

Frustrated Magnetism in the Quantum Kagome Herbertsmithite $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ Antiferromagnet

F. Bert¹, A. Olariu^{1,2}, A. Zorko^{1,3}, P. Mendels¹, J.C. Trombe⁴, F. Duc^{4,5}, M.A. de Vries⁶, A. Harrison⁷, A.D. Hillier⁸, J. Lord⁸, A. Amato⁹, C. Baines⁹.

¹Laboratoire de Physique des Solides, Univ Paris-Sud, UMR CNRS 8502, 91405 Orsay, France

²Institut de Physique de la Matière Complexe, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland

³Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

⁴Centre d'Élaboration des Matériaux et d'Études Structurales, CNRS UPR 8011, 31055 Toulouse, France

⁵Laboratoire National des Champs Magnétiques Pulsés, 143 avenue de Rangueil, 31400 Toulouse, France

⁶School of Physics & Astronomy, University of St Andrews, North Haugh, St Andrews KY16 9SS, UK

⁷Institut Laue Langevin, F38042 Grenoble, France

⁸ISIS Facility, CLRC Rutherford Appleton Laboratory Chilton, Didcot, Oxon OX11 0QX, UK

⁹Paul Scherrer Institut, Laboratory for Muon Spin Spectroscopy, CH-5232, Villigen PSI, Switzerland

E-mail: bert@lps.u-psud.fr

Abstract. The frustration of antiferromagnetic interactions on the kagome lattice of corner sharing triangles, 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. Only very recently, the model compound Herbertsmithite, $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$, a structurally perfect kagome antiferromagnet could be synthesized and allows close comparison to theories. Muon spin resonance investigation 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 ($J \simeq 180$ K). The kagome plane susceptibility could be accurately measured from the ^{17}O NMR lineshift. It goes through a broad maximum at $T \simeq J/2$ at variance with the diverging SQUID susceptibility which can be consistently interpreted as being dominated by a paramagnetic-like defect contribution arising from Zn/Cu intersite mixing. At lower temperatures ($T \simeq J/100$), the kagome susceptibility is found to saturate to a non zero value in agreement with the absence of a gap in relaxation measurements.

1. Introduction

Whereas the quantum kagome antiferromagnet model is believed to destabilize any conventional magnetic order [1], the exact nature of the ground state remains a debated theoretical issue, to which experiments could hardly contribute because of the absence of an experimental realization of the model. In the context of a longstanding quest for a model frustrated compound, the discovery [2] and synthesis in 2005 [3] of Herbertsmithite, the very first structurally perfect

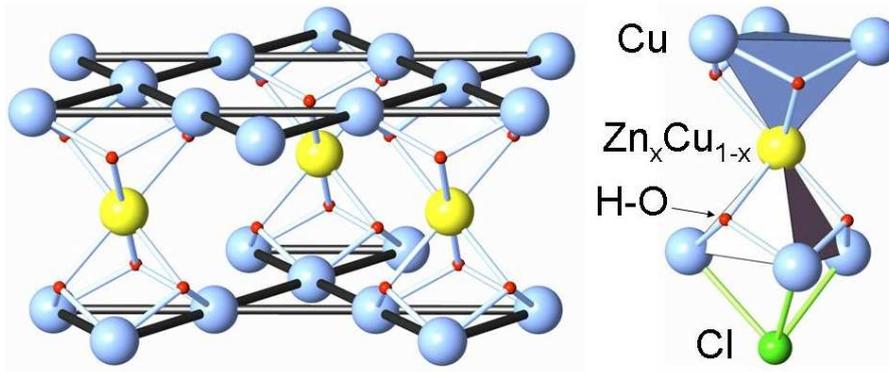


Figure 1. Crystallographic structure of the Zn paratacamite. For clarity, dark bonds that link nearest neighbor Cu emphasize the kagome magnetic lattice.

kagome quantum antiferromagnet has immediately triggered a great number of experimental investigations and novel theoretical developments [4, 5].

We review here some experimental features of the Herbertsmithite $\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$ compound which have been unraveled since 2005 from macroscopic magnetization measurements and local probe ^{17}O NMR, ESR and μSR studies: i) a liquid behavior down to at least 50 mK ii) the presence of complex magnetic defects arising from sizeable Cu/Zn intersite mixing iii) a non-gapped, finite $T \rightarrow 0$ susceptibility of the kagome planes in marked contrast with the monotonically increasing macroscopic susceptibility. The absence of a gap is likely to be related to a sizeable magnetic anisotropy of the Dzyaloshinsky-Moryia type.

