Spin-1/2 kagome compounds: volborthite vs herbertsmithite

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Abstract. Two kagome compounds, volborthite Cu₃V₂O₇(OH)₂·2H₂O and herbertsmithite
ZnCu₃(OH)₆Cl₂, are compared in order to derive information about the intrinsic properties of
the spin-1/2 kagome antiferromagnet. Observed for volborthite are a broad maximum at
T ~ J/4 and a large finite value approached at T = 0 in bulk magnetic susceptibility
χbulk as well as local one χlocal from the NMR measurements. These must be the intrinsic properties for
the spin-1/2 kagome antiferromagnet, as similar behavior was also reported in χlocal for
herbertsmithite [Olariu A et al. 2008 Phys. Rev. Lett., 100 087202]. Impurity effects that may
influence seriously the bulk properties are discussed.

1. Spin-1/2 kagome antiferromagnet
A kagome lattice is one of the typical playgrounds for frustration physics. Extensive theoretical and
experimental study has been carried out to understand the property of antiferromagnetically coupled
spins on the kagome lattice. However, the ground state (GS) of the most attracting kagome
antiferromagnet (KAFM) with S-1/2 Heisenberg spins seems to be beyond our understanding. This is
because of the inherent difficulty in theoretical treatments on the effects of frustration [1] as well as
the lack of ideal model compounds to study experimentally [2].

Theoretically expected for the GS of the S-1/2 KAFM is a sort of singlet state with an energy gap
in the spin excitation spectrum [1, 3-5]. Since the predicted magnitude of the gap Δ is so small, J / 4
to J / 20, that one assumes an unusual state covered by extended singlet pairs instead of local singlets
that are often observed in various compounds in which a bond alternation exists or is induced as a
result of a spin-lattice coupling. It is known that the size of singlet pairs or the correlation lengths ξ is
inversely proportional to Δ; the smaller the Δ, the larger the ξ. Determining how small the gap should
be is crucial for understanding the GS of the S-1/2 KAFM, though it seems difficult to estimate
precisely in theoretical treatments.

On the other hand, it is always an obstacle for materials scientists to find an ideal model compound.
Real compounds inevitably suffer from more or less disorder arising from defects in a crystal and
unwanted anisotropy or three dimensionality of interactions. Here we focus on the two candidate
compounds studied recently as approximately representing the S-1/2 KAFM. Both are copper
minerals with spin 1/2 carried by a Cu²⁺ ion. One is volborthite Cu₃V₂O₇(OH)₂·2H₂O [6-9] that
possesses such a kagome layer comprising of edge-sharing octahedra, as depicted in Fig. 1(a). Since it
crystallizes in a monoclinic structure [6], there is an anisotropy in magnetic interactions between
nearest-neighbour Cu²⁺ spins in the plane. The distances between two Cu atoms are 3.031 (Cu1-Cu2)

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and 2.937 Å (Cu2-Cu2). The Cu2 ion is located in an octahedron made of 4 O and 2 OH ions that is elongated horizontally in Fig. 1(a), while the octahedron of the Cu1 ion is deformed in the opposite way. Thus, it is reasonable to assume that an unpaired electron is in the $d_{z^2}$ orbital at Cu1, while in the $d_{x^2-y^2}$ orbital at Cu2, as schematically drawn in the inset of Fig. 1(a). As a result, moderately strong antiferromagnetic superexchange couplings are expected through bridging oxide ions with large Cu-O-Cu angles; 105.6° and 82.7° for $J_1$ between Cu1 and Cu2 spins, and 101.1° and 91.5° for $J_2$ between two Cu2 spins [6]. Although it is difficult to predict the magnitude of the magnetic couplings, the anisotropy may not be so large, because of this orbital arrangement. In fact, recent theoretical calculations on the magnetic susceptibility and specific heat of volborthite suggested that the lattice remains a great deal of frustration [10] and that the anisotropy can be less than 20% [11]. The average coupling $J_{av} = (2J_1 + J_2) / 3$ was estimated to be 84 K in our previous study [7]. On the one hand, an anisotropic kagome model has been studied theoretically, which found a rich phase diagram with a ferrimagnetic, incommensurate and decoupled chain phases [12].

