Spin Dynamics of the Spin-1/2 Kagome Lattice Antiferromagnet $ZnCu_3(OH)_6Cl_2$

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(Received 19 October 2006; published 9 March 2007)

We have performed thermodynamic and neutron scattering measurements on the $S = 1/2$ kagomé lattice antiferromagnet $ZnCu_3(OH)_6Cl_2$. The susceptibility indicates a Curie-Weiss temperature of $\theta_{CW} \simeq -300$ K; however, no magnetic order is observed down to 50 mK. Inelastic neutron scattering reveals a spectrum of low energy spin excitations with no observable gap down to 0.1 meV. The specific heat at low-T follows a power law temperature dependence. These results suggest that an unusual spin liquid state with essentially gapless excitations is realized in this kagomé lattice system.

DOI: 10.1103/PhysRevLett.98.107204 PACS numbers: 75.40.Gb, 75.25.+z, 78.70.Nx

An important challenge in condensed matter physics is the search for quantum disordered ground states in two-dimensional systems. Of particular interest is studying quantum spin liquids, an example of which is the "resonating valence bond" state proposed by Anderson [1]. These states are unusual in that neither translational nor spin rotational symmetries are broken. It is believed that the $S = 1/2$ Heisenberg antiferromagnet on a kagomé lattice (composed of corner sharing triangles) is an ideal system to look for spin liquid physics due to the high degree of frustration. There is broad theoretical consensus that the ground state of the $S = 1/2$ kagomé antiferromagnet is not magnetically ordered [2–8]. However, many basic properties are still under debate, such as the magnitude of the gap to the first triplet state. An intriguing possibility is the existence of deconfined $S = 1/2$ spinons as the fundamental excitations, as opposed to conventional $S = 1$ magnons.

Despite heavy theoretical interest, experimental studies of the $S = 1/2$ kagomé lattice have been hampered by the difficulty in synthesizing such materials. Here, we report thermodynamic and neutron scattering measurements on powder samples of $ZnCu_3(OH)_6Cl_2$, known as herbertsmithite [9]. As has been previously reported [10], $Zn_xCu_{4-x}(OH)_6Cl_2$ can be synthesized with variable Zn concentration, from $x = 0$ to $x = 1$ (herbertsmithite). Figure 1(a) represents the transformation from $Cu_2(OH)_3Cl$, which has a distorted pyrochlore structure, to $ZnCu_3(OH)_6Cl_2$, which consists of Cu kagomé layers separated by nonmagnetic Zn layers. Structurally, $ZnCu_3(OH)_6Cl_2$, with space group $R\bar{3}m$ and lattice parameters $a = b = 6.832$ Å and $c = 14.049$ Å, appears to be an excellent realization of the $S = 1/2$ kagomé lattice antiferromagnet. Initial evidence is the absence of long-range magnetic order, as shown in the neutron diffraction scans in Fig. 1(b). In $Cu_2(OH)_3Cl$, clear magnetic Bragg peaks are observed below ~ 6 K; whereas no magnetic Bragg peaks are observable down to 1.8 K in $ZnCu_3(OH)_6Cl_2$.

To further characterize the properties of $ZnCu_3(OH)_6Cl_2$, we performed magnetic susceptibility measurements on powder samples. The susceptibility, shown in Fig. 1(c), can be fit to a Curie-Weiss law at high temperatures ($T > 200$ K). The resulting Curie-Weiss temperature of -300 ± 20 K implies an antiferromagnetic exchange $J \simeq 17$ meV, calculated using the series expansion corrections for the kagomé lattice [11–13]. The susceptibility continually increases as the temperature is lowered down to 1.8 K. At first glance, this behavior may suggest the presence of several percent free spin-1/2 impurities yielding a Curie tail. This is certainly possible, but is not necessarily the case. From the chemical analyses, we calculate the stoichiometric coefficients to be 3.00 ± 0.04 on the Cu site and 1.00 ± 0.04 on the Zn site. Also, we have measured the ac susceptibility at temperatures down to 50 mK, as shown in the inset of Fig. 1(c). These data do not follow the simple Brillouin function behavior expected for free $S = 1/2$ spins. In particular, the susceptibility increase from 705 to 50 mK is much smaller than the free spin prediction. Recently, Ofer and co-workers [14] have shown that the muon Knight shift and transverse relaxation rate have T dependences similar to the measured susceptibility. Hence, the measured susceptibility may be intrinsic to the Cu kagomé system. We note that similar behavior is found for the frustrated $S = 1/2$ nuclear moments of ^{3}He films on graphite, where the susceptibility is found to continually increase with decreasing temperature down to $T \sim J/300$ [15]. Another recent μSR study [16] emphasizes the role of defects. The roles of impurities and exchange or Dzyaloshinskii-Moriya [17] anisotropies in

