Muon-spin spectroscopy of the organometallic spin-$\frac{1}{2}$ kagome-lattice compound Cu(1,3-benzenedicarboxylate)

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Using muon-spin resonance, we examine the organometallic hybrid compound Cu(1,3-benzenedicarboxylate) [Cu(1,3-bdc)], which has structurally perfect spin-$\frac{1}{2}$ copper kagome planes separated by pure organic linkers. This compound has antiferromagnetic interactions with Curie-Weiss temperature of -33 K. We found slowing down of spin fluctuations starting at $T=1.8$ K and that the state at $T \rightarrow 0$ is quasistatic with no long-range order and extremely slow spin fluctuations at a rate of 3.6 μs^{-1}. This indicates that Cu(1,3-bdc) behaves as expected from a kagome magnet and could serve as a model kagome compound.

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The experimental search for an ideal two dimensional, spin $\frac{1}{2}$, kagome compound, which has no out-of-plane interactions and no impurities on the kagome plane, has powered tremendous experimental effort in recent years.[1] Yet, all compounds studied today have shortcomings. Recently, a promising copper-based metal organic hybrid compound Cu(1,3-benzenedicarboxylate) [Cu(1,3-bdc)] was synthesized by Nytko *et al.*[2] This compound has an ideal kagome lattice structure as indicated by x ray, the spins are naturally $\frac{1}{2}$, and there are no Zn ions or any other candidates to substitute the Cu on the kagome plane. The goal of this Brief Report is to show that from a magnetic point of view Cu(1,3-bdc) shows the signatures of the high degree of frustration expected on the kagome lattice. This is done by demonstrating that the interplane interactions are small enough compared to the intraplane interactions that no long-range order is found at temperatures well below the interaction energy scale and by characterizing the ground-state properties. The experimental tool is muon-spin resonance (μSR). Our major finding is that the state at the lowest temperature investigated is quasistatic with extremely slow spin fluctuations. This type of behavior is similar to a huge class of frustrated magnets.[3,4] Therefore, Cu(1,3-bdc) could serve as a model spin-$\frac{1}{2}$ kagome compound.

Cu(1,3-bdc) is shorthand for Cu(1,3-benzenedicarboxylate). The kagome planes are separated by organic linkers, each linker being a benzene molecule with two corners featuring a carboxylate ion instead of the standard H ion. If one were to label the corners 1–6 consecutively, the two corners with the carboxylate ions would be the first and third. The Cu ions located on the kagome plane are linked by O-C-O ions while interplane Cu ions are linked by O-5C-O ions. The basic elements of Cu(1,3-bdc) are depicted in Fig. 1. Magnetization measurements found antiferromagnetic Curie-Weiss temperature of -33 K.[2] Strong antiferromagnetic exchange between Cu^{2+} ions linked by a carboxylate molecule was also found in the trinuclear compound Cu$_3$(O$_2$C$_{16}$H$_{23}$)·1.2C$_6$H$_{12}$.[5] Heat capacity shows a peak at $T \simeq 2$ K.[2]

The powder we examined contains Cu(1,3-bdc) in the form of blue crystalline plates. However, it is mixed with some green plates of copper-containing ligand oxidation by-product C$_{32}$H$_{24}$Cu$_6$O$_{26}$, which cannot be separated from the blue plates. To the naked eye it looks as if about 10% of the plates are green. However, as we demonstrate below, the μSR signal from Cu(1,3-bdc) can be separated from the C$_{32}$H$_{24}$Cu$_6$O$_{26}$ signal. Our sample was pressed into a Cu holder for good thermal contact.

