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Low-energy spin dynamics of the $s = 1/2$ kagome system herbertsmithite**

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Keywords:

neutron spectroscopy; antiferromagnetism; frustrated magnetism

Abstract

The low energy ($\epsilon = \hbar\omega < 1$ meV), low temperature ($T = 0.05$ K) spin dynamics of the $s = 1/2$ kagome candidate herbertsmithite are probed in the presence of magnetic fields up to 2.5 T. The zero-field spectra reveal a very weak continuum of scattering at $T = 10$ K and a broad inelastic peak centered at $\epsilon_{\max} = 0.2$ meV at lower temperatures, $T < 1$ K. The broad peak is found to be strongly damped, with a liquid-like structure factor implying correlations at length-scales up to $r = 6$ Å. The field dependence of the peak appears to follow the Zeeman splitting of $s = 1/2$ excitations, consistent with the weakly split “doublets” observed in low temperature specific heat. A possible explanation of these observations is a short-range correlated state involving defect spins between the kagome planes and moments in the kagome layers.

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Introduction

Despite decades of study, the $s = 1/2$ kagome Heisenberg antiferromagnet model still presents one of the greatest experimental and theoretical challenges in quantum magnetism. While recent numerical work^[1] has shown that the ground state is most likely a gapped spin liquid (a Z_2 topologically ordered state), a large cell valence bond crystal state^[2] and a $U(1)$ Dirac spinon liquid^[3, 4] are known to lie close to it in energy. In order to probe the ground state experimentally, there are thus tight constraints on the size of perturbing terms and amount of chemical disorder allowed in candidate realizations. Several such materials have been explored, including the monoclinically distorted compounds volborthite^[5] and vesignieite^[6], the vanadium oxyfluoride compound $[\text{NH}_4]_2[\text{C}_7\text{H}_{14}\text{N}][\text{V}_7\text{O}_6\text{F}_{18}]$ ^[7], as well as the polymorphs kapellasite^[8] and herbertsmithite^[9], $\text{Cu}_3\text{Zn}(\text{OH})_6\text{Cl}_2$. In the former two, the lowering of symmetry strongly affects the isotropy of magnetic exchange^[10, 11], whilst the vanadium oxyfluoride compound contains additional $\text{V}3^+$ ($s = 1$) between the kagome planes. In kapellasite, the arrangement of Cu octahedra results in a ferromagnetic nearest neighbour exchange^[12]. The premier realisation of the $s = 1/2$ kagome Heisenberg antiferromagnet thus remains herbertsmithite, despite the presence of anti-site disorder between the Cu and Zn sites^[9, 13, 14, 15, 16], which is thought to both dilute the kagome planes and result in weakly coupled interplane spins. This work, performed on a highly deuterated powder sample using inelastic time-of-flight neutron scattering at 50 mK and in magnetic fields up to 2.5 T, elucidates the low energy dynamics of these interplane spins, implying a short-range correlated fluctuating state at low temperature.

The crystal structure of herbertsmithite (figure 1) contains two distinct transition metal sites: the first makes up the kagome planes and is preferentially occupied by the Cu^{2+} ions due to the strong Jahn-

Teller distortion of the D_{4h} MO_4Cl_2 octahedra. The second is located directly above and below the centers of triangles in adjacent planes. This site is not Jahn-Teller distorted and is primarily occupied by Zn^{2+} . From previous studies using a variety of techniques (specific heat, C_p , and neutron diffraction^[14], static susceptibility, χ ,^[9] and ^{17}O NMR^[15]), the typical amount of intersite mixing has been estimated at 4 – 7% in Cu, meaning that around 12 – 21% of the interplane Zn sites are occupied by magnetic Cu^{2+} ions. One study, using anomalous X-ray scattering, has indicated no Zn on the intraplane site^[17], but this claim has been contested on the basis of ^{17}O NMR measurements^[16]. Due to the nearly 90° bridge between the intraplane and interplane sites, the exchange between them is expected to be weak, and possibly ferromagnetic. Indeed, $M(H)$ and $\chi(T)$ data suggest an energy scale $\mathcal{O}(1)$ K for the coupling between intra- and interplane sites^[13]. Further terms in the Hamiltonian potentially include a Dzyaloshinskii-Moriya (DM) term, the magnitude of which was estimated to be $\sim 0.08 J$ on the basis of ESR data^[18], and an axial exchange anisotropy $\Delta = -0.1 J$ derived from χ measurements on single crystals^[19].

