Dynamic Spin Fluctuations at $T \to 0$ in a Spin-$\frac{1}{2}$ Ferromagnetic Kagomé Lattice

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We report magnetization, electron spin resonance (ESR), and muon spin relaxation ($\mu$SR) measurements on single crystals of the $S = 1/2$ ($\text{Cu}^{+2}$) kagomé compound Cu(1,3-benzendicarboxylate). The $\mu$SR is carried to temperatures as low as 45 mK. The spin Hamiltonian parameters are determined from the analysis of the magnetization and ESR data. We find that this compound has anisotropic ferromagnetic interactions. Nevertheless, no spin freezing is observed even at temperatures two orders of magnitude lower than the coupling constants. In light of this finding, the relation between persistent spin dynamics and spin liquid are reexamined.

The search for different kinds of quantum spin liquids (SLs) continues to draw considerable experimental attention, and new candidate SLs are reported from time to time [1–9]. Much of the search is focused on compounds with a kagomé lattice. SL lack long range order and are classified according to the presence or absence of a gap to magnetic excitations. The gapless ones, or those with gap smaller than the lowest experimentally available temperature, are expected to have persistent spin dynamics (PSD) at $T \to 0$. A major experimental tool in the search for such states is the muon spin relaxation ($\mu$SR) technique. $\mu$SR is ideal for this task since it operates at zero external field, without affecting the rotation symmetry of the Hamiltonian. In addition, it can detect the presence or absence of long range order, and dynamic fluctuations. Therefore, PSD has been frequently used to identify materials as SL. However, $\mu$SR detected PSD in some compounds that are not expected to be SL such as: pyrochlores [10], molecular magnets [11], and other low dimensional systems [12]. This observation raises a question: can $\mu$SR give a false-positive observation when used to identify a SL?

To address this question we investigate the organometallic hybrid kagomé compound Cu(1,3-benzendicarboxylate) [Cu(1,3-bdc)], which was pointed out to be a ferromagnet (FM) at low temperatures [13]. Cu(1,3-bdc), with the chemical formula CuC$_6$H$_4$O$_4$, has the ideal qualities of a spin-1/2 kagomé featuring a non-magnetic 1,3-bdc ligand which links the Cu$^{+2}$ kagomé layers [13]. Initial magnetization measurements on polycrystalline samples of Cu(1,3-bdc) suggested that the mean nearest-neighbor super-exchange interaction is antiferromagnetic (AFM) in nature with a Curie-Weiss (CW) temperature of $\Theta_{\text{CW}} = -33$ K, yet at low temperatures the onset of a FM signal was observed [13]. Ferromagnetic correlation on a kagomé lattice means that the degree of frustration is low, and therefore the spins should freeze at low temperatures. Nevertheless, early $\mu$SR measurements showed only slowing down of the spin fluctuations below $T_s = 1.8$ K. The measurements were carried out only down to 0.9 K, where the magnetic state remains dynamic with no long range order [13].

Recently, single crystals were successfully synthesized in the form of millimeter size flakes. Here we combine direction dependent bulk magnetization and Electron Spin Resonance (ESR) measurements to characterize the spin Hamiltonian of these crystals. We show that Cu(1,3-bdc) is an anisotropic, slightly frustrated, ferromagnet; it is certainly not a SL. We also extend the temperature dependence of the previous $\mu$SR measurements and show...
that the dynamic fluctuations persist down to 45 mK. This result indicates that PSD detected by \(\mu\)SR can give a false-positive when used to identify a SL state. When the external field is in the \(\mathbf{z}\) direction, all sublattices are magnetized in that direction only, their moments are equal, and

\[
\mathbf{H}_{\text{eff}} = [H - z(J + D)M_z/(g\mu_B)^2]\mathbf{\hat{z}}
\]

regardless of \(d\); \(z\) is the number of neighbors. A solution of the implicit Eqs. 2 and 3 generates \(M_z(H, J, D, g||)\). We fit this \(M_z\) to the \(\mathbf{H} \parallel \mathbf{\hat{c}}\) data and find that

\[
J + D = -2.04(2) K
\]
and \(g|| = 2.51(1)\). The fit is plotted in Fig. 1 by the solid line. The calculated magnetization with interactions describes the data quite well. This calculation demonstrates that the interactions in the \(\mathbf{z}\) direction must be ferromagnetic on order of 1 K.

