Revealing quantum spin liquid in the herbertsmithite \( \text{ZnCu}_3(\text{OH})_6\text{Cl}_2 \)

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Based on experimental data and our theoretical analysis, we provide a strategy for unambiguous establishing of gapless quantum spin liquid state (QSL) in herbertsmithite and other materials. To clarify the nature of QSL, we recommend measurements of heat transport, low-energy inelastic neutron scattering and optical conductivity under the application of external magnetic field at low temperatures. We also suggest that artificially introduced inhomogeneity into \( \text{ZnCu}_3(\text{OH})_6\text{Cl}_2 \) can stabilize QSL, and serves as a test elucidating the contribution coming from impurities. We predict the results of these measurements in the case of gapless QSL.

PACS numbers: 64.70.Tg, 75.40.Gb, 78.20.-e, 71.10.Hf

In a geometrically frustrated magnet, spins are prevented from forming an ordered alignment, so that even at temperatures close to absolute zero they collapse into a liquid-like state called a quantum spin liquid (QSL). The herbertsmithite \( \text{ZnCu}_3(\text{OH})_6\text{Cl}_2 \) has been exposed as a gapless quantum spin liquid. The experimental data are derived from high-resolution low-energy inelastic neutron scattering on \( \text{ZnCu}_3(\text{OH})_6\text{Cl}_2 \) single-crystal. The impurity model assumes that the corresponding ensemble may be represented as a simple cubic lattice in the dilute limit below the percolation threshold. The model then suggests that in the absence of magnetic fields the bulk spin susceptibility \( \chi \) exhibits a divergent Curie-like tail, indicating that some of the \( \text{Cu} \) spins act like weakly coupled impurities [7, 17, 18]. The same behavior is recently reported in a new kagome quantum spin liquid candidate \( \text{Cu}_2\text{Zn}(\text{OH})_6\text{FBr} \) [20]. As a result, we observe a challenging contradiction between two sets of experimental data when some of them state the absence of a gap, while the other present evidences in the favor of gap.

Main goal of our letter is to attract attention to experimental studies of \( \text{ZnCu}_3(\text{OH})_6\text{Cl}_2 \) that can unambiguously reveal both the physics of QSL and the existence, or absence, of a possible gap in spinon excitations that form the thermodynamic, transport and relaxation properties. To unambiguously clarify the nature of QSL in herbertsmithite, we recommend the measurements of heat transport, low-energy inelastic neutron scattering and optical conductivity \( \sigma \) in \( \text{ZnCu}_3(\text{OH})_6\text{Cl}_2 \) subjected to external magnetic field. We suggest that the influence of impurities on the properties of \( \text{ZnCu}_3(\text{OH})_6\text{Cl}_2 \) can be tested by varying \( x \). We predict results of these measurements.

To analyze the QSL properties theoretically, we employ the strongly correlated quantum spin liquid (SCQSL) model [9, 11, 13]. A simple kagome lattice may have a dispersionless topologically protected branch of the quasi-particle spectrum with zero excitation energy, that is the
so-called flat band [9, 11, 21, 22]. In that case a topological fermion condensation quantum phase transition (FCQPT) can be considered as QCP of the ZnCu$_3$(OH)$_6$Cl$_2$, with SCQSL is composed of heavy fermions, or spinons, with zero charge and effective mass $M^*$, occupying the corresponding Fermi sphere with the Fermi momentum $p_F$. Consequently, the properties of insulating magnets coincide with those of heavy-fermion metals with one exception: Namely, typical insulator resists the electric current [9–13, 21].