Regarding the magnetic properties of herbertsmithite, no spin freezing is observed by any technique down to 50 mK, despite an estimated $J \sim 17(1)$ meV^[20]. The high energy spin dynamics at $T < 120$ K, as probed by neutron scattering, shows a continuum of scattering stretching between energy transfers $2 < \epsilon < 22$ meV ($\epsilon = \hbar\omega$), with a broad Q -dependence peaked at $\sim 1.4 \text{ \AA}^{-1}$ ^[21]. This response is nearly temperature independent in a broad range of T , implying unusual ω/T scaling of the dynamic susceptibility, $\chi''(\omega)$. A more detailed picture of the ω/T and H/T scaling was arrived at by neutron measurements at smaller incident energies, and *a.c.* susceptibility measurements^[20]; both $\chi''(\omega)$ and the real part of the *a.c.* susceptibility, $\chi'(H)$, were found to follow a universal scaling law χT^α , with $\alpha = 0.66$. These observations, as well as the low- T saturation of the intrinsic susceptibility extracted from ^{17}O NMR, can be qualitatively reproduced assuming a valence bond glass state induced by a small concentration of defects on the kagome plane^[22]. An alternative interpretation, placing less emphasis on the presence of antisite disorder, relates the gaplessness of spectrum, the presence of a Curie tail in $\chi(T)$, and a Schottky anomaly in $C_p(T)$ with the deconfined spinon ($s = 1/2$) excitations of the $U(1)$ liquid proposed in^[3, 4].

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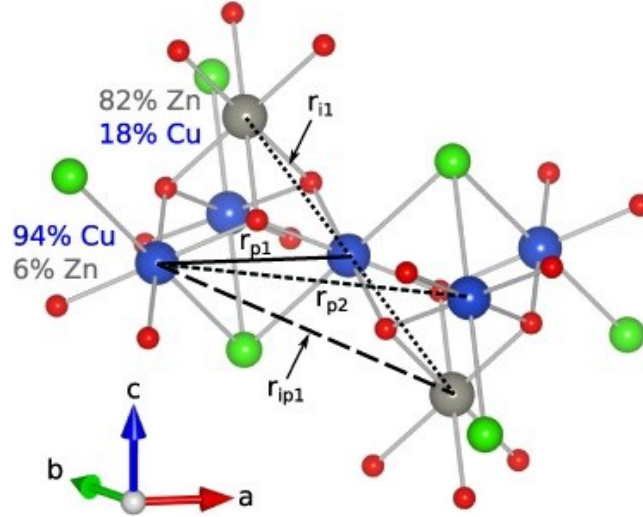


Figure 1. A view of the structure of herbertsmithite. The Cu^{2+} kagome layer sandwiches interplane Zn^{2+} . Distances used in the text are shown by solid and dashed lines.

While the interplane spins have (naturally) not been studied as intensively as the kagome planes, a few attempts have been made to understand their behaviour at low T . Fits of the Schottky anomaly in observed at $T < 5$ K in $C_p(T; H)$ imply that they are describable as $s = 1/2$ doublets with splittings narrowly distributed around ~ 2 K = 0.18 meV in zero magnetic field, and a Zeeman-like field dependence beyond $H = 2$ T^[14]. Furthermore, the interplane spins have been associated with a slowing down in spin fluctuations observed around $T \sim 1$ K by μ SR due to the strong correlation between the magnitude of this feature and the Cu occupation of the interplane site^[23]. Both of these sets of experiments imply the presence of a low energy response at $T < 1$ K in neutron scattering experiments, but this has until the present study not been confirmed.

