

## Dynamic Scaling in the Susceptibility of the Spin- $\frac{1}{2}$ Kagome Lattice Antiferromagnet Herbertsmithite

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The spin- $\frac{1}{2}$  kagome lattice antiferromagnet herbertsmithite,  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ , is a candidate material for a quantum spin liquid ground state. We show that the magnetic response of this material displays an unusual scaling relation in both the bulk ac susceptibility and the low energy dynamic susceptibility as measured by inelastic neutron scattering. The quantity  $\chi T^\alpha$  with  $\alpha \approx 0.66$  can be expressed as a universal function of  $H/T$  or  $\omega/T$ . This scaling is discussed in relation to similar behavior seen in systems influenced by disorder or by the proximity to a quantum critical point.

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A continuing challenge in the field of frustrated magnetism is the search for candidate materials which display quantum disordered ground states in two dimensions. In recent years, a great deal of attention has been given to the spin- $\frac{1}{2}$  nearest-neighbor Heisenberg antiferromagnet on the kagome lattice, consisting of corner sharing triangles. Given the high frustration of the lattice and the strength of quantum fluctuations arising from spin- $\frac{1}{2}$  moments, this system is a very promising candidate to display novel magnetic ground states, including the “resonating valence bond” (RVB) state proposed by Anderson [1]. A theoretical and numerical consensus has developed that the ground state of this system is not magnetically ordered [2–8], although the exact ground state is still a matter of some debate. Experimental studies of this system have long been hampered by a lack of suitable materials displaying this motif.

The mineral herbertsmithite [9,10],  $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ , is believed to be an excellent realization of a spin- $\frac{1}{2}$  kagome lattice antiferromagnet. The material consists of kagome lattice planes of spin- $\frac{1}{2}$   $\text{Cu}^{2+}$  ions. The superexchange interaction between nearest-neighbor spins leads to an antiferromagnetic coupling of  $J = 17 \pm 1$  meV. Extensive measurements on powder samples of herbertsmithite have found no evidence of long range magnetic order or spin freezing to temperatures of roughly 50 mK [11–13]. Magnetic excitations are effectively gapless, with a Curie-like susceptibility at low temperatures. The magnetic kagome planes are separated by layers of nonmagnetic  $\text{Zn}^{2+}$  ions; however, it has been suggested that there could be some site disorder between the Cu and Zn ions [14,15]. This possible site disorder, with  $\approx 5\%$  of the magnetic Cu ions residing on out-of-plane sites, as well as the presence of a Dzyaloshinskii-Moriya (DM) interaction [16], would likely influence the low energy magnetic response.

In this Letter we report a dynamic scaling analysis of the susceptibility of herbertsmithite as measured in both the bulk ac susceptibility and the low energy dynamic susceptibility measured by inelastic neutron scattering. In particular, we find that the quantity  $\chi T^\alpha$  can be expressed as a universal function in which the energy or field scale is set only by the temperature. This type of scaling behavior, when measured in quantum antiferromagnets [17] and heavy-fermion metals [18], has long been associated with proximity to a quantum critical point (QCP). Power law signatures in the susceptibility have also been associated with random systems such as Griffiths phase [19] or random singlet phase [20] systems. Such similarities could shed light on the relevant low energy interactions in herbertsmithite.

Figure 1(a) shows the ac magnetic susceptibility of a herbertsmithite powder sample as measured using a commercial ac magnetometer (Quantum Design). An oscillating field of 17 Oe, with a frequency of 100 Hz, was applied along with a range of dc fields up to  $\mu_0 H = 14$  T. The data were corrected for the diamagnetic contribution by use of Pascal’s constants. These results, for data sets with nonzero applied dc field, are plotted in Fig. 1(b) with  $\chi' T^\alpha$  (with  $\alpha = 0.66$ ) on the y axis and the unitless ratio  $\mu_B H / k_B T$  on the x axis. For this value of  $\alpha$ , the data collapse quite well onto a single curve for a range of  $\mu_B H / k_B T$  spanning well over two decades. Scaling plots with various exponent choices support  $\alpha = 0.66 \pm 0.02$ . This scaling remains roughly valid up to moderate temperatures, dependent upon the applied dc field. In the data taken with  $\mu_0 H = 0.5$  T, shown in Fig. 1, the scaling fails for temperatures greater than roughly  $T = 35$  K; under an applied field of  $\mu_0 H = 5$  T the scaling remains valid to about  $T = 55$  K. The functional form of this collapse is qualitatively similar to the generalized critical Curie-Weiss function seen in the heavy-fermion compound  $\text{CeCu}_{5.9}\text{Au}_{0.1}$  [21], but with deviations demonstrating that such a simple

