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Naturally tuned quantum critical point in the $S = 1$ kagomé $YCa_3(VO)_3(BO_3)_4$

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Although $S = 1/2$ kagomé systems have been intensely studied theoretically, and within the past decade been realized experimentally, much less is known about the $S = 1$ analogs. While the theoretical ground state is still under debate, it has been found experimentally that $S = 1$ kagomé systems either order at low temperatures or enter a spin glass state. In this work, $YCa_3(VO)_3(BO_3)_4$ (YCVBO) is presented, with trivalent vanadium. Owing to its unusual crystal structure, the metal-metal bonding is highly connected along all three crystallographic directions, atypical of other kagomé materials. Using neutron scattering it is shown that YCVBO fails to order down to at least 50 mK and exhibits broad and dispersionless excitations. ^{11}B NMR provides evidence of fluctuating spins at low temperatures while dc magnetization shows critical scaling that is also observed in systems near a quantum critical point such as Herbertsmithite, despite its insulating nature and $S = 1$ magnetism. The evidence shown indicates that YCVBO is naturally tuned to be a quantum disordered magnet in the limit of $T = 0$ K.

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I. INTRODUCTION

Phase transitions have been known since antiquity, but it was not until the development of statistical mechanics that they could be well described and understood physically. A phase transition occurs when some symmetry is broken which gives rise to an order parameter that can be measured experimentally. Critical exponents have been used to describe the overall symmetry and interactions of the system. In the limit of zero kelvin, most systems are found to exhibit ordering, but some systems cannot order due to the presence of quantum fluctuations. Such is the case for spin liquids, with perhaps none having been studied more than Herbertsmithite [1–5]. One strategy used for finding new materials that fail to magnetically order in the low temperature limit is to look for geometrically frustrated lattices: lattices where fluctuations are enhanced at low temperatures because the spins cannot simultaneously satisfy all of their energetic constraints due to the lattice geometry. So far, spin liquid behavior has only been discovered for kagomé and triangular lattices in two dimensions and hyperkagomé and pyrochlore lattices in three dimensions. Of those found, nearly all of them are $S = 1/2$ or effective $S = 1/2$ systems, where quantum fluctuations are large and many theoretical predications have been made for the ground state [6].

II. EXPERIMENTAL

In this manuscript we report on another material, $YCa_3(VO)_3(BO_3)_4$ (YCVBO), that fails to order in temperatures down to at least 50 mK—well beyond the previous limit of 1.5 K found for this material [7]. The preparation of phase-pure YCVBO is quite challenging. The method has been described in detail previously [7], which yielded tiny single crystals suitable for diffraction, with small but sizable V_2O_3, CaB_2O_4, and YBO_3 impurities. In our attempt, we used stoichiometric amounts of Y_2O_3, $CaCO_3$, V_2O_3, and B_2O_3 (enriched $^{11}B_2O_3$ for our samples used for neutron scattering and ^{11}B NMR) in a quartz tube coupled to a dynamic vacuum, and reacted at 1050 °C for 50 h with intermediate grindings. Phase pure polycrystalline samples resulted. We note that YCVBO is prone to oxidation upon exposure to air, but the process is quite slow and takes months before the sample is completely decomposed (denoted by a change in color due to the lack of the V^{3+} cation). Neutron scattering measurements were made on the Disc Chopper Spectrometer (DCS [8]) at the NIST Center for Neutron Research (Gaithersburg, MD) using wavelengths of 1.8 and 4.8 Å at 50 mK and 30 K in medium resolution mode on a three gram enriched ^{11}B sample of YCVBO. Heat capacity and dc magnetic susceptibility measurements were performed on a Physical Property Measurement System (PPMS) using the ^3He and vibrating sample magnetometer options, respectively. ^{11}B NMR data were recorded on a Bruker