2. Experimental

The highly deuterated ($\sim 98\%$) powder sample of herbertsmithite used in the present experiment was prepared by the method described by Shores *et. al.*^[9], substituting the protonated or hydrated starting materials with their deuterated and anhydrous counterparts, respectively. The Cu occupation of the interplane site was estimated at $\sim 20\%$ from the Curie tail of the magnetic susceptibility. 10 g of sample was loaded in a Cu can in cylindrical geometry, and mounted on a dilution refrigerator. Thermalization was achieved by condensing a small volume of liquid helium in the sample can at low temperature via a capillary. The data was acquired on the IN5 direct geometry time-of-flight spectrometer at ILL using an incident energy $E_i = 1.26$ meV, resulting in a (Q, ϵ) window of $0.28 < Q$

$< 1.4 \text{ \AA}^{-1}$ ($\epsilon = 0$) and $-1.24 < \epsilon < 1.01 \text{ meV}$, and an ϵ resolution of 0.01 meV , estimated by a Gaussian fit to the elastic line. Background due to the sample environment was partially corrected for by subtracting an empty can measurement from all the datasets. Finally, fields up to 2.5 T were achieved using a split-coil cryomagnet.

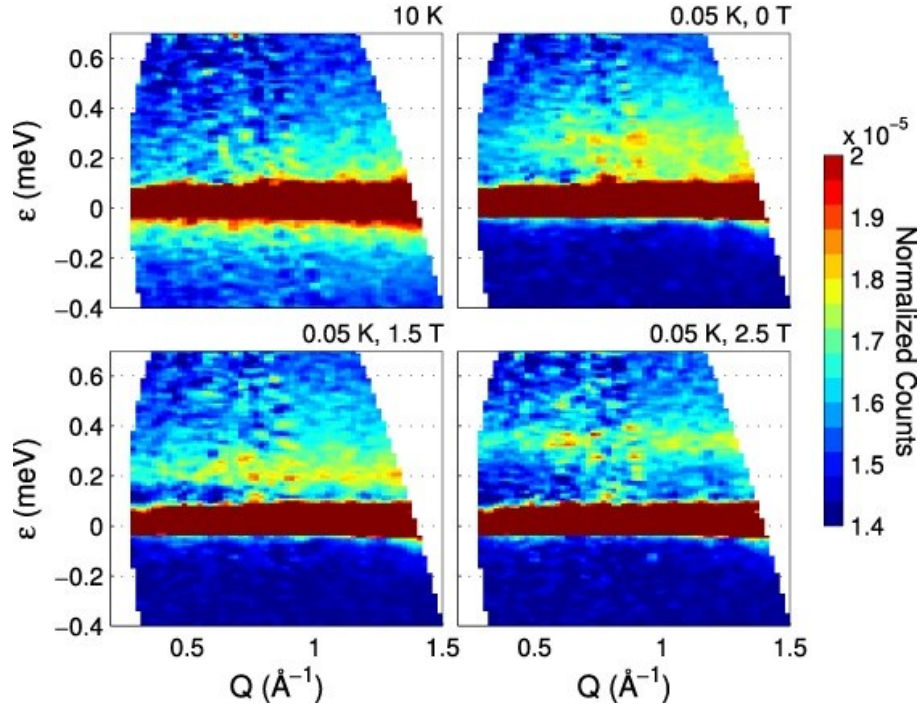


Figure 2. $S(Q, \epsilon)$ from IN5 at $T = 10 \text{ K}$ and 0.05 K , and fields of 1.5 T and 2.5 T for the latter temperature.

3. Results

Background-subtracted $S(Q, \epsilon)$ maps at 50 mK in fields of $0, 1.5, 2.5 \text{ T}$, and at 10 K , are shown in figure 2. At 10 K , $S(Q, \epsilon)$ hints at a weak column of scattering at high $Q \sim 1.2 \text{ \AA}^{-1}$ (see also figure 3(a)), similar to that observed at higher E_i in previous studies^[21]. A fit of the energy transfer integrated data ($0.15 < \epsilon < 0.6 \text{ meV}$) to the structure factor for a spin pair,

$$S(Q) \propto f^2(Q) \left(1 + \alpha \frac{\sin(Qr)}{Qr} \right), \quad (1)$$

where $f^2(Q)$ is the form factor of Cu^{2+} , results in antiferromagnetic ($\alpha < 0$) correlations at $r = 3.5(1) \text{ \AA}$, consistent with the nearest neighbour (nn) Cu-Cu distance within the kagome planes, $r_{p1} = 3.42 \text{ \AA}$, as found in previous measurements. The Q -integrated response ($0.4 < Q < 1.2 \text{ \AA}^{-1}$) was converted to the

