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Low temperature magnetization of the $S=\frac{1}{2}$ kagome antiferromagnet $ZnCu_3(OH)_6Cl_2$

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The dc magnetization of the unique $S=\frac{1}{2}$ kagome antiferromagnet Herbertsmithite has been measured down to 0.1 K. No sign of spin freezing is observed in agreement with former μSR and ac-susceptibility results. The low temperature magnetic response is dominated by a defect contribution which exhibits an energy scale $\simeq 1$ K, likely reflecting the coupling of the defects. The defect component is saturated at low temperature by $H \gtrsim 8$ T applied magnetic fields which enables us to estimate an upper bound for the nonsaturated intrinsic kagome susceptibility at $T=1.7$ K.

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In triangular lattices, the frustration of antiferromagnetic interactions associated to the enhancement of quantum fluctuations for $S=\frac{1}{2}$ spins was acknowledged long ago as a key-point to stabilize novel ground states of magnetic matter.[1] Numerous theoretical studies have since emphasized the $S=\frac{1}{2}$ nearest-neighbor Heisenberg antiferromagnet on the kagome lattice (KAH), a network of corner sharing triangles. Although numerical approaches are complicated by the huge degeneracy of the system, it is believed that the ground state could be a unique realization of a disordered two-dimensional quantum liquid at $T=0$, with a surprisingly small gap, if any, to unconventional unconfined spinon excitations and a gapless continuum of nonmagnetic excitations.[2–4] Concurrently, growing efforts were made to identify a model frustrated compound and find evidence for such an exotic spin liquid ground state. Key features have emerged from these experimental investigations like the suppression of magnetic order at the energy scale of the antiferromagnetic interaction, the persistence of spin dynamics at very low temperatures,[5,6] or a large density of low energy nonmagnetic states.[7] However, the frustrated compounds studied so far show strong deviations from the ideal KAH ($S>\frac{1}{2}$ spins, dilution of the magnetic lattice, anisotropic interactions). Besides, they often present marginal low T order or spin glass-like behavior which forbid a close comparison to theoretical expectations.[8]

Only very recently, Herbersmithite, $ZnCu_3(OH)_6Cl_2$, a structurally perfect kagome antiferromagnet decorated by Cu^{2+} $S=\frac{1}{2}$ spins could be synthesized.[9] It belongs to a large compound family $Zn_xCu_{4-x}(OH)_6Cl_2$ where the parent structure, clinoatacamite ($x=0$), is that of a distorted $S=\frac{1}{2}$ pyrochlore. The substitution of Zn^{2+} ions preferentially on the less Jahn-Teller distorted Cu^{2+} site located in between the kagome planes restores the threefold symmetry of the lattice for $x>1/3$. Eventually the Herbertsmithite compound ($x=1$) presents decoupled $S=\frac{1}{2}$ perfect kagome planes. Also, the magnetic order which sets in clinoatacamite at 19 K gradually disappears as $x \to 1$ and for $x=1$, muon spin resonance (μSR) investigation[10] has demonstrated the absence of any spin freezing at least down to 50 mK, an energy scale 4000 times smaller than the main antiferromagnetic interaction ($J \simeq 190$ K).

Once Herbertsmithite is acknowledged to be the first good candidate for the realization of the KAH model, the magnetic susceptibility and heat capacity are the first quantities of interest as they straightforwardly probe the nature of the ground state, either magnetic or not, and the excitation spectrum. At low T, these thermodynamic quantities show, respectively, a Curie-like tail[11,12] and a Schottky-type[11,13] anomaly. It was soon recognized that Dzyaloshinsky-Moriya interactions, which are allowed in Herbertsmithite structure, can yield such a drastic increase of the low T susceptibility.[14] However, magnetic defects could also account for these features, a scenario sustained by recent NMR data[15] and neutron diffraction refinements of the structure.[13,16] Despite poor sensitivity, these latter point at a large (6%–10%) Cu/Zn intersite mixing. This chemical disorder would likely reflect the finite energy of the Jahn-Teller process that selects the Zn substitution site. Both the resulting dilution of the kagome magnetic network and the interplane Cu^{2+} ions may contribute to the defect component. In this Brief Report, we report on a detailed investigation of the Herbertsmithite magnetization at low temperature ($T>0.1$ K) and up to moderately high fields ($H<14$ T). Both sets of data are consistently analyzed in terms of a large defect contribution. We show that the low T intrinsic susceptibility can be nonetheless estimated.

