Workshop on Muon Science Technology and Industry (MELODY 2023)

Exploration of quantum spin liquid ground state by MuSR

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Nov. 5 2023

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Curriculum Vitae

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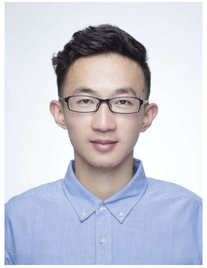
Group members

Graduate Student



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吴琼

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焦嘉琛

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王颖

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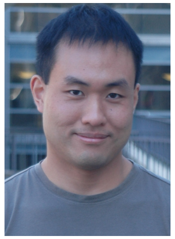
Alumni



丁兆峰

张建

谭程

杨燕兴

in Huang
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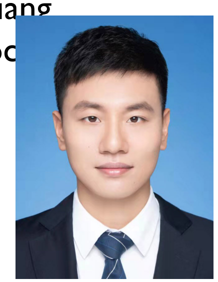

朱子浩

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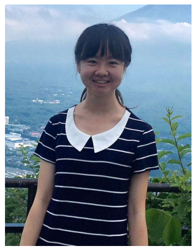
彭小冉

王冬逸

陈乐冰



臧佳伟

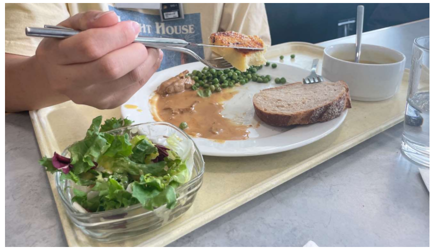
储玄婧

Best student talk award

MuSR Beam time

TRIUMF

PSI



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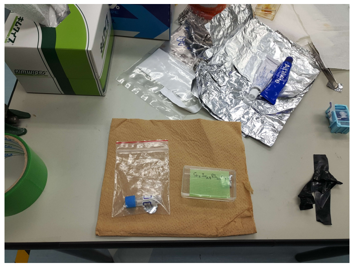
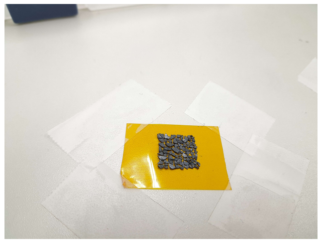
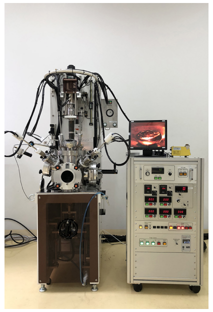
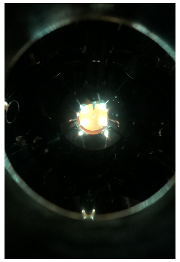




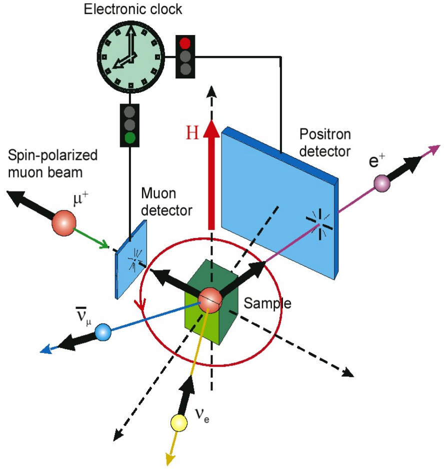
Research





MuSR

Electrical resistivity, magnetic resistivity, specific heat



Exotic behaviors of quantum materials

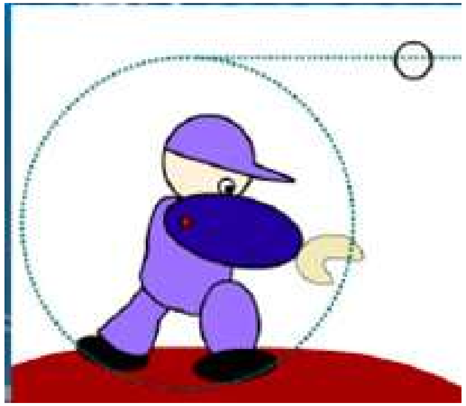
Heavy fermion

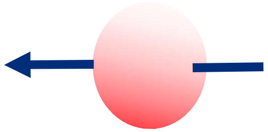
Superconductivity

Quantum spin liquid

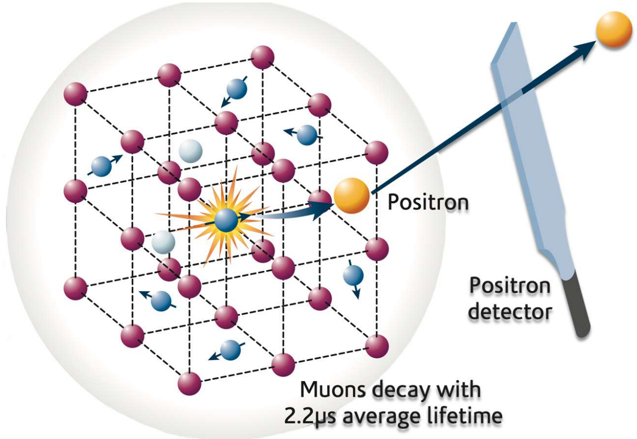
Principle of MuSR

Accelerator





Muon



$\mu^+ \rightarrow e^+ + \nu_e + \nu_\mu$

- Measuring the anisotropic distribution of the decay positrons from a bunch of muons deposited at the same condition

- Statistical average direction of the spin polarization (*P*) of the muon ensemble

- *P*(t) depends on the spatial distribution and dynamical fluctuations of the muon magnetic environment

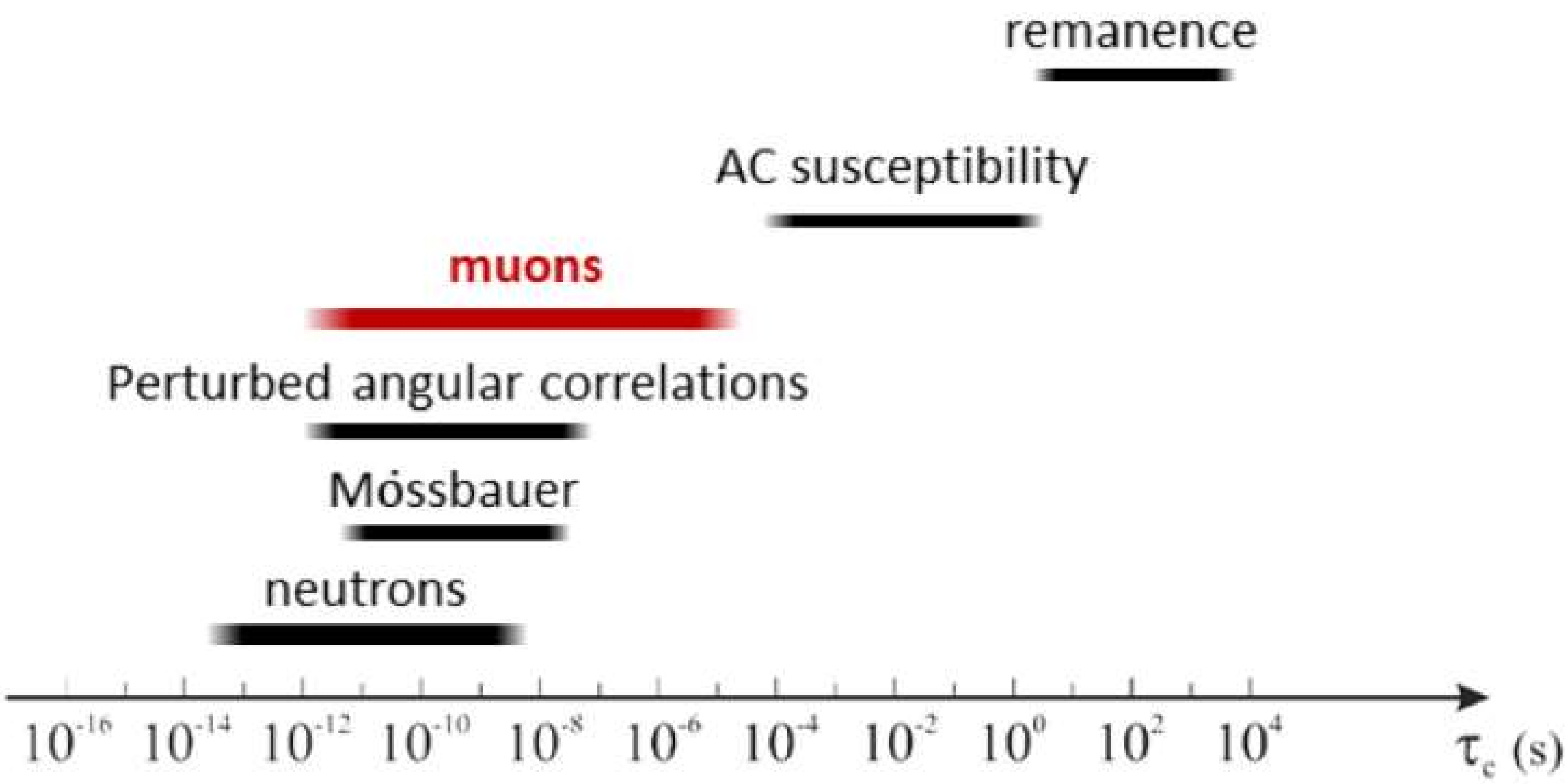


图 2.1-3 μSR 实验能有效填补多种实验对磁场频率覆盖的空白。图片由 A. Yaouanc 和 P. Dalmas De Réotier 所著专著[68]中第一章图 1.5 重新绘制。

Advantages and uniqueness of MuSR

Extreme sensitivity to small internal magnetic fields (0.1 G) -- able to detect fields of nuclear and electronic origin.

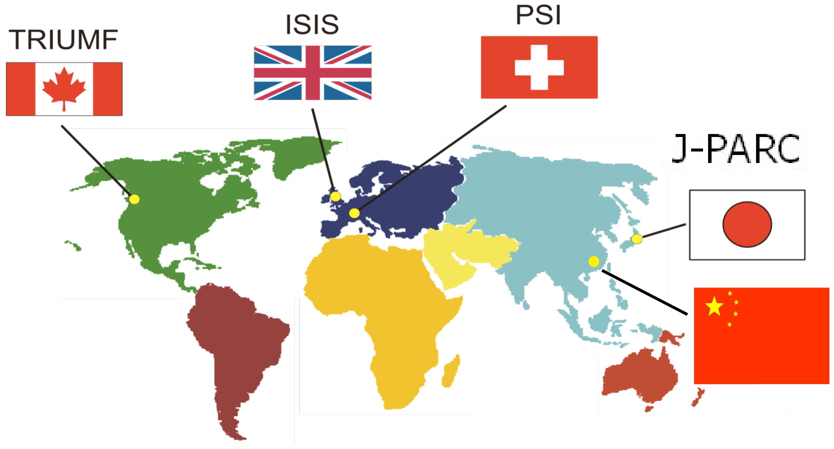
Obtain volume fraction of magnetic phase

Can measure magnetic fluctuation rates in the range 10^4 to 10^{12} Hz, depending on the size of the magnetic field at the muon site

Can be implanted into any material (gas, liquid or solid)

