Thermodynamic Properties of Kagome Antiferromagnets with different Perturbations

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Abstract. We discuss the results of several small perturbations to the thermodynamic properties of Kagome Lattice Heisenberg Model (KLHM) at high and intermediate temperatures, including Curie impurities, dilution, in-plane and out of plane Dzyaloshinsky-Moria (DM) anisotropies and exchange anisotropy. We examine the combined role of Curie impurities and dilution in the behavior of uniform susceptibility. We also study the changes in specific heat and entropy with various anisotropies. Their relevance to newly discovered materials ZnCu$_3$(OH)$_6$Cl$_2$ is explored. We find that the magnetic susceptibility is well described by about 6 percent impurity and dilution. We also find that the entropy difference between the material and KLHM is well described by the DM parameter $D_z/J \approx 0.1$.

The discovery of Herbertsmithite compounds ZnCu$_3$(OH)$_6$Cl$_2$ has led to considerable excitement [1]. It is an example of the long-sought antiferromagnetic spin-half Kagome Lattice Heisenberg Model (KLHM). Ideally speaking, the layered material consists of spin-half copper atoms arranged in structurally perfect Kagome planes, which are separated by non-magnetic planes. The latter contain only zinc atoms as the transition metal. This leads to the possibility of observing ideal KLHM behavior in the material. Indeed, in several ways the experimental observations [2, 3, 4, 5, 6, 7, 8, 9] appear promising for one of the highly anticipated but so far elusive states of matter, a two-dimensional spin-liquid with deconfined gapless spin-half excitations.

However, the situation is unsettled on both the experimental and theoretical fronts. On the theoretical front, it remains unclear that the ground state of KLHM is a gapless spin-liquid with deconfined spin-half excitations [10, 11, 12]. Evidence for absence of long-range order and a gap in the spin excitation spectrum has come from several numerical studies [13, 14, 15, 16, 17, 18, 19, 20, 21, 22]. Furthermore, a Valence Bond Crystal phase has been proposed [23, 24], which appears to have a lower energy [20, 21] than the proposed variational wave functions for the spin-liquid phases [10]. So the question remains, is the spin-liquid phase, either with Fermi points or with a true Fermi surface for spinons realized for KLHM? And, can it be stabilized by adding other smaller interactions to the KLHM [25]? This remains an active area of theoretical investigations.

On the experimental front, a key question is, do the experimental observations reflect the behavior of an ideal KLHM, or are they dominated by various perturbations, including quenched impurities [11, 12, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24]. The exchange constant of the material is approximately 200K [26, 27], yet the magnetic susceptibility continues to increase below 1K and saturates at even lower temperatures to a very large value, in dimensionless terms almost two orders of magnitude
larger than the known susceptibility for the square-lattice Heisenberg Model. Furthermore, the specific heat appears linear or even sub-linear at low temperatures, and is strongly magnetic-field dependent \[2\]. However, one should keep in mind that this very low temperature behavior reflects a tiny fraction of the full spin entropy of \(\ln(2)\) \[27\]. Hence, its relevance to the KLHM is doubtful. Among other experimental results, there is no signature of a spin-gap either in Neutron scattering, or in NMR or \(\mu\)SR measurements \[2, 3, 4, 5, 6, 7, 8, 9\]. Before interpreting the experiments in terms of various proposed ground state scenarios for the KLHM, it is important to ascertain how much of the behavior is intrinsic to the Kagome system and how much of it arises from quenched impurities.

There is growing evidence that these materials have significant antisite disorder \[5, 6, 7, 8, 9\]. This is related to interchange of copper and zinc atoms between the kagome and non-magnetic planes. It has been estimated that upto 6-10 percent of the copper atoms may be replaced by zinc atoms and themselves end up in the zinc planes. This can cause a large density of nearly free spins, which would be only weakly coupled to the spins in the kagome planes. Furthermore, it leads to dilution in the Kagome planes, a quenched disorder, which can significantly affect the thermodynamic properties in the plane, especially if large unit cell Valence Bond Crystal phases are relevant to the pure material.

The Kagome Lattice lacks inversion symmetry through midpoints of bonds and hence, always allows for Dzyaloshinsky-Moria (DM) interactions \[28, 29\], involving cross products between spins. In a structurally perfect purely two-dimensional Kagome-Lattice, the DM interactions are represented by a vector \(D_z\), which points out of the Kagome plane. However, in the real material, the three dimensional embedded structure has sufficiently low symmetry to allow two independent DM parameters. A \(D_z\), which points out of the plane and a \(D_p\), which points in the plane, is perpendicular to the bonds and hence rotates from bond to bond. A priori, either of these DM terms could be dominant in the materials. Recent ESR experiments have been interpreted in terms of a dominant \(D_z\) term, which is about ten percent of the exchange interaction \(J\) \[8\].

