Eur. Phys. J. B **59**, 305–309 (2007)
DOI: 10.1140/epjb/e2007-00301-6

THE EUROPEAN PHYSICAL JOURNAL B

Magnetic susceptibility and specific heat of the spin-$\frac{1}{2}$ Heisenberg model on the kagome lattice and experimental data on $ZnCu_3(OH)_6Cl_2$

G. Misguich[1,a] and P. Sindzingre[2]

[1] Service de Physique Théorique, CEA Saclay, 91191 Gif-sur-Yvette Cedex, France
[2] Laboratoire de Physique Théorique de la Matière Condensée, Univ. P. et M. Curie, 75252 Paris Cedex, France

Received 3 July 2007
Published online 1st November 2007

Abstract. We compute the magnetic susceptibility and specific heat of the spin-$\frac{1}{2}$ Heisenberg model on the kagome lattice with high-temperature expansions and exact diagonalizations. We compare the results with the experimental data on $ZnCu_3(OH)_6Cl_2$ obtained by Helton et al. [Phys. Rev. Lett. **98**, 107204 (2007)]. Down to $k_BT/J \simeq 0.2$, our calculations reproduce accurately the experimental susceptibility, with an exchange interaction $J \simeq 190$ K and a contribution of 3.7% of weakly interacting impurity spins. The comparison between our calculations of the specific heat and the experiments indicate that the low-temperature entropy (below ∼20 K) is smaller in $ZnCu_3(OH)_6Cl_2$ than in the kagome Heisenberg model, a likely signature of other interactions in the system.

PACS. 75.50.Ee Antiferromagnetics – 75.10.Jm Quantized spin models – 75.40.Cx Static properties

1 Introduction

After many years of theoretical investigations, the nature of the ground-state of the spin-$\frac{1}{2}$ Heisenberg model on the kagome lattice is still not known. Although all numerical studies have concluded to the absence of long-range magnetic (Néel) order [1–8], many basic questions such as the existence of spontaneously broken symmetries, or the existence of a finite gap to magnetic excitations remain open. In fact, many different states of matter have been proposed for the kagome Heisenberg antiferromagnet: $\mathbb{Z}_2$ gapped topological liquids [9,10], valence-bond crystals [11–14], critical spin liquids with gapless spinons [15,12].

Recently, a promising spin-$\frac{1}{2}$ antiferromagnetic insulator with an ideal kagome geometry, $ZnCu_3(OH)_6Cl_2$, has been synthesized and studied for its magnetic properties [16–20]. Because these studies did not detect any kind ordering (nor spin freezing) down to 50 mK, it could represent one of the first and most remarkable realization of a 2D quantum spin liquid [21,22].

To extract some information about the low-energy physics of the kagome Heisenberg model from the experiments on $ZnCu_3(OH)_6Cl_2$, it is important to first analyze in a quantitative way the possible role of magnetic defects (and other "perturbations" to this model) in this compound. In this paper we compare the experimental data for the magnetic susceptibility χ and specific heat c_v obtained by Helton et al. [16] with calculations for the spin-$\frac{1}{2}$ Heisenberg model on the kagome lattice based on exact diagonalization (ED) data (partial spectrum of a 36-site cluster and full spectrum for 24-site and 18-sites clusters) and high-temperature series expansion [23,24]. Down to temperature $k_BT/J = 0.2$, the experimental susceptibility $\chi_{\rm exp}(T)$ can be very well fitted by that of the kagome lattice Heisenberg model with $J \simeq 190$ K plus a contribution of about 4% of impurity spins with weak mutual interactions (modeled by a ferromagnetic Curie-Weiss temperature of $\simeq -6$ K), likely mostly due to antisite disorder (Cu substituted to Zn on sites between the kagome planes) [20,25]. The low temperature specific heat is dominated by impurities (and other perturbations) below 2 K and by phonons above 15 K. In the intermediate range, the calculated specific heat appears to be larger than in the experiment. We comment on this feature at the end of the paper.

2 Uniform static susceptibility

The spin-$\frac{1}{2}$ Heisenberg model reads:

$$\mathcal{H} = J \sum_{\langle i,j \rangle} \boldsymbol{S}_i \cdot \boldsymbol{S}_j - g\mu_B H \sum_i S_i^z \qquad (1)$$

where the sum runs over pairs of nearest neighbor sites on the kagome lattice and H is an external magnetic field.

