Application of muon spectroscopy to the study of low-dimensional molecular materials

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Outline of talk

- Introduction
- Using LF-μSR to study spin dynamics in low-dimensional materials
- Low-dimensional molecular spin liquids:

  $Cu_3(HOTP)_2$ (S = 1/2, 2D kagome)

  $EtMe_3Sb[Pd(dmit)_2]_2$ (S = 1/2, 2D triangular $\rightarrow$ 1D chain)

- Summary

Collaborators

$Cu_3(HOTP)_2$

Diego López-Alcalá	ICMol, Valencia
Victor Garcia-Lopez	ICMol, Valencia
Miguel Clemente-León	ICMol, Valencia
Jose Baldoví	ICMol, Valencia
Eugenio Coronado	ICMol, Valencia

$EtMe_3Sb[Pd(dmit)_2]_2$

Yugo Oshima	RIKEN
Yasuyuki Ishii	Shibaura Institute of Technology
Isao Watanabe	RIKEN
Hitoshi Seo	RIKEN
Takao Tsumuraya	Kumamoto University
Tsuyoshi Miyazaki	NIMS, Tsukuba
Reizo Kato	RIKEN

Types of μSR measurement

Main methods
- **ZF-μSR**
- **TF-μSR**
- **LF-μSR**

Other methods
- RF-μSR
- Photoexcited μSR
- Negative muons (μ^-SR)

Main μSR measurements and their uses

ZF-μSR

- Test for spin ordering or spin freezing (down to mK temperatures)
- Measuring ionic diffusion in energy materials

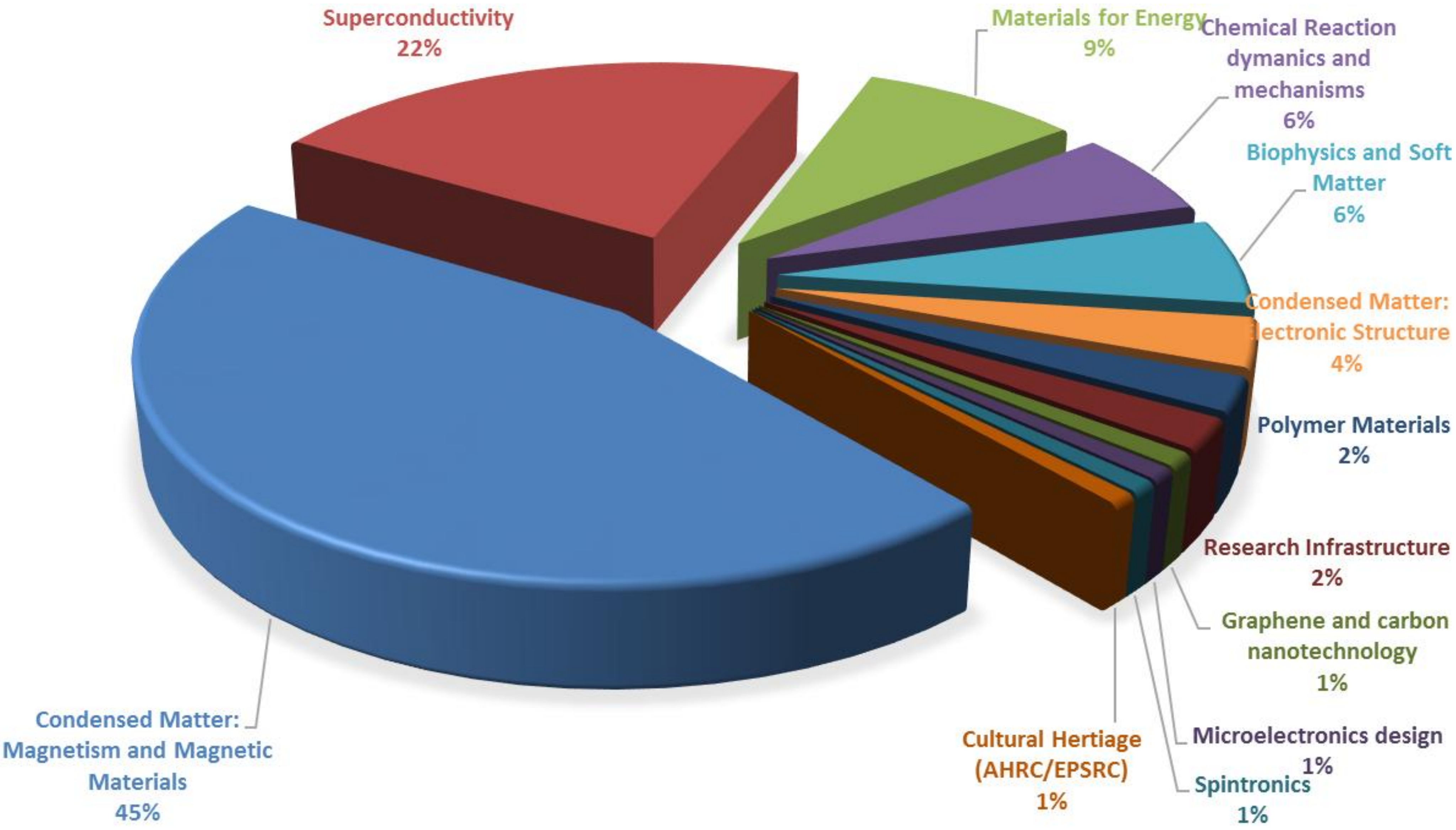
TF-μSR

- Exploring phase diagrams: closing gaps, crossing QCPs etc.
- Following field-induced spectral broadening and satellite features
- Exploring muonium chemistry

LF-μSR

- Providing information about spin dynamics to test against models
- Resolving contributions from different relaxation mechanisms
- Giving information about quantum entanglement

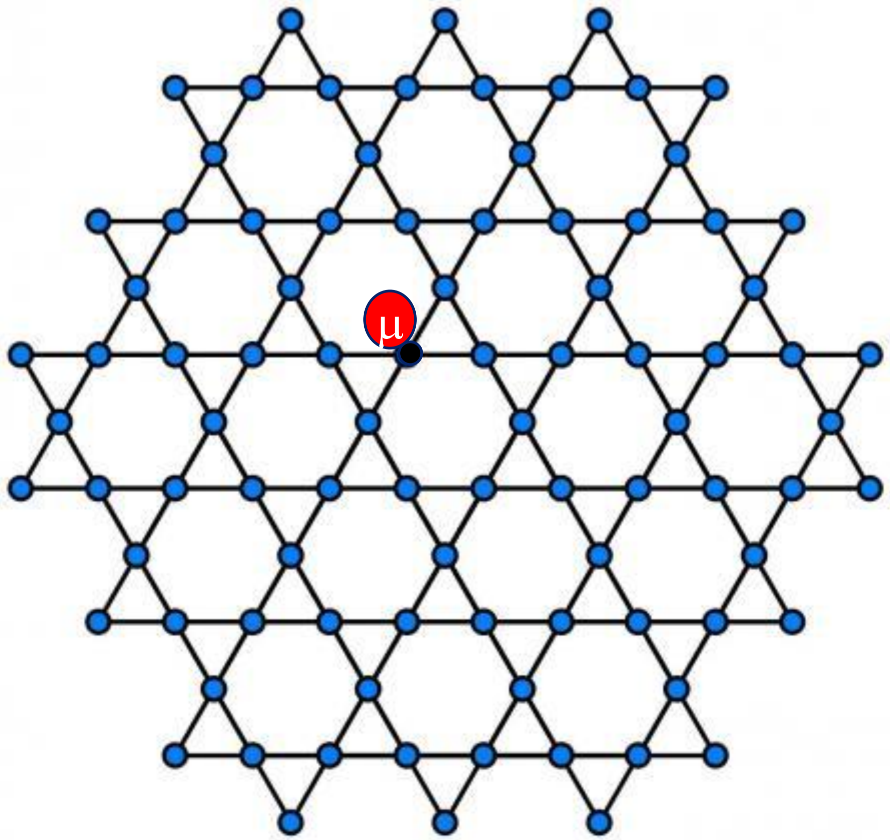
Science Themes for Muon Proposals at ISIS



Using LF-μSR to probe diffusive spin dynamics

Key ideas:

- Random walk for the unpaired spin that propagates via the nearest neighbour exchange interaction
- Intermittent hyperfine interaction with the static muon sitting at one probe point in the structure
- Spin autocorrelation function $S(t)$ follows from all possible diffusion paths that return to the muon site
- Spectral density of spin fluctuations $J(\omega)$ is the Fourier transform of $S(t)$
- Spectral density is probed at a frequency ω that tracks the applied field



Diffusive spin dynamics in low dimensional materials

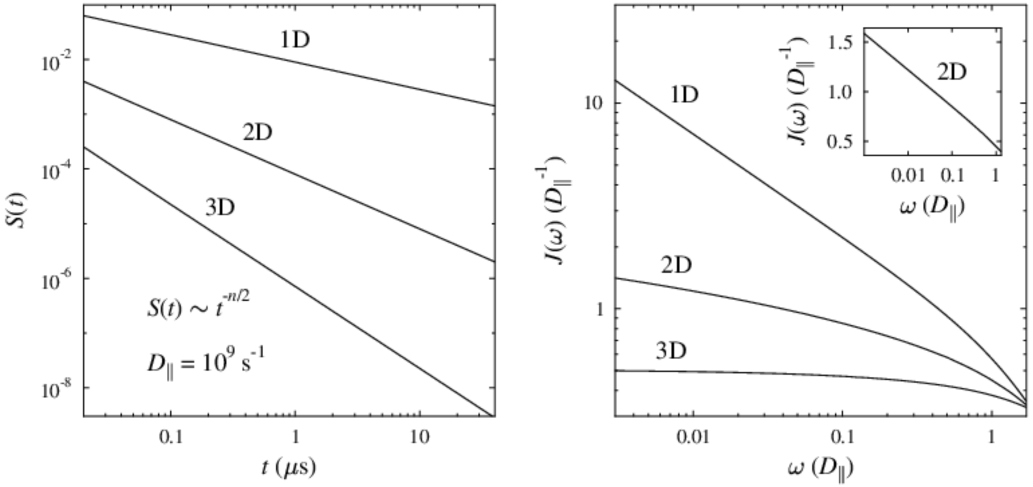
Autocorrelation function for *n* dimensional diffusion $S_n(t) = [e^{-2tD_{\parallel}} I_0(2tD_{\parallel})]^n$

Corresponding spectral density $J(\omega) = 2\int_0^\infty S_n(t)\cos\omega t \; dt$

LF-μSR relaxation rate

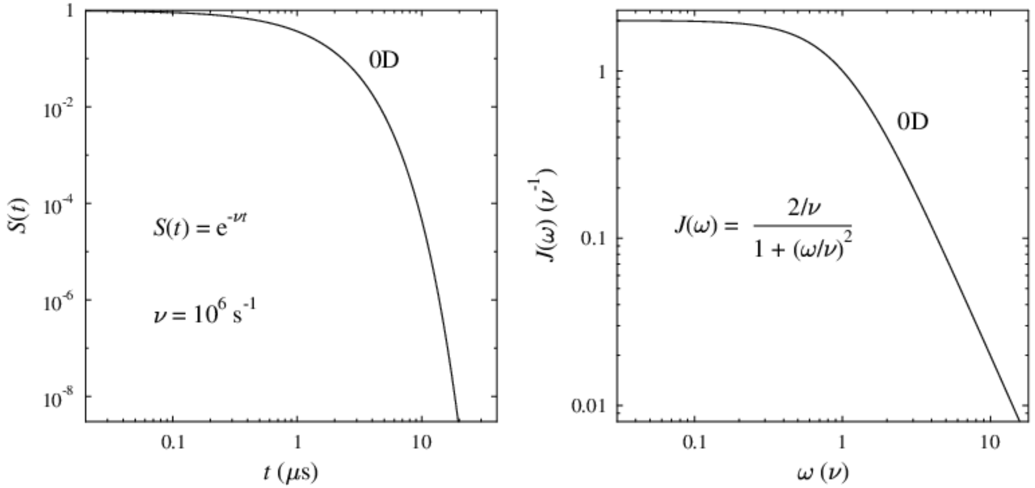
$\lambda \propto J(\omega)$ $\omega \propto B_{LF}$

Diffusion for
n = 1 to 3



Spin diffusion

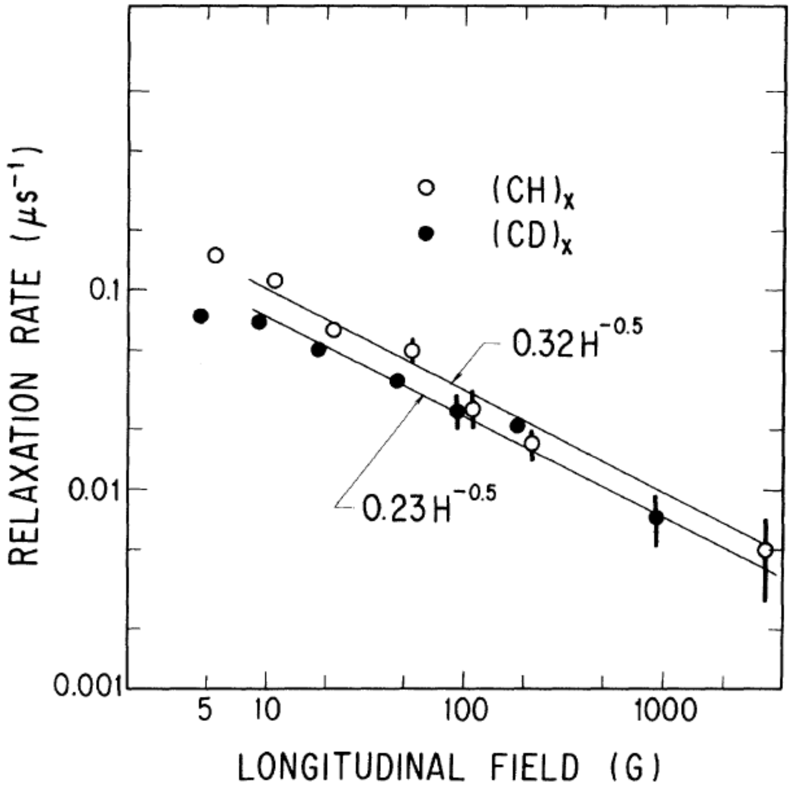
Comparison
with localised
fluctuations
(*n* = 0)



BPP/Redfield
model (NMR)

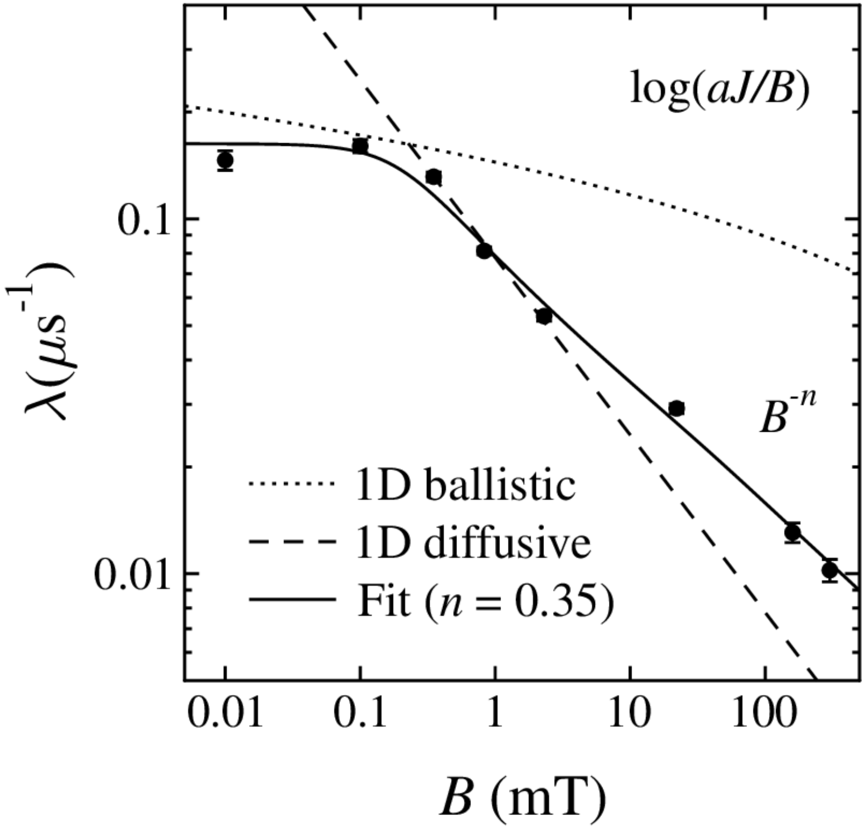
Diffusive 1D Spin Dynamics: Polymers and Spin Chains

