Thermodynamic properties of the Spin-1/2 Heisenberg Antiferromagnet with Anisotropic Exchange on the Kagomé Lattice: Comparison with Volborthite

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Thermodynamic properties such as magnetic susceptibility and specific heat have been computed for the Heisenberg Antiferromagnet with spatially anisotropic exchange on the kagomé lattice on clusters up to $N = 24$ spins from the full spectra obtained by exact diagonalization. This approach is shown to provide a good representation of these thermodynamic properties above temperatures of about $J_{rr}/5$ where $J_{rr}$ is an average of the coupling constants. Comparison with experimental Volborthite data obtained by Hiroi et al. [J. Phys. Soc. Jpn. 70, 3377 (2001)] shows that Volborthite is best described by a model with nearly isotropic exchanges in spite of the significant distortion of the kagomé lattice of magnetic sites in this compound and suggests that additional interactions are present. Comparison of the specific heat at low temperature raise the possibility that the density of states at low energy in Volborthite might be much lower than in the Heisenberg model. Magnetization curves under an applied field of the model are also investigated. The $M = 1/3$ plateau is found to subsist in the anisotropic case and extend to lower field with increased anisotropy. For sufficient anisotropy, this plateau would then be observable for a field reasonably accessible to experiment. The absence of a plateau well below $\sim 70$ Teslas would further support a nearly isotropic model.

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I. INTRODUCTION

Frustrated quantum magnetic insulators have received a large attention since many years, due to the possibility of observing unconventional behavior. Amongst these, antiferromagnets with a kagomé lattice of spin-1/2 appear to be promising candidates. However, despite numerous theoretical investigations, the nature of the ground-state of such spin systems remain an open question. In the most studied case of the spin-1/2 Heisenberg model, numerical studies have concluded to the absence of long-range magnetic (Néel) order and the presence of an unusually large density of states at low energy. But many questions such as the existence of spontaneously broken symmetries or even the existence of a finite gap to magnetic excitations are not settled.

In recent years, two promising experimental realizations of a spin-1/2 kagomé antiferromagnet have been synthesized and studied for their magnetic properties: Cu$_3$V$_2$O$_7$(OH)$_2$·2H$_2$O (Volborthite) and recently ZnCu$_3$(OH)$_6$Cl$_2$ (Herbertsmithite). Both compounds do not show any signs of ordering down to temperatures well below the exchange coupling strength and could be amongst the first realizations of a 2D quantum spin liquid. Yet they appear to deviate somewhat from a perfect realization of the kagomé Heisenberg model. They differ in different ways. Herbertsmithite has a perfect kagomé geometry but contains a significant (probably intrinsic) percentage of impurity spins arising from antisite disorder and may also deviates from the Heisenberg model due to the presence of additional interactions, possibly Dzyaloshinskii-Moriya interactions. In particular, the effect of the impurity spins which have significant interactions between themselves and with the spins residing on the kagomé sites seems to be not easy to modelize. This complicates the analysis of the experimental data and the determination of the relevant model describing Herbertsmithite. By contrast, Volborthite has the advantage of being available with a very low impurity content. However, it presents a deformed kagomé geometry. There, the equilateral kagomé triangles are distorted into isosceles triangles which suggest that two of the nearest neighbor exchange constants are different from the third. But to which extent the exchange couplings differ and whether an Heisenberg model with such a spatial anisotropy of exchange couplings is sufficient to describe Volborthite remained an open question.