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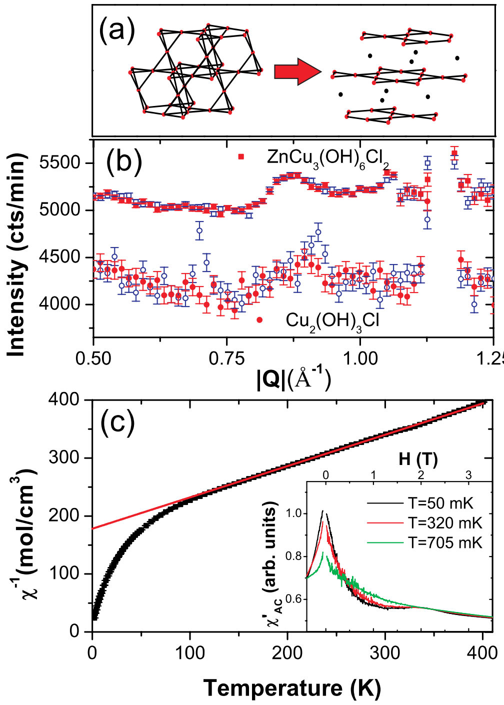

FIG. 1 (color online). (a) The chemical transformation from the pyrochlorelike lattice of $Cu_2(OH)_3Cl$ to the kagomé layers of $ZnCu_3(OH)_6Cl_2$. (b) Magnetic diffraction scans of the two systems at $T = 1.4$ K (open) and 20 K (filled). The $Cu_2(OH)_3Cl$ data show magnetic Bragg peaks at $Q \simeq 0.70$ and $Q \simeq 0.92$, which are absent for the $ZnCu_3(OH)_6Cl_2$ data (which have been shifted by 2300 counts/ min for clarity). (c) Magnetic susceptibility of $ZnCu_3(OH)_6Cl_2$ measured using a SQUID magnetometer plotted as $1/\chi$, where mole refers to a formula unit. The line denotes a Curie-Weiss fit. Inset: ac susceptibility (at 654 Hz) at low temperatures measured at the NHMFL in Tallahassee, FL.

this system remain important topics for further investigation. We also observe a small peak in the ac susceptibility near $H = 2$ T at 50 mK which disappears upon warming to 705 mK. The overall susceptibility data indicate the absence of magnetic order or a spin gap down to 50 mK.

The specific heat $C(T)$ of $ZnCu_3(OH)_6Cl_2$ is shown in Fig. 2(a) in various applied fields. For temperatures of a few Kelvin and higher, the lattice contribution to the specific heat (proportional to $\sim T^3$) is the most significant contribution, as shown in the inset. However, this contribution diminishes at low temperatures, and below $\sim$5 K, an additional contribution is clearly observed which arises from the Cu spin system. Magnetic fields of a few Tesla can significantly affect the low-T behavior, and fields of 10 T and higher strongly suppress the specific heat below 3 K. The difficulty in synthesizing an isostructural nonmagnetic compound makes it hard to subtract the lattice contribution precisely. However, the magnetic field dependence suggests that the specific heat in zero applied field below 1 K is predominately magnetic in origin. As a rough measure of the spin entropy, the field-induced change in specific heat below 3 K, obtained by subtracting the 14 T data from the zero field data, accounts for about 5% of the total entropy of the spin system.

