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μSR insight into the impurity problem in quantum kagome antiferromagnets

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Impurities, which are unavoidable in real materials, may play an important role in the magnetism of frustrated spin systems with a spin-liquid ground state. We address the impurity issue in quantum kagome antiferromagnets by investigating $ZnCu_3(OH)_6SO_4$ (Zn-brochantite) by means of muon spin spectroscopy. We show that muons dominantly couple to impurities, originating from Cu-Zn intersite disorder, and that the impurity spins are highly correlated with the kagome spins, allowing us to probe the host kagome physics via a Kondo-like effect. The low-temperature plateau in the impurity susceptibility suggests that the kagome spin-liquid ground state is gapless. The corresponding spin fluctuations exhibit an unconventional spectral density and a nontrivial field dependence.

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The two-dimensional Heisenberg quantum kagome antiferromagnet (QKA), the paradigm of geometrical frustration, has been the focus of attention for several years [1,2]. Theoretical studies have lately converged on a spin-liquid (SL) ground state [3–8], most likely with a finite gap to magnetic spinon excitations [5–7]. Although early experiments, on the contrary, spoke in favor of a gapless ground state [9–12], experimental evidence of a gapped SL has also recently been presented [13,14]. The confusion about the gap likely stems from the fact that all known QKA representatives contain a significant amount of defects that may affect their ground state, on top of other perturbations, such as magnetic anisotropy [15–19] and exchange interactions beyond the nearest neighbors [10,19–22]. In particular, it is difficult to discern the magnetic response of the impurity spins from that of the kagome spins, which makes identification of their influence on the ground state elusive [23–28].

In herbertsmithite, the most extensively studied QKA representative to date [29], a sizable amount (5%–10%) of Cu-Zn intersite disorder is present [9,30,31]. The general consensus is that these defects contribute significantly to the bulk magnetic response, but only at low energies ($E \lesssim 0.7$ meV) and at low temperatures ($T/J \lesssim 1/20$) [14,32–34]. Even though the defects are often described as quasifree spin-$\frac{1}{2}$ impurities [29], their relation with the kagome spins is yet unsettled [13,14,35,36]. It is important to resolve this issue, because a strong coupling would mean that defects could be intimately involved in the selection of a particular ground state of the QKA.

We provide a unique perspective on the impurity problem by investigating another QKA representative, the recently synthesized $ZnCu_3(OH)_6SO_4$ (Zn-brochantite) [12], which bears a resemblance to herbertsmithite in many respects. Despite a sizable average intraplane exchange interaction of $J = 65$ K [12], it remains magnetically disordered down to at least $T/J = 1/3000$ [37]. Moreover, just as herbertsmithite [32], it exhibits scale-free magnetic fluctuations at high T's that are reminiscent of a critical correlated state [37]. Finally, the two compounds are also similar regarding defects. The amount of the Cu-Zn intersite disorder (6%–9%) and the effective Weiss temperature of impurities ($\sim$1 K) in Zn-brochantite [12] both match those in herbertsmithite [29]. However, the SL behavior of Zn-brochantite is even more perplexing, as two SL instabilities have recently been found at different temperatures [37]. Here, the impurities may play an important role by pinning spinons at low T's and thus enabling a spinon-instability mechanism.

We tackle the impurity problem in QKA's by performing muon spin relaxation and rotation (μSR) measurements on Zn-brochantite. At low T's, the muons are expected to be dominantly influenced by impurities through the long-range dipolar interaction [37]. Such a scenario was indeed confirmed in herbertsmithite, where, however, the presence of a coupling between the impurity spins and the kagome spins remains unresolved [35]. If the impurities are coupled to the correlated state of the host, as they are in high-T_c superconductors and in many other strongly correlated electron systems [38,39], the muons may indirectly probe subtle correlations of the host state. Moreover, the screening response of spinon excitations to impurities should strongly depend on the particular SL ground state [40], which could then be determined by μSR. Here, we demonstrate that in Zn-brochantite muons detect the impurity magnetism at low T's and that intrinsic correlations between the impurity spins and the kagome spins due to a Kondo-like effect are indeed present. The observed low-T local-susceptibility plateau is consistent with a gapless host SL featuring a spinon Fermi surface [40]. Moreover, this SL state is characterized by unusual spin dynamics with an intriguing magnetic field dependence.