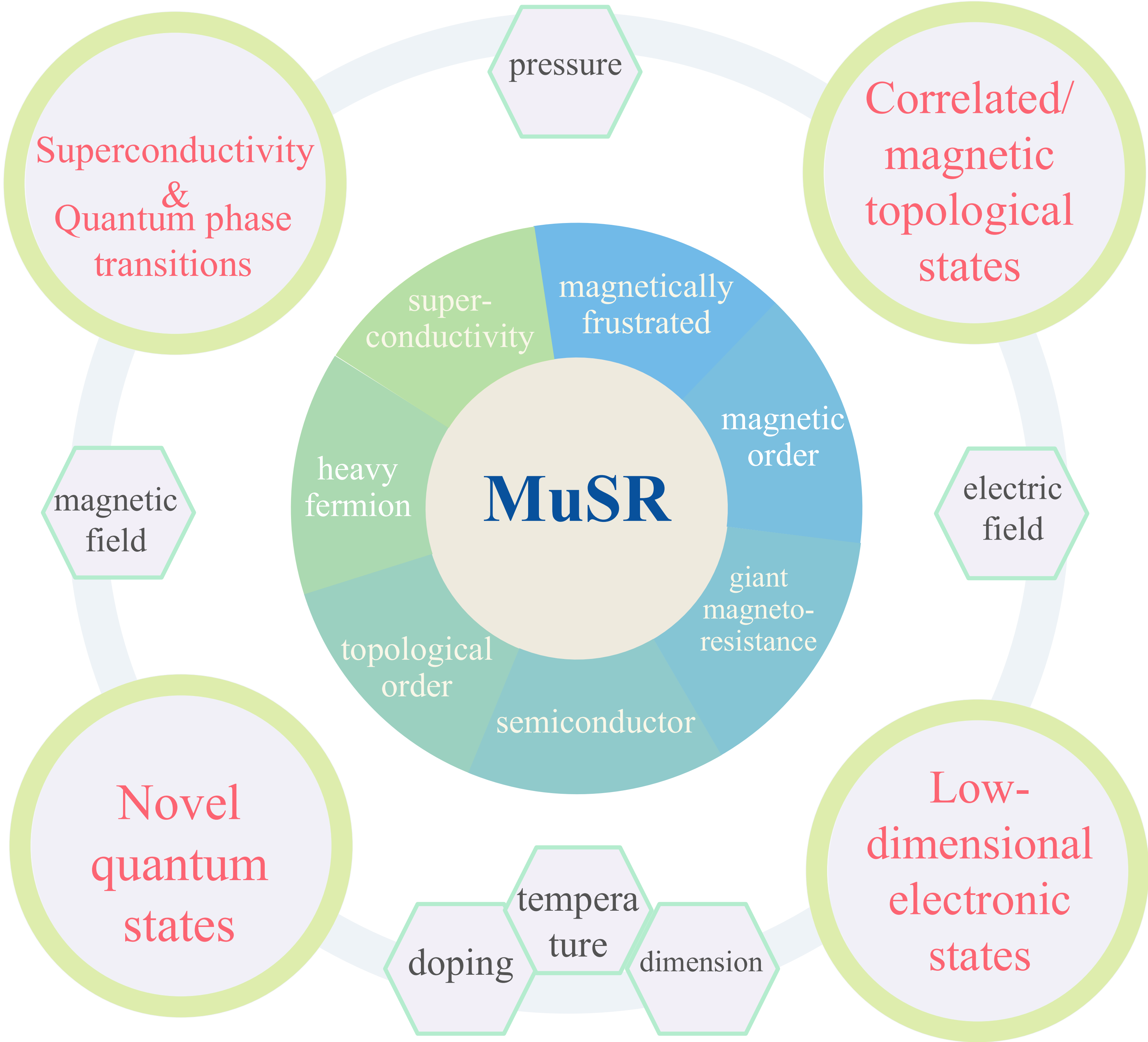
Can be applied to single crystals, polycrystalline samples and thin films

In a large variety of environments (e.g. any temperature, magnetic fields up to 8T, electric fields, high pressure, irradiated with light, applied RF pulses etc

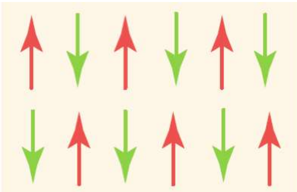
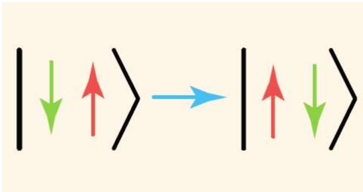


More MuSR Facilities!!

A. D. Hillier…**L. Shu**…et. al., "Muon spin spectroscopy", Nature Reviews Methods Primers 2022
殳蕾、倪晓杰、潘子文，"MuSR 技术在凝聚态物理中的应用"，物理 2021
Z. H. Zhu and **L. Shu**, "Muon Spin Relaxation Studies on Quantum Spin Liquid Candidates", Progress in Physics 2020


pressure
Superconductivity & Quantum phase transitions
Correlated/ magnetic topological states
super-conductivity
magnetically frustrated
magnetic order
heavy fermion
MuSR
magnetic field
electric field
giant magneto-resistance
topological order
semiconductor
Novel quantum states
Low-dimensional electronic states
tempera ture
doping
dimension

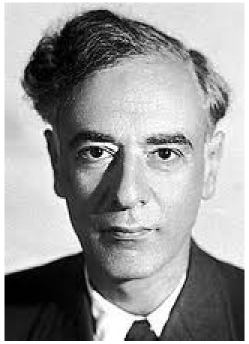
History of quantum spin liquid

1970

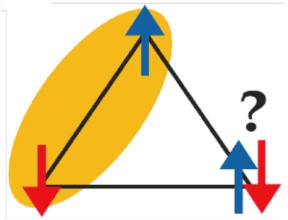
L. E. F. Neel

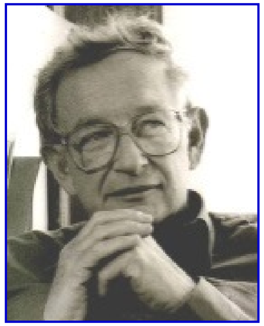
vs.



L. D. Landau

1962





P. W. Anderson

1977

The concept of quantum spin liquid: RVB state

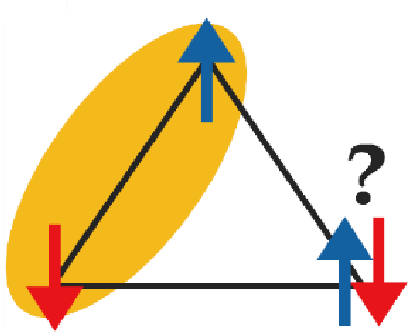
RESONATING VALENCE BONDS: A NEW KIND OF INSULATOR?*

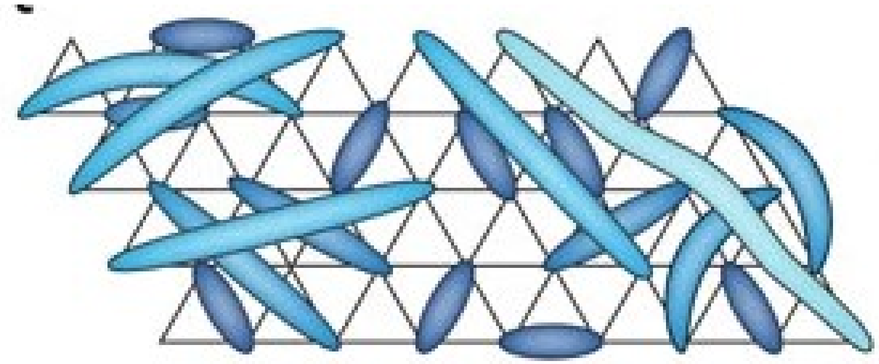
P. W. Anderson
Bell Laboratories, Murray Hill, New Jersey 07974
and
Cavendish Laboratory, Cambridge, England

(Received December 5, 1972; Invited**)

ABSTRACT

The possibility of a new kind of electronic state is pointed out, corresponding roughly to Pauling's idea of "resonating valence bonds" in metals. As observed by Pauling, a pure state of this type would be insulating; it would represent an alternative state to the Néel antiferromagnetic state for S = 1/2. An estimate of its energy is made in one case.





P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973)

QSL and high-T_c superconductors

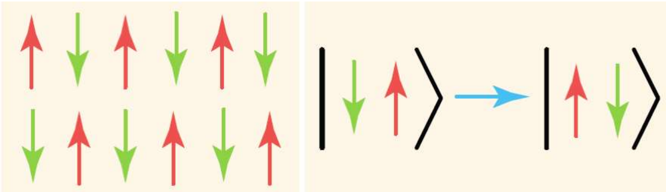
The Resonating Valence Bond State in La_2CuO_4 and Superconductivity

P. W. ANDERSON

The oxide superconductors, particularly those recently discovered that are based on La_2CuO_4, have a set of peculiarities that suggest a common, unique mechanism: they tend in every case to occur near a metal-insulator transition into an odd-electron insulator with peculiar magnetic properties. This insulating phase is proposed to be the long-sought "resonating-valence-bond" state or "quantum spin liquid" hypothesized in 1973. This insulating magnetic phase is favored by low spin, low dimensionality, and magnetic frustration. The preexisting magnetic singlet pairs of the insulating state become charged superconducting pairs when the insulator is doped sufficiently strongly. The mechanism for superconductivity is hence predominantly electronic and magnetic, although weak phonon interactions may favor the state. Many unusual properties are predicted, especially of the insulating state.

P. W. Anderson, Science **235**, 1196 (1987)

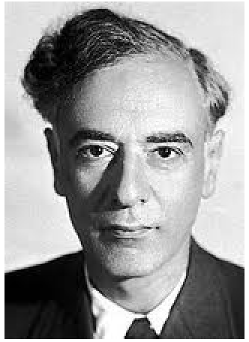
History of quantum spin liquid



1970

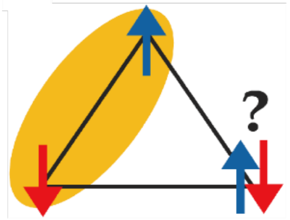
L. E. F. Neel

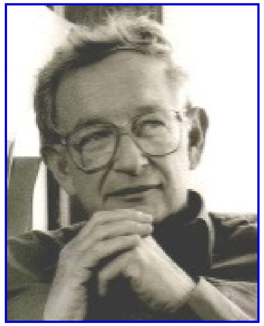
vs.



L. D. Landau

1962





1977

P. W. Anderson

Topological order

Xiaogang Wen
Buckley prize
Dirac medal

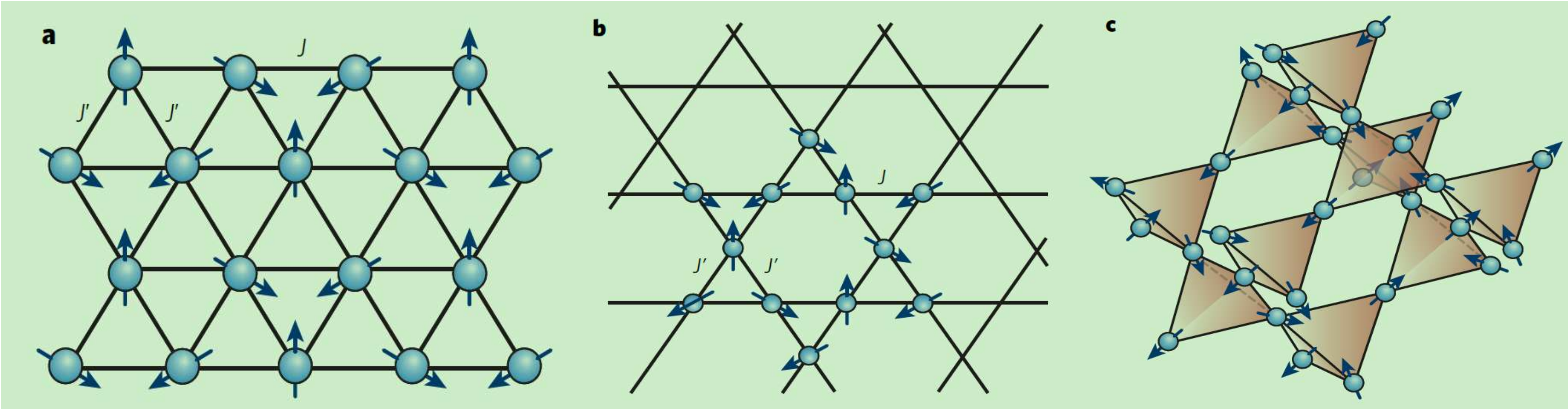
Topological quantum computation

Kitaev model

A. Kitaev
Buckley prize
Dirac medal

Real materials

Searching for QSL materials



Triangular **Kagomé** **Pyrochlore**

Frustration leads to the formation of fluid-like states of matter, i.e. spin liquids. Spins highly correlate but still fluctuate strongly when $T \to 0$.
Fractional magnetic excitations, i.e. spinons are expected.