At $B = 0$, contrary to the Landau Fermi liquid (LFL) behavior, where the effective mass $M^*$ is approximately constant, this quantity becomes strongly temperature dependent, demonstrating the non-Fermi liquid (NFL) behavior [9]

$$M^*(T) \simeq a_T T^{-2/3}. \quad (1)$$

At finite $T$, the system transits to the LFL behavior, being subjected to the magnetic field

$$M^*(B) \simeq a_B B^{-2/3}. \quad (2)$$

The introduction of “internal” (or natural) scales greatly simplifies understanding the thermodynamic, transport and relaxation properties [9]. Namely, near FCQPT the effective mass $M^*(B, T)$ reaches its maximal value $M^*_M$ at certain temperature $T_M \propto B$. Hence, to measure the effective mass and temperature, it is convenient to introduce the scales $M^*_M$ and $T_M$ respectively, see Fig. 1. This generates the normalized effective mass $M^*_N = M^*/M^*_M$ and the temperature $T_N = T/T_M$. Near FCQPT the normalized effective mass $M^*_N(T_N)$ can be well approximated by a simple universal interpolating function. The interpolation occurs between the LFL and NFL states, reflecting the universal scaling behavior of $M^*_N$ [9]

$$M^*_N(y) \approx c_0 \frac{1 + c_1 y^2}{1 + c_2 y^{8/3}}. \quad (3)$$

Here, $y = T_N = T/T_M$, $c_0 = (1 + c_2)/(1 + c_1)$, where $c_1$ and $c_2$ are free parameters. The magnetic field $B$ enters only in the combination $\mu_B B/T$, making $T_M \sim \mu_B B$. It follows from Eq. (3) that

$$T_M \simeq a_1 \mu_B B, \quad (4)$$

where $a_1$ is a dimensionless factor, $\mu_B$ is the Bohr magneton. Thus, in the presence of magnetic field the variable $y$ becomes $y = T/T_M \sim T/\mu_B B$. Expression (4) permits to conclude that Eq. (3) describes the scaling behavior of the effective mass as a function of $T$ and $B$. The curves $M^*_N$ at different magnetic fields $B$ merge into a single one in terms of the normalized variable $y = T/T_M$. Since the variables $T$ and $B$ enter symmetrically, Eq. (3) also describes the scaling behavior of $M^*_N(B, T)$ as a function of $B$ at fixed $T$.

To examine the impurity model, we first refer to the experimental behavior of the magnetic susceptibility $\chi$ of herbertsmithite. It is seen from Fig. 1 that the magnetic susceptibility diverges $\chi(T) \propto T^{-2/3}$ in magnetic fields
that LFL behavior of the magnetic susceptibility $\chi$ is demonstrated at least for $B \geq 3$ T and low temperatures $T$. At such temperatures and magnetic fields the impurities should become fully polarized. Thus, assuming the impurities are fully polarized and hence do not contribute to $\chi$, one has simply $\chi_{kag}(T) = \chi(T)$. Analogous behavior of the heat capacity follows from Fig. 3. LFL behavior of $C_{mag}/T$ emerges under the application of the same fields. Consequently, we may conclude that at least at $B \geq 3$ T and $0.2 \leq T \leq 2$ K, the contributions to both $\chi$ and $C_{mag}/T$ from the impurities are negligible; rather, one expects them to be dominated by the kagome lattice, exhibiting a spin gap in the kagome layers \cite{7,16,17}. Thus, one would expect both $\chi(T)$ and $C_{mag}(T)/T$ to approach zero at $T \leq 2$ K and $B \geq 3$ T. It is clear from Figs. 1, 2, and 3, that this is not the case. These conclusions agree with recent experimental findings that the low-temperature plateau in local susceptibility identifies the spin-liquid ground state as gapless one \cite{24}, while recent theoretical analysis confirms the absence of a gap \cite{15,25}. Moreover, we suggest that the growing $x$, elevating randomness and inhomogeneity of the lattice and therefore facilitating the frustration of the lattice, can stabilize QSL. This observation can be tested in experiments on samples of herbertsmithite with different $x$ under the application of magnetic field.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3}
\caption{(Color online) Specific heat $C_{mag}/T$ measured on powder \cite{2,3} and single-crystal \cite{4-6} samples of herbertsmithite is displayed as a function of temperature $T$ for fields $B$ shown in the legend.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig4}
\caption{(Color online) Scaling behavior of the normalized dynamic spin susceptibility ($T^{2/3}/\chi'')_{N}$. Data are extracted from measurements on the herbertsmithite ZnCu$_3$(OH)$_6$Cl$_2$ \cite{1}. Solid curve: Theoretical calculations based on Eq. (6) \cite{10,12}.}
\end{figure}

