Exploring the 3D spin-1/2 system $Y_3Cu_2Sb_3O_{14}$ for possible QSL behaviour

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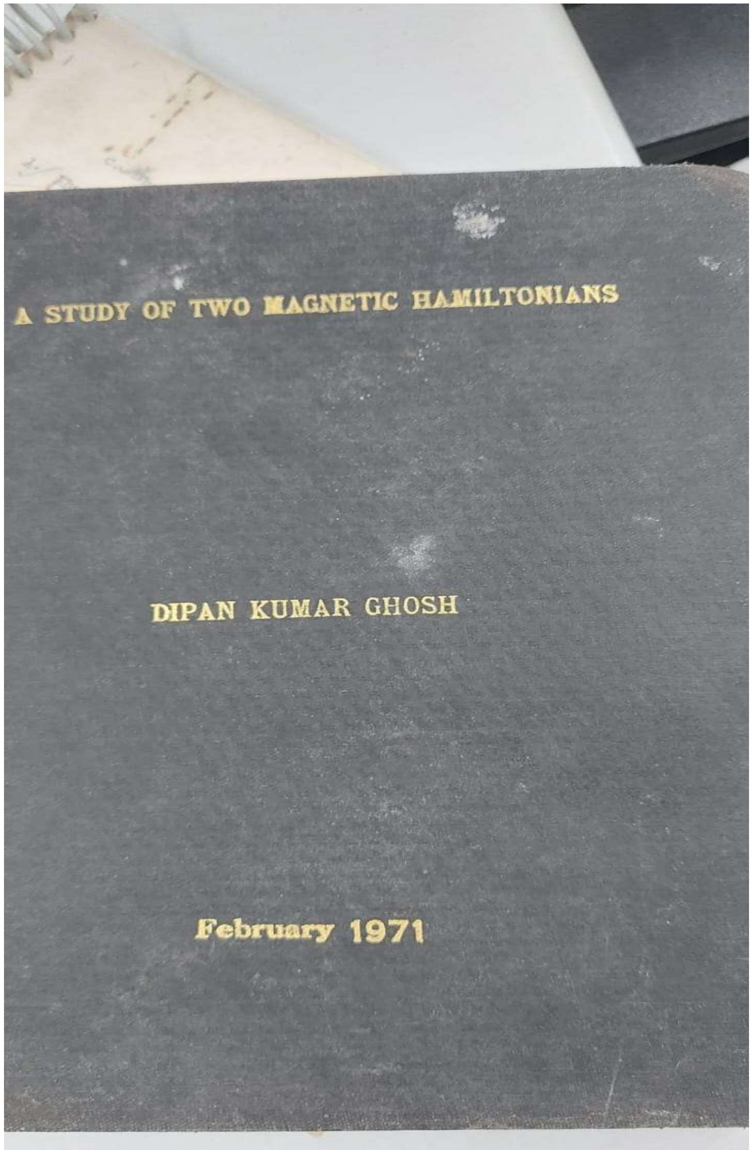

Majumdar-Ghosh model

Prof. Ghosh retired about 20 years ago from the Physics dept at IIT Bombay

Acknowledgments

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- IIT Bombay Central Facilities

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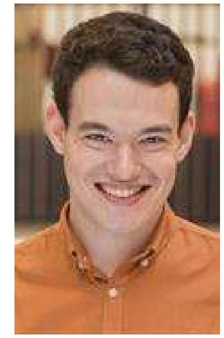

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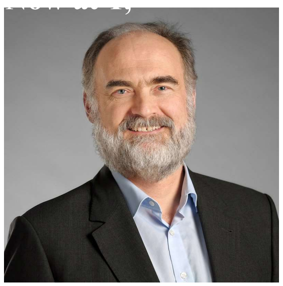

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Context and motivation for the current work

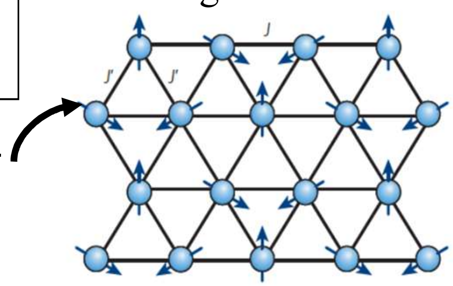
- The genesis of the field is perhaps in the exotic properties of quasi-1D Heisenberg AF systems
- Discovery of high-Tc in cuprates (already 40 years old!) reignited interest in 1D and 2D systems
- This then evolved into a focus on frustrated systems and an emergence of the field of Quantum Spin Liquids
- Current pursuit of QSL is through the routes of bond anisotropy and geometric frustration

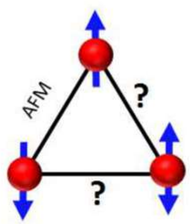
Geometrical Frustration

Anderson and Fazekas (1973)

Triangular lattice

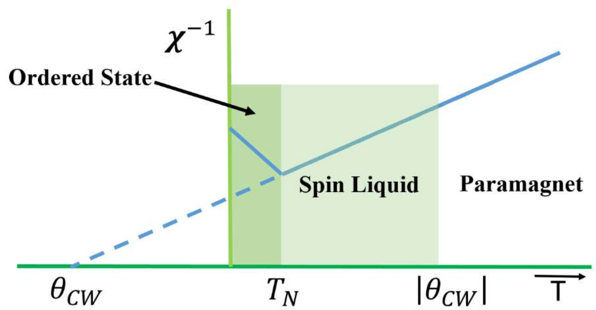
$\mathbf{S}=\frac{1}{2}$





Frustration parameter,

$$f = \frac{|\theta_{CW}|}{T_N}$$



Few examples:
(a) Triangular: k-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, **Sr$_3$CuSb$_2$O$_9$ and Y$_2$CuTiO$_6$** **(b)** Kagome: ZnCu$_3$(OH)$_6$Cl$_2$ (c) Hyperkagome: Na$_4$Ir$_3$O$_8$ (d) Pyrochlore: Y$_2$Mo$_2$O$_7$, Ho$_2$Ti$_2$O$_7$

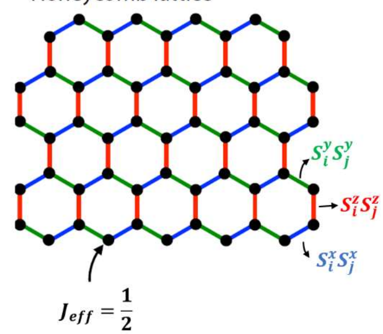
Leon Balents, Nature 464.7286 (2010), pages 199–208.

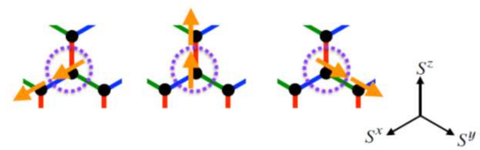
Bond-anisotropy driven frustration

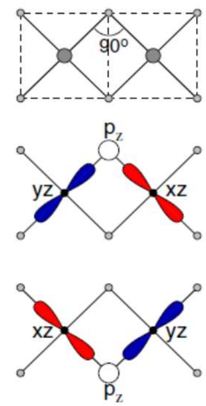
Alexei Y. Kitaev (2006)

$$\mathcal{H} = -J_x \sum_{<ij>x} S_i^x S_j^x - J_y \sum_{<ij>y} S_i^y S_j^y - J_z \sum_{<ij>z} S_i^z S_j^z$$