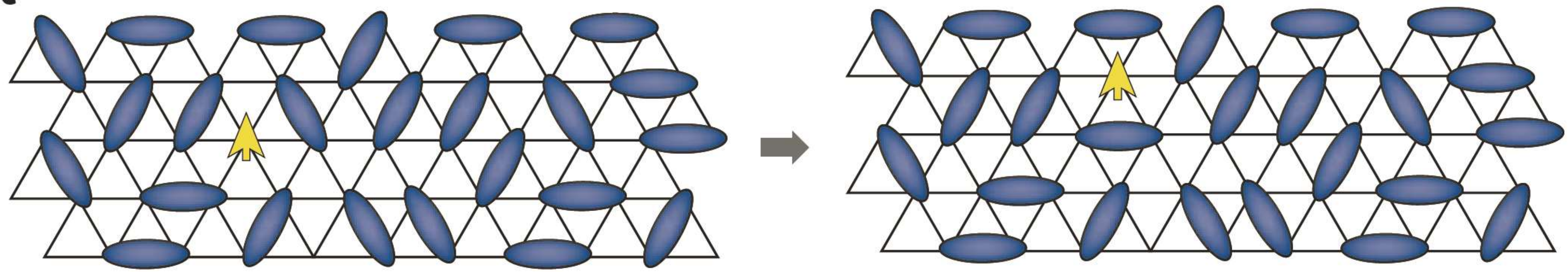
L Balents, Nature **464**, 199 (2010)
P. W. Anderson, Science **235**, 1196 (1987)
P. W. Anderson, Mater. Res. Bull. **8**, 153 (1973)

Searching for QSL materials

Table 1 | Some experimental materials studied in the search for QSLs

Material	Lattice	S	Status or explanation
κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$	Triangular†	½	Possible QSL
EtMe$_3$Sb[Pd(dmit)$_2$]$_2$	Triangular†	½	Possible QSL
Cu$_3$V$_2$O$_7$(OH)$_2$•2H$_2$O (volborthite)	Kagomé†	½	Magnetic
ZnCu$_3$(OH)$_6$Cl$_2$ (herbertsmithite)	Kagomé	½	Possible QSL
BaCu$_3$V$_2$O$_8$(OH)$_2$ (vesignieite)	Kagomé†	½	Possible QSL
Na$_4$Ir$_3$O$_8$	Hyperkagomé	½	Possible QSL
Cs$_2$CuCl$_4$	Triangular†	½	Dimensional reduction
FeSc$_2$S$_4$	Diamond	2	Quantum criticality

c

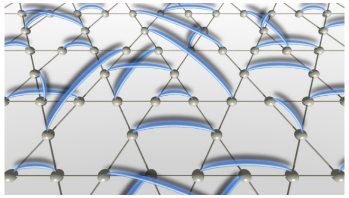


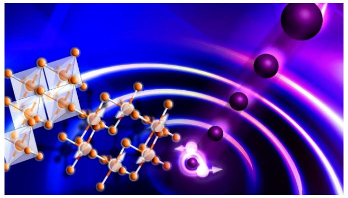
L. Balents, Nature **464**, 199 (2010)

Quantum Spin Liquid

FM, AFM

Quantum Spin Liquid





REVIEW

QUANTUM MATERIALS

Quantum spin liquids

C. Broholm[1], R. J. Cava[2], S. A. Kivelson[3], D. G. Nocera[4], M. R. Norman[5*], T. Senthil[6]

Spin liquids are quantum phases of matter with a variety of unusual features arising from their topological character, including "fractionalization"—elementary excitations that behave as fractions of an electron. Although there is not yet universally accepted experimental evidence that establishes that any single material has a spin liquid ground state, in the past few years a number of materials have been shown to exhibit distinctive properties that are expected of a quantum spin liquid. Here, we review theoretical and experimental progress in this area.

Broholm *et al.*, *Science* **367**, eaay0668 (2020)

- No magnetic order at $T = 0$ K
- Highly entangled spins
- Beyond Landau's symmetry breaking paradigm
- Fractionalized excitations & emergent gauge structure

- Exotic quantum magnetic ground state
- Important fundamental research
- Potential application on quantum computation

How to identify a quantum spin liquid?

Step I： Role out magnetic order、 spin glass
μSR, magnetic susceptibility, specific heat, NMR, elastic neutron scattering…

Step II： Detect the spinon excitation				
inelastic neutron scattering	**specific heat**	**thermal conductivity**	**thermal Hall**	**μSR**
continuum	power law/linear term	linear term	quantized	strong spin dynamics
Kagome $ZnCu_3(OH)_6Cl_2$ Nature 492, 406 (2012)	triangular κ-(BEDT-$TTF)_2Cu_2(CN)_3$ Nat. Phys. 4, 459 (2008)	triangular $EtMe_3Sb[Pd(dmit)_2]_2$ Science 328, 1246 (2010)	honeycomb α-$RuCl_3$ Nature 559, 227 (2018)	triangular $YbMgGaO_4$ PRL 117 097201 (2016)

Quantum Spin liquid

- Absence of magnetic long range order down to zero temperature
- Highly entangled spin system

What can you measure with MuSR

- Absence of magnetic orders (long/short range, spin glass)
- Spin dynamics T_1

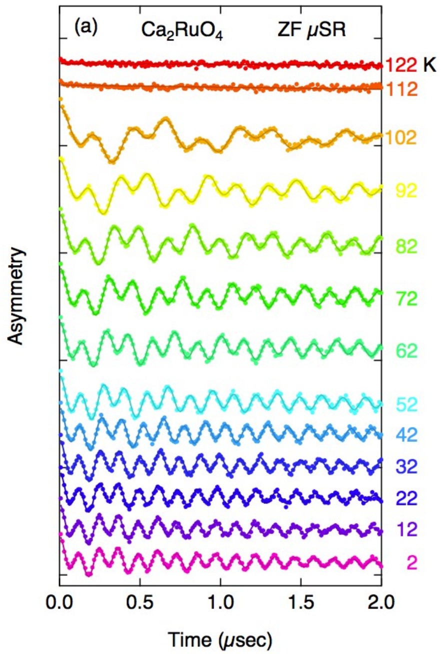
Magnetic order, volume fraction

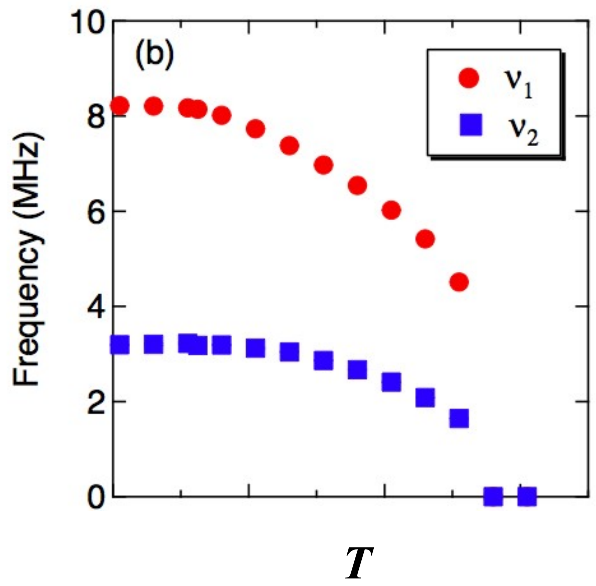
- Long-range order leads to coherent oscillations
- Measuring $\omega_\mu = \gamma_\mu |B|$ vs. T gives order parameter

nature materials ARTICLES
PUBLISHED ONLINE: 19 FEBRUARY 2012 | DOI: 10.1038/NMAT3236

New magnetic phase diagram of $(Sr,Ca)_2RuO_4$

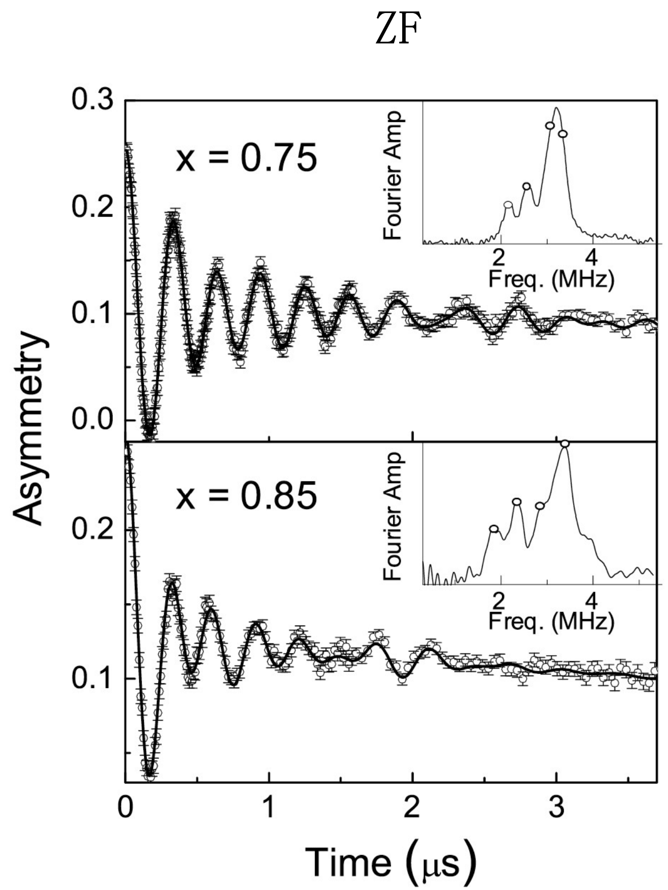
J. P. Carlo[1,2], T. Goko[1,3], I. M. Gat-Malureanu[1,4], P. L. Russo[1], A. T. Savici[1], A. A. Aczel[5], G. J. MacDougall[5], J. A. Rodriguez[5], T. J. Williams[5], G. M. Luke[5], C. R. Wiebe[1,5], Y. Yoshida[6], S. Nakatsuji[7,8], Y. Maeno[7], T. Taniguchi[9] and Y. J. Uemura[1]*

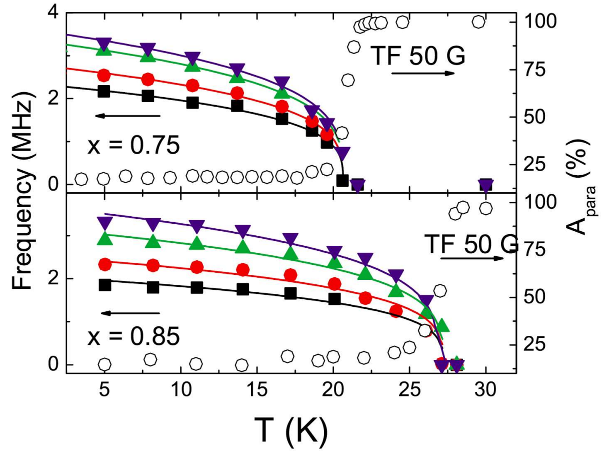


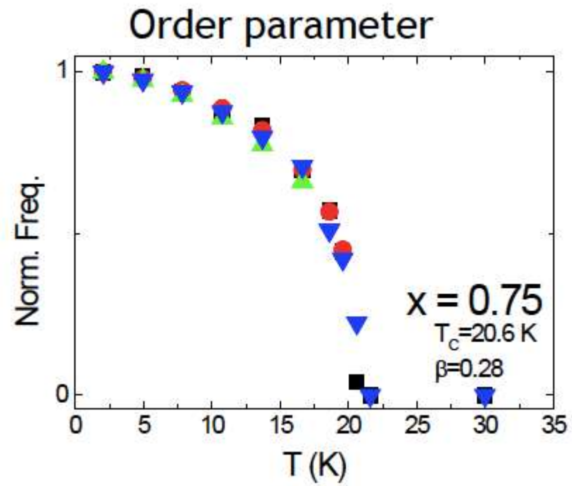


J. P. Carlo et al. Nature Materials 11, 323-328 (2012)

Magnetic Phase Transitions in NaxCoO2







- **Textbook** MuSR signature of a phase transition to an ordered magnetic state

- Fitting function: $A(t) = A_0 e^{-\lambda t} \cos(\omega_{\mu t} + \Phi)$

P. Mendels *et al.* PRL 94 136403 (2005)

Spin Waves of Honeycomb Iridate Na_2IrO_3

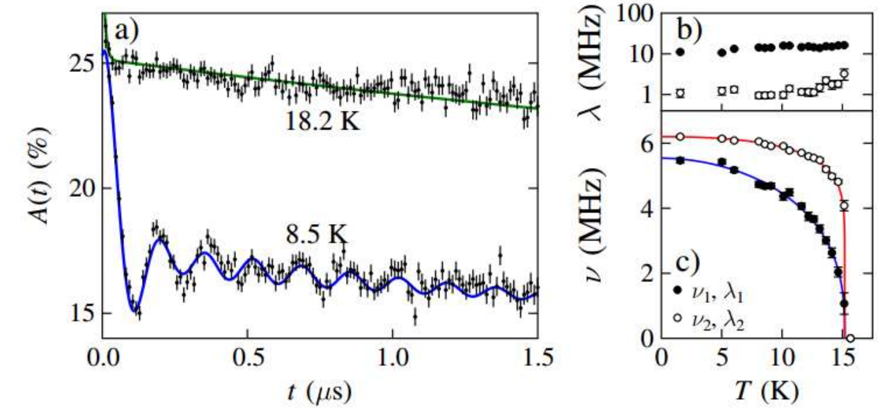
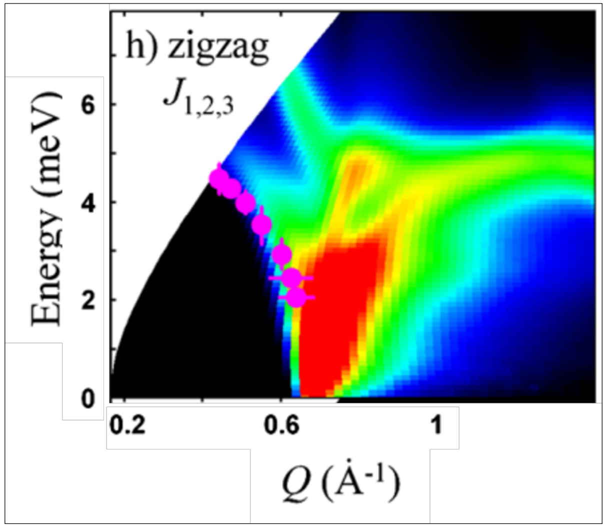


FIG. 2 (color online). (a) ZF μ^+SR spectra on a polycrystalline sample of Na_2IrO_3 above and below T_N. Solid lines are (top) a guide to the eye and (bottom) a fit described in the text. (b),(c) Fitted parameters as a function of temperature.



