

## Dilution in volborthite $S = 1/2$ frustrated magnet: a $\mu$ SR and NMR study

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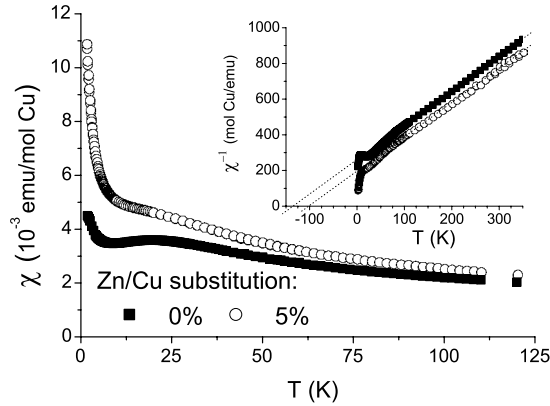
### Abstract

Volborthite,  $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ , is a natural frustrated antiferromagnet ( $\theta_{\text{CW}} \simeq 130$  K) with  $S = 1/2$  spins ( $\text{Cu}^{2+}$ ) sitting at the vertices of a Kagomé-like lattice built on isosceles triangles. We report on the static (SQUID,  $^{51}\text{V}$  NMR) magnetic properties of the pure and 5% Zn/Cu substituted compounds and on an extensive  $\mu$ SR study of the dilution effect (up to 15% Zn substitutions) on the spin dynamics. Although volborthite shares most of the unusual features already exhibited in Kagomé bilayer compounds, namely a dynamical state as  $T \rightarrow 0$  and a low temperature maximum in the local susceptibility, we found some surprising specificities. The  $T \rightarrow 0$  dynamical state is less robust against dilution and the low temperature local susceptibility studied by means of NMR also strongly depends on dilution. Such a sensitivity to dilution questions the role of the asymmetry of the exchange constants.

### 1. Introduction

Over the last decade, a great effort was made in material science to develop a new compound meeting the theoretical requirements for the existence of a spin liquid ground state. Two main features have been put forward for destabilizing any magnetic ordering: first, a depleted triangular (Kagomé) or tetrahedral (pyrochlore) lattice to increase dramatically the ground state degeneracy and, second,  $S = 1/2$  Heisenberg spins to enhance the quantum fluctuations. The recent rediscovery of volborthite [1], a natural frustrated antiferromagnet, could be an important step forward in this quest.

The magnetic sublattice of volborthite  $\text{Cu}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$  consists of  $S = 1/2$  ( $\text{Cu}^{2+}$ ) spins sitting at the vertices of well-separated ( $c = 7.2$  Å) Kagomé-like planes. In contrast to the ideal Kagomé case, the lattice is rather built on isosceles triangles, which probably leads to a dissymmetry in the Cu–Cu super-exchange constants  $J_1 \neq J_2$ . However, a former



**Figure 1.** Susceptibility of the pure and 5% Zn substituted samples measured as a function of temperature in a 100 G magnetic field. In the inset, the inverse of the susceptibility is represented to single out the extended Curie–Weiss regime. The susceptibilities have been renormalized by the Cu content of each sample.

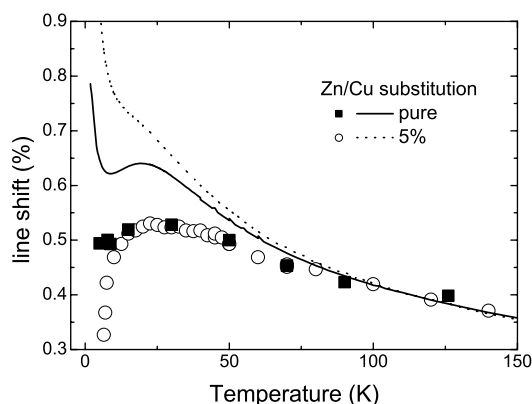
study [2] of this compound proved that this network retains enough frustration that no transition towards an ordered state is detected down to 1.8 K, despite strong antiferromagnetic interactions ( $\theta_{CW} \simeq 130$  K). Thus, with its simple 2D, 100% covered magnetic lattice,  $S = 1/2$  spins and a frustration parameter  $f = \theta_{CW}/T_c$  larger than 60, volborthite appears as an important candidate for showing the occurrence of a spin liquid ground state.