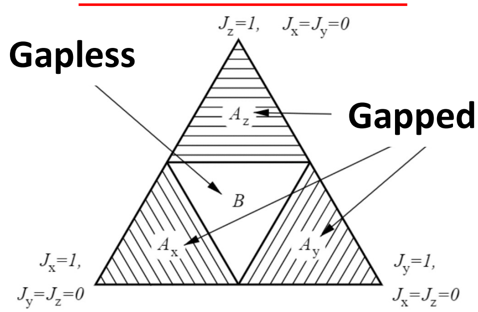
Honeycomb lattice



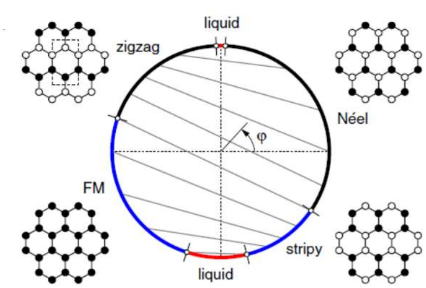




Kitaev Ground State



Heisenberg-Kitaev Model

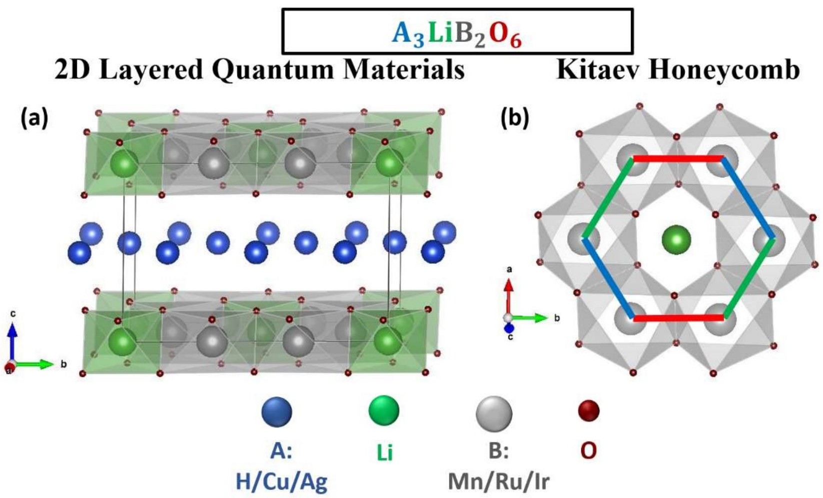


Excitations:

1. **Z_2 flux (localized Majorana)**
2. **Itinerant Majorana Fermions**

Few examples:
(a) Honeycomb: **α-RuCl$_3$** (KQSL above 8 Tesla), **H$_3$LiIr$_2$O$_6$** and more recently **(H,Li)$_6$Ru$_2$O$_6$**

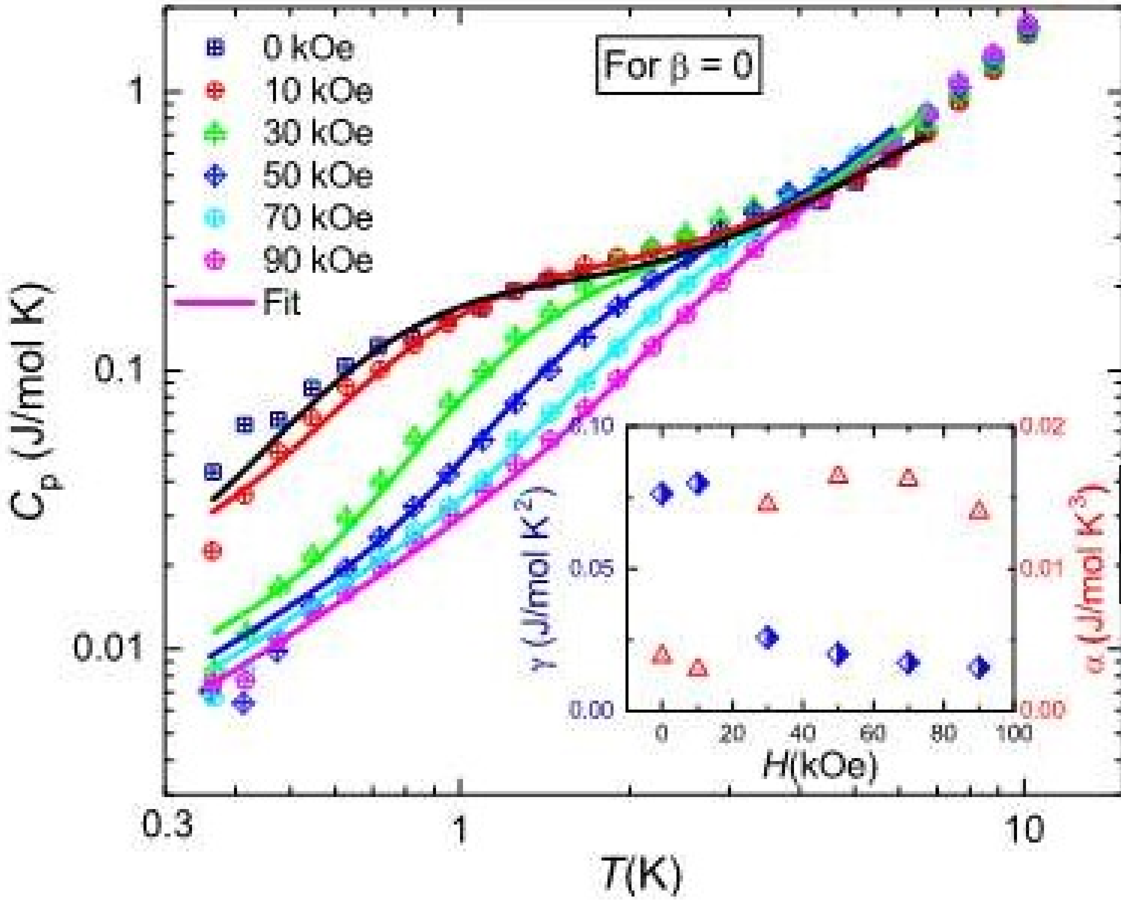
Our work on honeycomb systems



Space Group: C2/m

Compounds \ Lattice parameters	a (Å)	b (Å)	c (Å)	β (°)
$Ag_3LiIr_2O_6$ (Ir^{4+}, J_{eff}=1/2)	5.27(7)	9.13(6)	6.49(3)	106.0(1)
(*)$Ag_3LiIr_{1.4}Ru_{0.6}O_6$ (Ir^{4+}, J_{eff}=1/2 and Ru^{4+}, S=1)	5.26(1)	9.11(0)	6.50(1)	105.9(1)
$Ag_3LiRu_2O_6$ (Ru^{4+}, S=1)	5.22(4)	9.04(5)	6.51(0)	105.5(1)
$Ag_3LiMn_2O_6$ (Mn^{4+}, S=1)	5.06(9)	8.78(6)	6.37(5)	105.0(6)
(*)$Cu_3LiRu_2O_6$ (Ru^{4+}, J_{eff}=1)	5.18(2)	8.92(6)	6.05(2)	106.5(9)
(*)$H_{5.9}Li_{0.1}Ru_2O_6$ (Ru^{3+}, J_{eff}=1/2)	5.09(1)	8.92(0)	5.01(1)	107.2(0)
$H_3LiIr_2O_6$ (Ir^{4+}, J_{eff}=1/2)	5.34(8)	9.24(3)	4.87(3)	111.4(4)

1. Ag3LiRu2O6, PRB **99**, 054417 (2019)
2. Ag3LiMn2O6, PRB **99**, 144429 (2019)
3. Ag3LiIr2O6, PRB **104**, 115106 (2021)
4. (H, Li)6Ru2O6, PRB Letters **110**, L241102 (2024)
5. Cu3LiRu2O6, PRB Letters **111**, L100403 (2025)
6. Ru-doped Ag3LiIr2O6, PRB **112**, 035142 (2025)



Experimental data

$$C_p = \gamma T + \alpha T^2 + \ \beta T^3 + C_{Schottky}$$

Theory

In a DSL ansatz

$$\frac{C(T)}{k_B} \approx 2.292\frac{(k_B T)^2}{J^2} + 0.696\frac{(k_B T)\left(\frac{g\mu_B |H|}{2}\right)}{J^2}$$