A zigzag phase was suggested by powder INS

◆ Magnetic order at low T, T_N = 15.3 K

◆ Fitting function: $A(t) = A_1 e^{-\lambda_1 t}\cos(2\pi\nu_1 t + \phi_1) + A_2 e^{-\lambda_2 t}\cos(2\pi\nu_2 t + \phi_2) + A_3 e^{-\Lambda t} + A_{bg}$

S. K. Choi *et al.* PRL 108 127204 (2012)

Spin glass behavior in $Sr_4Cu_6O_{10}$

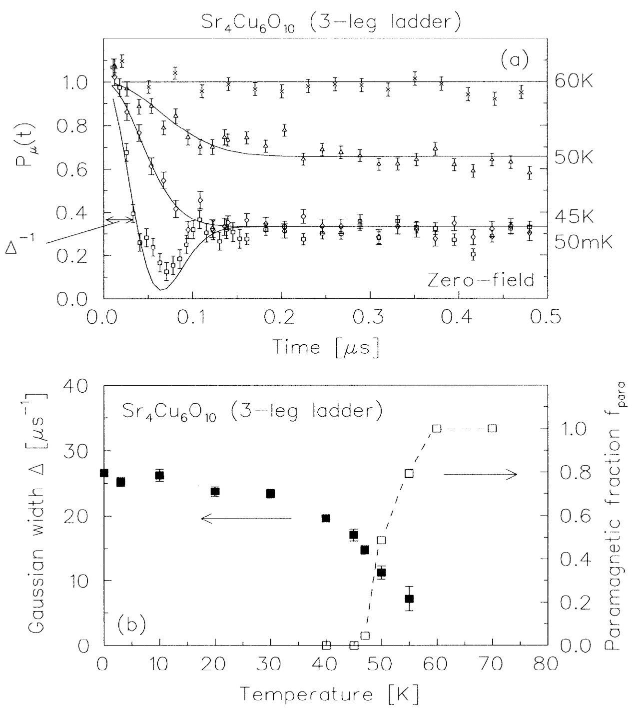


FIG. 2. (a) Zero-field μSR spectra in the 3-leg ladder system. The solid lines are the fit with the model function, Eq. (1). (b) Temperature dependence of the Gaussian field-distribution width (Δ) and the paramagnetic volume fraction (f_{para}). The broken line is a guide to the eye.

- Fitting function: $P_\mu = f_{\text{para}} + (1 - f_{\text{para}})G_{\text{static}}(t, \Delta)$

- A recovery of the polarization to 1/3 at low *T*, static magnetism,

- Absence of procession: magnetic order is a random freezing of moments.

K. Kojima *et al.* PRL. (1995)

Spin dynamics in $YbMgGaO_4$

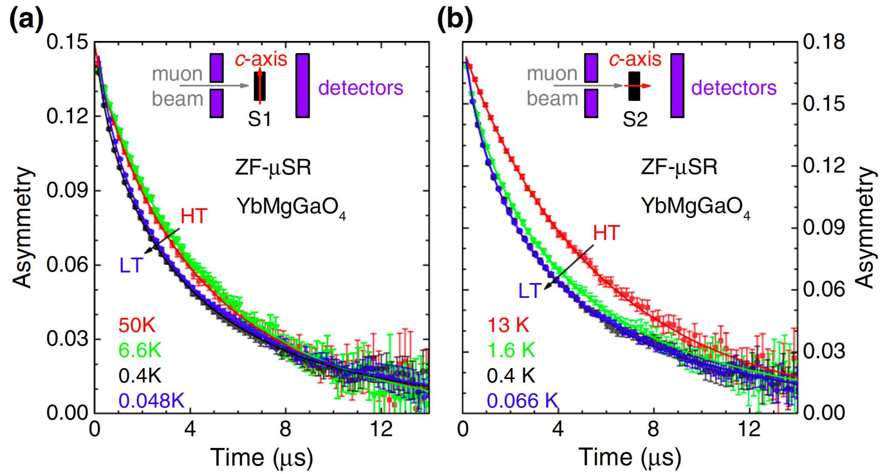
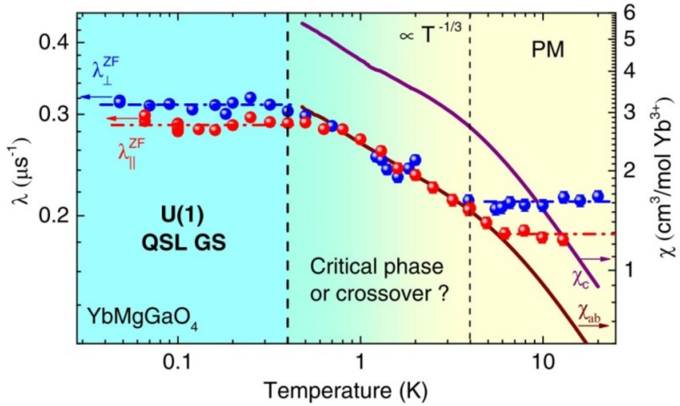


FIG. 2. Selected background-subtracted ZF-μSR signals with the incident beam (a) perpendicular ($\perp$) and (b) parallel ($\|$) to the c axis. The colored lines are the corresponding fits to the data using Eq. (1). The insets show relevant experimental geometries.



- No magnetic order
- Lack of a recovery of the polarization to 1/3 at low *T*, no spin glass
- *T* independent plateau of muon spin relaxation rate

Y. Li *et al.* PRL 117 097201. 2016)

Spin dynamics in $YbMgGaO_4$

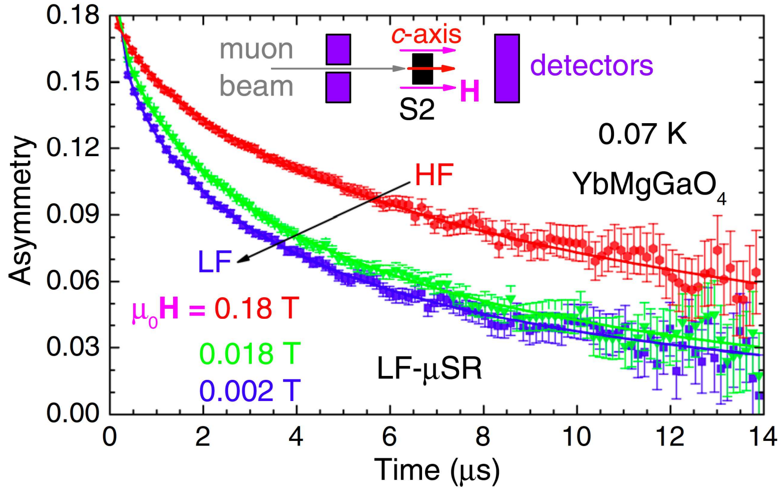
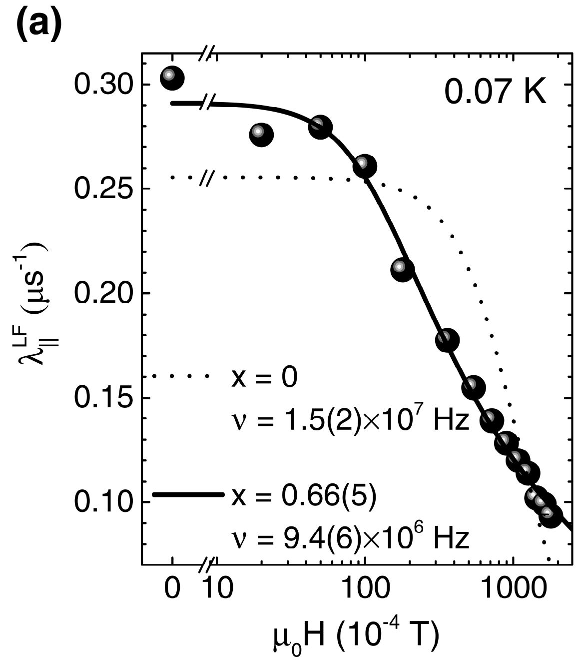


FIG. 3. Selected LF-μSR signals (background-subtracted) at 0.07 K. The colored lines are fits to the data using Eq. (1). The insets show the experimental geometries.