The same outcomes can be drawn from the results of neutron-scattering measurements of the dynamic spin susceptibility $\chi(q, \omega, T) = \chi'(q, \omega, T) + i\chi''(q, \omega, T)$ as a function of momentum $q$, frequency $\omega$, and temperature $T$. Indeed, these results play a crucial role in identifying the properties of the quasiparticle excitations involved.
At low temperatures, such measurements reveal that the corresponding quasiparticles—of a new type—inulator—are represented by spinons, form a continuum, and populate an approximately flat band crossing the Fermi level [26]. The imaginary part $\chi''(T, \omega_1)$ satisfies the equation [10, 12]

$$T^{2/3}\chi''(T, \omega_1) \simeq \frac{a_1 \omega_1}{1 + a_2 \omega_1^2}, \quad (5)$$

where $a_1$ and $a_2$ are constants and $\omega_1 = \omega/(T)^{2/3}$. It is seen from Eq. (5) that $T^{2/3}\chi''(T, \omega_1)$ has a maximum $(T^{2/3}\chi''(T, \omega_1))_{\text{max}}$ at some $\omega_{\text{max}}$ and depends on the only variable $\omega_1$. Equation (5) confirms the scaling behavior of $\chi'' T^{0.66}$ experimentally established in Ref. [1].

Similar to Eq. (3), we introduce the dimensionless function $(T^{2/3}\chi''(T, \omega_1))_{\text{max}} = T^{2/3}\chi''/(T^{2/3}\chi''_{\text{max}})$ and the (dimensionless) variable $\omega_N = \omega_1/\omega_{\text{max}}$. In this case, Eq. (5) is modified to read

$$\left(T^{2/3}\chi''(T, \omega_1)\right)_{\text{max}} \simeq \frac{b_1 \omega_N}{1 + b_2 \omega_N^2}, \quad (6)$$

with $b_1$ and $b_2$ being fitting parameters. Their role is to adjust the function on the right hand side of Eq. (6) to reach its maximum value 1 at $\omega_N = 1$. In such a situation it is expected that the dimensionless normalized susceptibility $(T^{2/3}\chi'')(T, \omega_1))_{\text{max}} = T^{2/3}\chi''/(T^{2/3}\chi''_{\text{max}})$ exhibits scaling as a function of the dimensionless energy variable $\omega_N$, as it is seen from Fig. 4. We predict that if measurements of $\chi''$ are taken at fixed $T$ as a function of $B$, then with respect to Eq. (2), we again obtain that the function $B^{2/3}\chi''(\omega)$ exhibits the scaling behavior with $\omega_N = \omega_1/\omega_{\text{max}}$

$$(B^{2/3}\chi''(\omega))_{\text{max}} \simeq \frac{d_1 \omega_N}{1 + d_2 \omega_N^2}, \quad (7)$$

Similarly, $d_1$ and $d_2$ are fitting parameters adjusted such that the function $(B^{2/3}\chi'')(T, \omega_1))_{\text{max}}$ reaches unity at $\omega_N = 1$. If the system is exactly at a FCQPT point, the above scaling is valid down to lowest temperatures. It would also be crucial to carry out the measurements of low energy inelastic neutron scattering on ZnCu$_3$(OH)$_6$Cl$_2$ single crystals under the application of relatively high magnetic fields. Latter measurements permit to directly observe possible gap since in this case the contribution from supposed impurities is negligible, as we have seen above in the case of the spin susceptibility $\chi$.

Measurements of heat transport are particularly salient in that they probe the low-lying elementary excitations of QSL in ZnCu$_3$(OH)$_6$Cl$_2$ and potentially reveal itinerant spinons that are mainly responsible for the heat transport. Surely, the overall heat transport is contaminated by the phonon contribution; however, this contribution is hardly affected by the magnetic field $B$. SCQSL in herbertsmithite behaves like the electron liquid in HF metals—provided the charge of an electron is set to zero. As a result, the thermal resistivity $w$ of the SCQSL is given by [10, 13, 14]

$$w - w_0 = W_r T^2 \propto \rho - \rho_0 \propto (M^*)^2 T^2, \quad (8)$$

where $W_r T^2$ represents the contribution of spinon-spinon scattering to thermal transport, being analogous to the contribution $AT^2$ from electron-electron scattering to charge transport, and $\rho$ is the longitudinal magnetoresistivity (LMR). Also, $w_0$ and $\rho_0$ are the residual thermal and electric resistivity respectively. Now, we consider the effect of a magnetic field $B$ on the spin-lattice relaxation rate $1/(T_1 T)$.