The main purpose of this paper is to study this question by comparing the thermodynamic quantities measured by Hiroi et al. with the results obtained from exact diagonalization (ED) of an anisotropic Heisenberg model (AHM), described by the Hamiltonian:

$$\mathcal{H}_{\text{AHM}} = J \sum_{[i,j]} S_i S_j + J' \sum_{(k,i)} S_k S_i. \ (1)$$

where the symbols $[i,j]$ note pair of nearest neighbour sites on the horizontal chains with exchange coupling $J$ and $(k,i)$ pair of nearest neighbour sites between the middle sites and sites on the chains with exchange coupling $J'$ (see Fig. 1). $J$ and $J'$ are taken antiferromagnetic (positive). The ratio $\alpha = J/J'$ will be used to measure the anisotropy of the couplings and the average $J_{rr} = (J + 2J')/3$ to set the energy scale. The classical AHM has a ferrimagnetic ground-state for $\alpha \leq 0.5$. 

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which subsists for the spin-1/2 model over nearly the same range of values $\alpha$. We shall thus limit ourselves to the region $\alpha \gtrsim 0.5$, where the ground state has zero magnetization. Thermodynamic properties were computed from the full spectra of clusters up to $N = 24$ spins which is shown to yield results that may be considered as reliable estimate of these quantities in the thermodynamic limit down to temperatures $T \sim 0.2J_{\text{av}}$ or even below.

We focus on the comparison of the experimental and numerical magnetic susceptibility $\chi$, accurately measured by Hiroi et al over a large range of temperatures $T$, since it is presently the best known of the thermodynamic quantities. As discussed below, the comparison indicates that Volborthite is best described by the Heisenberg model with at most a small anisotropy and reveals that additional interactions are present in Volborthite besides the nearest neighbour couplings.

Besides the magnetic susceptibility, this paper reports the results obtained from these ED calculation for the magnetic heat capacity $C_v(T)$ and the magnetization curves $M(H)$ under an applied magnetic field $H$. The available data for Volborthite are however still limited, which hinder the use of this quantities for the determination of the model which could be relevant to describe Volborthite. The total heat capacity was measured by Hiroi et al but the magnetic part is somewhat uncertain, especially at high temperatures, since the lattice part is poorly known. Yet, as discussed below, the comparison at low temperature raises the possibility that the density of states at low energy in Volborthite might be much lower than in the Heisenberg model. The magnetization of Volborthite was only measured by Hiroi et al under low fields (up to a few Tesla) which only gives access to the very low part of the magnetization curve. As shown below, the anisotropic Heisenberg model show a plateau at one third of the saturation of the magnetization which starts at a field that decrease with increasing anisotropy. Its location (or absence) will provide further information on the nature of the model which is relevant to Volborthite.

This paper does not address the question of the nature of the ground state of the AHM which has been studied recently by Yavors’kii, Apel and Everts or Wang using mean field approaches. The analysis of the low energy spectrum of the AHM and this question will be the subject of a forthcoming manuscript. ED results for the magnetic susceptibility and the heat capacity have been reported by Wang but where not compared to the experimental data and where obtained only for a cluster of $N = 12$ spins. Whether this very small size systems could be sufficient for the comparison with experimental data was unclear.

The paper is organized as follows. Numerical results obtained from the AHM model for the magnetic susceptibility and the heat capacity are compared with experiment in Sec. II and Sec. III respectively. The magnetization curves of the AHM model and the possibility of the detection of a magnetization plateau experimentally are considered in Sec. IV. Sec. V summarizes the results.

II. MAGNETIC SUSCEPTIBILITY

ED results for the magnetic susceptibility $\chi(T)$ for different cluster sizes and selected values of the anisotropy $J$ are plotted in Fig. 2 to gather with the experimental data scaled with $J_{\text{av}} = 84.1K$. This scaling was found by Hiroi et al to enable a fit of the data to the high-temperature series expansion of the isotropic model for $T \gtrsim 2.5$.

A comparison of the $\chi(T)$ obtained for $J = 0.6, 1, 2$ at the different sizes indicate that the ED results become to be well converged to their thermodynamic values down to temperature below $T/J_{\text{av}} \sim 0.2$ once $N \geq 18$ whereas the convergence of the $N = 12$ results is slightly poorer. We can thus safely compare the $N = 18$ numerical data for $0.6 \leq J \leq 2$ with experiment over this range of temperature. Having assessed the convergence of the ED results, we examine the effect of the anisotropy of $\chi$ and compare with experiment.