Solitons in *trans*-polyacetylene



Nagamine et al, PRL 53, 1763 (1984)

Spinons in DEOCC-TCNQF_4



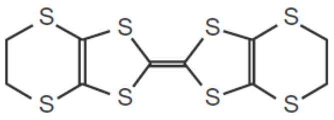
Pratt et al, PRL 96, 247203 (2006)

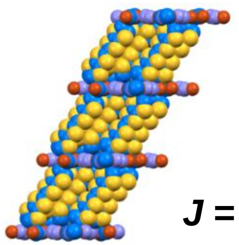
2D Quantum spin liquids

- Original Anderson 1973 RVB theory for a QSL was on the S=1/2 HAF triangular lattice
- However, nearest neighbour exchange interactions on their own give 120° AF order
- We need higher order interactions such as ring-exchange to stabilise a QSL
- Kagome lattice also provides simple framework for supporting the QSL state

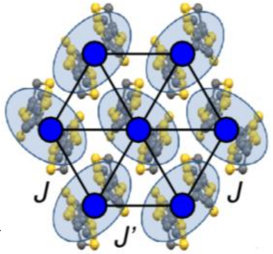
Molecular systems

e.g. radical dimers
κ-$(ET)_2Cu_2(CN)_3$ and
κ-$(ET)_2Ag_2(CN)_3$

ET: 

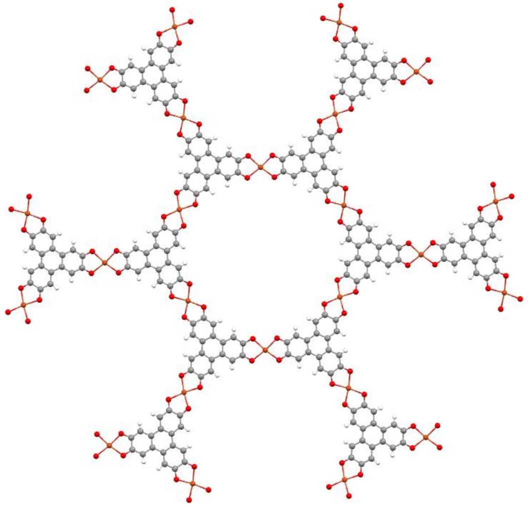


J = 250 K



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

Metal-organic-frameworks (MOFs)



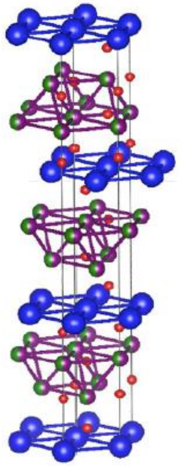
Kagome: $Cu_3(HOTP)_2$

Inorganic systems

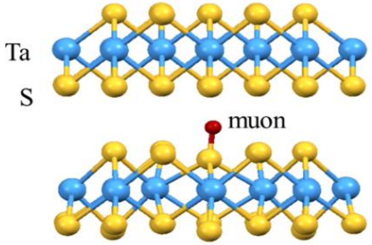
e.g.

$YbMGaO_4$ (M=Mg,Zn) and $YbZn_2GaO_5$

$J \approx 2$ K



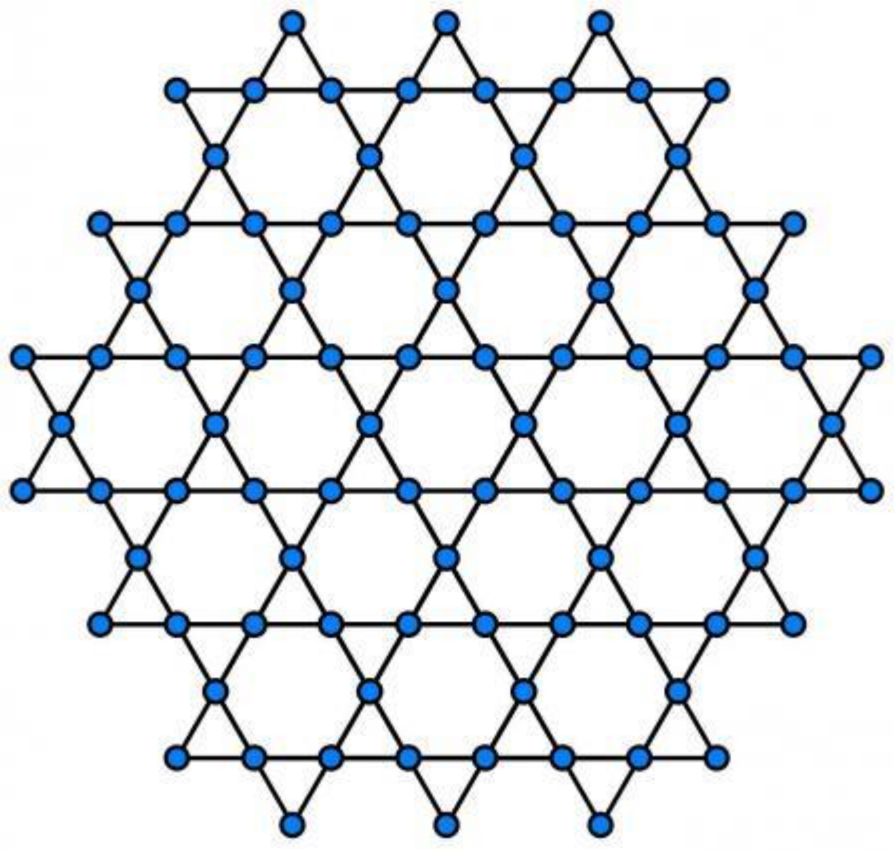
1T-TaS_2



Kagome-lattice 2D Quantum Spin Liquids

Theory for the nature of the QSL state in the *S*=1/2 kagome lattice is not at all settled:

- Gapped or gapless?
- U(1) or Z_2 gauge symmetry?
- Chiral or not?
- Spinon Fermi surface or quadratic or linearly dispersing spinons?



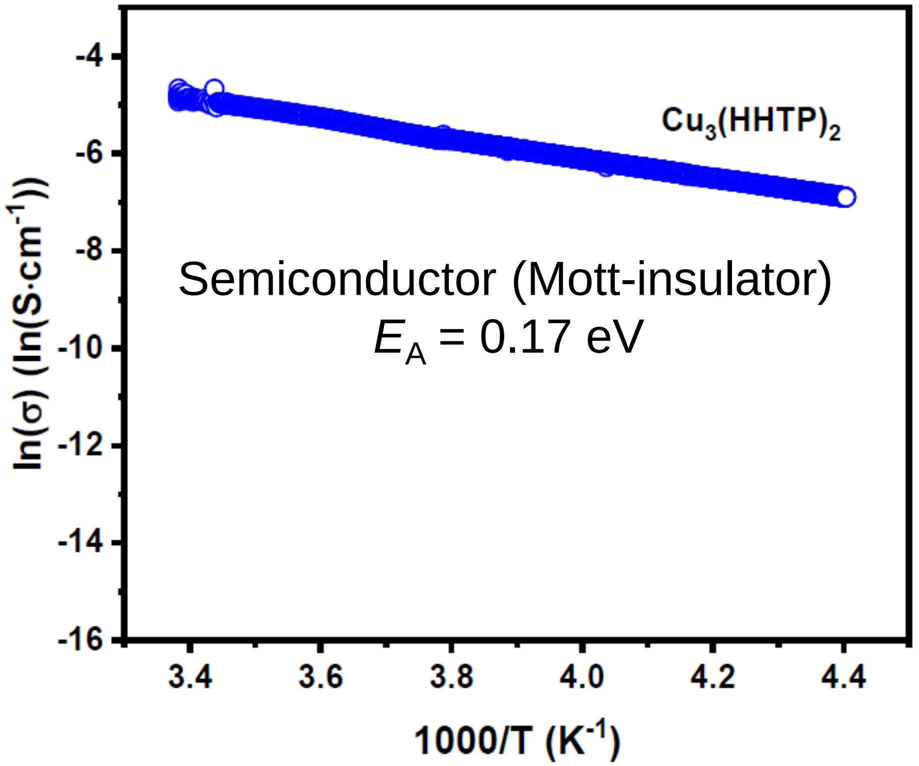
The **experimental** situation for the ideal kagome lattice is also often unclear, e.g. due to site mixing and non-symmetric lattices in mineral-based kagome systems

MOFs provide a promising new avenue

Kagome MOF system $Cu_3(HOTP)_2$

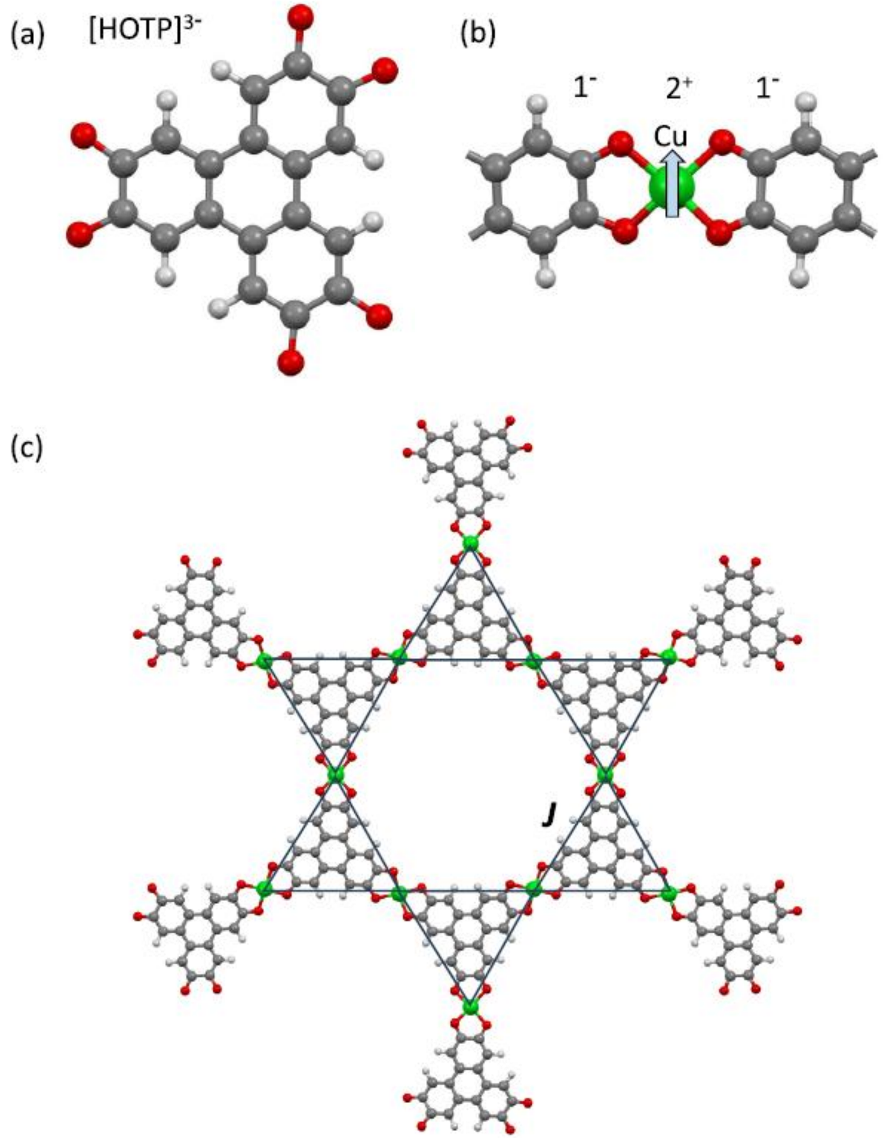
Kagome-lattice of $S = ½$ Cu in the
Metal-Organic-Framework (MOF) $Cu_3(HOTP)_2$

also known as $Cu_3(HHTP)_2$

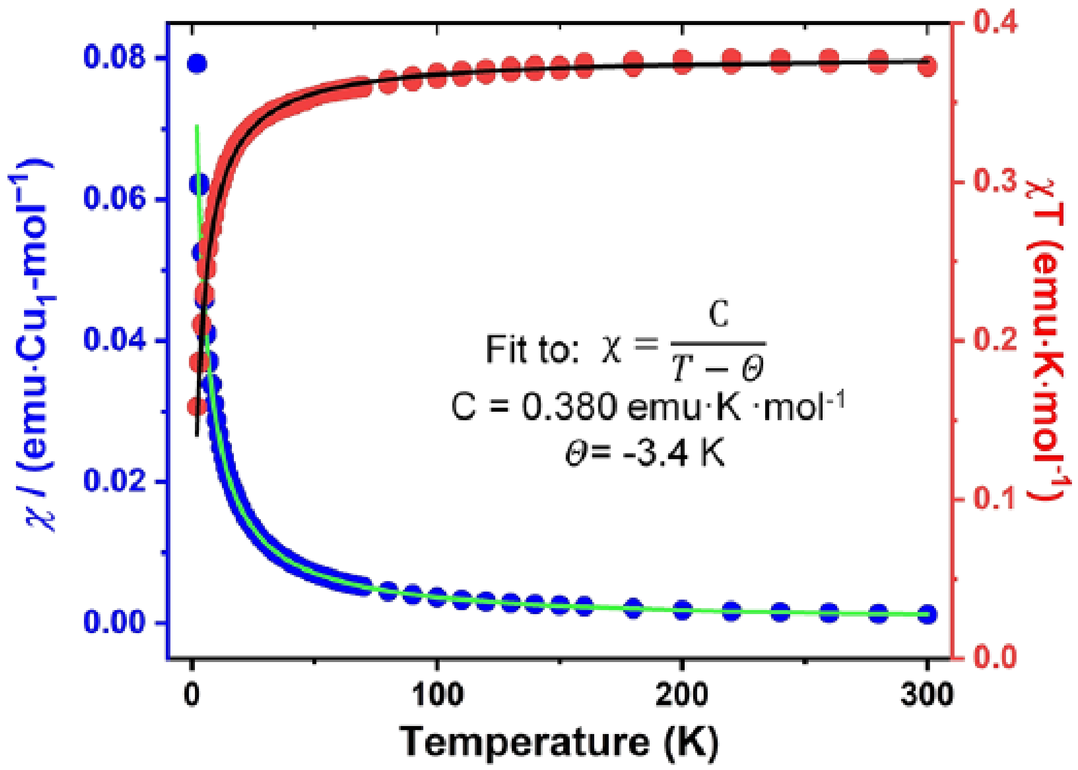


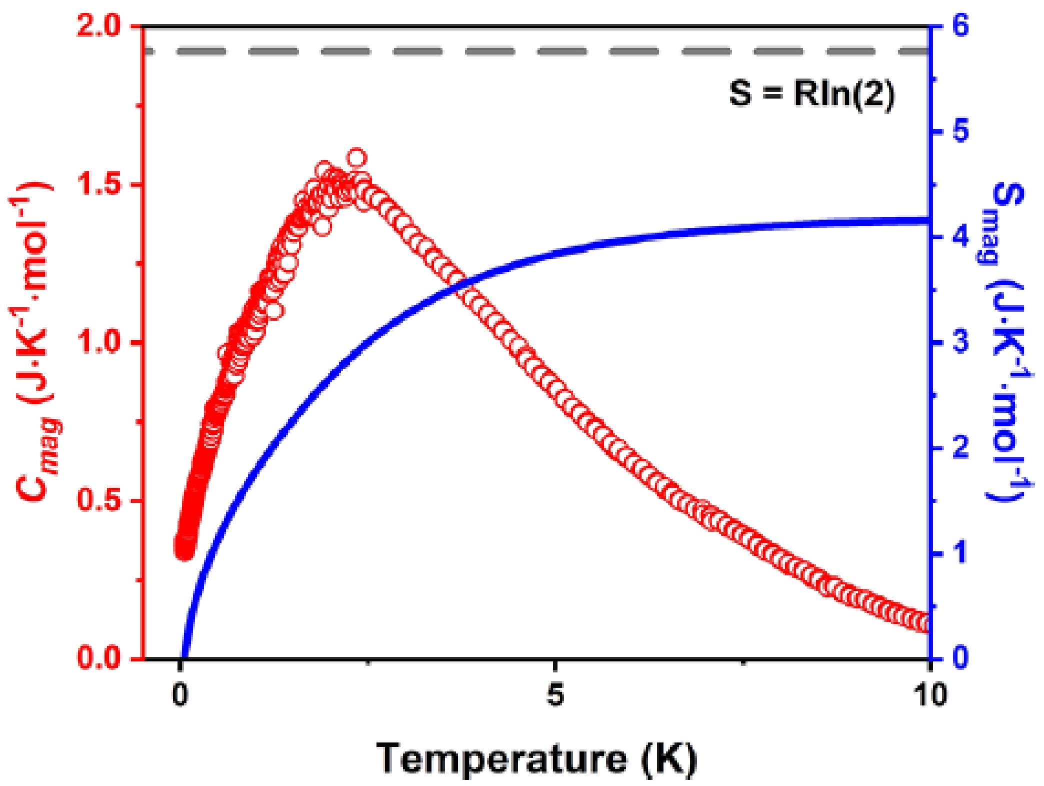
Misumi et al, J. Am. Chem. Soc. 142, 16513 (2020)