$J/k_B = 51$ K

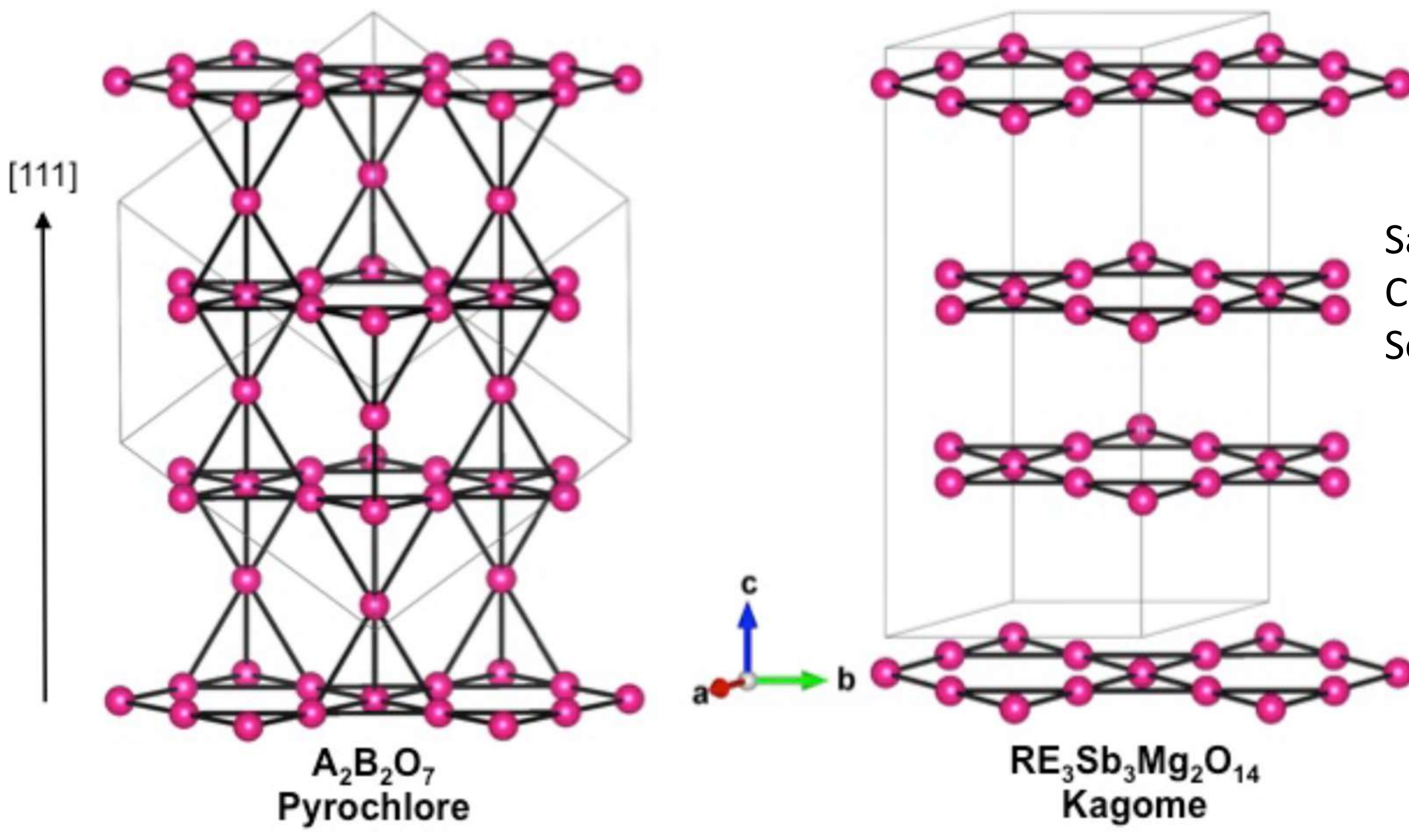
$Sr_3CuSb_2O_9$ TLAF

S. Kundu et al. PRL **125**, 267202 (2020)

Y_2CuTiO_6 TLAF

S. Kundu et al. PRL **125**, 117206 (2020)

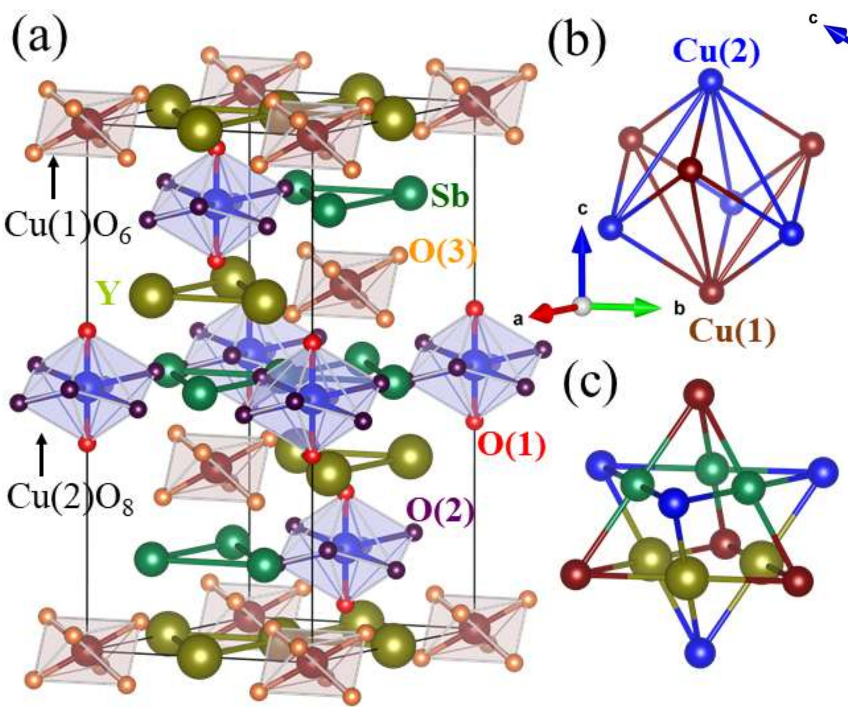
- The focus of this talk is on a geometrically frustrated system



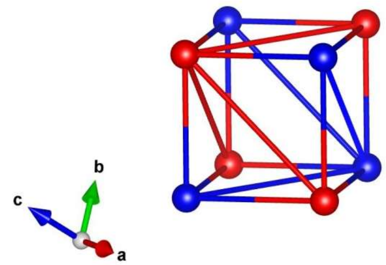
Sanders et al. and Cava Physica Status Solidi, 2016

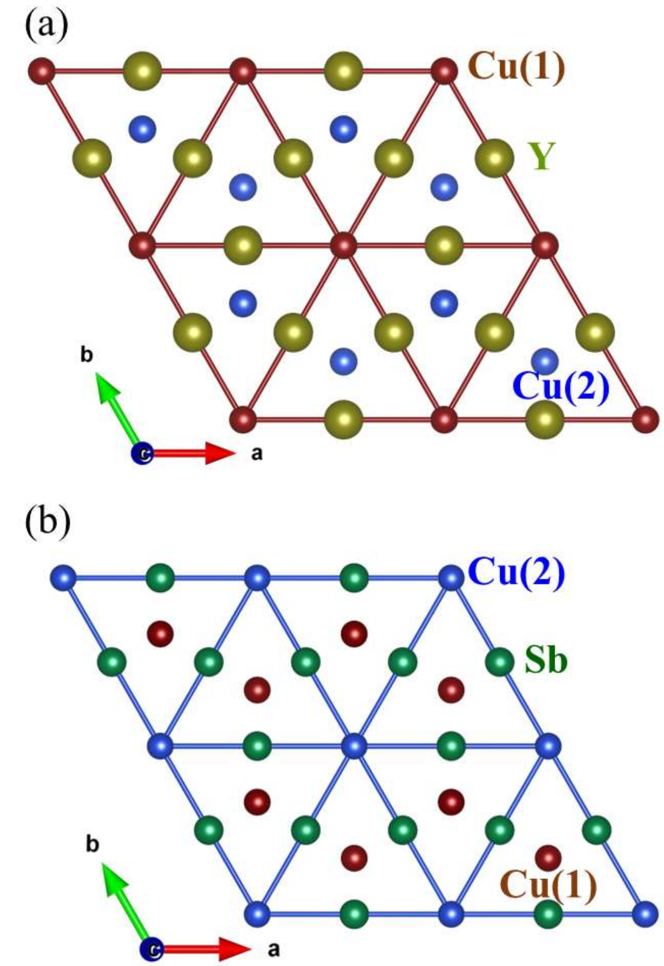
RE = La, Pr, Sm, Eu, Tb, Ho

$Y_3Cu_2Sb_3O_{14}$ (YCSO)



Crystal structure consisting $Cu(1)O_6$ octahedra and $Cu(2)O_8$ hexagonal bipyramids





Triangular lattices formed by (a) $Cu^{2+}(1)$ and (b) $Cu^{2+}(2)$ ions in the *ab* plane. The position of in-plane Y^{3+} and Sb^{5+} are also shown. Each Cu(2) site is centred in equilateral Cu(1) triangles in adjacent layers, and the same valid for Cu(1) sites.