**Figure 1.** Kagome lattices of volborthite (a) and herbertsmithite (b). The two drawings are in the same scale. The inset on each drawing expands a triangle of Cu ions to show a possible arrangement of 3$d$ orbitals carrying unpaired electrons.

The other compound is herbertsmithite ZnCu3(OH)6Cl2 that was claimed to be a structurally perfect KAFM [13]. In fact, it crystallizes a hexagonal structure as depicted in Fig. 1(b) comprising an equilateral triangle made of Cu$^{2+}$ ions [14]. The Cu-Cu distance is 3.414 Å, more than 10% larger than those of volborthite. Magnetic couplings should be isotropic through a nearest-neighbour superexchange $J$ via a Cu-O-Cu path based on the $d_{x^2-y^2}$ orbitals arranged symmetrically along the threefold axis. The magnitude of $J$ was estimated to be 170 ~ 190 K [15-17], more than double of the $J_{av}$ of volborthite, which is due to the larger bond angle of 119° [18]. Although the compound looks like perfect, its Achilles heel is a mutual exchange between Cu$^{2+}$ and nonmagnetic Zn$^{2+}$ ions [19-21]. It was reported that 6 - 10% of the Cu site in the kagome plane is replaced by Zn, which means that 18 - 30% of the Zn site is occupied by the kicked out Cu ions. This may be caused by the similarity in the ionic radius between Cu$^{2+}$ and Zn$^{2+}$ and also the same valence state of the two ions. The associated disorder effects in the kagome plane must disturb the GS seriously. Moreover, the almost free Cu spins at the Zn site mask the intrinsic properties in bulk measurements: a superexchange between two neighboring Cu spins at the Cu and Zn sites is expected to be relatively much smaller because of the particular Cu-O-Zn bond angle of 96.9° [18]. Such a chemical substitution is not the case for...
volborthite, because a mutual exchange between aliovalent Cu$^{2+}$ and V$^{5+}$ ions is unfavourable in terms of Madelung energy.

Both the compounds exhibit no long-range order down to 50 mK and have been supposed to be in a spin liquid state [8, 22]. In this paper, we compare the uniform and local magnetic susceptibilities of the two compounds and try to clarify the similarity and differences between them. Through the comparison, we discuss a possible GS for the ideal spin-1/2 KAFM.

2. Experimental
Polycrystalline samples of volborthite and herbertsmithite were prepared as previously reported for each compound [7, 13, 14]. Magnetic susceptibility was measured by a commercial SQUID magnetometer in magnetic fields of 1 and 10 kOe between 2 and 400 K.

3. Magnetic susceptibility
Figure 2 compares magnetic susceptibility $\chi$ for the two compounds. Marked features are a broad maximum observed at around $T_{\text{peak}} = 22$ K for volborthite and a large Curie tail at low temperatures for herbertsmithite. The former may be associated with the development of antiferromagnetic short-range-order (SRO) [7], and the latter is apparently due to free spins mostly at the Zn site. Both compounds exhibit Curie-Weiss (CW) behaviour at high temperatures, as clearly evidenced in the inverse-$\chi$ plot shown in the inset. The Weiss temperature $\Theta_W$ and the Lande $g$ factor are $\Theta_W = -115$ K and $g = 2.26$ for volborthite and $\Theta_W = -241$ K and $g = 2.23$ for herbertsmithite. The latter value is slightly smaller than $\Theta_W \sim -300$ K reported previously [13, 15]. The difference in the magnitude at high temperatures apparently comes from a difference in the Weiss temperature and thus the antiferromagnetic interaction.

Figure 2. Magnetic susceptibility $\chi$ per 1 mole of Cu for volborthite and herbertsmithite measured at $H = 10$ kOe on heating. The inset shows the same data plotted as $1/\chi$. The line through each data set denotes a Curie-Weiss fit.