In Fig. 2(a) one sees that the ED $\chi(T)$ are unsensitive to the anisotropy for $T/J_{\text{av}} \gtrsim 1$ and coincide very well with the experimental data. However, anisotropy has a large effect on $\chi(T)$ at lower $T$. Between $T/J_{\text{av}} \sim 1$ and $T/J_{\text{av}} \sim 0.1 – 0.2$, where the ED results are subjected to little size effects and can be trusted as converged, one observes a strong increase of $\chi$ with anisotropy which for $\alpha = 0.6$ or 2 reach several times its value for $\alpha = 1$ and the experimental value. Qualitatively, this increase of the susceptibility can be understood as follows: (i) as $\alpha$ decreases toward 0.5, the system approaches the ferrimagnetic phase where $\chi$ diverges at $T = 0$, (ii) for large $\alpha$ the middle spins become quasi disconnected from the chain spins and from one another, behaving as quasi free
FIG. 2: (color online) Magnetic susceptibility $\chi$ vs temperature $T$ scaled to $J_{av} = (J + 2J')/3$ (see Eqn. (1)). The curves obtained from exact diagonalization (ED) for different values of the anisotropy $\alpha = J/J'$ and number of spins $N$ are shown by light coloured lines, specified by different symbols, as indicated in the legend. The black heavy line connects the experimental data of Hiroi et al with $T$ scaled to $J_{av} = 84.1K$. (a) includes ED results for $0.6 \leq \alpha \leq 2$ and cluster sizes $N = 12, 18, 24$. (b) displays an enlarged region of (a) for a better comparison of the ED data at small anisotropy with experimental data (only part of the ED data at large anisotropy are shown for clarity).

As shown in Fig. 2(a) such a large increase of $\chi$ at low $T$ does not occur in Volborthite. This leads to conclude that a AHM with a large anisotropy is not appropriate to describe Volborthite. However, as can be seen in Fig. 2(b), a AHM with $\alpha \sim 1$ is neither fully satisfactory. The shape of the ED $\chi(T)$ curves differ somewhat from the experimental one. The AHM displays a bump in $\chi(T)$ at $T/J_{av} \sim 1$ absent in Volborthite. For small or moderate anisotropy the ED $\chi(T)$ are slightly smaller than the experimental $\chi(T)$ in the range $0.2 \lesssim T/J_{av} \lesssim 1$. In the AHM, the maximum of $\chi(T)$ always occurs at a lower temperature than in Volborthite. This reveals the presence in Volborthite of additional interactions between the spins besides those included in the AHM.

FIG. 3: (color online) Specific heat $C_v$ vs temperature $T$. (a): results of exact diagonalizations (ED) –see caption of Fig. 2–. (b): experimental results of Hiroi et al with $T$ scaled to $J_{av} = 84.1K$. $C_{tot}^v$ is the total specific heat measured. $C_{mag}^v$ is the magnetic part derived by Hiroi et al by subtracting from $C_{tot}^v$ the lattice contribution estimated from a Debye model.
shown below in Fig. 3 (b). The ED and experimental results in Fig. 3 (a) for the same values of the anisotropy $\alpha$ of the isotropic model, the finite size effects are subject to some uncertainties. The size effects $S$ i.e. wether there exist one (or more) extra peak at low $T$ with increased anisotropy but only very slightly. This is the usual main peak, associated to large energy excitations, rather insensitive to the detail of the interactions in the AHM. However, the integrated entropy under this peak $\sim S(T = \infty) - S(T = 0.2J_{av})$ (see Fig. 4) is only about 1/2 of the total entropy. Thus, as already found in the isotropic case, an unusually large part of the entropy is located at low temperature, which reveals a large density of states at low energy. For all values of the anisotropy, such a feature is seen to be a plateau was also exhibited at low $T$ (see Fig. 3). The integrated entropy (see Fig. 4). The comparison between $C_v^{mag}$ which is only accurate at low $T$ and the ED $C_v$ which are only converged at high $T$ is not easy. $C_v^{mag}$ is quite different from the ED $C_v$ of Fig. 3(a). $C_v^{mag}$ exhibits a peak at $T \sim 30K$. The height of this peak is about twice larger than the height of the main peak of the ED results. If the temperature of the experiment are scaled to $J_{av}=84.1K$, this peak is located at a temperature $T/J_{av} \sim 0.3$ This is about half of the temperature of the main peak of the ED $C_v$. The differences for $T/J_{av} \sim 0.2$ are thus quite large. But $C_v^{mag}$ is rather uncertain in this range of temperature. Most likely, the peak of the real $C_v^{mag}$ is located at a temperature higher than $\sim 30K$. Yet one may notice that the integrated entropy up to $T=60K$ (see Fig. 4) is similar to the one found for the AHM up to $T/J_{av} \sim 0.7$.