A $ZnCu_3(OH)_6Cl_2$ powder sample was prepared by the hydrothermal method described in Refs. 9 and 10. Low temperature dc-magnetization ($0.1\ \text{K}<T<3$ K) was measured in a homemade superconducting quantum interference device (SQUID) magnetometer for fixed external magnetic fields up to 0.7 T. For $T>0.3$ K, each data point was obtained by extracting the sample through the pick-up coils. To avoid heating effect, for $0.1\ \text{K}<T<0.4$ K, the sample was kept at a fixed position in the pick-up coils and we measured the SQUID voltage variation as a result of the T-dependent sample magnetization. Besides, dc-magnetization curves were recordered versus field ($0<H<14$ T) at constant temperature in a commercial vibrating sample magnetometer (VSM). Standard SQUID data up to 5 T and for $T>1.8$ K were also used to complement and calibrate the low T data.

The temperature dependence of the dc magnetic susceptibility χ of Herbertsmithite measured in a 0.1 T applied field

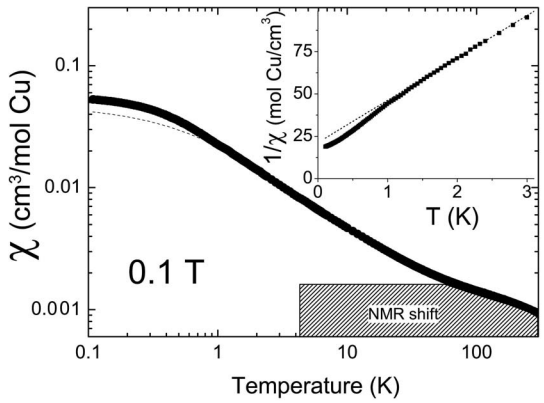

FIG. 1. Molar dc susceptibility of Herbertsmithite versus temperature in a 0.1 T external field on a log-log plot. The local susceptibility measured by a ^{35}Cl NMR line shift falls in the shaded area (Ref. 15). The dashed line is a Curie Weiss fit for 1.5 K$<T<$3 K (see text). Inset: T-dependence of the inverse of the susceptibility at low temperature.

is presented in Fig. 1 in the whole studied temperature range (0.1 K$<T<$300 K). At high temperature ($T\gtrsim$150 K), the susceptibility shows a Curie-Weiss behavior which yields the exchange constant $J\simeq$190 K.[11,17] At lower temperature, the susceptibility increases much more rapidly down to $\simeq$0.5 K where it eventually flattens. Down to the lowest temperature of the experiment T=0.1 K, there is no sign of a magnetic transition in agreement with former μSR[10] and ac-susceptibility[11] measurements. The T-dependence of the total dc-magnetization M has been also measured between 0.1 and 3 K for fixed applied fields H in the range 0.05–0.7 T. Characteristic plots of M/H versus T are presented in Fig. 2. At low temperature, saturation effects are evidenced by the decrease of M/H with increasing fields. More precisely, the field dependence of the magnetization measured at 0.2 K is plotted in the inset of Fig. 2. At this temperature, the data are well-described by the linear $M=\chi(0.2\text{ K})H$ relation for low fields $H\leqslant$0.1 T while saturation effects are clearly observed for $H\geqslant$0.2 T. Therefore the flattening at low temperature of $M/H\simeq\chi$ measured for H=0.1 T in Fig. 1 cannot be ascribed to a field effect.

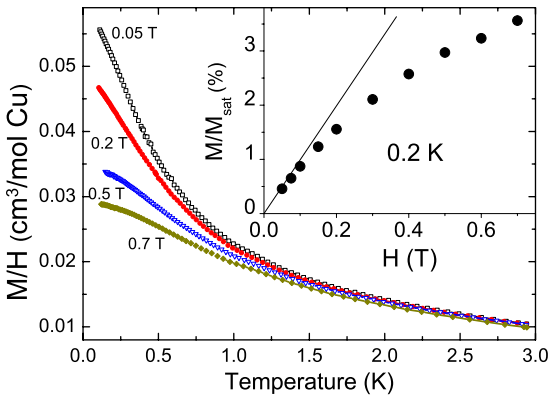

FIG. 2. (Color online) M/H as a function of temperature for different H. Inset: M normalized by the saturated magnetization of 1 mol of $S=\frac{1}{2}$ spins (Cu^{2+}) M_{sat}=5583 emu, at 0.2 K as a function of H. The data are extracted from the temperature scans of the main panel. The straight line is a plot of χ(0.2 K)H.