HOTP is hexaoxytriphenylene



Exchange Coupling and Residual Entropy





From Curie-Weiss fit: $J = 2\theta/z = 1.7$ K

From high T series expansion: $J = 2.0$ K

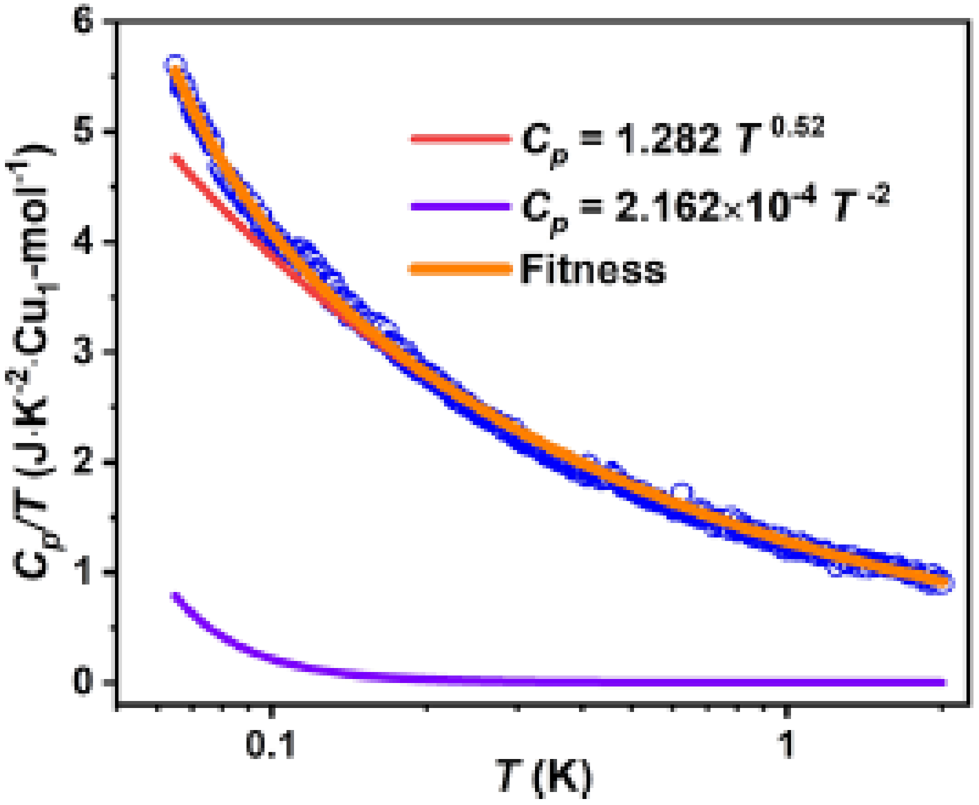
Residual entropy is 30% of *R* ln 2

Consistent with a QSL ground state (prediction is 40 %)

Misumi et al, J. Am. Chem. Soc. 142, 16513 (2020)

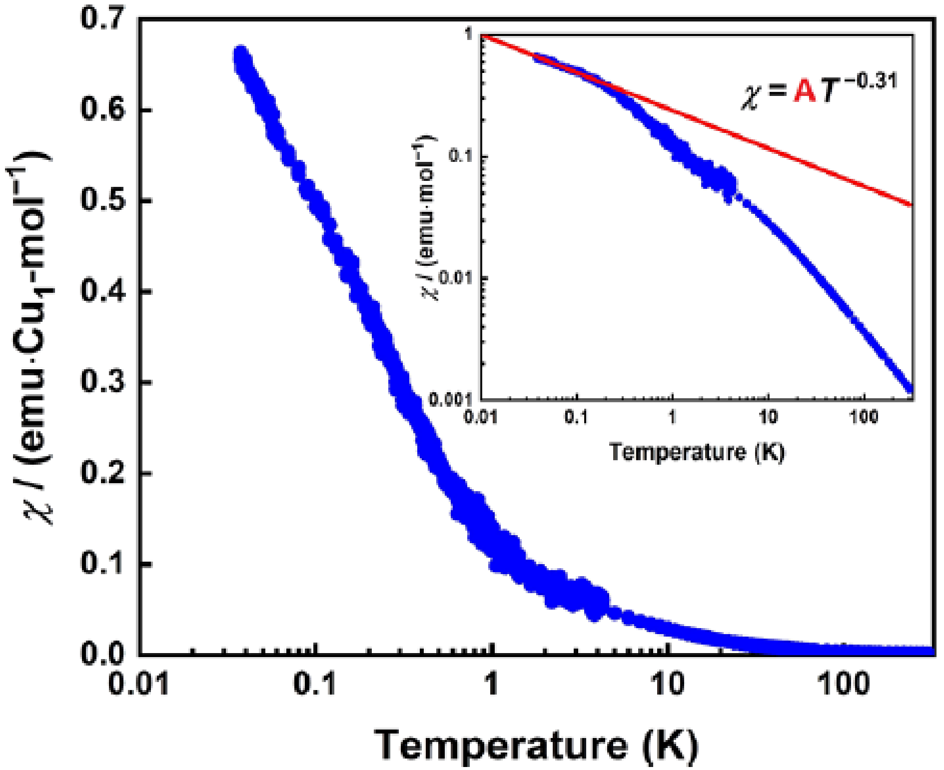
Power Laws for Specific Heat and Magnetic Susceptibility

Low temperature specific heat



Power law $n_C = 0.52$

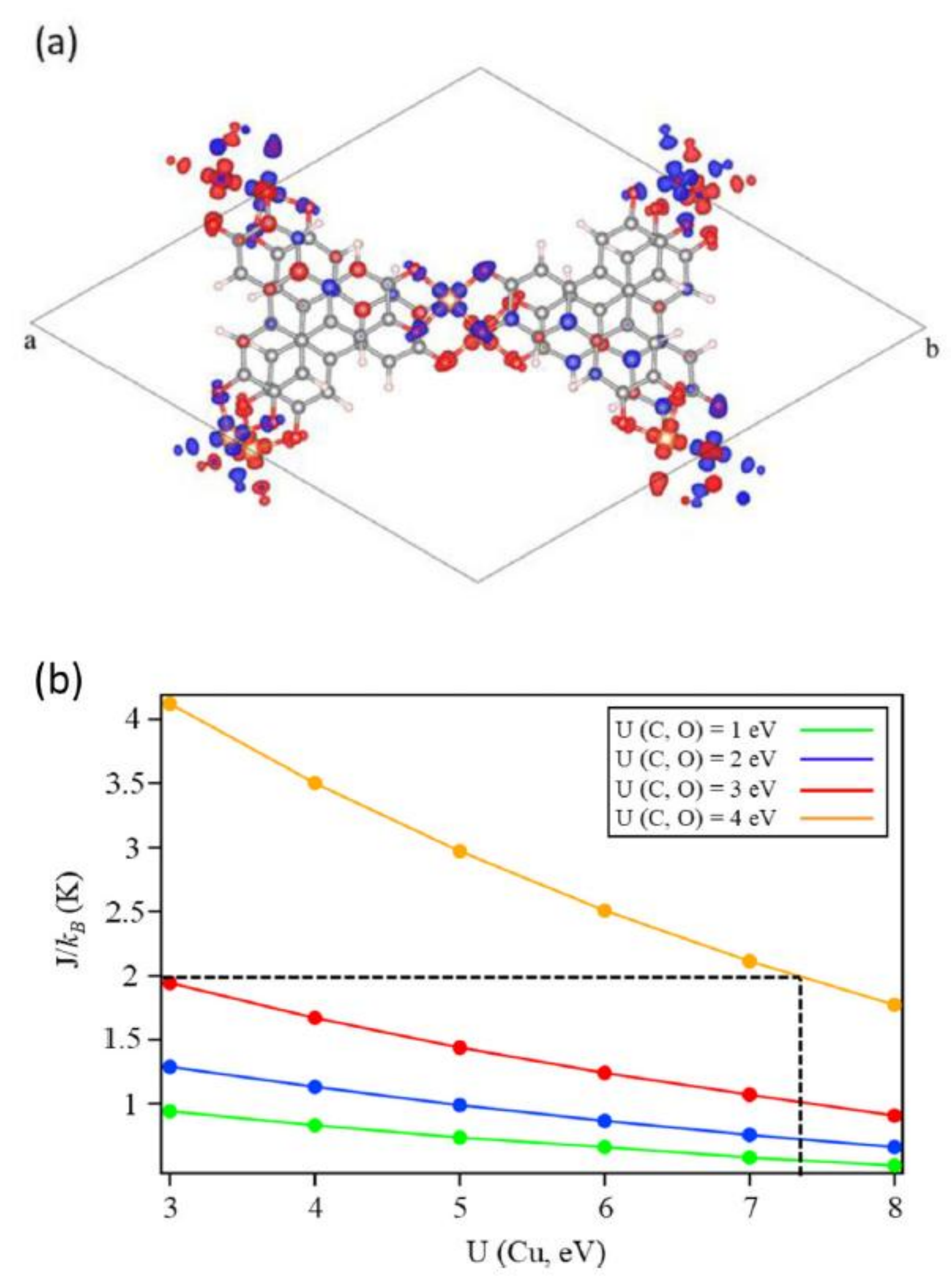
Low temperature magnetic susceptibility



Power law $n_\chi = -0.31$

Misumi et al, J. Am. Chem. Soc. 142, 16513 (2020)

Electronic Structure from DFT



Spin density is 79% on Cu with the rest mainly on the O ligands

Slipped configuration between adjacent layers is more stable than the eclipsed configuration by ~1 eV

(note that there are 12 equivalent slip directions for a pair of layers)

Broken symmetry DFT+U calculations allow the exchange coupling *J* to be calculated

The experimental value *J* ~ 2 eV is matched for the reasonable U parameter values of 7.3 eV on Cu and 4 eV on C and O

Interlayer exchange coupling is 0.13 eV and interlayer dipolar coupling is -0.07 eV, giving a combined interlayer coupling of 0.06 eV

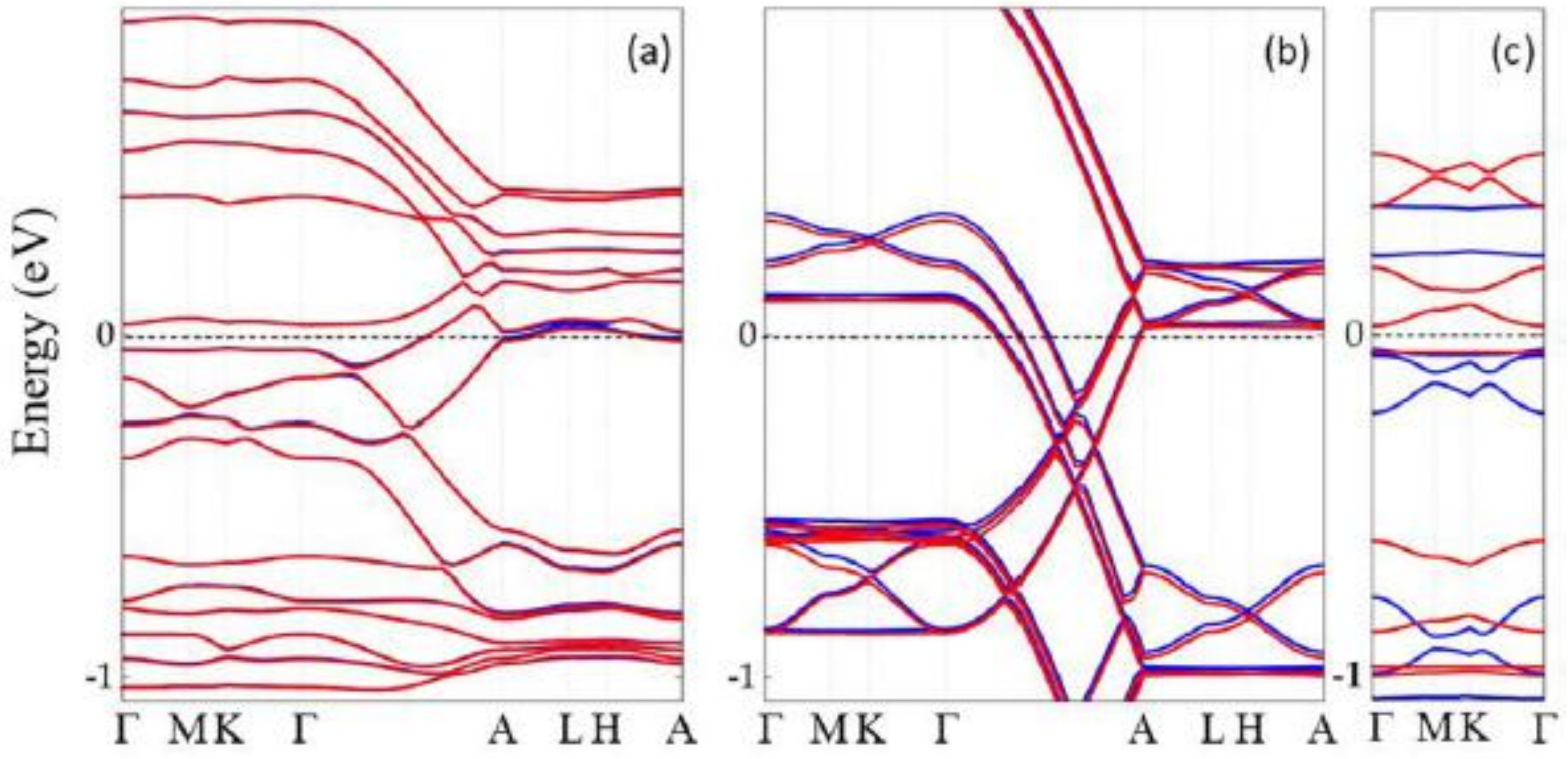
The predicted anisotropy ratio for intralayer versus interlayer diffusion is then $D_{\parallel}/D_{\perp}$ = 2.0/0.06 = 33

