

**Ground State of the Kagomé-Like  $S = 1 / 2$   
Antiferromagnet Volborthite  $Cu_3 V_2 O_7 (OH)_2 \times$   
 $2H_2O$**

F. Bert, D. Bono, P. Mendels, F. Ladieu, F. Duc, J.-C. Trombe, P. Millet

► **To cite this version:**

F. Bert, D. Bono, P. Mendels, F. Ladieu, F. Duc, et al.. Ground State of the Kagomé-Like  $S = 1 / 2$  Antiferromagnet Volborthite  $Cu_3 V_2 O_7 (OH)_2 \times 2H_2O$ . Physical Review Letters, American Physical Society, 2005, 95, pp.087203. 10.1103/PhysRevLett.95.087203 . cea-01395314

**HAL Id: cea-01395314**

**<https://hal-cea.archives-ouvertes.fr/cea-01395314>**

Submitted on 10 Nov 2016

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Ground state of the Kagomé-like S=1/2 antiferromagnet, Volborthite $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$

F. Bert,<sup>1</sup> D. Bono,<sup>1</sup> P. Mendels,<sup>1</sup> F. Ladieu,<sup>2</sup> F. Duc,<sup>3</sup> J.-C. Trombe,<sup>3</sup> and P. Millet<sup>3</sup>

<sup>1</sup>*Laboratoire de Physique des Solides, UMR 8502, Université Paris-Sud, 91405 Orsay, France.*

<sup>2</sup>*Service de Physique de l'État Condensé, DSM, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France.*

<sup>3</sup>*Centre d'Élaboration des Matériaux et d'Études Structurales, CNRS UPR 8011, 31055 Toulouse, France.*

(Dated: January 7, 2014)

Volborthite compound is one of the very few realizations of S=1/2 quantum spins on a highly frustrated kagomé-like lattice. Low-T SQUID measurements reveal a broad magnetic transition below 2 K which is further confirmed by a peak in the  $^{51}\text{V}$  nuclear spin relaxation rate ( $1/T_1$ ) at  $1.4 \text{ K} \pm 0.2 \text{ K}$ . Through  $^{51}\text{V}$  NMR, the ground state (GS) appears to be a mixture of different spin configurations, among which 20% correspond to a well defined short range order, possibly of the  $\sqrt{3} \times \sqrt{3}$  type. While the freezing involve all the  $\text{Cu}^{2+}$  spins, only 40% of the copper moment is actually frozen which suggests that quantum fluctuations strongly renormalize the GS.

PACS numbers: 75.30.Cr, 75.50.Lk, 76.60.-k

In the quest for novel states of condensed matter, frustration has emerged as a key concept [1]. In magnetic systems, competitive interactions resulting from the geometry of the lattice, especially for corner sharing networks, can lead to a macroscopic entropy at  $T=0 \text{ K}$  and could favor a novel spin liquid state. Theoretically, Heisenberg S=1/2 antiferromagnet on a 2D kagome lattice is predicted to lead to such an exotic quantum state [2, 3]. Actually very few real systems approach this model. So far, the  $\text{Cr}^{3+}$  (S=3/2) kagomé bilayer compounds  $\text{SrCr}_{9p}\text{Ga}_{12-9p}\text{O}_{19}$  (SCGO) and  $\text{Ba}_2\text{Sn}_2\text{ZnGa}_{10-7p}\text{Cr}_{7p}\text{O}_{22}$  ( $p < 0.97$ ) have been the experimental archetypes of Heisenberg frustrated antiferromagnets. In this context, the recent rediscovery of Volborthite  $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  [5, 6] is a major step towards a realization of the theoretical model. The magnetic lattice of this natural antiferromagnet consists of quantum S=1/2 ( $\text{Cu}^{2+}$ ) spins sitting at the vertices of well separated ( $7.2\text{Å}$ ) kagome-like planes. The lattice displays a monoclinic distortion, possibly yielding two Cu-Cu interaction constants  $J_1 \neq J_2$ , which does not seem to impact on the characteristic fingerprints of frustration. Indeed, despite strong antiferromagnetic interactions ( $J \simeq 90 \text{ K}$ ), no transition towards an ordered state has been detected down to 1.8 K, neither in susceptibility nor in heat capacity measurements [6]. Instead, a maximum in both these quantities is observed around 20 K, probably reflecting the enhancement of short range correlations, and defines a new low energy scale as a result of frustration [7, 8]. Besides, as in kagomé bilayers [4], muon spin relaxation ( $\mu\text{SR}$ ) experiments detected no sign of static spin freezing but rather temperature independent spin fluctuations persisting down to 50 mK, indicative of a fluctuating quantum GS [9]. Only in one ESR study the existence of an internal field was evidenced at 1.8 K which was interpreted as short range order [10].