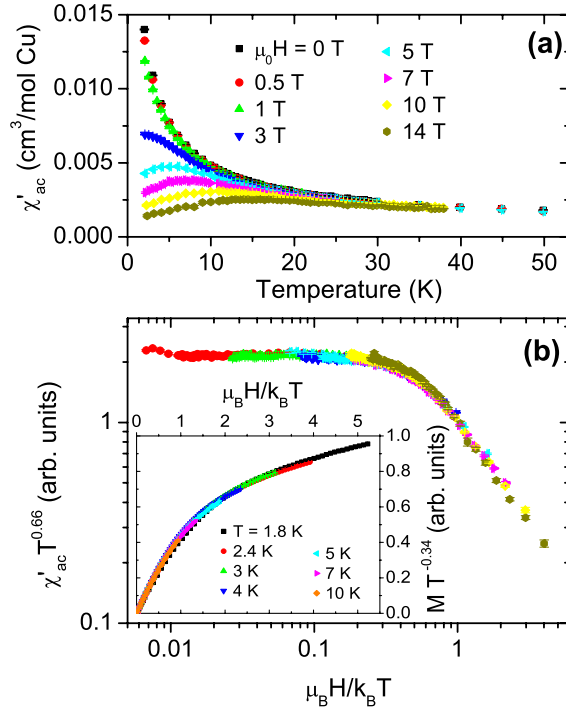


FIG. 1 (color online). (a) The in-phase component of the ac susceptibility, measured at 100 Hz with an oscillating field of 17 Oe. (b) A scaled plot of the ac susceptibility data measured at nonzero applied field, plotted as  $\chi'_{ac} T^\alpha$  with  $\alpha = 0.66$  on the y axis and  $\mu_B H / k_B T$  on the x axis. Inset: A scaled plot of the dc magnetization, showing  $MT^{-0.34}$  vs  $\mu_B H / k_B T$ .

response function is not quite adequate. It should also be pointed out that in herbertsmithite the entire bulk susceptibility obeys this scaling relation, while in  $\text{CeCu}_{5.9}\text{Au}_{0.1}$  it is only the estimated local contribution,  $\chi_L(T) = [\chi(T)^{-1} - \chi(T=0)^{-1}]^{-1}$ , that obeys scaling. A susceptibility of this form will imply a similar scaling in the bulk dc magnetization of the sample, with  $MT^{\alpha-1}$  expressible as a function of  $H/T$ . As a complementary measurement, such a scaling is shown in the inset to Fig. 1(b). The dc magnetization was measured up to  $\mu_0 H = 14$  T at temperatures ranging from  $T = 1.8$  K to 10 K, and is plotted as  $MT^{-0.34}$  vs  $\mu_B H / k_B T$ .

The inelastic neutron scattering spectrum of herbertsmithite was measured on the time-of-flight Disk Chopper Spectrometer at the NIST Center for Neutron Research. A deuterated powder sample of mass 7.5 g was measured using a dilution refrigerator with an incident neutron wavelength of 5 Å. Measurements were taken at six different temperatures, with roughly logarithmic spacing, ranging from 77 mK to 42 K. The scattering data were integrated over a wide range of momentum transfers,  $0.5 \leq Q \leq 1.9 \text{ Å}^{-1}$ , to give a measure of the local response. The momentum integrated dynamic scattering structure factor,  $S(\omega)$ , is shown in Fig. 2(a). Similar to previous reports on the neutron scattering spectrum of herbertsmithite [11], the data show a broad inelastic spectrum with no discernable spin gap and only a weak tem-