Electronic Structure from DFT: Regular Stacking Models

Regular AB zigzag slipped stacking

Regular AA eclipsed stacking

Decoupled
2D layers

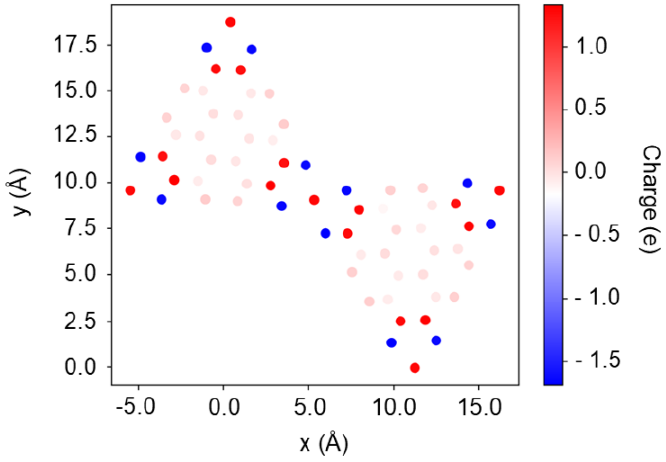


1D metal

Very 1D metal

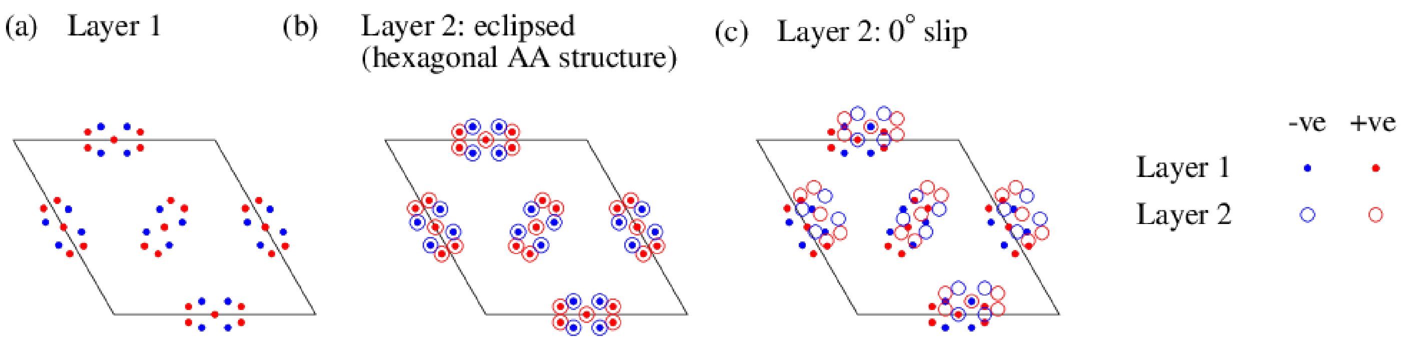
Small gap 2D semiconductor

Frustrated layer stacking - first layer



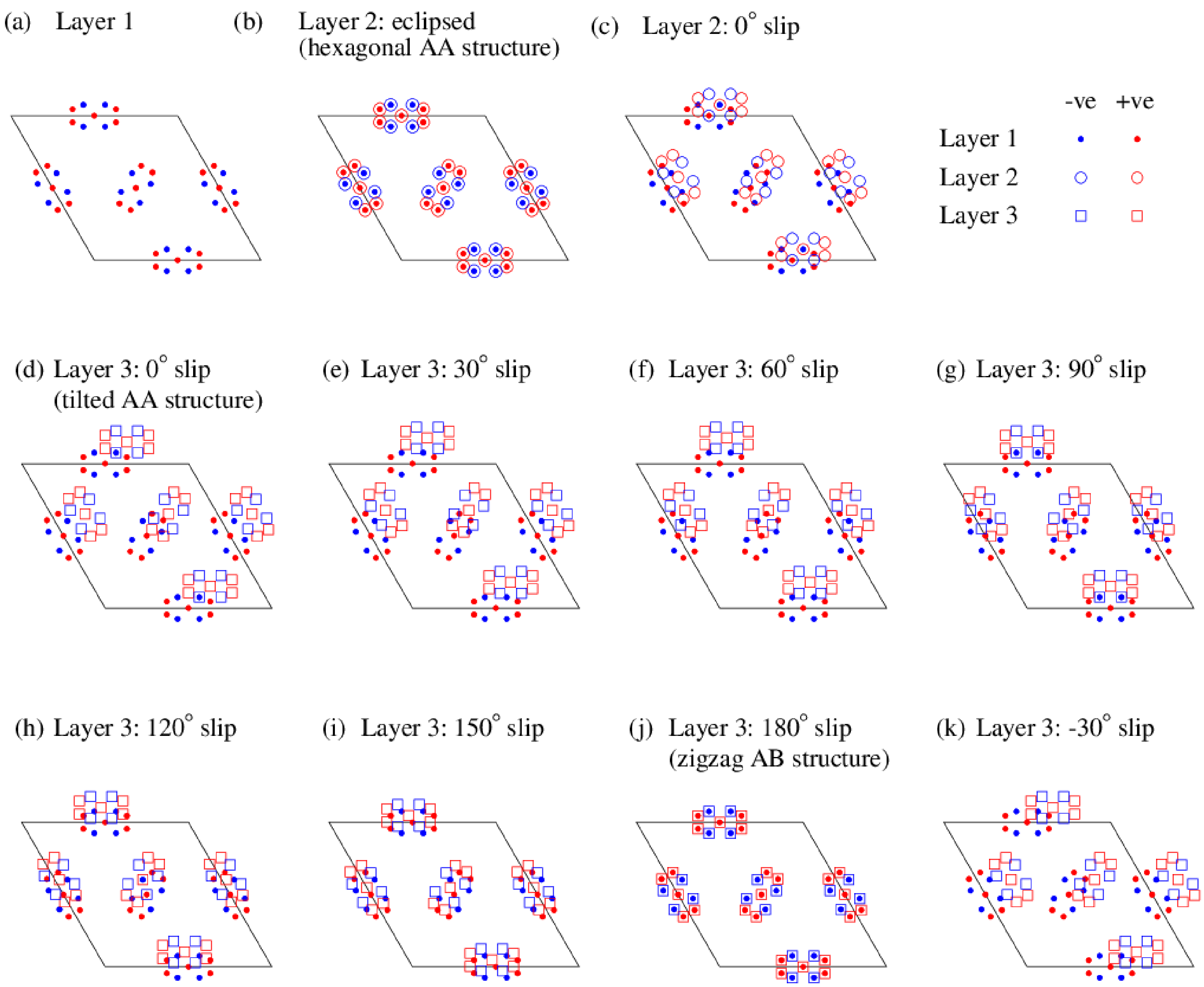
Charge distribution in the layer

Frustrated layer stacking – second layer



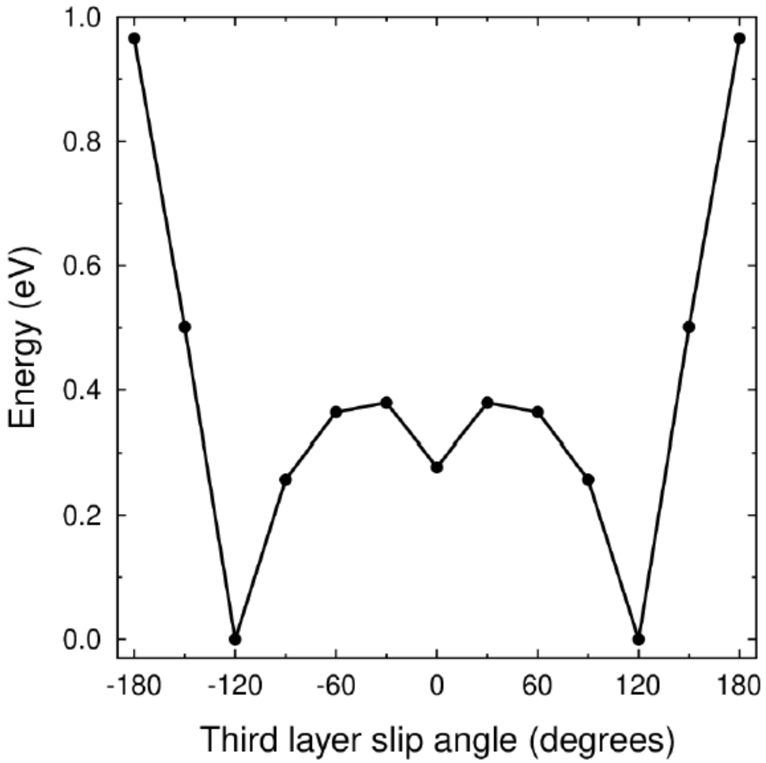
12 equivalent
slip directions

Frustrated layer stacking – third layer



slip directions for third layer now inequivalent versus NNN layer interaction

Frustrated layer stacking



Two-fold degeneracy for the slip angle of each successive layer

Result is random stacking which kills coherent interlayer transport

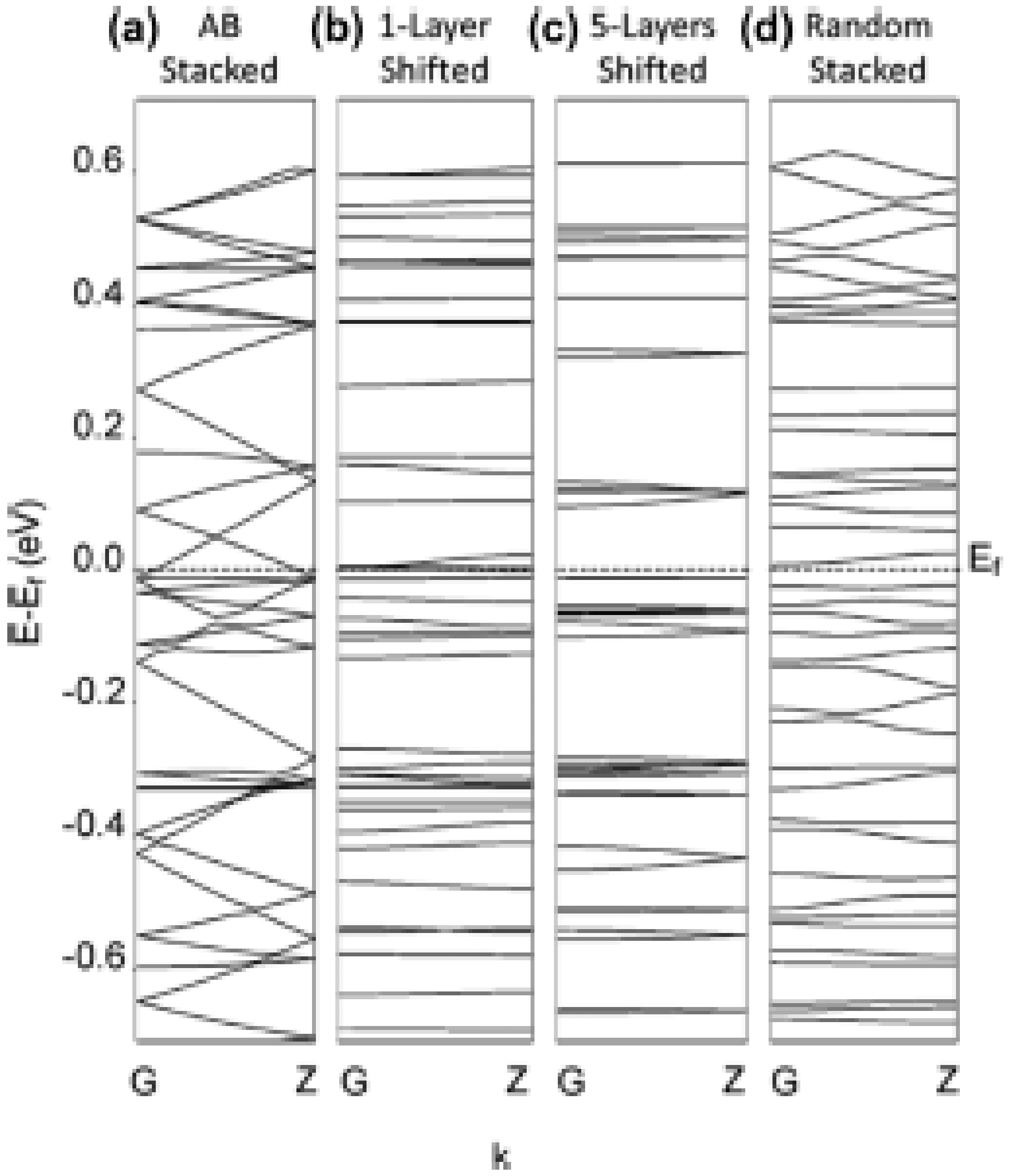
Effect of random stacking on electronic properties

Theoretical study of $Ni_3(HITP)_2$

(in HITP NH replaces the O in HOTP)

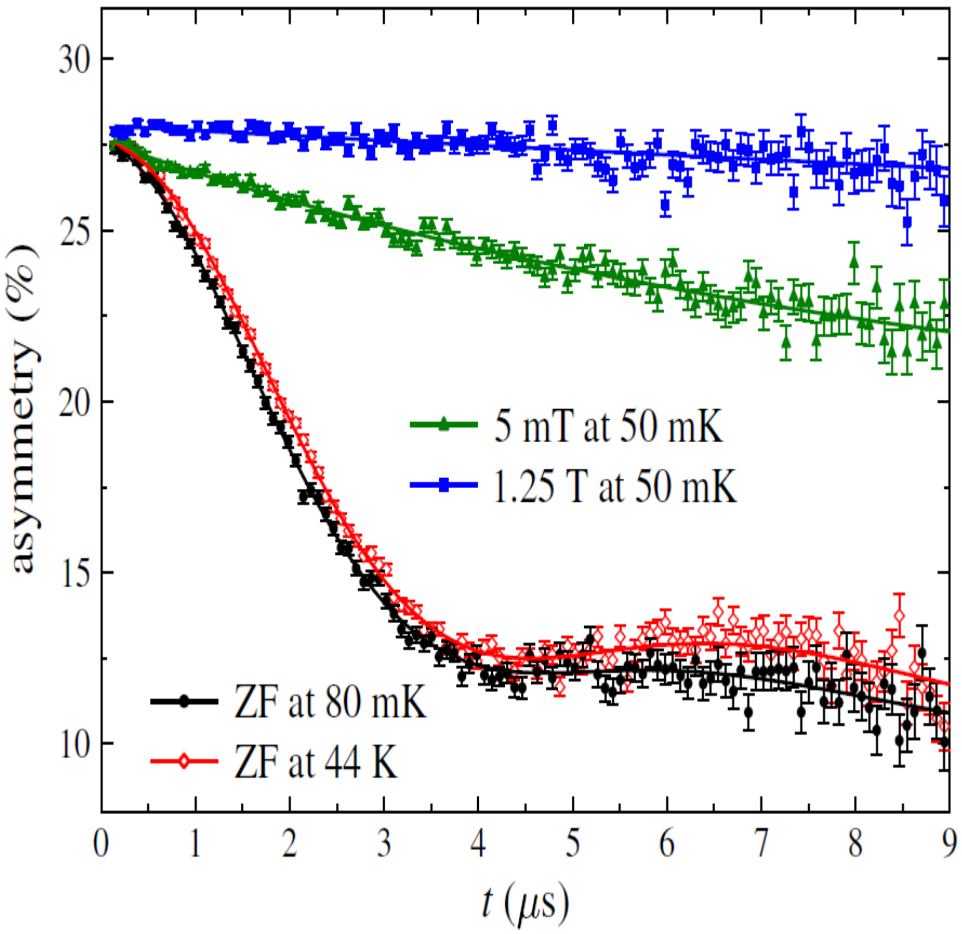
Foster et al, J. Phys. Chem. Lett. 9, 481 (2018)

Effect of layer displacement on inter-layer dispersion within a 10-layer unit cell

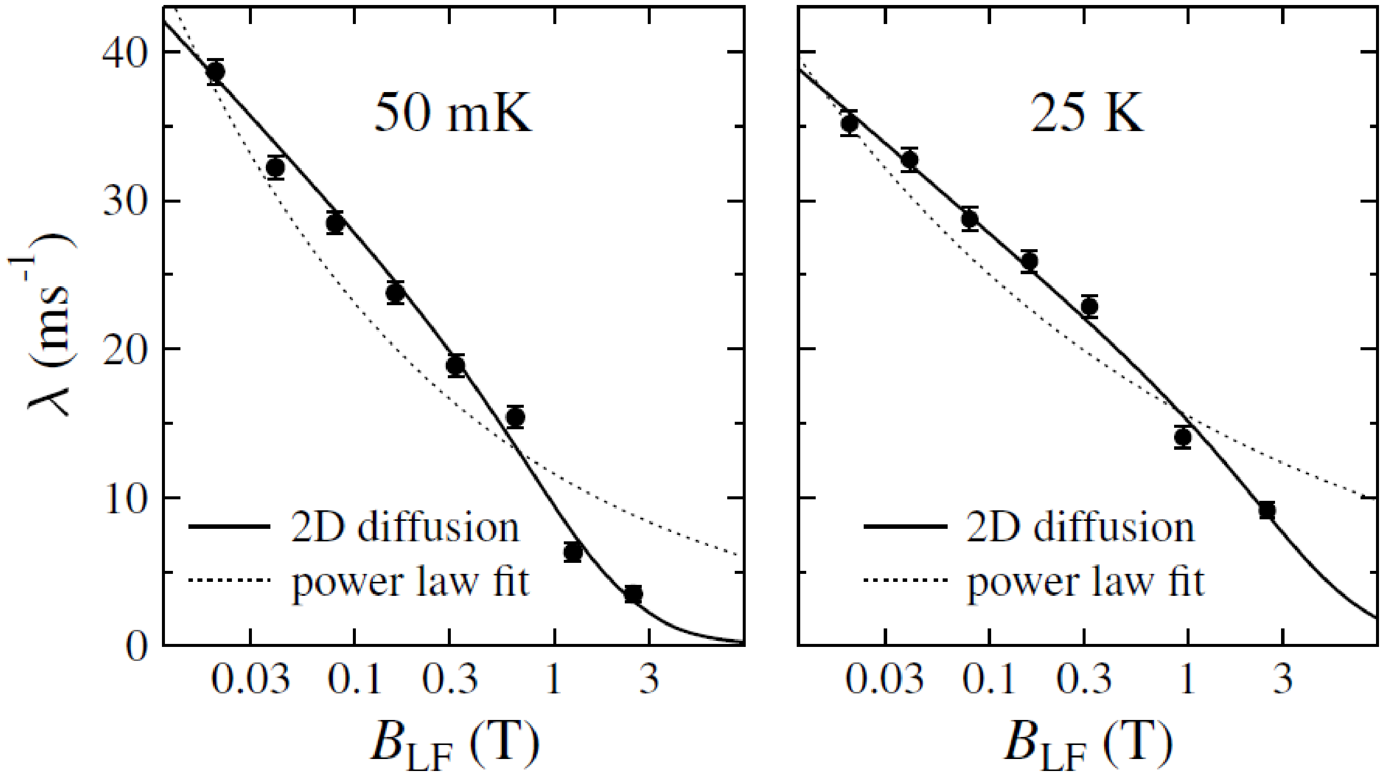


μSR Data from the HiFi Instrument at ISIS

- No evidence for ordering or freezing in ZF down to 50 mK
- Nuclear relaxation contribution quenched in LF
- Electronic relaxation revealed in the form of a slow Lorentzian
- Relaxation persists to high field signifying fast spin dynamics



Spin Dynamics from LF-μSR



2D spin diffusion describes the LF-μSR relaxation well at all *T*

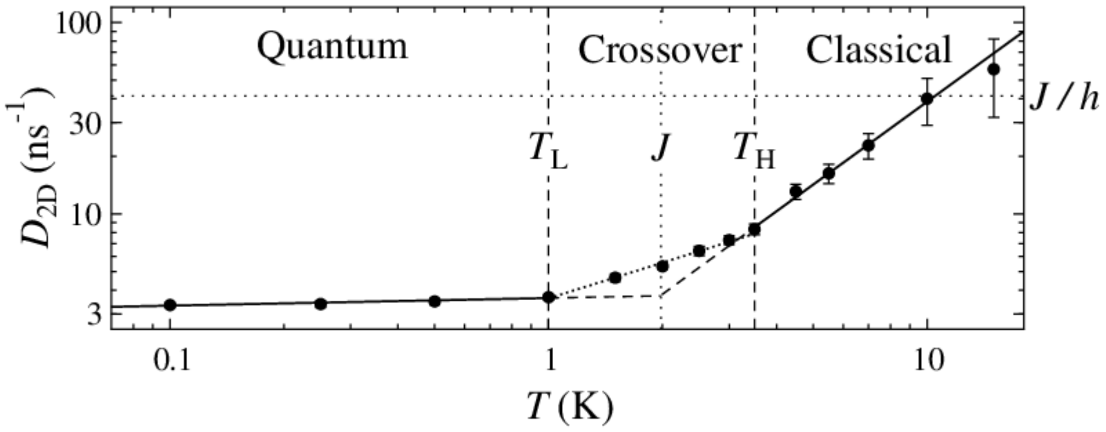
(it is not a 1D metal!)