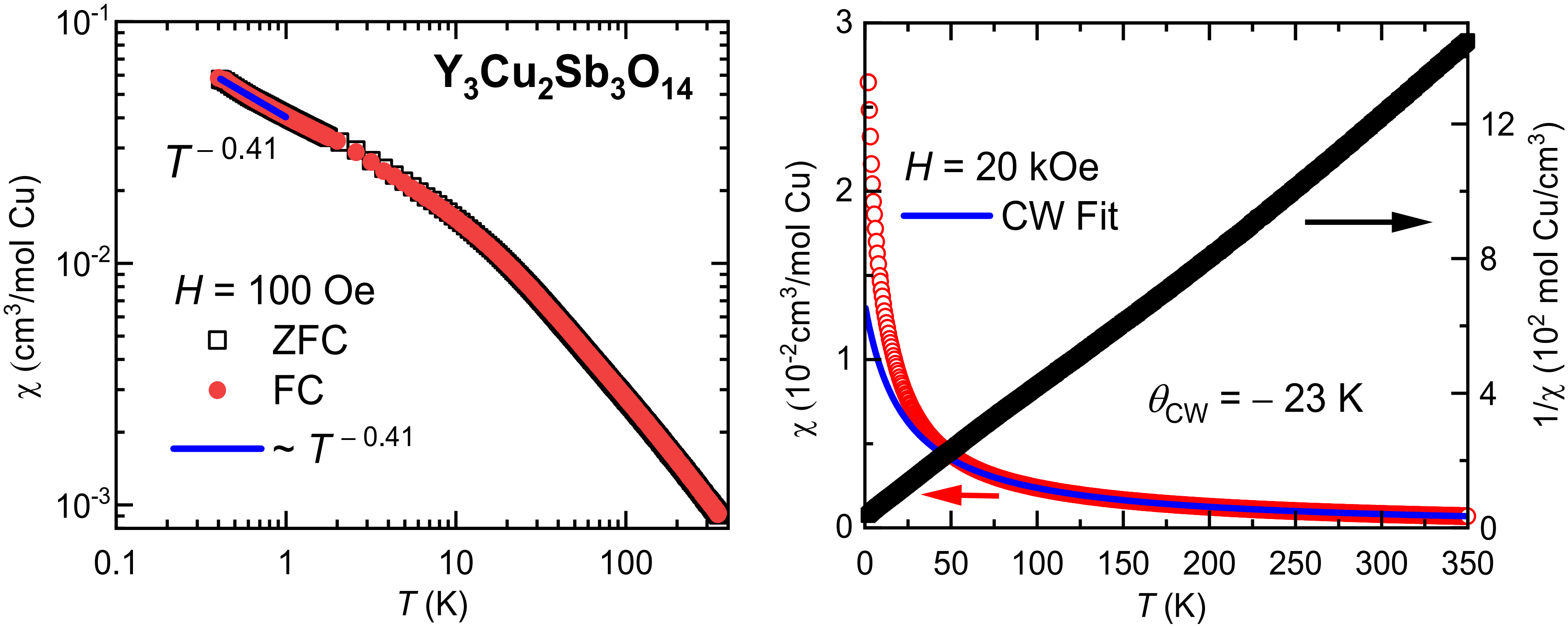
So, what are the properties of $Y_3Cu_2Sb_3O_{14}$?

We have done a comprehensive investigation

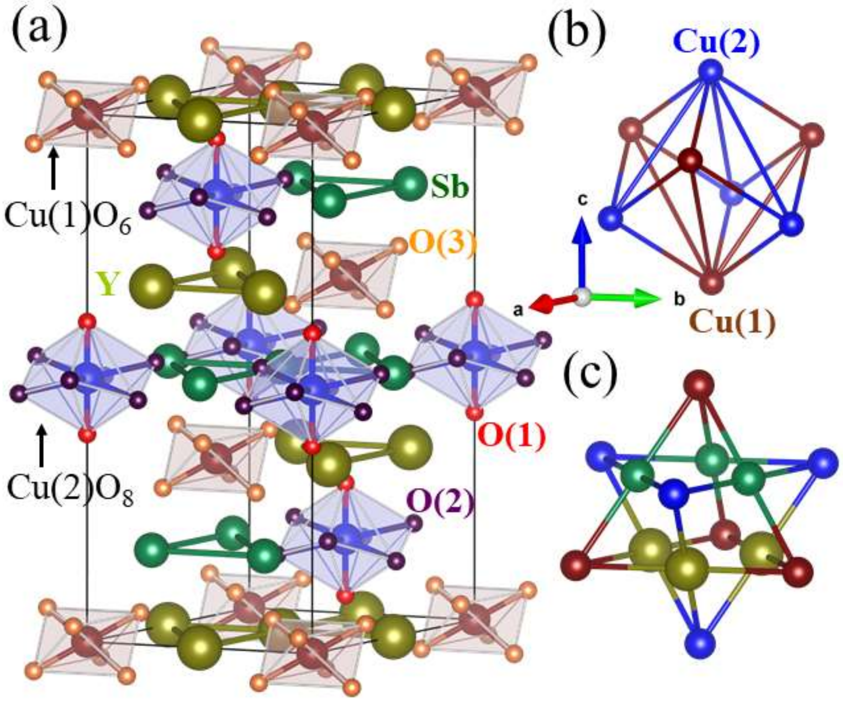
- Magnetisation/susceptibility
- ^{89}Y nuclear magnetic resonance (NMR)
- Electron spin resonance (ESR)
- Muon spin relaxation (μSR)
- Specific heat

- First principle electronic structure calculations through Density Functional Theory

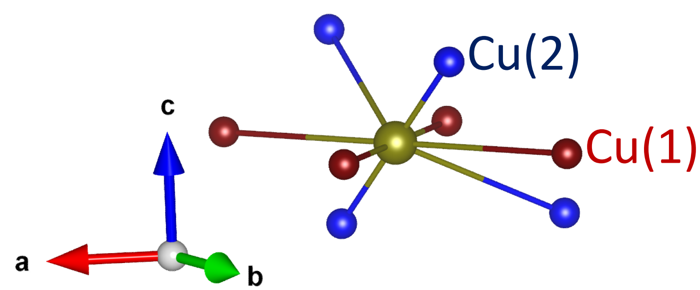
Susceptibility

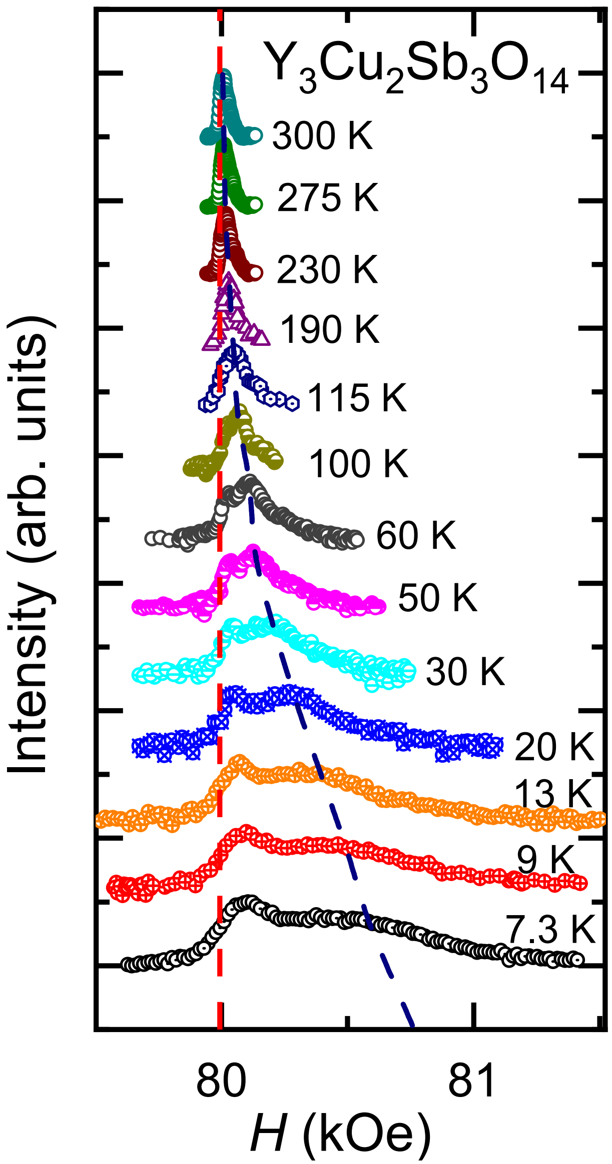


- μ_{eff} = 1.57 μ_B which is somewhat smaller than the 1.73 μ_B expected for Cu^{2+}
- No bifurcation between the ZFC and FC susceptibility, $\chi(T)$.
- No clear indication of any long-range magnetic ordering is observed down to 0.4 K.