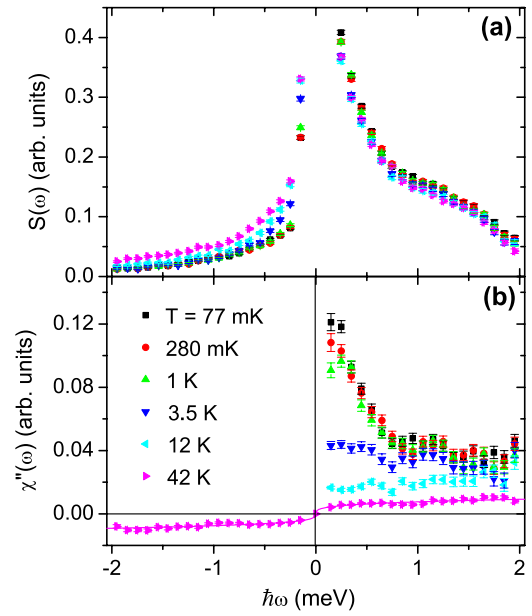


FIG. 2 (color online). (a) Neutron scattering structure factor  $S(\omega)$ , measured using the Disk Chopper Spectrometer integrated over wave vectors  $0.5 \leq Q \leq 1.9 \text{ Å}^{-1}$ . (b) The local dynamic susceptibility  $\chi''(\omega)$ , determined as described in the text. Uncertainties where indicated in this article are statistical in origin and represent 1 standard deviation.

perature dependence for positive energy transfer scattering. The negative energy transfer scattering intensity is suppressed at low temperatures due to detailed balance. The imaginary part of the dynamic susceptibility is related to the scattering structure factor through the fluctuation-dissipation theorem,  $\chi''(\omega) = S(\omega)(1 - e^{-\hbar\omega/k_B T})$ . The dynamic susceptibility can then be determined in a manner similar to that used previously [11]. For the two lowest temperatures measured, detailed balance considerations will effectively suppress scattering at negative energy transfer for values of  $|\hbar\omega| \geq 0.15$  meV. Thus these data sets are averaged together and treated as background. This background is subtracted from the  $T = 42$  K data, for which the detailed balance suppression is not pronounced below  $|\hbar\omega| = 2$  meV. From this,  $\chi''(\omega; T = 42 \text{ K})$  is calculated for negative  $\omega$ , and the values for positive  $\omega$  are easily determined from the fact that  $\chi''(\omega)$  is an odd function of  $\omega$ . The dynamic susceptibility at the other temperatures is calculated by determining the difference in scattering intensity relative to the  $T = 42$  K data set. It is reasonably assumed that the elastic incoherent scattering and any other background scattering are effectively temperature independent. The calculated values of  $\chi''(\omega)$  at all measured temperatures are shown in Fig. 2(b). The  $T = 42$  K scattering data and  $\chi''(\omega)$  were fit to smooth functions for use in calculating the susceptibility at other temperatures so that statistical errors would not be propagated throughout the data; the smooth function of  $\chi''(\omega; T = 42 \text{ K})$  used in the calculation is also shown in the figure.

The resulting values for  $\chi''(\omega)$  follow a similar scaling relation as the ac susceptibility, where the ratio  $\hbar\omega/k_B T$  replaces  $\mu_B H/k_B T$ . In Fig. 3 we show  $\chi''(\omega)T^{0.66}$  on the y axis and the unitless ratio  $\hbar\omega/k_B T$  on the x axis. The scaled data collapse fairly well onto a single curve over almost four decades of  $\hbar\omega/k_B T$ . Here we have used the same exponent  $\alpha = 0.66$  that was observed in the scaling of the ac susceptibility. However, the error bars on the data allow for a wider range of exponents ( $\alpha = 0.55$  to  $0.75$ ) with reasonable scaling behavior. The collapse of the  $\chi''(\omega)$  data is again reminiscent of the behavior observed in certain heavy-fermion metals, including the shape of the functional form of the scaling function. Let us assume that  $\chi''(\omega)T^\alpha \propto F(\omega/T)$ . The heavy-fermion metal  $\text{CeCu}_{5.9}\text{Au}_{0.1}$  displays a scaling [21,22] that could be fit to the functional form  $F(\omega/T) = \sin[\alpha \tan^{-1}(\omega/T)]/[(\omega/T)^2 + 1]^{\alpha/2}$ . A fit to this functional form is shown as a dashed blue line in Fig. 3. This simple form does not fit the herbertsmithite data well for low values of  $\omega/T$ . Other heavy-fermion metals [23,24], display a scaling relation that can be fit to the functional form  $F(\omega/T) = (T/\omega)^\alpha \tanh(\omega/\beta T)$ ; this functional form is similar to that used to fit the dynamic susceptibility in  $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_4$  [25]. This functional form fits our data much better, shown (with fit parameter  $\beta = 1.66$ ) as the dark red line in Fig. 3. This function is somewhat unusual, in that for low values of  $\omega/T$  it is proportional to  $(\omega/T)^{1-\alpha}$  rather than the expected  $\omega/T$  [17]; of course such a dependence might be recovered at still smaller values of  $\omega$ . For larger values of  $\omega/T$ , this curve approaches a power law dependence with  $\chi''(\omega) \propto \omega^{-\alpha}$ . This is consistent with the low temperature ( $T = 35$  mK) behavior of the dynamic susceptibility of herbertsmithite reported earlier [11].