2. Herbertsmithite as the end member of the paratacamite family

Herbertsmithite consists of a stacking of Cu^{2+} ($S=1/2$) kagome planes separated from each other by non magnetic Zn^{2+} triangular planes (see Fig. 1). Superexchange through the OH group is responsible for the dominant nearest neighbor interaction of the magnetic Cu^{2+} . The structure is described in the rhombohedral $R\bar{3}m$ space group which ensures the isotropy of the in-plane magnetic interaction and thus makes the magnetic lattice a perfect kagome one. The 119° Cu-OH-Cu bond angle yields moderate antiferromagnetic interactions $J \simeq 180(10)$ K determined from the fit of the high temperature dc-susceptibility to series expansion calculation for the kagome case [6, 7].

A wider family of frustrated compounds, the $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$ Zn-paratacamite, is achieved by progressive substitution of the inter-kagome planes Zn^{2+} ions by additional Cu^{2+} . The interlayer magnetic Cu^{2+} bridge the kagome planes and break the 2D character of Herbertsmithite. While the substitution rate is increased, a ferromagnetic-like component shows up below $T \lesssim 7$ K in magnetization measurements although the dominant magnetic interaction remains antiferromagnetic as demonstrated by the high temperature Curie-Weiss behavior observed for all x [3]. For $x < 0.3$, a Jahn-Teller distortion lowers the symmetry of the structure to the monoclinic space group $\text{P}2_1/n$. The magnetic lattice of the fully substituted clinoatacamite ($x = 0$) can thus be viewed as a 3D network of corner-sharing distorted tetrahedra or as weakly coupled ($J' \simeq 0.1\text{J}$) distorted kagome planes with 3 inequivalent interactions on each triangle [8].

Due to the high sensitivity of muon spins to magnetic fields, μSR is a unique technique to track at the microscopic scale the development of order parameters or to reveal subtle short range ordering. Thus zero field μSR experiments enabled us to demonstrate unambiguously the

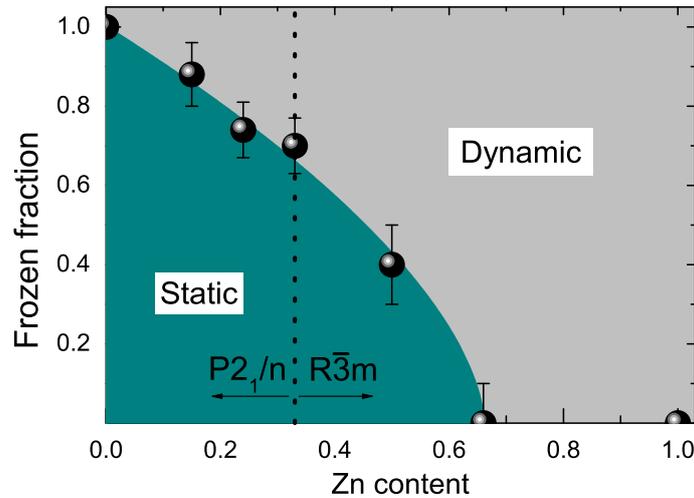


Figure 2. Magnetic phase diagram of the paratacamites drawn from μ SR spectra analysis at $T \sim 1$ K.

absence of any spin freezing in Herbertsmithite down to at least 50 mK with an upper bound of $6 \times 10^{-4} \mu_B$ for the frozen moment of the Cu^{2+} [9]. At the other end of the phase diagram, Clinoatacamite was shown to fully order at 18 K and then to undergo a subsequent transition at 6.4 K where the ferromagnetic component develops [10, 11]. For intermediate Zn rates, the low temperature phase appears to be locally inhomogeneous yielding a two component μ SR signal; one from frozen magnetic environment reminiscent of the ordered phase in clinoatacamite but getting more and more disordered as x increases, and one from a dynamical environment of the muon, reminiscent of the Herbertsmithite signal but with slower spin dynamics. As a local probe technique, the magnitude of the μ SR signal is directly proportional to the volume fraction which is probed. A two component fit of the μ SR relaxation signal at base temperature allows us to measure the volume fraction of the sample that is magnetically frozen [9]. The evolution of this frozen fraction is plotted in Fig. 2. Interestingly for $x > 0.66$, the frozen fraction gets lower than our experimental accuracy (a few percent) and we are left with a fully liquid phase although $1/3^d$ of the inter-layer 3D coupling paths are still active. The large domain of stability of a liquid phase in the phase diagram of the paratacamite likely relates to the weakness of the interplane coupling as well as the shortness of the in plane correlation length.