μSR is a sensitive probe of magnetism that can easily distinguish between static and dynamic local magnetic fields B_μ [41]. In our previous μSR study in a small longitudinal field (LF) applied along the initial muon polarization, we showed that a dynamical magnetic state remains present in Zn-brochantite at least down to 21 mK [37]. Here, we build on this investigation by performing muon spin rotation measurements in a transverse magnetic field (TF) of 0.3 T, as well as muon spin relaxation measurements in various LFs. The magnetic field B_0 was applied along the muon beam

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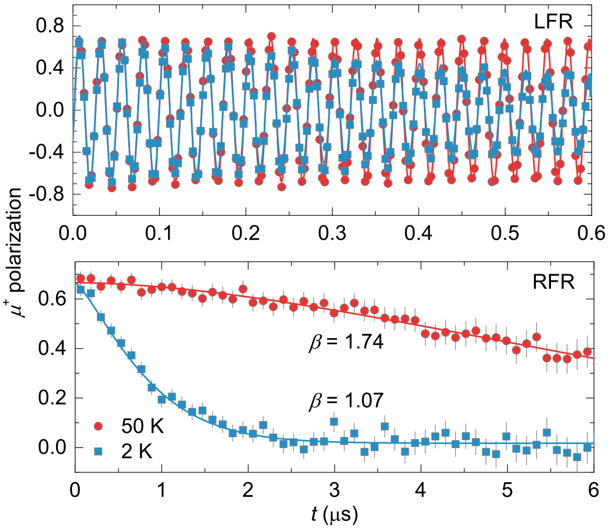

FIG. 1. The μ^+ polarization in Zn-brochantite in a TF of 0.3 T in the laboratory frame of reference (LFR; upper panel) and in the rotating frame of reference (RFR; lower panel), the latter rotating with the Larmor frequency ν and thus displaying the envelope of the oscillations in the LFR. Symbols show the measurements and solid lines depict the fits, which are further explained in the text.

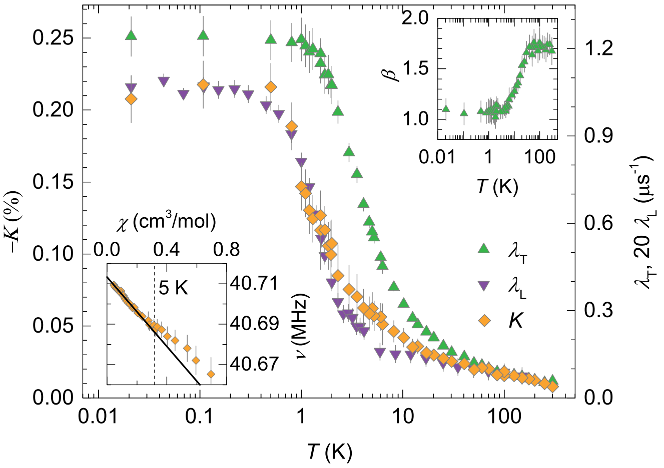

FIG. 2. The T dependence of the Knight shift K and the transverse relaxation rate λ_T in Zn-brochantite in a TF of 0.3 T. The data for the longitudinal relaxation rate λ_L in a magnetic field of 8 mT are reproduced from Ref. [37]. The lower inset displays the linear scaling of the mean precession frequency with the bulk susceptibility [12] at low susceptibility values (high T's). The extrapolation line yields $\nu_0 = 40.713$ MHz. The upper inset shows the T dependence of the stretching exponent in the TF experiment.

direction, with the initial muon polarization parallel to it in the LF experiment and tilted by ~45° from it in the TF experiment. μSR measurements were conducted on the General Purpose Surface Muon (GPS) and the Low Temperature Facility (LTF) instruments at the Paul Scherrer Institute, Switzerland on a ~100% deuterated Zn-brochantite powder sample from the same batch as the one used in our previous study [37]. A deuterated sample was used to minimize muon relaxation due to nuclear magnetic fields [37]. The GPS instrument was operated in the veto mode, which minimized the amount of background signal below the detection limit, while the background in the LTF experiment (~20% of the total signal) was determined by comparing the muon polarization curves from GPS and LTF and then subtracted from raw data.

Typical TF μSR polarization curves for low and high T's are shown in Fig. 1. In the TF experiment the muon polarization $P(t)$ precesses around the direction of B_0 with the Larmor frequency ν. The TF data are well described by the model $P_{\mathrm{TF}}(t) = P_0 \cos(2\pi\nu t - \phi) e^{-(\lambda_{\mathrm{T}} t)^\beta}$, where $\phi \sim \pi/2$, $P_0 = 0.70$ is the projection of the initial muon polarization on the plane perpendicular to B_0, λ_{T} is the transverse muon spin relaxation rate, and β is the stretching exponent, which characterizes the distribution of static local fields B_μ induced by the applied field B_0. In principle, λ_{T} is also affected by dynamic fluctuations of B_μ. Yet, this effect is of the order of λ_{L}, i.e., the relaxation that is purely dynamical in origin [37]. Since in Zn-brochantite λ_{L} is more than an order of magnitude below λ_{T} (Fig. 2), the latter is obviously dominated by static effects.