At lower $T$, however, the lattice contribution is small and $C_v^{mag}$ more accurate. But there also, one sees quite distinct behavior. $C_v^{mag}$ increases much less rapidly with $T$. There is no low $T$ peak. As a result the shapes of the integrated entropy widely differs (see Fig. 4). The integrated entropy obtained from $C_v^{mag}$ is much smaller than in the AHM which reveals that the density of states at low energy could be much smaller in Volborthite than in the AHM model. This may further suggest that some modification of the AHM are needed to describe Volborthite.

### III. SPECIFIC HEAT

ED results for the specific heat $C_v(T)$ are displayed in Fig. 3 (a) for the same values of the anisotropy $\alpha$ as in Fig. 2. For the sake of clarity experimental data are shown below in Fig. 3 (b). The ED and experimental results for the integrated entropy $S(T) = \int_0^T c_v(x)/dx$ are plotted in Fig. 4.

The ED results for $C_v$ show little size effects and can be considered as (quasi)converged for $T/J_{av} \gtrsim 0.2$ like those obtained for the susceptibility $\chi$. In this range of temperature $C_v$ exhibit a broad peak around $T/J_{av} \sim 0.6 - 0.8$ which increases and shift to higher $T$ with increased anisotropy but only very slightly. This is the usual main peak, associated to large energy excitations, rather insensitive to the detail of the interactions in the AHM. However, the integrated entropy under this peak $\sim S(T = \infty) - S(T = 0.2J_{av})$ (see Fig. 4) is only about 1/2 of the total entropy. Thus, as already found in the isotropic case, an unusually large part of the entropy is located at low temperature, which reveals a large density of states at low energy. For all values of the anisotropy, such a feature is seen to be a plateau was also exhibited at low $T$ (see Fig. 3). The integrated entropy (see Fig. 4). The comparison between $C_v^{mag}$ which is only accurate at low $T$ and the ED $C_v$ which are only converged at high $T$ is not easy. $C_v^{mag}$ is quite different from the ED $C_v$ of Fig. 3(a). $C_v^{mag}$ exhibits a peak at $T \sim 30K$. The height of this peak is about twice larger than the height of the main peak of the ED results. If the temperature of the experiment are scaled to $J_{av}=84.1K$, this peak is located at a temperature $T/J_{av} \sim 0.3$ This is about half of the temperature of the main peak of the ED $C_v$. The differences for $T/J_{av} \sim 0.2$ are thus quite large. But $C_v^{mag}$ is rather uncertain in this range of temperature. Most likely, the peak of the real $C_v^{mag}$ is located at a temperature higher than $\sim 30K$. Yet one may notice that the integrated entropy up to $T=60K$ (see Fig. 4) is similar to the one found for the AHM up to $T/J_{av} \sim 0.7$.