dynamical susceptibility, $\chi''(\epsilon)$, using the fluctuation-dissipation theorem $\chi''(\epsilon) = (1 - e^{-\epsilon/k_B T}) S(\epsilon)$. By comparing the neutron energy gain and loss sides, it is found that detailed balance breaks down at $\epsilon = 0.13$ meV, below which multiple scattering from the sample environment dominates. Above this energy, $\chi''(\epsilon)$ is flat within error bars, as also observed in^[24].

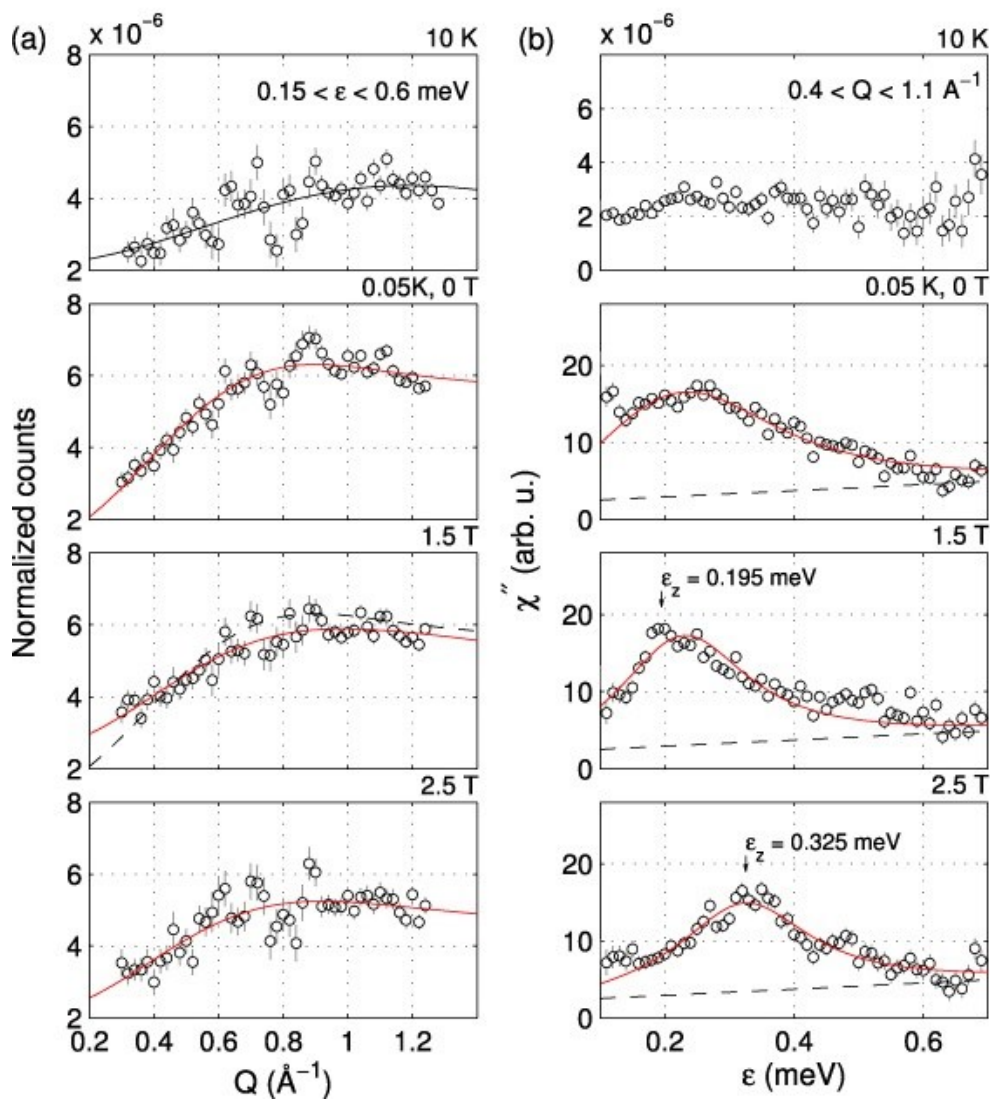


Figure 3. (a) Q - and (b) ϵ -cuts of the data at all T and H . The ϵ -dependence has been converted to $\chi''(\epsilon)$ using the fluctuation-dissipation theorem. The integration ranges used are 0.15 – 0.6 meV and 0.4 – 1.2 \AA in energy and momentum transfer, respectively. Fits in (a) include one nn for the upper curve (black line) and two for the lower 3 curves (red), with the second distance consistent with r_{p2} , r_{i1} , and r_{ip1} (figure 1). The low temperature, zero-field field fit is reproduced in the 1.5 T panel to illustrate the slight shift of intensity towards $Q = 0$ in applied magnetic field. The lines in (b) correspond to damped harmonic oscillator fits, as described in the text.

As the sample is further cooled to 50 mK in zero field, an increase in spectral weight is observed at low energy transfers, taking the form of a broad, apparently non-dispersive feature centered at $E_{\max} \sim 0.25$ meV, and extending up to at least 0.6 meV. The maximum in the scattering is found at a lower $Q_{\max} \sim 0.8 \text{ \AA}^{-1}$ with respect to the 10 K data, indicating antiferromagnetic correlations at distances

longer than r_{p1} . Extending the fit with another $\alpha \sin \frac{\alpha \sin(Qr)}{(Qr)}$ term to include these, the observed shift can be accounted for assuming either correlations between an interplane spin and a next nn spin in the kagome plane, $r_{ip1} = 5.07 \text{ \AA}$, in-plane next nearest neighbours, $r_{p2} = 5.7 \text{ \AA}$, or two nn interplane spins, $r_{i1} = 6.1 \text{ \AA}$ (figure 2) – at 20% occupation of the interplane site, each will on average have 1.2 nearest neighbours. The Q -integrated ϵ dependence (at this temperature and energy range identical to $\chi''(\epsilon)$) appears to be independent of energy transfer, and can be described by a damped harmonic oscillator form

