

Magneto-thermodynamics of the Spin- $\frac{1}{2}$ Kagomé Antiferromagnet

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In this paper, we use a new hybrid method to compute the thermodynamic behavior of the spin- $\frac{1}{2}$ Kagomé antiferromagnet under the influence of a large external magnetic field. We find a T^2 low-temperature behavior and a very low sensitivity of the specific heat to a strong external magnetic field. We display clear evidence that this low-temperature magnetothermal effect is associated with the existence of low-lying fluctuating singlets, but also that the whole picture (T^2 behavior of C_v and the thermally activated spin susceptibility) implies contribution of both nonmagnetic and magnetic excitations. Comparison with experiments is made.

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Introduction.—Spin systems with strong geometrical frustration exhibit a generic feature: the deviation of their spin susceptibility from the Curie law occurs at a much lower temperature than for nonfrustrated ones and is often accompanied by very peculiar low-temperature properties [1]. The two-dimensional spin- $\frac{1}{2}$ Kagomé antiferromagnet (KAFM) is an example of such systems.

All theoretical and numerical treatments point to a disordered spin-liquid ground state [2–5], with a small spin gap estimated to be of the order of $1/20$ of the coupling constant. But contrarily to what prevails in 1D or ladders spin liquids, we have shown that the first excitations of this system have a spin 0. The spectrum of these many-particle $S_{\text{tot}} = 0$ eigenstates forms a continuum adjacent to the ground state, which extends smoothly up to energies higher than the spin gap [6,7]. In this paper we report some thermodynamic consequences of this property and focus on the magnetothermal effects which are seemingly a unique signature of this kind of spin liquids.

Numerical method.—The $\frac{1}{2}$ spins on the Kagomé lattice interact through the Hamiltonian

$$\mathcal{H} = J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - \gamma H \sum_i S_i^z, \quad (1)$$

where the double sum is limited to first neighbors. The temperature T and the magnetic field H are measured in coupling constant units ($J = 1, \gamma = 1$). Up to now two kinds of methods were available to obtain thermodynamic quantities: high temperature series and exact diagonalizations. The first [8] gives essentially exact results down to temperatures of the order of $J/2$, but unhappily no direct information on the range of temperature of interest in this work. The second allows the exact computation of the thermodynamics properties at all values of T , but for a set of sizes limited to $N \leq 21$. For such sizes and in spite of the supposed-to-be short range spin-spin correlations [4,5], there might be some uncertainties on the low T thermodynamic properties related to the discrete nature

of the finite size spectra. To deal with larger sizes and in order to obtain significant information on the effect of an applied field at low T ($T \sim 0.05 \dots 0.2$), we have devised an hybrid method which takes advantage of both previous approaches. An approximate density of states in each irreducible representation (IR) of the complete symmetry group of the lattice and Hamiltonian is reconstructed via a maximum entropy procedure. It uses exact diagonalization data to fix the edges of the density of states and the six first moments of the Hamiltonian in each given subspace. In the $N = 36$ sample there are 264 different IR and thus the procedure involves a very large amount of exact results. Most of the low T physics comes from the relative position, weight and general shape of the different IR, which are an essential input of our method. The knowledge of these quantities for each IR of SU(2) allows a straightforward computation of the effect of any magnetic field. We have checked on different frustrated spin problems that this approach gives reliable information on the intermediate temperature range and on multiple-peak structures [9].

Numerical results.—High temperature range down to $T = 0.2$: Numerical results are summarized in Fig. 1, together with the Padé approximant of the high-temperature series of Elstner and Young [8]. In this range of temperature, the spin susceptibility χ shows a shoulder at $T \sim 1$ and the specific heat C_v a high T peak around $T = 2/3$. The Padé approximants cannot be distinguished from the $N = 18$ results down to $T = 0.4$ and then merge smoothly with the exact $N = 24$ low T results. We thus infer that above $T = 0.4$ these different data give a very good approximation of the thermodynamic limit. It should be noticed that there is only 50% of the total entropy in the high T peak above $T = 0.2$, whereas the Néel ordered Heisenberg magnet on the triangular lattice develops 50% of the total entropy above $T = 1$, and only $\sim 6\%$ below $T = 0.2$. The low T entropy is indeed a distinctive mark of exotic spin liquids [10] and the KAFM represents an extreme situation.