[a] e-mail: gregoire.misguich@cea.fr

To fix the notations, we define the (zero-field) uniform susceptibility per site $\chi(T)$ as $\chi(T) = \frac{g\mu_B}{N} \left.\frac{\partial \sum_i \langle S_i^z \rangle}{\partial H}\right|_{H=0}$ where N is the total number of spins.

The high-temperature expansion of χ has been computed up to order $\mathcal{O}\left(T^{-15}\right)$ (included) by Elstner and Young [23]:

$$\chi(T) = \frac{4C_0}{J}\chi_{\rm th}(t = k_B T/J)$$
$$\chi_{\rm th}(t) = (1/4)t^{-1} - (1/4)t^{-2} + \dots \qquad (2)$$

where $C_0 = 0.25(g\mu_B)^2$ is the Curie constant and t the reduced temperature. The truncated series $\chi_n(t) = \sum_{i=0}^{n} c_i t^{-i}$ at order $n = 14$ and $n = 15$ agree with a relative error smaller than 10^{-2} for $t > 1$. Down to this temperature, they already provide good approximations to $\chi_{\rm th}(t)$. The convergence of high-T series can be improved using Padé approximants (PA). In the present case the PA provide a reliable estimate of $\chi_{\rm th}(t)$ at least down to $t \sim 0.5$.[1] One representative PA (numerator of degree 8 and denominator of degree 7) is displayed Figure 1.

On a small enough system, it is possible to obtain by ED the *full* spectrum (2^N energy levels for N spins). We have done so for two 18-site and 24-site kagome clusters (with periodic boundary conditions). Then thermodynamic quantities can be computed exactly as a function of T. For bigger systems, where one can still compute some eigenstates by ED, one may use the approximate method described in reference [26] to compute thermodynamic quantities.[2]

The results for the susceptibility $\chi(t)$ are shown in Figure 1. Above $t = 0.2$, the relative difference between the (exact) $N = 18$ and $N = 24$ curves is smaller than 0.5%. We therefore make the (rather safe) assumption that our finite-size results are good approximations to the thermodynamic limit down to $t_{\rm min} \simeq 0.2$. This represents a small gain over the coupled-cluster expansion of reference [27], which is valid above $t \sim 0.3$.

The $\chi(t)$ obtained with the approximate method for $N = 36$ sites also agrees (with a relative error smaller than 2%) with the $N = 24$ results down to $t \simeq 0.2$. Slightly below, the 36-site susceptibility is still increasing and might be a better approximation to the infinite-size limit than the 24-site curve. Still, it is not possible decide at which t finite-size (and/or errors due to the approximation in the density of states) will become too important. Safely, we only use the theoretical results (noted $\chi_{\rm th}$) above $t \simeq 0.2$ to fit the experimental data $\chi_{\rm exp}$ for the susceptibility.

