## HOT NEW SPIN-1/2 PERFECT KAGOMÉ COMPOUND

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## Outline

- Kagomé, what is it ? Why is it interesting ?
- The search for kagomé realization.
- $\Box$  Cu(1,3-bdc) compound.
- Research questions.
- Experimental methods and their results.
- □ Summary.

#### Frustration !?



Antiferromagentic (AFM) arrangement of spins can be easily provided in a square lattice.



#### Frustration?

AFM arrangement of spins in a triangle cannot be satisfied. The frustration is caused by the geometry of the lattice.



Geometrical frustration is a phenomenon in condensed matter in which the geometrical properties of the crystal lattice forbid simultaneous minimization of all interactions. This may lead to highly degenerate ground state with a nonzero entropy at zero temperature. Kagmé lattice is one form of frustrated lattices.

#### Kagomé, what is it? Why is it interesting?

The 2D antiferromagnetic (AFM) kagomé lattice is a highly frustrated lattice, being comprised of corner sharing triangles.

#### The classical ground state :

The energy can be minimized by providing the 120<sup>0</sup> condition.

<u>Kagomé has a unique property:</u> The spins can oscillate but still maintain the  $120^{\circ}$  condition even at a lowest temperature of T $\rightarrow$ 0.

The ground state of a kagomé AFM is infinitely degenerate.



T → 0: dynamics + no long-range order.

## The search for kagomé realization

- SCGO Spin 3/2, alternating kagome and triangle planes.
- Volborthite distortion.
- Jarosite large spin number, long-range order.
- Vesignieite –impurities.
- Herbertsmithite impurities.

# $Cu(1,3-bdc) - C_8H_4CuO_4$

Cu(1,3-bdc) is shorthand for Cu(1,3-benzendicarboxylate). Synthesized by Nytko et al. at MIT.

The organometallic hybrid compound Cu(1,3bdc), which has structurally perfect spin 1/2 copper kagomé planes separated by pure organic linkers.

Each linker contains a benzene molecule.

#### What does Cu(1,3-bdc) mean ?

- $\Theta cw = -33 K.$
- C (heat capacity) has a peak at 1.8K.
- $\chi$  saturates at 1.8K



Cu(1,3-bdc)



### **Research Questions**

Does this compound behave as expected from a kagome compound:

- Does it have a long-range order?
- Is the limit of  $T \rightarrow 0$  dynamic?

Does it have anisotropic behavior ?
 What is the Hamiltonian of this compound ? Can we characterize it?

## Muon Spin Resonance (µSR)



- Perfectly spin polarized muons.
- Muons are implanted into the sample.
- Muons rotate at a larmor frequency,  $\omega = \gamma_{\mu} H$ .
- The Muons decay after mean-life-time of 2.2µsec.
- Positrons are emitted preferentially in the muon spin direction.
- We can reconstruct the muon polarization.

#### Principals of µSR



Time

Does this compound behave as expected from a kagome compound:

Does it have a long-range order?

 $\Box$  Is the limit of T $\rightarrow$  0 dynamics?

Fast Fourier Transform (FFT) of the TF data at H=1kOe. : T = 6K, there is a wide asymmetric peak.

This peak separates into two different peaks as we lower the temperature down to 3.5K. At even lower temperature the low frequency peak vanishes.



L. Marcipar et al. PRB 80 132402 (2009)

Does this compound behave as expected from a

kagome compound:

Does it have a long-range order?

 $\Box$  Is the limit of T $\rightarrow$  0 dynamics?

Transverse Field (TF) measurements: 0.9K < T < 6K, H=1kOe.

TF data displayed in rotating-reference-frame, H=800Oe.