Various fittings to the $\chi$ data have been carried out, as shown in Fig. 3. The $J_{av}$ of volborthite is determined to be $J_{av} / k_B = 86$ K by fitting the data above $T = 150$ K to the calculations by high-temperature series expansions (HTSE) for the kagome lattice based on the spin Hamiltonian $J\sum S_i \cdot S_j$ [3]. A Bonner-Fisher (BF) curve assuming $J_{av} / k_B = 136$ K cannot reproduce the observed steep increase at low temperatures as well as the sharper peak, which means that the Heisenberg chain model is far from the reality. Taking into account couplings between the chains would improve the result and may reach a less anisotropic case on the kagome lattice, as discussed before [11]. It is important to note that the $\chi$ may remain at a large finite value at $T = 0$, implying the absence of a spin gap in the GS. After subtracting a small upturn at low temperatures that is ascribed
to 0.5% free spins, the remaining value becomes $2.7 \times 10^3$ cm$^3$ / mol-Cu. If there was a gap of $J / 4$ as predicted by the finite-cluster calculations [3], the $\chi$ should steeply decrease after a maximum at $J / 6 \sim 14$ K, as shown in Fig. 3(a). Thus, we can safely exclude the presence of such a large gap. Very recently, we extended our measurements down to 60 mK on a higher-quality sample and found a nearly $T$-independent $\chi$ [23]. Therefore, it is plausible to conclude that the GS of volborthite is gapless or, more carefully, that the spin gap would be less than $J / 1500$, if any.

![Figure 3](image)

**Figure 3.** Various analyses on the magnetic susceptibilities of volborthite (a) and herbertsmithite (b). Shown in (a) are fits to the Curie-Weiss (CW) form, the Heisenberg chain model expressed by the Bonner-Fisher (BF) curve [24], and the uniform kagome lattice model by the high-temperature series expansions (HTSE) [3]. The $T$ dependence expected for $\Delta = J / 4$ by the finite cluster calculations is also plotted in (a). The inset of (b) expands the low-temperature part, where fitting to the form $\chi = \chi_{\text{imp}} + \chi_{\text{bulk}}$ is shown. Thus separated contributions are shown in the main panel below the data. The HTSE fits at high temperatures yield $J_{\text{av}} / k_B = 86$ K for volborthite and $J / k_B = 199$ K for herbertsmithite.