Other Hamiltonian parameters are obtained from ESR. The ESR measurement were done in the X-band \((\omega_0 = 9.5\, \text{GHz})\) at \(15 \leq T \leq 300\, \text{K}\). The applied field was swept between 0.9 \(\leq H \leq 6\, \text{kG}\). The inset in Fig. 2 plots a representative raw ESR data taken at \(T = 295\, \text{K}\) of the sample with a DPPH reference. To obtain the absorption line, we subtract the reference signal, and integrate the raw ESR signal over the applied field. The main panel of
to a Lorenzian function, $\chi''(H) = \frac{A_{\parallel,\perp}}{\pi} \frac{\delta}{\delta^2 + (H - H_{\parallel,\perp})^2}$ \hspace{1cm} (5)

where $2\delta$ is the full width-half maximum and $H_{\parallel,\perp} = \omega_0/(g_{\parallel,\perp}\mu_B)$ is the resonance field. We find that $g_{\perp} = 2.164(2)$ and $g_{\parallel} = 2.181(2)$. $\delta_{\parallel} = 0.432(1) \text{ kG}$ and $\delta_{\perp} = 0.867(22) \text{ kG}$. The $\delta$ and $g$-factor do not have temperature dependence down to 15 K. The area $A$ of the $H_{\perp,\parallel}$ measurement is highest, consistent with the magnetization data, and increases upon cooling as expected. The ESR $g_{\parallel,\perp}$ factors are larger than 2 but lower than the value determined by the magnetization measurement. The cause of the discrepancy between the magnetization and ESR $g$ factors is not clear to us.

At temperature higher than typical interaction strength, the widths $\delta_{\parallel}$ and $\delta_{\perp}$ are related to the three Hamiltonian parameters via the moments according to

$$g_{\parallel,\perp}\mu_B \delta_{\parallel,\perp} = \frac{\pi}{3} \frac{M_{2,\parallel,\perp}^{\parallel,\perp}}{M_{4,\parallel,\perp}^{\parallel,\perp}}$$ \hspace{1cm} (6)

where $M_{2,\parallel,\perp}^{\parallel,\perp} = -Tr ([\mathcal{H}, S_{\parallel,\perp}^z] / T_{\parallel,\perp} (S_{\parallel,\perp}^z)^2)$ and $M_{4,\parallel,\perp}^{\parallel,\perp} = Tr ([\mathcal{H}, [\mathcal{H}, S_{\parallel,\perp}^z]] / T_{\parallel,\perp} (S_{\parallel,\perp}^z)^2)$ are the second and fourth moments respectively, and $S_{\parallel,\perp}^z$ stands for the spin component perpendicular or parallel to the applied field respectively. For the Hamiltonian of Eq. 4 for a kagomé lattice, and for each of the field orientation, we obtain the second and fourth moments as given in the supplementary material. When taking $F = 0$ the second

FIG. 3. (Color online) The temperature dependence of the inverse susceptibility $\chi^{-1}(T)$, measured at two directions: $H_{\parallel,\perp}$ (filled symbols) and $H_{\perp,\parallel}$ (hollow symbols), the solid lines are fits to the inverse Curie-Weiss law. The inset shows the residuals from the fit at low temperatures.

FIG. 4. (Color online) (a) The raw $\mu$SR data with applied longitudinal field of 50 to 800 G, the solid lines demonstrate the fit to Eq. 11. (b) A semi-log scale of the spins fluctuation rate $\nu$ obtained in Ref. 4 with the added points at 240 mK and 45 mK. Inset: the kagome unit cell (bold red) with its three sublatices (a,b and c) the corresponding magnetic moment ($M^a$, $M^b$ and $M^c$) and angles ($\alpha$, $\beta$, $\gamma$).

moments are given by

$$M_{2,\parallel} = 4E^2$$ \hspace{1cm} (7)
$$M_{2,\perp} = E^2 + D^2,$$ \hspace{1cm} (8)

and the fourth moments up to second order in anisotropies are given by

$$M_{4,\parallel} = 18J^2E^2$$ \hspace{1cm} (9)
$$M_{4,\perp} = \frac{9}{2}J^2E^2 + 3J^2D^2$$ \hspace{1cm} (10)

We numerically solve Eqs. 5 and 6. All the possible solutions of these equations are given in Table I. In both solutions $J + D < 0$ and $J \pm E < 0$ and, as stated above, the interactions between spins are ferromagnetic in all directions.