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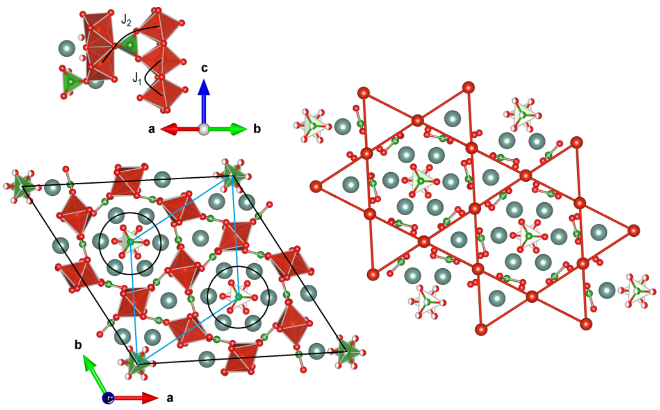

FIG. 1. Structure of YCVBO contains rigid VO$_6$ (red octahedra) and BO$_3$ (green trimers) units. Y and Ca ions are denoted by the large spheres and occupy those sites randomly. The smaller light blue unit cell shows the typical gaudefroyite subcell and the larger black unit cell denotes the supercell of YCVBO formed by BO$_3$ stack ordering at the positions encircled. Atoms in the BO$_3$ units at the YCVBO unit cell origin are shown with half-circles, denoting that the positions of the trimers are statistically half-occupied rather than the positions of the atoms (for example, there are no BO or BO$_2$ units). The kagomé lattice is nearly perfect and is shown with red bonds. VO$_6$ octahedra are edge sharing along the crystal *c* axis, with BO$_3$ units cross linking the infinite VO$_6$ chains that make up the kagomé network. Exchange pathways J$_1$ and J$_2$ as described in the text are indicated, but it should be noted that this is likely an oversimplification of the structure.

Avance-II spectrometer at 4.7 T magnetic field. 30 mg of sample was packed into a 1.8 mm Si$_3$N$_4$ rotor which was spun in a homebuilt cryoMAS probe using compressed helium gas [9]. A sample spinning rate of 30 kHz was used from room temperature to 64 K, where the rate was gradually decreased to 10 kHz by 16 K.

III. RESULTS AND DISCUSSION

YCVBO is a member of the gaudefroyite [Ca$_4$(MnO)$_3$(BO$_3$)$_3$CO$_3$] family. In gaudefroyite and other related minerals such as YCa$_3$(MnO)$_3$(BO$_3$)$_4$ (YCMBO [10]), the system adopts $P6_3/m$ symmetry, although the space group assignment has been debated previously in the natural mineral [10–12]. MnO$_6$ octahedra are edge sharing along the *c* axis forming infinite-chain structures, which are probably the largest component of the magnetic exchange. Within the *ab* plane, MnO$_6$ are arranged on a perfect kagomé lattice. BO$_3$ (and CO$_3$ in the natural mineral) trimer units are stacked in a disordered arrangement in the center of each kagomé star. The remaining BO$_3$ units serve to interconnect the infinite chains—the result is a system of well connected, highly interacting kagomé planes with in plane exchange of J$_2$ and out of plane exchange J$_1$ (see Fig. 1). Both materials have mixed antiferromagnetic and ferromagnetic interactions, but magnetically order at 7.5 K for YCMBO and 1.8 K for natural gaudefroyite [10]. On the other hand, YCVBO adopts a supercell structure formed by partial chemical ordering of the BO$_3$ units in the kagomé star center [7], which lowers the symmetry to $P\bar{3}$ (Fig. 1). It has been argued in previous work that, for YCVBO, a larger antiferromagnetic exchange exists along the chain axis while ferromagnetic exchange exists within the *ab* plane [7]. Naively, one would expect YCVBO to magnetically order at low temperatures, given the large and negative Curie Weiss temperature (−453 K). Instead, we find that YCVBO fails to order down to mK temperatures, and has a broad inelastic response at low temperatures in neutron scattering experiments that is reminiscent of Herbertsmithite. The supercell in YCVBO implies a higher degree of chemical of order in this material than typical gaudefroyites, which in turn should result in a tendency towards magnetic disorder as demonstrated by Wills *et al.* [13].