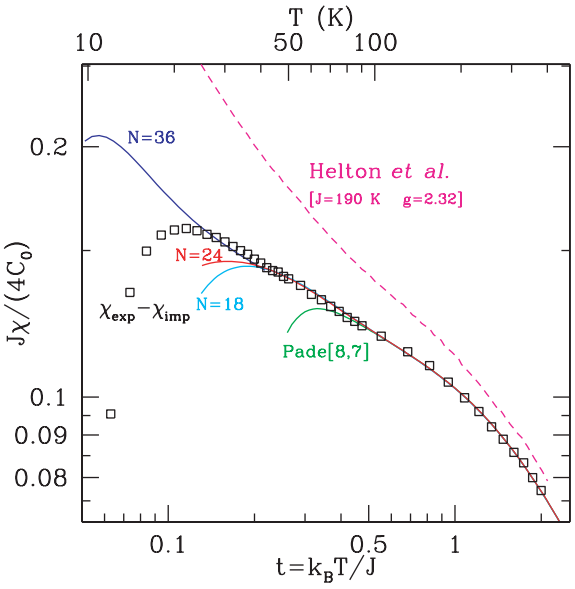

Fig. 1. (Color online) Magnetic susceptibility per spin as a function of temperature. Dashed (magenta) curve: experimental data (Helton et al.), multiplied by $J/(4C_0)$ as a function of k_BT/J with $J \simeq 190$ K and $C_0 = 0.504$ K cm^3/(mol of Cu). Black squares: $\chi_{\rm s} = \frac{J}{4C_0}(\chi_{\rm exp}(T) - \chi_{\rm imp}(T))$, obtained from the experimental data $\chi_{\rm exp}$ by subtracting the contribution $\chi_{\rm imp}$ of a concentration $x = 0.03655$ of impurity spins with a Curie-Weiss temperature $\theta_{\rm imp} = -6.1$ K. Red (resp. cyan) curve: Exact $\chi_{\rm th}$ for a $N = 24$ (resp. 18) site kagome cluster with periodic boundary conditions. Blue curve: Results for $N = 36$ spins obtained with the (approximate) method of reference [26]. Green curve: Padé approximant from the high-temperature expansion at order t^{-15}. The Padé approximant is not converged below $t \simeq 0.4$ whereas the finite-size curves are practically converged to the thermodynamic limit down to $t \simeq 0.2$. Below $t = 0.2J$, the later curves are only indicative.

We fit $\chi_{\rm exp}$ to a sum of contributions from the kagome spins $\chi_{\rm s}$ and the impurities $\chi_{\rm imp}$ in the following way:

$$\chi_{\rm exp}(T) = \frac{4C_0}{J}\chi_{\rm s}(k_BT/J) + \chi_{\rm imp}(T) \qquad (3)$$
$$\text{with } \chi_{\rm imp}(T) = \frac{xC_0}{T + \theta_{\rm imp}} \qquad (4)$$

where J is the (unknown) magnetic exchange in between the spins in the kagome planes, x an impurity concentration, $C_0 = 0.25(g\mu_B)^2/k_B$ the Curie constant and $\theta_{\rm imp}$ the Curie-Weiss temperature of the system of impurities. Equation 4 is the leading term in a high-temperature expansion for the system of impurities, which provides a simplified picture of their interactions. To be applicable, T should therefore be large compared to $\theta_{\rm imp}$. We assume that the system of impurities does not perturb the the kagome spins.

We optimized numerically the parameters so that $\chi_{\rm s}$ fits the theoretical results $\chi_{\rm th}$ for $t \geq 0.2$. As can be seen

[1] Comparing the PA and the exact curves for 18 and 24-site clusters shows that the PA is in fact correct down to $T \sim 0.4J$, see Figure 1.

[2] In this method, one constructs the density of states in each symmetry sector from the exact low and high energy states obtained from ED and approximating in between the unknown part of the spectrum with a smooth density of states. This smooth part is constructed so that the first moments of the density of states ($Tr[H^n]$), in each symmetry sector of the finite cluster, are exact up to $n = 5$. This Ansatz guaranties that the thermodynamics becomes exact at low T (when thermal excitations only involve the eigenstates computed exactly) as well as at high T (when a re-summed high-temperature expansion up to T^{-5} is valid).

in Figure 1, an almost perfect agreement can be obtained between $\chi_s = \frac{J}{4C_0}(\chi_{exp}(T) - \chi_{imp}(T))$ (squares) and the theoretical estimates for the kagome susceptibility χ_{th} with the following parameters: $C_0 = 0.504$ K cm^3/(mol of Cu) (equivalent to a gyromagnetic factor $g = 2.32$), $J = 190.4$ K, $x = 0.03655$ and $\theta_{imp} = -6.1$ K. We note that the value of J is in rough agreement with the values reported in reference [16] (17 meV $\simeq$ 200 K) and [27] (170 K). We also check a posteriori that the lowest temperature of the fit ($t = 0.2 \simeq 38$ K) is much bigger than $|\theta_{imp}|$, so that a Curie-Weiss approximation for the impurities is justified. 6 K is also approximatively the transition temperature reported in $Zn_xCu_{4-x}(OH)_6Cl_3$ for $x < 0.6$ (replacing some Zn by Cu between the kagome planes) [17], so this energy scale may correspond to some couplings for spins located between the planes, where magnetic impurities could sit. We eventually notice that down to $t = 0.15$ (that is below the lowest temperature used for the fit), $\chi_{exp} - \chi_{imp}$ continues to increase and to follow the $N = 36$ curve. This suggests that the maximum of the kagome susceptibility could indeed be below $t = 0.15$.