Classical to Quantum Crossover

$$D = \frac{1}{2}v^2\tau = \frac{1}{2}vl = D_{2D}l^2$$

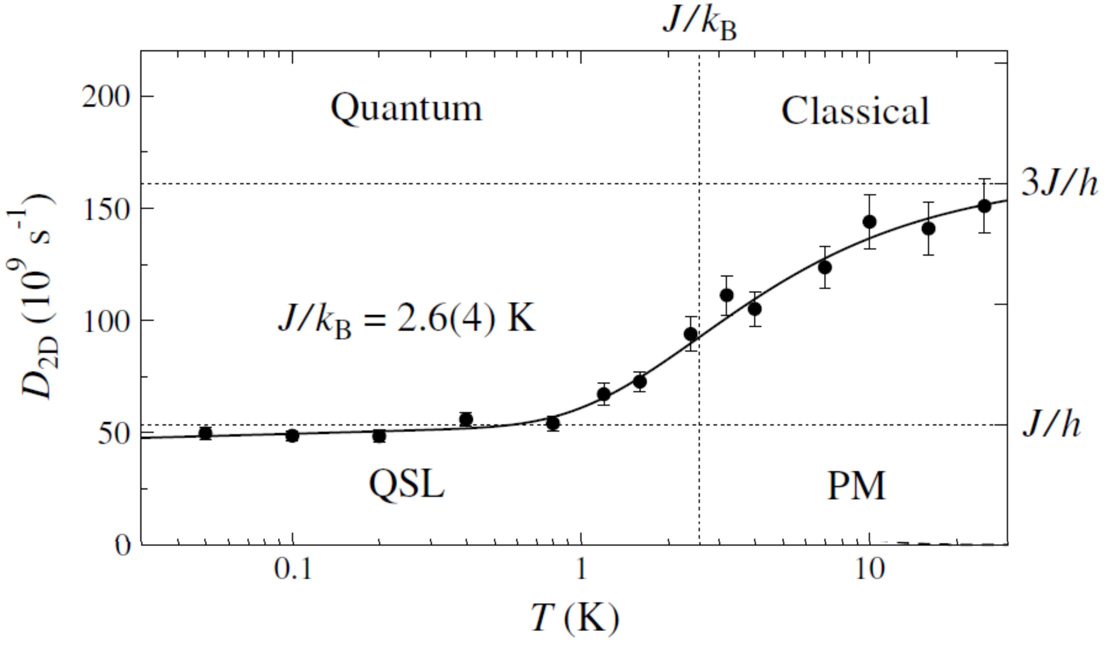
$$D_{2D} = \frac{v}{2l}$$

High T classical region:
$v = (2J/h)\,a$ and $l = a$
so $D_{2D} = J/h$



YbZnGaO$_4$ PRB 106, L060401 (2022)

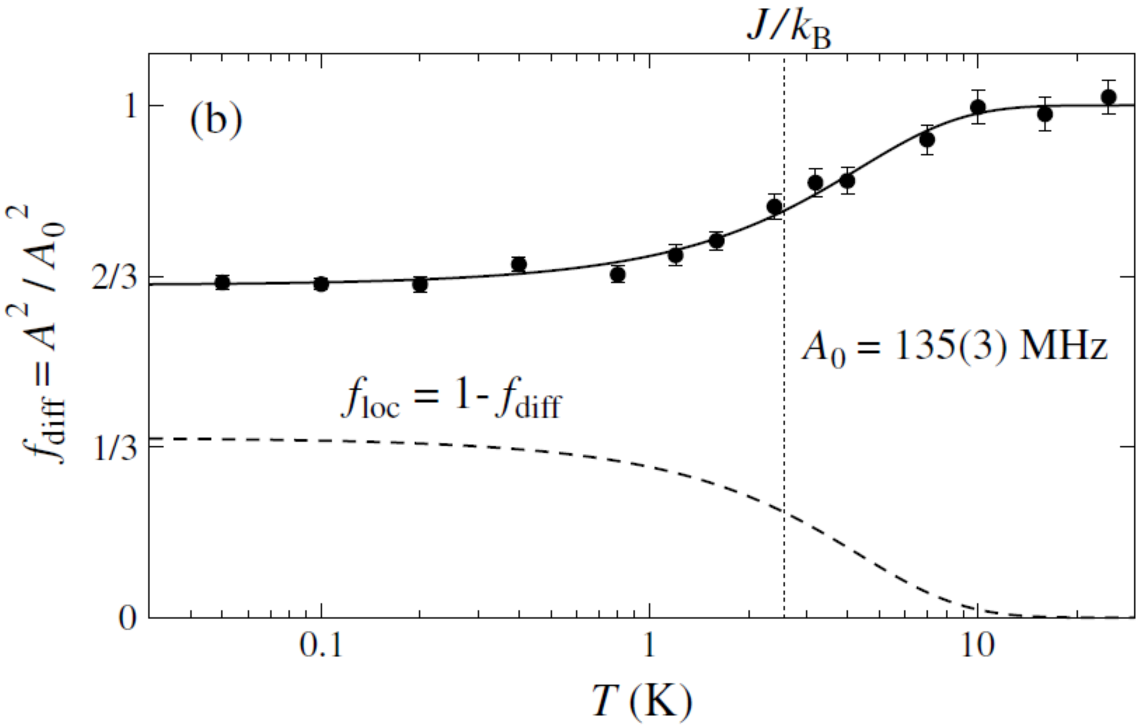
Cu$_3$(HOTP)$_2$



Line is fit to $D_{2D}(T) = D_0T^n + D_1\exp(-J/T)$

J = 2.6(4) K and n = 0.03(3)

HFC of Muon Probe and Localised versus Diffusive states



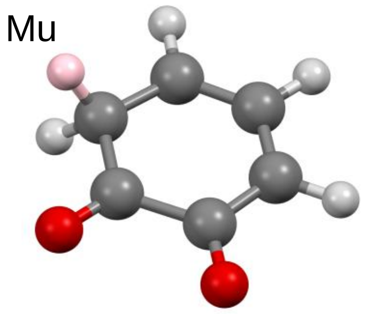
A is not expected to vary strongly with *T*

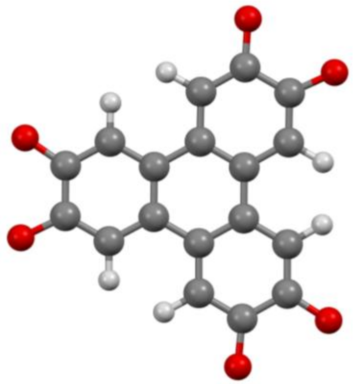
The apparent drop in *A* at low *T* coincides with the emergence of a non-diffusive term in the spectral density

This reflects localised excitations that are only present in the quantum region

The localised term has a Lorentzian spectral density with a low field cut-off below 20 mT

Use 1,2-dioxyphenylene as a model for 1/3 of HOTP

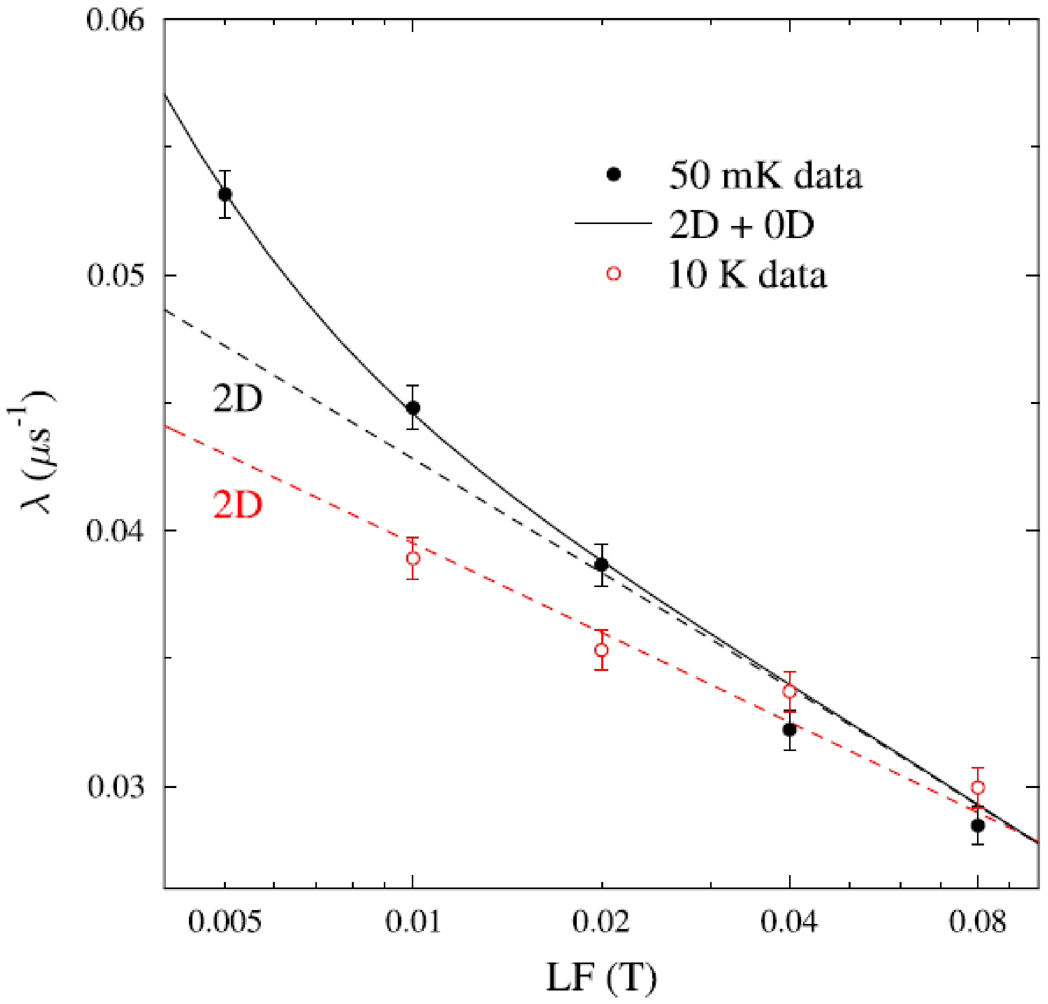




DFT+μ for addition of Mu to the molecule using Gaussian16 (B3LYP/cc-pVDZ) gives a bare HFC value of A = 110 MHz

This becomes A = 135 MHz after quantum correction for the muon zero-point motion, matching the observed A_0

Further Evidence for Localised States at Low Field



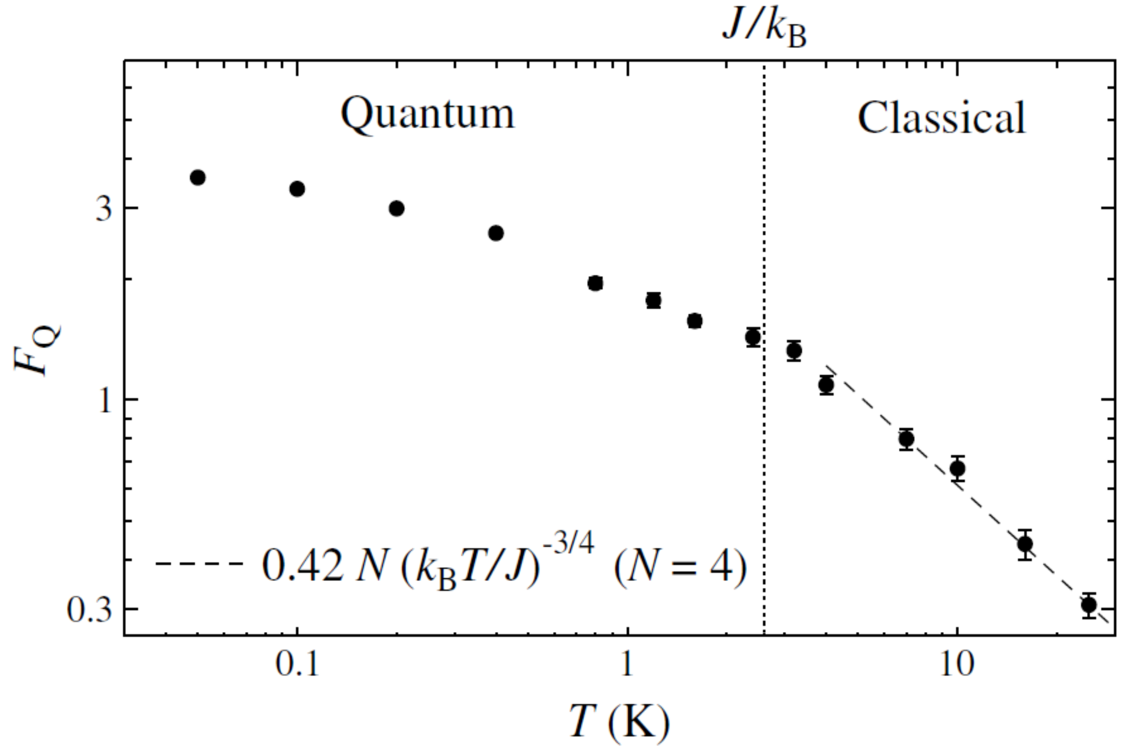
Comparison of low-field part of the LF data measured at 50 mK and 10 K. The dashed lines show the extrapolation of the 2D field dependence derived from fitting the full field range of the data. At 50 mK there is a significant deviation from the 2D fit at 0.01 T and below, signifying the presence of a slowly fluctuating localized 0D term in the spectral density.