Muon-spin rotation and relaxation (μSR) measurements were performed at the Paul Scherrer Institute, Switzerland (PSI) in the low-temperature facility spectrometer with a dilution refrigerator. The measurements were carried out with the muon spin tilted at 45° relative to the beam direction. Positrons emitted from the muon decay were collected simultaneously in the forward-backward (longitudinal) and the up-down (transverse) detectors with respect to the beam direction. Transverse-field (TF) measurements, where the field is perpendicular to the muon-spin direction, were taken at
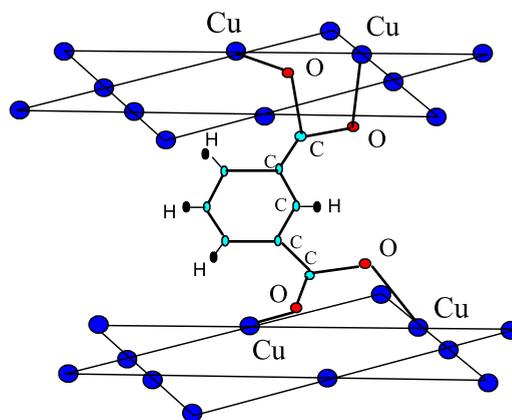
FIG. 1. (Color online) The Cu(1,3-bdc) structure showing the kagome planes and the interplane and intraplane superexchange path.
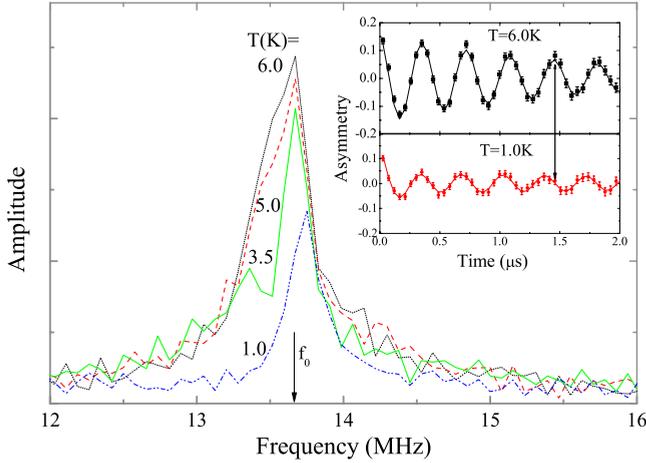
FIG. 2. (Color online) FFT of the asymmetry data in a field of 1 kOe transverse to the initial muon-spin direction. f_s is the reference frequency in pure silver. Inset: transverse-field asymmetry in the time domain and a rotating reference frame.

FIG. 3. (Color online) The muon shift from $C_{32}H_{24}Cu_6O_{26}$ K_1 and from Cu(1,3-bdc) K_2, and the relaxation rate from Cu(1,3-bdc) R_2 versus temperature.

temperatures ranging from 0.9 to 6.0 K with a constant applied field of $H=1$ kOe. Zero-field (ZF) measurements were taken in the longitudinal configuration at a temperature ranging from 0.9 to 2.8 K. The longitudinal-field (LF) measurements, where the field is parallel to the muon-spin direction, were taken at several different fields between 50 Oe and 3.2 kOe with a constant temperature of 0.9 K. We also performed a field calibration measurement using a blank silver plate providing the muon rotation frequency f_s =13.67 MHz at the applied TF of 1 kOe.

In the inset of Fig. 2 we depict by symbols the muon decay asymmetry in a reference frame rotated at H =200 Oe less than the TF. In the main panel of Fig. 2 we show the fast Fourier transform (FFT) of the TF data at some selected temperatures. The FFT of the highest temperature, 6 K, shows a wide asymmetric peak with extra weight toward low frequencies. At 3 K the wide asymmetric peak separates into two different peaks shifting in opposite directions. At even lower temperatures the low-frequency peak vanishes. We assign the latter peak to muons that stop in Cu(1,3-bdc) since such a wipe out of the signal is typical of slowing down of spin fluctuations, which in Cu(1,3-bdc) is expected near 2 K.

Despite the disappearance of the second peak in the frequency domain, its contribution in the time domain is clear. The high-frequency peak in the main panel of Fig. 2 corresponds to the signal surviving for a long time in both insets of Fig. 2. The broad and disappearing peak in the main panel corresponds to the fast decaying signal in the first 0.2 μs seen in the lower inset. The arrow in the inset demonstrates the frequency shift. Consequently we fit the function

$$A_{TF}(t) = A_1 e^{-(R_1 t)^2/2} \cos(\omega_1 t + \varphi) + A_2 e^{-R_2 t} \cos(\omega_2 t + \varphi) + B_g \tag{1}$$

to our data in the time-domain globally, where the parameters R_1 and ω_1 are the relaxation and angular frequency of the byproduct, and R_2 and ω_2 are the relaxation and angular
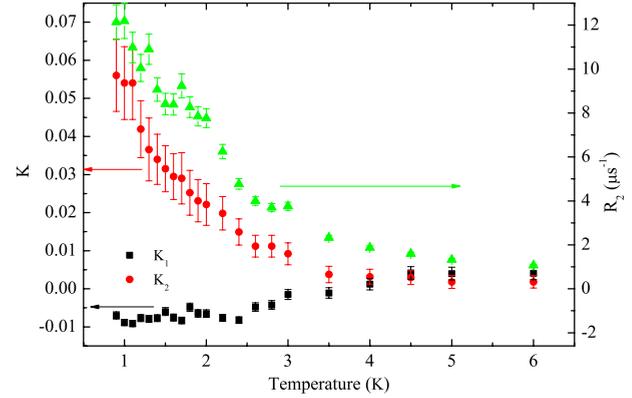
frequency of the kagome part. The parameters $A_1=0.049(4)$, $A_2=0.125(3)$, $R_1=0.13(1)$ (μs^{-1}), φ, and B_g are shared in the fit while R_2, ω_1, and ω_2 are free. The quality of the fit is represented in the inset of Fig. 2 by the solid lines. The ratio of A_1 to A_2 supports the assignment of the fast relaxing signal to Cu(1,3-bdc).