We find that the shape of the B_μ distribution changes significantly between 40 and 4 K, as β decreases progressively from its high-T value of 1.75 to its low-T value of 1.05 (upper inset in Fig. 2). This change is clearly seen in the bottom panel of Fig. 1, which shows the polarization data in a rotating frame of reference. The distribution of static B_μ is close to Gaussian ($\beta = 2$) at high T's, but turns into Lorentzian ($\beta = 1$) at low T's. A Gaussian-like distribution of static fields is expected for dense disordered systems and a Lorentzian-like distribution for dilute systems [41]. The observed crossover is thus in line with the fact that in Zn-brochantite the bulk magnetic susceptibility χ is dominated by dense kagome spins at high T's, whereas at low T's the diluted impurities yield the dominant contribution to χ [12]. This suggests that the muons mainly detect the magnetism of the impurity spins at low T's.

The precession frequency ν is shifted from $\nu_0 = \gamma_\mu/2\pi \times B_0$ ($\gamma_\mu = 2\pi \times 135.5$MHz/T is the muon gyromagnetic ratio) due to induced static B_μ. It scales linearly with the bulk susceptibility (lower inset in Fig. 2) up to $\chi \sim 0.3$ cm^3/mol, i.e., down to $T \sim 5$ K, which confirms the dominant coupling of the muons to the kagome spins at high T's, in line with the high-T value of β. The corresponding Knight shift

$$K = \frac{\nu - \nu_0}{\nu_0} = A\chi_\mu \qquad (1)$$

is proportional to the local susceptibility χ_μ, where A is the coupling constant between the electron and the muon magnetic moments. Even though A is of dipolar origin, one expects $A \neq 0$ for powder Cu-based samples, because of a sizable anisotropy of the magnetic response imposed by anisotropic g factors, which typically span the interval 2.05–2.3 [42]. The scaling of K with χ changes around 5 K (Fig. 3) and reveals that the average coupling of the muons to the impurity spins $A_{\mathrm{i}} = 36$ mT/μ_{B} is somewhat smaller than their coupling to the kagome spins $A_{\mathrm{k}} = 44$ mT/μ_{B}. The observed scaling of K with χ below 5 K, where χ is mainly due to impurities [12], and the change in β unquestionably show that at these temperatures the μSR response is indeed dominated by impurities. This is in sharp contrast to NMR measurements [37], where the

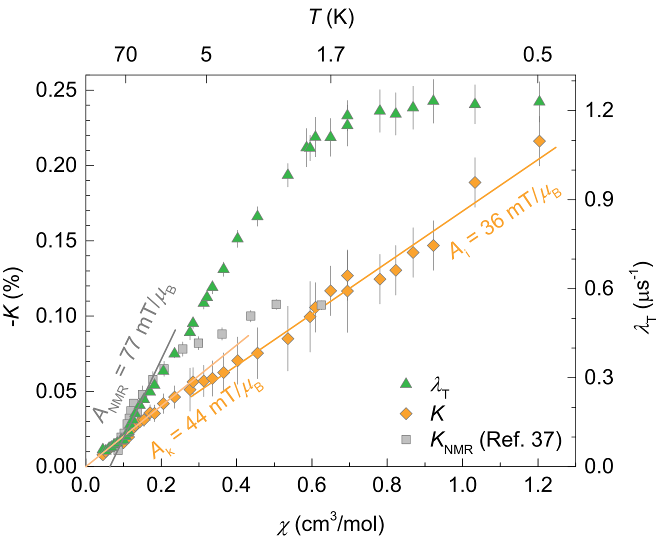

FIG. 3. The scaling of the Knight shift K and the transverse muon relaxation rate $\lambda_{\rm T}$ with the bulk susceptibility χ in Zn-brochantite. The solid lines give the coupling $A_{\rm k}(A_{\rm i})$ between the muons and the kagome (impurity) moments. The NMR Knight-shift data $K_{\rm NMR}$ are reproduced from Ref. [37].

^{2}D Knight shift revealed that the magnetic coupling with the impurity spins is much smaller than with the kagome spins [note the low-T leveling off of the curve $K_{\rm NMR}(\chi)$ in Fig. 3]. This can be explained by the difference in the dominant coupling mechanism of the two probes with electron magnetic moments, i.e., the short-ranged hyperfine coupling in NMR versus the long-ranged dipolar coupling in μSR.

K saturates below $\sim$0.5 K, while the saturation of $\lambda_{\rm T}$ occurs at a $\sim$3 times higher temperature (Fig. 2). This dichotomy is even more obvious when comparing the variation of $\lambda_{\rm T}$ and K with χ (Fig. 3). Both of these parameters reflect the static properties of the B_μ distribution: K the average field value and $\lambda_{\rm T}$ the distribution width. In a paramagnet with inhomogeneous broadening due to anisotropic powder averaging, one should find $\lambda_{\rm T} \propto K \propto \chi$. However, if antiferromagnetic (AFM) correlations start developing they can affect the shape of the local field distribution. Such an AFM correlated regime can therefore lead to a situation where $\lambda_{\rm T} \not\propto K \propto \chi$. The saturation of $\lambda_{\rm T}$ below $\sim$1.5 K is thus a sign of quasistatic AFM correlations involving the impurity spins, as they dominate the system's magnetic response at low T's. This temperature corresponds well to the effective Weiss temperature $\theta_{\rm i}^{\rm CW} \approx -1.2$ K of the impurity spins at low T's [12]. Furthermore, the $\lambda_{\rm T}(\chi)$ dependence exhibits an anomalous slope change already at 70 K (Fig. 3), a temperature that is close to the Weiss temperature $\theta_{\rm k}^{\rm CW} = -79$ K of the kagome spins [12]. This anomaly is thus likely due to the development of quasistatic spin correlations among the intrinsic kagome spins, which are also reflected in increased ^{2}D NMR linewidth [37].