Additional specific heat measurements at zero field at temperatures down to 106 mK were performed at the National High Magnetic Field Laboratory (NHMFL) and the combined data are shown in Fig. 2(b). The specific heat at low temperatures ($T < 1$ K) appears to be governed by a power law with an exponent which is less than or equal to 1. In a 2D ordered magnet, magnon excitations would give $C \sim T^2$. The kagomé-like compound $SrCr_{8-x}Ga_{4+x}O_{19}$ (SCGO) [18] and other 2D frustrated magnets [19] are also observed to have $C \sim T^2$ even in the absence of long-range order [20,21]. The behavior that we observe in $ZnCu_3(OH)_6Cl_2$ below 1 K stands in marked contrast. We can fit our data to the power law $C = \gamma T^{\alpha}$, though we note that the exponent α is sensitive to the chosen range of temperatures that are fit. The blue line in this figure represents a linear fit with $\alpha = 1$ over the temperature range 106 mK $< T <$ 400 mK. The fitted value for γ is 240 ± 20 mJ/K^2 Cu mole. If we include higher temperatures, the red line represents a fit with $\alpha = 2/3$ over the temperature range 106 mK $< T <$ 600 mK. Extending the fitted range to even higher temperatures can yield α values as low as 0.5.

Finally, inelastic neutron scattering measurements of the low energy spin excitations were performed on deuterated powder samples of $ZnCu_3(OD)_6Cl_2$. High resolution mea-

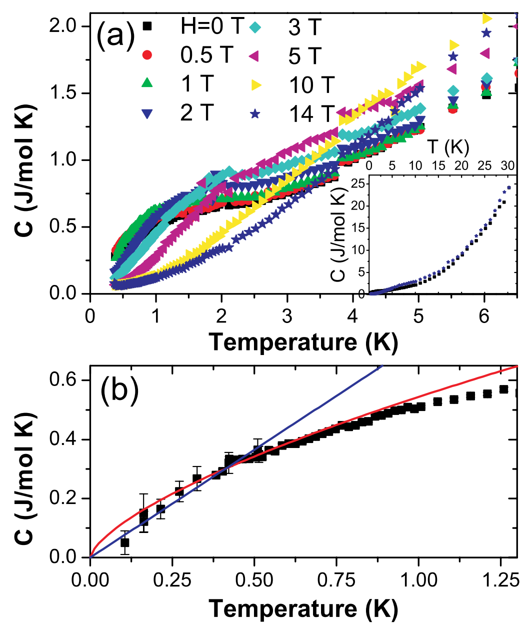

FIG. 2 (color online). (a) The specific heat $C(T)$ of $ZnCu_3(OH)_6Cl_2$ in various applied fields, measured using a Physical Property Measurement System. Inset: $C(T)$ plotted over a wider temperature range in applied fields of 0 T (square) and 14 T (star). (b) $C(T)$ in zero field measured down to 106 mK. The lines represent power law fits as described in the text.

surements were taken on the time-of-flight Disk Chopper Spectrometer (DCS) at the NIST Center for Neutron Research in Gaithersburg, MD. A sample with mass 9 g was cooled in a dilution refrigerator and studied with incident neutrons of wavelength 7 Å, yielding an instrumental energy resolution of 0.02 meV (half-width at half-maximum). As shown in Fig. 3(a), the spin excitations form a broad spectrum at low energies. A notable observation is the near temperature independence of the scattering for positive energy transfers. The excitation spectrum on the negative energy-transfer side is suppressed at low temperatures due to detailed balance.