In this Letter, we show, for the first time, that volborthite undergoes, around 1.3 K, a transition to a frozen

state which we characterize using  $^{51}\text{V}$  NMR as a local probe of magnetism. Note that, so far, NMR investigation of the GS in the kagomé bilayers had proved to be impossible because of a wipe out of the NMR intensity at low T [11]. The volborthite powder samples were prepared by refluxing an aqueous suspension of  $\text{V}_2\text{O}_5$  and a basic copper (II) carbonate salt  $\text{Cu}(\text{OH})_2\text{-Cu}(\text{CO}_3)$  for several days. No spurious phase was detected in X-ray measurements. SQUID and NMR measurements above 2 K and  $\mu\text{SR}$  experiments on these samples [12] were similar to the above described published data.

The low T static susceptibility of volborthite is presented in Fig. 1 (top panel). Below 2 K, the separation between the field cooled (FC) and zero field cooled (ZFC) susceptibilities reveals a spin freezing process. At 1.2 K, "ageing" effects [13] have been observed (not shown here) which ascertains the glassy nature of the GS. At variance with textbook spin glass transition, the FC susceptibility does not level off below the transition and the hardly detectable broad maximum on the ZFC branch occurs below the FC/ZFC separation [19]. This suggests a rather broad distribution of freezing temperatures as, for instance, in super-paramagnets where spin clusters get progressively blocked on lowering T.

To address the important issue of the intrinsic character of this glassy low-T phase, the susceptibility of two zinc substituted samples is also reproduced in Fig. 1. Zn atoms enter Volborthite lattice without noticeable distortion. Since  $\text{Zn}^{2+}$  is non-magnetic, the Zn/Cu substitution results in diluting the kagome magnetic lattice. The freezing temperature  $T_g$ , defined here as the temperature of the ZFC maxima, are plotted in the inset of Fig. 1 as a function of the magnetic lattice dilution and compared to the same data for SCGO compounds [11]. In marked contrast with SCGO,  $T_g$  for Volborthite is strongly affected by dilution. This reminds us of the drastic reduction upon dilution of the dynamical plateau value seen in  $\mu\text{SR}$  experiments [12] and suggests that the bilayer topology

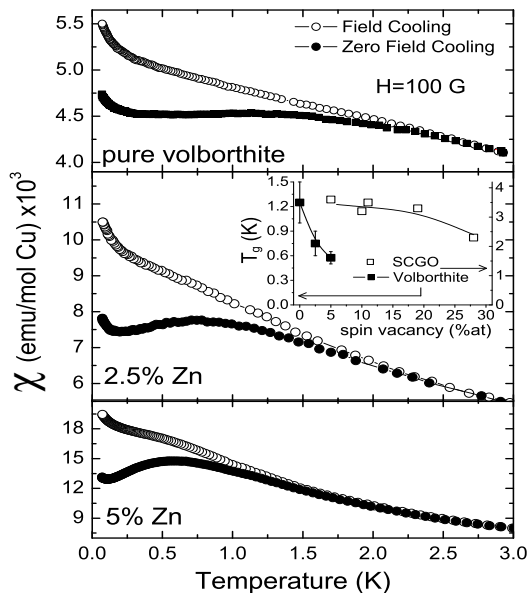


FIG. 1: SQUID dc susceptibility in  $\text{Cu}_{3(1-x)}\text{Zn}_{3x}\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  measured after two cooling protocols, with (open symbols) and without (full symbols) a 100 Oe applied field. Inset: comparison of  $T_g$  versus  $S=0$  impurity dilution rate in volborthite and SCGO bilayer compounds.

likely better accommodates defects than the single layer one in volborthite. Nonetheless, in both systems, the random dilution of the magnetic network reduces  $T_g$  and hence simple magnetic dilution as a source of disorder cannot explain, alone, the spin-glass like transition.