In Fig. 3 we plot the shift, $K_{1,2}=(\omega_s-\omega_{1,2})/\omega_s$, versus temperature, where $\omega_s=2\pi f_s$. As expected K_2 increases with decreasing temperatures. The small decrease in K_1 is not expected and is not clear to us at the moment. The muon transverse relaxation, R_2, is also presented in Fig. 3. It has roughly the same temperature behavior as the shift, K_2. However, at $T=1.8$ K R_2 seems to flatten out before increasing again around 1 K. This is somewhat surprising.

The field at the muon site is given by $\mathbf{B}=\mathbf{H}-\Sigma_k \widetilde{A}_k \langle \mathbf{S}_k \rangle$, where $\langle \mathbf{S}_k \rangle$ is the thermal average of the spins neighboring the muon and $\widetilde{A}_k$ is the hyperfine interaction with each neighboring spin. Assuming a distribution of hyperfine fields in the $\hat{z}$ direction one can write $\widetilde{A}_k$ as a sum of a mean value $\overline{A}_k$ plus a fluctuating component δA_k. For the distribution

$$\rho(\delta A_k) = \frac{1}{\pi} \frac{\sigma_k}{(\delta A_k)^2 + \sigma_k^2} \tag{2}$$

one finds that the shift is given by $K_2=\langle \mathbf{S}_k \rangle \Sigma_k \overline{A}_k / H$ and $R_2 = \gamma_\mu \langle \mathbf{S}_k \rangle \Sigma_k \sigma_k$.[6] To test this derivation it is customary to plot the macroscopic magnetization M measured with a superconducting quantum interference device magnetometer versus K_2. This is depicted in Fig. 4(a). The magnetization is also measured at 1 kOe. The plot indicates that in the temperature range where both M and K_2 are available they are proportional to each other. Therefore, $\Sigma_k \overline{A}_k$ is temperature independent.

If the σ_k are also temperature-independent parameters we expect $R_2 \propto K_2$. A plot of R_2 versus K_2, shown in Fig. 4(b), indicates that R_2 is not proportional to or even does not depend linearly on K_2 and a kink is observed at $T_0=1.8$ K. This result suggests a change in the hyperfine fields distribution at T_0. An interesting possible explanation for such a change is a response of the lattice to the magnetic interactions via a magnetoelastic coupling.[7] However, unlike a simi-
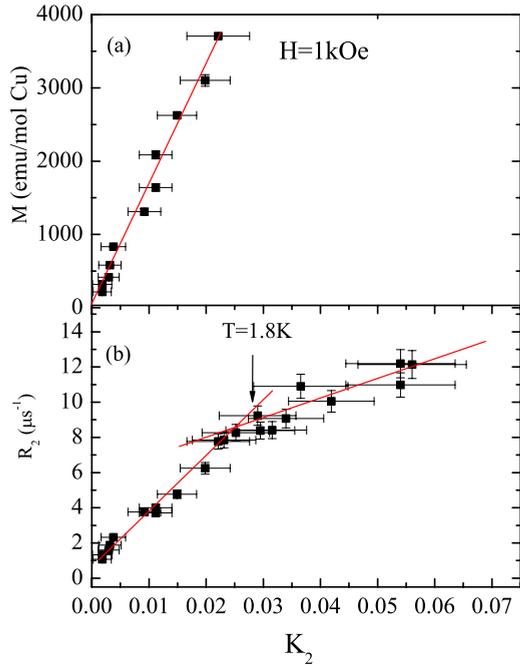
FIG. 4. (Color online) (a) Magnetization versus the muon shift in Cu(1,3-bdc). (b) The muon relaxation rate versus the muon shift in Cu(1,3-bdc).

lar situation in a pyrochlore lattice,[8] it seems that here the lattice is becoming more ordered upon cooling since the rate of growth of R_2 below T_0 is lower than at higher temperatures.