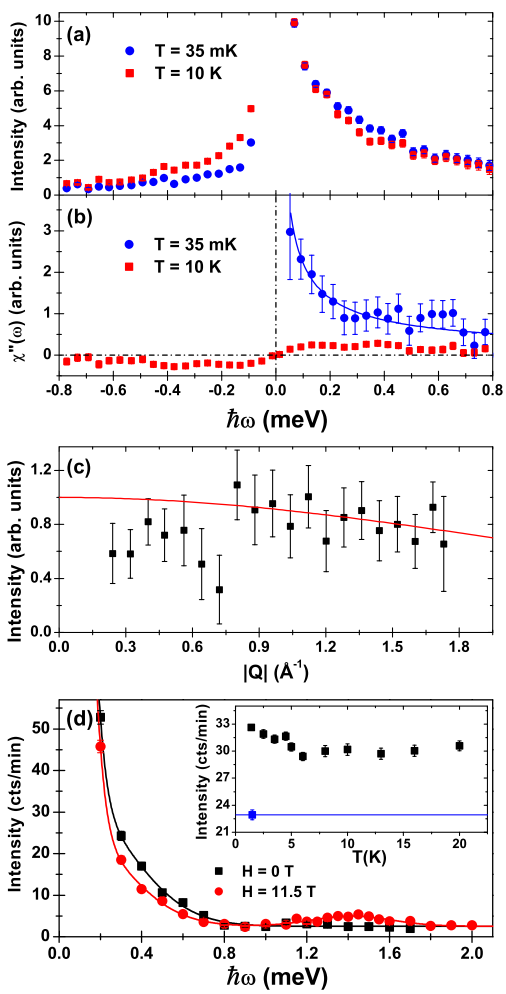

FIG. 3 (color online). (a) Inelastic neutron scattering data taken on DCS, integrated over momentum transfers $0.25 \leq |\vec{Q}| \leq 1.5$ Å^{-1}. (b) $\chi''(\omega)$, extracted from the data as described in the text. The line denotes a power law fit. (c) The Q-dependence of the scattering, integrated over energy transfers $-0.5 \leq \hbar\omega \leq -0.22$ meV. (d) Energy scans taken on SPINS at zero field and 11.5 T at $|\vec{Q}| = 0.6$ Å^{-1} and $T = 1.2$ K. The lines are guides to the eye. Inset: Temperature dependence of the scattering for $0.3 \leq \hbar\omega \leq 0.5$ meV and $|\vec{Q}| = 0.9$ Å^{-1}. The blue data point and line indicate the background, measured on the energy loss side at $T = 1.5$ K.

The magnetic scattering intensity is proportional to the dynamic structure factor $S(\vec{Q}, \omega) = [n(\omega) + 1]\chi''(\vec{Q}, \omega)$, where $n(\omega)$ is the Bose occupation factor and $\chi''(\vec{Q}, \omega)$ is the imaginary part of the dynamical susceptibility. We find that part of the measured intensity for positive energy transfers below 0.4 meV is spurious background scattering, probably caused by multiple scattering of neutrons within the sample environment. Therefore, to extract the intrinsic scattering from the sample, the following procedure was used. For negative energy transfers, $\chi''(\omega, T = 10\text{ K})$ can be obtained by subtracting the 35 mK data (which is essentially background) from the 10 K data and dividing by the Bose factor. Here, $\chi''(\omega)$ represents the dynamical susceptibility integrated over momentum transfers $0.25 \leq |\vec{Q}| \leq 1.5$ Å^{-1} and is a good measure of the local response function. This is plotted in Fig. 3(b), where the positive ω data is obtained by using the fact that $\chi''(\omega)$ is an odd function of ω. Then, $\chi''(\omega, T = 35\text{ mK})$ can be extracted from the positive energy-transfer data using $S(\omega; T = 35\text{ mK}) - S(\omega; T = 10\text{ K}) = I(\omega; T = 35\text{ mK}) - I(\omega; T = 10\text{ K})$, where $I(\omega)$ is the measured intensity and the background is assumed to be temperature independent between 35 mK and 10 K. As seen in Fig. 3(b), the data for $\chi''(\omega)$ at $T = 35$ mK increase with decreasing ω, indicating the absence of a spin gap down to 0.1 meV. Moreover, the data may be described by a simple power law; the solid line represents a fit to the form $\chi''(\omega) \propto \omega^{\gamma}$ with an exponent $\gamma = -0.7 \pm 0.3$. This apparently divergent behavior is unusual and again differs markedly from measurements on SCGO [22] which yield $\gamma \simeq 0$. Of course, within the errors, we cannot rule out other functional forms for $\chi''(\omega)$.