Rigol and Singh [27] analyzed the same experimental data with another high-temperature method (coupled cluster expansion) and obtained a somewhat different conclusion. They argued that Dzyaloshinskii-Moriya (DM) interactions provide a better description of the low-temperature increase of the susceptibility than impurities. Although we agree that DM interactions are certainly present in $ZnCu_3(OH)_6Cl_2$ and that they should affect the physics of the system (at least at low-temperatures), it is also clear that a few percent of impurities must be present too and should have a visible effect on the susceptibility, even at rather high temperatures. According to reference [27], *free* impurities cannot explain the sharp increase of χ_{exp} below 60 K. In our analysis, this issue is solved by allowing for a small *ferromagnetic* Curie-Weiss temperature $\theta_{imp} \simeq -6$ K for the impurities[3]. One can indeed see that, once χ_{imp} has been subtracted, the experimental results show a saturation of χ around 20 K, in rough agreement with the measurements of reference [19]. The location of the maximum we obtain is however quite sensitive to the value x of the impurity concentration.

3 Specific heat

The experimental data for the specific heat $c_v(T)$ are only available at very low temperature where the size effects on the ED results are large. We therefore also applied the high-temperature entropy method [28]. It combines three pieces of information about the system: 1) The high temperature series expansion of $c_v(T)$, up to T^{-17} [23,24]. 2) The ground-state energy per site e_0 of the Hamiltonian. Here we use the following estimate

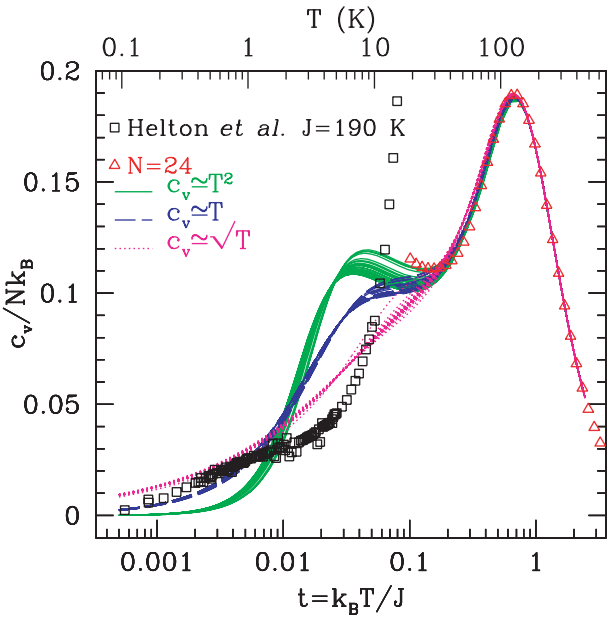

Fig. 2. (Color online) Specific heat c_v vs. temperature T. Black squares: experimental data from Helton et al. [16], assuming $J \simeq 190$ K. Red triangles: exact specific heat of a 24-site kagome cluster. Green (full), blue(dashed) and magenta(dotted) curves: c_v calculated by the entropy method for three different values of the low-temperature exponent ($\alpha = 2$, 1 and 0.5). All valid PA from order 14 to 17 with numerator and denominator of degrees ≥ 3 are shown. For a given α and at each temperature, their dispersion provides a rough estimate of the error bars.

$e_0 = 2\langle 0|\boldsymbol{S}_i \cdot \boldsymbol{S}_j|0\rangle = -0.44$ [24]. 3) The exponent α describing the low-temperature behavior of the specific heat: $c_v(t \to 0) \sim t^\alpha$. The method then provides a set of $c_v(t)$ curves (for different Padé approximants) which all satisfy exactly the following properties: i) $c_v(T \to 0) \sim T^\alpha$, ii) $c_v(T \to \infty) \sim$ the series expansion, iii) $\int_0^\infty c_v(T)dT = -Ne_0$, and iv) $\int_0^\infty c_v(T)/TdT = Nk_B \ln(2)$. When the value of e_0 and α are both correct, one usually gets a large number of very similar curves but if either is *incorrect*, only a few and scattered curves will be obtained (more details in Refs. [28,24]). In the case of the kagome antiferromagnet, the value of α is not known and the entropy method gives a reasonable convergence for $\alpha = 1$ and $\alpha = 2$ [24]. Motivated by the experimental observation [16] of a low-temperature c_v with an exponent smaller than one, we also include here a calculation with $\alpha = 0.5$.