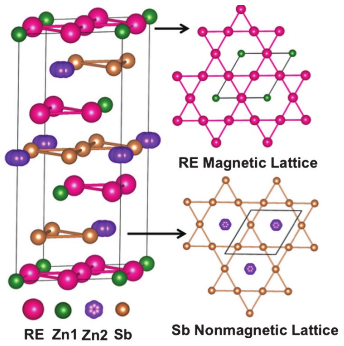


- LF spectra change moderately when field increase from 0 to 0.18 T

Y. Li *et al.* PRL 117 097201 (2016)

Searching for quantum spin liquid candidates

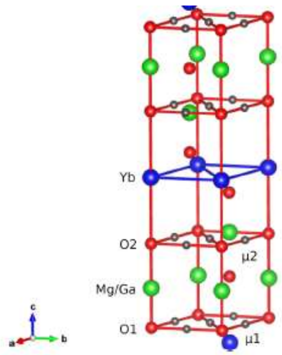
$Tm_3Sb_3Zn_2O_{14}$



Possible QSL ground state: a $\mathbb{Z}_2$ QSL

Z. F. Ding… L. Shu* PRB 2018

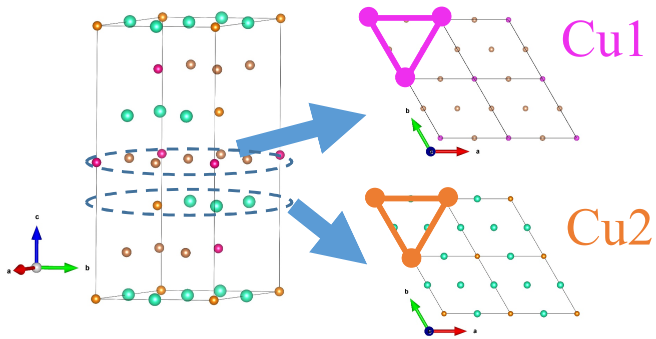
$YbMgGaO_4$



Persistent spin dynamics and absence of spin freezing

Z. F. Ding… L. Shu* PRB 2020

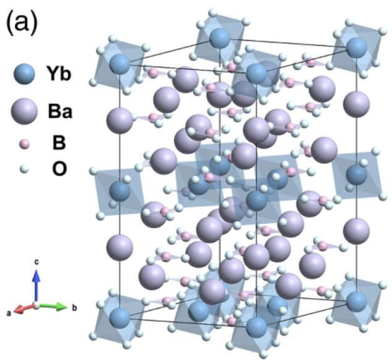
$Lu_3Sb_3Cu_2O_{14}$



Intrinsic properties of spin-liquids due to very high purity

Y. X. Yang…L. Shu*, arXiv:2102.09271

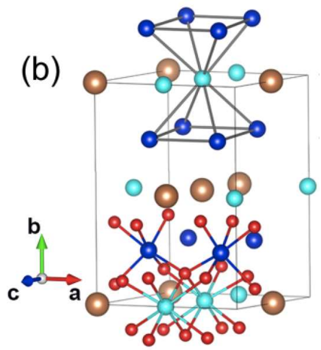
$Yb(BaBO_3)O_3$



Quantum magnet, dipole-dipole interaction dominant

C. Y. Jiang…L. Shu* PRB 2022

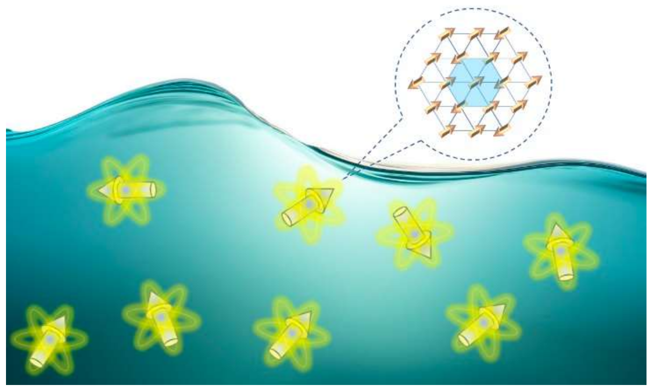
Tm_3SbO_7



Explained by a transverse field Ising model

Y. X. Yang…L. Shu* PRB 2022

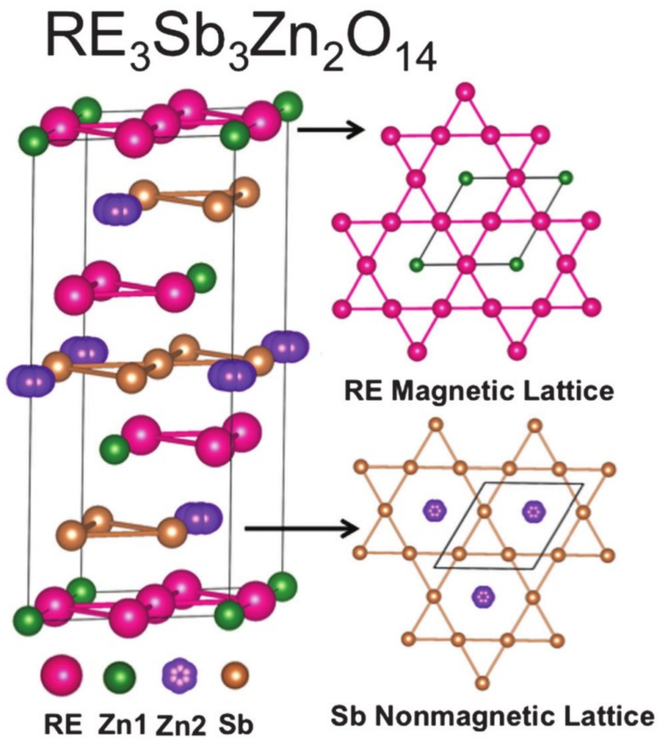
$NaYbSe_2$



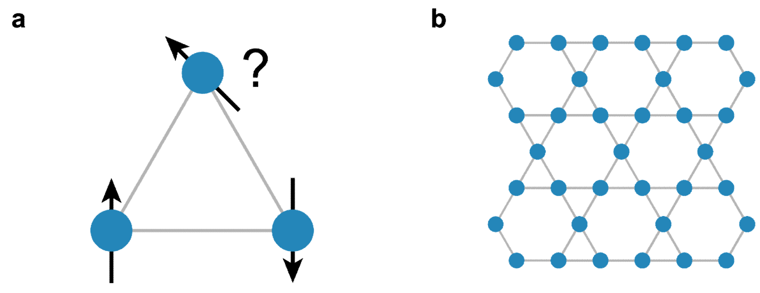
Classic droplets in the quantum order

Z. H. Zhu…L. Shu*, the Innovation 2023

Rare-earth Kagomê lattice magnet $Tm_3Sb_3Zn_2O_{14}$



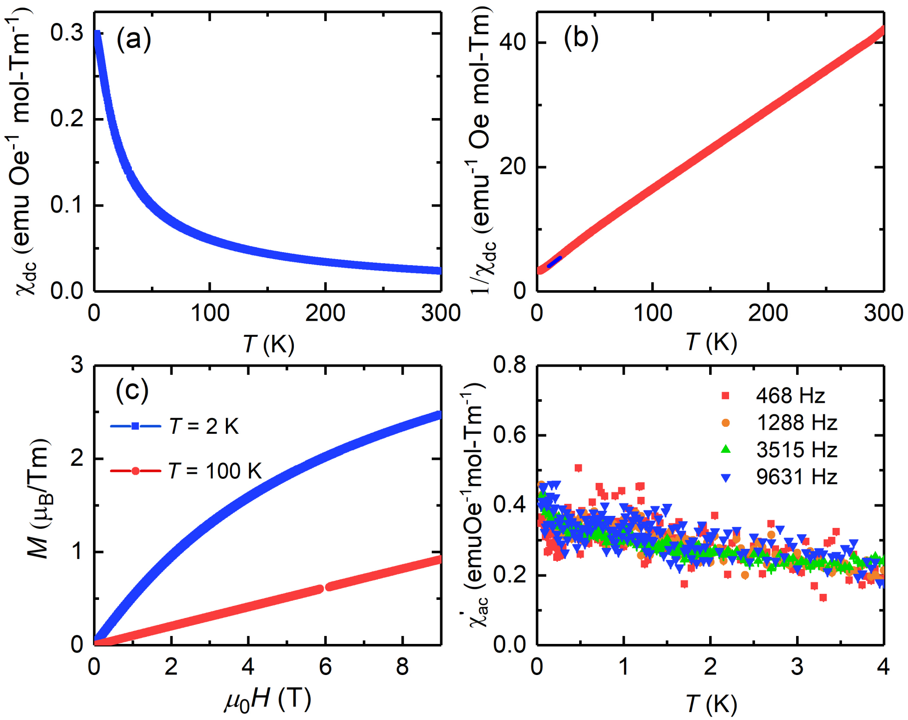
Geometrical frustration



- The Tm kagomê layers, separated by non-magnetic Zn, Sb and O atoms
- The nearest Tm-Tm bond between two neighboring layers is 6.06 Å, while within the kagomê layers, the nearest Tm-Tm bond is 3.68 Å, quasi-2D

Z. F. Ding… L. Shu* PRB 2018

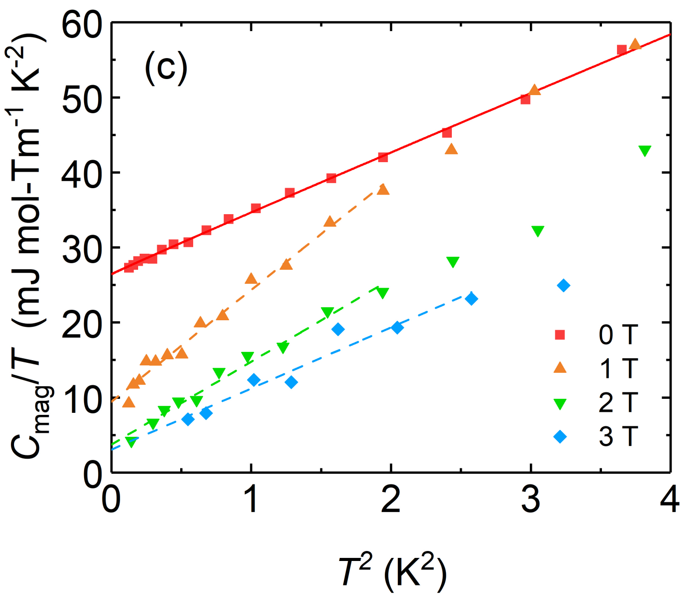
Rare-earth Kagomê lattice magnet $Tm_3Sb_3Zn_2O_{14}$

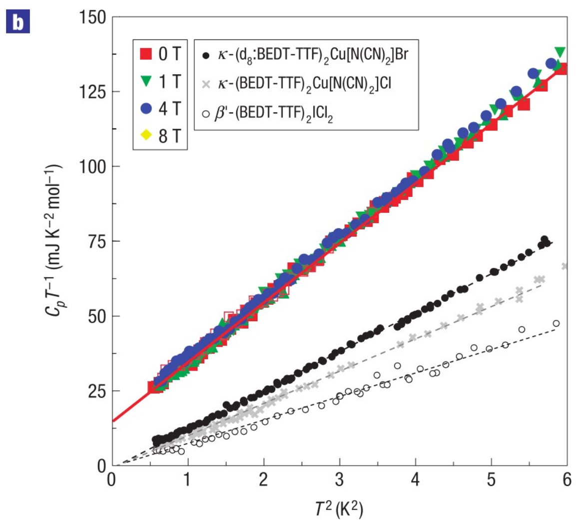


- **Absence of magnetic order in susceptibility**
- **Absence of spin freezing** behaviors such as spin glass
- Isothermal magnetization at 2 K: the low energy scale of the interaction between the low-lying non-Kamers doublets of Tm^{3+}, effective spin-1/2 moment

Z. F. Ding… L. Shu* PRB 2018

Rare-earth Kagomê lattice magnet $Tm_3Sb_3Zn_2O_{14}$





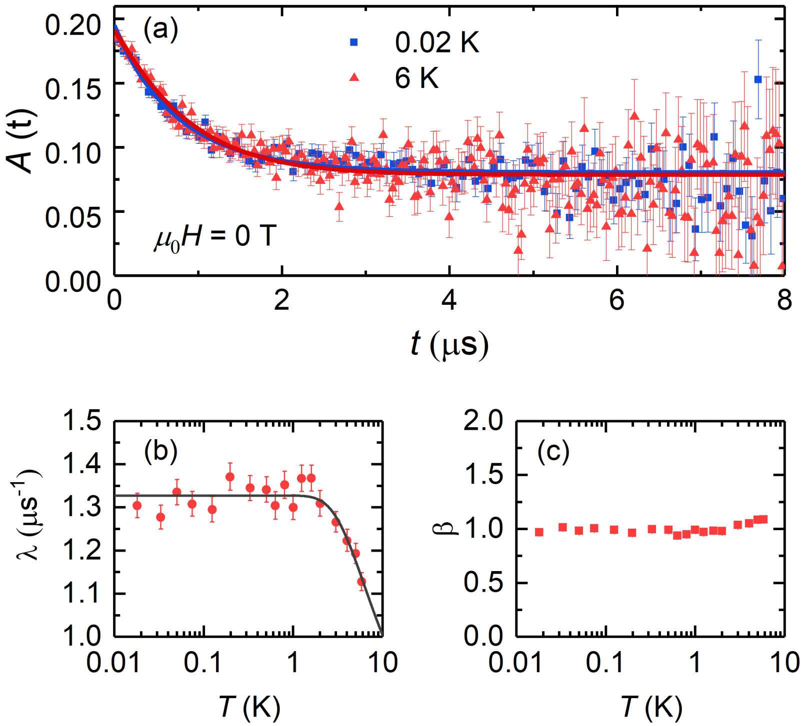
S. Yamashita *et al.* Nat. Phys. 4, 459 (2008)

- $\gamma(0)$ is gradually suppressed by field, which means that part of $\gamma(0)$ could be induced by the (quenched) disorders
- The robust $\gamma(0)$ (**26.6(1) mJ mol Tm^{-1} K^{-2}**) : constant density of states at low energies
- For higher magnetic field applied $C_p \sim e^{-\Delta/T}$

a spin liquid state?

Z. F. Ding… L. Shu* PRB 2018

Rare-earth Kagomê lattice magnet $Tm_3Sb_3Zn_2O_{14}$



- No magnetic order down to 20 mK
- **The low temperature plateau** of λ indicates the persistent spin dynamics and large density of states at low energies.
- The observed stretched exponent $\beta \sim 1$, almost *T* independent: the absence of obvious disorder/impurity induced.
- The persistent spin dynamics is consistent with the large density of states from a QSL state, gapless.