The NMR line shift of chlorine in Herbertsmithite was measured recently.[15] This local probe investigation is thought to give the intrinsic susceptibility χ_i which is found to strongly deviate from the macroscopic SQUID data χ for $T\lesssim$50 K. Indeed, despite large error bars due to the broadening of the NMR line, χ_i shows a broad maximum or at least a saturation below $\simeq$50 K. One can then put an upper limit to the intrinsic susceptibility $\chi_i<1.5\times10^{-3}$ cm^3/mol Cu as represented by the shaded area in Fig. 1. The maximum of χ_i likely reflects a moderate enhancement of the short range antiferromagnetic (AF) correlations as in the well-studied kagome bilayer case.[18–20] Once these correlations have developed, it is doubtful that there will be a subsequent rise of the susceptibility at lower temperature and we assume that the above upper limit for χ_i also stands down to 0 K. The low temperature dc susceptibility which is the subject of this Brief Report is therefore mainly dominated by a defect contribution. In the following we will make the simplest assumption that the intrinsic and defect contributions are uncorrelated and therefore $\chi=\chi_d+\chi_i$ with $\chi_i/\chi_d<0.1$ for $T<$2 K. As previously mentioned, one can anticipate two types of defects in the structure which can both show a paramagneticlike behavior and which both contribute to χ_d in our analysis. First some Cu^{2+} ions could lie on the interplane site. Their coupling to the kagome planes is likely very weak, maybe slightly ferromagnetic, as discussed in Ref. 9. Second, the dilution of the kagome magnetic lattice by Zn^{2+} ions is believed to locally stabilize dimers and to induce a weak staggered magnetization on further neighboring sites.[21] This nontrivial extended response of the system around a spin vacancy constitutes the second magnetic defect. In the closely related copper based anisotropic kagome structure of Volborthite,[22] the controlled magnetic dilution by Zn/Cu substitution indeed yields a Curie-like tail that scales with the Zn content.[23]

We first consider the intermediate temperature range 1.5–10 K. As shown in the inset of Fig. 1, $1/\chi\simeq1/\chi_d$ does not extrapolate to 0 when $T\to0$ as would be expected for free spins following a Curie law. Instead χ_d rather shows a Curie-Weiss behavior $\chi_d=C_d/(T+\theta_d)$. A proper fit of the low T data requires an accurate knowledge of $\chi_i(T)$. In the absence of such data, we fit with a constant χ_i in the two extreme cases; $\chi_i=0$ which yields θ_d=0.85 K and C_d=0.040 cm^3/mol Cu/K (fit range 1.5 K$<T<$3 K) and $\chi_i=1.5\times10^{-3}$ cm^3/mol Cu which yields θ_d=0.80 K and C_d=0.0345 cm^3/mol Cu/K (fit range 2 K$<T<$10 K). A fit of the high temperature ($T>$150 K) data gives a Curie-Weiss constant $C_{CW}\simeq$0.5 cm^3/mol Cu. If one assumes that the magnetic defects behave as $S=\frac{1}{2}$ spins, their contribution corresponds to $\sim$7% of weakly coupled $S=\frac{1}{2}$ spins out of the total Cu^{2+} contribution. This number is remarkably similar to the estimated number of two level systems which contribute to the Schottky anomaly in heat capacity measurements[13] and also of misplaced Cu^{2+} from neutron diffraction refinement.[13,16] This latter finding suggests that the main contribution to χ_d comes from the interplane Cu^{2+} ($S=\frac{1}{2}$ de-

