The Herbertsmithite Hamiltonian: μSR measurements on single crystals

Citation: Ofer, Oren et al. "The Herbertsmithite Hamiltonian: μSR Measurements on Single Crystals." Journal of Physics: Condensed Matter 23.16 (2011): 164207.

As Published: http://dx.doi.org/10.1088/0953-8984/23/16/164207

Publisher: IOP Publishing

Persistent URL: http://hdl.handle.net/1721.1/76640

Version: Author's final manuscript: final author's manuscript post peer review, without publisher's formatting or copy editing

The Herbertsmithite Hamiltonian: μSR measurements on single crystals

Oren Ofer[1], **Amit Keren**[2], **Jess H. Brewer**[3], **Tianheng H. Han**[4] **and Young S. Lee**[4]

Abstract. We present transverse field muon spin rotation/relaxation measurements on single crystals of the spin-1/2 kagome antiferromagnet Herbertsmithite. We find that the spins are more easily polarized when the field is perpendicular to the kagome plane. We demonstrate that the difference in magnetization between the different directions cannot be accounted for by Dzyaloshinksii-Moriya type interactions alone, and that anisotropic axial interaction is present.

[1] TRIUMF, 4004 Wesbrook Mall, Vancouver, BC V6T2A3, Canada

E-mail: `oren@triumf.ca`
[2] Department of Physics, Technion, Haifa 32000, Israel
[3] Department of Physics and Astronomy, University of British Columbia, Vancouver, V6T1Z1 Canada
[4] Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA

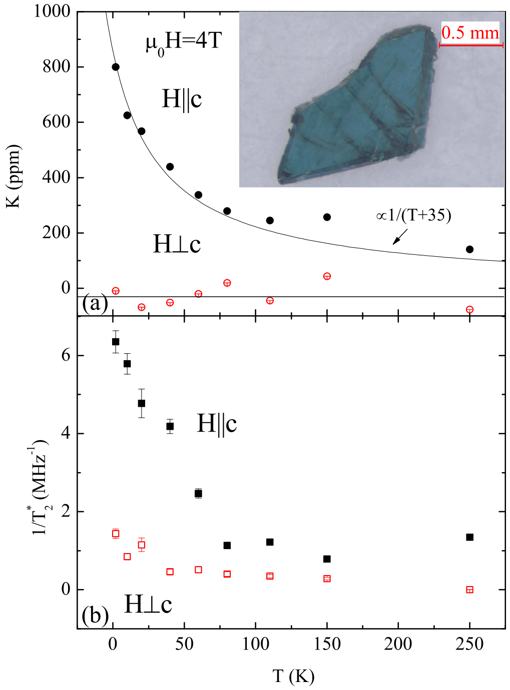

Figure 1. (Color online) The temperature dependence of (a) the muon frequency shift K (errors are smaller than the symbol) and (b) relaxation rate $1/T_2^*$, for two orientations of the crystals (filled symbols for $\vec{\mathbf{H}} \parallel \widehat{\mathbf{c}}$, hollow for $\vec{\mathbf{H}} \perp \widehat{\mathbf{c}}$). The solid line represent a Curie-Weiss type law. The inset shows a typical crystal.

After many years of searching for a good model compound for the spin-1/2 antiferromagnetic kagome magnet, it seems that the community is converging on Herbertsmithite, $ZnCu_3(OH)_6Cl_2$, as the system closest to ideal. Recently, a major scepticism was removed when it was shown that the Zn ions in single crystals do not reside in the kagome plane [1]. However, it is not yet clear what exactly is the Hamiltonian controlling the behavior of this system. Are the interactions isotropic or not? Is the Dzyaloshinskii Moriya (DM) interaction [2] relevant?

To address these questions the research must advance to single crystals. These are available, but their size is still small, limiting the experiments available for them. The high transverse field muon spin rotation (μSR) technique is capable of overcoming this size problem, since the high field helps focus the muon beam onto the small crystals. Here we report such measurements. We find that the magnetic response of Herbertsmithite is very anisotropic. We then analyze the magnetization data and show that a non-isotropic diagonal interaction must be present in $ZnCu_3(OH)_6Cl_2$.