Possible QSL ground state: a $\mathbb{Z}_2$ QSL

Z. F. Ding… L. Shu* PRB 2018

Rare-earth Kagomê lattice magnet $Tm_3Sb_3Zn_2O_{14}$

$Tm_3Sb_3Zn_2O_{14}$ Tm/Zn site-mixing disorder: 17%

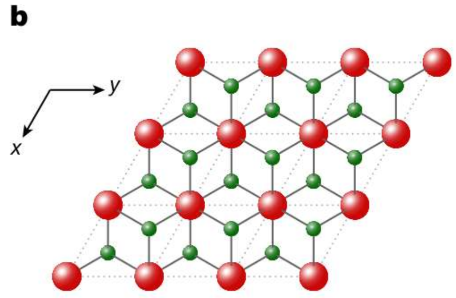
$Tm_3Sb_3Mg_2O_{14}$ Tm/Mg site-mixing disorder: 2%

- Spin-liquid like behaviors are not observed in $Tm_3Sb_3Mg_2O_{14}$
- Samples with perfect geometrical frustration are in urgent demand

Z. F. Ding… L. Shu* PRB 2018 Y. X. Yang… L. Shu* CPL 2022

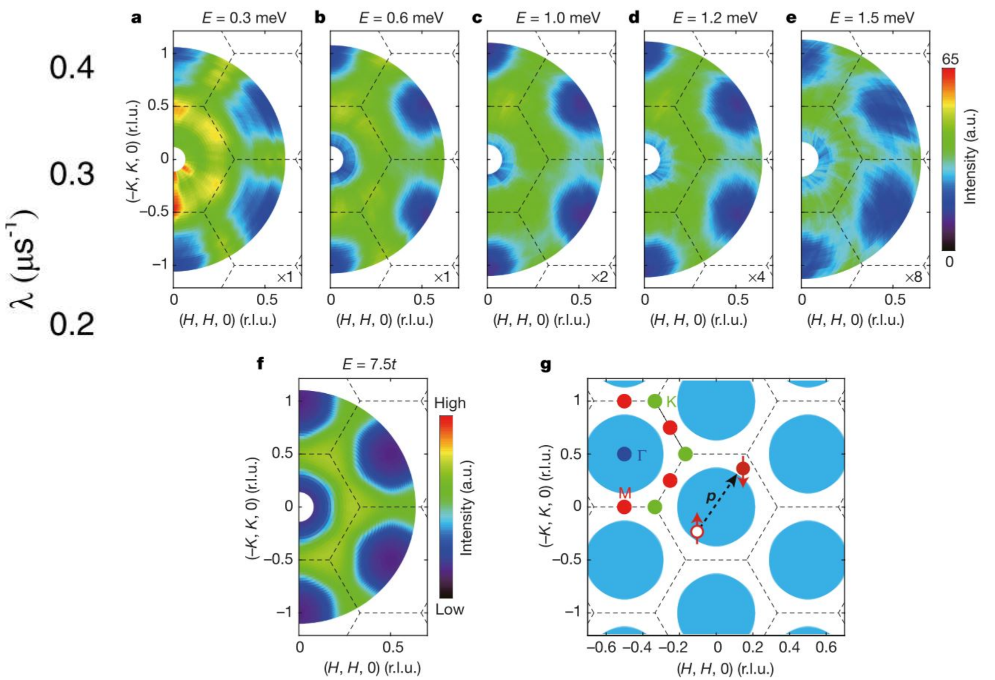
2D triangular antiferromagnet $YbMgGaO_4$

- Yb^{3+}: $J_{\mathrm{eff}} = 1/2$
- Triangular lattice
- No magnetic order down to 60 mK
- Mg-Ga site mixing



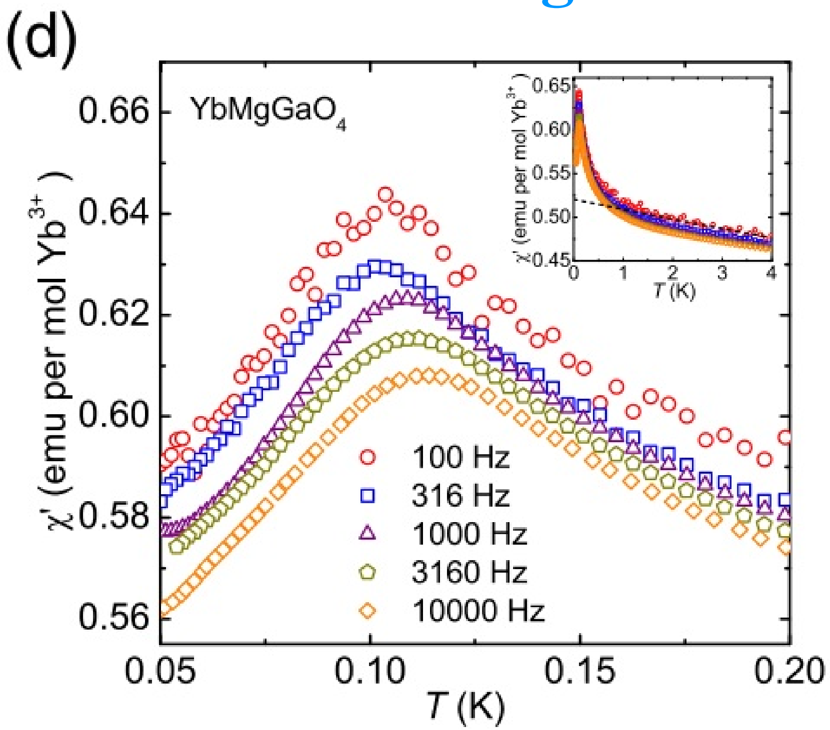
Paddinson *et al.*, NP (2017)

U(1) QSL?



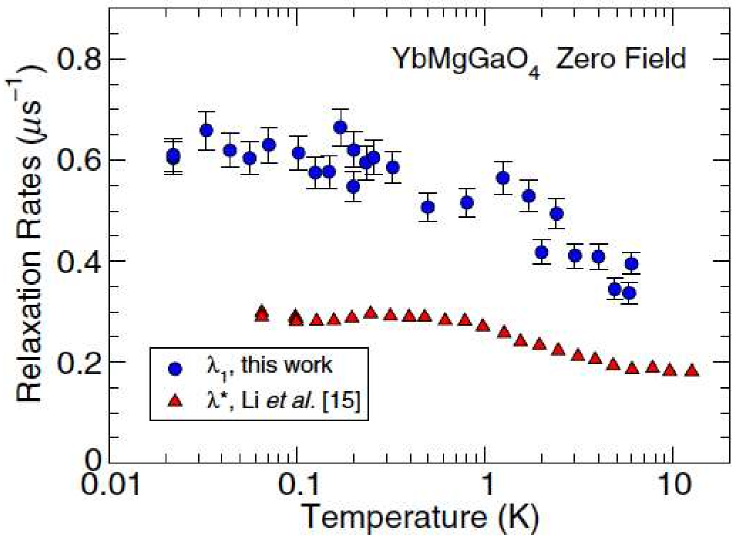
Li *et al.*, Sci. Rep. (2015)
Li *et al.*, PRL (2016)
Shen *et al.*, Nature (2016)

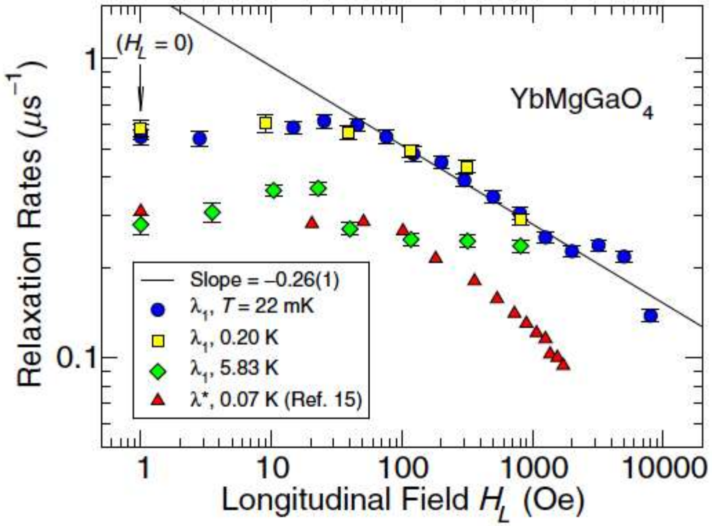
Random singlet



Xu *et al.*, PRL (2016)
Ma *et al.*, PRL (2018)
Kimchi *et al.*, PRX (2018)

2D triangular antiferromagnet $YbMgGaO_4$



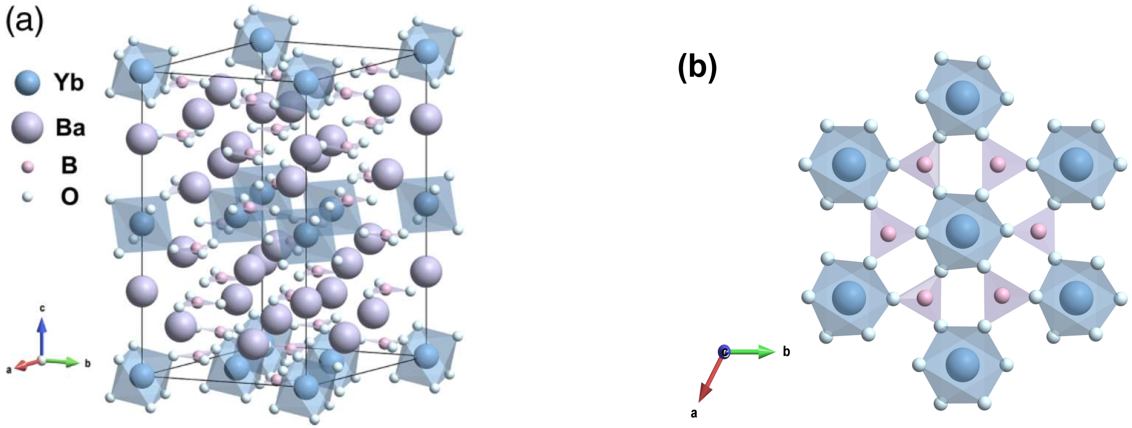


- "Persistent" spin dynamics and absence of spin freezing
- a power-law fit to the $T = 22$ mK data for 25 Oe $< H_L <$ 2 kOe, slow spin dynamics

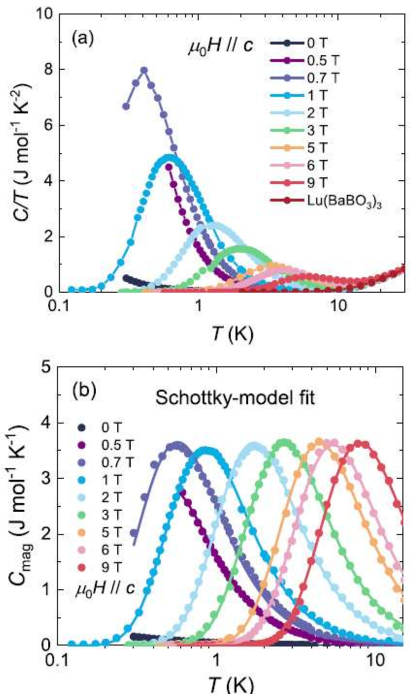
Random singlet

Z. F. Ding… L. Shu* PRB 2020

Quantum dipolar magnet $Yb(BaBO_3)_3$



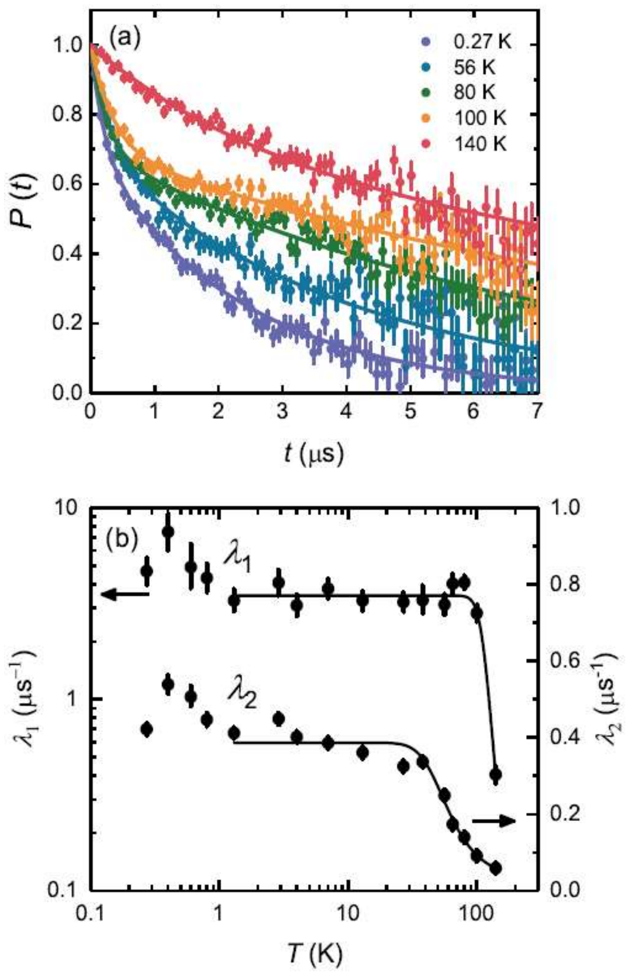
Free of disorder

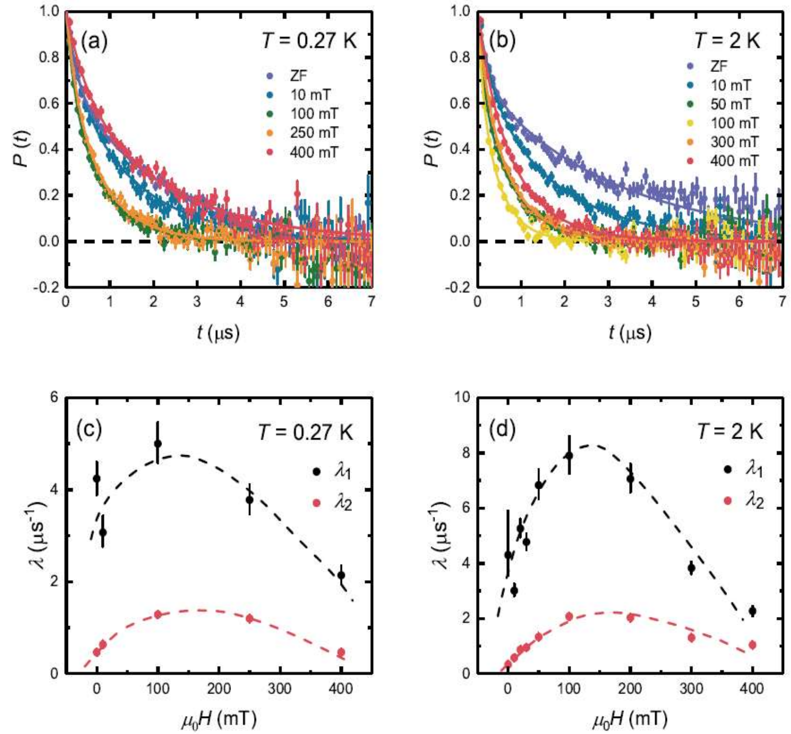


- Degeneration of ground state doublet be affected (ZF and low magnetic fields)
- Ground state doublet well opened (higher magnetic fields)