 $A_{TF}(t) = A_{1}e^{-\frac{(R_{1}t)^{2}}{2}} \cos(\omega_{1}t + \varphi) + A_{2}e^{-R_{2}t}\cos(\omega_{2}t + \varphi) + Bg_{1}$ 

 $\omega_1, R_1 - By \ product$  $\omega_2, R_2 - kagome \ part$ 



L. Marcipar et al. PRB 80 132402 (2009)

Does this compound behave as expected from a

kagome compound:

- Does it have a long-range order?
- $\Box$  Is the limit of T $\rightarrow$  0 dynamics?

 $\Box$  The muon shift of the kagomé part , K<sub>2</sub>, increases with decreasing the temperature

 $\rightarrow$  as expected.

 $\Box$  The muon transverse relaxation,  $R_2$ , has the same temperature behavior as the shift,  $K_{2.}$ 



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Does this compound behave as expected from a

kagome compound:

 $K_2$ 

- Does it have a long-range order?
- $\Box$  Is the limit of T $\rightarrow$  0 dynamics?

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$$\left\langle S \right\rangle = M = \chi H$$

$$R_2 = \gamma_{\mu} \left\langle S \right\rangle_k \sigma_k , \quad K_2 = \frac{\left\langle S \right\rangle}{H} \sum_k \overline{A}_k \left( r \right) \right\} R_2 \circ$$



$$R_{2} \not\sim K_{2}$$

This result suggests a change in the hyperfine field distribution at  $T_0$ . There is a change in the hyperfine coupling  $\sum_k \overline{A}_k(r)$ due to change in the distance between the muon spin and the electron.





#### Theoretical expectations – ZF $\mu$ SR

Long-range order in a system  $\rightarrow$  the muons oscillate several times. Typical data in a system with long range order:



## Static random internal field (H=0).

The muons hardly complete an oscillation but saturate at 1/3 of the initial asymmetry due to parallel internal fields.

Expected behavior ( $\Delta$  field distribution width):





#### Dynamic random internal fields (H=0)

The muons hardly complete an oscillation and can't even saturate. Expected behavior (v is fluctuation rate) :

 $\Box$  The 1/3 recovery is lost.

 $\Box$   $v \gg \Delta$  the relaxation becomes exponential.



## With longitudinal field (H>0)

Expected behavior 
$$(\omega_L = \gamma_\mu H)$$
:

The dip is due to the presence of a typical field scale around which the muon spin nearly completes an oscillation. However, wide field distribution causes quick damping of the oscillations.

**The recovery** is due to the fact that some muons experience nearly static field during the measurement.

 $\Box \omega_L >> \Delta$ , the field at the muon site is nearly parallel to the initial muon spin direction  $\rightarrow$  the muon does not relax.



Does this compound behave as expected from a kagome compound:

- Does it have a long-range order?
- $\Box$  Is the limit of T $\rightarrow$  0 dynamics?

#### L. Marcipar et al. PRB 80 132402 (2009)

#### Zero-Field(ZF) measurements: 0.9K< T < 2.8K .



•No long range order at 0.9K (and below).

- •Relaxation increases as T decrease.
- •There is a dip at around  $0.1 \mu sec.$
- •The ZF data fits the expected theory.

### Longitudinal-Field(LF) measurements: 50Oe < H < 3.2kOe, T=0.9K.



•The asymmetry recovers at more than 1/3 of the height.

• The LF data fits the same expected theory.

All those fits are done with one function , The Dynamical Gaussian Kubo Toyabe with one free parameter, v(t).

These are unusual µSR data in a kagomé magnet.

Other kagomé magnets show the same general behavior but without this dip.

The data indicates the absence of long-range order and the presence of quasi-static field fluctuation.

We can extract the fluctuation rate v.

#### Spin fluctuation rate

Does this compound behave as expected from a

kagome compound:

Does it have a long-range order?

 $\Box$  Is the limit of T $\rightarrow$  0 dynamics?

J. Robert et al. PRL 101 117207 (2009), L. Marcipar et al. PRB 80 132402 (2009)

 $\Box$  T < T<sub>0</sub> =1.8K, V decreases but saturates below 1K.