3. ^{17}O NMR spectrum and Cu/Zn intersite mixing

In order to address the pending theoretical questions regarding the nature of the ground state and the structure of the excitation spectrum of the quantum kagome antiferromagnet, we used the ^{17}O nucleus as a local probe of the magnetic properties of Herbertsmithite [12]. A typical powder NMR spectrum of ^{17}O measured in Herbertsmithite at $T \sim J$, a temperature which realizes a compromise for a good signal to noise ratio and weak magnetic broadening, is plotted on Fig. 3. The clear shift of the spectrum with respect to the reference line, much larger than usual chemical shifts for ^{17}O , evidences large transferred hyperfine fields. Indeed, since the dominant superexchange interaction is mediated by the OH group, a good overlap of the Cu and O electronic orbitals is expected, and gives rise to a large hyperfine coupling of ^{17}O nuclear spin to the two neighboring Cu spins, which is for instance 26 times larger than the one of Cl nuclei [13].

^{17}O bears a $I=5/2$ nuclear spins which yields one central line and two pairs of satellite lines

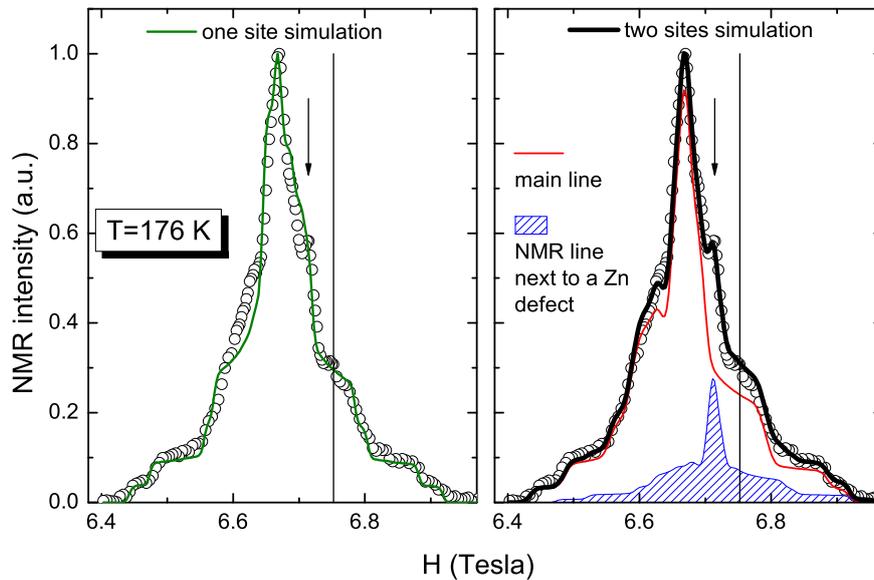


Figure 3. ^{17}O NMR spectrum of Herbertsmithite at $T = 176$ K. The vertical line is the reference resonance line for ^{17}O . The vertical arrow points at a peak feature in the experimental spectrum (see text). Left panel: the solid green line is a typical simulation assuming one single oxygen site. Right panel: the black line is the sum of two contributions from oxygen located far (red) and close (blue) to a magnetic vacancy in the kagome planes. Note that the parameters used for simulating the main lines in both panels are different.

as a consequence of quadrupolar interactions. The positions of these lines depend on the relative orientation of the external magnetic field and the quadrupolar and magnetic shift tensors. Due to the low symmetry of the oxygen site in Herbertsmithite structure, both tensors are anisotropic and they are not diagonal in the same reference frame, although symmetry considerations suggest that they should share the Cu-Cu direction as a common eigenvector. As a result of the powder average, the NMR line shows many singularities which correspond to singular orientations of both tensors. To our surprise, despite 6 free parameters, we were unable to reproduce the position of all the singularities of the experimental spectrum in our simulations. A typical tentative simulation is shown on the left panel of fig. 3. In particular, the peak at the position marked by the vertical arrow is systematically absent in the simulated NMR lines.