The saturation of K below $\sim$0.5 K (Fig. 2), the lowest temperature of bulk χ measurements [12], indicates that the local susceptibility in a magnetic field of 0.3 T reaches a plateau value of $\chi_\mu \sim 1.2$ cm^3/mol for $T \lesssim 0.5$ K (Fig. 3). Comparing this with the calculated normalized saturation magnetization $M_{\rm s}/H = 70$ cm^3/mol reveals an average magnetic moment of $0.017\mu_{\rm B}$ per Cu site, which is much smaller than the full moment of $\sim 1\mu_{\rm B}$. It is significantly decreased from the full moment even if that is rescaled to 6%–9% spin-$\frac{1}{2}$ impurity concentration [12]. Therefore, the impurity moments are obviously not saturated despite the plateau in χ_μ below $\sim$0.5 K. Furthermore, the plateau in λ_L, indicating a saturation in magnetic fluctuations even at 8 mT, occurs at the same temperature (Fig. 2, Ref. [37]). Both plateaus must thus be related to the low-T SL state of the investigated compound which sets in around 0.6 K [12,37]. This unambiguously demonstrates a significant coupling of the impurity spins with the kagome spins. Interestingly, a low-T saturation of $\lambda_{\rm L}$ [35,43] and a small average magnetic moment [44] were also found in herbertsmithite.

In order to corroborate the intimate connection of the impurity spins with the intrinsic kagome spins, as implied by the low-T plateaus in $K(T)$ and $\lambda_{\rm L}(T)$, we performed additional LF μSR experiments at 110 mK, i.e., deep in the saturated regime. The polarization curves (inset in Fig. 4) are described by the stretched-exponential form $P_{\rm LF}(t) = P_0 e^{-(\lambda_{\rm L} t)^\beta}$, where the stretching exponent $\beta = 0.86$ was fixed to the value found in our previous LF study [37]. The inverse relaxation rate exhibits a power-law dependence on the applied field,

$$1/\lambda_{\rm L} \propto B^p, \tag{2}$$

with two notably different regions. The power $p = 0.20(1)$ is found for magnetic fields below $B_c \sim 0.4$ T and $p = 2.5(4)$ for higher magnetic fields. We note that the muon relaxation due to nuclear magnetic fields in Zn-brochantite is negligible for $B \gtrsim 4$ mT [37], therefore, the observed relaxation is entirely due to magnetic fields arising from the electron magnetic moments.

The sublinear field dependence of $1/\lambda_{\rm L}$ for $B < B_c$ is rather unusual. The conventional exponential decay of the local-field autocorrelation function $\mathcal{S}(t) \propto e^{-t/\tau}$, characteristic of a single-correlation-time (τ) Markovian local-field evolution,

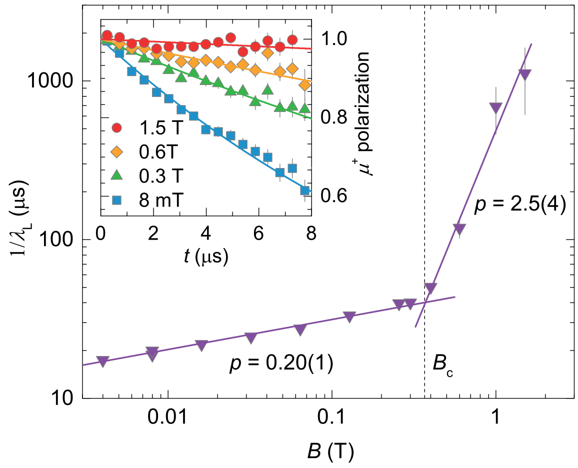

FIG. 4. The scaling of the inverse longitudinal muon relaxation rate with the applied LF in Zn-brochantite at 110 mK. Two power-law regimes are indicated by solid lines. The inset shows the corresponding polarization curves (symbols) and stretched-exponential fits (solid lines).

yields a Lorentzian spectral density $\mathcal{S}(\omega)$, where $1/\lambda_{\mathrm{L}} \propto \mathcal{S}(\omega)^{-1} \propto (\gamma_\mu B)^2$ [45]. The high-field value $p = 2.5(4)$ is indeed close to 2. The experimentally observed $p = 0.2$ at low fields, however, suggests a more exotic spectral density $\mathcal{S}(\omega) \propto \omega^{-p} = \omega^{-0.2}$, where temporal correlations decay algebraically as $\mathcal{S}(t) \propto t^{-(1-p)} = t^{-0.8}$ [46]. A similar situation with $p \leqslant 1$ was observed on a few occasions in different SL phases of spin chains [46], pyrochlores [47], and QKA's [35,48].