Microscopic insight into this ground state is provided by our low-T  $^{51}\text{V}$  NMR experiments. The non-magnetic  $\text{V}^{5+}$  ions are situated above or below the center of the stars which constitutes the kagomé lattice. They thus probe symmetrically the magnetism of six  $\text{Cu}^{2+}$  ions belonging to the same hexagon through an hyperfine coupling, estimated to be  $A \simeq 7.7$  kOe from susceptibility versus NMR shift measurements (see Ref. [12]) above 90 K in agreement with the value estimated in Ref. [6].

The nuclear spin lattice relaxation has been measured by the saturation-recovery method and fitted to a sum, with T-independent coefficients, of four exponential terms with relaxation rates proportional to  $1/T_1$  as expected for a  $S=7/2$  nuclear spin [14] in the case of partial saturation of the NMR line. The divergence of  $1/T_1$  at  $1.4 \text{ K} \pm 0.2 \text{ K}$  (Fig. 3, inset) is a strong evidence that the vanadium probe indeed feels a transition in agreement with our susceptibility measurements. Following the analysis of Ref. [9] of the zero field  $\mu\text{SR}$  relaxation rate below 1 K ( $\lambda = 5 \mu\text{s}^{-1}$  in our sample [12]), we get 3.5 MHz for the copper spin fluctuation rate. From the hyperfine coupling  $A$ , we would then expect the corresponding  $^{51}\text{V}$   $1/T_1$  to be  $\simeq 20 \text{ ms}^{-1}$ , much higher than the value actually measured. This suggests that spin fluctua-

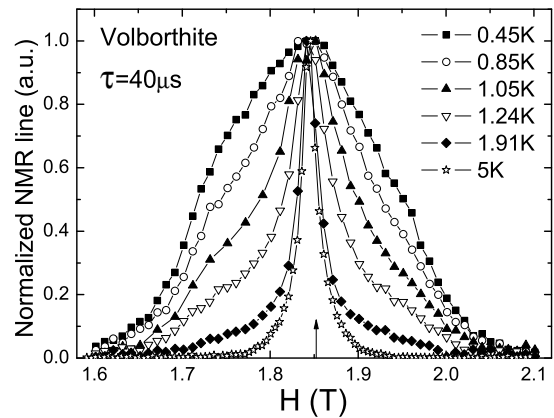


FIG. 2:  $^{51}\text{V}$  NMR spectra measured at 20.733 MHz as a function of the applied field. For clarity, the spectra have been normalized to their maximum value. The vertical arrow shows the position  $H_0$  of the unshifted reference line.

tions, seen in  $\mu\text{SR}$ , are efficiently filtered by the nuclear probe. We shall come back to this point later.

Characteristic  $^{51}\text{V}$  ( $\gamma/2\pi = 11.1923 \text{ MHz/T}$ ) NMR spectra measured at  $\nu_0 = 20.733 \text{ MHz}$ , below 5 K, are presented in Fig. 2. At these low T, the quadrupolar splitting of the  $S=7/2$  vanadium NMR line is masked by a large magnetic broadening which reflects the width of the field distribution at the vanadium site. On lowering T, the NMR line broadens drastically around 1.5 K and then saturates below 0.6 K. At a lower 12.548 MHz irradiating frequency, we checked that this saturation is field independent, and therefore reflects, as expected, a frozen field distribution in the GS. Upon closer inspection of the T-dependence of the lineshape, we note first the appearance of a broad background feature below 1.5 K. In order to track qualitatively this broad component we chose rather arbitrarily to plot the half width at  $1/5^{\text{th}}$  of the maximum in Fig. 3. Then the main central line, which width is roughly the width at half maximum of the spectra (open symbols in Fig. 3), starts to broaden rapidly and below 1 K, its lineshape changes from lorentzian-like to gaussian-like. The two distinct features, broad background and central line, in the low-T spectra suggest that the NMR line, below 1.5 K, is no more homogenous but results from at least two different types of magnetic environments of vanadium. This is probably related, as well, to the progressive freezing observed in macroscopic susceptibility. It is an important finding of this study as it demands a special magnetic ordering in the GS leading to two different V sites.