Although oxygen occupies only one crystallographic site in the Herbertsmithite structure, we were bound to attribute this peak to the central line of a second oxygen site. As depicted in the right panel of fig. 3, a very good fit is then obtained if one assumes that the magnetic shift of the second site is half the one of the main contribution. Reminding that one oxygen is linked to two copper ions, the presence of this second half shifted oxygen site demands that spin vacancies are present in the kagome planes. On the kagome lattice, one spin vacancy is neighboring four oxygen sites, which are thus probing only one Cu^{2+} spin. From the $\sim 20\%$ relative intensity of this second line, we thus estimate a rather large magnetic dilution of the kagome plane of about 5%. Interestingly, the NMR lineshape can be satisfyingly reproduced in exact diagonalization of small spin cluster on the kagome lattice with random spin vacancies [14].

A natural source of dilution of the kagome magnetic lattice of Herbertsmithite is inter-site mixing defects of Cu and Zn species. Namely, part of the non-magnetic Zn^{2+} substitutes copper on the kagome plane, and respectively, to preserve stoichiometry, the same amount of copper substitute zinc on the inter-plane site. Direct confirmation of a large amount 7-10% of such inter-

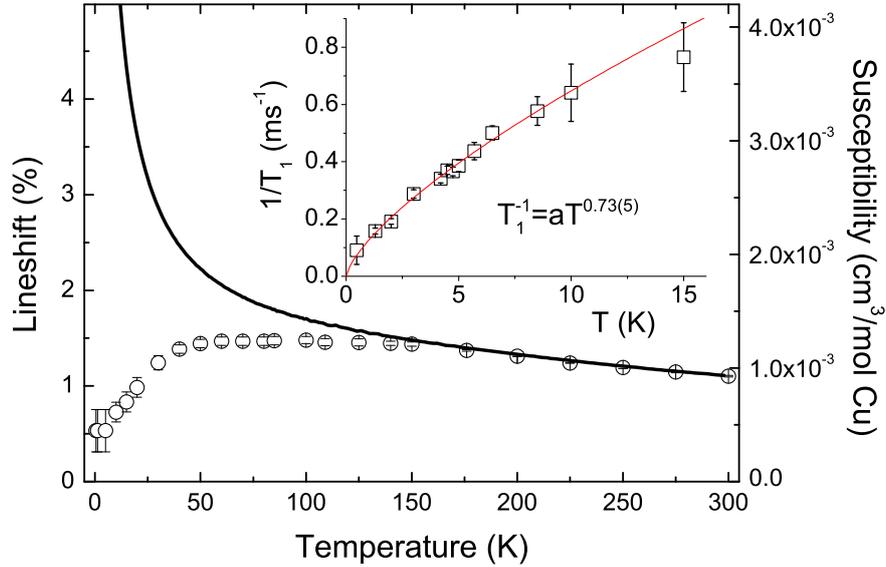


Figure 4. Thermal variation of the susceptibility of the kagome planes measured from the shift of the main ^{17}O NMR line (open symbols) compared to the macroscopic susceptibility (solid line). Inset: Longitudinal nuclear relaxation rate $^{17}\text{O}/T_1$ and fit to a sublinear thermal dependence.

site mixing defects is given by refinement of neutron diffraction data [15, 16]. More indirectly, low temperature features of thermodynamical measurements such as a Schottky-like anomaly in heat capacity [15] or spurious contributions to susceptibility [7] or magnetization [17] (see last section) were attributed to nearly free Cu^{2+} spins on the zinc site.

4. Magnetism of the kagome planes

The magnetic shift of the main contribution to the ^{17}O NMR line measured from 300 K down to 0.45 K is represented on fig. 4. The high temperature shift, $T \gtrsim J$, is proportional to the macroscopic Curie-Weiss susceptibility and the scaling of both data yields the large hyperfine coupling constant $70(5) \text{ kOe}/\mu_B$. Below $T \sim J$, the line shift levels off and shows a broad maximum around $J/2$ before a sharp decrease below ~ 50 K. This low temperature $T < J$ behavior of the shift is in striking contrast with the Curie like upturn of the macroscopic susceptibility below $\sim J/2$. Thus the low temperature Curie tail does not arise from the Cu^{2+} spins of the kagome planes which are probed by ^{17}O NMR and should be attributed to the 5 – 10% nearly free Cu^{2+} spins on the inter-plane Zn sites. Note that the weakness of the superexchange coupling of coppers located in the kagome and in the triangular Zn planes yields a weak hyperfine coupling of ^{17}O to the misplaced coppers¹. Therefore, ^{17}O nuclei mainly probe the magnetism of the kagome plane, far (main line) and close (second line) to a non-magnetic Zn impurity.