Quantum Entanglement: Quantum Fisher Information

Quantum Fisher Information (QFI) as an Entanglement Witness

$$F_{\mathrm{Q}} = \frac{4}{\pi} \int_0^{\infty} \tanh^2 \left(\frac{\hbar\omega}{2k_{\mathrm{B}}T} \right) J(\omega) d\omega,$$

Hauke et al, Nat. Phys. 12, 778 (2016)
Laurel et al, PRL 127, 037201 (2021)



Quantum entanglement length

Entanglement length ξ_E

Verstraete et al, PRL 92, 027901 (2004)

From F_Q:

$$\xi_E \propto F_Q^{1/2}$$

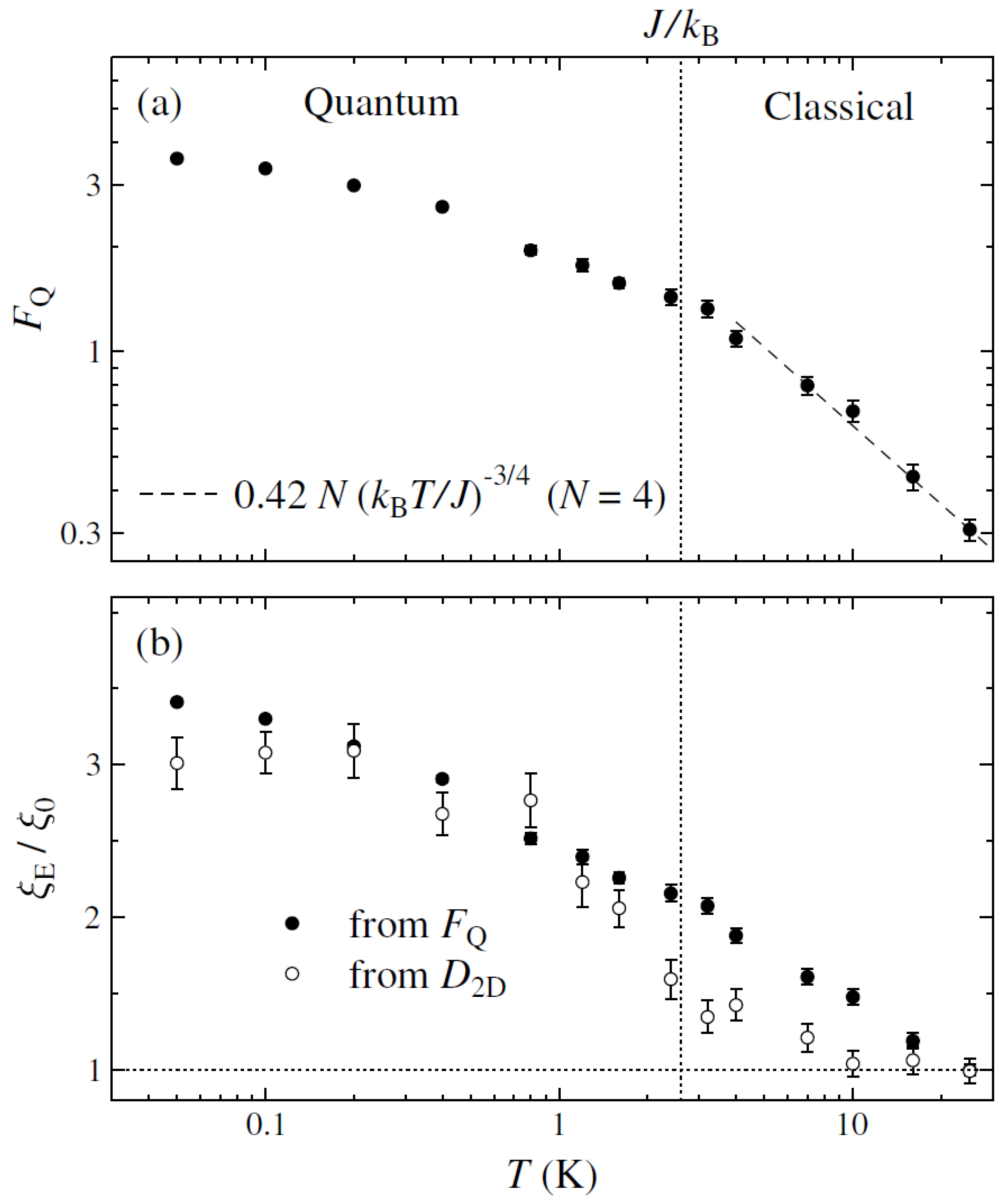
From D_{2D}:

$$D_{2D} = 0.5\, v / l$$

When v is independent of T (e.g. FS or linear nodal QSL)

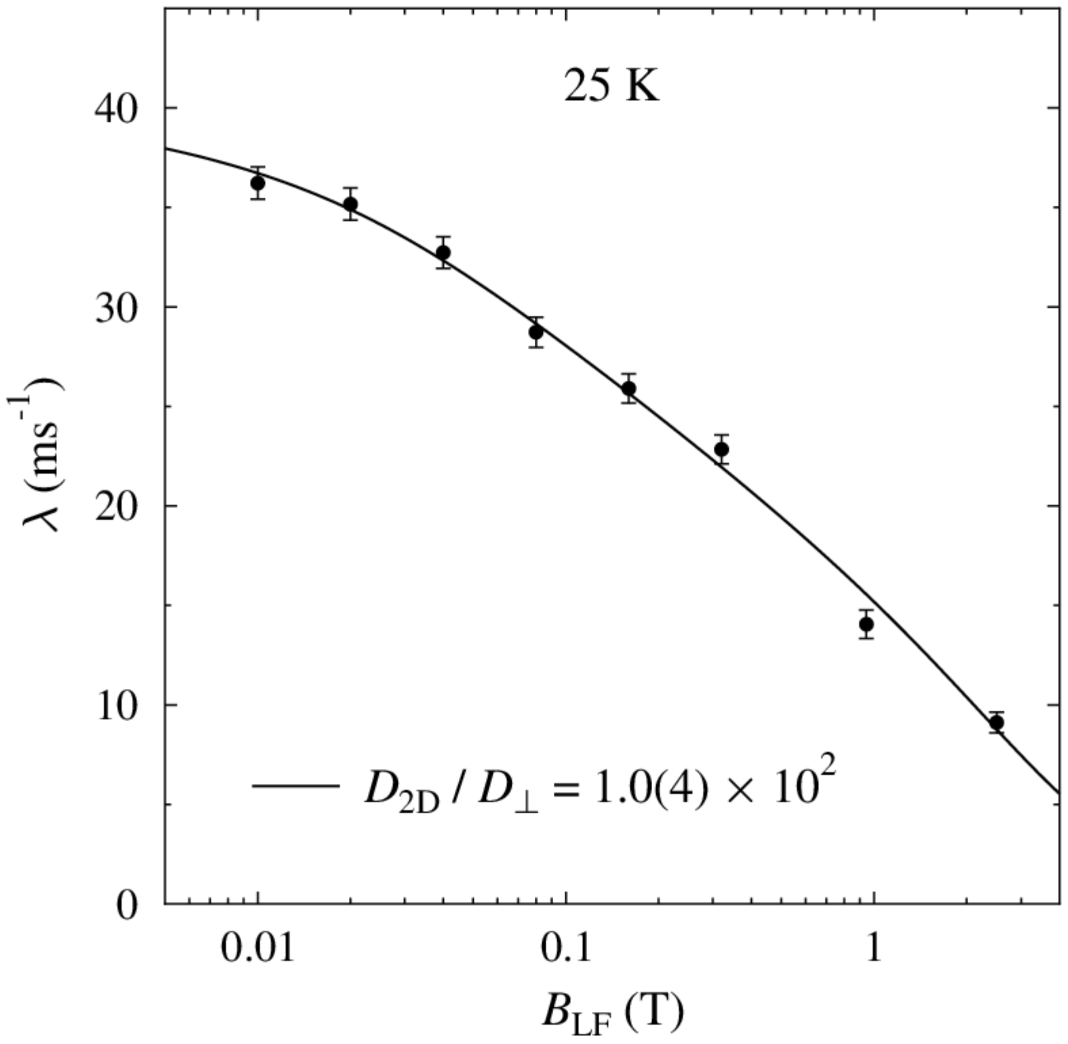
$D_{2D} \sim 1/l$ and can associate l with entanglement length ξ_E

$$\xi_E \propto 1 / D_{2D}$$



Just how 2D is it?

With slow interlayer hopping we get a modified autocorrelation function: $S_{3D}(t) = \exp(-2D_{\perp}t)I_0(2D_{\perp}t)S_{2D}(t)$



We can then fit the spectral density to this modified model:

At 25 K, the fitted ratio $D_{2D} / D_{\perp}$ is 10^2

Indicates an inter-layer coupling of 0.02(1) K
(the DFT estimate was a bit larger at 0.06 K)

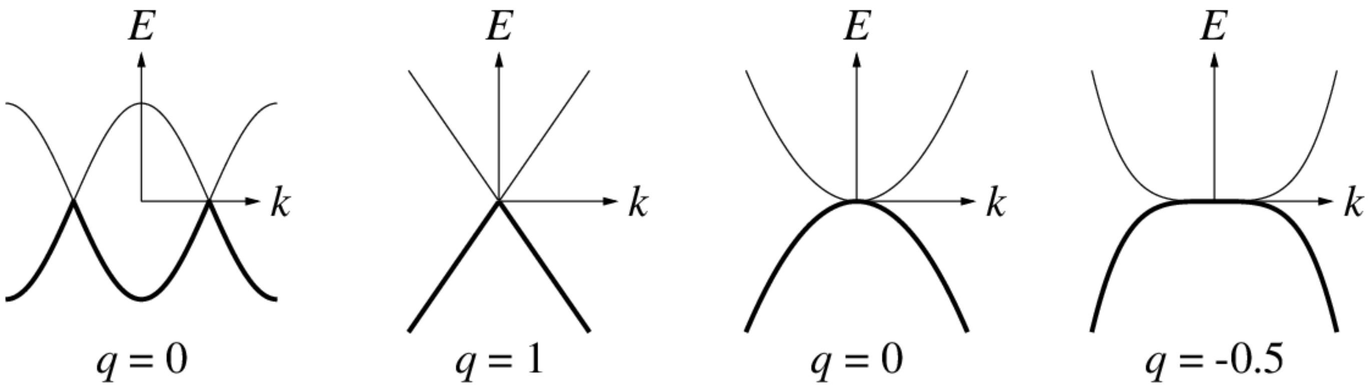
At 50 mK, the lower limit for $D_{2D} / D_{\perp}$ is even larger at 10^4

Quantum entanglement is further suppressing
the inter-layer interaction

Power Laws, Quantum Criticality and Dispersion

For low-energy dispersion of form $E \propto k^m$

Density of states: $\quad$ DOS $\propto E^q$ $\quad$ where $q = 2/m-1$



Quantum Critical power laws

Spin Diffusion: $\quad n_D = 2/\nu - 2$ $\quad$ from $n_D = 0.03(3)$, we get $\nu = 0.673(7)$

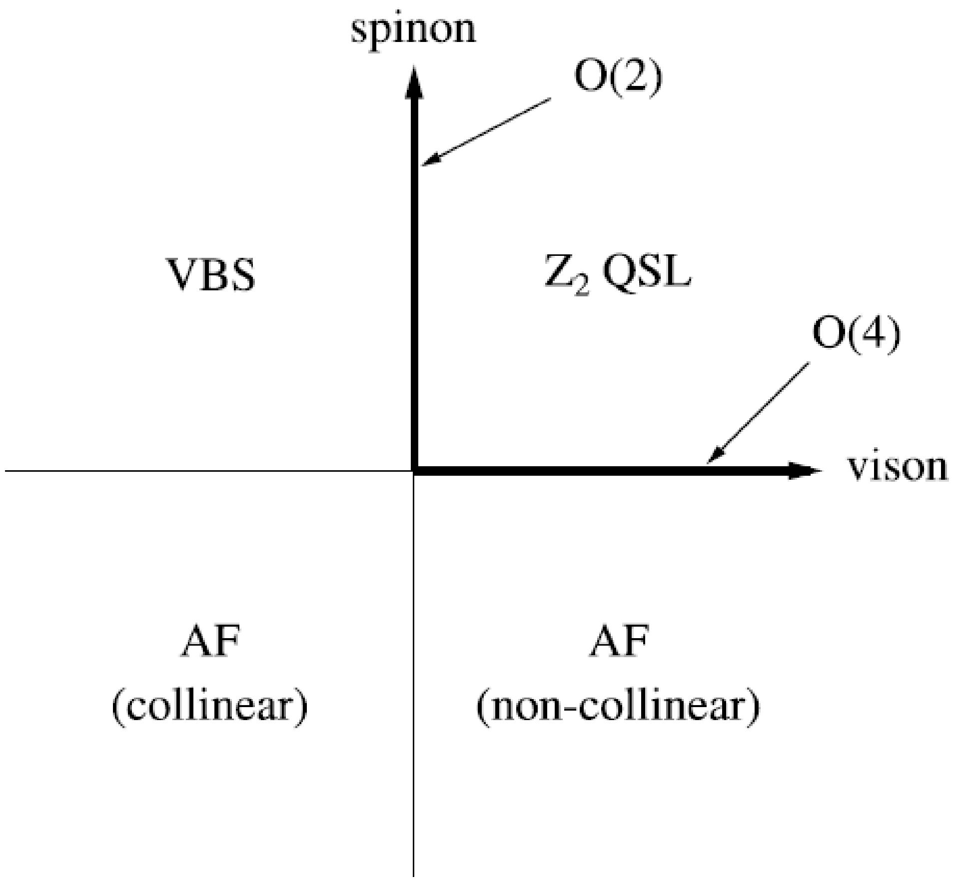
c.f. 0.672 for O(2)

0.748 for O(4)

Magnetic susceptibility: $\quad n_\chi = -(2 - \eta)\nu + q$ $\quad$ from $n_\chi = -0.31$ and $\eta = 0.04$, $\nu = 0.673$ we get $q = 1.0$

Specific heat: $\quad n_C = 3\nu - 1 + q$ $\quad$ from $n_C = 0.52$ and $\nu = 0.673$ we get $q = -0.5$

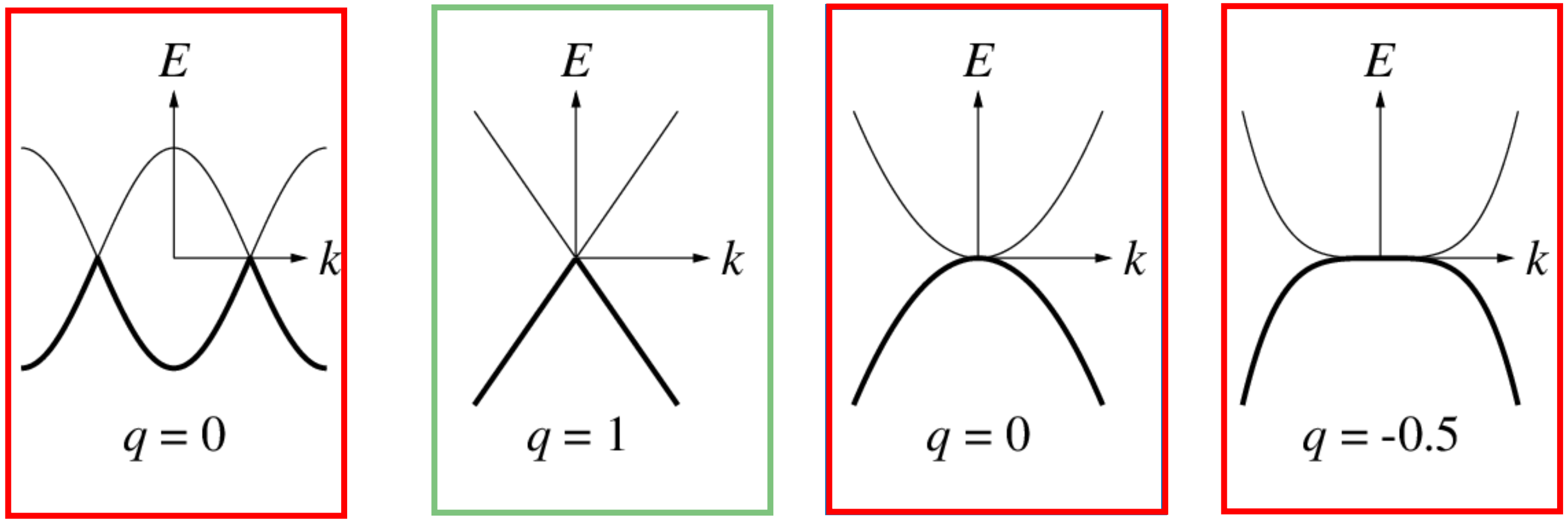
O(2) versus O(4) criticality in a Z_2 QSL



Phase diagram for a Z_2 QSL spinon-vison double Chern-Simons model

Xu and Sachdev, Phys. Rev. B 79, 064405 (2009)

Low energy excitations versus experiment



	q	ν	n_D	n_χ	n_C
1. Spinon (FS)	0		0	0	1
2. Spinon (FS+GF)	0		0.33		0.67
3. Spinon (quartic)	-0.5	0.673	0.03	-1.81	0.52
4. Spinon (quadratic)	0	0.673	0.03	-1.31	1.02
5. Spinon (linear)	1	0.673	**0.03**	**-0.31**	2.02
6. Singlet (quadratic)	0	0.51			**0.52**
7. Experiment			**0.03**	**-0.31**	**0.52**

n_c=2.02 for Dirac spinons would be very hard to separate from the vibrational term

Z_2-linear QSL with Dirac spinons and specific heat dominated by non-magnetic singlet excitations

Summary for Kagome MOF QSL

- Electronic structure of the kagome MOF $Cu_3(HOTP)_2$ was studied using DFT+U, reproducing the exchange coupling $J = 2$ K and demonstrating the frustrated stacking and weak inter-layer coupling
- QSL properties were confirmed experimentally in ZF-μSR and a detailed LF-μSR study was carried out to characterise the spin dynamics
- 2D spin diffusion provides a good description of the spin dynamics, implying that the kagome layers are well decoupled magnetically as well as electronically
- Classical to quantum crossover was observed at $k_B T \sim J$ and changes in the diffusion rate and spectral density function were linked to quantum entanglement
- When low-temperature thermodynamic, magnetic and spin transport properties are compared, evidence is found for Dirac-type linear nodal dispersion of the spin excitations