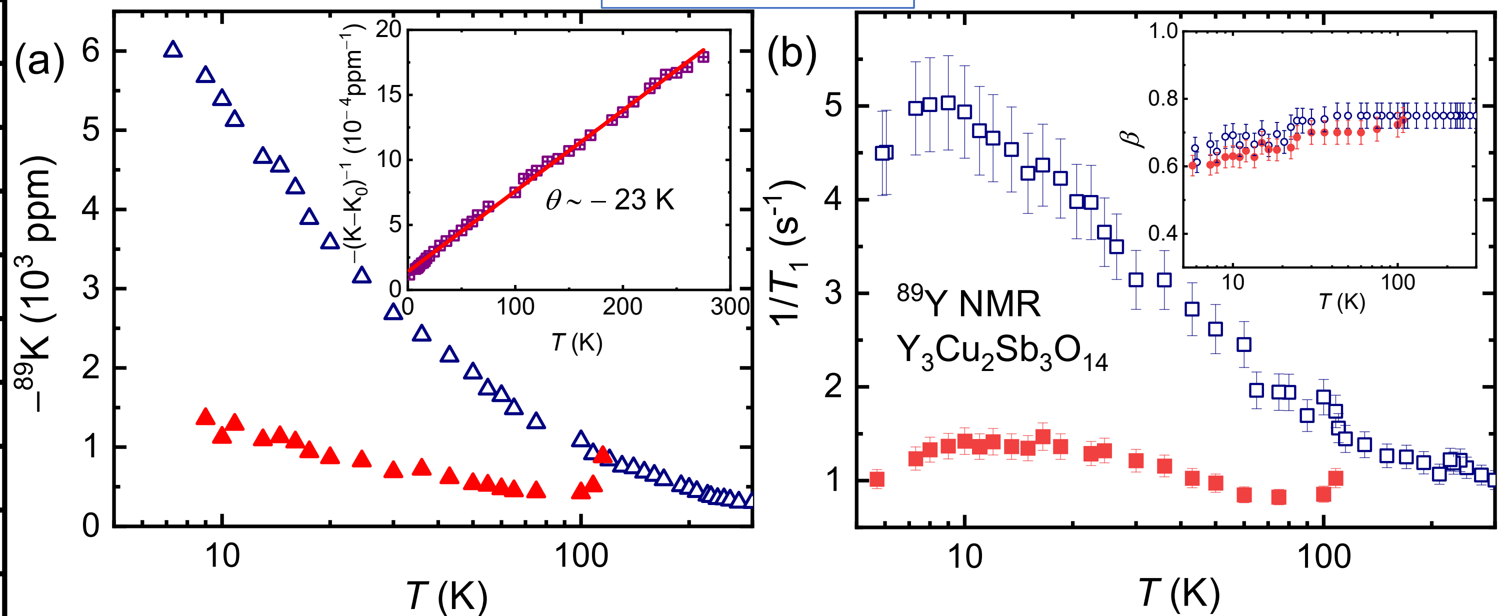


Y neighbourhood



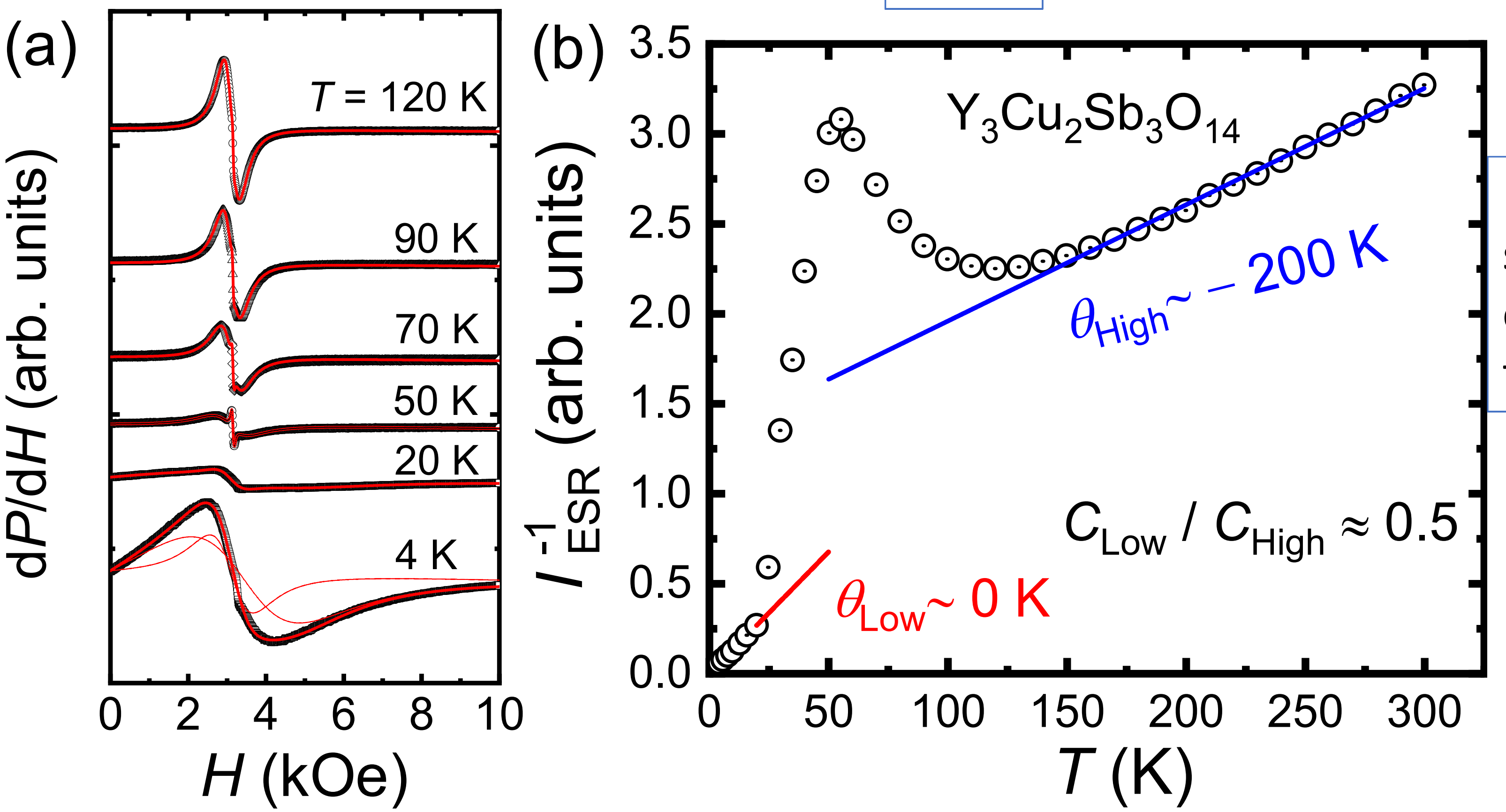


^{89}Y NMR



^{89}Y NMR we find evidence of a transition at about 120 K which we suggest arises from a fraction of the spins condensing into a singlet (a valence bond solid or perhaps a spin liquid) state. While the remaining spins also condense into a QSL state below 1 K.