The μSR LF data including ZF are presented in Fig. 5. The LF data at the lowest temperature of 0.9 K are depicted in panel (a). At this temperature and a field of 50 Oe, the muon asymmetry shows a minimum at around 0.1 μs. At longer times the asymmetry recovers. The origin of this dip is the presence of a typical field scale around which the muon spin nearly completes an oscillation. However, the field distribution is so wide that the oscillation is damped quickly. The origin of the recovery is the fact that some of the muons experience nearly static field in their initial field direction during the entire measured time. These muons do
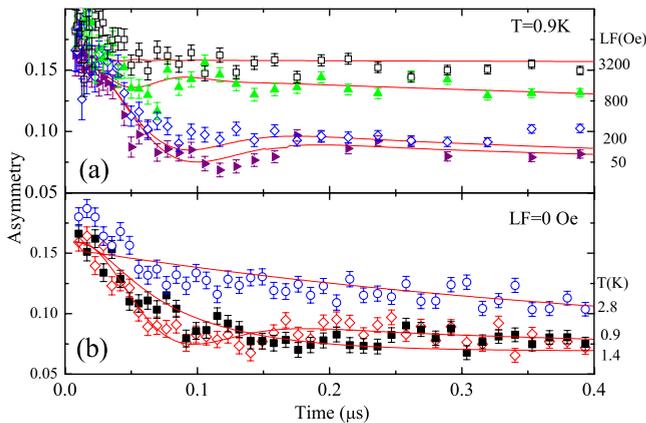
FIG. 5. (Color online) (a) The asymmetry at various longitudinal fields and $T=0.9$ K. (b) The asymmetry at zero field and various temperatures.

not lose their polarization while others do. When the external field increases, the dip moves to earlier times (as the field scale increases) and the asymptotic value of the asymmetry increases as well (as more muons do not relax).

The ZF data at three different temperatures are shown in Fig. 5(b). As the temperature decreases the relaxation rate increases due to the slowing down of spin fluctuations, until at the lowest temperature the dip appears. We saw no difference in the raw data between 1.0 and 0.9 K and therefore did not cool any further.

These are unusual μSR data in a kagome magnet, in the sense that the spin fluctuations are slow enough compared to the internal field scale to expose the static nature of the muon-spin relaxation function, namely, the dip, and to allow calibration of the internal field distribution. Other kagome magnets show the same general behavior but without this dip.[3] The data indicate the absence of long-range order and the presence of quasistatic field fluctuation. If the ground state had long-range order, the muon would have oscillated several times due to the internal magnetic field. Similarly, if the ground state was dynamic we would *not* have seen a recovery of the muon polarization after a long time.

To analyze this type of muon-spin-relaxation function, a theoretical polarization function $P(\nu,\Delta,H,t)$ must be generated. It depends on the random-field distribution $\rho(\mathbf{B})$, the spin fluctuations rate ν defined by $\langle\mathbf{B}(t)\mathbf{B}(0)\rangle=\langle B^2\rangle e^{-2\nu t}$, where B is the internal local field, and the LF H. In ZF or small LF field, standard perturbation methods for calculating relaxation functions do not apply and a special method for calculating P is required. This function is produced in two steps. In the first step the static muon polarization is generated using the double projection expression

$$\bar{P}_z(0,\Delta,H,t) = \int \rho(\mathbf{B})\left[\frac{B_z^2}{\mathbf{B}^2} + \frac{B_x^2 + B_y^2}{\mathbf{B}^2}\cos(\gamma_\mu|\mathbf{B}|t)\right]d^3\mathbf{B}.$$

(3)

We found that the Gaussian field distribution

$$\rho(\mathbf{B}) = \frac{\gamma_\mu^3}{(2\pi)^{3/2}\Delta^3}\exp\left(-\frac{\gamma_\mu^2[\mathbf{B} - H\hat{z}]^2}{2\Delta^2}\right)$$

(4)

works best. This $\bar{P}_z(0,\Delta,H,t)$ is known as the static Gaussian Kubo-Toyabe LF relaxation function.[9]

In the second step the dynamic fluctuations are introduced. One method of doing so is using the Voltera equation of the second kind[10]

$$\bar{P}_z(\nu,H,\Delta,t) = e^{-\nu t}\bar{P}_z(0,H,\Delta,t)$$
$$+ \nu\int_0^t dt'\bar{P}_z(\nu,H,\Delta,t-t')e^{-\nu t'}\bar{P}_z(0,H,\Delta,t').$$

(5)