The low temperature behavior of the KLHM is characterized by high near degeneracy between many putative ground states. Thus the system is clearly going to be highly sensitive to small perturbations. The \(D_z\) interactions lift the high ground state degeneracy at the classical level, leading to planar order with definite chirality \[30\]. Recently, these \(D_z\) interactions have been studied numerically for the spin-half system by Cepas et al \[31\], who find a phase transition from a non-magnetic phase to a magnetically ordered phase at a critical ratio of \(D_z/J\) of approximately ten percent. This puts the material \(\text{ZnCu}_3(\text{OH})_6\text{Cl}_2\) close to this quantum critical point.

In contrast to the \(D_z\) interactions, the \(D_p\) interactions are much more complex. At the classical level, they can favor a weakly ferromagnetic canted state \[30\]. For the quantum system, it is likely that they may not lead to long-range order even for sufficiently strong \(D_p/J\) ratio. In fact, the finite temperature behavior of the entropy function shows \[32\] that while an increasing \(D_z\) leads to a clear reduction of entropy with respect to the pure KLHM, an increasing \(D_p\) even to values as large as \(J/4\) hardly changes the entropy function. Numerical studies also found that \(D_p\) interactions can lead to enhanced ferromagnetic susceptibilities, which could play a role in explaining the experimental observations \[26, 32\].

In addition to DM anisotropy, the possibility of relatively strong Ising anisotropy in these systems has also been suggested \[33, 34\]. The pure Ising model on the Kagome Lattice is exactly soluble and leads to a large ground state entropy. Since a fraction of the ground states have a finite magnetization, this system has a divergent Curie-like susceptibility as \(T \to 0\). Moving away from the Ising model, by adding \(XY\) exchange terms leads to (i) a lifting of the ground state degeneracy, (ii) a robust second peak in the specific heat at low temperatures, and (iii) a cut-off for the Curie susceptibility as \(T \to 0\) \[35, 36\]. Such a behavior has indeed been reported in the experiments. Besides the high temperature susceptibility of oriented samples shows vastly
different Curie-Weiss temperatures along and perpendicular to the kagome planes [34]. Thus, substantial Ising anisotropy cannot be ruled out for these materials.

In this paper, our focus is going to be on the thermodynamic properties at relatively high temperatures, which can be studied in a controlled manner by High Temperature Expansions (HTE) [37], Numerical Linked-cluster Expansions (NLC) [35, 36], as well as by Exact Diagonalization (ED) of finite systems [27]. In an earlier paper, we had studied various perturbations individually including DM and exchange anisotropy, impurities and dilution [32]. There, our assumptions were that much of the observed behavior was intrinsic to the materials and was not due to quenched impurities and that anisotropies were relatively small, that is, the system was close to being KLHM. Thus, while we did look at impurity, dilution and small Ising and XY anisotropy, we focused primarily on the DM interactions as the primary reason for the large increase in the magnetic susceptibility. This led to suggestions of large DM interactions, which were primarily of $D_p$ character.

Here we look again at these perturbations, relaxing the assumption that quenched impurities are not playing a role. In fact, we believe, quenched impurities do play an increasingly important role at low temperatures. Unfortunately, this makes it difficult to select a unique set of parameters from a comparison between theory and thermodynamic experimental properties. We can combine free spins with dilution to get an excellent agreement with the susceptibility data at intermediate and high temperatures, without the need for any anisotropies. This is shown in Fig. 1, where one can see that when about six percent free Curie impurities are subtracted from the experimental data, it agrees remarkably well with the susceptibility of the KLHM with about six percent dilution [32]. It is not useful to add further DM interactions to study the susceptibility with impurity, dilution and DM interactions as proliferation of free parameters makes such an exercise meaningless. However, we should note that impurity plus dilution cannot be the full answer to ZnCu$_3$(OH)$_6$Cl$_2$ down to lowest temperatures as ultimately the Curie behavior goes away and the susceptibility saturates. The absence of Curie-like growth shows up in the subtracted curves in Fig. 1 as a rapid downturn in the susceptibility. This

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**Figure 1.** Experimental susceptibility (Exp.) of the material ZnCu$_3$(OH)$_6$Cl$_2$ compared with those of the Kagome Lattice Heisenberg Model (KLHM) with $J=170K$. Also shown is the experimental susceptibility after subtraction of Curie terms. The latter are fit remarkably well with the susceptibility of a diluted KLHM with $J=210K$. 
Figure 2. Entropy and Specific Heat, per spin, of the Heisenberg-Ising Model on the Kagome Lattice for several values of $J_\perp$ with $J_z = 1$.

quenching of the impurity susceptibility requires a coupling between the impurity spins and the rest of the system and cannot be understood if the rest of the system has a spin-gap.