Time of flight neutron scattering was used to measure the magnetic inelastic excitations of YCVBO at low temperatures. For single crystal samples, a four-dimensional data set is obtained that includes the diffraction pattern and the inelastic dispersion curve. For the case of YCVBO powders, all of the excitations are powder averaged, resulting in a three-dimensional data set of intensity as a function of reciprocal space and energy, $I(Q,\omega)$ [Figs. 2(a) and 2(b)].

The intensity is directly proportional to the dynamical structure factor, $S(Q,\omega)$. The fluctuation dissipation theorem can be used to obtain the dynamical susceptibility from the magnetic scattering intensity via $S(Q,\omega) = [n(\omega)+1]\chi''(Q,\omega)$, where $n(\omega)$ is the Bose occupation factor. Spurious background signals are known to contribute to the positive energy transfer spectral weight between zero and approximately 0.4 meV on the DCS [15,16]. Instead, $\chi''(Q,\omega)$ can be obtained for 30 K using the negative energy transfer side. First, the data is integrated over $Q = [0.42, 2.07]$ Å^{-1} to obtain $S(\omega)$ at each temperature. At low temperatures, the probability of creating an excitation from a scattering event far exceeds that for the destruction of an excitation, resulting in almost no signal on the negative energy transfer side other than background. The intensity at 50 mK is then subtracted from 30 K and the result is divided by the Bose factor to obtain $\chi''(\omega)$ at 30 K for the negative energy transfer side. Since $\chi''(\omega)$ is an odd function, the positive energy transfer side is $\chi''(\omega > 0) = -\chi''(\omega < 0)$. $\chi''(\omega)$ at 50 mK is found by $S(\omega, \mathrm{T} = 50\ \mathrm{mK}) - S(\omega, \mathrm{T} = 30\ \mathrm{K})$ on the positive energy transfer side, where it is assumed that the background intensity is invariant with temperature. Figure 2(c) shows the result, which is the development broad and apparently dispersionless excitations. The damped harmonic oscillator model was used to fit the excitation as previously done for Herbertsmithite [14] as a guide to the eye. This resulted in a center at 0.71(2) meV with a large width of 0.39(4) meV (much larger than the instrumental resolution at this wavelength of approximately 0.1 meV). A similar excitation was observed in Herbertsmithite; however, both the energy and width are more than doubled in YCVBO. Such a large width could be due to strong spin fluctuations or intrinsic disorder [14]. However, YCVBO is fundamentally different from Herbertsmithite in that the disorder mainly arises from the nonmagnetic ions: Y/Ca occupation of the vacancies and BO$_3$ stacking faults that are disconnected from the magnetic sublattice. No magnetic reflections and no diffuse scattering are observed at 50 mK (including magnetic V$_2$O$_3$ reflections, which were found in a previous study [7]), indicating no transition into long-range magnetic order [Fig. 2(d)].

As a comparison of the magnetic response measured via neutron scattering, the magnetic susceptibility was measured