$\mathcal{S}(\omega) \propto \omega^{-0.2}$ could be due to a distribution of correlation times of the impurity spins. The impurities could still be decoupled from the SL properties of the kagome spins and the power law $\mathcal{S}(\omega)$ could be due to a presence of impurity-impurity couplings with a distribution of strengths arising from the randomness of impurity positions. However, the drastic change of the spectral density at B_c strongly suggests a more involved scenario.

The sudden sizable increase of p at $B_c \sim 0.4$ T is rather intriguing. It cannot be accounted for by field-induced polarization of the impurity spins, which would yield gradual changes. It rather strengthens the conclusion from the saturation of the muon Knight shift that the impurities are coupled to the SL phase of the kagome spins. The properties of the SL phase obviously abruptly change at B_c. Therefore, in addition to the well documented T-induced instabilities in Zn-brochantite [37], the low-T SL state could also exhibit a field-induced instability at the critical field B_c. This calls for future in-depth studies, as field-induced instability appears to be a common feature of frustrated antiferromagnets [49,50], yet its origin remains unknown.

The correlations between the impurity and the kagome spins in the SL state can be understood as a Kondo-like effect, which can emerge on frustrated spin lattices from either fermionic or bosonic spinon excitations [40,51–53]. The resulting screening generally leads to Curie-Weiss behavior of impurity susceptibility at $T \gtrsim T_{\mathrm{K}}$, where the Kondo temperature T_{K} is of the order of $|\theta_{\mathrm{i}}^{\mathrm{CW}}|$ [54]. Therefore, the observed low-T Curie-Weiss behavior [12] does not require impurity-impurity interactions. Below $T \sim T_{\mathrm{K}}$ the Curie-Weiss behavior should break down [54], which nicely corresponds to the onset of the plateau in the impurity susceptibility χ_μ at ∼0.5 K. Moreover, the Kondo effect can help to differentiate between different candidate SL ground states. In particular, the finite χ_μ at $T \to 0$ observed in Zn-brochantite is consistent with predictions for a gapless SL with a spinon Fermi surface [40,53], while it contradicts the divergent behavior expected for gapless Dirac $U(1)$ SLs and the exponentially suppressed impurity response of gapped Z_2 SLs [40]. Our observations are thus in accord with previous hints about the nature of the SL in Zn-brochantite from bulk heat-capacity measurements [12].

The evidently gapless SL in Zn-brochantite is at odds with the apparently gapped SL in herbertsmithite [13]. Moreover, the experimentally detected correlations between the impurity and kagome spins in the SL state of Zn-brochantite stand in contrast to the recent inelastic neutron scattering results on herbertsmithite [14], which advocated that a diluted impurity lattice with random-bond Heisenberg interactions may be effectively decoupled from the intrinsic kagome physics at $T/J \sim 1/100$. The differences between the two compounds may have various origins; the perturbing magnetic anisotropies [15] are not necessarily the same, the position of the Zn (impurity) site is different [12], and the kagome lattice in Zn-brochantite is slightly distorted [12].

In conclusion, by performing μSR on Zn-brochantite, we have shown that this technique can comprehensively address the impurity magnetism that generally dominates the bulk response of QKA representatives at low T's. Our results reveal that the low-T kagome-lattice SL state in the investigated compound is reflected in the magnetic behavior of the impurity spins, implying strong correlations between the impurity and the kagome spins. Our findings thus suggest a Kondo-like description of impurity spins on the kagome lattice, a description that is also applicable to other quantum SL systems, e.g., the organic triangular-lattice antiferromagnets [40] and the Kitaev quantum SLs [55–57]. Based on theoretical predictions for the Kondo effect in SLs, details of the observed impurity behavior enable us to confirm a gapless SL with a spinon Fermi surface as the ground state of Zn-brochantite. Impurities thus indeed prove to be salient local probes and may turn out to be essential for finally fully understanding the ground state of the QKA.

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[1] *Introduction to Frustrated Magnetism: Materials, Experiments, Theory*, edited by C. Lacroix, P. Mendels, and F. Mila (Springer, Berlin, 2011).

[2] L. Balents, Spin liquids in frustrated magnets, Nature (London) **464**, 199 (2010).

[3] Y. Ran, M. Hermele, P. A. Lee, and X.-G. Wen, Projected-Wave-Function Study of the Spin-1/2 Heisenberg Model on the Kagomé Lattice, Phys. Rev. Lett. **98**, 117205 (2007).