The function $\bar{P}_z(0,H,\Delta,t')$ is taken from the first step. The factor $e^{-\nu t}$ is the probability to have no field changes up to time t. The factor $e^{-\nu t'}\nu dt'$ is the probability density to experience a field change only between t' and $t'+dt'$. The first term on the right-hand side (rhs) is the polarization at time t due to muons that did not experience any field changes. The second term on the rhs is the contribution from those muons
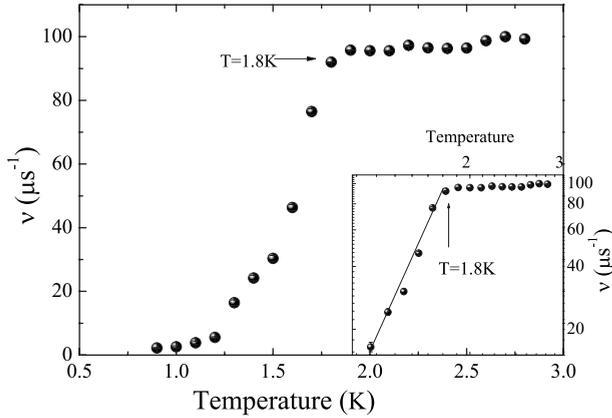
FIG. 6. The fluctuation rate ν versus temperature. Inset: ν near 1.8 K on a log-log scale. The error bars are smaller than the symbol size.

that experienced their first field change at time t'. The factor $e^{-\nu t'}\bar{P}_z(0,H,\Delta,t')\nu dt'$ is the amplitude for the polarization function evolving from time t' to t, which can include more field changes recursively. This equation can be solved numerically[11] and $\bar{P}_z(\nu,H,\Delta,t)$ is known as the dynamic Gaussian Kubo-Toyabe LF relaxation function.[9]

The experimental asymmetry is fitted with $A_{LF} = A_0\bar{P}_z(\nu,H,\Delta,t)+B_g$. The relaxation from the second green phase is very small and is absorbed in the background factor B_g. In the fit of the field-dependence experiment at the lowest temperature, presented in Fig. 5(a) by the solid lines, Δ, ν, A_0, and B_g are shared parameters. We found $\Delta = 19.8(4)$ MHz and $\nu=3.6(2)$ μs^{-1}. This indicates that the spins are not completely frozen even at the lowest temperature.

When analyzing the ZF data at a variety of temperatures, shown in Fig. 5(b) by the solid lines, we permit only ν to vary. The fit is good at the low temperatures but does not capture the 2.8 K data at early times accurately. However, the discrepancy is not big enough to justify adding more fit parameters. We plot the temperature dependence of the fluctuation rate in Fig. 6. ν hardly changes while the temperature decreases from $T=2.8$ K down to $T_0=1.8$ K. From T_0, ν decreases with decreasing temperatures, but saturates below

1 K. This type of behavior was observed in a variety of frustrated kagome (Ref. 3) and pyrochlore (Ref. 4) lattices. It is somewhat different from classical numerical simulations where ν decreases with no saturation.[12,13] In fact, the numerical ν is a linear function of the temperature over 3 orders of magnitude in T.[13]

The inset of Fig. 6 shows ν as a function of temperature near T_0 on a log-log scale where slowing down begins. Only near T_0 are our data consistent with a linear relation

$$\nu - \nu_\infty = \nu_0(T-T_0),$$

where ν_∞ is the high-temperature fluctuation rate. The discrepancy with the numerical work might be because μSR probes field correlations involving several spins nearing the muon while the simulations concentrate on spin-spin autocorrelations (with a decay Γ_a compared here with ν). At our lowest temperature the rotations of ensemble of spins are already coherent therefore field and spin correlations are not identical. Another possibility is that the saturation of ν with decreasing T is a pure quantum effect not captured by the classical simulations.

To summarize, we found that Cu(1,3-bdc) has a special temperature $T_0=1.8$ K. Upon cooling, the susceptibility, as measured by the μSR, grows monotonically even past this temperature. The muon-spin linewidth also grows but halts around this temperature. This might be explained by a subtle structural transition but low-temperature structural data are required. At T_0 the slowing down of spin fluctuations begins but the spins remain dynamic with no long-range order. The rate of the spin fluctuations appears to be linear near T_0 but becomes saturated at the lowest T. This general behavior is similar to other kagome compounds, though different features are seen here. Therefore, considering its lattice, Cu(1,3-bdc) could serve as a model compound for spin-$\frac{1}{2}$ kagome magnet.

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