We report here on a comparison of the static (SQUID susceptibility,  $^{51}\text{V}$  NMR lineshift) and dynamical ( $\mu\text{SR}$ ) magnetic properties of the pure compound and Zn/Cu substituted samples. The controlled dilution of the magnetic structure by non-magnetic impurities has indeed proven to be a powerful tool for unravelling the intrinsic properties and more generally for investigating the nature of the magnetic correlations in those exotic systems [3, 4]. The pure and diluted powder samples (2.5%, 5%, 10% and 15% Zn/Cu substitution) were all prepared at the CEMES by hydrothermal synthesis. For the macroscopic and local susceptibility, we will concentrate on the comparison of the pure and 5% diluted samples whereas we will present an extensive study of the effect of dilution on the dynamics ( $\mu\text{SR}$  experiments).

## 2. SQUID macroscopic susceptibility

As shown in the inset of figure 1, at high temperatures, the macroscopic susceptibility of the pure and diluted samples follows a Curie–Weiss law. From the slopes of  $\chi^{-1}(T)$  we deduce a Curie–Weiss constant  $C_{CW} = 0.52$  emu K/mol Cu which leads to a reasonable value of  $2.0 \mu_B/\text{Cu}^{2+}$  ( $1.73 \mu_B$  is predicted theoretically). From the intercept with the temperature axis we deduce the Curie–Weiss temperatures  $\theta_{CW}^{0\%} = 133 \pm 3$  K for the pure sample and  $\theta_{CW}^{5\%} = 105 \pm 5$  K for the 5% Zn substituted one. This last finding is very surprising since, from the mean field theory, one would naively expect  $\theta_{CW} = zJS(S+1)/3k_B$  where  $z$  is the number of nearest magnetic neighbours and  $J$  the average coupling energy, i.e. in our case,  $\theta_{CW} = (1-p)J/k_B$  where  $p$  is the amount of Zn dilution.  $\theta_{CW}^{5\%}$  being much smaller than  $0.95\theta_{CW}^{0\%}$ , this seems to imply that the effect of a vacancy in the magnetic lattice extends further than its nearest neighbours.

This high temperature regime extends well below the Curie–Weiss temperature indicating a strong frustration of the antiferromagnetic interactions. It then exhibits a maximum at around 20 K that probably reflects a strong enhancement of the local antiferromagnetic correlations.



**Figure 2.** NMR lineshift as a function of the temperature in the pure and 5% Zn diluted samples. The solid curves show the corresponding macroscopic susceptibilities in arbitrary units.

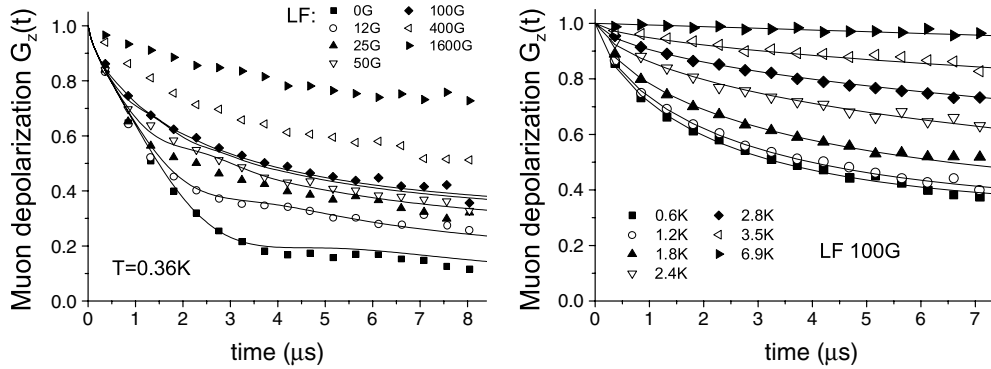
At still lower temperatures the susceptibility becomes Curie-like. As in previously studied Kagomé systems [4, 5], the dilution of the magnetic network by non-magnetic impurities leads to an even larger Curie tail indicating that it is most probably a defect contribution.

### 3. $^{51}\text{V}$ NMR lineshift

In order to distinguish between the intrinsic magnetism of the Kagomé layers and a possible defect contribution, we used  $^{51}\text{V}$  NMR as a local probe of the magnetic properties.  $^{51}\text{V}$  nuclei are ideal probes for this purpose since they are situated in the centre of the hexagons of the Kagomé lattice, and are therefore coupled to six  $\text{Cu}^{2+}$  ions in the pure compound. The NMR lineshape of the pure sample is reasonably symmetric over the whole temperature range. In contrast, whereas it is also symmetric above 50 K for the diluted samples, it then becomes asymmetric at lower temperature with a sizable shift of the spectral weight towards higher resonance frequencies. This contribution probably arises from the  $^{51}\text{V}$  nuclei close to dilution defects. A detailed analysis of the NMR lineshape of the diluted samples will be presented elsewhere. We will concentrate here on just the lineshift, i.e. the local susceptibility. We define it, reliably down to 6 K, as the frequency shift of the maximum of the NMR line, which, we believe, is associated with  $^{51}\text{V}$  nuclei surrounded by six  $\text{Cu}^{2+}$  ions and far from the non-magnetic Zn impurities.