[4] Y. Iqbal, F. Becca, and D. Poilblanc, Projected wave function study of $\mathbb{Z}_2$ spin liquids on the kagome lattice for the spin-$\frac{1}{2}$ quantum Heisenberg antiferromagnet, Phys. Rev. B **84**, 020407(R) (2011).

[5] S. Yan, D. A. Huse, and S. R. White, Spin-liquid ground state of the $S = 1/2$ kagome Heisenberg antiferromagnet, Science **332**, 1173 (2011).

[6] S. Depenbrock, I. P. McCulloch, and U. Schollwöck, Nature of the Spin-Liquid Ground State of the $S = 1/2$ Heisenberg Model on the Kagome Lattice, Phys. Rev. Lett. **109**, 067201 (2012).

[7] H.-C. Jiang, Z. Wang, and L. Balents, Identifying topological order by entanglement entropy, Nat. Phys. **8**, 902 (2012).

[8] Y. Iqbal, F. Becca, S. Sorella, and D. Poilblanc, Gapless spin-liquid phase in the kagome spin-$\frac{1}{2}$ Heisenberg antiferromagnet, Phys. Rev. B **87**, 060405 (2013).

[9] A. Olariu, P. Mendels, F. Bert, F. Duc, J. C. Trombe, M. A. de Vries, and A. Harrison, ^{17}O NMR Study of the Intrinsic Magnetic Susceptibility and Spin Dynamics of the Quantum Kagome Antiferromagnet $ZnCu_3(OH)_6Cl_2$, Phys. Rev. Lett. **100**, 087202 (2008).

[10] B. Fåk, E. Kermarrec, L. Messio, B. Bernu, C. Lhuillier, F. Bert, P. Mendels, B. Koteswararao, F. Bouquet, J. Ollivier, A. D. Hillier, A. Amato, R. H. Colman, and A. S. Wills, Kapellasite: A Kagome Quantum Spin Liquid with Competing Interactions, Phys. Rev. Lett. **109**, 037208 (2012).

[11] L. Clark, J. C. Orain, F. Bert, M. A. De Vries, F. H. Aidoudi, R. E. Morris, P. Lightfoot, J. S. Lord, M. T. F. Telling, P. Bonville, J. P. Attfield, P. Mendels, and A. Harrison, Gapless Spin Liquid Ground State in the $S = 1/2$ Vanadium Oxyfluoride Kagome Antiferromagnet $[NH_4]_2[C_7H_{14}N][V_7O_6F_{18}]$, Phys. Rev. Lett. **110**, 207208 (2013).

[12] Y. Li, B. Pan, S. Li, W. Tong, L. Ling, Z. Yang, J. Wang, Z. Chen, Z. Wu, and Q. M. Zhang, Gapless quantum spin liquid in the $S = 1/2$ anisotropic kagome antiferromagnet $ZnCu_3(OH)_6SO_4$, New J. Phys. **16**, 093011 (2014).

[13] M. Fu, T. Imai, T.-H. Han, and Y. S. Lee, Evidence for a gapped spin-liquid ground state in a kagome Heisenberg antiferromagnet, Science **350**, 655 (2015).

[14] T.-H. Han, M. R. Norman, J.-J. Wen, J. A. Rodriguez-Rivera, J. S. Helton, C. Broholm, and Y. S. Lee, Correlated impurities and intrinsic spin liquid physics in the kagome material Herbertsmithite, arXiv:1512.06807.

[15] A. Zorko, S. Nellutla, J. van Tol, L. C. Brunel, F. Bert, F. Duc, J.-C. Trombe, M. A. de Vries, A. Harrison, and P. Mendels, Dzyaloshinsky-Moriya Anisotropy in the Spin-1/2 Kagome Compound $ZnCu_3(OH)_6Cl_2$, Phys. Rev. Lett. **101**, 026405 (2008).

[16] O. Cépas, C. M. Fong, P. W. Leung, and C. Lhuillier, Quantum phase transition induced by Dzyaloshinskii-Moriya interactions in the kagome antiferromagnet, Phys. Rev. B **78**, 140405 (2008).

[17] Y. Huh, L. Fritz, and S. Sachdev, Quantum criticality of the kagome antiferromagnet with Dzyaloshinskii-Moriya interactions, Phys. Rev. B **81**, 144432 (2010).

[18] A. Zorko, F. Bert, A. Ozarowski, J. van Tol, D. Boldrin, A. S. Wills, and P. Mendels, Dzyaloshinsky-Moriya interaction in vesignieite: A route to freezing in a quantum kagome antiferromagnet, Phys. Rev. B **88**, 144419 (2013).

[19] Y.-C. He and Y. Chen, Distinct Spin Liquids and their Transitions in Spin-1/2 XXZ Kagome Antiferromagnets, Phys. Rev. Lett. **114**, 037201 (2015).