 $\Box V$  remains small  $\rightarrow$  the spins remain dynamic with <u>no long-</u> <u>range order</u>.

$$v=3.6(2)\,\mu s^{-1}$$



## Spin fluctuation rate



### **Research Questions**

Does this compound behave as expected from a kagome compound:
 Does it have a long-or er? NO
 Is the limit of T O ynamics? YES

Does it have anisotropic behavior ?
What is the Hamiltonian of this compound ? Can we characterize it?

- Does it have anisotropy behavior?
- What is the Hamiltonian of this compound ?

Can we characterize it?

Measure sample magnetization with SQUID (Superconducting Quantum Interference Device)

Susceptibility measurements are the first step towards the Hamiltonian characterization.

- Does it have anisotropy behavior?
- What is the Hamiltonian of this compound ?

Can we characterize it?

Н straw straw Gluing the single-crystal  $\hat{c}$ plates allow us  $\hat{c}$ to perform magnetization measurements at different directions. (a) (b)

- Does it have anisotropy behavior?
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$$\chi_{\perp,\parallel}^{-1} = \frac{3k_B}{\left(g\,\mu_B\right)^2 S(S+1)} \left(T - \theta_{\perp,\parallel}^{cw}\right)$$

Using the curie-wiess law we can determine  $\theta_{CW}^{\parallel} = 4.03(1)K$ . The perpendicular direction could not be fitted to a linear function.  $\theta_{CW}^{\perp}$  is not reliable.

Indications of ferromagnetic interactions





## Electron Spin Resonance (ESR)

- ESR is a technique for studying species that have one or more unpaired electrons.
- No magnetic field onergy states of the electron are degenerate.
- Applying an external magnetic field, those electron energy levels split into 2 energy levels.

We use fixed microwave radiation and sweep the magnetic field. Once the resonance condition  $\Delta E = g_e \mu_B B_0$ is satisfied,

energy is absorbed by the sample and we get the absorption line.



## Continuous Wave (CW) ESR

- CW ESR consists a source of microwave radiation, a resonator cavity and a detector.
- The frequency, ω, is fixed (~9.5GHz) and the magnetic field
   H, is swept. The absorption power:

$$\frac{\Delta P_c}{P_w} \simeq \chi "\eta Q_u$$

- $\Delta P_{c}$  the change in the reflected power
- P<sub>w</sub> the power reaching the sample

- $Q_u$  unloaded quality factor
- $\eta$  filling factor
- $\chi^{''}$  the imaginary part of the susceptibility

## CW ESR

Modulation field is used to improve sensitivity:

$$H = St + H_{m} \cos(\omega_{m} t)$$
  
$$\chi''(H, \omega) = \chi''(St, \omega) + \frac{\partial \chi''(H, \omega)}{\partial H} H_{m} \cos(\omega_{m} t)$$

A lock-in detects the amplitude of the fast modulations in the absorption power, therefore the outcome of the measurement is:

 $rac{\partial \chi\,"ig(H,\omegaig)}{\partial H}$ 

 $\frac{2}{1} \rightarrow INTEGRATION$ 

 $\chi"(H,\omega)$ 



## ESR Results

- Does it have anisotropy behavior?
- What is the Hamiltonian of this compound ?

Can we characterize it?

#### □ 15K < T< 300K.

- Distinct anisotropy seen in the ESR results. consistent with susceptibility measurements.
- Intensity increase as T decrease. Expected behavior.



## ESR Results

- Does it have anisotropy behavior?
- What is the Hamiltonian of this compound ?

Can we characterize it?

The g-factor at each temperature can be calculated by

$$g_{\perp,\parallel} = \frac{\Delta H}{H_r} \cdot 2.0023 + 2.0023$$

- $\rm H_r$  -resonance field of a reference sample
- $\Delta$ H- difference between resonance fields of the sample and the reference

 $g_{\perp} = 2.158(5), g_{\parallel} = 2.175(5)$ 

- Two different g-factors and two absorption line-widths.
- Temperature independence.