Although the susceptibility of the $S=1/2$ kagome antiferromagnet is expected to decrease at some low temperature, high T series expansion improved by using Padé approximants, exact diagonalization [7] and coupled-cluster expansion [18] predict a monotonous increase of the susceptibility as the temperature is lowered down to at least $T \sim 0.2 - 0.3J$. Therefore, the

¹ The weak superexchange constant $J'/J \sim 0.1$ was attributed to the proximity of the corresponding Cu-OH-Cu bond angle 97° to the antiferromagnetic/ferromagnetic limit according to Goodenough-Kanamori analysis [3].

observed broad maximum of the lineshift below $T \sim J$ demands that additional terms to the nearest neighbor Heisenberg Hamiltonian are introduced to describe the magnetic properties of the kagome planes of Herbertsmithite. First, due to the rather strong dilution of the magnetic lattice it is possible that none of the copper ions in the plane can be considered as being far from a spin vacancy. The lineshift should then likely be compared to the site-averaged susceptibility of a diluted kagome lattice. Second, the absence of a center of inversion in between two near-neighbor sites on the kagome lattice allows magnetic anisotropy of the Dzyaloshinsky-Moryia (DM) type. Such anisotropy may strongly affect the magnetic properties as first discussed by Rigol *et al* [18], initially in order to account for the low T Curie upturn of the susceptibility. Through ESR lineshape analysis, an experimental estimate of the DM interactions could be recently extracted [19]. The DM vector is found to be mainly perpendicular to the kagome plane with a rather large magnitude of $\sim 0.1J$. A detailed comparison of the measured lineshift to the dilute kagome model with DM anisotropy has not yet been performed.

At still lower temperature, the NMR spectrum broadens magnetically and the shift is less accurately determined. Nonetheless, the spectrum stays clearly shifted away from the reference line, out the error bars. Also the 0.45 K and 1.3 K spectra are found to be identical so that there is no relative variation of the shift below 1.3 K. Quite certainly, we can thus conclude that the $T \rightarrow 0$ kagome plane susceptibility of Herbertsmithite is finite, and in particular it is gapless. In order to get more insight into the structure of the excitation spectrum, we have performed T_1 relaxation measurements at the position of the main central line. The thermal dependence of the relaxation rate is plotted in the inset of fig. 4. It can be fitted to a power law with the sublinear exponent 0.73(5). Quite strikingly the high field relaxation rate of Cl and Cu nuclei follow the same rather unusual variation [20, 13]. This may point at a rather high density of low energy excitations with weak q dependence. The gapless behavior confirms the lineshift analysis and is also in agreement with the absence of a gap larger than 0.1 meV evidenced by inelastic neutron scattering [6].

As mentioned previously, the theoretical question of the presence of a gap in the magnetic excitation spectrum of the Heisenberg model on the quantum kagome lattice is still open. Indeed one faces the difficult problem of extrapolating exact diagonalization results on small clusters to the thermodynamic limit and only an upper bound of $J/20$ for the gap value is established [21]. Our experimental finding may not help to settle directly this debate as, even if a gap were present in the purely Heisenberg model, the additional DM term in Herbertsmithite would likely mix the singlet and triplet states and lead to the observed gapless susceptibility.

5. Magnetic defects contribution to macroscopic magnetization

The intersite mixing is responsible for two kinds of magnetic defects that can show up in the susceptibility of Herbertsmithite. First the misplaced Zn^{2+} in the kagome plane act as non magnetic impurities which are likely to induce a staggered magnetization of the nearby Cu^{2+} spins as commonly observed in strongly correlated systems [22]. Note however that for the quantum kagome lattice, the situation is more subtle as, in addition to the staggered magnetization picture, the spins in the very close vicinity to the defect tend to form non magnetic dimers [23, 12]. As observed in the kagome-like $S=1/2$ Volborthite compound, where non magnetic impurities can be introduced in a controlled manner, one can then expect that the whole extended defect around the spin vacancy will behave as a paramagnetic center with a small effective moment [24]. Second, the misplaced Cu^{2+} on the Zn interlayer site are weakly coupled to the kagome planes and can be considered as free $S=1/2$ spins. While the first type of defects is well studied by ^{17}O NMR, through the second, minority, line of the spectrum (see section 3) [12], the second type with its larger moment should contribute, especially at low temperature to the macroscopic susceptibility.