We now focus on the  $T=0.35 \text{ K}$  spectra (Fig. 4) in the well established GS of volborthite. By comparison of the integrated intensity with  $T > 2 \text{ K}$  data, we checked that all sites are detected at this low-T and we therefore probe the bulk properties of the sample. The top and bottom spectra have been obtained in the same condi-

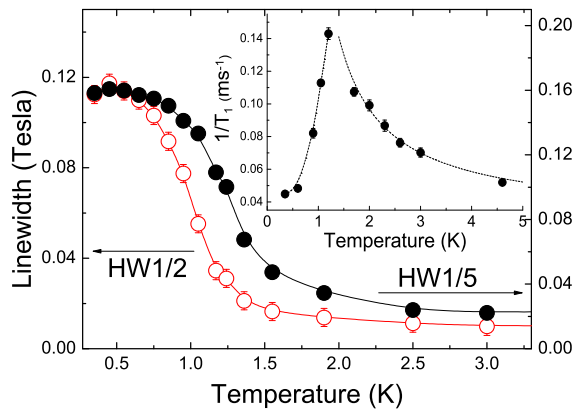


FIG. 3: Half widths of the NMR spectra measured at 1/2 (HW1/2, open symbols) and 1/5 (HW1/5, full symbols) of the maximum height. Inset :  $T$ -dependence of the  $^{51}\text{V}$  spin-lattice relaxation rate ( $1/T_1$ ) measured at the maximum intensity of the spectra ( $H=1.85$  T). Lines are guides for the eye.

tions except for a different duration  $\tau$  in the pulse sequence  $\pi/2 - \tau - \pi/2$ . This contrast procedure allows us to separate the two components of the spectrum. They indeed prove to have different spin-spin relaxation times  $T_2$  which we determined by standard  $T_2$  measurements at  $H = 1.845$  T and  $H = 1.955$  T.

In the long time spectrum (top panel), the slowly relaxing ( $T_2 = 105 \mu\text{s}$ ) broad background clearly stands out, without the fast relaxing ( $T_2 = 60 \mu\text{s}$ ) gaussian-like component and appears to be rectangular shaped. An unshifted narrower line also appears on this spectrum. However, because of its much longer  $T_2 = 240 \mu\text{s}$ , it eventually represents less than 1% of the total sample and probably arises from some small impurity phase. The rectangular lineshape is a clear signature of the presence of one well defined frozen field  $H_f$  at the vanadium site arising from the neighboring copper moments. The resonance condition writes  $H_0 = 2\pi\nu_0/\gamma = \|\mathbf{H} + \mathbf{H}_f\|$  where  $H$  is the applied field. Due to powder distribution,  $\mathbf{H}_f$  is randomly oriented with respect to  $\mathbf{H}$ . In the limit  $H_f \ll H_0$  one would expect a rectangular lineshape with cut-offs at  $H_0 \pm H_f$ . An exact derivation of the NMR line  $P(H)$  yields

$$P(H) = (H_0^2 + H^2 - H_f^2)/(4H_f H^2) \quad (1)$$

for  $|H - H_0| < H_f$ . The component labelled "ordered" in Fig. 4 is a fit with such a model with  $H_f = 0.16$  T and a narrow distribution (0.02 T HWHM) of this frozen field. The solid line in the top panel is a global fit to the NMR line, including the impurity phase. In order to produce a well-defined amplitude of the frozen field at the vanadium site, short-range order of the six neighboring  $\text{Cu}^{2+}$  moments must exist. In a classical picture, the energy is minimized on the kagomé lattice, when the spins are at  $120^\circ$  from each other on each triangle. Following most of the theoretical works [15], we assume a  $\sqrt{3} \times \sqrt{3}$  type