To check our conclusion, and to verify the assumption made so far, we use the calculated Hamiltonian param-
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1. Introduction

The study focuses on the effect of applied fields on the magnetization of a system. The Hamiltonian parameters derived from the solution of the equations are presented in Table I. The parameters are used to generate the expected field-dependent magnetization in the perpendicular direction ($M_\perp$) and compared to the data in Fig. 1. For this purpose, we fit all data without the need to introduce a solution.

We attempt to confirm these results by temperature-dependent susceptibility measurements. The inverse susceptibility $\chi^{-1}$ is a function of temperature, with different values for each field orientation and an applied field of 0.1 K. The $\chi^{-1}$ is clearly different between the two directions. We performed a high temperature fit to the inverse Curie-Weiss (CW) law, $\chi(T)^{-1} = (T - \Theta_{CW})/C$, where $C$ is the Curie constant, and $\Theta_{CW}$ is the CW temperature. For the two experiments, the fit was applied in two temperature ranges: low-T (5 K, 30 K) and high-T (50 K, 100 K). Above 100 K, $\chi(T)^{-1}$ is no longer linear with $T$ for both directions. The CW temperature for $H || \hat{c}$ from the high-T range is $-1.0(8)$ K, and from the low-T range is $\Theta_{CW} = 4.03$ K. The CW temperature for $H \perp \hat{c}$ from the high-T is $\Theta_{CW} = -49(2)$ K. For low-T, $H \perp \hat{c}$, the data is not linear and could not be fitted reliably. The inset of Fig. 3 displays the difference between the fitted curve and the experimental data. It is clear that above $\approx 15$ K, this difference for $(\chi(T)^{\perp})^{-1}$ deviates greatly from 0, whereas the difference for $(\chi(T)^{\parallel})^{-1}$ is close to 0. This type of analysis provides a reliable $\Theta_{CW}$ only when the temperature range used in the fit is much larger than the CW temperature obtained by the fit. For $H \perp \hat{c}$ this condition is not obeyed in the high temperature range. Therefore $\Theta_{CW}$ is ambiguous. For $H || \hat{c}$ both temperature ranges are valid, but give conflicting values of $\Theta_{CW}^\parallel$.

The situation is even more confusing when analyzing the Curie constant for the different directions and temperature ranges. We have that both temperature ranges, the Curie constant is substantially different between the different directions, and much smaller than expected from localized spin 1/2 on each Cu site. We therefore abandon susceptibility measurements as a mean of characterizing the Hamiltonian.

We now turn to discuss the longitudinal fields (LF) $\mu$SR results. The data were collected at the M15 surface muon beamline at TRIUMF using a dilution refrigerator spectrometer. The spectra were gathered at $T = 45$ mK and $T = 240$ mK. In the LF-mode the external field is applied along the initial muon spin direction. When the internal fields fluctuate in space and time, the muon spin polarization is expected to complete less than one full oscillation, and then to relax. The frequency of oscillation increases and the relaxation rate decreases as the field increases. This behavior is described by the dynamical LF Kubo-Toyabe (DLFKT) function $G(\Delta, \nu, t, H_{LF})$, where $\nu$ is the field fluctuation rate, $\Delta$ is the static width of the local field distribution, and $H_{LF}$ is the applied field.