It is curious to know whether the broad maximum in $\chi$ observed for volborthite is a general feature for the spin-1/2 HAFM. In the case of herbertsmithite, the large Curie tail might have absorbed it into the background, even if it exists. Thus, it is reasonable to assume that $\chi = \chi_{\text{imp}} + \chi_{\text{bulk}}$, where $\chi_{\text{imp}} = C/(T - \Theta)$. We fit the data between 2 and 17 K by assuming that the $\chi_{\text{bulk}}$ is constant at that $T$ range to estimate the concentration of nearly free spins $x_{\text{imp}}$. The fitting yields $x_{\text{imp}} = 10.9(4)$% with $\Theta = 1.1(1) \times 10^3$ cm$^3$ / mol-Cu and $\Theta = -2.2(1)$ K, which means that the actual compositions are Cu$_{0.9}$Zn$_{0.1}$ and Zn$_{0.7}$Cu$_{0.3}$ at the kagome Cu site and the Zn site, respectively, in good agreement with previous results from structural refinements [19, 20]. After subtraction of this large impurity contribution, the rest $\chi_{\text{bulk}}$ turns to be more flat but does not exhibit clearly a broad peak as in volborthite. It is likely, however, that the ambiguity of estimating $\chi_{\text{imp}}$ at low temperatures has obscured a possible gradual decrease below $\sim 50$ K. By fitting the $\chi_{\text{bulk}}$ between 200 and 350 K to the result of the HTSE, we obtain $J = 199(1)$ K assuming $g = 2.23$ from the CW fitting at high temperatures. This $J$ value is close to those reported previously [15-17]. Thus, the energy scale is more than two times larger in herbertsmithite than in volborthite.
In the case that the $\chi_{\text{bulk}}$ is influenced by impurity contributions, the NMR Knight shift $K$ often provides a good local probe to estimate $\chi_{\text{local}}$. In the case of volborthite, $\chi_{\text{bulk}}$ and $K$ from V NMR signals gave similar $T$ dependences that are plotted together in Fig. 4(a), taking into account the hyperfine coupling constant $A = 6.6$ kOe / $\mu_B$ in the relation of $K = A\chi / N_A$ [7]. Thus, the presence of a broad peak in magnetic susceptibility is clearly evidenced, though the $T_{\text{peak}}$ at the maximum seems to be slightly different between $\chi_{\text{bulk}}$ and $\chi_{\text{local}}$. Very recent $^{17}$O NMR experiments on herbertsmithite by Olariu et al. successfully determined the local susceptibility of the kagome lattice and found that $K$ decreases below 50 K and approaches approximately one-third of the maximum value at 50 K [21]. Their $\chi_{\text{local}}$ data is compared with our $\chi_{\text{bulk}}$ data in Fig. 4 using $A = 35$ kOe / $\mu_B$. Note that the $T_{\text{peak}}$ of herbertsmithite is considerably higher than that of volborthite, reflecting the larger $J$ value. Figure 4(b) shows an alternative plot after normalization using $J / k_B = 86 (199)$ K and $g = 2.26 (2.23)$ for volborthite (herbertsmithite). All the data except the $\chi_{\text{bulk}}$ of herbertsmithite merge into a universal curve at high temperatures, whereas their low-temperature behaviors seem different. However, we can say qualitatively that there is a broad maximum at around $T \sim J / 4$, indicating the development of SRO, and also that a large value remains at $T = 0$, supporting a gapless GS.

**Figure 4.** (a) Local magnetic susceptibility $\chi_{\text{local}}$ estimated from the Knight shift obtained by previous NMR measurements [7, 21]. The original Knight shift data were measured at $H \sim 80$ kOe for volborthite and $\sim 70$ kOe for herbertsmithite, while the magnetic susceptibility was obtained at $H = 10$ kOe. The $\chi_{\text{bulk}}$ data has been divided by 0.9 for comparison, taking into account the missing 10% spins from the kagome plane. (b) The same data plotted after normalization using $J / k_B = 86 (199)$ K and $g = 2.26 (2.23)$ for volborthite (herbertsmithite).

### 4. Impurity effects
As a matter of fact, the impurity effects are inevitable in real materials and may be crucial for understanding the true GS of the kagome compounds. Bert et al. found a spin-glass transition at 1.2 K for volborthite [25], as reproduced in Fig. 5. Their sample seems to contain more impurity spins than ours, judging from the larger Curie tail. Recently, we also observed a similar spin-glass transition in $\chi$ measurements down to 60 mK in our samples [23]. In the previous NMR study down to 1.7 K, we obtained a characteristic NMR spectrum that is composed of a sharp central peak and a broad hump, as...
reproduced in Fig. 6 [7]. Bert et al also found a similar NMR spectrum and suggested that 20% of Cu spins are in SRO and 40% are frozen [25]. In contrast, we ascribed the broad hump to field-induced paramagnetic moments, because its line width appeared to vanish at zero field, as reproduced in the inset of Fig. 6 [7]. It is known for spin-1/2 Heisenberg chains such as Sr$_2$CuO$_3$ that local staggered magnetization is induced by magnetic field near chain ends or defects, which gives a similar spectrum [26]. On the analogy of this, we think that the broad hump comes from Cu spins that are located near and affected by a defect, as schematically illustrated in Fig. 7, and the sharp central peak from the rest of intact spins that must carry the intrinsic information of the kagome lattice. It is considered that the spin glass transition observed at low temperatures is related to this defect induced moments. Possibly, an impurity-affected domain spreading over the distance $\xi$ from a defect grows with decreasing temperature and finally overlaps with nearby domains to be connected to each other percolatively, resulting in the spin glass transition.