Pioneering measurements on Herbertsmithite indicated a Curie-Weiss (CW) temperature $\theta = -314$ K and a broad deviation from the high-temperature CW behavior starting at $T \approx 75$ K. The nearest-neighbor super-exchange interaction leads to a coupling of $J \approx 190$ K [3]. Extensive measurements on powder samples have found no

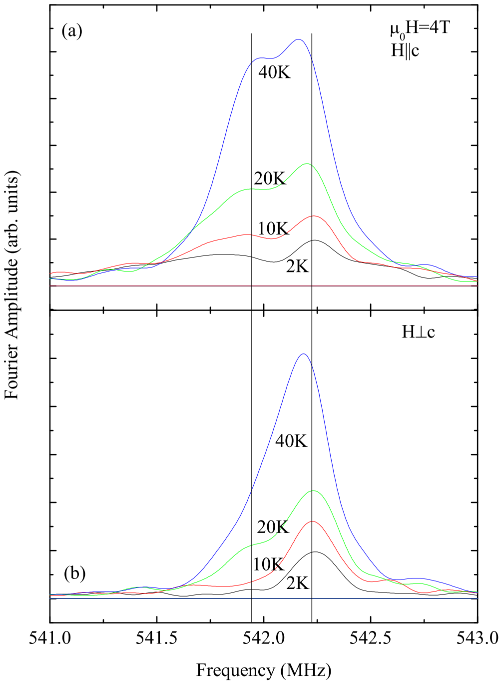

Figure 2. (Color online) The temperature dependence of the Fourier transform of the μSR asymmetry data in a field of 4 T. (a) The spectra obtained when the field $\vec{\mathbf{H}}$ is parallel to the $\widehat{\mathbf{c}}$-axis, which is normal to the mosaic (and thus to the kagome plane) (b) The spectra obtained when the field $\vec{\mathbf{H}}$ is perpendicular to the $\widehat{\mathbf{c}}$-axis.

evidence for long-range magnetic ordering or spin freezing down to 20 mK [4, 5], or a gap to excitations [6, 7]. A recent Raman spectroscopic study on single crystals gives further evidence for a gapless spin liquid state [8]. Analysis of electron spin resonance spectra using DM interactions *only* suggests a sizable DM vector of $D_z = 15$ K [9]. Nuclear magnetic resonance spectra, analyzed again using DM interactions *only*, but with the addition of defects arising from site-exchange, claimed $11 \leq D \leq 19$ K [10]. However, magnetization measurements on oriented powders discovered a dramatic difference in the magnetization between different directions [11] and demonstrated that DM is not the only perturbation to the Heisenberg Hamiltonian. The measurements performed here on single crystals are a clear improvement on the experiments with oriented powders.

The single crystals were measured by X-ray diffraction using a Bruker D8 AXS single crystal diffractometer in order to reveal their crystallographic axes. Subsequently a mosaic of 6 single crystals was created. In the mosaic, the $\widehat{\mathbf{c}}$ axis is off by few degrees between crystals, and we did not manage to keep a particular orientation of the a-b plane. One face of a crystals is shown in the inset of Fig. 1. In general, all faces had similar size and the crystals shape is closer to a cube rather than a slab or a needle. The dark lines seen on the crystal are likely cracks or uneven steps, however x-ray refinement do find a single phase. The $\widehat{\mathbf{c}}$ axis of the crystal is the direction perpendicular to the kagome plane.

The mosaic, held by a thin Mylar tape, was placed onto a low-background sample holder on the M15 surface muon channel at TRIUMF, Canada. Transverse field (TF) μSR spectra, where the field is applied perpendicular to the muon spin direction, were gathered in the T range between 2 K and 250 K in a constant field of $\mu_0 H = 4$ T. Thereafter, the mosaic was rotated by 90° to probe the second orientation of the crystals. A TF-μSR experiment is a sensitive probe of the magnetization M of the specimen through the precession frequency of the muon spin. The frequency shift $K^{\alpha\alpha}(T)$ for a field in the α direction is proportional to M^{α}/H^{α} defined here as $\chi^{\alpha\alpha}(T)$. However, it should be noted that the ratio of shifts in different directions is not the same as the ratio of susceptibilities in those directions, since the shift is also determined by the muon-spin to electronic-spin coupling. This coupling has a significant dipolar character.

