Low temperature magnetization of the S=1/2 kagome antiferromagnet 
ZnCu$_3$(OH)$_6$Cl$_2$

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The dc-magnetization of the unique S=1/2 kagome antiferromagnet Herbertsmithite has been measured down to 0.1 K. No sign of spin freezing is observed in agreement with former $\mu$SR and ac-susceptibility results. The low temperature magnetic response is dominated by a defect contribution which exhibits a new 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 non saturated 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=1/2 spins was acknowledged long ago as a keypoint to stabilize novel ground states of magnetic matter. Numerous theoretical studies have since then emphasized the S=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 non magnetic excitations. Concurrently, growing efforts were made to identify a model frustrated compound and find evidences 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 or a large density of low energy non magnetic states. However, the frustrated compounds studied so far show strong deviations from the ideal KAH (S> 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.

Only very recently, Herbertsmithite, ZnCu$_3$(OH)$_6$Cl$_2$, a structurally perfect kagome antiferromagnet decorated by Cu$^{2+}$ S=1/2 spins could be synthesized. It belongs to a large compound family Zn$_x$Cu$_{4-x}$(OH)$_6$Cl$_2$ where the parent structure, clinoacanthite (x=0), is that of a distorted S=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 three fold symmetry of the lattice for $x > 1/3$. Eventually the Herbertsmithite compound ($x = 1$) presents decoupled S=1/2 perfect kagome planes. Also, the magnetic order which sets in clinoacanthite at 19 K gradually disappears as $x \to 1$ and for $x = 1$, muon spin resonance ($\mu$SR) investigations 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 and a Schottky-type 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. However magnetic defects could also account for these features, a scenario sustained by recent NMR data and neutron diffraction refinements of the structure. Despite a 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 paper, 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)$_6$Cl$_2$ powder sample was prepared by the hydrothermal method described in Ref. Low temperature dc-magnetization ($0.1$ K $< T < 3$ K) was measured in a home made 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 $0.1$ K $< T < 0.4$ K, the sample was kept at a fixed position in the pick-up coils and we measured the SQUID...
The low temperature dependence of the dc magnetic susceptibility $\chi$ of Herbertsmithite measured in a 0.1 T applied field is presented on Fig. 1 in the whole studied temperature range. The susceptibility shows a Curie-Weiss behavior which yields the exchange constant $J \simeq 190$ K. 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 and ac-susceptibility measurements. The $T$-dependence of the total dc-magnetization $M$ has been also measured between 0.1 K 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 $H \leq 0.1$ T while saturation effects are clearly observed for $H \geq 0.2$ T. Therefore, the flattening at low temperature of $M/H \simeq \chi$ measured for $H = 0.1$ T in Fig. 1 can not be ascribed to a field effect.

The NMR lineshift of chlorine in Herbertsmithite was measured recently. This local probe investigation is thought to give the intrinsic susceptibility $\chi_i$ which is found to strongly deviate from the macroscopic SQUID data $\chi$ for $T \lesssim 50$ K. Indeed, despite large error bars due to the broadening of the NMR line, $\chi_i$ shows a broad maximum or at least a saturation below $\simeq 50$ K. One can then put an upper limit to the intrinsic susceptibility $\chi_i < 1.5 \times 10^{-3}$ cm$^3$/mol Cu as represented by the shaded area in Fig. 1. The maximum of $\chi_i$ likely reflects a moderate enhancement of the short range AF correlations as in the well studied kagome bilayer case. 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 $\chi_i$ also stands down to 0 K. The low temperature dc-susceptibility which is the subject of this 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 $\chi = \chi_d + \chi_i$. $\chi_i/\chi_d < 0.1$ for $T < 2$ K. As previously mentioned, one can anticipate two types of defects in the structure which can both show a paramagnetic-like behavior and which both contribute to $\chi_d$ 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. 2. 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. This non trivial 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, the controlled magnetic dilution by Zn/Cu substitution indeed yields a Curie-like tail that scales with the Zn content.