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### IV. MAGNETIZATION CURVES

The magnetization of the isotropic model $\alpha = 1$ has already been the subject of many studies. The model displays a plateau at $M = m/m_s = 1/3$ of the saturated magnetization $m_s$, which was interpreted as valence bond state with a $\sqrt{3} \times \sqrt{3}$ superstructure and a jump of height $\delta M = 2/9$ to saturation which arises degenerate localized magnons. The $M = 1/3$ plateau was aslo
reported to subsist in the anisotropic case\textsuperscript{\ref{not}1}. But this case remained much less studied.

The magnetization curves obtained from the ED spectra are plotted in Fig. 5 for different value of the anisotropy $\alpha$ in function of $H/H_s$ where $H_s$ is the saturation field. The $M = 1/3$ plateau subsist in the anisotropic case. The magnetization jump close to saturation disappear for $\alpha < 1$ and is replaced for $\alpha > 1$ by a smaller jump (proportional to the number of horizontal lines in the cluster) which will disappear in the thermodynamic limit. The spin structure in the $M = 1/3$ plateau corresponds, for $\alpha < 1$, to the ferrimagnetic phase (present in zero field for $\alpha \lesssim 0.5$), whereas for $\alpha > 1$ it corresponds to full polarization of the middle spins. One may notice that the width of the $M = 1/3$ plateau increases and the lower field $H_1$, for which it appears decreases with increased anisotropy. For a large anisotropy this field become quite low. The value of $H_s$ is $3J'/3J_{av}(2 + \alpha)/(2 + \alpha)$ if $\alpha < 1$ and $2(J' + 2J) = 3J_{av}(1 + 2\alpha)/(2 + \alpha)$ if $\alpha > 1$ (with $H_s = 3J_{av} = 3J$ if $\alpha = 1$). Fig. 5 indicate that $H_1 \sim 0.3H_s$ if $\alpha = 1$ but becomes $\lesssim 0.1H_s$ for $\alpha \lesssim 0.7$ or $\alpha \gtrsim 2$. If $J_{av} = 84K$, $H_s \sim 200$ Teslas, so $H_1 \sim 70$ Teslas if $\alpha \sim 1$, but for a large anisotropy $H_1$ could be $\sim 20$ Teslas i.e. in a range accessible to experiments. If a compound would be well described by the AHM Hamiltonian, the presence of a large anisotropy would be signaled by an observable magnetization plateau at low field, to gether with a large peak in the magnetic susceptibility at low temperature(as seen in Sec. II). Additional interactions to the AHM Hamiltonian may have different effects on the location of the $M = 1/3$ plateau and the susceptibility. But most likely a magnetization plateau at low field would imply a large peak in the magnetic susceptibility at low temperature. Since the latter feature is not found in Volborthite, it is probable that the $M = 1/3$ plateau (if any) is not located at low field but around $\sim 70$ Teslas. Presently, the magnetization has been only measured for fields up to 7 Teslas\textsuperscript{\ref{not}2} (and no plateau has been seen). Measurements at higher fields may be worth. The absence of a plateau up to $\sim 70$ Teslas would confirm a small anisotropy. If a plateau is observed below, its location would be a valu-

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig5}
\caption{(color online) Magnetization curves for different value of the anisotropy $\alpha$, obtained from exact diagonalization on clusters of $N = 18$ (dotted red lines) and $N = 24$ (dashed blue lines) spins. The magnetization $M$ is normalized to 1. $H_s$ the saturation field.}
\end{figure}

able information for the determination of the model appropriate to Volborthite.

\section{Summary}

In this work, we have investigated the thermodynamic properties of the spin-1/2 spatially anisotropic Heisenberg model on the kagomé lattice by means of exact diagonalization in order to compare with available experimental data for Volborthite.