Figure 2 depicts the Fourier transforms of the μSR data obtained at $T \leq 40$ K. At the highest T (not shown) a symmetric peak at 542.1 MHz is seen for both field orientations. Below 150 K the peak becomes asymmetric (not shown). Below 40 K, two clear peaks show up in the $\vec{\mathbf{H}} \parallel \widehat{\mathbf{c}}$ measurement [panel (a)]. This happens only at 20 K in the $\vec{\mathbf{H}} \perp \widehat{\mathbf{c}}$ measurement [panel (b)]. In both cases, the emerging lower intensity peak appears below 542.1 MHz. As the temperature is lowered, the low intensity peak in the $\vec{\mathbf{H}} \parallel \widehat{\mathbf{c}}$ spectrum shifts to even lower frequencies and broadens. In contrast, the low intensity peak for $\vec{\mathbf{H}} \perp \widehat{\mathbf{c}}$ smears out quickly, and is unseen at 2 K. The high intensity peak does not shift in either case. The solid vertical lines help assess the shift. The low frequency peaks can be assigned to muons that are influenced by the magnetic kagome planes, since such a wipe out of the signal is typical of slowing down of spin fluctuations, which is expected as T decreases.

Raw data in the time domain for the $T = 2$ K and $T = 250$ K are shown in Fig. 3. These data are presented in a rotating reference frame of 539 MHz. The vertical line indicates that in the $\vec{\mathbf{H}} \perp \widehat{\mathbf{c}}$ case [panel (a)] no change in the rotation frequency is detected and only an increase in the relaxation is observed. In the $\vec{\mathbf{H}} \parallel \widehat{\mathbf{c}}$ case [panel (b)] the frequency does shifts and the relaxation increases. The reason for the apparent increase in the frequency in Fig. 3b is that in the time domain one sees the mean frequency. In the $\vec{\mathbf{H}} \parallel \widehat{\mathbf{c}}$ case the mean frequency shifts upward since the low frequency peak diminishes faster than the high frequency peak. This is not the case for $\vec{\mathbf{H}} \perp \widehat{\mathbf{c}}$. In light of the Fourier transform the function

$$\begin{aligned} A_{\mathrm{TF}}(t) = A_{\parallel,\perp} \exp(-\sqrt{t/T^{*}_{2\parallel,\perp}}) \cos(\omega_{\parallel,\perp} t + \varphi_{\parallel,\perp}) \\ + A_2 \exp(-(\sigma t)^2/2) \cos(\omega_2 t + \varphi_2) \qquad (1) \end{aligned}$$

is fitted to these data globally. The fit is also shown in Fig. 3 using solid lines. The two terms represent an oscillating signal relaxing as a root exponential, originating from the kagome planes, and a Gaussian-relaxing signal stemming from a paramagnetic site. A, T_2^*, σ and ω are the corresponding Asymmetry, relaxation times, relaxation rate and frequencies for each peak in each geometry, respectively. The total asymmetry is a common parameter in the global fit. The ratio $A_{\parallel,\perp}/A_2 = 3(1)$ indicates that most