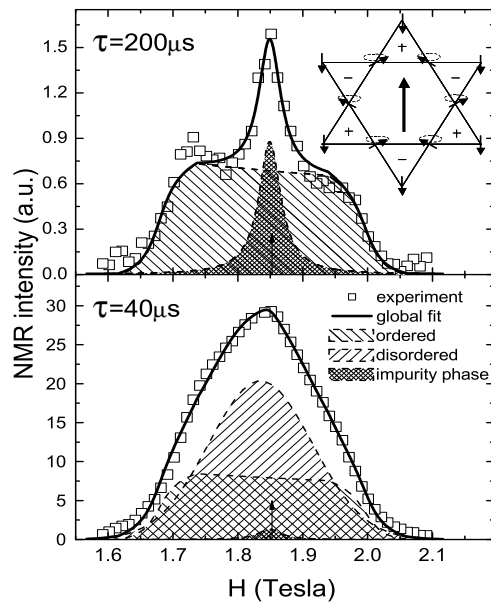


FIG. 4:  $^{51}\text{V}$  NMR spectra measured for two different delays  $\tau$  at  $T=0.35$  K. Note the different scales in the top and bottom panel. The solid lines are fits to the data and result from the sum of three components (dashed, dashed-dotted and dotted lines) as explained in the text. Inset: scheme of the proposed  $\sqrt{3} \times \sqrt{3}$  local order responsible for the ordered component (dashed line). The vector at the center of the hexagon stands for the resulting frozen field at the vanadium site.

short range order, sketched in the inset of Fig. 4, which corresponds to alternating chiralities (+ and - signs) on neighboring triangles. Such a short range order indeed leads to a well defined  $H_f = 3H_{Cu}$  resulting field at the vanadium site, where  $H_{Cu}$  is the frozen field arising from each  $\text{Cu}^{2+}$ . On the contrary, a uniform chirality order ( $\mathbf{q} = 0$ ) would lead to a null field at the vanadium site which cannot reproduce our NMR data. In addition, the classical  $\sqrt{3} \times \sqrt{3}$  order favors local collective excitations made of a coherent out-of-plane rotation of the six spins belonging to a same hexagon as depicted in the inset of Fig. 4. It is remarkable that such excitations, which cost zero energy, do not affect the resulting field at the vanadium site, neither by hyperfine nor dipolar coupling, and are, therefore, "filtered" out at the symmetric vanadium site. This could explain why we measured a small  $1/T_1$  which, besides, decreases at low temperature, as in usual static phases, whereas, in  $\mu\text{SR}$  experiments, muons which sit in less symmetric positions, still feel a strong dynamics which persists below  $T_g$  [9, 12]. From  $H_f$  and the hyperfine coupling constant, we get  $0.41\mu_B$  for the frozen  $\text{Cu}^{2+}$  moment contributing to this slow relaxing component. This small value, compared to  $1\mu_B$  expected for a spin 1/2, demonstrates that zero point quantum fluctuations strongly affect the volborthite GS.

In the bottom panel, combining the formerly discussed slow relaxing components with a frozen gaussian-like

component ("disordered" label) results in the solid line which reproduces well the short time experimental spectra. Taking into account the different  $T_2$  values, we evaluate the corresponding sample fractions, in the limit  $\tau \rightarrow 0$ , to be  $\simeq 80\%$  for the gaussian like component and  $\simeq 20\%$  for the rectangular-shaped one. A gaussian-like frozen component is easily obtained provided that the  $\text{Cu}^{2+}$  frozen moments belonging to a same hexagon are randomly oriented as in the case of a spin glass. In this random picture, we extract also a small  $0.44\mu_B$  value for the frozen copper moment consistent with the previous one. A gaussian like component could also come from several frozen field values, smaller than in the  $\sqrt{3} \times \sqrt{3}$  case and slightly distributed, arising from various other spin configurations. A crude illustration of this scenario can be obtained if one assumes a random distribution of the chiralities on the kagomé lattice. One finds then that 4% of the hexagons are in the  $\sqrt{3} \times \sqrt{3}$  configurations while the other configurations lead to either  $H_f = 0$  (54%) or  $H_f = \sqrt{3}H_{Cu}$  (41%). Our experimental value already indicates that, within this classical framework, the  $\sqrt{3} \times \sqrt{3}$  configuration has to be favored by some mechanism. An exact quantum calculation of the possible states in a finite kagomé spin 1/2 cluster would certainly allow a better quantitative understanding of this gaussian-like component in this scenario. At the nanoscopic scale of the NMR probe, it is difficult to decide whether these two vanadium sites in the GS reveal different domains or appear as a mixture in a single phase. However, both configurations freeze at approximately the same temperature and, for both, we found a similar frozen fraction of the  $\text{Cu}^{2+}$  moments. Both arguments favor an original single phase description.