ESR

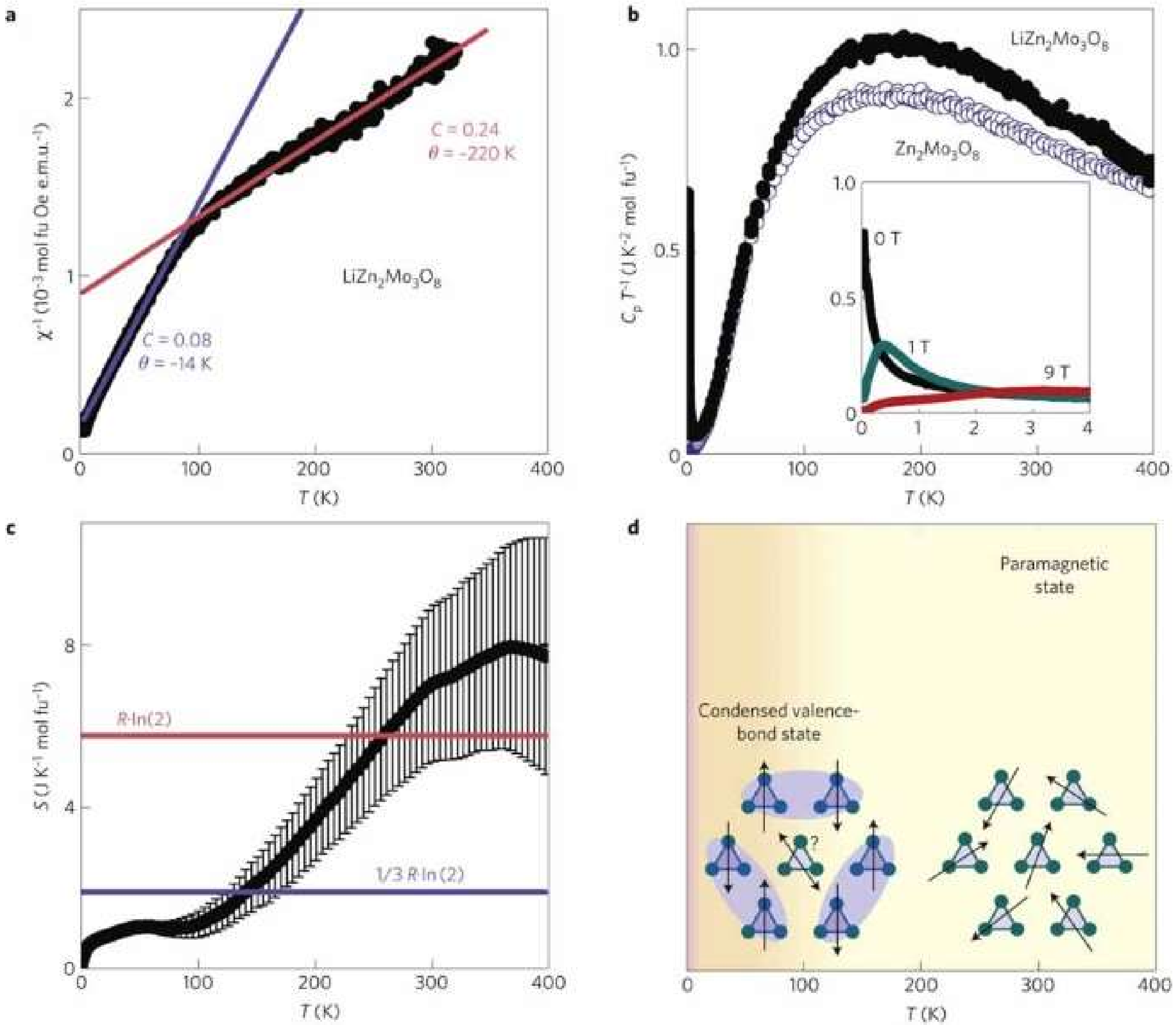


Note that at high-T signal arises from only about 20% of the spins

- On cooling down through 120 K, the ESR spectra split off into two signals.

Collaborator: J. Sichelschmidt, MPI- Dresden
M. Hemmida, H.-A. Krug von Nidda , University of Augsburg

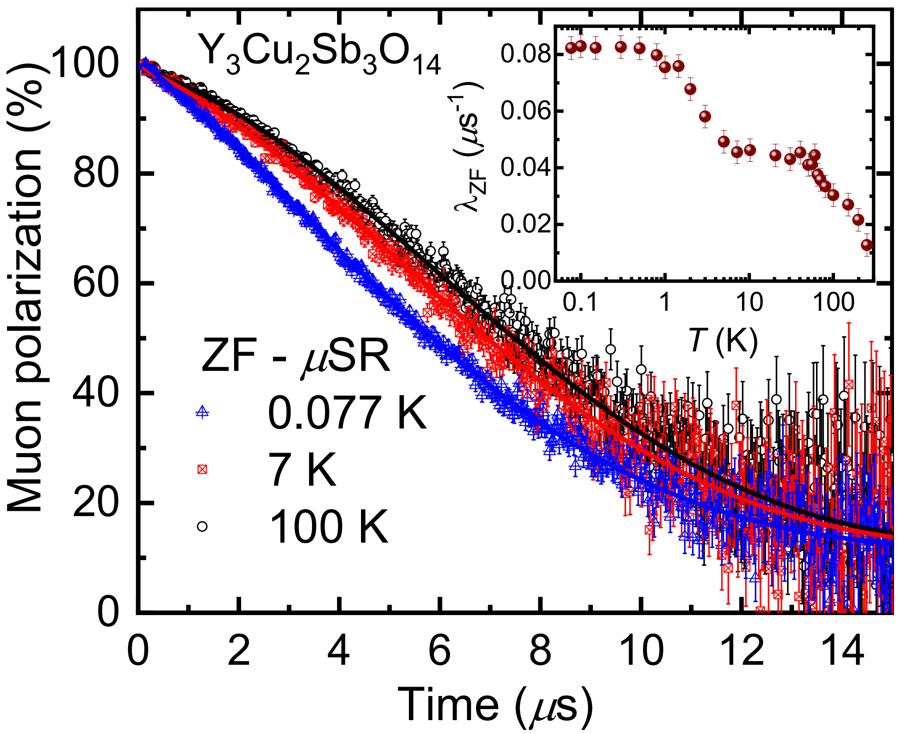
- The temperature dependence of I^{-1}_{ESR} (I_{ESR} = integrated ESR intensity) follows a CW law and from fits in the high-*T* and low-*T* regions, we find that the Curie constant at low-*T* reduces to about one-half of the high- *T* value.



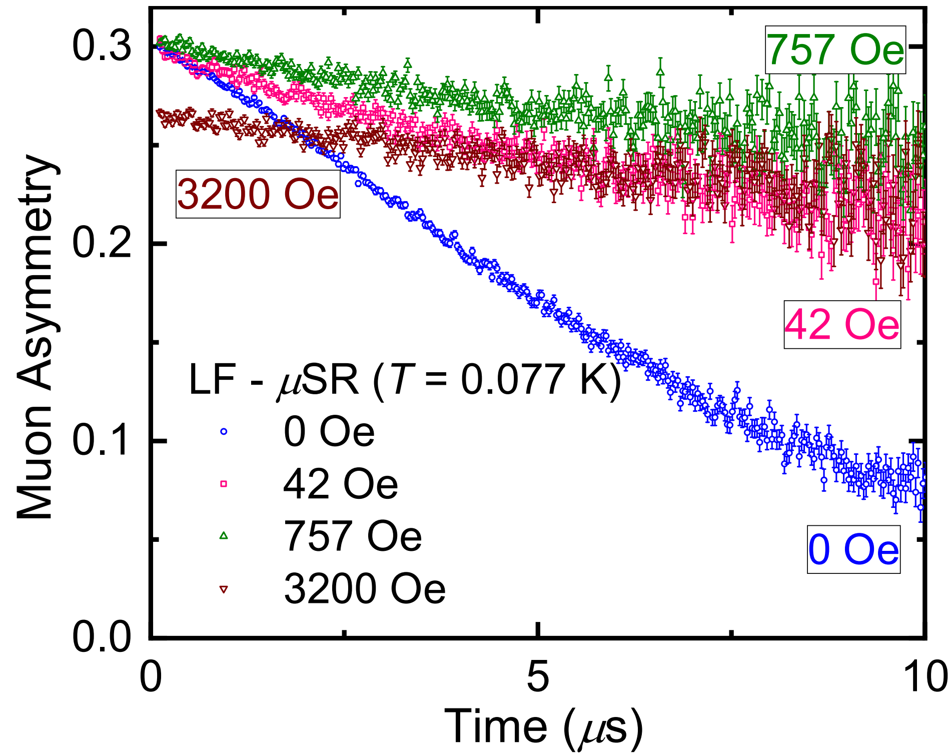
LiZn2Mo3O8

Schekelton et al. Nature Materials 2012

The spins on the vertices of the hexagon condense into a VBS state below about 96 K while the centre spin remains paramagnetic