The exact diagonalization results for the magnetic susceptibility and specific heat are found to be well converged to their values in the thermodynamic limit down to temperatures $\sim 0.2J_{av}$ (and perhaps below) for clusters of $N = 24$ spins. The range of temperature is significantly larger than the one accessible with present high temperature series expansion calculation\textsuperscript{\ref{not}28,32} and also somewhat larger than with other methods such as the linked cluster expansion of Ref.\textsuperscript{\ref{not}22,23}.

The comparison of the computed magnetic susceptibility with the experimental data show that Volborthite is best described by an Heisenberg model with at most a weak anisotropy. This suggests that the spatial anisotropy of the couplings in Volborthite is weak in spite of the significant distortion of the kagomé lattice in this compound. It also reveals the necessity to introduce in the present model other interactions in addition to the nearest neighbor exchanges to allow a good fit to the magnetic susceptibility of Volborthite below $\sim J_{av}$.

The comparison of the numerical specific heat with experimental data reveal quite large differences but is uneasy since the latter are rather uncertain, especially at high temperature. At low temperature, the integrated entropy of Volborthite appears to be much smaller than in the model. This suggests that the high density of states at low energy, which is a caracteristic of the Heisenberg model may not be present in Volborthite. Although, more accurate experimental data will be necessary to check this assumption, this may indicate some significan
differences between the physics of the Heisenberg model and Volborthite at low energy. In Herbertsmithite, where the magnetic specific heat is also uncertain, a simi-

lar comparison of the integrated entropy at low temperature leads to an analogous conclusion\textsuperscript{\ref{not}18}. For both compounds, this point seems worth further experimental investigation and will put constraint on the additional in-
interactions which are to be introduced in the Heisenberg model in order to better describe these compounds.

An other characteristic property of the kagomé Heisenberg model is the presence of a magnetization plateau at one third of the saturated magnetization. Because of the large value of the average exchange in Volborthite (~ 84K), the saturation field may be larger than 200 Teslas and the experimental study of the magnetization is uneasy. For weak anisotropy the plateau appears around ~ 70 Teslas and its width may not be large. Yet, the width of the plateau is found to increase with anisotropy and for large anisotropy this plateau starts at an applied field which may reach very small value more accessible to experiment. In view of the experimental data for the susceptibility, the detection of a plateau at low field seems however unlikely. Presently, the magnetization has been measured for fields up to 7 Teslas and the experimental study of the magnetization is uneasy. For weak anisotropy the plateau may appear more accessible to experiment. In view of the experimental data for the susceptibility, the detection of a plateau at low field seems however unlikely. Presently, the magnetization has been measured for fields up to 7 Teslas and its width may not be large. Yet, the width of the plateau is found to increase with anisotropy and for large anisotropy this plateau starts at an applied field which may reach very small value more accessible to experiment. In view of the experimental data for the susceptibility, the detection of a plateau at low field seems however unlikely. Presently, the magnetization has been measured for fields up to 7 Teslas and no plateau has been seen. The absence (or the presence) of a plateau up to much higher fields would provide further inside into the model that can describe Volborthite.

Although, it may not allow a perfect description of Volborthite, the anisotropic Heisenberg model provide a starting point and a reference for the understanding of this compound (or compounds with a distorted kagomé geometry that would be identified in the future) and thus remain worth consideration. In order to get insight into the influence of the anisotropy on the nature of the ground state and the low energy excitations, exact diagonalization have been carried out for clusters up to \( N = 36 \) spins which will be reported in an other paper. Preliminary investigations of the modification to the Heisenberg model that are required for a better description of Volborthite have been also started and will be be pursued. First principle investigations might help to provide further inside into this question and more experimental data would be very useful.

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expansions which would consist to fit the coefficients of the expansion to the ED results over the range of temperatures where the ED results may be considered as converged. Note that in this range of temperature two different values of $\alpha$, one $> 1$ and the other $< 1$ lead to rather similar $\chi(T)$. It is uneasy to differentiate between the two case on the sole basis of the magnetic susceptibility.