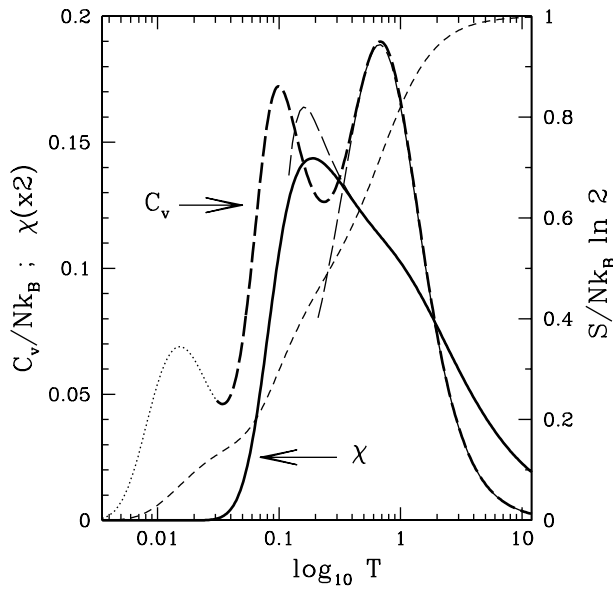


FIG. 1. Specific heat C_v , spin susceptibility χ , and entropy S of the $N = 18$ Kagomé antiferromagnet versus temperature T . Dashed line: C_v/Nk_B ; continuous line: $\chi \times 2$; short-dashed line: $S/k_B \ln 2$. The light dashes represent the Padé approximants to C_v and χ of Ref. [8]: they cannot be distinguished from the $N = 18$ and 24 results down to $T = 0.4$. For $T \leq 0.03$ the numerical results are exact but cannot be informative on the thermodynamic limit, because of the finite size effect.

From $T = 0.2$ down to $T \sim 0.2\Delta$: when cooling down the KAFM, one encounters a second energy scale Δ related to the spin gap [11]. In the range of sizes presently studied, the gap is still decreasing [7] and Δ varies from $\Delta_{18} = 0.104$ to $\Delta_{36} = 0.074$ which explains the evolution of C_v in Figs. 2 and 3. From the study of spin-spin correlations [4,5] and of finite size effects on the spin-gap one might expect that the $N = 36$ sample is not very far from the thermodynamic limit. Remembering that 50% of the total entropy has to be accounted for below $T = 0.2$, one expects the low T peak in C_v to remain for $N \rightarrow \infty$.

The spin gap clearly explains the thermally activated spin susceptibility χ . However, C_v (in contrast to χ) does not decrease exponentially in the gap. For the larger samples ($N = 18-36$), C_v below the peak is well fitted by a T^2 law in the range $T = (0.3-0.6)\Delta$ (Fig. 2). The non-exponential behavior of C_v is indeed due to the presence of singlets in the gap, but, as can be seen in Fig. 3, higher spin channels do contribute to approximately one-half of C_v in this range of temperature and the T^2 behavior appears as a cooperative effect due to different spin channels. This fact contradicts an intuitive expectation: from our knowledge of fully gapped systems one would naively expect an absence of contribution of the triplets for temperatures lower than the spin gap. In fact, C_v , at temperature T , essentially measures the energy fluctuations around the average energy $e(T)$. In a fully gapped system, when T is lower than the spin gap, the ground state alone is populated and the energy fluctuations are thermally activated. In the present

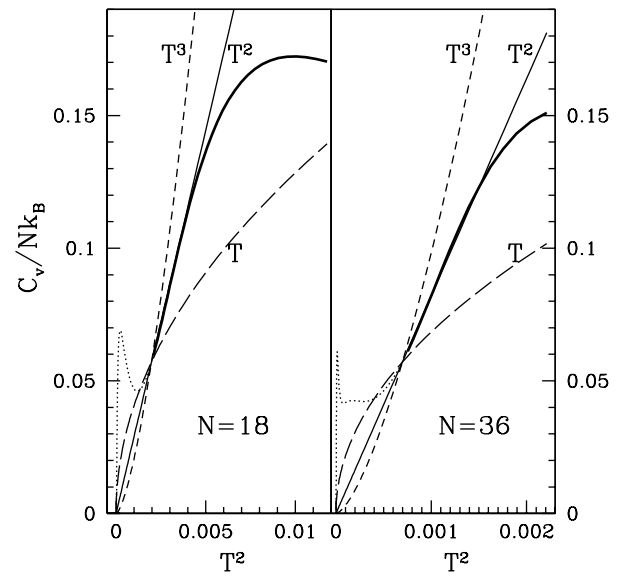


FIG. 2. Low-temperature specific heat C_v (full lines for $T \geq 0.3\Delta$, dotted lines below) versus the square of the temperature ($N = 18$ and 36 samples). C_v is well fitted by a T^2 law (light line) in the range $T = (0.3-0.6)\Delta$ and deviates from higher or lower power laws.

case, the thermal population at a temperature T is dominated by the singlet states with an energy $\sim e(T)$: this large number of relay levels in the spin gap and the very large number of low-lying triplets are at the origin of this surprising behavior.