PHYSICAL REVIEW RESEARCH 7, 023007 (2025)

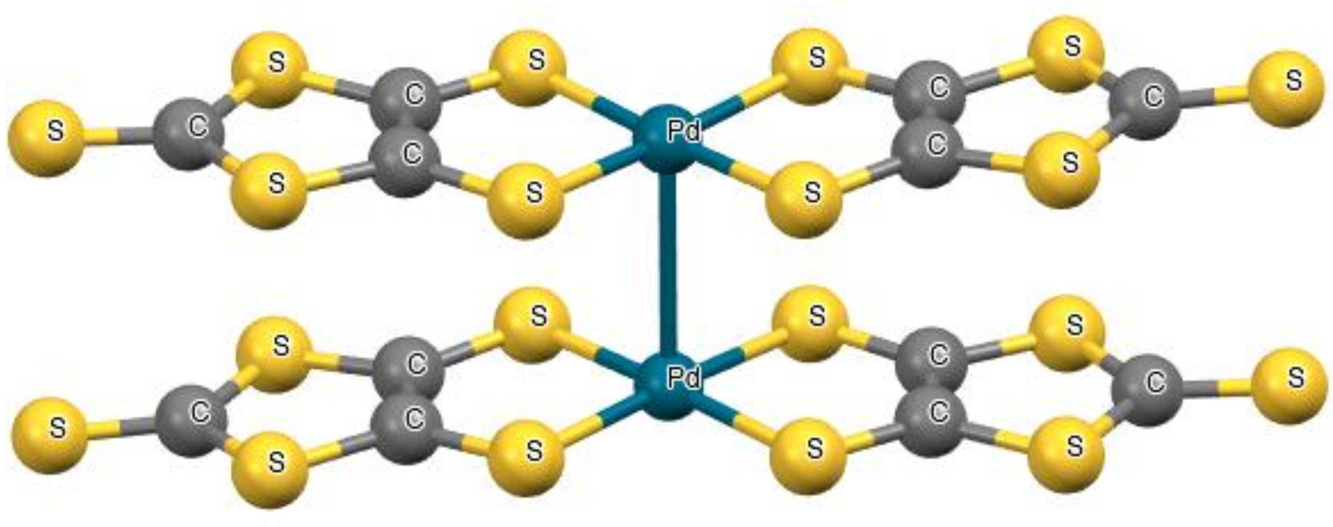
The Triangular-lattice QSL System $EtMe_3Sb[Pd(dmit)_2]_2$

$EtMe_3Sb[Pd(dmit)_2]_2$

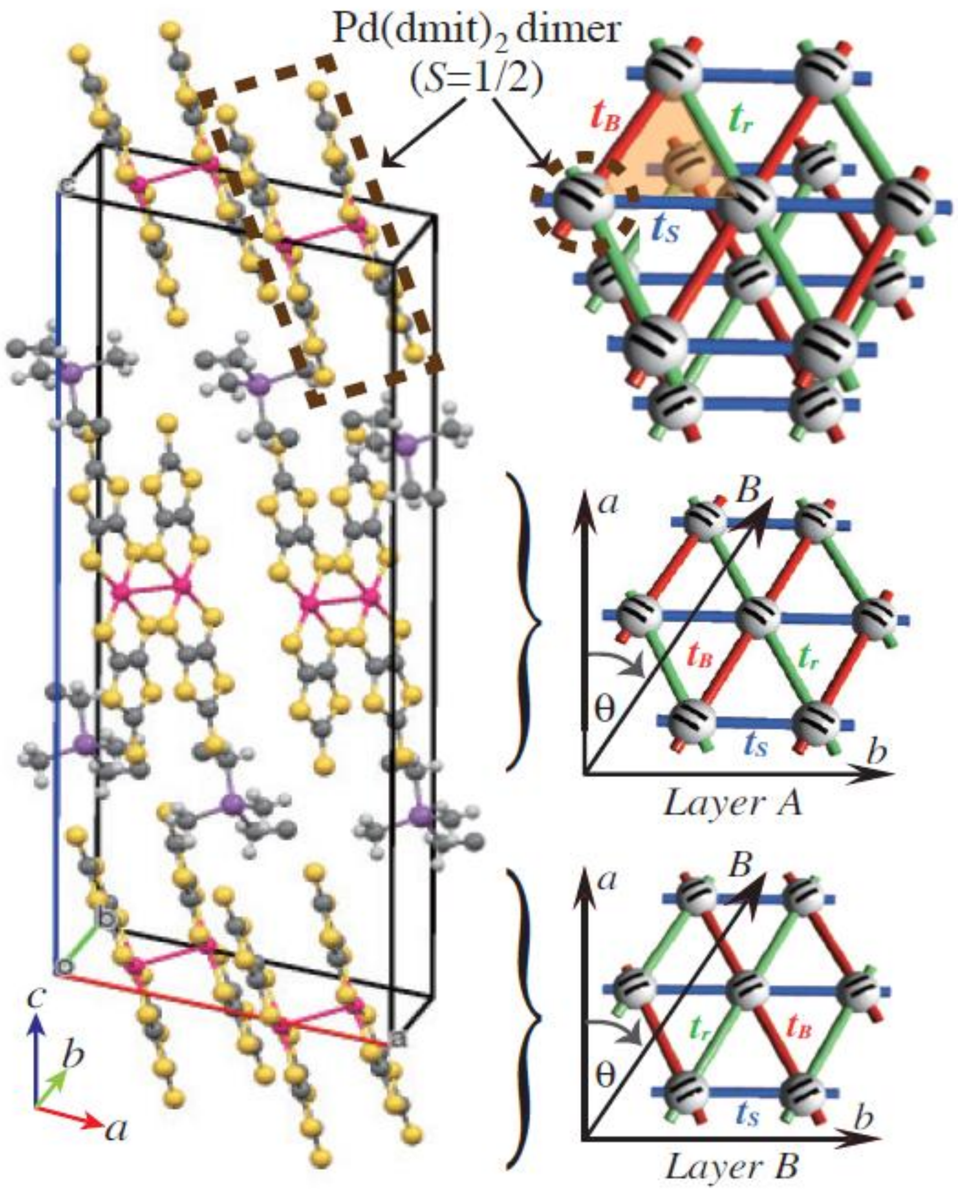
2D triangular-lattice QSL based on S=1/2 radical dimers

Long regarded to be one of the best candidates for a 2D QSL with no ordering down to 40 mK

However: thermal conductivity properties have been controversial



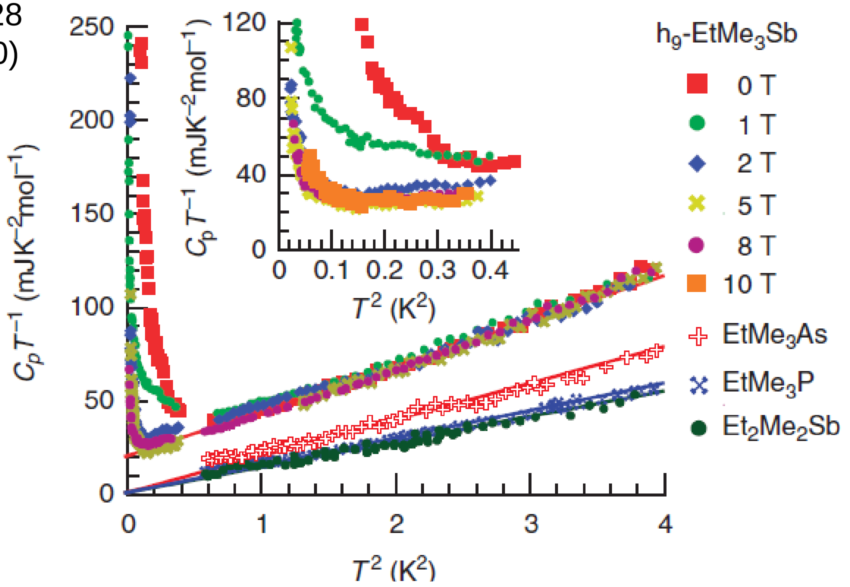
$[Pd(dmit)_2]_2$



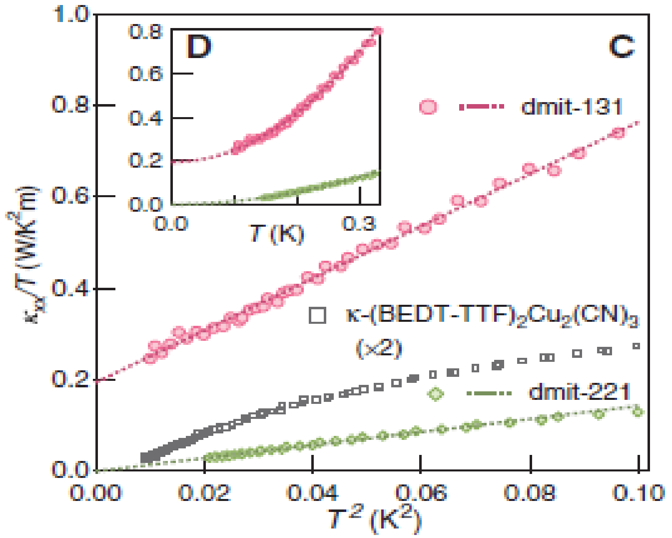
QSL Properties of $EtMe_3Sb[Pd(dmit)_2]_2$

Original Kyoto results for C_p and κ

Science 328 1246 (2010)

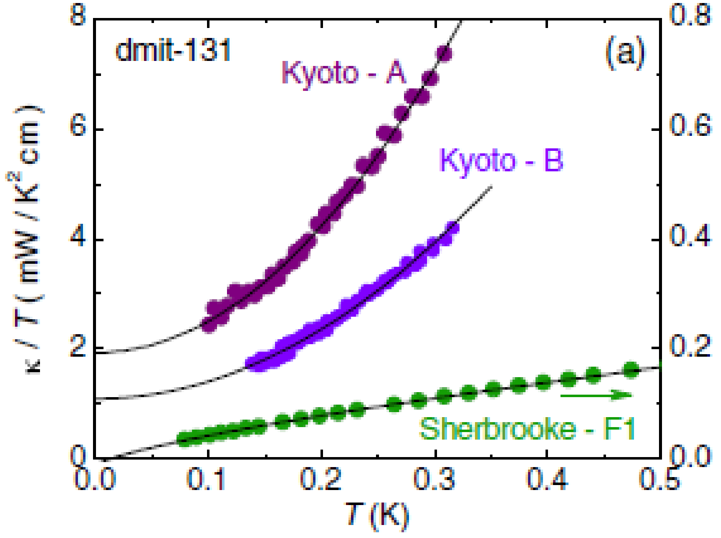


Nat. Comms. 1274 (2011)

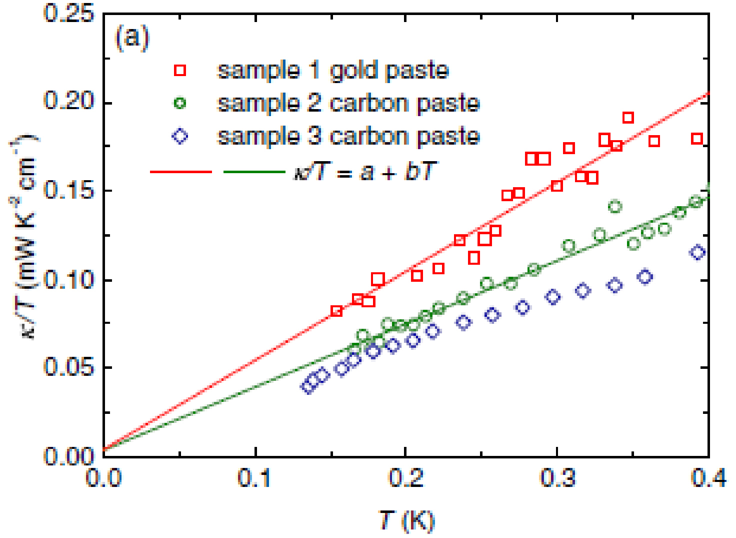


More recent results for thermal conductivity

PRX 9,041051 (2019)



PRL 123, 247204 (2019)

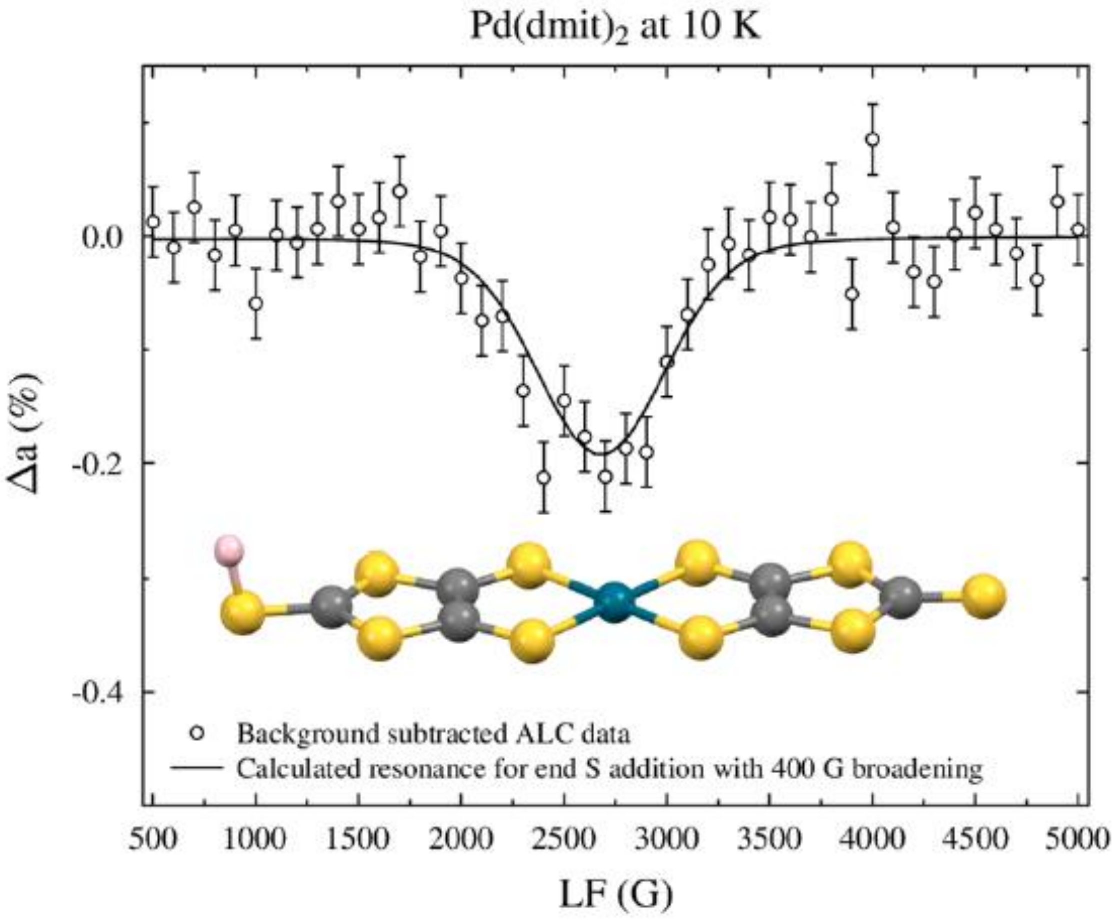


μSR Study: Starting off with the Muon Probe State

DFT+μ:

Addition site	Relative energy (eV)	A (MHz)	D (MHz)
Inner C	0.013	40.5	2.7
Outer C	0.632	-4.4	18.2
Inner S	0.000	48.9	4.0
Outer S	1.356	9.8	2.0
End S	0.000	72.7	3.0

Measurement of the characteristic resonance confirms the muon addition site predicted by DFT as being at the end S position