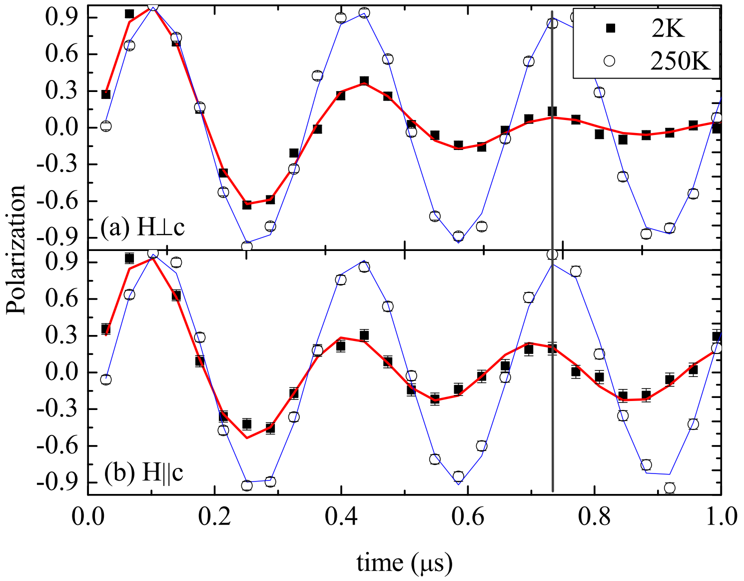

Figure 3. (Color online) μSR data in the time domain using a rotating reference frame of 539 MHz, for the two different field directions and two different temperatures: 250 and 2 K. (a) $\vec{\mathbf{H}} \perp \widehat{\mathbf{c}}$; no shift is detected between the two temperatures, but an increase in relaxation is observed. (b) $\vec{\mathbf{H}} \parallel \widehat{\mathbf{c}}$; a shift in the frequency and increase in relaxation are observed. The solid lines are fits of Eq. 1 to the data. The solid vertical line show when a shift is present and when it is not.

muons sense the kagome planes. The very fast relaxation at early times makes the data in the time domain look as if some asymmetry is lost. This translates to a reduced Fourier amplitude in Fig. 2 upon cooling. A fit in the time domain with a fixed $A_{\mathrm{TF}}(0)$ for all temperatures overcomes this problem.

In Fig. 1(a) we plot the frequency shift, $K_{\parallel,\perp} = (\omega_2 - \omega_{\parallel,\perp})/\omega_2$, versus temperature. The shifts $K_{\parallel}$ and $K_{\perp}$ behave very differently with decreasing temperature. $K_{\parallel}$ increases rapidly with decreasing T below 100 K and reaches 800 ppm at 2 K. In contrast, $K_{\perp}$ fluctuates and is very small. The behavior of $K_{\perp}$ is not understood at the moment; however, the temperature average $\overline{K_{\perp}(T)} = -30(50)$ ppm hints that these might be muon site fluctuations. $K_{\parallel}$ is an order of magnitude larger than the macroscopic suscetibility χ at the same applied field as measured by a SQUID [12]. The fact that $K_{\parallel} \sim 4\pi\chi$ is, *a priori*, a cause for concern. It might indicate that the muons are working as a magnetometer and that the difference between $K_{\parallel}$ and $K_{\perp}$ is due to differences in the sample's demagnetization factor D in different directions. However, the two lines, clearly resolved at 20 K for each direction, indicates that the muons in the site with a shift is sensing the local susceptibility. If the muons were only experiencing $D\chi$, we would not see different behavior at different sites. Moreover, we do not expect differences in D for different directions due to the crystals shape. Thus, the behavior of $K_{\perp}$ and $K_{\parallel}$ indicates a very small spin response when the field is in the kagome plane compared to a field perpendicular to this plane.

Since the temperature dependence of the shift is proportional to the local susceptibility these results indicates that Herbertsmithite has an easy axis. We fit $K_{\|}(T)$ to a CW type law and find $\theta_{cw} = -35$ K. We also fit our $K_{\|}(T)$ data to a CW law with an offset. We examined a free offset and an offset set by the $\overline{K_{\perp}}$ data. We found that θ_{cw} either does not change or becomes more negative. We will continue our discussion using the minimal $|\theta_{cw}|$ since it is sufficient for the conclusions of this paper. This θ_{cw} is different from the one obtained by a SQUID on powders. However, in Herbertsmithite different probes gave different behavior [6, 7, 11, 13, 9] upon cooling so having a new CW is not so surprising.

Finally, in Fig. 1(b) we present the relaxation rate $1/T^{*}_{2\|,\perp}$. The relaxation in both directions is flat and small down to 70 K and then it increases. However, at low T, the relaxation is very different for the two directions. Since $1/T^{*}_{2}$ is also proportional to the susceptibility [14] the relaxation measurement indicate, again, that the system is anisotropic.

