High-field magnetic ground state in $S = 1/2$ kagome lattice antiferromagnet ZnCu$_3$(OH)$_6$Cl$_2$
An exciting field of modern condensed matter physics is the quantum spin liquid, in which strong frustration leads to the lack of magnetic ordering and the emergence of novel physical phenomena in the ground state. The \( S = \frac{1}{2} \) kagome lattice antiferromagnet is considered to be a likely candidate of spin liquid by a number of recent experiments. The high-field magnetization of the kagome lattice is complicated due to the presence of a few percent of extra Cu impurities sitting on the interlayer metallic sites. To determine the magnetic ground state of the kagome lattice, we measured the magnetization of a single crystalline \( \text{ZnCu}_3(\text{OH})_6\text{Cl}_2 \) using torque magnetometry down to the base temperatures 20 mK in intense magnetic field as high as 31 T. The high-field intrinsic magnetization from the kagome lattice turns out to be linear with magnetic field, and the magnetic susceptibility is independent of temperature at 20 mK \( \lesssim 5 \) K. Moreover, below 2 K, several field-induced anomalies are observed in between 7 T and 15 T.

DOI: 10.1103/PhysRevB.90.064417  PACS number(s): 75.30.Cr, 75.30.Kz, 75.50.Ee

High-field magnetic ground state in \( S = \frac{1}{2} \) kagome lattice antiferromagnet \( \text{ZnCu}_3(\text{OH})_6\text{Cl}_2 \)

Tomoya Asaba, 1 Tian-Heng Han, 2,3,4 B. J. Lawson, 1 F. Yu, 1 C. Tinsman, 1 Z. Xiang, 1,5 G. Li, 1 Young S. Lee, 2 and Lu Li 1,∗

1Department of Physics, University of Michigan, Ann Arbor, Michigan 48109, USA
2Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
3James Franck Institute and Department of Physics, University of Chicago, Chicago, Illinois 60637, USA
4Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, USA
5Department of Physics, University of Science and Technology of China, Hefei, Anhui 230026, China

(Received 1 May 2014; revised manuscript received 4 August 2014; published 18 August 2014)

Herbertsmithite \( \text{ZnCu}_3(\text{OH})_6\text{Cl}_2 \) is a kagome lattice antiferromagnet with spin-1/2 and has been demonstrated to be a likely candidate of spin liquid by a number of recent experiments. The high-field magnetization of the kagome lattice is complicated due to the presence of a few percent of extra Cu impurities sitting on the interlayer metallic sites. To determine the magnetic ground state of the kagome lattice, we measured the magnetization of a single crystalline \( \text{ZnCu}_3(\text{OH})_6\text{Cl}_2 \) using torque magnetometry down to the base temperatures 20 mK in intense magnetic field as high as 31 T. The high-field intrinsic magnetization from the kagome lattice turns out to be linear with magnetic field, and the magnetic susceptibility is independent of temperature at 20 mK \( \lesssim 5 \) K. Moreover, below 2 K, several field-induced anomalies are observed in between 7 T and 15 T.

Publisher: American Physical Society

1098-0121/2014/90(6)/064417(5) 064417-1 ©2014 American Physical Society
The tilt angle is defined by the angle between the field $H$ and the kagome lattice normal axis ($\vec{z}$ axis). The torque $\tau$ generated by the sample $\vec{m} \times \vec{B}$ is along the axis coming out of sketch page, and the torque deflects the cantilever so that the capacitance changes between the metallic cantilever and the gold film underneath. The torque responses from herbertsmithite sample A in selected $T$ between 0.3 K and 30 K. The tilt angle $\phi = 20^\circ$.

cantilevers with $c$ axis facing up and the magnetic torque was measured capacitively, as shown in Fig. 1(a).

Example curves of the field dependence of the magnetic torque $\tau$ are shown in Fig. 1(b), measured on sample A at selected temperatures $T$ between 0.3 K and 30 K. The tilt angle $\phi$ is $20^\circ$. In Fig. 1(b), the positive sign of $\tau$ is consistent with the sign in Eq. (2), which means that the torque component from the $c$-axis magnetization $M_c H_c$ is smaller than that from the in-plane magnetization $M_p H_p$. As shown in Fig. 1(b), the torque response becomes quadratic at higher $T$ and torque changes sign around $T \approx 15$ K. Those facts are consistent with previous measurements [13,18] in which the $c$-axis susceptibility $\chi_c$ was shown to be slightly larger than the in-plane susceptibility $\chi_p$ at $T \geq 15$ K.

At low $T$, the $\tau-H$ curve shows two sets of interesting features: (1) $\tau-H$ is nonmonotonic; (2) at $\mu_0 T \sim 8$ T, a number of kinks are observed in the $\tau-H$ curves. We focus on the kinks that suggest magnetic-field-driven anomalies, then analyze the magnetization curves in intense magnetic fields. The high-field magnetic susceptibility is found to be $H$ independent and $T$ independent (Pauli-like) in the $S = \frac{1}{2}$ kagome system below 5 K.