In order to ascertain this picture, we have measured the low T magnetization of

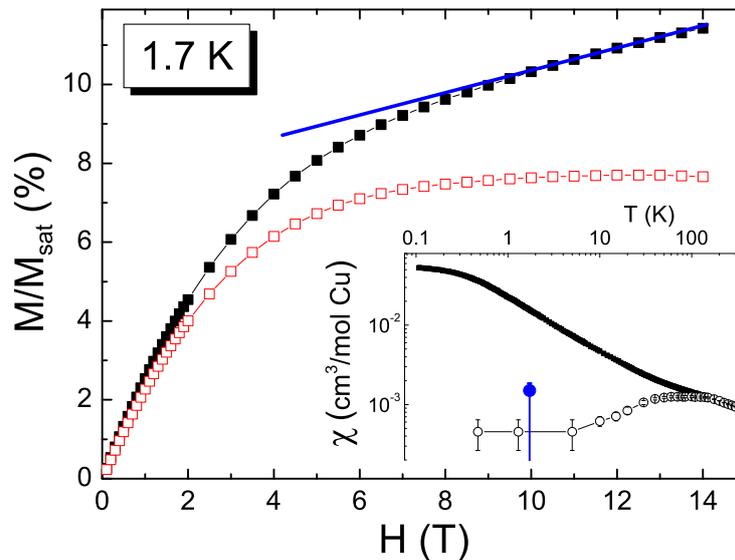


Figure 5. Field dependence of the 1.7 K macroscopic magnetization (black squares) of Herbertsmithite normalized to the saturated magnetization of 1 mole of Cu^{2+} $S=1/2$ spins. The magnetization of the defective inter-layer Cu^{2+} spins (red open squares) is estimated by subtracting the linear contribution of the kagome planes (blue line) from the total magnetization. Inset : the kagome plane susceptibility at 1.7 K is shown as the blue circle with large downward error bar on the plot of the macroscopic susceptibility (black curve) and ^{17}O NMR lineshift reproduced from fig. 4.

Herbertsmithite in strong magnetic fields (see fig. 5) [17]. The magnetization is linear at low field and shows a pronounced downward curvature above ~ 2 T as expected for the Brillouin type saturation of free spins, although a saturation plateau at higher field is not observed. Instead, the magnetization for $H \gtrsim 8$ T increases rather linearly with the applied field. As a first approximation, one can split the total magnetization as the sum of two terms.

First a linear term that is likely to arise from the susceptibility of the Cu^{2+} spins of the kagome planes. Due to their strong antiferromagnetic interactions, their magnetization is not expected to deviate from linearity up to very high fields $g\mu_B H \sim J$. As shown in the inset of fig. 5, this kagome plane susceptibility is much lower than the macroscopic susceptibility at the same $T = 1.7$ K but significantly higher than the local susceptibility obtained from ^{17}O NMR. However if the effective moment of the extended paramagnetic defects induced by spin vacancies in the kagome lattice is small, they may not be saturated in the maximum applied field of 14 T and they then also contribute to the linear magnetization. As a result the extracted susceptibility must be considered as an upper bound to the intrinsic kagome plane susceptibility measured accurately from the shift of the NMR main central line.

Second, a saturated magnetization which can be isolated by subtraction of the high field linear contribution (discussed above) from the measured total magnetization (see red curve in Fig. 5). This part of the magnetization resembles a Brillouin function for a spin 1/2 although the saturation is reached at a slightly higher field suggesting some residual antiferromagnetic interactions of ~ 1 K [17, 9, 15]. This second contribution can be safely attributed to the interlayer Cu^{2+} defects. From the value of the saturated magnetization we get about 7% of such defects out of the total number of Cu, in perfect agreement with the previously mentioned direct and indirect estimations from other studies.

6. Conclusion

The discovery of Herbertsmithite has already triggered many experimental studies. We have made a very partial review of the results focusing mainly on our contribution to the understanding of this unique compound. We can now draw a consistent picture of its magnetic properties. The macroscopic susceptibility is dominated at low T by Cu^{2+} magnetic defects substituted at the interlayer Zn^{2+} sites, which behave as nearly free spins. The local susceptibility of the kagome planes is gapless and should be described within the minimal framework of the Heisenberg Hamiltonian, sizeable DM anisotropy ($\sim 0.1J$) and magnetic dilution (5 – 10%).

The recently evidenced large DM anisotropy opens a new area of research to understand the ground state of Herbertsmithite and more generally the interplay of frustration, DM perturbation and quantum fluctuations. Indeed, at variance with the classical case [25], quantum fluctuations on the kagome lattice seem to stabilize a wide liquid phase up to DM interaction of the order of $0.1J$ [26]. The detailed study of this new phase diagram, closely related to Herbertsmithite physics, has yet to be performed.

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