There has been in the past many speculations about the origin of the T^2 behavior in SrCrGaO and in the

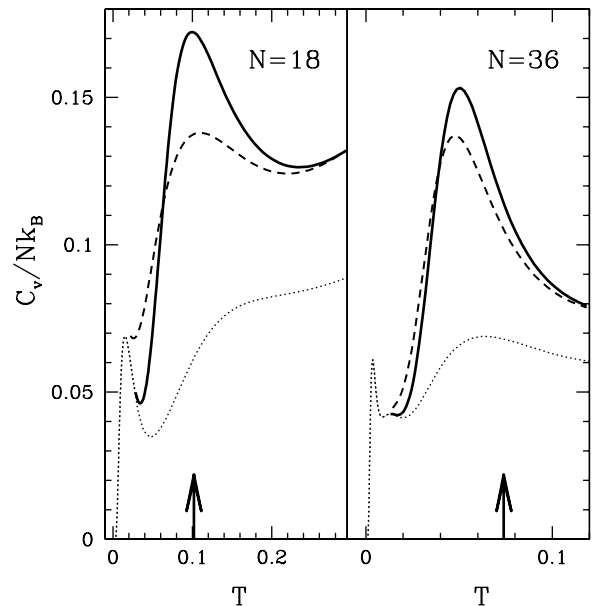


FIG. 3. Contribution of the singlet ($S_{\text{tot}} = 0$) states (dotted lines) to the total specific heat (full lines) and effect of a magnetic field H equivalent to the 6 T experiment of Ramirez *et al.* [24] (dashed lines). The arrows indicate the value of Δ for each sample.

jarosites: simple or nematic spin-wave modes have been suggested [12,13]. Strictly speaking the presence of a spin gap precludes such an explanation in the spin- $\frac{1}{2}$ case, but the small spin gap is a proof that the spin- $\frac{1}{2}$ KAFM is relatively near a quantum critical point. An alternative explanation can also be featured by focusing on the resonating-valence-bound picture of the singlets [3,14,15]: in such a picture the modes are associated with the dimer-dimer long range orientational order (“resonons” of Rokhsar and Kivelson [14]). Such a picture gives a T^2 behavior of C_v provided that the dimer-dimer structure factor is linear in k at small wave vectors. This would imply an algebraic decrease of the dimer-dimer correlations. Regarding the range of sizes available, this hypothesis cannot be completely discarded (dimer-dimer correlations at distance 6 are of the order of 10^{-2} in the spin- $\frac{1}{2}$ KAFM [5], whereas they are about 10^{-4} in the spin liquid phase of the multiple spin exchange model on the triangular lattice studied in Ref. [10]). In this last hypothesis, a global picture involving both singlet and magnetic excitations should be worked out.

Temperatures lower than 0.2Δ : The C_v curves for $N = 18$ and $N = 36$ are numerically exact in this temperature range. The entropy of the singlet excitations in the spin gap ($\sim 15\%$) is certainly a significant information in the thermodynamic limit. But the low-temperature peak (dots in Figs. 1, 2, and 3) is unphysical and a consequence of the discreteness of the spectra. Large size effects in the lowest part of the energy spectrum preclude its extrapolation for $N \rightarrow \infty$; in particular, they make it impossible to decide the exact value of the entropy at $T = 0$ and the very low T behavior of C_v in the thermodynamic limit.

Comparison with experimental results.—The comparison with experimental results is only indicative, insofar as only pseudo-spin-1 [16], spin- $\frac{3}{2}$ [17–20], and spin- $\frac{5}{2}$ [21,22] Kagomé lattices have been realized and studied in the laboratory.

Pseudo spin-1: The organic compound m -MPYNN · BF₄ studied by Wada and co-workers [16] may behave at low enough temperatures as a spin-1 KAFM. χ has been measured in a large range of temperature. There are similarities with the present spin- $\frac{1}{2}$ results: A shoulder at $T \sim 1$, a thermally activated behavior with a spin gap of the order of 7.7×10^{-2} . It might be noticed that the experimental gap is large enough compared to the spin- $\frac{1}{2}$ case; half integer and integer spin systems might indeed behave differently.

Spin-3/2 systems: We will concentrate here on SrCrGaO which displays the most convincing example of a non-conventional low-temperature behavior [18–20]. From the magnetic point of view, it is not clear whether SrCrGaO is a good representative of a system of Kagomé planes (with intervening dilute triangular Heisenberg planes) or whether it is better described as a stack of two-dimensional slabs of pyrochlore. However, on the qualitative level these

two theoretical models display similarities, absence of long range order, resonating valence-bond ground state, so that a comparison of the experimental results for SrCrGaO with our numerical results might be justified [23].