The field-driven anomalies are emphasized by taking derivatives of torque $\tau$ with respect to field $H$. Figure 2(a) shows the angular dependence of derivative $\tau/\mu_0 T$ from $\phi = -3^\circ$ to $74^\circ$ at 0.3 K. In high magnetic fields, we have observed four possible field-induced anomalies. They are marked by two pairs of arrows, at $\mu_0 H \sim 7$ T and 10 T, and $\mu_0 H \sim 13$ T and 15 T. The first pair is so pronounced that there are clear slope changes in the $\tau-H$ curves in Fig. 1(b).

The anomaly fields are almost independent of the magnetic field orientation, which is consistent with the Heisenberg model. As the field tilt angle changes from $-3^\circ$ to $74^\circ$, the peaks and dips shift as little as $1$ T, compared with the anomaly field values on the order of $\sim 10$ T. Moreover, measurements at different $T$ show that the anomaly fields are almost $T$ independent. Figure 2(b) shows the $\tau/\mu_0 T$ at selected $T$ between 0.3 K and 10 K. The field locations for these anomalies do not show noticeable changes for $T < 1$ K. The pair of higher-field features (13 T and 15 T) disappear at $T > 1.2$ K, while the pair of lower-field features disappear at $T > 1.6$ K. Below 2 K, all the anomaly field values are almost $T$ independent. For sample B, we further cool down to 20 mK. The derivative $\tau/\mu_0 T$ is almost independent of $T$ between 20 mK and 330 mK.

The trend of low $T$ torque signal is consistent with earlier magnetization measurements [13]. We find that the increase of the magnetization contribution from impurity would make the torque signal more positive, whereas the increase of the kagome plane magnetization would make the torque signal more negative. In the earlier magnetization measurements [13] at $1.8 \leq T \leq 300$ K, $(\chi_c/\chi_p)_\text{imp} < 1$ and $(\chi_c/\chi_p)_\text{kagome} > 1$.

To further understand the competition between $M_c$ and $M_p$, we look at the effective transverse magnetization $M_T$, which is defined as

$$M_T = \frac{\tau}{\mu_0 H V}.$$  \hspace{1cm} (3)

The resulting $M_T$ curves are shown in Fig. 3(a). Above 1 K at zero field the slope of the $M_T$ vs $H$ curves increases greatly as $T$ decreases, following the Curie-Weiss law, which is consistent with early results [12,19]. At higher fields, the slope becomes negative, because the intrinsic kagome moments prefer to stay along the crystalline $c$ axis, i.e., have larger contribution from $M_c$. Furthermore, the fact that the slope
above 10 T does not change when $T$ increases suggests that the intrinsic magnetic susceptibility from the kagome lattice is $T$ independent below 5 K.

To further illustrate this point, the effective magnetic susceptibility is defined as $\chi_{\text{eff}} \equiv \frac{1}{\mu_0} \frac{dM_T}{dH}$. Figure 4(a) displays $\chi_{\text{eff}}$ vs field $H$ using the 31 T data shown in Fig. 3(b). At $H \geq 15$ T, $\chi_{\text{eff}}$ stays constant at $T \leq 5$ K. We have measured the high-field $\chi_{\text{eff}}$ in the sample B in two temperature ranges, first above 300 mK using a helium-3 refrigerator, and then down to 20 mK taken in a dilution-refrigerator. Figure 4(b) displays the $T$ dependence of the absolute value of the high-field susceptibility $\chi_{\text{eff}}$, which is the slope of the $M_T$ vs $H$ curves at $H \geq 15$ T. As shown in Fig. 4(b), the high-field magnetic susceptibility is almost independent of $T$ below 5 K. This is consistent with the presence of a spinon Fermi surface as is also observed in triangular organic antiferromagnetic systems [20].

We note that the effective magnetic susceptibility detects only the anisotropic part of the magnetic susceptibility. Assuming the anisotropy stays the same for the kagome lattice at different $H$, we infer that the magnetic susceptibility itself is $T$ independent and $H$ independent in the intense fields. In triangular organic antiferromagnetic systems [20], torque measurement has demonstrated that the intrinsic magnetic susceptibility is proportional to the effective magnetic susceptibility.

Figure 4(c) summarizes the phase diagram of herbertsmithite. At $\mu_0 H < 7$ T, the magnetic signal of herbertsmithite consists of the kagome plane signal $M_z$ and the impurity contributions $M_{\text{imp}}$ from the interlayered Cu magnetic moments. The impurity contribution quickly saturates as $H$ increases. As $H$ increases to 7 T, the magnetizations of all the impurities become constant. At $8 T < H < 16$ T, we observe that two pairs of field-induced anomalies are independent of $T$ at 20 mK $\leq T \leq 1.6$ K.