- Does it have anisotropy behavior ?
- What is the Hamiltonian of this compound Can we characterize it?

The data can be fitted to Lorentzian:

Ζ

 $\pi$ 

$$f(x) = \frac{1}{\pi} \frac{\delta}{\delta^2 + (x - x_0)^2}$$



The nth moment of a resonance curve (Lorentzian):

 $M_n \equiv \int \left(x - x_0\right)^n f(x) dx$ 

A cut-off must be used to calculate  $M_2$  and  $M_4$ .

$$|x - x_0| \le \alpha , \ \alpha \gg \delta$$
$$M_{-} = \frac{2\alpha\delta}{M_{-}} = \frac{2\alpha^3\delta}{M_{-}} \implies \delta = \frac{\pi}{M_{-}} \frac{M_{-}}{M_{-}}$$

 $3\pi$ 

- Does it have anisotropy behavior ?
- What is the Hamiltonian of this compound Can we characterize it?

$$G_{1} = \left\langle \left\{ S_{\alpha}^{I}(t), S_{\beta}^{I}(0) \right\} \right\rangle; \ S_{\alpha}^{I} = e^{-\frac{i\mathcal{H}_{\text{int}}t}{\hbar}} S_{\alpha} e^{\frac{i\mathcal{H}_{\text{int}}t}{\hbar}}$$
$$\zeta \frac{\chi^{"}(H, \omega)}{\omega} = \int_{-\infty}^{\infty} G_{1}(t) \exp(i\omega t) dt$$
$$\text{We measure: } \chi^{"}(H, \omega) \rightarrow \frac{\chi^{"}(H, \omega)}{H}$$



We did fit to:  

$$\frac{\chi''(H,\omega)}{H} = \frac{2A}{\pi} \frac{\delta}{(H-H_0)^2 + \delta^2}$$
We assume that:  

$$\frac{\chi''(H_0,\omega)}{\omega} = \frac{2A}{\pi} \frac{\gamma\delta}{(\omega - \gamma H_0)^2 + (\gamma\delta)^2}$$

$$G_{1} \equiv \left\langle \left\{ S_{\alpha}^{I}(t), S_{\beta}^{I}(0) \right\} \right\rangle; \ S_{\alpha}^{I} = e^{-\frac{i\mathcal{H}_{\text{int}}t}{\hbar}} S_{\alpha} e^{\frac{i\mathcal{H}_{\text{int}}t}{\hbar}}$$
$$\zeta \frac{\chi^{"}(H, \omega)}{\omega} = \int_{-\infty}^{\infty} G_{1}(t) \exp(i\omega t) dt$$
$$G_{1} = \frac{1}{2\pi\zeta} \int_{-\infty}^{\infty} \frac{\chi^{"}(0, \omega)}{\omega} \exp(-i\omega t) d\omega$$
$$M_{n} \equiv \int_{-\infty}^{\infty} \frac{\chi^{"}(0, \omega)}{\omega} \omega^{n} d\omega \rightarrow M_{2n} = \frac{\left(-1\right)^{n} \left(\frac{d^{2n}G_{1}(t)}{dt^{2n}}\right)}{G_{1}(0)}$$

$$\left(\frac{d^{n}G_{1}(t)}{dt^{n}}\right)_{t=0} = (i)^{n} \begin{cases} \left[\mathcal{H}_{1}, \left[\mathcal{H}_{1}, \left[\mathcal{H}_{1}, \left[\mathcal{H}_{1}, S_{x}\right] \dots\right]\right], S_{x} \right] \\ \overbrace{n \ times} \end{cases}$$

t = 0

- Does it have anisotropy behavior ?
- What is the Hamiltonian of this compound Can we characterize it?