Other works on kagome lattice systems have shown evidence for similar behavior of the susceptibility. The dynamic susceptibility in the kagome bilayer compound SCGO has been shown to display power law behavior [26] and has been fit to a form [27] identical to that shown as the dark red line in Fig. 3 with  $\alpha = 0.4$ . Both SCGO and BSGZCO [28] demonstrate anomalous power law behavior in their bulk susceptibilities. Also, an early dynamical mean-field theory study of a kagome RVB state [29] predicted such a scaling of the dynamic susceptibility. A recent paper [30] on herbertsmithite found that  $S(\omega)$  was roughly independent of both temperature and energy transfer for values of  $\omega$  greater than 2 meV. This simpler  $\omega/T$  scaling is different from what we measure here in the low energy susceptibility.

Similar scaling has been reported in other quantum antiferromagnets, many of which are believed to be close to a quantum phase transition [17]. The neutron scattering results on the spin glass  $\text{La}_{1.96}\text{Sr}_{0.04}\text{CuO}_4$  show a scaling that at small values of  $\omega$  worked best with  $\alpha = 0.41 \pm 0.05$  [17], while at higher energy transfers the data followed a pure  $\omega/T$  scaling [25] with  $\alpha = 0$ .

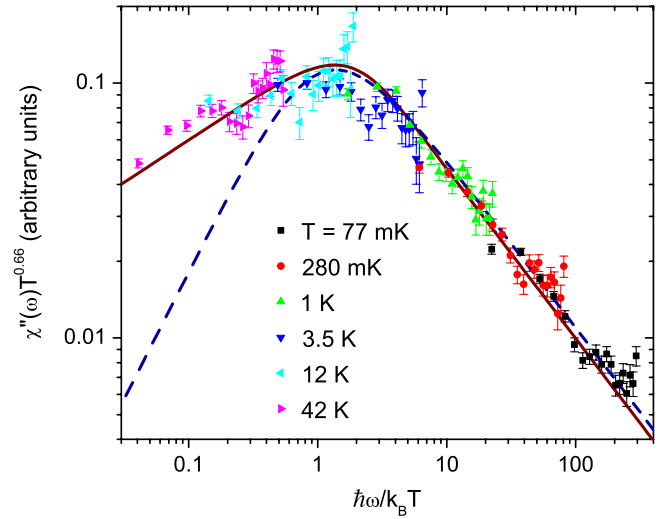


FIG. 3 (color online). The quantity  $\chi''(\omega)T^\alpha$  with  $\alpha = 0.66$  plotted against  $\hbar\omega/k_B T$  on a log-log scale. The data collapse onto a single curve. The lines are fits as described in the text.

