustogow Spectroscopy Lab

Conclusion

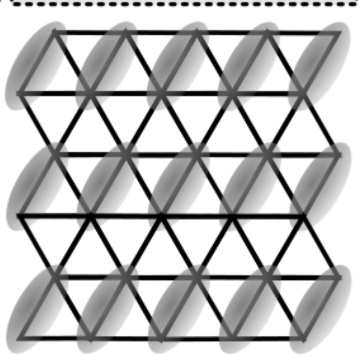
solids

Review

Thirty-Year Anniversary of κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$: Reconciling the Spin Gap in a Spin-Liquid Candidate

Andrej Pustogow

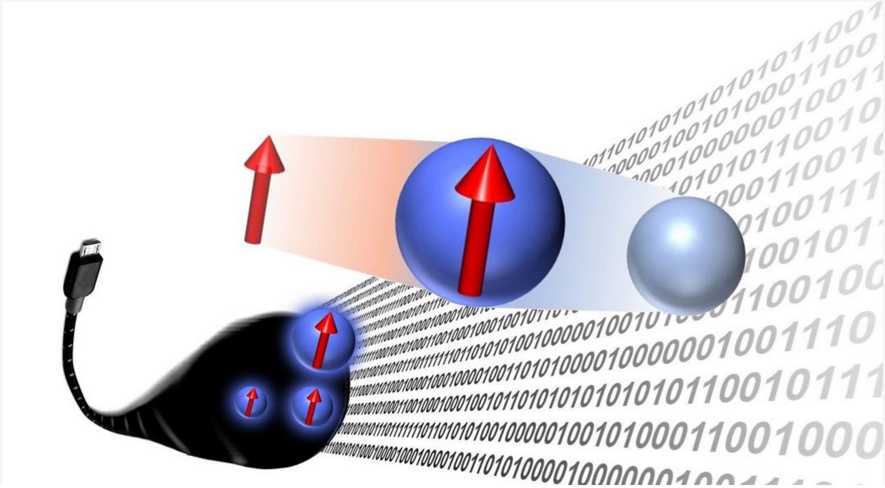
Solids **3**, 93–110 (2022)



26. April 2021

New measurements call spin liquids into question

Is it possible to transmit information through a material in the form of electron spins? New measurements show: not in the way that scientists had been working on for decades.



https://www.tuwien.at/en/tu-wien/news/news/neue-messungen-stellen-spin-fluessigkeiten-in-frage

2021

REPORT Science

MAGNETISM

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