In order to understand this behavior we turn to an anisotropic Heisenberg Hamiltonian with a DM interaction which we write as

$$\mathcal{H} = \sum_{i} g\mu_B \vec{\mathbf{S}}_i \cdot \vec{\mathbf{H}} - \sum_{j\neq i} J_{\perp} \vec{\mathbf{S}}^{\perp}_{i} \cdot \vec{\mathbf{S}}^{\perp}_{j} + J_z S^z_i S^z_j + \vec{\mathbf{D}}_{ij} \cdot (\vec{\mathbf{S}}_j \times \vec{\mathbf{S}}_i) \ , \tag{2}$$

where $\vec{\mathbf{D}}_{ij}$ are the DM vectors and the second sum is over neighboring spins (not bonds). This Hamiltonian can be written as $\mathcal{H} = g\mu_B \sum_i \vec{\mathbf{S}}_i \cdot \vec{\mathbf{H}}^{\text{eff}}_i$, where the effective field is

$$\vec{\mathbf{H}}^{\text{eff}}_i = \vec{\mathbf{H}} - \frac{1}{g\mu_B} (\sum_{j\neq i} \tilde{\mathbf{J}} \vec{\mathbf{S}}_j + \vec{\mathbf{D}}_{ij} \times \vec{\mathbf{S}}_j) \tag{3}$$

and the anisotropic diagonal coupling is given by

$$\tilde{\mathbf{J}} = \begin{pmatrix} J_{\perp} & 0 & 0 \\ 0 & J_{\perp} & 0 \\ 0 & 0 & J_z \end{pmatrix} . \tag{4}$$

When expressing $\vec{\mathbf{H}}^{\text{eff}}$ one has to be careful about the convention of $\vec{\mathbf{D}}_{ij}$ [2]. We continue with the mean-field approximation ($\vec{\mathbf{S}} \to -\vec{\mathbf{M}}/g\mu_B$). In principle the kagome unit cell has three different atoms and we should allow a different $\vec{\mathbf{M}}$ for each site. However, we are interested in the high temperature limit where it is reasonable to assume that the magnetization of all ions is the same. We will check this assumption at the end of the calculation. Thus

$$\vec{\mathbf{H}}^{eff}_i = \vec{\mathbf{H}} + \frac{Z}{(g\mu_B)^2} \left(\tilde{\mathbf{J}} \vec{\mathbf{M}} + \vec{\mathbf{D}}_i \times \vec{\mathbf{M}} \right) \ , \tag{5}$$

where $\vec{\mathbf{D}}_i = \frac{1}{Z} \sum_j \vec{\mathbf{D}}_{ij}$ and Z is the number of near neighbors. The magnetization is given by a self consistent solution of the equation $\vec{\mathbf{M}}_i = \frac{C}{T} \vec{\mathbf{H}}^{eff}_i$ where $C = (g\mu_B)^2 \ S(S+1)/(3k_B)$ is the Curie constant. The solution is given by

$$\chi^{\perp\perp}_i = C \frac{(T-\theta_{\perp})(T-\theta_z) + D^{\perp\prime 2}_i}{(T-\theta_z)(T-\theta_{\perp})^2 + T\vec{\mathbf{D}}^{\prime 2}_i - \vec{\mathbf{D}}^{\perp\prime 2}_i \theta_{\perp} - D^{z\prime 2}_i \theta_z} \ ,$$

$$\chi_i^{zz} = C\frac{(T-\theta_\perp)^2 + D_i^{z\prime 2}}{(T-\theta_z)(T-\theta_\perp)^2 + T\vec{\mathbf{D}}_i^{\prime 2} - \vec{\mathbf{D}}_i^{\perp\prime 2}\theta_\perp - D_i^{z\prime 2}\theta_z}\ , \tag{6}$$

where

$$\vec{\mathbf{D}}^{z,\perp\prime} = \frac{CZ}{(g\mu_B)^2}\vec{\mathbf{D}}^{z,\perp}\ .$$

Here $\vec{\mathbf{D}}^{z,\perp}$ are the DM components in the z direction and in the kagome plane, respectively.