The disorder of the GS is a challenge to our understanding of highly frustrated magnets, given that volborthite is probably the purest model system known so far. From a comparison with Zn diluted samples, we estimated an upper limit of 1% spin vacancy like defects in the pure volborthite sample. Theoretical works [16, 17] have put forward the possibility of an intrinsic "topological" spin glass state arising from frustration alone contrary to usual spin glasses where both frustration and disorder are responsible for glassiness. Alternatively, in Ref. [18], it was argued that a small amount of disorder could induce a spin glass like state provided that a coherent RVB background couples very efficiently the de-

fect centers. This scenario naturally explains the simultaneous occurrence of the glassy-like transition and the dynamical plateau in  $\mu\text{SR}$  experiments and is consistent with our finding of a two component NMR signal, arising from vanadium nuclei far and close to a defect.

In conclusion, volborthite which presents all the well established signatures of a spin liquid, namely no freezing at  $T \simeq \theta_{CW}$  and a dynamical plateau at  $T \rightarrow 0$ , allows, for the first time, a detailed NMR local investigation of the GS. This enabled us to study the internal field configurations and their dynamics. Further, this opens new avenues for refined theoretical calculations which are necessary to reveal the influence of the possible dissymmetry of the interactions and the actual texture of the GS.

- 
- [1] A. P. Ramirez, *Handbook on Magnetic Materials* (Elsevier Science, Amsterdam, 2001), vol. 13, p. 423, KJH Busch ed.
  - [2] G. Misguich and C. Lhuillier, *Frustration in Two-Dimensional Quantum Antiferromagnets* (World Scientific, 2003), cond-mat/0310405.
  - [3] F. Mila, Phys. Rev. Lett. **81**, 2356 (1998).
  - [4] Y. Uemura *et al.*, Phys. Rev. Lett. **73**, 3306 (1994).
  - [5] M. A. Lafontaine, A. L. Bail, and G. Férey, J. Solid State Chem. **85**, 220 (1990).
  - [6] Z. Hiroi *et al.*, J. Phys. Soc. Jpn. **70**, 3377 (2001).
  - [7] P. Mendels *et al.*, Phys. Rev. Lett. **85**, 3496 (2000).
  - [8] D. Bono, P. Mendels, G. Collin, and N. Blanchard, Phys. Rev. Lett. **92**, 217202 (2004).
  - [9] A. Fukaya *et al.*, Phys. Rev. Lett. **91**, 207603 (2003).
  - [10] S. Okubo *et al.*, Physica B **294–295**, 75 (2001).
  - [11] L. Limot *et al.*, Phys. Rev. B **65**, 144447 (2002).
  - [12] F. Bert *et al.*, J. Phys.: Condens. Matter **16**, S829 (2004).
  - [13] E. Vincent *et al.*, *Complex Behaviour of Glassy Systems* (Springer Verlag, 1997), pp. 184–219, cond-mat/9607224.
  - [14] A. Narath, Phys. Rev. **162**, 320 (1967).
  - [15] J. N. Reimers and A. J. Berlinsky, Phys. Rev. B **48**, 9539 (1993).
  - [16] P. Chandra, P. Coleman, and I. Ritchey, J. Phys. I **3**, 591 (1993).
  - [17] M. Ferrero, F. Becca, and F. Mila, Phys. Rev. B **68**, 214431 (2003).
  - [18] D. Bono *et al.*, Phys. Rev. Lett. **93**, 187201 (2004).
  - [19] The up-turn at  $T < 0.1$  K, is due to few ppm magnetic impurities in the grease used to ensure thermalization.