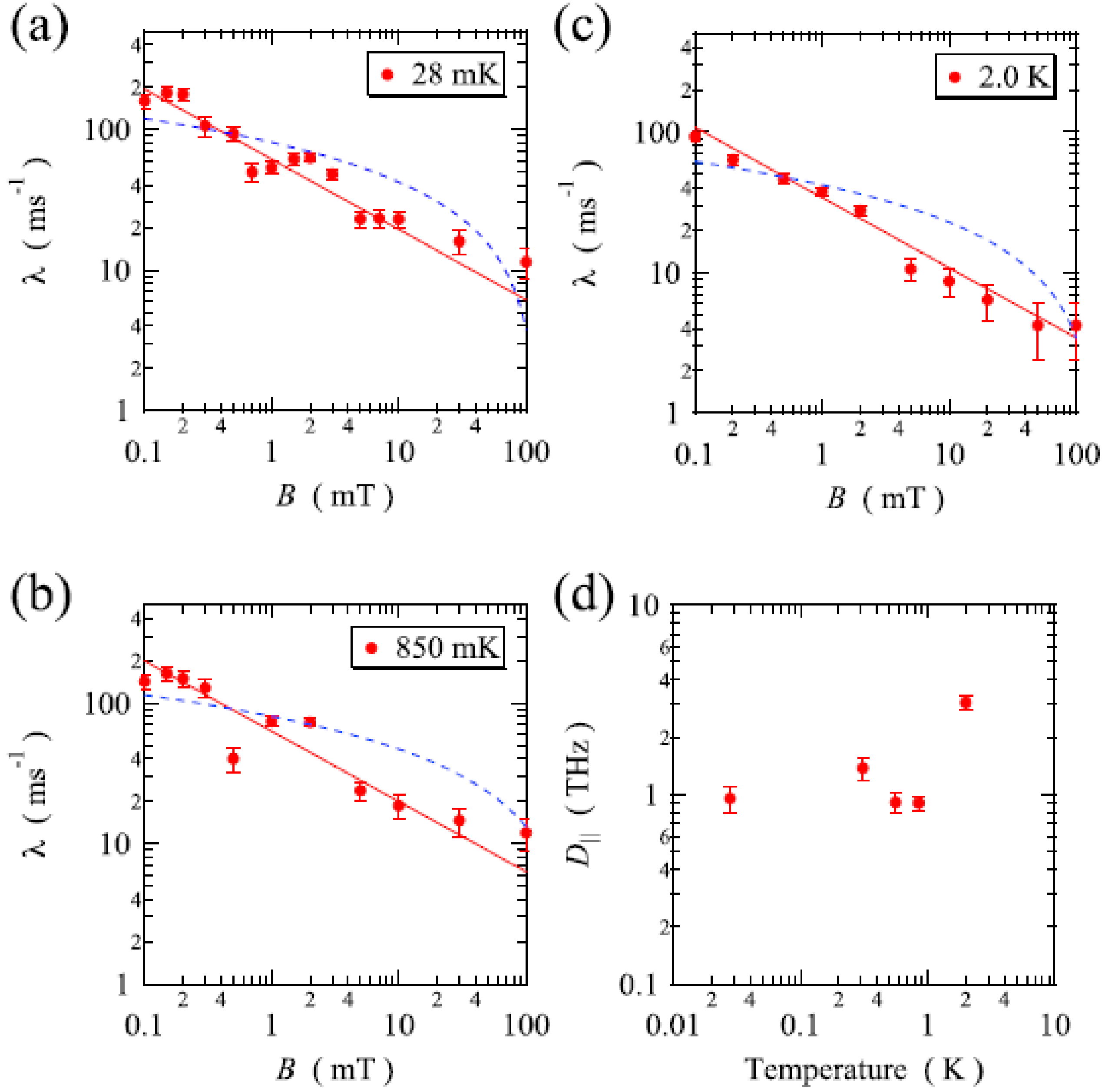


$Pd(dmit)_2$ + Mu (as studied here)

is equivalent to

$[Pd(dmit)_2]_2^-$ + Mu^+ (as studied in the QSL)

Diffusive 1D Spin Dynamics found in LF-μSR



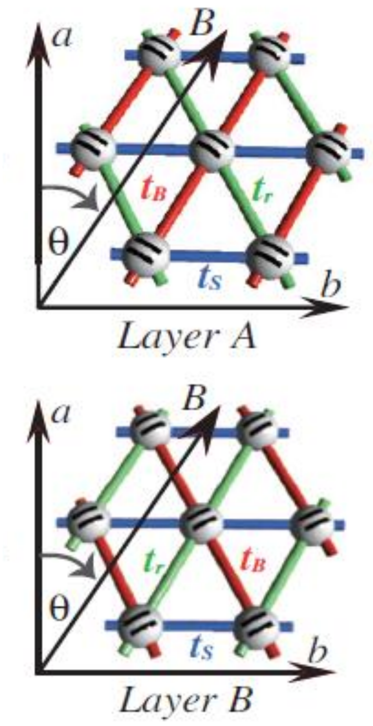
The 2D model gives very poor fit, whereas the 1D model fits very well

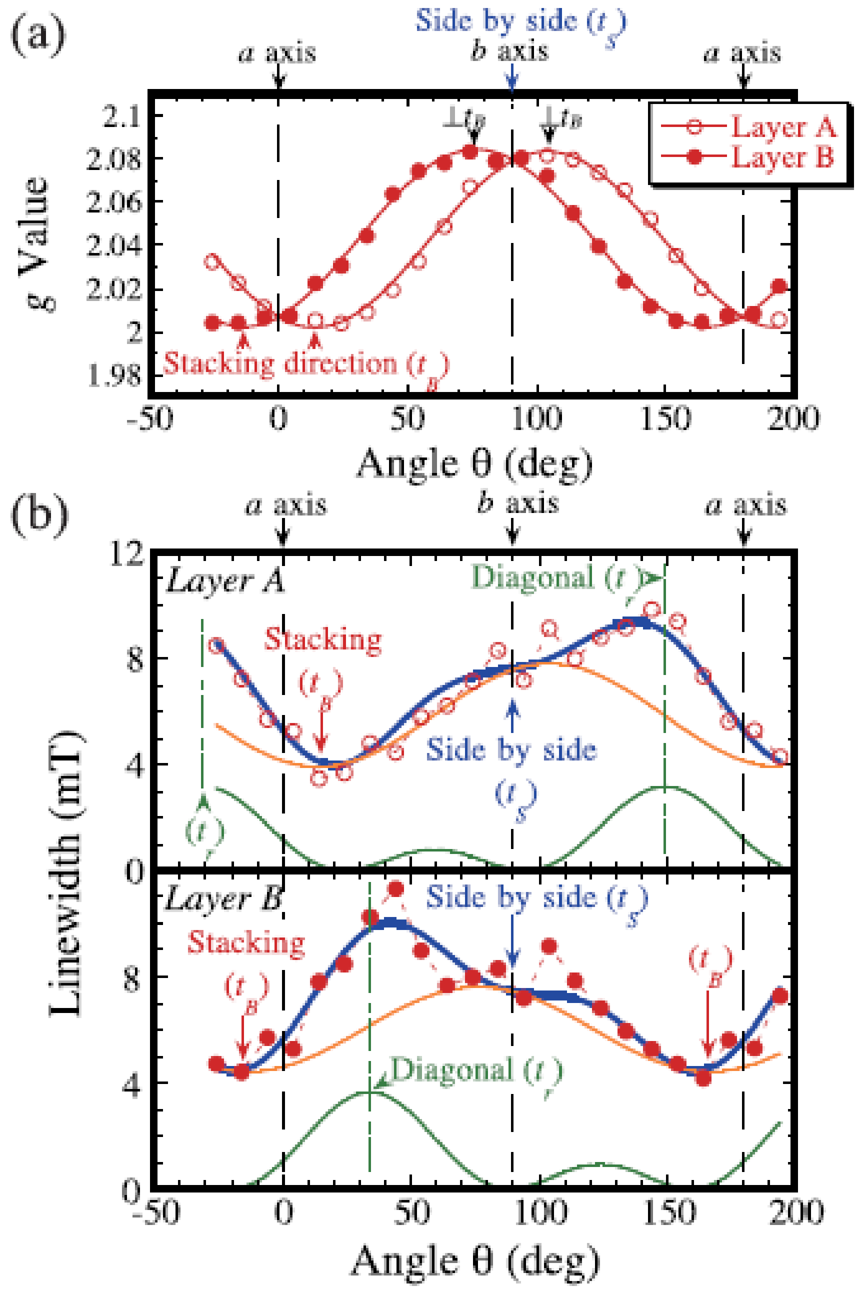
Lower limit for anisotropy is

$$D_{\parallel} / D_{\perp} > 10^4$$

These LF-μSR results indicate that a 2D →1D dimensional reduction is taking place

Angle-dependent in-plane EPR Linewidth and g Value





Characteristic $(3\cos^2\theta - 1)^2$ angular dependence of a strongly one-dimensional system

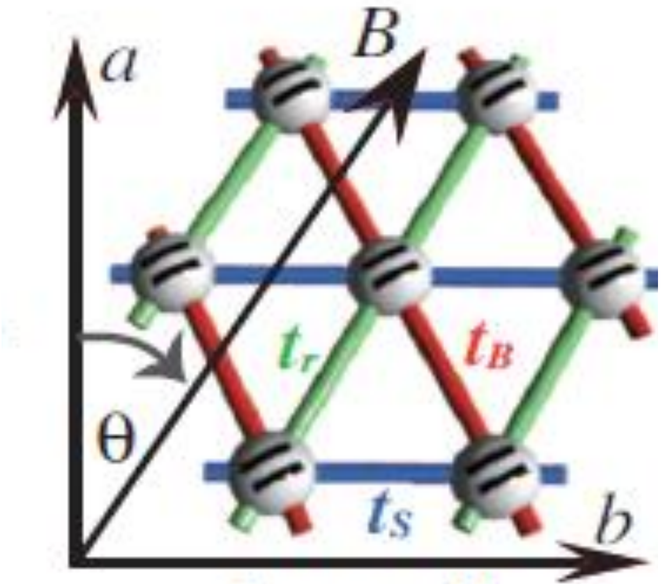
The fast diffusion direction is along the diagonal direction t_r

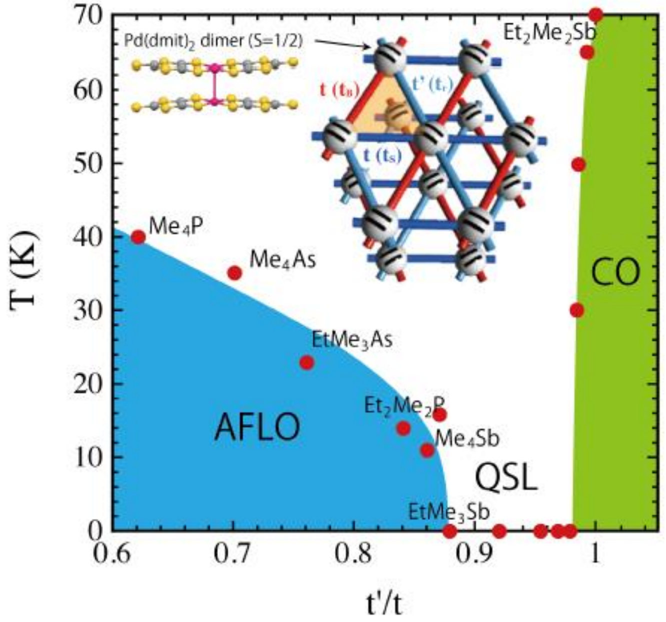
This is the weakest interaction direction according to previous DFT

Improved Calculation of the Interdimer Interactions

TABLE I. Interdimer transfer integrals (in meV) along the three directions of the triangular lattice of β'-$EtMe_3Sb[Pd(dmit)_2]_2$ evaluated by different methods. The low-temperature crystal structure data has been used for our calculation. FP, TB, and EHM stand for first-principles calculation, tight-binding, and extended Hubbard models, respectively. The number of bands included in the analysis is indicated.

Methods	t_B	t_S	t_r	Ref.
Extended Hückel	34	33	26	[17]
FP + TB (6-band)	54	45	40	[18]
FP + TB (2-band)	49	45	37	[19]
FP + TB (2-band)	55	47	39	[20]
FP + TB (2-band)	57	45	40	[21]
FP + TB (2-band)	57	45	40	[22]
FP + TB (8-band) + EHM	31	28	36	Present study





Dimensional Reduction

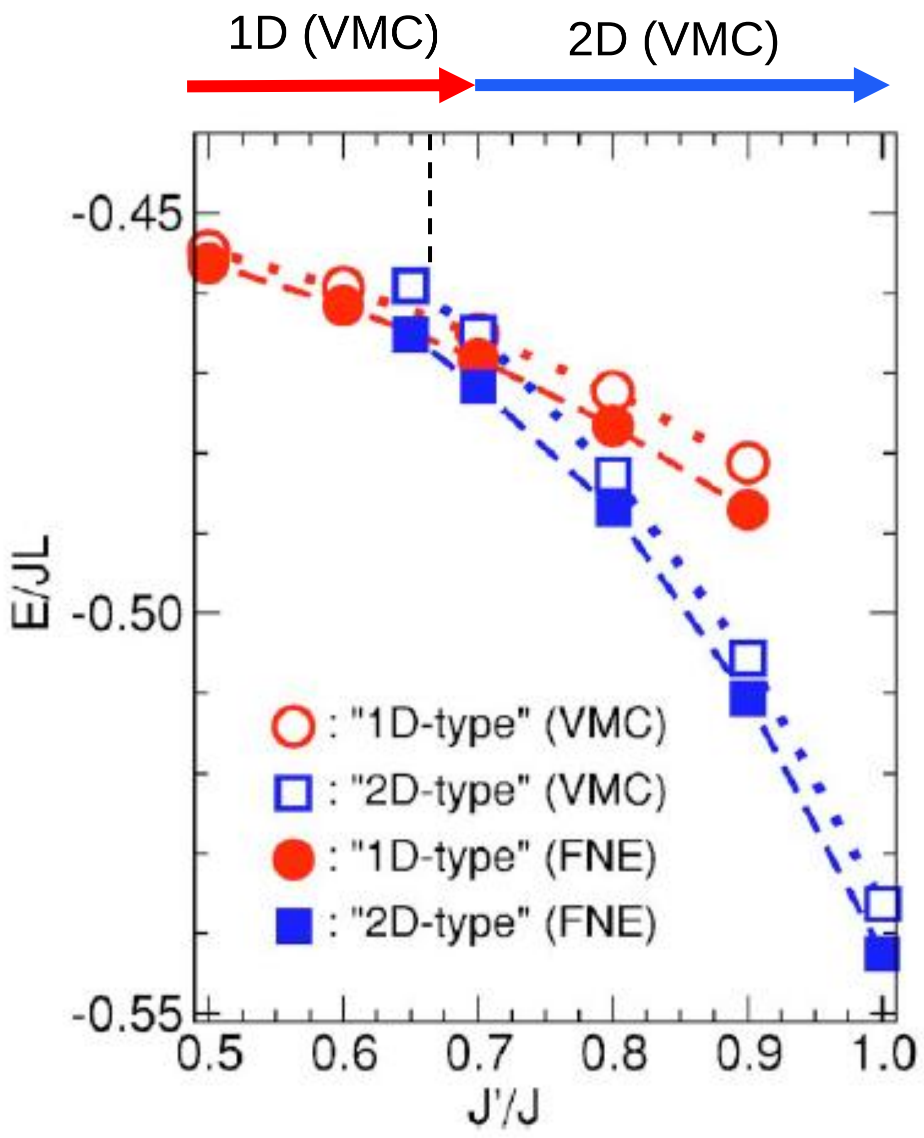
The previous Extended Huckel calculation gave t’/t = 0.87, J’/J = 0.75

Our new DFT calculation gives t’/t = 0.82, J’/J = 0.67

Cs_2CuCl_4 is a well-known triangular-lattice example where dimensional reduction takes place for parameter ratio J’/J ~ 0.4

The theoretical range for dimensional reduction is not yet established, but one RVB-type study* has given a range of up to J’/J = 0.65-0.70, for the 1D QSL, which would be consistent with our result

*S. Yunoki and S. Sorella, Phys. Rev. B 74, 014408 (2006)



Summary for $EtMe_3Sb[Pd(dmit)_2]_2$

- From μSR and EPR studies of the low-dimensional spin dynamics we have a resolution of the recent controversy about its status as a 2D QSL
- Dimensional reduction takes place, giving a 1D QSL rather than a 2D QSL
- The 1D direction found experimentally is not the one previously calculated to be the strongest interaction direction
- More accurate DFT calculations now show the correct 1D direction as t_r
- The J'/J ratio is the largest so far seen for this 2D to 1D dimensional reduction, which provides an important constraint for theoretical descriptions of the effect

PHYSICAL REVIEW LETTERS 133, 236702 (2024)

Overall Summary

- LF-μSR can be a powerful probe of spin dynamics and its dimensionality

- Diffusive models are best for non-ordered liquid-like states such as the QSL
  (compare with the quasistatic local fields plus coherent spin waves seen in ordered states)

- LF-μSR can follow the classical-quantum crossover and probe quantum entanglement

- Properties of the kagome-lattice MOF system $Cu_3(HOTP)_2$ were compared with QSL models, finding the best match for Dirac-type linearly-dispersing spin excitations

- From its low-dimensional diffusive spin-dynamics, we found that $EtMe_3Sb[Pd(dmit)_2]_2$ is actually a 1D QSL, rather than the previously conjectured 2D QSL