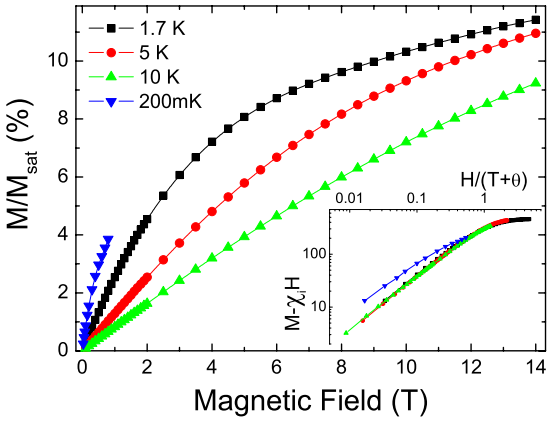

FIG. 3. (Color online) Normalized magnetization (M_{sat} =5583 emu) measured versus field in a VSM for three characteristic temperatures. The magnetization data at 0.2 K are also reported from the inset of Fig. 2. In the inset, for the same temperatures, $M-\chi_i H$ versus $H/(T+\theta)$ with $\chi_i=1.25\times10^{-3}$ cm^3/mol Cu and θ =1.3 K.

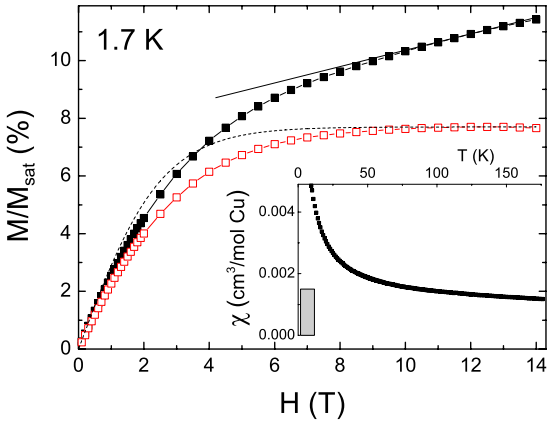

FIG. 4. (Color online) Closed squares: normalized magnetization of Herbertsmithite measured at 1.7 K versus field. The solid line is a linear fit of the data for $H>10$ T which likely reflects the nonsaturated intrinsic susceptibility χ_i. Open squares: the defect contribution obtained by subtracting the above linear contribution from the closed square magnetization curve. Dashed line: Brillouin function for 7.7% of free $S=1/2$ spins. Inset: the shaded area on the SQUID $\chi(T)$ plot represents the possible values of χ_i from this study.

fects) whereas the integrated staggered magnetization around a Zn^{2+} amounts to a rather small moment.

More puzzling is the behavior below 1 K where a subsequent enhancement of the susceptibility appears (Fig. 1, inset). The above described Curie-Weiss regime accounts then only qualitatively for the flattening of $\chi(T)$ (see dashed line in main panel and inset). At 0.1 K the rise of χ with respect to the extrapolated Curie-Weiss behavior is about 1.3×10^{-2} cm^3/mol Cu, i.e., one order of magnitude larger than the upper limit of χ_i. This enhancement is therefore also related to the defect contribution χ_d. No field cooling-zero field cooling opening could be detected below 1 K. Moreover, χ does not show any peak or divergence that would signal long range ordering. Thus the rise of χ for $T\simeq\theta_d$ probably reflects a strengthening of some ferromagneticlike correlations between the magnetic defects rather than some kind of ordering. It is noticeable that a slight slowing down of the electronic spin fluctuation is detected at this same temperature $T\simeq\theta_d$ in μSR experiments. This nicely corroborates the correlation strengthening picture. θ_d is also close to the temperature of the maximum of the Schottky anomaly in zero field heat capacity data. Therefore $k_B\theta_d$ appears as an energy scale for Herbertsmithite, most likely related to the magnetic defect system.