[20] J.-C. Domenge, P. Sindzingre, C. Lhuillier, and L. Pierre, Twelve sublattice ordered phase in the $J_1 - J_2$ model on the kagomé lattice, Phys. Rev. B **72**, 024433 (2005).

[21] R. Suttner, C. Platt, J. Reuther, and R. Thomale, Renormalization group analysis of competing quantum phases in the $J_1 - J_2$ Heisenberg model on the kagome lattice, Phys. Rev. B **89**, 020408(R) (2014).

[22] Y. Iqbal, H. O. Jeschke, J. Reuther, R. Valentí, I. I. Mazin, M. Greiter, and R. Thomale, Paramagnetism in the kagome compounds $(Zn,Mg,Cd)Cu_3(OH)_6Cl_2$, Phys. Rev. B **92**, 220404(R) (2015).

[23] S. Dommange, M. Mambrini, B. Normand, and F. Mila, Static impurities in the $S = 1/2$ kagome lattice: Dimer freezing and mutual repulsion, Phys. Rev. B **68**, 224416 (2003).

[24] I. Rousochatzakis, S. R. Manmana, A. M. Läuchli, B. Normand, and F. Mila, Dzyaloshinskii-Moriya anisotropy and nonmagnetic impurities in the $s = \frac{1}{2}$ kagome system $ZnCu_3(OH)_6Cl_2$, Phys. Rev. B **79**, 214415 (2009).

[25] R. R. P. Singh, Valence Bond Glass Phase in Dilute Kagome Antiferromagnets, Phys. Rev. Lett. **104**, 177203 (2010).

[26] D. Poilblanc and A. Ralko, Impurity-doped kagome antiferromagnet: A quantum dimer model approach, Phys. Rev. B **82**, 174424 (2010).

[27] H. Kawamura, K. Watanabe, and T. Shimokawa, Quantum spin-liquid behavior in the spin-1/2 random-bond Heisenberg antiferromagnet on the kagome lattice, J. Phys. Soc. Jpn. **83**, 103704 (2014).

[28] T. Shimokawa, K. Watanabe, and H. Kawamura, Static and dynamical spin correlations of the $S = \frac{1}{2}$ random-bond antiferromagnetic Heisenberg model on the triangular and kagome lattices, Phys. Rev. B **92**, 134407 (2015).

[29] P. Mendels and F. Bert, Quantum kagome antiferromagnet $ZnCu_3(OH)_6Cl_2$, J. Phys. Soc. Jpn. **79**, 011001 (2010).

[30] F. Bert, S. Nakamae, F. Ladieu, D. L'Hôte, P. Bonville, F. Duc, J.-C. Trombe, and P. Mendels, Low temperature magnetization of the $S = \frac{1}{2}$ kagome antiferromagnet $ZnCu_3(OH)_6Cl_2$, Phys. Rev. B **76**, 132411 (2007).

[31] M. A. de Vries, K. V. Kamenev, W. A. Kockelmann, J. Sanchez-Benitez, and A. Harrison, Magnetic Ground State of an Experimental $S = 1/2$ Kagome Antiferromagnet, Phys. Rev. Lett. **100**, 157205 (2008).

[32] M. A. de Vries, J. R. Stewart, P. P. Deen, J. O. Piatek, G. J. Nilsen, H. M. Rønnow, and A. Harrison, Scale-Free Antiferromagnetic Fluctuations in the $s = 1/2$ Kagome Antiferromagnet Herbertsmithite, Phys. Rev. Lett. **103**, 237201 (2009).

[33] T.-H. Han, J. S. Helton, S. Chu, D. G. Nocera, J. A. Rodriguez-Rivera, C. Broholm, and Y. S. Lee, Fractionalized excitations in the spin-liquid state of a kagome-lattice antiferromagnet, Nature (London) **492**, 406 (2012).

[34] G. J. Nilsen, M. A. de Vries, J. R. Stewart, A. Harrison, and H. M. Rønnow, Low-energy spin dynamics of the $s = 1/2$ kagome system herbertsmithite, J. Phys.: Condens. Matter **25**, 106001 (2013).

[35] E. Kermarrec, P. Mendels, F. Bert, R. H. Colman, A. S. Wills, P. Strobel, P. Bonville, A. Hillier, and A. Amato, Spin-liquid ground state in the frustrated kagome antiferromagnet $MgCu_3(OH)_6Cl_2$, Phys. Rev. B **84**, 100401 (2011).

[36] V. R. Shaginyan, M. Ya. Amusia, J. W. Clark, G. S. Japaridze, A. Z. Msezane, and K. G. Popov, Comment on "Correlated impurities and intrinsic spin liquid physics in the kagome material Herbertsmithite" (T. H. Han, M. R. Norman, J. J. Wen, J. A. Rodriguez-Rivera, J. S. Helton, C. Broholm, and Y. S. Lee, arXiv:1512.06807), arXiv:1602.03330.