**Figure 5.** Comparison of magnetic susceptibility at $H = 1$ kOe of volborthite for sample A studied in the present paper and sample B obtained by annealing in a hydrothermal condition. The amounts of impurity spins are estimated from the Curie tails to be 0.5% and 0.07%, respectively. The $\chi$ data given by Bert et al. is also plotted [25], which exhibits a thermal hysteresis due to a spin-glass transition.

**Figure 6.** $^{51}$V powder NMR spectrum of volborthite measured at $T = 1.7$ K and $f = 12.8$ MHz [7]. The inset shows the field dependence of the full width at 1/2, 1/10 and 1/20 of the peak height.

Therefore, critically important is to reduce the amount of impurity spins or defects as much as possible. Very recently, we have tried to improve the sample quality of volborthite and succeeded it by annealing in a hydrothermal condition after the initial precipitation [23]. The x-ray diffraction peaks from the annealed sample becomes much sharper, and the particle size gets bigger as 100 $\mu$m. The $\chi$ measured on the new sample is shown in Fig. 5, which exhibits a much smaller Curie tail and more pronounced decrease below $T_{\text{peak}}$ (sample B). The estimation of $x_{\text{imp}}$ gives 0.07%, reduced by one order of magnitude compared with the present sample A. The entity of the defects in volborthite is not known, but maybe associated with certain crystalline defects produced near the particle surface or at a stacking fault, as is often the case for such a layered compound. Various experiments are in progress on the clean sample to elucidate more clearly the nature of the GS of volborthite.

In strong contrast, it seems difficult to control the impurity level in herbertsmithite: mutual exchange between Cu and Zn atoms may occur to attain a high-entropy state at preparation temperatures. We found approximately 10% Cu spins missing from the kagome plane. Previous specific heat and NMR measurements found it approximately 6% [20, 21]. It was suggested that about
20% of the remaining spins behave differently from the majority spins, because each defect directly affects nearby 4 Cu spins [21]. The situation for the 10% exchange is schematically depicted in Fig. 7, which clearly illustrates how imperfect the kagome plane of the herbertsmithite is. As observed in volborthite, even less than 1% defects disturb the surrounding spins within a large distance. One has to be careful to interpret experimental results from such a diluted kagome lattice.

Figure 7. Schematic drawings of the kagome lattice for volborthite (left) and herbertsmithite (right) exemplifying how much defects are included in actual samples. Small balls represent Cu atoms, and larger closed circles some defects for volborthite and Zn atoms for herbertsmithite. It is assumed for volborthite that two defects exist among approximately 300 Cu ions, so that $x_{\text{imp}} \sim 0.7\%$, while, for herbertsmithite, that Zn occupies 10% of the Cu sites randomly. Since 4 Cu spins next to a defect that are marked by open circles lose their neighbours and are affected seriously, the number of intact spins decreases rapidly with increasing $x_{\text{imp}}$. Even in a case with less defects as in volborthite, the influence of defects on the background of singlet "sea" may spread over within a correlation length $\xi$ that should increase with decreasing temperature until it is limited by the average separation of defects.

5. Concluding remarks
The GS of the spin-1/2 HAFM is still mysterious. The broad maximum and the finite value in $\chi_{\text{bulk}}$ as well as in $\chi_{\text{local}}$ observed in volborthite must be its intrinsic properties, as also observed in $\chi_{\text{local}}$ for herbertsmithite. Thus, SRO develops below $T \sim J / 4$, and the spin excitation at $T = 0$ may be gapless, in disagreement with theoretical predictions. The correlation length may increase with decreasing temperature rapidly, more rapidly than in one-dimensional systems, and saturate at a very large value, so that even a small amount of defects must influence seriously the surroundings. This may be common for all the frustrated systems that lack long-range order. In the absence of defects, the GS is considered to be a sort of long-range RVB state or a spin liquid, if you like, which contains various ranges of singlet pairs in long distances. We believe that there must be an extremely slow spin dynamics originating from frustration and quantum fluctuations in the spin-1/2 KAFM, which will be addressed in future study using a higher-quality powder sample or, hopefully, a single crystal of volborthite, or other more ideal compounds to be explored in future work.