μSR

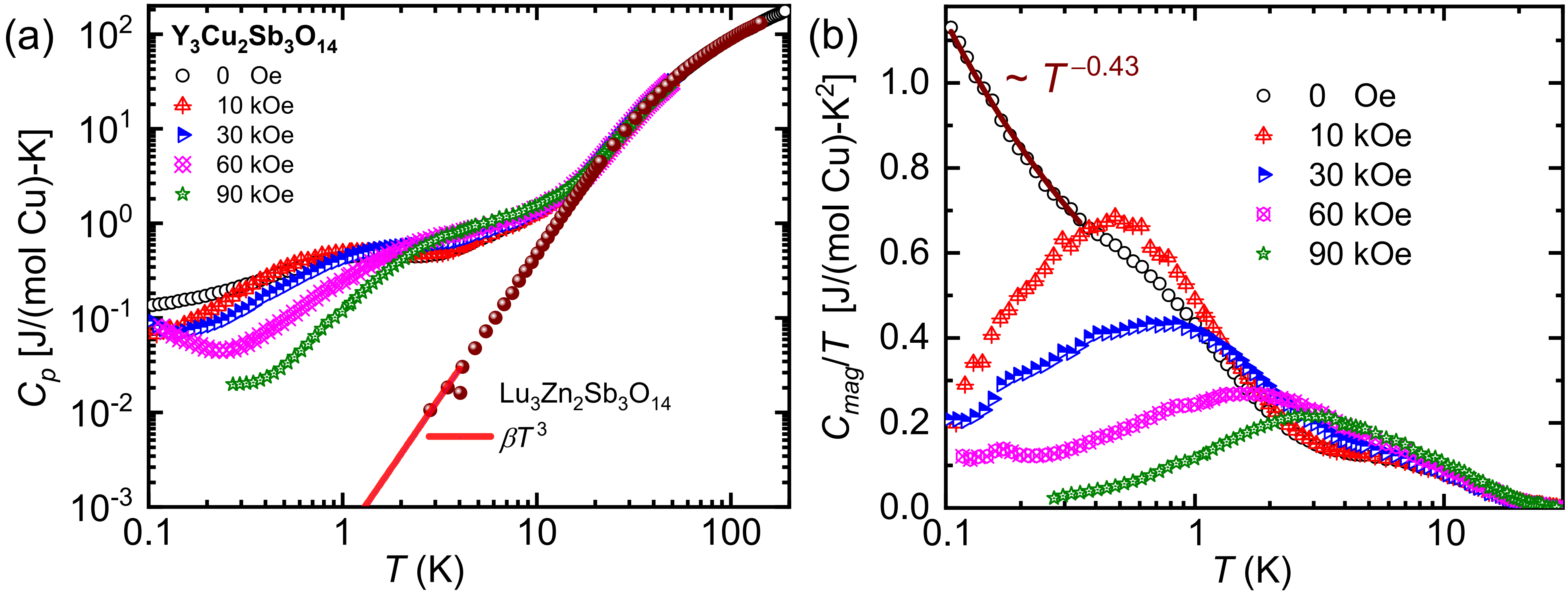


We do not observe oscillations in muon asymmetry spectra at temperatures down to 77 mK.

The ZF-μSR spectra are described by the Gaussian Kubo-Toyabe function $G_{KT}(\sigma, t)$ multiplied by an exponential function, with the relation $A(t) = A_1 e^{-\lambda_{ZF} t} G_{KT}(\sigma, t) + A_{BG}$.

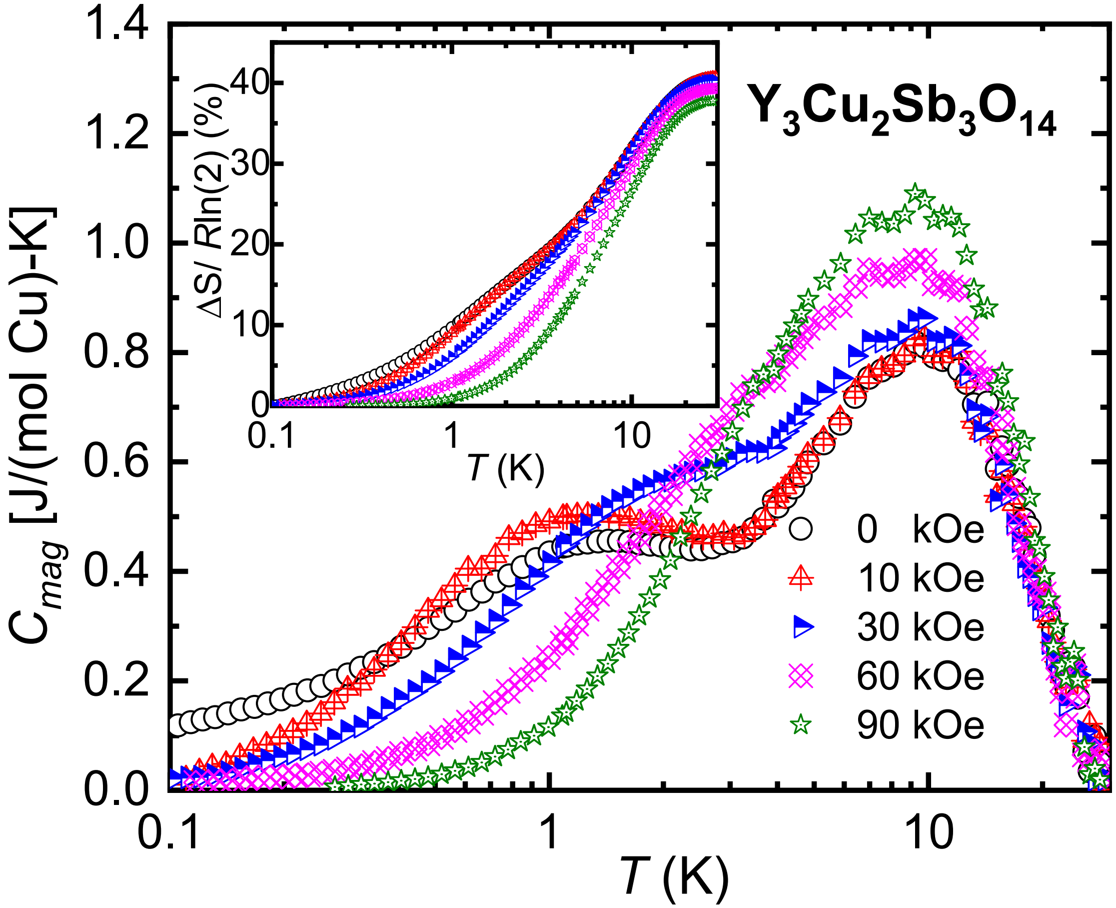
We do not observe any decoupling behavior under the 3200 LF at T = 0.077 K