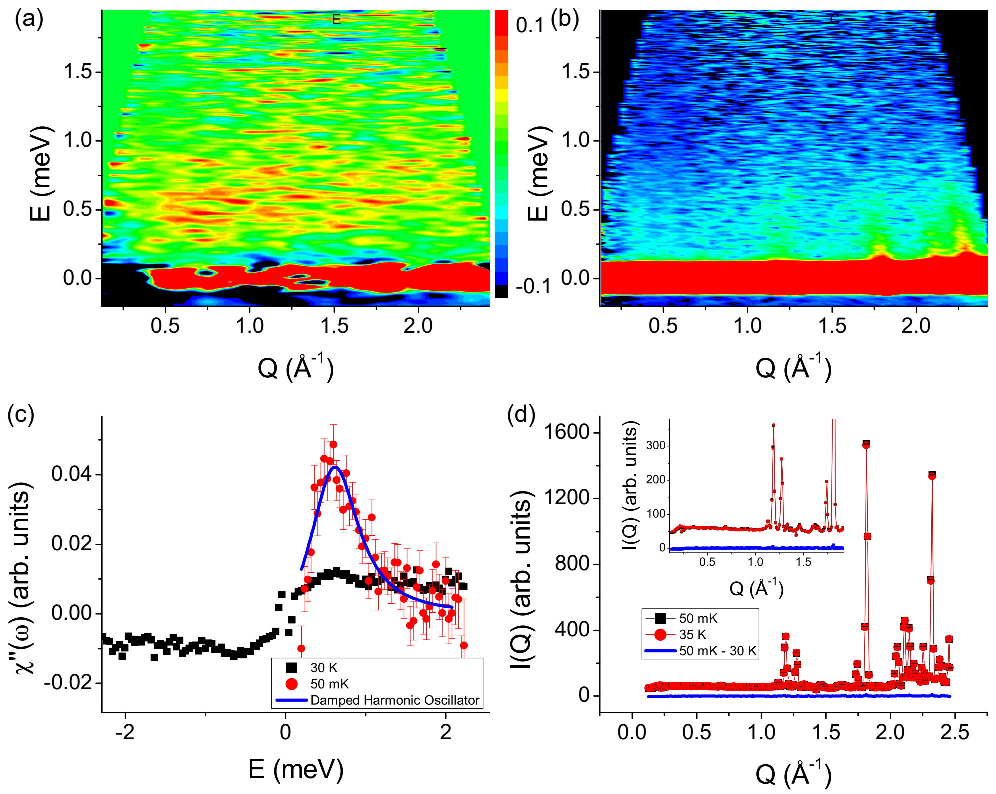

FIG. 2. (a) Magnetic signal at 50 mK can be isolated by subtracting off the data at 30 K, where phonon contributions dominate. This figure has been smoothed so that the broad excitation is better observed; (b) the raw signal at 50 mK with only an empty can subtraction is shown here. Phonons that are created by the incident neutrons can be observed; (c) the dynamic susceptibility is found through the process described in the text. The damped harmonic oscillator model used in [14] was used to fit the excitation at 50 mK as a guide to the eye; (d) no additional Bragg peaks or diffuse scattering are observed, even at 50 mK. The inset is a closeup view of a portion of the data. Error bars represent one standard deviation.

for our samples. The critical scaling dependence of the dc susceptibility is presented in Figs. 3(a) and 3(b). The magnetization at various temperatures is shown to completely collapse onto a single curve scaled by the temperature with critical exponents. Approximating the dc susceptibility as the low-frequency ac susceptibility, the dc susceptibility follows a relatively smooth curve when scaled by $T^{0.70(2)}$ against the unitless ratio $\mu_B H/k_B T$ for data to within almost three decades. The scaling law is valid in small fields for temperatures below 35 K, but the range increases with the field. This type of behavior is expected for systems near quantum critical points such as heavy fermion magnets [17] or quantum antiferromagnets [16,18,19]. As the field is increased and the temperature is lowered, the divergence of the susceptibility decreases as the quantum critical point is approached and traversed. The observed scaling bears striking agreement to the unusual scaling observed in Herbertsmithite [16]. For Herbertsmithite, the scaling was also observed in the inelastic neutron scattering excitation spectrum as a function of ω/T. While our neutron scattering data collapses on the same curve predicted by the scaling law, more temperatures are needed to make such a claim with any real degree of certainty. This is difficult to do for any system where the magnetism stems from an element with low scattering power, in this case V, because of the amount of counting time needed to obtain adequate statistics. Such a power law behavior has also been observed in other disordered kagomé systems such as $SrCr_{9x}Ga_{12-9x}O_{19}$ [20] and $Ba_2Sn_2Ga_{10-7x}ZnCr_{7x}O_{22}$ [21], which could be evidence of magnetic disorder. This scenario could be envisioned in YCVBO with oxygen vacancies, resulting in mixed V oxidation states, but positional disorder is unlikely due to size constraints [11]. Adding these defects was not found to improve the fit in joint x-ray/neutron structure refinements previously, and we observe no other evidence of multiple V valence states [7]. Because the scaling in Herbertsmithite is regarded as a key signature of its unique ground state, the unexpected appearance of this behavior in an $S = 1$ insulator is remarkable.