It is simple to see that there are three different $\vec{\mathbf{D}}_i$ in the lattice. Therefore, χ_i^{zz} and $\chi_i^{\perp\perp}$ or $\vec{\mathbf{M}}_i$ must be site dependent, unless we are in the limit of high temperatures, $(T-\theta)^2 \gg (\mathbf{D}_i^{z,\perp\prime})^2$ where

$$\chi^{zz} = \frac{C}{(T-\theta_z)} \text{ and } \chi^{\perp\perp} = \frac{\mathrm{C}}{\mathrm{T}-\theta_\perp}. \tag{7}$$

In this case the DM interaction does not affect the CW temperatures which are determined from the high T data. In our experiment at $T = 65$ K, $T - \theta_{cw} = 100$ K and $\mathbf{D}_{ij}$ is estimated to be on the order of 10 K [9]. Therefore, $(T-\theta_{cw})^2$ is two order of magnitude larger than $(\mathbf{D}_i^{z,\perp\prime})^2$, and the high temperature limit is valid. Since the shifts, hence the susceptibilities in the two directions are different at $T = 65$ K we conclude that $\theta_z \neq \theta_\perp$, that J must have axial anisotropy, and that DM interaction cannot explain the anisotropy in the measurements. This does not mean that the DM interaction, which is allowed by the symmetry of the kagome lattice, is not present in addition to the axial anisotropy [15].

In conclusions, μSR measurements were performed on single crystals of Herbertsmithite. We find no clear signature of a magnetic transition down to $T < 10^{-2}J$, as was found for powders (down to $10^{-4}J$). Anisotropic spin susceptibility with an easy axis is revealed. By mean-field approximations, we show that this phenomenon cannot be due to DM interactions alone, and an anisotropic super-exchange J is needed. Our data calls for more work on larger crystals where one can avoid using a mosaic of crystal and the anisotropy can be measured more accurately. Such crystal are becoming available. It will also be useful to have theoretical work on the high temperature behavior of the magnetization in different directions, using Eq. 2 and more accurate methods than mean field.

Acknowledgments

We are grateful to the staff of the TRIUMF CMMS Facility for assistance with the μ^+SR experiments. We are also grateful to P. Mendels for helpful discussion. AK and YSL would like to thank the Israel-US Binational Science Foundation for funding this work. JHB is supported at UBC by NSERC of Canada and (through TRIUMF) by NRC of Canada.

References

[1] Freedman D E Han T H Prodi A Muller P Huang Q-Z Chen Y-S Webb S M Lee Y S McQueen T M Nocera D G 2010 *J. Am. Chem. Soc.* **132** 16185

[2] Rigol M Singh R R P 2007 *Phys. Rev. B* **76** 184403

[3] Helton J S Matan K Shores M P Nytko E A Bartlett B M Yoshida Y Takano Y Qiu Y Chung J H Nocera D G Lee Y S 2007 *Phys. Rev. Lett.* **98** 107204

[4] Mendels P Bert F de Vries M A Olariu A Harrison A Duc F Trombe J C Lord J S Amato A Baines C 2007 *Phys. Rev. Lett.* **98** 077204

[5] Bert F Nakamae S Ladieu F L'Hute D Bonville P Duc F Trombe J C Mendels P 2007 *Phys. Rev. B* **76**, 132411

[6] Ofer O Keren A Nytko E A Shores M P Bartlett B M Nocera D G Baines C Amato A 2006 (*Preprint* cond-mat/0610540)

[7] Olariu A Mendels P Bert F Duc F Trombe J C de Vries M A Harrison A 2008 *Phys. Rev. Lett.* **100** 087202

[8] Wulferding D Lemmens P Scheib P Roder J Mendels P Chu S Han T Lee Y S 2010 *Phys. Rev. B* **82** 144412

[9] Zorko A Nellutla S. van Tol J Brunel L C Bert F Duc F Trombe J C de Vries M A Harrison A Mendels P 2008 *Phys. Rev. Lett.* **101** 026405

[10] Rousochatzakis I Manmana S R Luchli A M Normand B Mila F 2009 *Phys. Rev. B* **79**, 214415

[11] Ofer O Keren A 2009 *Phys. Rev. B* **79**, 134424

[12] Han T and Lee Y S, in preparation.

[13] Imai T Nytko E A Bartlett B M Shores M P Nocera D G 2008 *Phys. Rev. Lett.* **100**, 077203

[14] Kalvius G M Noakes D R and Hartmann O 2001 *Handbook on the Physics and Chemistry of Rare Earths* vol 32 (North-Holland, Amsterdam, 2001); J. H. Brewer, *Encyclopedia of Applied Physics* vol 11 (VCH 1994) p 23-53

[15] Elhajal M Canals B Lacroix C 2002 *Phys. Rev. B* **66** 014422