The Q dependence of the scattering is shown in Fig. 3(c). These data were obtained by integrating over energy transfers $-0.5 \leq \hbar\omega \leq -0.22$ meV and subtracting the 35 mK data set from the 10 K data set. We find that the data appear to be only weakly dependent on $|\vec{Q}|$. Note that due to the polycrystalline form of the sample, the data represents the powder average of the scattering from a crystal. The solid line represents the squared form factor $|F|^2$ for the Cu^{2+} ion. The deviations of the data from $|F|^2$ suggest that the structure factor is not completely independent of $|\vec{Q}|$. That is, some degree of spin correlations are necessary to account for the relative reduction in scattering at small $|\vec{Q}|$. The overall diffuse nature of the scattering points to the absence of a well-defined length scale to describe these correlations.

Further measurements were taken using the triple-axis SPINS spectrometer at the NCNR with the sample mounted inside a superconducting magnet, as shown in Fig. 3(d). The instrument was configured in a horizontally focusing analyzer geometry with $E_f = 3.05$ meV and collimations of guide-80′-radial-open. A BeO filter was placed in the scattered beam to reduce higher-order neutron contamination. The resulting instrumental energy resolution was about 0.06 meV. An applied field of 11.5 T transfers spectral weight from lower to higher energies. This demonstrates that a significant fraction of the low energy scattering is magnetic in origin, since the incoherent and phonon background would not respond to the applied field in this manner. The magnetic signal in zero field extends down to below 0.2 meV, consistent with the analysis of the above DCS data. In 11.5 T, the magnetic signal becomes peaked around $\hbar\omega \simeq 1.4$ meV, which is close to the Zeeman energy $g\mu_B H$. However, the half-width of this peak of about 0.21 meV is significantly broader than the resolution. Therefore, the peak does not simply originate from Zeeman excitations of noninteracting spins, which would result in a narrow energy peak, but involve spins which are part of the interacting system. The integrated spectral weight of the zero field magnetic signal for $\hbar\omega < 1$ meV accounts for at most 20% of the total scattering expected from a $S = 1/2$ spin system (an estimate made by normalization to the incoherent elastic scattering from the sample and also to a vanadium standard). The inset of Fig. 3(d) shows the temperature dependence of the inelastic signal with energy transfers integrated over the range $0.3 \leq \hbar\omega \leq 0.5$ meV. There is a small increase in the signal when the sample is cooled below $\sim$5 K, though, for the most part, the intensity is largely independent of temperature in this range.

Our experimental results suggest an intriguing picture for the ground state properties of the $S = 1/2$ kagomé lattice antiferromagnet. A hallmark of the quantum spin liquid in two dimensions is the existence of deconfined $S = 1/2$ spinons as the fundamental magnetic excitation. A rich variety of spin liquid states have been theoretically proposed in which the spinons can be described as bosonic [6,8,23], fermionic [24,25], or even as Dirac fermions [26]. We note that several of these theories are based on triangular lattice Hamiltonians, and they may not have clear extensions to the kagomé lattice antiferromagnet. Using a naive comparison to a generic model of fermionic spinons with a Fermi surface, one would expect $C = \gamma T$. From our linear fit below 400 mK, the value of γ indicates a Fermi temperature of $T_F \sim 110$ K. However, other forms for the specific heat (such as $C \propto T^2$ [26]) may hold at higher temperatures where the lattice contribution prevents us from clearly identifying the magnetic contribution.