However, if the system is in close proximity to a quantum critical point, then one would expect persistent spin fluctuations to exist as the transition is approached. To look for unambiguous evidence of such fluctuations, solid-state ^{11}B NMR was used and is presented in Fig. 4. Line I belongs to the B sites connecting magnetic chains of VO_6 octahedra, while line II corresponds to the B in the middle of the kagomé stars. There is a clear difference in the temperature dependence of both of these lines. Whereas line I gradually broadens with decreasing temperature (in fact becoming too broad to be detected with our technique convincingly below 30 K) and shifts (see Fig. 5 inset), line II does not show any remarkable temperature dependence or shift. The double-peak structure of line II is caused by coupling of the ^{11}B nuclear spin 3/2 with the

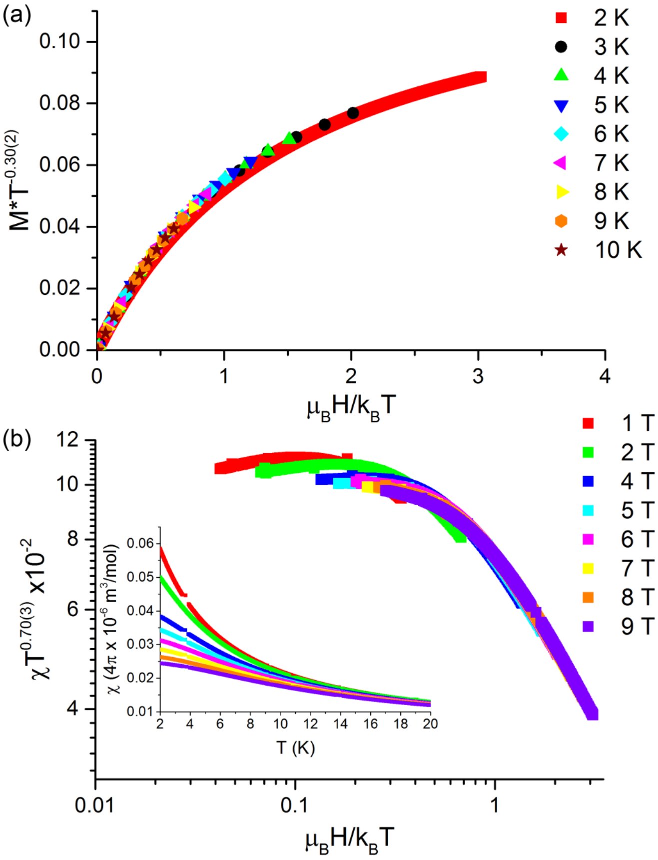

FIG. 3. (a) Scaling of the magnetization completely collapses onto the same curve in a remarkably similar manner to that of Herbertsmithite [16], which indicates the proximity of a quantum critical point; (b) approximating the dc susceptibility as the low frequency ac susceptibility, it can be seen that the scaling law holds here as well. The range of data shown is slightly beyond that for which the scaling law remains valid. The inset shows the dc susceptibility corrected for diamagnetism.