$$\chi''(\epsilon) \propto \frac{4}{\pi} \frac{\Gamma \epsilon}{(\epsilon^2 - \epsilon_0^2)^2 + 4\Gamma^2 \epsilon^2}, \quad (2)$$

centred at $\epsilon_0 = 0.290(5)$ meV, and a large $\Gamma = 0.19(1)$ meV. The latter value is an order of magnitude greater than the resolution, and could be connected with a combination of damping due to strong spin fluctuations, known to persist at low T in herbertsmithite, and an intrinsic width caused by, for example, a distribution of energy levels due to disorder.

In an applied field of 1.5 T, the low energy ($\epsilon < 0.2$ meV) spectral weight observed in zero field shifts up in energy, and the spectrum becomes more sharply peaked at $\epsilon_{\max} = 0.20(1)$ meV, which corresponds to the expected Zeeman splitting for $s = 1/2$ spins, $\epsilon_Z = g\mu_B H = 0.1952$ meV ($g = 2.25$ [18]). Indeed, a comparison of the width of the feature in ϵ with the zero-field spectrum reveals a considerable narrowing, with $\Gamma(1.5 \text{ T}) = 0.12(1)$ meV, while still remaining broader than resolution. One possible source of the large Γ given the Zeeman-like field dependence is g -factor anisotropy, but the experimental $\delta g = 0.1$ [18] only translates to an energy splitting ~ 0.01 meV. Furthermore, the Q -dependence indicates some flattening versus the zero field data, with slightly more intensity towards $Q = 0$. Fitting the simple model above, this may be interpreted as a weakening of antiferromagnetic correlations at $r > r_{p1}$, with correlations at r_{p1} remaining similar in strength.

A recent ^{17}O NMR study revealed a transition to a frozen, possibly glassy, state of the kagome spins at $H_c = 1.5 \text{ T}$ [25]. In the Q range covered by our data, we observe no additional features corresponding to this state. This is not surprising, as the frozen moment is expected to be very small close to H_c . In addition, the measured ϵ_{\max} is considerably larger than that estimated from NMR ($0.4 \text{ K} = 0.034$ meV).