Our NMR results on the pure and 5% diluted samples are presented in figure 2 and compared to the macroscopic susceptibilities measured by the SQUID. Whereas the macroscopic and local susceptibilities coincide at high temperature with, for both, a Curie–Weiss behaviour followed by a maximum at around 20 K, striking differences appear at lower temperature. In contrast to the SQUID susceptibility, the NMR shift does not show any Curie upturn but keeps on decreasing below the maximum. Without entering into too much detail about the NMR lineshape, it should be noticed that it is, instead, the width of the NMR line that follows a Curie law. These observations are reminiscent of the results obtained on Kagomé bilayer compounds such as  $\text{SrCr}_9\text{Ga}_{12-9p}\text{O}_{19}$  (SCGO) [6, 4] and  $\text{Ba}_2\text{Sn}_2\text{ZnGa}_{10-7p}\text{Cr}_{7p}\text{O}_{22}$  (BSZCGO) [5]. As in these former studies, we conclude that the Curie term is defect induced and not intrinsic to the magnetism of the Kagomé layers.

More surprisingly, the dilution of the magnetic lattice appears to lead to a much sharper decrease of the low  $T$  susceptibility. Such a spin gap opening, as a result of dilution, contrasts



**Figure 3.** Field (left panel) and temperature (right panel) dependences of the muon depolarization in the 5% Zn/Cu substituted volborthite sample. The solid curves in the left figure are fits to the 0, 12.5, 25, 50 and 100 G data curves with one static and one dynamic component. In the right-hand figure, the solid curves are fits of the data with a stretched exponential plus a constant non-relaxing (decoupled) component.

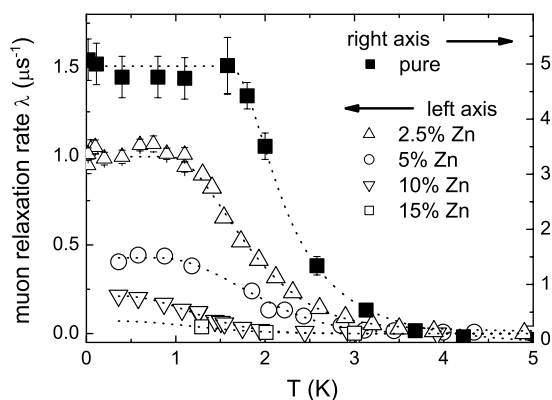
strikingly with the formerly studied Kagomé bilayer compounds where the low  $T$  shift is hardly dependent on the dilution. One could wonder whether this sensitivity of volborthite to dilution is related to the asymmetry of the exchange constants or to the single-layered lattice which could be less robust against dilution than the archetype Kagomé bilayer compounds.

#### 4. Dynamical magnetic properties

To check the landmark of a ‘liquid’ ground state, namely a persisting spin dynamics when  $T \rightarrow 0$  [7], we performed  $\mu$ SR experiments at the PSI (pure and 2.5% dilution: fast relaxation) and ISIS (5%, 10% and 15% dilution: slow relaxation) muon facilities. The experiments were performed in the longitudinal field (LF) configuration, i.e. with the magnetic field, if any, in the direction of the initial muon polarization. On general grounds, in these  $\mu$ SR experiments, a fully polarized beam of  $S = 1/2$  muons is stopped in the sample. Due to local magnetic fields, the muons then start to depolarize. After an average lifetime of  $2.2 \mu\text{s}$ , they decay into positrons which are preferentially emitted in the direction of the muon spins at the time of their decay. These positrons are collected in forward and backward detectors which permits one to record the muon depolarization as a function of the time they have spent in the sample.

As a representative example, the muon depolarization curves  $G_z(t)$  are shown in figure 3 for the 5% Zn diluted sample. We first performed a ‘decoupling’ experiment at the lowest temperature  $T = 0.36$  K which consists in studying the effect of a LF on the muon depolarization in order to distinguish between static and dynamic relaxation processes. Were the sample in a frozen magnetic state, in zero field,  $G_z(t)$  would show a dip at  $t \simeq 1/\gamma_\mu H_{\text{int}}$  where  $\gamma_\mu/2\pi = 13.5 \text{ MHz kG}^{-1}$  is the muon gyromagnetic constant and  $H_{\text{int}}$  is the average internal field, and would completely decouple, i.e. the muon would not depolarize any more, in a field of about  $5H_{\text{int}}$ .