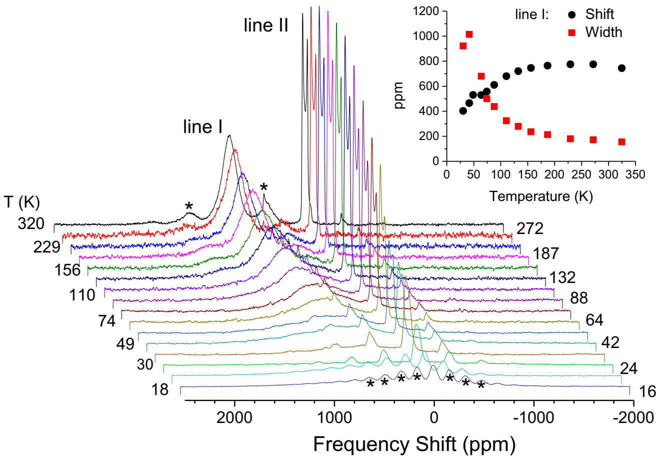

FIG. 4. ^{11}B MAS NMR spectra of YCVBO as a function of temperature. These spectra are referenced to the resonance frequency of BF_3Et_2O solution. The asterisks denote spinning sidebands, repeating the shift behavior of the central/isotropic line and determined in number and intensity just by the spinning rate at a given temperature. The inset shows the temperature dependence of the magnetic shift (in ppm from the reference) and linewidth (FWHM in ppm) of the line I.

local electric field gradient. The broadening of line I is due to a magnetic hyperfine shift caused by the intrinsic magnetic susceptibility of the sample. Furthermore, the temperature dependence of this shift clearly does not follow Curie-Weiss behavior, which agrees with the dc susceptibility data and indicates that the fluctuating moments are indeed strongly interacting, and more reminiscent of a spin liquid system [22,23] or of an $S = 1$ spin chain.

Scaling near quantum critical points has been studied intensely over the past few decades, with varying exponents α depending upon the system studied. Further complicating this field is the experimental difficulty of finding systems that are naturally tuned to such points. Typically, chemical doping or magnetic fields need to be used as tuning probes to study this phenomena. For the heavy fermion metals $CeCu_{6-x}Au_x$, critical scaling has been found for $CeCu_{5.9}Au_{0.1}$ with $\alpha = 0.74(5)$ [17], whereas for the organic spin liquid κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$, $\alpha = 0.83(6)$ [24]. Our value of $\alpha = 0.70(3)$ is certainly within this range of values, and is within error as the value for $CeCu_{5.9}Au_{0.1}$. The observation of this unusual exponent which deviates from the value of $\alpha = 1$ expected for conventional insulating magnets suggests that exotic physics is at play in YCVBO, and that this system is naturally tuned to the proximity of a quantum critical point without chemical doping.

Given that Herbertsmithite is an ideally two dimensional $S = 1/2$ kagomé while YCVBO is an $S = 1$ system of spin chains highly connected in kagomé-like fashion, the comparisons between the two might seem overstated. However, it is important to consider other possible ground states of $S = 1$ and V-kagomé materials. Most V kagomé systems are $S = 1$, but $S = 1/2$ V^{4+} kagomé compounds can be made via ionothermal synthesis, which essentially uses organic scaffolding agents to construct well-separated two-dimensional lattices [25]. $(NH_4)_2(C_7H_{14}N)(V_7O_6F_{18})$ is gapless and fails to order in the limit of low temperatures [26]. $S = 1$ kagomé compounds, including V^{3+} containing jarosite [27,28], $KV_3Ge_2O_9$ [29], $(NH_4)_2(C_2H_8N)$-$[V_3F_{12}]$ [30], $[C_6N_2H_8][NH_4]_2[Ni_3F_6(SO_4)_2]$ [31], and $BaNi_3(OH)_2(VO_4)_2$ [32] all either order in the limit of low temperatures or exhibit spin glass freezing. Typically, these systems are gapped antiferromagnets with their susceptibilities collapsing to zero with a maximum in the specific heat at around half the antiferromagnetic exchange coupling energy. Theoretically, $S = 1$ kagomé lattices have not received as much attention as their $S = 1/2$ counterparts. Many ground states have been proposed for these systems including, but not limited to, long-range order [33], a trimerized state [34], and a hexagon valence bond solid [35]. We also note that to our knowledge no current $S = 1$ spin-chain model predicts the experimental behavior observed here. There are recent predictions of the $S = 1$ kagomé lattice having a ground state of a topological paramagnet at low temperatures [36]. Future experiments to verify this claim would be necessary.