Heat Capacity

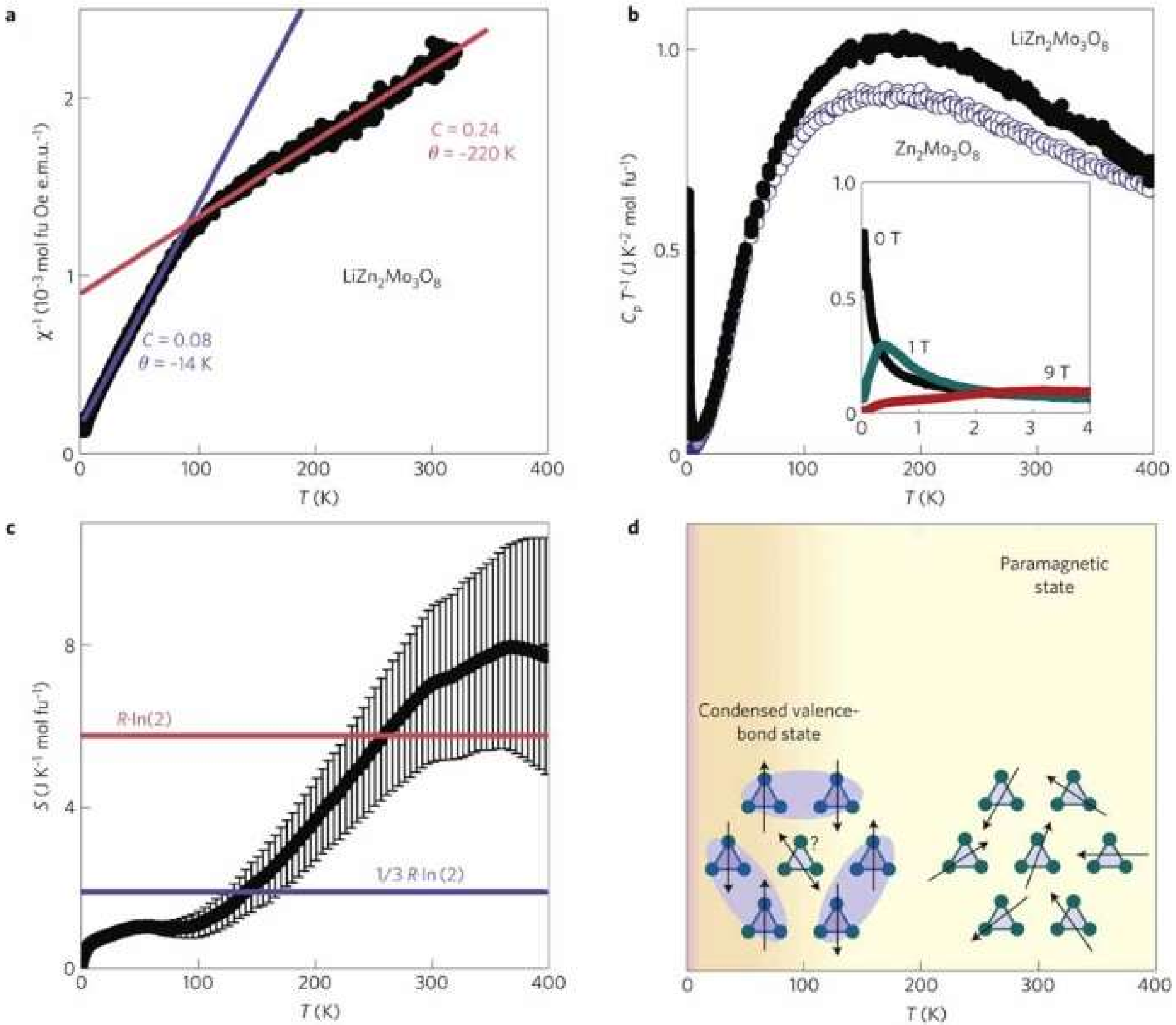


- C_{mag} shows no evidence for a transition to magnetic long-range order down to 0.1 K.
- The zero field C_{mag}/T *vs* T data shows a power law behaviour ($T^{-\alpha}$) with an exponent α = 0.43 at low temperatures, possibly related to random singlets.

Heat Capacity



- Two step entropy release
- Close to 40 % of the entropy (compared to Rln2) is recovered by about 20 K.

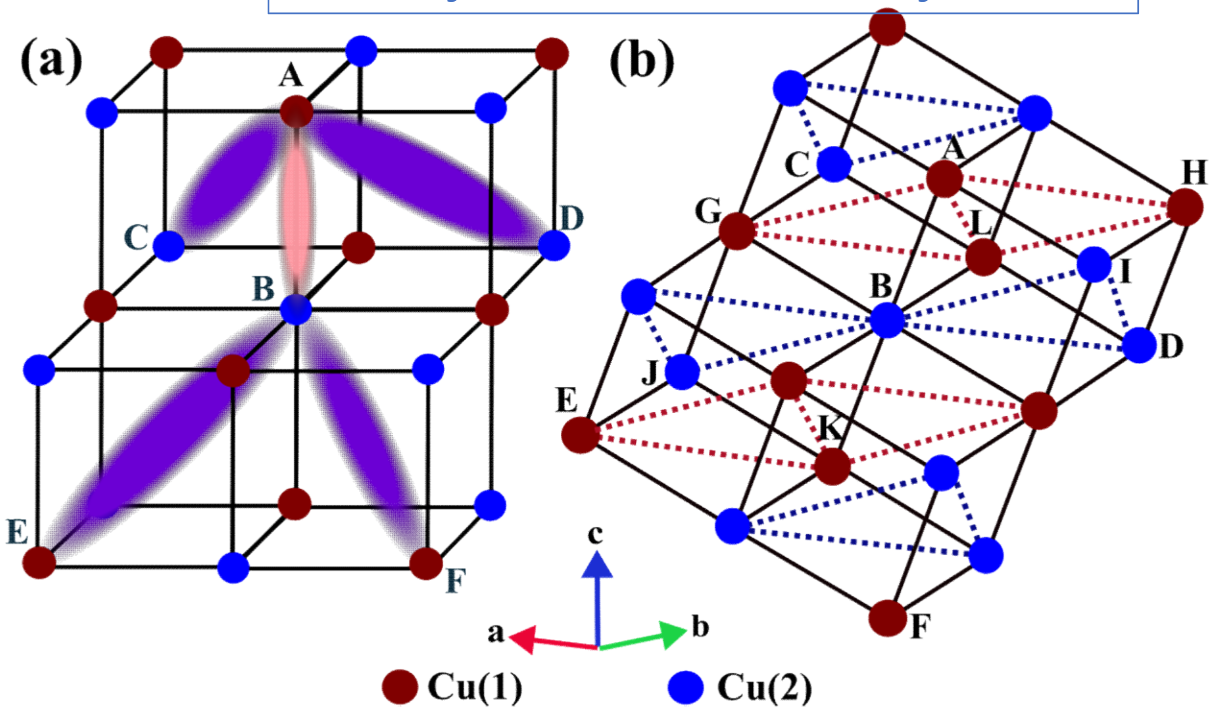


LiZn2Mo3O8

Schekelton et al. Nature Materials 2012

The spins on the vertices of the hexagon condense into a VBS state below about 96 K while the centre spin remains paramagnetic

Density Functional Theory results



Collaborator: Rounak Das, Indra Dasgupta,
Indian Association for the Cultivation of Science

TABLE I. Exchange parameters along the body diagonals.

J	Cu-Cu distance (Å)	Exchange Parameter (meV)
J_{AC}	9.01	3.6
J_{AD}	9.01	4.6
J_{BE}	9.01	3.6
J_{BF}	8.58	3.0
J_{AB}	5.14	0.2

TABLE II. Exchange parameters along the face diagonals or in the Cu(1) planes and Cu(2) planes.

J	Cu-Cu distance (Å)	Exchange Parameter (meV)
J_{AH}	7.40	2.2
J_{AL}	7.40	1.6
J_{HL}	7.40	1.5
J_{BI}	7.40	2.0
J_{ID}	7.40	2.1
J_{BD}	7.40	1.7

- The dominant exchange interactions are along the body diagonals of the cube, forming dimers where the inter-dimer exchange interaction (J_{AB}) is negligible compared to the intra-dimer exchange interactions. This opens up the possibility for the formation of VBS within our system.

- The antiferromagnetic interaction along the face diagonal of the cube forming a triangular network for Cu(1) and Cu(2) introduces frustration and prohibits long-range ordering

Conclusions

- **$Y_3Cu_2Sb_3O_{14}$** is a **3D** spin-1/2 QSL and is not found to order down to 77 mK.

- ^{89}Y NMR we find evidence of a transition at about 120 K which we suggest arises from a fraction of the spins condensing into a singlet (a valence bond solid or perhaps a spin liquid) state. While the remaining spins also condense into a QSL state below 1 K.

- Similar behavior (though with only the high-temperature transition) has been seen in $LiZn_2Mo_3O_8$ which is 2D system while ours is a 3D system.

- A plateau in the muon relaxation rate is observed between 60 K and 10 K (signifying the VBS/QSL state from a fraction of the spins) followed by an increase and another plateau below about 1 K (presumably signifying the VBS/QSL state from all the spins).

- Our DFT calculations find a dominant AF interaction along the body diagonal with inequivalent Cu(1) and Cu(2) ions alternately occupying the corners of the cube. All other near neighbour interactions between the Cu ions are also found to be antiferromagnetic and are thought to drive the frustration.

Thank You