In the volborthite compounds, there seem to be two distinct muon relaxation processes: a nearly static component with a dip at  $t \simeq 4 \mu\text{s}$  and which is already decoupled within 50 G; and a dynamical component which is hardly decoupled with a 1600 G field. These two processes are possibly related to two different muon sites. One could correspond to muons bound to water molecules located in between the Kagomé planes, where the muons should mainly feel the proton nuclear dipole field (static component). The other one would then arise from muons



**Figure 4.** Muon depolarization rate  $\lambda$  as a function of the temperature for all the samples studied. The pure sample data are associated with the right-hand axis.

bound to the oxygens embedded in the Kagomé layer and muons stopping next to them are probably much more sensitive to the  $\text{Cu}^{2+}$  electronic spin magnetism. The fact that this latter is not easily decoupled with an external field proves that the volborthite compounds *remain dynamic at the lowest temperatures*. As a first attempt we thus fitted, in the left panel of figure 3, the LF dependence experiment with two components: a static Kubo–Toyabe component and a stretched exponential accounting for the dynamical component isolated in a 100 G field.

The right-hand panel of figure 3 shows the temperature dependence of the muon depolarization in the 5% Zn diluted sample. For all the samples, we applied a 100 G longitudinal field in order to isolate the dynamical component. Above 5 K, the muons in all the samples are nearly not depolarized, meaning that the spin fluctuations are too fast to couple to the muon spin. As the temperature is lowered, the spin dynamics seems to slow down and couples efficiently to the muon spin leading to larger muon depolarization rates. However, below about 1 K, the depolarization curves do not evolve any more (see for instance the 0.6 and 1.2 K curves). As in the Kagomé bilayer compounds, the magnetic system seems to reach a slow dynamics state from which it can no longer pursue its freezing process.

In order to quantify this temperature effect we have represented in figure 4 the muon depolarization rate  $\lambda$  as a function of the temperature for all the samples. In the absence of a simple model for fitting the muon depolarization curves, we simply defined  $\lambda$  such that  $G_z(t = 1/\lambda) = 1/e$ . As in formerly studied SCGO [3] and BSZCGO [5], the dilution of the magnetic network slows the muon depolarization down, i.e. enhances the spin dynamics. It is however noticeable that the dilution by 15% of the volborthite magnetic network already suppresses the specific features of the frustrated systems, namely a strong slowing down followed by a low  $T$  persisting dynamics. In contrast, in the Kagomé bilayer compounds, these features disappear only around the percolation threshold, i.e. at about 50% dilution of the magnetic network. For comparison, in volborthite, this threshold is around 35% dilution [8].

## 5. Conclusion

From our SQUID,  $^{51}\text{V}$  NMR and  $\mu\text{SR}$  experiments, it appears that volborthite shares most of the unusual features already exhibited in the Kagomé bilayer compounds, namely a dynamical state as  $T \rightarrow 0$  and a maximum in the local susceptibility in agreement with previously published NMR studies [2, 6]. However, the detailed study of the dilution of the magnetic

network by non-magnetic impurities reveals some striking differences. The susceptibility, NMR data and  $\mu$ SR experiments show that volborthite magnetic structure seems to be less robust against dilution than the Kagomé bilayer compound. Whether this dilution sensitivity arises from the single-layered structure or is related to the anisotropy of the coupling constants has still to be studied. In this latter case, volborthite should be best described as a network of chains coupled through frustrated interactions.

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### References

- [1] Lafontaine M A, Bail A L and Férey G 1990 *J. Solid State Chem.* **85** 220
- [2] Hiroi Z, Hanawa M, Kobayashi N, Nohara M, Takagi H, Kato Y and Takigawa M 2001 *J. Phys. Soc. Japan* **70** 3377
- [3] Keren A, Uemura Y J, Luke G, Mendels P, Mekata M and Asano T 2000 *Phys. Rev. Lett.* **84** 3450
- [4] Limot L, Mendels P, Collin G, Mondelli P, Ouladdiaf B, Mutka H, Blanchard N and Mekata M 2002 *Phys. Rev. B* **65** 144447
- [5] See Bono D, Mendels P, Collin G, Blanchard N, Baines C and Amato A 2004 *J. Phys.: Condens. Matter* **16** S817
- [6] Mendels P, Keren A, Limot L, Mekata M, Collin G and Horvatić M 2000 *Phys. Rev. Lett.* **85** 3496
- [7] Uemura Y J *et al* 1994 *Phys. Rev. Lett.* **73** 3306
- [8] Henley C L 2001 *Can. J. Phys.* **79** 1307