#### We obtain the $M_2$ and $M_4$ :

$$\begin{bmatrix} M_{2}^{\perp,\parallel} = -\frac{Tr\left(\left[\mathcal{H}, S_{z,x}\right]^{2}\right)}{Tr\left(S_{z,x}^{2}\right)}, & M_{4}^{\perp,\parallel} = \frac{Tr\left(\left[\mathcal{H}, \left[\mathcal{H}, S_{z,x}\right]\right]^{2}\right)}{Tr\left(S_{z,x}^{2}\right)} \end{bmatrix}$$

Let us consider the simplest anisotropy Hamiltonian:

$$\mathcal{H} = \sum_{j < k} \left( J_{jk} \vec{S}_j \cdot \vec{S}_k + D_{jk} S_{jz} S_{kz} + E_{jk} \left( S_{jx} S_{kx} - S_{jy} S_{ky} \right) \right)$$



#### Method of Moments – kagome lattice

Therefore, the  $2^{nd}$  and  $4^{th}$  moments for kagome lattice is given by:

$$M_{2}^{\parallel} = 4\left(D^{2} + E^{2}\right)$$

$$M_{2}^{\perp} = 16E^{2}$$

$$M_{4}^{\parallel} = \frac{7D^{2}}{4} + 2D^{3}J - DE^{2}J + D^{2}\left(4E^{2} + 3J^{2}\right) + \frac{1}{2}E^{2}\left(5E^{2} + 9J^{2}\right)$$

$$M_{4}^{\perp} = 2E^{2}\left(4D^{2} + 9DJ + 8\left(E^{2} + J^{2}\right)\right)$$

Acknowledgement to Dr. Ravi Chandra and Dr. Daniel Podolsky for the calculations.

- Does it have anisotropy behavior ?
- What is the Hamiltonian of this compound Can we characterize it?

The Method of Moments allows us to connect the susceptibility and ESR measurements along with theoretical calculations in order to get the Hamiltonian parameters J, D and E.

$$\begin{aligned} -2 \cdot \theta_{CW}^{\parallel} &= J + D = -2 \cdot 4.03K \\ \frac{2\pi f}{20.048 \cdot H_{\perp}} \cdot \delta_{\perp} &= \frac{\pi}{2\sqrt{3}} M_{2}^{\perp} \cdot \sqrt{\frac{M_{2}^{\perp}}{M_{4}^{\perp}}} \\ \frac{2\pi f}{20.048 \cdot H_{\parallel}} \cdot \delta_{\parallel} &= \frac{\pi}{2\sqrt{3}} M_{2}^{\parallel} \cdot \sqrt{\frac{M_{2}^{\parallel}}{M_{4}^{\parallel}}} \end{aligned}$$

Solving numerically these three equations yiels  $F_{erromagnetic}$  interactions ???  $(J = -9.273K, D = 1.213, E = \pm 0.477K)$  $(J = -6.975K, D = -1.085K, E = \pm 0.449K)$ 

#### Discussion – ferromagnetic interactions?

- ESR method depends on the cut-off selection, the cut-off affects the moments calculations. Wrong selection of the cut-off. In order to get AFM interactions we need a robust change in this cut-off.
- 2. In our model we consider simplest anisotropy Hamiltonian which takes into account only n.n. interactions. Maybe n.n.n. interactions or/and DMI interactions needs to be considered.
- If the cut-off selection is correct we found new phase of matter. Kagomé with ferromagnetic interactions with no long-range order and dynamic ground state.

# Summary

Does this compound behave as expected from a kagome compound?

✓ There is no long range order

 $\checkmark$  The state at the lowest temperature is quasi-static with extremely slow spin fluctuations.

 $\checkmark$  A distinct anisotropy behavior detected by magnetization and ESR measurements.

? We are able to characterize the spin Hamiltonian?? FM interactions??? Thank you for your attention!