C. Y. Jiang…L. Shu* PRB 2022

Quantum dipolar magnet $Yb(BaBO_3)_3$





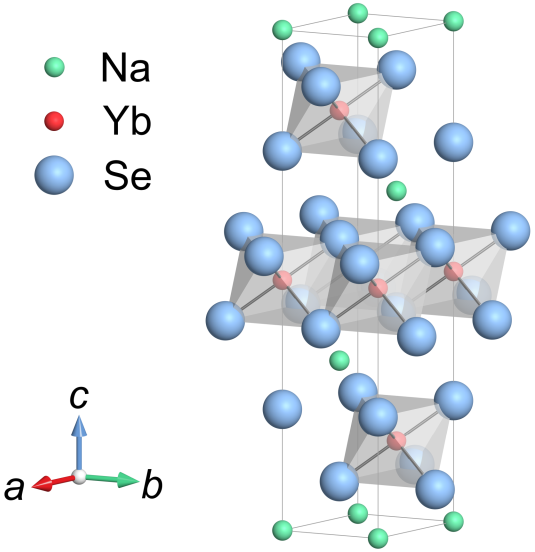
Field-induced increase of the density of spin excitations

Quantum magnet, dipole-dipole interaction dominant

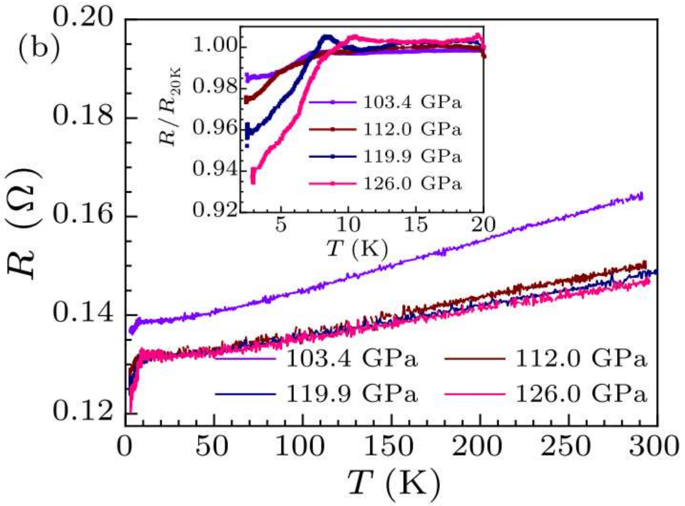
C. Y. Jiang…L. Shu* PRB 2022

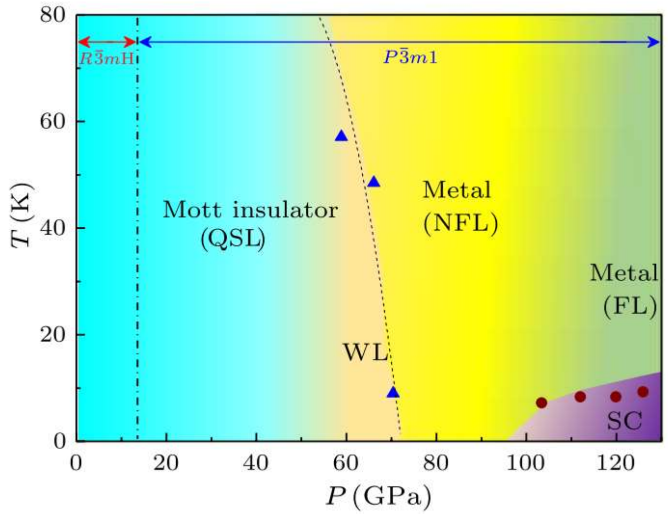
Triangular antiferromagnet $NaYbSe_2$

- Yb^{3+} triangular lattice
- No site-mixing
- ~10% site-mixing (Na-Yb)



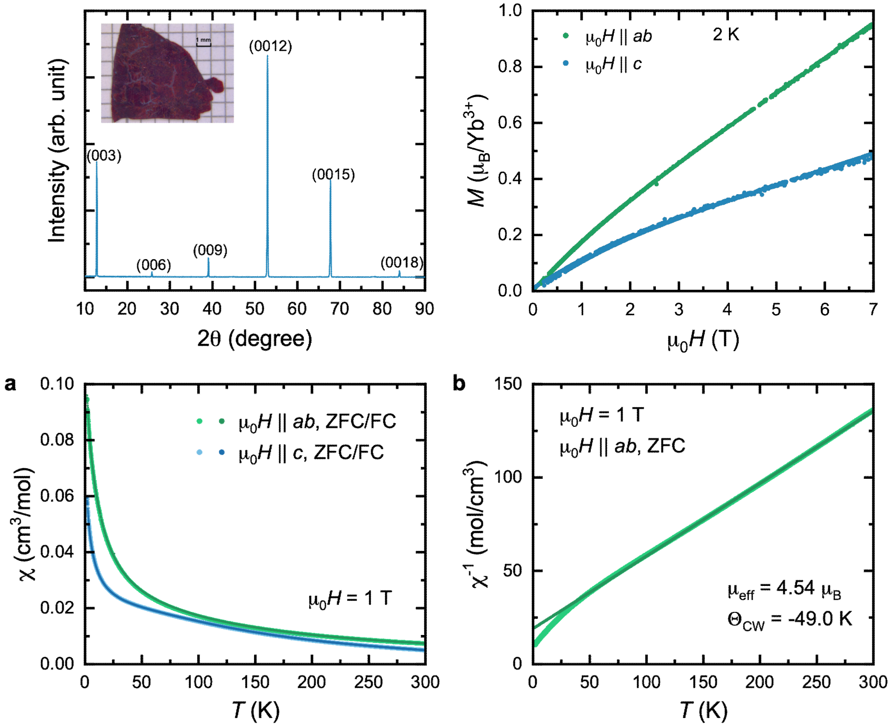
Pressure induced SC





Jia *et al*., CPL (2020)
Zhang *et al*., arXiv:2020.11479

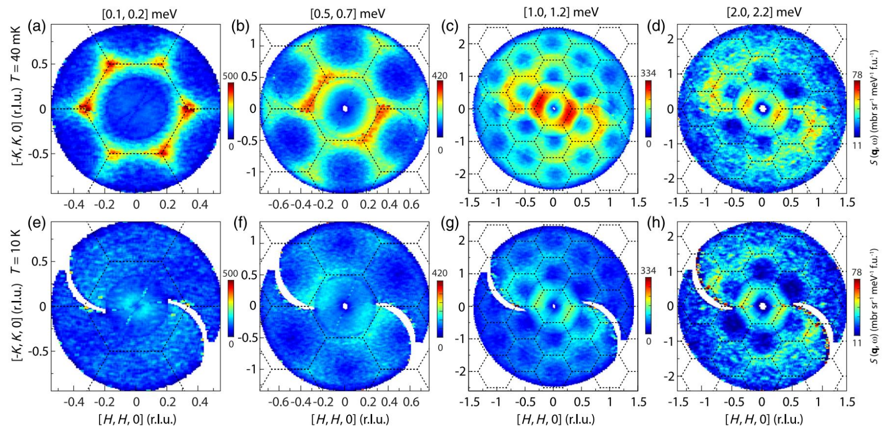
$NaYbSe_2$



Spinon Fermi Surface Spin Liquid in a Triangular Lattice Antiferromagnet $NaYbSe_2$

Peng-Ling Dai, Gaoning Zhang, Yaofeng Xie, Chunruo Duan, Yonghao Gao, Zihao Zhu, Erxi Feng, Zhen Tao, Chien-Lung Huang, Huibo Cao, Andrey Podlesnyak, Garrett E. Granroth, Michelle S. Everett, Joerg C. Neuefeind, David Voneshen, Shun Wang, Guotai Tan, Emilia Morosan, Xia Wang, Hai-Qing Lin, Lei Shu, Gang Chen, Yanfeng Guo, Xingye Lu, and Pengcheng Dai

Phys. Rev. X **11**, 021044 – Published 27 May 2021



- Single crystal
- NaCl-flux

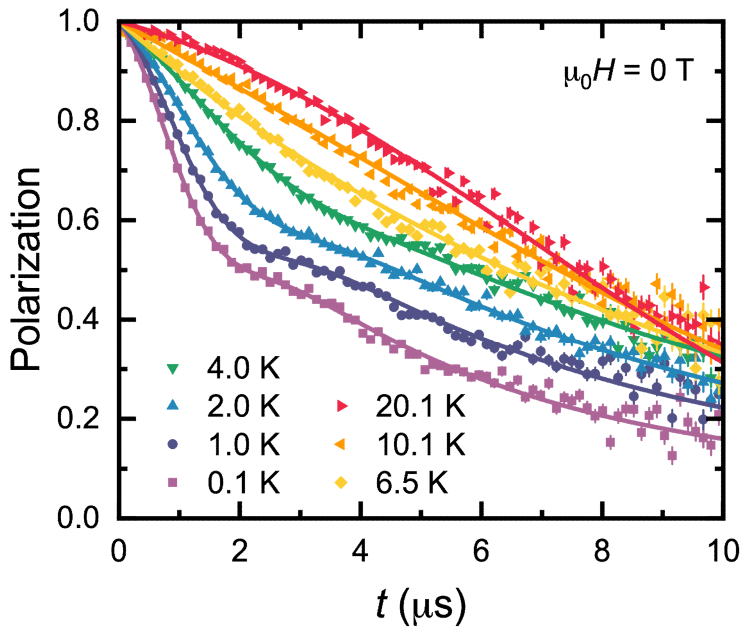
- No magnetic order
- No spin freezing

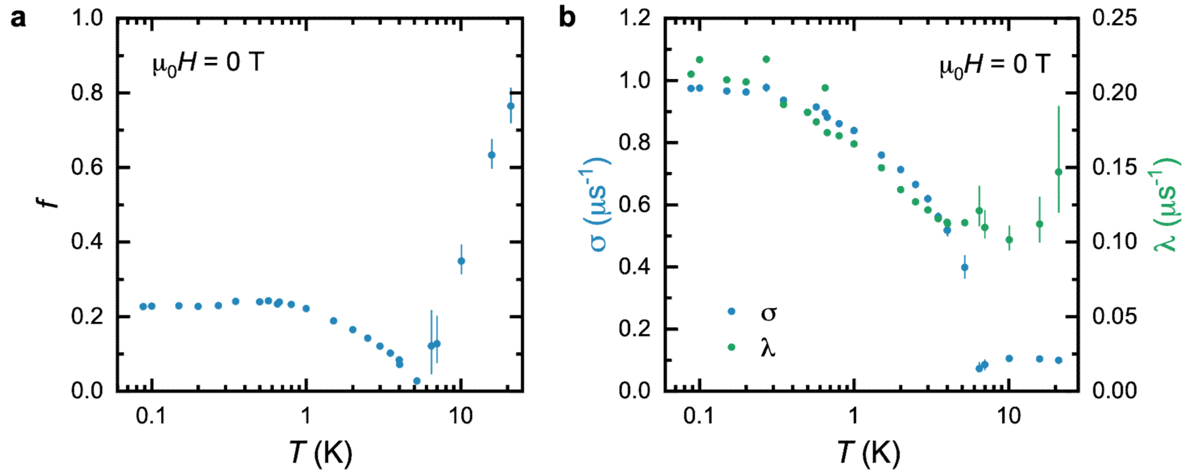
Z. H. Zhu…L. Shu*, the Innovation 2023

- a clear signature of magnetic excitation continuum extending from 0.1 to 2.5 meV

- a spinon Fermi surface.