As seen from Fig. 5 A for $B \leq B_{\text{inf}}$ (or $B_N \leq 1$) the normalized relaxation rate $1/(T_1 T)_{\text{N}}$ depends weakly on the magnetic field. Data for $(1/T_1 T)_{\text{N}}$ at different temperatures [29] listed in the legend. The inflection point at which the normalization is taken is indicated by the arrow. Panel (B). Magnetic field dependence of the normalized magnetoresistance $\rho_N$, extracted from LMR of YbRh$_2$Si$_2$ at different temperatures [29] is depicted by the same solid curve, tracing the scaling behavior of $W_r \propto (M^*)^2$ (see Eqs. (8) and (9)).
Thus, we predict that the application of a magnetic field $B$ leads to a crossover from NFL to LFL behavior and to a significant reduction in both the relaxation rate and the thermal resistivity, as the normalized LMR of YbRh$_2$Si$_2$ does, see Fig. 5 B.

Our next step is analysis of the herbertsmithite low-frequency optical conductivity $\sigma$. To avoid the contribution of phonon absorption into the conductivity, we consider low temperatures $T$ and frequencies $\omega$ [30]. This is because the above contribution becomes substantial at elevated $T$ and $\omega$ [31]. In the case of QSL the optical conductivity is given by [30]

$$\sigma(\omega) \propto \omega \chi''(\omega) \propto \omega^2(M^*)^2.$$  \hfill (10)

It follows from Eq. (10) that $\sigma(\omega) \propto \omega^2$, and that behavior is consistent with experimental facts obtained in measurements on ZnCu$_3$(OH)$_6$Cl$_2$ and EtMe$_3$Sb[Pd(dmit)$_2$]$_2$ representing the best candidates for identification as a material that hosts QSL [31, 32]. It is seen from Eqs. (1) and (10), that at elevated temperatures the low-frequency optical conductivity is a decreasing function of $T$. This observation is consistent with the experimental data [31], see also [33]. It also follows from Eqs. (2) and (10) that $\sigma(\omega)$ diminishes under the application of magnetic fields. This observation seems to contradict the experimental results since no systematic magnetic field dependence is observed [31]. To elucidate the magnetic field dependence of $\sigma(B)$, we note that measurements of $\sigma(B)$ have been taken at 6 K and the magnetic fields $B \leq 7$ T [31]. In such a case the system is still in the transition regime and does not enter into the LFL state at which the effective mass $M^*$ is given by Eq. (2) [9]. Therefore, in this case the effective mass behavior is determined by Eq. (1), rather than by Eq. (2), and the $\sigma(B)$ dependence cannot be observed. As a result, we predict that the $B$-dependence of $\sigma$ can be observed at $B \simeq 7$ T provided that $T \leq 1$ K. In that case, as it seen from Fig. 3, at $T \leq 1$ K the effective mass $M^* \propto C_{\text{mag}}/T$ is a diminishing function of the applied magnetic field. Thus, we predict that $\sigma(B)$ diminishes at growing magnetic fields, as it follows from Eqs. (2) and (10). We note that the above experiments on measurements of the heat transport and optical conductivity can be carried out on samples with different $x$. As a result, these experiments allow us to test the influence of impurities on the value of the gap. We predict that at moderate $x \sim 20\%$ QSL remains robust, for both the inhomogeneity and randomness facilitate frustration.

In summary, the main message of our paper is to suggest performing the above discussed heat transport, low energy inelastic neutron scattering, and optical conductivity $\sigma$ measurements on ZnCu$_3$(OH)$_6$Cl$_2$ subjected to external magnetic fields. We have suggested that growing $x$, characterizing % of the Zn sites that are occupied by Cu, can facilitate the frustration of the lattice, and thus can stabilize QSL. This observation can be tested in experiments on samples of herbertsmithite with different $x$. Considered measurements can give an unambiguous answer if a real gap in spinon excitations, determining the thermodynamic, transport and relaxation properties of insulating magnets, exists, or does not exists, and how it depends on impurities. Such measurements pave a new avenue for technological applications of the magnets.