We first consider the intermediate temperature range
1.5 K–10 K. As shown in the inset of Fig. 1, $1/\chi \simeq 1/\chi_d$ does not extrapolate to 0 when $T \rightarrow 0$ as would be expected for free spins following a Curie law. Instead $\chi_d$ 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 $\chi_i$ in the two extreme cases; $\chi_i = 0$ which yields $\theta_d = 0.85$ K and $C_d = 0.040$ cm$^3$/mol Cu/K (fit range 1.5 K $< T < 3$ K) and $\chi_i = 1.5 \times 10^{-3}$ cm$^3$/mol Cu which yields $\theta_d = 0.80$ 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=1/2 spins, their contribution corresponds to $\sim 7\%$ of weakly coupled S=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 $\chi_d$ comes from the interplane Cu$^{2+}$ (S=1/2 defects) 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. 2 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 $\chi$ with respect to the extrapolated Curie-Weiss behavior is about $1.3 \times 10^{-2}$ cm$^3$/mol Cu, i.e. one order of magnitude larger than the upper limit of $\chi_i$. This enhancement is therefore also related to the defect contribution $\chi_d$. No Field Cooling-Zero Field Cooling opening could be detected below 1 K. Moreover $\chi$ does not show any peak or divergence that would signal long range ordering. Thus, the rise of $\chi$ for $T \simeq \theta_d$, probably reflects a strengthening of some ferromagnetic-like 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. $\theta_d$ is also close to the temperature of the maximum of the Schottky anomaly in zero field heat capacity data. Therefore, $k_BT_\theta$ appears as a new 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 dependencies 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 $J \simeq 190$ 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 K–25 K. Characteristic results are shown in Fig. 3. At 1.7 K, a strong saturation effect is observed above $\sim 2$ T and up to $\sim 8$ 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

![FIG. 3: (Color online) Normalized magnetization ($M_{sat} = 5583$ emu) measured versus field in a VSM for 3 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 $\chi_i = 1.25 \times 10^{-5}$ cm$^3$/mol Cu and $\theta = 1.3$ K.](image)

![FIG. 4: (Color online) Full squares : normalized magnetization of Herbertsmithiite 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 non saturated intrinsic susceptibility $\chi_i$. Open squares : the defect contribution obtained by subtracting the above linear contribution from the full 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 $\chi_i$ from this study.](image)
\[ M_d(H, T) = \chi_i(T)H \] 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 \(\chi_i(1.7\ K)\). In Fig. 4 the straight line corresponds to \(\chi_i(1.7\ K) = 1.5 \times 10^{-5}\ \text{cm}^3/\text{mol}\ \text{Cu}\). 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 \(\sim 8\%\) of the saturated magnetization of one \(\text{Cu}^{2+}\) mole, in perfect agreement with the \(\sim 7\%\) 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 \(\chi_i\) value is therefore only the upper limit of the kagome susceptibility at low temperature. The possible values of \(\chi_i\) for \(T \geq 1.7\ K\) 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 \(M_d = M - \chi_iH\). Possible reasons for this are that 1) the magnetic defects are complex objects involving the point defect itself, likely a misplaced \(\text{Zn}/\text{Cu}\) 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, 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. 4 the \(M_d(T, H)\) data for \(1.7\ K < T < 10\ K\) merge on a same curve if one uses the scaling variable \(H/(T+\theta)\) which accounts phenomenologically for the AF coupling. Good scaling is obtained for \(\chi_i = 0.00125 \pm 0.00025\ \text{cm}^3/\text{mol}\ \text{Cu}\) and \(\theta = 1.1 \pm 0.2\ K\) in agreement with \(\theta_{\text{CW}}\) 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 \(\chi_i\) and \(\theta\) 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 \((S \neq 1/2)\). Signature of the coupling energy \(\sim 1\ K\) are 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 \(\text{Zn}/\text{Cu}\) 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 \(\sim 10\ T\) external fields used in this study is not clearly known, our results are compatible with a finite kagome susceptibility at \(T \sim J/100\) 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 polarisability of the ground state of this unique realization of a S=1/2 kagome system.

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