The double peak structure in C_v has not been seen in these compounds: this is not a surprise in the light of present results. In SrCrGaO the Curie-Weiss temperature is of the order of 500 K, the coupling constant of Eq. (1) is thus of the order of 100 K, and from results shown in Fig. 3 we expect the low- T peak to appear at $T \sim 0.05J \sim 5$ K or below. On the other hand, the scale for the semiclassical behavior is given by $S(S + 1)J$: we thus predict that the high T peak in SrCrGaO should appear around 350 K, but experimental data extend only to 40 K. We might notice that in SrCrGaO as in the $S = \frac{1}{2}$ numerical data, the low- T peak in C_v accounts for half of the total entropy of the spin system [24]. Lastly, the T^2 behavior of C_v is consistent with the experimental data.

The stronger argument in favor of a parentage between the spin- $\frac{1}{2}$ KAFM and SrCrGaO is *the quasi-absence of sensitivity of C_v to applied magnetic fields H as large as twice the temperature* reported by Ramirez *et al.* [24].

This is a highly surprising result, which cannot be explained in any of the following hypothesis: Néel long range order, ordinary spin glass, spin liquid with a full gap for both magnetic and nonmagnetic excitations.

(i) Since a Néel-ordered system spontaneously breaks the rotational invariance, the ground states (and the first excitations) are superpositions of quasidegenerate eigenstates with a *different total spin*. In such a case, χ goes to a constant at low T . Though the magnetization per spin vanishes, the typical spin is not zero: $S_{\text{tot}}^2 \sim N\chi(T = 0)$. This gives a H dependent C_v .

(ii) On the other hand, in a fully gapped spin liquid, as soon as the applied field is large enough to match the gap, C_v is completely washed out, as, for example, in the spin-Peierls compounds.

In SrCrGaO a field of 8 to 11 tesla is large enough to excite magnetic excitations (as can be seen in looking at the nonzero values of χ at equivalent temperature), and nevertheless there is no effect on C_v . We show on the spin- $\frac{1}{2}$ example below that the presence of an important background of nonmagnetic excitations is enough to drastically decrease the effect of the field on C_v .

The magnetothermal effect on spin- $\frac{1}{2}$ KAFM is displayed in Fig. 3 for a field equal to the temperature of the peak T_p (corresponding approximately to the 6 T experiments of Ramirez *et al.* [24]).

(i) The contribution of singlet excitations to C_v is displayed on the same graph. In the interesting range of temperature, the singlets account for only half of C_v .

(ii) The higher spin channels are responsible for the missing half of C_v . These higher spin channels are indeed fully sensitive to H . If these magnetic levels were separated from the singlet ground state by a spin-gap void

of singlet excitations, the decrease of the C_v peak would be 3 times larger than it is in the present situation. Here again, the presence of the background of singlets brings a great change in the fluctuation spectrum of this system and explains its paradoxical low sensitivity to H .

(iii) The effect of a field of the order of T_p seems larger in the spin- $\frac{1}{2}$ KAFM than in SrCrGaO: this suggests that in this range of T the relative weight of the singlets is larger in SrCrGaO than it is for spin- $\frac{1}{2}$. We suggest the following conjecture: SrCrGaO, as a spin- $\frac{3}{2}$ system, is closer to the quantum critical transition than the spin- $\frac{1}{2}$ KAFM. Its spin gap, if not zero is certainly smaller than that of the spin- $\frac{1}{2}$ KAFM, and there may be a collapse of the different low-energy scales appearing in the low S_{tot} sectors of the spin- $\frac{1}{2}$ system (see Fig. 3). In such a situation we expect a weaker sensitivity of C_v to H .

An important issue in experimental systems is the problem of dilution. We have checked the effect of quenched disorder on the spin- $\frac{1}{2}$ KAFM by including 1 or 3 non-magnetic sites in a $N = 21$ sample. The general qualitative properties of the KAFM (thermally activated χ , low- T peak in C_v , and singlets in the spin gap) do not disappear with such dilutions. This seems an interesting indication that the thermodynamic features we have been describing in this paper are rather robust.

Conclusion.—In this paper we describe the results of a numerical investigation of the magnetothermal properties of the spin- $\frac{1}{2}$ KAFM. We show that the specificities of its low-energy spectrum induce a very low sensitivity of the specific heat to the external magnetic field. Such an effect is a very strong signature of a large weight of singlet excitations and would not be present in a Néel ordered system, in a standard spin glass, or in a dimerized Spin-Peierls like system. We have verified that this effect is qualitatively insensitive to quenched disorder. The qualitative similarities to the Ramirez *et al.* results on SrCrGaO are probably more than a coincidence, but a new independent proof advocating for the presence of low-lying fluctuating singlets in this spin- $\frac{3}{2}$ compound. The precise nature of the lattice (Kagomé or pyrochlore slab) might not be a central issue. We have preliminary results showing that similar spin-liquid behavior does appear on many other lattices. We now suspect this behavior to be a generic feature of one class of spin liquids.

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