ZF-μSR





- Coexistence of quasi-static and dynamic spins

No magnetic order

$$P(t) = fG_{KT}(\sigma, t) + (1-f)\exp(-\lambda t)$$

$$G_{KT}(\sigma, t) = \frac{1}{3} + \frac{2}{3}(1-\sigma^2 t^2)\exp\left(-\frac{1}{2}\sigma^2 t^2\right)$$

- 23% quasi-static spins
- $\sigma/\gamma_\mu = 1.14\ \mathrm{mT}$
- T-independent $\lambda \rightarrow$ Persistent spin dynamics

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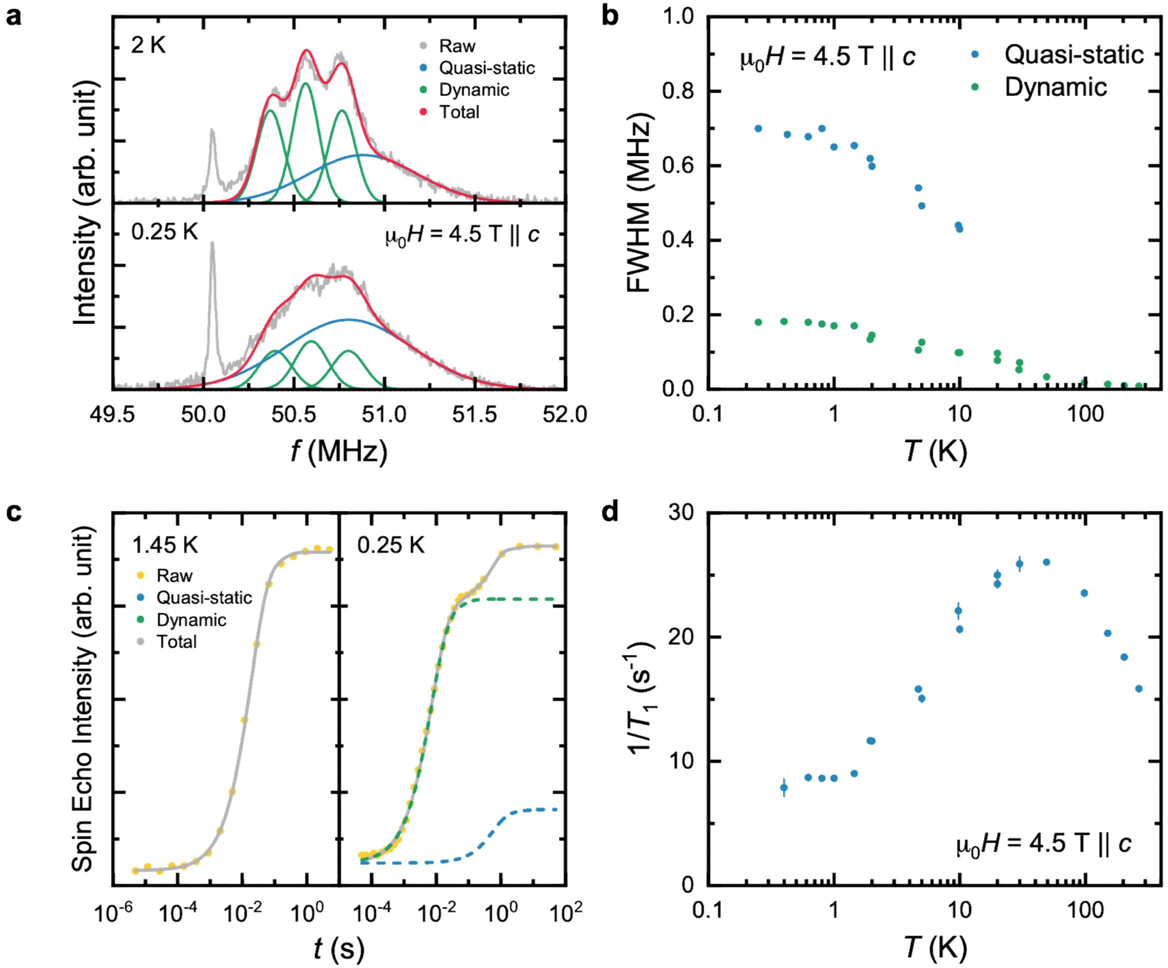
NMR & Thermal conductivity

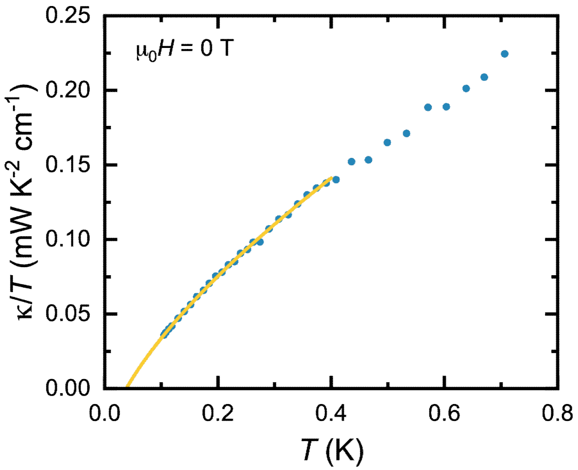
NMR

- ➢ Two groups of peaks
- ➢ Two step relaxation
- ➢ $1/T_1 \rightarrow$ Persistent spin dynamics

Thermal conductivity

- ➢ Negligible residual linear term
- ➢ No iterant excitations





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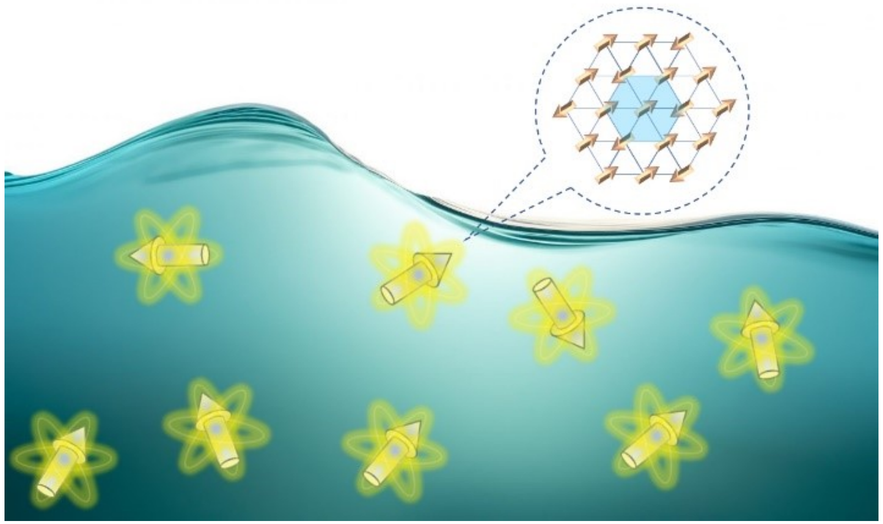
Comparison of all results: QSL or not?

Proposed picture

- Fluctuating magnetic droplets immersed in a sea of QSL

- 23% quasi-static spins with short-range correlation
- Not spin glass by susceptibility
- Slow fluctuation by NMR
- Droplets with "up-up-down" structure

- A majority dynamic spins
- Possible spinon Fermi surface



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Quantum Spin liquid

What can you measure with MuSR

- Absence of magnetic orders (long/short range, spin glass)

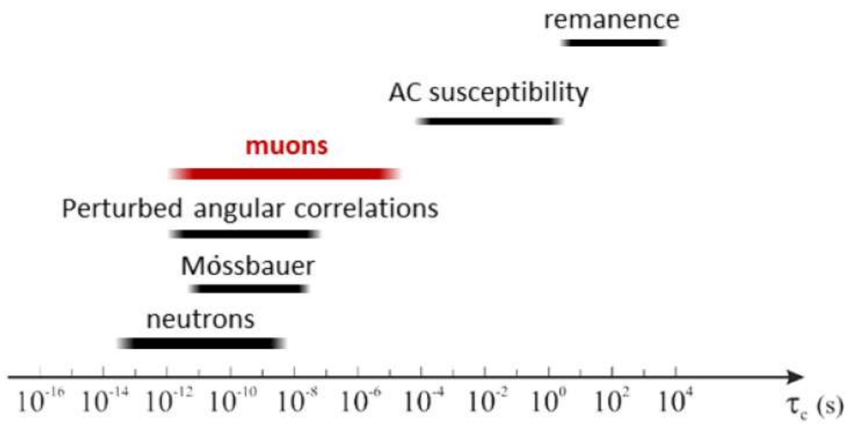
  No oscillation

  No initial asymmetry loss

  No KT-term due to electrical spin

- Spin dynamics T_1

  Persistent spin dynamics



MuSR facilities

	PSI	Triumf	ISIS	JPARC	CSNS
Power of proton	1.4 MW	70 kW	144 kW	1 MW	20 kW
Surface muon intensity (/s)	$10^7 \sim 10^9$	2×10^6	$10^7 \sim 10^8$	1.5×10^7	$10^5 \sim 10^6$
Polarization (%)	> 95	> 90	> 90	> 95	95
Positron (%)	< 1	< 1	< 1	< 1	< 1
Frequency	CW	CW	40 Hz	25 Hz	1 Hz
Asy	0.3	0.28	0.28	0.25	0.32
Counting rate (Mevents/h on 1 cm×1 cm sample)	~ 25	~ 15	~ 100 (EMU) ~1400 (Super-MuSR)	~ 55	~ 40
$C^* A^2$	2.25	1.176	7.84 (EMU) 109.76 (Super-MuSR)	3.43	2.048

Sample environment

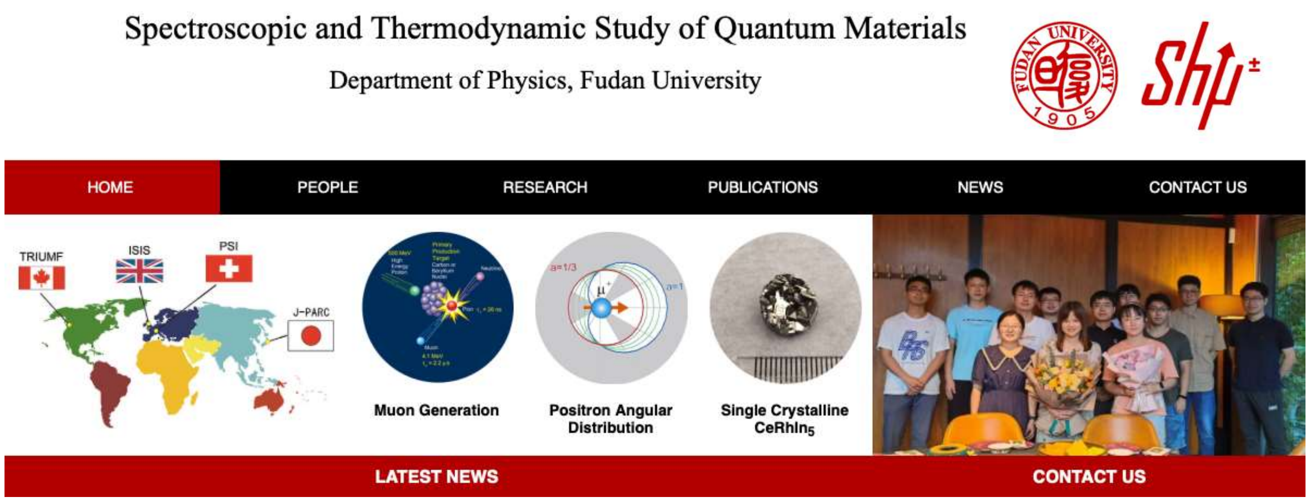
- Temperature：**2 K**-300 K (PSI-GPS、TRIUMF-LAMPF)

  DR/He^3 (PSI-Dolly、FLAME、TRIUMF-DR)

- Pressure: PSI-GPD (0-0.65 T, 0.23-500 K, 2.8 GPa)

- Low-energy: PSI-LEM (0-0.3 T, 2.5-325 K)

Thank you!



http://www.physics.fudan.edu.cn/tps/people/leishu/GroupHomepage.html