## Muon shift

The field at the muon site given by:  $B=H-\sum ilde{A}_k\left(r
ight)ig\langle S_kig
angle$ Assuming a distribution field in the z direction:  $\tilde{A}_{\mu} = \overline{A}_{\mu} + \delta A_{\mu}$  $\rho(\delta A_k) = \frac{1}{\pi} \frac{\sigma_k}{\left(\delta A_k\right)^2 + \sigma_k^2}$ Using the distribution:  $B = rac{\omega_k}{\gamma}$  ,  $H = rac{\omega_s}{\gamma}$  $\langle S \rangle = M = \chi H$  $\Rightarrow B = H - M \cdot \sum_{k} \overline{A}_{k} \qquad \Rightarrow \frac{A_{eff} \cdot M}{H} = \frac{H - B}{H} \Rightarrow A_{eff} \cdot \chi = \underbrace{\frac{\omega_{s} - \omega_{k}}{\omega_{s}}}_{S}$  $\overline{P}_{\mu}(t) = P_0 \cos\left[\gamma_{\mu}\left(1 + \overline{A}\chi\right)H_{TF}t\right] \int \cos\left(\gamma_{\mu}\delta A\chi H_{TF}t\right)\rho(\delta A)d(\delta A)$  $\Rightarrow R_2 = \gamma_\mu \chi H_{TF} \sum_k \sigma_k$ 



## Static Gaussian Kubo Toyabe

B-local magnetic field

$$P_{z}(t) = \cos^{2} \theta + \sin^{2} \theta \cos(\gamma_{\mu} |B|t)$$

$$\overline{P}_{z}(t) = \frac{1}{3} + \frac{2}{3}\cos\left(\gamma_{\mu} |B|t\right)$$



$$\overline{P}_{z}(t) = \frac{1}{3} + \frac{2}{3} \left(1 - \Delta^{2} t^{2}\right) \exp\left(-\frac{1}{2} \Delta^{2} t^{2}\right)$$



## Dynamical Gaussian Kubo Toyabe

The static Gaussian LF KT:

$$\overline{P}_{z}\left(0,\mathrm{H},\Delta,t\right) = 1 - \frac{2\Delta^{2}}{\left(\omega_{L}\right)^{2}} \left[1 - \exp\left(-\frac{1}{2}\Delta^{2}t^{2}\right)\cos\left(\omega_{L}t\right)\right] + \frac{2\Delta^{4}}{\left(\omega_{L}\right)^{3}}\int_{0}^{t} \exp\left(-\frac{1}{2}\Delta^{2}\tau^{2}\right)\sin\left(\omega_{L}\tau\right)d\tau$$

#### The dynamic Gaussian KT:

$$\overline{P}_{z}(\nu,\mathrm{H},\Delta,t) = \underbrace{e^{-\nu t}\overline{P}_{z}(0,\mathrm{H},\Delta,t)}_{0} + \nu \int_{0}^{t} dt' \overline{P}_{z}(\nu,\mathrm{H},\Delta,t-t') e^{-\nu t'} \overline{P}_{z}(0,\mathrm{H},\Delta,t')$$

The polarization at time t due to muons that did not experience any field change.

Contribution from those muons that experienced their first field change at time t'.



## Filling factor and Q factor

**Filling factor** 

$$\eta = rac{\int\limits_{V_s} B_1^2 dV}{\int\limits_{V_C} B_1^2 dV}$$

 $B_1$  – the microwave magnetic field intensity.

**Quality factor** 

Maximum microwave energy stored in the resonator

$$Q=2\pi$$

Energy dissipated per microwave cycle

#### Change in the reflected power

$$B = B_1 \sin(\omega t) \to M' = \chi' \sin(\omega t), M'' = -\chi' \cos(\omega t)$$
$$E = \vec{B} \cdot \vec{M} ; P = B \cdot \frac{dM}{dt} \Longrightarrow \frac{1}{T} \int_0^T B \cdot \left(\frac{dM}{dt}\right) dt = \frac{1}{2} \omega \chi'' B_1$$



## g-factor calculation