The impurity spins should be nearly free at temperatures above their coupling scale. In this case, the temperature dependence of the specific heat and entropy should come from the rest of the system. We will try to use this to get a handle on the anisotropies. There has been a long theoretical debate about the specific heat of the pure KLHM and whether it has a second low temperature peak in addition to the high temperature peak associated with short-range order [37, 38]. This issue is not settled yet. For KLHM the extrapolation of High Temperature Expansion (HTE) by Misguich and Sindzingre allows one to reliably calculate entropy down to $T/J = 0.06$ [27], which is considerably lower than what we can get reliably by Numerical Linked Cluster (NLC) expansions. This is because the extrapolation method developed by Bernu and Misguich [39] allows them to incorporate a lot of information about the $T = 0$ properties of the system into the HTE study. Hence, in this case, we simply quote several results from their paper. First, around $T/J = 0.1$ the specific heat of the KLHM, per copper site is 0.1 (We take $k_B = 1$). Second, integrating the experimental specific heat from $T = 0$ to obtain the entropy as a function of temperature shows that at $T/J = 0.06$ the entropy of the experimental system falls below that of KLHM by at least 0.05. Misguich and Sindzingre suggest that this implies that additional terms in the experimental material help quench part of the large low temperature entropy of the system. The issue of the lower temperature peak in specific heat of KLHM is sensitive to assumptions about the low temperature behavior of the model and is not resolved in their study.

In Fig. 2, we show the entropy and specific heat of the Heisenberg-Ising model on the kagome lattice as obtained by NLC [35, 36]. While for the Heisenberg model, the existence of a two-
Figure 3. Entropy reduction with respect to KLHM due to DM interactions, for several values of the DM parameters. Two curves are shown for each parameter set. The thick dashed lines are from exact diagonalization of a 15-site cluster, whereas the thin black lines are from exact diagonalization of a 12-site cluster. The diamond represents the entropy reduction in ZnCu$_3$(OH)$_6$Cl$_2$ inferred from the study of Misguich and Sindzingre.

peaked specific heat remains under debate, there is no question that such a behavior arises for the Heisenberg-Ising model. For the pure Ising model, the entropy saturates to its ground state value at relatively high temperatures and the specific heat becomes exponentially small at lower temperatures. If we add a small XY coupling ($J_{\perp}$) to the Ising model, at high temperatures the behavior resembles that of the Ising model. But at lower temperatures, when $J_{\perp}$ becomes relevant, the specific heat develops a second peak and the ground state entropy is lifted by the perturbation. For a range of large anisotropy, the specific heat has a minimum around $T/J = 10$.

From an experimental point of view it has been very difficult to obtain the specific heat at temperatures above 10K (roughly $J/20$). This is because, the phonon contributions become very large above this temperature and it is difficult to reliably subtract them. However, such a subtraction has been attempted by Helton and Lee [40] and their data suggests that the specific heat has a minimum around $J/10$. However, the experimental behavior cannot be taken as evidence for Ising anisotropy for two reasons. First, as seen in Fig. 2, Ising anisotropy increases the entropy at any temperature with respect to the Heisenberg model, whereas the experimental entropy is lower. And, second, below the peak the specific heat of the Heisenberg-Ising model rises to a level above 0.1, whereas the experimental value is only about 0.03 [27, 40].

To look for reduction in entropy with respect to KLHM, we turn to the DM anisotropies. We consider a whole range of DM parameters ($D_p$ and $D_z$). For each case, we use exact diagonalization of small clusters of size 12 and 15 to obtain the entropy function [32]. For any temperature, we define the reduction in entropy with respect to the Heisenberg model as

$$\Delta S = S(D_z = 0, D_p = 0) - S(D_z, D_p).$$

Note that $\Delta S > 0$ means the entropy of the system with the DM interactions is lower than that of KLHM. The quantity $\Delta S$ is plotted in Fig. 3. The experimental value inferred in the study of Misguich and Sindzingre [27] is shown by a diamond. The main message from this plot is that the reduction in entropy is very insensitive to $D_p$ and depends primarily on $D_z$. So, if we
assume that the reduction in entropy is due to DM interactions, a $D_z$ value of order ten percent is likely. This is consistent with the experimental finding.

In conclusions, in this paper we have looked at the role of various perturbations to KLHM in the finite temperature thermodynamic properties and their relevance to ZnCu$_3$(OH)$_6$Cl$_2$. The susceptibility data at intermediate and high temperatures can be rather well fit with six percent Curie impurities along with a six percent dilution in the Kagome planes. The reduction in entropy with respect to KLHM below $T/J = 0.1$ suggests $D_z/J \approx 0.1$ in these materials. These findings are consistent with other experimental studies. The very low temperature behavior of these materials are likely dominated by impurities, which are weakly coupled to the system. Together with the anisotropies considered here, they may lead to a very different ground state than the one expected for the pure KLHM. This is beyond the scope of the current work.

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