The magnetic response of the defects strongly dominates the total susceptibility at low temperature and it is difficult to extract any information on the KAH contribution. However, one can expect different field dependences for the two contributions. Namely, the weakly coupled magnetic defects should be more easily saturated than the Cu^{2+} spins belonging to the perfect kagome network with the stronger $J\simeq190$ K coupling. To further investigate the field dependence of the magnetization we measured $M(H)$ curves in a vibrating sample magnetometer up to 14 T for constant temperatures in the range 1.7–25 K. Characteristic results are shown in Fig. 3. At 1.7 K, a strong saturation effect is observed above ~2 T and up to ~8 T where $M(H)$ reaches a linear regime. At higher temperature, the saturation effect gradually disappears and at 10 K a nearly linear dependence is recovered. This behavior is compatible with a simple decomposition of the magnetization into a defect and an intrinsic contribution $M=M_d+M_i$. One then assumes that for moderately high fields ($H<14$ T) with respect to the coupling energy scale J, the linear $M_i(H,T)=\chi_i(T)H$ relation holds and that the defect magnetization M_d follows a Brillouin-like saturation. In this scenario, at 1.7 K, the regime for $H>10$ T, where the magnetization is a linear function of H, is explained by the complete saturation of the magnetic defects and the slope of $M(H)$ is a direct measure of the intrinsic susceptibility χ_i(1.7 K). In Fig. 4 the straight line corresponds to $\chi_i(1.7\text{ K})=1.5\times10^{-3}$ cm^3/mol Cu. It is the largest possible value for the intrinsic susceptibility so that the remaining defect magnetization extracted from our data (open squares) does not decrease at high fields. It is noticeable that the fully saturated defect magnetization amounts then to ~8% of the saturated magnetization of one Cu^{2+} mole, in perfect agreement with the ~7% estimate given by the low T Curie-Weiss behavior of the defect susceptibility. However, one cannot exclude that the complex magnetic defects at play in Herbertsmithite are not completely saturated even at the lowest temperature and highest field of this study. Part of or the whole linear regime could then be ascribed to the defect contribution. The extracted χ_i value is therefore only the upper limit of the kagome susceptibility at low temperature. The possible values of χ_i for $T\gtrsim1.7$ K from this analysis are represented by the shaded area in the inset of Fig. 4.

As shown by the dashed line in Fig. 4, a simple $S=1/2$ Brillouin function fails to capture the field dependence of the defect magnetization $M_d=M-\chi_i H$. Possible reasons for this are that (1) the magnetic defects are complex objects involving the point defect itself, likely a misplaced Zn/Cu atom, and the local screening of the defect by the neighboring spins, so that one does not expect a simple $S=1/2$ effective

spin value, and (2) the magnetic defects are slightly antiferromagnetically coupled which tends to reduce the field effect with respect to the H/T dependence of free spins. Note that unconstraining the spin value of the Brillouin function does not give either a good fit of the H and T dependence of M_d. As shown in the inset of Fig. 3, the $M_d(T,H)$ data for $1.7\ \mathrm{K}<T<10\ \mathrm{K}$ merge on the same curve if one uses the scaling variable $H/(T+\theta)$ which accounts phenomenologically for the AF coupling. Good scaling is obtained for $\chi_i = 0.001\ 25 \pm 0.000\ 25\ \mathrm{cm}^3/\mathrm{mol}$ Cu and $\theta = 1.1 \pm 0.2$ K in agreement with θ_{CW} extracted from the low T Curie Weiss fit of the susceptibility. It is noticeable that below 1 K, deviations from this scaling appear gradually. Eventually, the 0.2 K curve can not be made to fall on the $T>1$ K ones, even with different χ_i and θ values. It suggests that the effective defect moment does change below 1 K which corroborates the enhanced correlations scenario drawn from the analysis of the T dependence of the susceptibility.

In summary, from a detailed study of the temperature and field dependence of the magnetization at low T, we can draw a coherent picture of the Herbertsmithite magnetic behavior. The Curie-like tail in the susceptibility can be safely attributed to a defect contribution. The magnetic defects, probably of two kinds, behave in average as weakly coupled spins ($S \neq 1/2$). The signature of the coupling energy $\simeq 1$ K is found ubiquitously in thermodynamics measurements as well as in the spin dynamics. The complex nature of the defects challenges both chemistry to achieve a better control of Zn/Cu site occupation and theory to describe their magnetic behavior. Remarkably, such a large quantity of defects does not seem to alter the underlying KAH physics. Besides, although the effect of the $\simeq 10$ T external fields used in this study is not clearly known, our results are compatible with a finite kagome susceptibility at $T \simeq J/100$ and thus question the ground state nature and the presence of a gap. Although we showed in this study that the low T up turn of the macroscopic susceptibility can be explained in a defect scenario without Dzyaloshinsky-Moriya perturbation terms contrary to the initial proposal of Ref. 14, they could nonetheless impact the low T intrinsic properties and possibly increase the polarizability of the ground state of this unique realization of a $S=1/2$ kagome system.

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