[37] M. Gomilšek, M. Klanjšek, M. Pregelj, F. C. Coomer, H. Luetkens, O. Zaharko, T. Fennell, Y. Li, Q. M. Zhang, and A. Zorko, Instabilities of spin-liquid states in a quantum kagome antiferromagnet, Phys. Rev. B **93**, 060405(R) (2016).

[38] H. Alloul, J. Bobroff, M. Gabay, and P. J. Hirschfeld, Defects in Correlated Metals and Superconductors, Rev. Mod. Phys. **81**, 45 (2009).

[39] A. Georges, The beauty of impurities: Two revivals of Friedel's virtual bound-state concept, C. R. Phys. **17**, 430 (2016).

[40] A. Kolezhuk, S. Sachdev, R. R. Biswas, and P. Chen, Theory of quantum impurities in spin liquids, Phys. Rev. B **74**, 165114 (2006).

[41] A. Yaouanc and P. D. De Réotier, *Muon Spin Rotation, Relaxation, and Resonance: Applications to Condensed Matter* (Oxford University Press, Oxford, U.K., 2011).

[42] A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).

[43] P. Mendels, F. Bert, M. A. de Vries, A. Olariu, A. Harrison, F. Duc, J. C. Trombe, J. S. Lord, A. Amato, and C. Baines, Quantum Magnetism in the Paratacamite Family: Towards an Ideal Kagomé Lattice, Phys. Rev. Lett. **98**, 077204 (2007).

[44] O. Ofer and A. Keren, Symmetry of the spin Hamiltonian for herbertsmithite: A spin-$\frac{1}{2}$ kagome lattice, Phys. Rev. B **79**, 134424 (2009).

[45] R. S. Hayano, Y. J. Uemura, J. Imazato, N. Nishida, T. Yamazaki, and R. Kubo, Zero-and low-field spin relaxation studied by positive muons, Phys. Rev. B **20**, 850 (1979).

[46] F. L. Pratt, S. J. Blundell, T. Lancaster, C. Baines, and S. Takagi, Low-Temperature Spin Diffusion in a Highly Ideal $S = \frac{1}{2}$ Heisenberg Antiferromagnetic Chain Studied by Muon Spin Relaxation, Phys. Rev. Lett. **96**, 247203 (2006).

[47] A. Keren, J. S. Gardner, G. Ehlers, A. Fukaya, E. Segal, and Y. J. Uemura, Dynamic Properties of a Diluted Pyrochlore Cooperative Paramagnet $(\mathrm{Tb}_p\mathrm{Y}_{1-p})_2\mathrm{Ti}_2\mathrm{O}_7$, Phys. Rev. Lett. **92**, 107204 (2004).

[48] E. Kermarrec, A. Zorko, F. Bert, R. H. Colman, B. Koteswararao, F. Bouquet, P. Bonville, A. Hillier, A. Amato, J. van Tol, A. Ozarowski, A. S. Wills, and P. Mendels, Spin dynamics and disorder effects in the $S = \frac{1}{2}$ kagome Heisenberg spin-liquid phase of kapellasite, Phys. Rev. B **90**, 205103 (2014).

[49] F. L. Pratt, P. J. Baker, S. J. Blundell, T. Lancaster, S. Ohira-Kawamura, C. Baines, Y. Shimizu, K. Kanoda, I. Watanabe, and G. Saito, Magnetic and nonmagnetic phases of a quantum spin liquid, Nature (London) **471**, 612 (2011).

[50] M. Jeong, F. Bert, P. Mendels, F. Duc, J. C. Trombe, M. A. de Vries, and A. Harrison, Field-Induced Freezing of a Quantum Spin Liquid on the Kagome Lattice, Phys. Rev. Lett. **107**, 237201 (2011).

[51] S. Florens, L. Fritz, and M. Vojta, Kondo Effect in Bosonic Spin Liquids, Phys. Rev. Lett. **96**, 036601 (2006).

[52] K.-S. Kim and M. D. Kim, Kondo physics in the algebraic spin liquid, J. Phys.: Condens. Matter **20**, 125206 (2008).

[53] P. Ribeiro and P. A. Lee, Magnetic impurity in a $U(1)$ spin liquid with a spinon Fermi surface, Phys. Rev. B **83**, 235119 (2011).

[54] A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, Cambridge, U.K., 1997).

[55] A. J. Willans, J. T. Chalker, and R. Moessner, Disorder in a Quantum Spin Liquid: Flux Binding and Local Moment Formation, Phys. Rev. Lett. **104**, 237203 (2010).

[56] K. Dhochak, R. Shankar, and V. Tripathi, Magnetic Impurities in the Honeycomb Kitaev Model, Phys. Rev. Lett. **105**, 117201 (2010).

[57] G. J. Sreejith, S. Bhattacharjee, and R. Moessner, Vacancies in Kitaev quantum spin liquids on the three-dimensional hyperhoneycomb lattice, Phys. Rev. B **93**, 064433 (2016).