We are grateful to V.A. Khodel for valuable discussions. This work was partly supported by U.S. DOE, Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research. JWC acknowledges support from the McDonnell Center for the Space Sciences, and expresses gratitude to the University of Madeira and its branch of Centro de Investigação em Matemática e Aplicações (CIMA) for gracious hospitality during periods of extended residence.

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References:

[1] J.S. Helton et al., Phys. Rev. Lett. 104, 147201 (2010).
[2] J.S. Helton et al., Phys. Rev. Lett. 98, 107204 (2007).
[3] M.A. deVries et al., Phys. Rev. Lett. 100, 157205 (2008).
[4] T.H. Han et al., Phys. Rev. B 83, 100402(R) (2011).
[5] T.H. Han, S. Chu, and Y.S. Lee, Phys. Rev. Lett. 108, 157202 (2012).
[6] T.H. Han et al., arXiv:1402.2693 (2014).
[7] T.H. Han et al., Phys. Rev. B 94, 060409(R) (2016).
[8] H. Yamaguchi et al., Scient. Rep. 7, article number: 16144 (2017) doi:10.1038/s41598-017-16431-0.
[9] V.R. Shaginyan, M.Ya. Amusia, A.Z. Msezane, and K.G. Popov, Phys. Rep. 492, 31 (2010).
[10] M.Ya. Amusia, K.G. Popov, V.R. Shaginyan, and V.A. Stephanovich, Theory of Heavy-Fermion Compounds, Springer Series in Solid-State Sciences 182 (2015).
[11] V.R. Shaginyan, A.Z. Msezane, and K.G. Popov, Phys. Rev. B 84, 060401(R) (2011).
[12] V.R. Shaginyan, A.Z. Msezane, K.G. Popov, and V.A. Khodel, Phys. Lett. A 376, 2622 (2012).
[13] V.R. Shaginyan et al., Europhys. Lett. 97, 56001 (2012).
[14] V.R. Shaginyan et al., Europhys. Lett. 103, 67006 (2013).
[15] H.J. Liao et al., Phys. Rev. Lett. 118, 137202 (2017).
[16] M. Fu, T. Imai, T.H. Han, and Y.S. Lee, Science 350, 655 (2015).
[17] T. Imai, M. Fu, T.H. Han, and Y.S. Lee, Phys. Rev. B 84, 020411(R) (2011).
[18] M.R. Norman, Rev. Mod. Phys. 88, 041002 (2016).
[19] Y. Zhou, K. Kanoda, and T.-K. Ng, Rev. Mod. Phys. 89, 025003 (2017).
[20] Z. Feng et al., Chin. Phys. Lett. 34, 077502 (2017).
[21] V.R. Shaginyan et al., J. Low Temp. Phys. 189, 410 (2017).
[22] D. Green, L. Santos, and C. Chamon, Phys. Rev. B 82, 075104 (2010).
[23] P. Gegenwart et al., New J. Phys. 8, 171 (2006).
[24] M. Gomilsek et al., Phys. Rev. B 94, 024438 (2016).
[25] H.J. Liao et al., Phys. Rev. Lett. 118, 137202 (2017).
[26] T.H. Han et al., Nature 492, 406 (2012).
[27] T. Imai et al., Phys. Rev. Lett. 100, 077203 (2008).
[28] P. Carretta, R. Pasero, M. Giovannini, and C. Baines, Phys. Rev. B 79, 020401(R) (2009).
[29] P. Gegenwart et al., Science 315, 969 (2007).
[30] V.R. Shaginyan et al., J. Low Temp. Phys. 191, 4 (2018).
[31] D.V. Pilon et al., Phys. Rev. Lett. 111, 127401 (2013).
[32] A. Pustogow et al., arXiv:1803.01553.
[33] T.-K. Ng and P. A. Lee, Phys. Rev. Lett. 99, 156402 (2007).