The neutron scattering measurements of the excitation spectrum at low temperatures are also consistent with expectations of deconfined spinons in a spin liquid. We find no evidence of a spin gap down to $\sim J/170$, much lower than the prediction from exact diagonalization studies for a spin gap of $\sim J/20$ [7]. The power law behavior of $\chi''(\omega)$ is interesting and may indicate a spin liquid with critical spin correlations [27]. Our observation of a diffuse Q dependence for the inelastic scattering suggests that if a singlet spin liquid picture is correct, then the singlets are not restricted to nearest neighbor dimers, since no well-defined length scale is indicated by the data. The near temperature independence of $S(\vec{Q}, \omega)$, similar to observations in f-electron systems [28], may indicate the proximity to a quantum critical point. Many of the current theories for 2D spin liquids were formulated to describe experimental results [29,30] for $S = 1/2$ triangular lattice systems. More theoretical studies based explicitly on the $S = 1/2$ kagomé Heisenberg antiferromagnet (including the possible effects of impurities and exchange or Dzyaloshinskii-Moriya anisotropies) are certainly important for further comparisons with experimental results.

We thank P. A. Lee, A. Keren, J. W. Lynn, Q. Huang, T. Senthil, and X.-G. Wen for useful discussions and E. Palm and T. Murphy for help with the measurements at the NHMFL. The work at MIT was supported by the NSF under Grant No. DMR 0239377, and in part by the MRSEC program under Grant No. DMR 02-13282. This work used facilities supported in part by the NSF under Agreement No. DMR-0454672. A portion of this work was performed at the NHMFL, which is supported by NSF Cooperative Agreement No. DMR-0084173, by the State of Florida, and by the DOE.

[1] P. W. Anderson, Science **235**, 1196 (1987).
[2] G. Misguich and C. Lhuillier, in *Frustrated Spin Systems*, edited by H. T. Diep (World Scientific, Singapore, 2004).
[3] C. Zeng and V. Elser, Phys. Rev. B **42**, 8436 (1990).
[4] J. Marston and C. Zeng, J. Appl. Phys. **69**, 5962 (1991).
[5] R. Singh and D. Huse, Phys. Rev. Lett. **68**, 1766 (1992).
[6] S. Sachdev, Phys. Rev. B **45**, 12 377 (1992).
[7] C. Waldtmann *et al.*, Eur. Phys. J. B **2**, 501 (1998).
[8] F. Wang and A. Vishwanath, cond-mat/0608129.
[9] R. Braithwaite *et al.*, Mineral. Mag. **68**, 527 (2004).
[10] M. Shores *et al.*, J. Am. Chem. Soc. **127**, 13 462 (2005).
[11] A. B. Harris *et al.*, Phys. Rev. B **45**, 2899 (1992).
[12] D. Grohol *et al.*, Nat. Mater. **4**, 323 (2005).
[13] K. Matan *et al.*, Phys. Rev. Lett. **96**, 247201 (2006).
[14] O. Ofer and A. Keren *et al.*, cond-mat/0610540.
[15] R. Masutomi *et al.*, Phys. Rev. Lett. **92**, 025301 (2004).
[16] P. Mendels *et al.*, cond-mat/0610565.
[17] M. Rigol and R. R. P. Singh, cond-mat/0701087.
[18] A. P. Ramirez *et al.*, Phys. Rev. Lett. **64**, 2070 (1990).
[19] S. Nakatsuji *et al.*, Science **309**, 1697 (2005).
[20] P. Sindzingre *et al.*, Phys. Rev. Lett. **84**, 2953 (2000).
[21] G. Misguich and B. Bernu, Phys. Rev. B **71**, 014417 (2005).
[22] C. Broholm *et al.*, Phys. Rev. Lett. **65**, 3173 (1990).
[23] S. Isakov *et al.*, Phys. Rev. B **72**, 174417 (2005).
[24] S. Lee and P. Lee, Phys. Rev. Lett. **95**, 036403 (2005).
[25] O. I. Motrunich, Phys. Rev. B **72**, 045105 (2005).
[26] Y. Ran *et al.*, cond-mat/0611414.
[27] B. Altshuler *et al.*, Phys. Rev. B **50**, 14 048 (1994).
[28] M. C. Aronson *et al.*, Phys. Rev. Lett. **75**, 725 (1995).
[29] R. Coldea *et al.*, Phys. Rev. B **68**, 134424 (2003).
[30] Y. Shimizu *et al.*, Phys. Rev. Lett. **91**, 107001 (2003).