Figure 4(a) shows the spectra obtained with different fields at $T = 45$ mK. The data exhibits a typical DLFKT behavior in every respect. We fit the function

$$A(t) = A_0 G(\Delta, \nu, t, H_{LF}) + B_0$$

(11)

to the data where $A(t)$ is the muon asymmetry, and $B_0$ is a non-relaxing background due to muons stopping in the sample holder. All the fit parameters are shared for all the data sets at a given temperature. The instantaneous internal field distribution is assumed to be Gaussian. The fit is demonstrated by the solid lines in Fig. 4(a). We obtain that $\nu = 0.43(2) \mu$s$^{-1}$ and $\Delta = 19.3450(4)$ MHz. The value for $\Delta$ is consistent with previous measurements [14] indicating the same field distribution from the millikelvin to few Kelvin range. In contrast, $\nu$ decreases by a factor of $\approx 8$ relative to data obtained before at a temperature 20 times larger (0.9 K) [14]. We add the new $\nu$ values to the previous results in Fig. 4(b). The full picture clearly shows dramatic slowing of the spin fluctuations below $\approx 1.8$ K. However the system continues to fluctuate even at 0.05 K with no signs of freezing. Between 240 mK and 45 mK $\nu$ is finite, clearly measurable by $\mu$SR, and temperature independent.

It should be pointed out that the analysis of the $\mu$SR data was done assuming that the muon experiences only the external field. However, in a ferromagnet the internal field is larger than the external field. Unfortunately, without proper knowledge of the muon stopping site it is difficult to estimate the internal field. Analysis of the muon data with a field larger than $H_{LF}$ could only lead to higher values of $\nu$. Therefore, the $\nu$ in Fig. 4(b) should be considered as lower limit on the real values.

Finite fluctuation rate $\nu$ at $T \rightarrow 0$, with different time scales, was observed in many kagomé lattices with antiferromagnetic interactions such as SCGO [1], Volborthite [2], Herbertsmithite [3, 5], Nd$_3$Ga$_5$SiO$_{14}$ [6], Langasite [7], Kapellasite [8], and vanadium-oxyfluoride [9]. All these compounds are considered to be SL. However the Hamiltonian in Eq. 1 with the parameters in Table I gives a ground state that is fundamentally different from these spin liquids. Since $D > |E|$ the spin lie in the xy plane. This allows us to define one angle per spin as

| Sol. # | J (K)  | D (K)  | E (K)  |
|-------|--------|--------|--------|
| 1     | -2.3822| 0.3421 | ± 0.14217 |
| 2     | -1.7470| 0.2930 | ± 0.12175 |
shown in the inset of Fig. 4(b). For positive or negative $\alpha$ the spins would like to lie parallel or perpendicular to a bond, respectively. However, the ground state energy minimum is reached when two spins make the angles $\alpha = -\beta = -\sqrt{3}E/(6J - E)$ with a bond, and the third spin has $\gamma = 0$ and is 60 degrees away from a bond (see supplementary material). This is a slightly frustrated spin arrangement. A new energy minimum for all the spins on the lattice is found every 60 degrees, but there is no local continuous degeneracy. The energy minimum is shallow and it takes $\sim 10$ mK per unit cell to overcome the potential barrier and move the entire spin system collectively between local energy minima. This means that Cu(1,3-bdc) should order magnetically and it is not a spin liquid.

In summary, the Cu(1,3-bdc), with Cu$^{2+}$ spin-1/2 situated on kagomé lattice, exhibits anisotropic but ferromagnetic interactions in all direction. $\mu$SR indicates persistent spin dynamics down to 45 mK as expected from a spin liquid. The same behavior was observed in many kagomé lattices with AFM interactions. This is very surprising given that a kagomé lattice with ferromagnetic interactions has very small degree of frustration, lacks continuous local degeneracy, and is not a spin liquid. Therefore, $\mu$SR can falsely identify a spin liquid.

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I. SUPPLEMENTARY MATERIAL

A. Moments

The evaluation of the linewidths in ESR at high temperatures involves calculating the second and fourth order moments to be used in Eq. 6 in the main text. Thus we need to evaluate the first and second order commutators of the total spin component in a given direction and the Hamiltonian. It is straightforward to see that for a spin-1/2 Hamiltonian the first order commutator gives rise to two-spin terms. The second order commutator gives rise to single spin or three spin terms depending on whether a bond term, from the Hamiltonian, and a two spin term from the first order commutator, share two sites or one.

The evaluation of the traces involves careful bookkeeping of all the different terms possible. We accomplished that by writing a Mathematica program which evaluates all the terms that can arise and computes the trace. The program evaluates the moments for a general Hamiltonian of spin-1/2 sites. It is assumed that the lattice can be grouped into clusters of sites, which can be seen as sublattices corresponding to a particular Bravais lattice site. The Hamiltonian is then specified as the sum of interactions within a cluster and between clusters. Thus we assume that the Hamiltonian has translation invariance.