Other differences between YCVBO and Herbertsmithite are worth examining further. The critical exponents for the scaling are slightly different: $\alpha = 0.70(3)$ for YCVBO compared to $\alpha = 0.66$ for Herbertsmithite. However, within the Helton

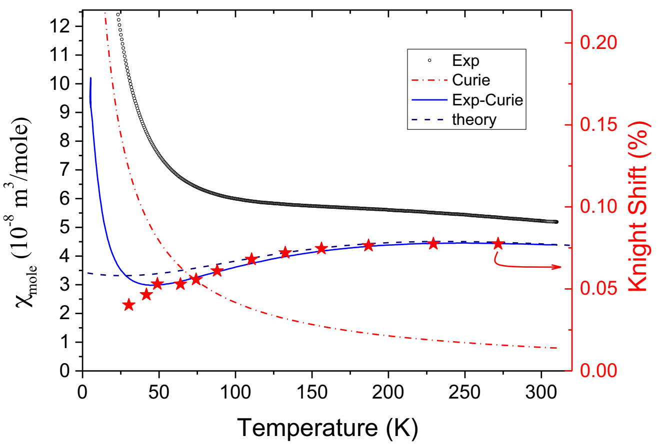

FIG. 5. Temperature dependence of the magnetic susceptibility of YCVBO. The magnetic susceptibility was measured (PPMS-VSM) in an external field of 4.7 T, a close field to the one used for NMR. The full line (blue) represents the susceptibility curve where the Curie tail (red dash-dot line, corresponding to paramagnetic impurities per V ion of 7% of V^{3+} or 4% of V^{2+}) is subtracted from the experimental data (small circles). The red stars denote ^{11}B Knight shift values (scale in the right); the dashed line is the theoretical function for the magnetic susceptibility for the 1D-HAF chain described in the text.

et al. paper, it is acknowledged that the error on α is large for Herbertsmithite, suggesting a range between 0.55 and 0.75 [16]. This would place our compound, YCVBO, within the same universality class. Another natural explanation could be that the interactions along the c direction in YCVBO could play a role in the selection of a ground state, and the magnetic behavior might be better explained as a $S = 1$ spin-chain system (with a Haldane-like gap). To explore this possibility, the magnetic susceptibility of YCVBO was measured in an external field of 4.7 T, which is close to the field used in our NMR work and is shown in Fig. 5. The behavior is clearly non-Curie-Weiss–like up to 300 K with a broad maximum. While many forms could possibly fit this data, we have attempted to fit our data with a 1D Heisenberg antiferromagnetic chain model [37], using a small Curie-Weiss term at low temperatures:

$$\chi_M = A\frac{2+0.0194x+0.777x^2}{3+4.346x+3.232x^2+5.834x^3}, \tag{1}$$

where the dashed (navy) curve in Fig. 5 is calculated with $A = 4.6(9) \times 10^{-5}$ m^3/mole and $|J|/k = 180(10)$ K. This suggests that our system might be represented by a 1D chain along the c direction, with the low-temperature behavior naturally explained by the proximity to a quantum critical point. While the origin of the quantum criticality may be different in this case, the scaling analysis is still valid in the low temperature limit. However, this is only one interpretation of the data. Future experiments on single crystals are needed to confirm or deny these different origins for the quantum critical behavior. What is clear is that Curie-Weiss fits to the data should be treated with caution at temperatures less than 300 K. From our fits to the dc susceptibility, we estimate the nearest neighbor exchange to be approximately on the scale of 200 K. This would give YCVBO a frustration index greater than 4000, which would make YCVBO one of the most frustrated systems known.

YCVBO appears to display novel behavior for an $S = 1$ kagomé system: no magnetic order was found down to at least 50 mK and no elastic diffuse scattering was observed. Although this could imply a singlet ground state, which could vindicate the hexagon singlet scenario, the incoherent background due to V is substantial and would likely mask any magnetic diffuse scattering. Indeed, the scaling of the susceptibility and the spin fluctuations observed imply the presence of a quantum critical point, indicating that the ground state could be an extremely rare example of a critical $S = 1$ spin liquid.

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