Discussion. For Cu spins with $g$ factor of 2, 10 T magnetic field corresponds to $\sim 0.07 J$, where $J$ is the exchange energy of this material. It is worth emphasizing that the strong applied field introduces a Zeeman energy of $\sim 0.1 J$. This complicates a direct comparison with theories considering only a Heisenberg term [10]. A recent high-field specific heat study on a single crystal herbertsmithite indicates a strong field dependence below 9 T which significantly weakens from 9 T to 18 T [21]. This corroborates with our torque measurements, both of which are consistent with herbertsmithite entering a high-field regime at $\mu_0 H > 10$ T.

Our field-induced anomalies extend from 20 mK to 1.6 K and stay at certain field magnitudes. This is distinct from...
those observations in NMR on powder samples [22], which have field dependent transition temperatures that stay below 0.6 K up to 12 T. The origin of the anomalies is still an open question. These anomalies can arise from the interlayered Cu magnetic moments, potentially through coupling with the kagome planes. The caveat of this simple explanation is that the anomaly fields are not correlated with the concentration level of the interlayered Cu.

At low \( T \), the \( T \)-independent kagome-intrinsic susceptibility is consistent with a spinon Fermi surface state at high fields. Similar behaviors have been observed on an organic spin liquid featuring a triangular spin lattice [20]. The existence of a spinon Fermi surface at high fields is also supported by the large \( \Gamma \) term of specific heat in high fields [21], as well as the early \( ^{17}\text{O} \) NMR studies [23]. The latest theories predict magnetic ordering at higher field [24], including a field-induced spontaneous breaking of spin rotational symmetry on a kagome gapless Dirac spin liquid [25]. The transition temperature and ordered moment both scale with the applied field, at odds with our torque data and the high-field specific heat measurements [21]. For a kagome spin lattice, a magnetization plateau may exist at 1/9 of the saturation [26], which corresponds to \( \mu_0 H \sim 50 \text{T} \) [21], much higher than our anomaly fields. We further note that the anomaly fields stay almost the same as \( \vec{H} \) changes from along the \( c \) axis to the \( ab \) plane, suggesting the Heisenberg symmetry is behind these anomalies.

Although being dominated by an isotropic Heisenberg exchange, the actual spin Hamiltonian of herbertsmithite is complicated by perturbations. The leading terms are likely the Dzyaloshinskii-Moriya (DM) interaction [18,27,28], easy-axis anisotropic exchange energy [13], and coupling energy to the impurities [11], whose magnitudes are consistent with the 10% variation of the anomalous field values when rotating the crystal in field. Other perturbations are present but may be smaller, such as kagome-kagome direct coupling and second-nearest-neighbor interaction in plane [29]. In the \( T \rightarrow 0 \text{ K} \) limit, the DM interaction, for various combinations of in-plane and normal-to-plane components, causes an increasing easy-axis magnetization anisotropy [30,31]. The quantitative determination of this is hampered at \( T < 30 \text{ K} \) by the spin-cluster size. Differently, the effect of an exchange anisotropy on magnetization anisotropy shows a vanishing tendency as \( T \rightarrow 0 \text{ K} \). The combined effect of easy-axis kagome-intrinsic magnetization anisotropy due to the DM term and the easy-plane magnetization anisotropy of the impurities, both of which are on the order of 10%, might explain the weak sample magnetization anisotropy at low \( T \).

The anomaly fields are comparable to the energy scale of major perturbations. The closeness in energy may have produced those two pairs of anomalies and opened up new possibilities to explain the nature of the observed crossovers. Additional theories which include at least one of the major perturbations on a large lattice cluster are strongly desired. Further, torque magnetometry is only sensitive to magnetization anisotropy. A better understanding of our torque data requires a precise determination of uniform susceptibility in the same temperature and dc field ranges. When quantum fluctuations and geometric frustration prohibit the system from long-range spin ordering, the dynamic spin correlations at low frequencies contain essential clues which provide supplementary information to thermodynamic studies. This calls for further neutron scattering experiments at low energies and high fields. Both works are currently in progress.

**Conclusion.** We studied the high-field magnetic torque of kagome lattice single crystalline \( \text{ZnCu}_3(\text{OH})_6\text{Cl}_2 \) and observed field-induced anomalies. The field-induced anomalies that are observed between 7 T and 15 T hint at subtle changes to the correlations of the moments of interlayered Cu. The effective magnetic susceptibility is almost independent of temperature at \( 20 \text{ mK} \leq T \leq 5 \text{ K} \) at intense magnetic fields, indicating a gapless spin liquid state.

**Acknowledgments.** This work at the University of Michigan is supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering under Grant No. DE-SC0008110. The work at MIT is supported by the U.S. Department of Energy under Grant No. DE-FG02-07ER46134. T.A. acknowledges the support from the Nakajima Foundation. T.-H.H. acknowledges the support by the Grainger Fellowship from the Department of Physics, University of Chicago during data analysis and manuscript writing. B.J.L. acknowledges the support from the National Science Foundation Graduate Fellowship Grant No. F031543. We are grateful for the discussions with P.A. Lee, S. Sachdev, and Kai Sun. The high-field experiments were performed at the National High Magnetic Field Laboratory, which is supported by NSF Cooperative Agreement No. DMR-084173, by the State of Florida, and by the DOE.