The input to the program specifies all the site indices and coupling coefficients (9 in number, for $S_{i\alpha}S_{j\beta}$) for all the different bonds involving spins from the Bravais lattice site at the origin. The rest of the bonds on the lattice and their contributions to the trace can be evaluated given the translation invariance. Thus the evaluation is quite general and can be extended to several other systems with more general Hamiltonians such as those containing all the components of the DM interaction and also longer range exchange interactions.

The moments in this paper have been evaluated for the anisotropic kagomé Hamiltonian with three exchange coupling constants and a Dzyaloshinskii-Moriya (DM) term given in Eq. 1 of the main text. They are given by:

$$M_2^\parallel = 4E^2$$
$$M_2^\perp = F^2 + E^2 + D^2$$
$$M_4^\parallel = 18J^2E^2 + 28E^4 + 10F^2E^2 + 8\sqrt{3}FE^2J + 4\sqrt{3}FE^2D + 20JDE^2 + 8E^2D^2$$
$$M_4^\perp = \frac{11}{2}F^4 - JDE^2 + \frac{9}{2}J^2E^2 + 3J^2D^2$$
$$+ 2JD^3 - \frac{5\sqrt{3}}{2}FE^2D + \frac{13}{4}E^4 + \frac{5}{4}D^4$$
$$+ \frac{41}{4}F^2E^2 + 2F^2J^2 + 3F^2D^2 + \frac{25}{4}E^2D^2$$

B. Effective Fields

The kagomé lattice is constructed from three sublattices. They are presented in Fig. B(b) of the paper. The effective fields in the three different sublattices are:

$$\mathbf{H}_{\text{eff}}^a = \mathbf{H} - \frac{2J}{g^2\mu_B^2}(\mathbf{M}^b + \mathbf{M}^c) - \frac{E}{g^2\mu_B^2}\left(2M_x^b\right)$$
$$- M_x^c + \sqrt{3}M_y^c - 2M_y^b + M_y^a + \sqrt{3}M_x^a$$

$$\mathbf{H}_{\text{eff}}^b = \mathbf{H} - \frac{2J}{g^2\mu_B^2}(\mathbf{M}^a + \mathbf{M}^c) - \frac{E}{g^2\mu_B^2}\left(2M_x^a\right)$$
$$- M_x^c - \sqrt{3}M_y^c - 2M_y^a + M_y^b - \sqrt{3}M_x^b$$

$$\mathbf{H}_{\text{eff}}^c = \mathbf{H} - \frac{2J}{g^2\mu_B^2}(\mathbf{M}^b + \mathbf{M}^a) - \frac{E}{g^2\mu_B^2}\left(-M_x^a\right)$$
$$- M_x^b + \sqrt{3}M_y^b - \sqrt{3}M_x^b - M_y^b + \sqrt{3}M_y^b - \sqrt{3}M_x^b$$
C. Ground state

We determine the ground state in the mean field approximation by writing

\[ M^a = M(\cos \alpha, \sin \alpha) \]

\[ M^b = M(\cos \beta, \sin \beta) \]

\[ M^c = M(\cos \gamma, \sin \gamma). \]

The Hamiltonian per unit cell \( H = \) external field it is given by

\[ H = -\frac{M^2}{2(\gamma_B)^2} \{ J [4 \cos(\beta - \alpha) + 4 \cos(\gamma - \beta) + 4 \cos(\alpha - \gamma)] + \]

\[ E[4 \cos(\alpha + \beta) + 2\sqrt{3} \sin(\alpha + \gamma) - 2\sqrt{3} \sin(\beta + \gamma)] \]

\[ -2 \cos(\alpha + \gamma) - 2 \cos(\beta + \gamma) \right\} \]

This Hamiltonian is invariant under rotations by 120 degrees and cyclic permutations of the angles. A numerical search for the minimum shows that it occurs at \( \alpha = -\beta, \) and \( \gamma = 0. \) Given these relations, and that for each sublattice \( H_{\text{eff}}^d \) is parallel to \( M^d, \) we find that \( \alpha = -\beta = -\sqrt{3}E/(6J - E). \)

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