Further comparisons can be made to neutron results on various heavy-fermion metals with doping levels that place them near a transition to a spin-glass or antiferromagnetically ordered state [22–24,31]. In addition, a scaling of the ac susceptibility similar to that reported here was seen in  $\text{CeCu}_{5.9}\text{Au}_{0.1}$  [21] and  $\text{Ce}(\text{Ru}_{0.5}\text{Rh}_{0.5})_2\text{Si}_2$  [32]. Recent exact diagonalization work [33] has suggested that the ground state of the spin- $\frac{1}{2}$  kagome lattice antiferromagnet with a Dzyaloshinskii-Moriya interaction will be a quantum disordered state for the Heisenberg Hamiltonian, but a Néel ordered state when the component of the Dzyaloshinskii-Moriya vector perpendicular to the kagome lattice plane exceeds  $\approx J/10$ . The presence of a nearby QCP is also possible in models without a DM interaction [34]. Furthermore, several of the theoretically proposed ground states for the spin- $\frac{1}{2}$  kagome lattice antiferromagnet [35,36] are critical or algebraic spin liquid states. These proposed quantum ground states would possibly display excitations that are similar to fluctuations near a QCP. Thus, the observed low energy scaling behavior in herbertsmithite might signify quantum critical behavior [37] or a critical spin liquid ground state.

In many doped heavy-fermion metals, the observed non-Fermi liquid behavior is likely related to disorder. In herbertsmithite, the low temperature susceptibility roughly resembles a Curie tail, and it has been suggested [14,15] that this is attributable to  $S = 1/2$  impurities (consisting of  $\approx 5\%$  of all magnetic ions) with weak couplings to the rest of the system. We find that the scaling behavior seen in herbertsmithite does have features in common with the disordered heavy-fermion metals, such as  $\chi''(\omega)$  proportional to  $(\omega/T)^{1-\alpha}$  at low values of  $\omega/T$  rather than linear in  $\omega/T$ . The divergence of the low temperature susceptibility may also be indicative of a random magnetic system, such as a Griffiths phase [19,38] or random singlet phase [20]. A collection of impurity spins subject to a broad



distribution of couplings,  $P(J_{\text{imp}})$  may result in a power law susceptibility at sufficiently low temperatures [39]; however, the scaling presented here describes the entire measured susceptibility rather than the response of a small impurity fraction. In this scenario, the scaling of the ac susceptibility, with  $\chi' T^{0.66} \propto F(H/T)$ , would be useful in determining the distribution of couplings experienced by the impurity spins in herbertsmithite. The disordered heavy-fermion metal  $\text{Ce}(\text{Ru}_{0.5}\text{Rh}_{0.5})_2\text{Si}_2$  displays a scaling of the ac susceptibility [32] that is remarkably similar to that in herbertsmithite, except with a considerably larger effective moment [a much smaller field will suppress the low temperature susceptibility of  $\text{Ce}(\text{Ru}_{0.5}\text{Rh}_{0.5})_2\text{Si}_2$ ]. That scaling was attributed to a broad distribution of coupling strengths that likewise diverges at low coupling, quite likely with a power law distribution [40]:  $P(J_{\text{imp}}) \propto J_{\text{imp}}^{-\alpha}$ . In terms of our data, this would imply a distribution of impurity couplings which extend to several meV, which is surprisingly large for the assumed out-of-plane impurity ions. A further prediction in this scenario is that the distribution of local susceptibilities would diverge at low temperatures [19] such that the width of the Knight shift,  $\delta K$ , as measured by NMR would go as  $\frac{\delta K}{K} \propto T^{-\lambda}$  with  $\lambda \approx 0.17$ . The observed NMR signal certainly broadens at low temperatures [41], and it would be most interesting to see if it follows this specific power law. Thermal transport measurements would be important to help differentiate between scenarios where the scale-invariant spin excitations are localized near impurities or extended (as in the aforementioned criticality scenarios).

In conclusion, we have shown that the low energy dynamic susceptibility of the spin- $\frac{1}{2}$  kagome lattice antiferromagnet herbertsmithite displays an unusual scaling relation such that  $\chi T^\alpha$  with  $\alpha \approx 0.66$  depends only on the thermal energy scale  $k_B T$  over a wide range of temperature, energy, and applied magnetic field. This behavior is remarkably similar to the data seen in certain quantum antiferromagnets and heavy-fermion metals as a signature of proximity to a quantum critical point. In addition to scenarios based on impurities, the results may indicate that the spin- $\frac{1}{2}$  kagome lattice antiferromagnet is near a QCP, or that the ground state of herbertsmithite may behave like a critical spin liquid.

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