Increasing the field to 2.5 T, the broad feature is again found to shift in ϵ , consistent with the Zeeman splitting. The overall peakshape also grows more symmetric, with a similar $\Gamma = 0.125(4)$ meV to the

1.5 T data. The key parameters describing $\chi''(\epsilon)$ and fits to (1) and (2) at all fields are summarised in Table 1.

H (T)	$-\alpha(3.4 \text{ \AA})$	$-\alpha(5.4 \text{ \AA})$	ϵ_{\max}	ϵ_Z (meV)	ϵ_0 (meV)	Γ (meV)
0	0.45(2)	0.37(5)	0.25(1)	0	0.290(5)	0.19(1)
1.5	0.42(2)	0.20(5)	0.20(1)	0.1952	0.260(5)	0.13(1)
2.5	0.38(3)	0.25(7)	0.33(1)	0.3253	0.345(5)	0.125(7)

Table 1. Field dependence of fitting parameters for equations (1) and (2) at $T = 0.05$ K. ϵ_{\max} , the observed peak maximum and ϵ_0 , the centre of (2), differ in the strongly damped regime $\Gamma \sim \epsilon_0$. A g -factor of 2.25 is assumed in the calculation of the Zeeman splitting energy of $s = 1/2$ spins, ϵ_Z .

4. Discussion

The broad inelastic feature at ~ 0.2 meV observed at $T = 0.05$ K in our experiments is most naturally associated with the interplane spins discussed in the introduction. Their involvement is inferred primarily from the energy scale and field dependence of the feature, which are consistent with both the zero-field- and Zeeman-split $S = 1/2$ doublets observed in the heat capacity^[14], as well as the estimates for inter- to intra- plane coupling strength derived from $M(H)$ and χ ^[13]. While the observed field dependence could also be compatible with deconfined spinons, as proposed in^[3,4], neither the small apparent bandwidth, nor the structure factor can be accounted for in this framework.

Two possibilities for how the zero-field splitting of the aforementioned doublets could arise are: 1) coupling to short range order or fluctuations in the kagome planes, or 2) oligomerisation of the interplane spins with neighbouring spins on the kagome plane *i.e.* formation of trimers or heptamers, as observed in materials like MgCr_2O_4 ^[26]. Although the Q -dependence of the feature is consistent with both of these possibilities, we will consider only the first here, as it most consistently accounts for the field dependence of the spectrum. As mentioned previously, a field-induced transition to a frozen state is observed in NMR at $H_c = 1.5$ T^[25]; the interplane spins ought to provide a sensitive probe of the kagome planes going across this transition. In our experiments, two major changes are seen in the spectrum at H_c : the apparent collapse of the splitting regime observed at zero field and a large drop in Γ . The first can be explained if the spin freezing on the planes involves, at least locally, a 120° arrangement of the spins on the kagome triangles. This appears likely from studies of pressure-induced magnetic order in herbertsmithite, where a $\mathbf{q} = \sqrt{3} \times \sqrt{3}$ order is adopted beyond $P = 2.5$

GPa^[27]. In this scenario, the mean exchange energy $J \sum_i^z s_i \langle s_j \rangle$ at the interplane site vanishes,

effectively decoupling the interplane spins and leading to the shift of scattering towards smaller Q and Zeeman-like field dependence. Furthermore, the reduction in Γ observed at the transition reflects the reduction of the fluctuating moment accompanying the freezing, and perhaps also the narrower distribution of moment directions in the plane. Remaining correlations could involve *e.g.* defects in the kagome planes.

5. Conclusion

We have carried out an inelastic neutron scattering study to probe the low energy dynamics of herbertsmithite at low temperatures and in magnetic fields. Beyond the characteristic column of scattering observed in previous neutron experiments, which we find to extend down to at least 0.13 meV, an additional broad component peaked at $\epsilon_{\max} = 0.25$ meV appears at low T . We associate this mode with the higher energy level of the weakly coupled interplane spins. A possible signature of the magnetic ordering phase transition observed in NMR is indirectly observed through the field dependence of ϵ_{\max} and the damping, Γ . Further neutron scattering investigations over a broader Q - and ϵ -range, preferably using single crystals, are required to confirm this suggestion.

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