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References

[1] Misguich G and Lhuillier C, in *Frustrated Spin Systems*, edited by H. T. Diep (World Scientific, Singapore, 2005), pp. 229.
[2] Ramirez A P 1994 *Annu. Rev. Mater. Sci.* **24** 453
[3] Elstner N and Young A P 1994 *Phys. Rev. B* **50** 6871
[4] Waldmann C, Everts H-U, Bernu B, Lhuillier C, Sindzingre P, Lecheminant P and Pierre L 1998 *Eur. Phys. J. B* **2** 501
[5] Mila F 1998 *Phys. Rev. Lett.* **81** 2356
[6] Lafontaine M A, Bail A L and Férey G 1990 *J. Solid State Chem.* **85** 220
[7] Hiroi Z, Kobayashi N, Hanawa M, Nohara M, Takagi H, Kato Y and Takigawa M 2001 *J. Phys. Soc. Jpn.* **70** 3377
[8] Fukaya A, Fudamoto Y, Gat I M, Ito T, Larkin M I, Savici A T, Uemura Y J, Kyriakou P P, Luke G M, Rovers M T, Kojima K M, Keren A, Hanawa M and Hiroi Z 1998 *Phys. Rev. Lett.* **91** 207603
[9] Okubo S, Ohta H, Hazuki K, Sakurai T, Kobayashi N and Hiroi Z 2001 *Physica B* **294-295** 75
[10] Wang F, Vishwanath A and Kim Y B 2007 *Phys. Rev. B* **76** 094421
[11] Sindzingre P 2008 *arXiv:0707.4264*
[12] Yavors'kii T, Apel W and Everts H-U 2008 *Phys. Rev. B* **76** 064430
[13] Shores M P, Nytko E A, Bartlett B M and Nocera D G 2005 *J. Am. Chem. Soc.* **127** 13462
[14] Braithwaite R S W, Mereiter K, Paar W H and Clark A M 2004 *Mineralogical Magazine* **68** 527
[15] Helton J S, Matan K, Shores M P, Nytko E A, Bartlett B M, Yoshida Y, Takano Y, Suslov A, Qiu Y, Chung J H, Nocera D G and Lee Y S 2007 *Phys. Rev. Lett.* **98** 107204
[16] Rigol M and Singh R R P 2007 *Phys. Rev. Lett.* **98** 207204
[17] Misguich G and Sindzingre P 2007 *Eur. Phys. J. B* **59** 305
[18] Mizuno Y, Tohyama T, Maekawa S, Osafune T, Motoyama N, Eisaki H and Uchida S 1998 *Phys. Rev. B* **57** 5326
[19] Lee S-H, Kikuchi H, Qiu Y, Lake B, Huang Q, Habicht K and Kiefer K 2007 *Nat. Mater.* **6** 853
[20] de Vries M A, Kamenev K V, Cockelmann W A, Sanchez-Benitez J and Harrison A 2008 *Phys. Rev. Lett.* **100** 157205
[21] Olariu A, Mendels P, Bert F, Duc F, Trombe J C, Vries M A d and Harrison A 2008 *Phys. Rev. Lett.* **100** 087202
[22] Mendels P, Bert F, Vries M A d, Olariu A, Harrison A, Duc F, Trombe J C, Lord J S, Amato A and Baines C 2007 *Phys. Rev. Lett.* **98** 077204
[23] Yoshida H, Okamoto Y, Tayama T, Sakakibara T and Hiroi Z in *preparation*
[24] Bonner J C and Fisher M E 1964 *Phys. Rev.* **135** A640
[25] Bert F, Bono D, Mendels P, Ladieu F, Duc F, Trombe J-C and Millet P 2005 *Phys. Rev. Lett.* **95** 087203
[26] Takigawa M, Motoyama N, Eisaki H and Uchida S 1997 *Phys. Rev. B* **55** 14129