The results for some valid PA from orders 14 to 17 are displayed in Figure 2[4] together with the exact result obtained by ED of the full spectrum of a 24-site kagome cluster. For $t > 0.3$, these results are practically exact.

[3] The Curie-Weiss temperature is an *average* of the different exchange constants. However, due to the complexity of the interactions between impurities (disorder), the ferromagnetic sign of θ_{imp} does not necessarily imply that they behave ferromagnetically at *low* temperatures.

[4] By the entropy method, the entropy $s(e)$ is obtained as the power $\alpha/(\alpha+1)$ of a rational fraction (PA) of the energy per site e. The specific heat curve is then obtained parametrically through $T(e) = 1/s'(e)$ and $c_v(e) = -s'(e)^2/s''(e)$. Only the PA which satisfy $s(e) > 0$, $s'(e) > 0$ and $s''(e) < 0$ in the range $]e_0, 0[$ are physically "valid".

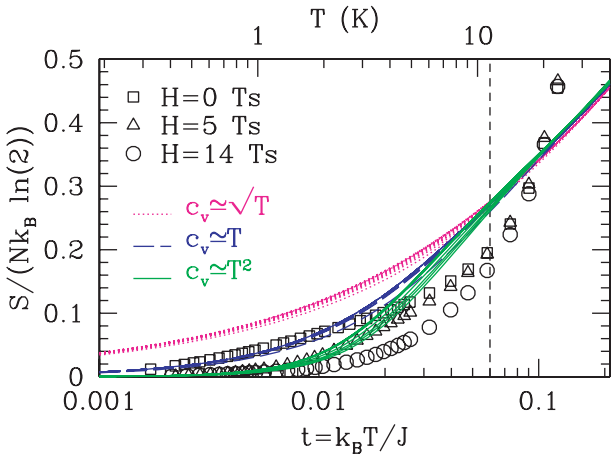

Fig. 3. (Color online) Entropy S vs. temperature. Square, triangles and circles: experimental data from Helton et al. [16] with magnetic field $B = 0$, 5 and 14 Teslas, plotted as a function of k_BT/J with $J = 190$ K. Green (full), blue(dashed) and magenta(dotted) curves: entropy calculated by the entropy method for $\alpha = 2$, $\alpha = 1$ and $\alpha = 0.5$ (same PA as in Fig. 2).

In the two scenarios $\alpha = 1$ and 2 there is a significant dispersion of the results for $t < 0.3$ from one PA to another [24]. [5] In both case, c_v show a low-t peak or shoulder as found from ED of finite-size systems. The choice $\alpha = 0.5$ leads to a smoother $c_v(t)$ and improves significantly the convergence. It is however not clear if this improved convergence for small values of α ($0.5 \lesssim \alpha \lesssim 1$) indicates that α is actually smaller than one or an artifact of the present entropy method, which might be "slower" to stabilize a low-t peak (as with $\alpha = 2$, see Fig. 2), than a smooth curve (as with $\alpha = 0.5$). In any case, this is clearly related to the unusually large low-temperature entropy of the kagome system.

Figure 2 also displays the experimental results (black squares) obtained by Helton et al. [16] The only parameter here is the exchange constant, taken to be $J \simeq 190$ K from the fits of the susceptibility data. Above 15 K, the phonon contribution is dominant and we have to focus on the lower temperatures to analyze the magnetic contribution. Below 15 K the order of magnitude agrees with our calculation but there is no quantitative agreement. Several "perturbations" such as weakly interacting magnetic impurities or magnetic anisotropies should indeed contribute to the specific heat at such low temperatures.

Results for the integrated entropy $S(T) = \int_0^T c_v(x)/x dx$ are plotted in Figure 3, where one sees that the choice of the low-T exponent α of c_v has practically no influence on the theoretical $S(t = k_BT/J)$ above $t \simeq 0.06$ and that, around this temperature, the experimental value is significantly *lower* than in our calculations. Of course, subtracting the contribution of the phonons (hard to estimate quantitatively) and from the impurities would make the discrepancy even larger. Concerning the impurities, one sees in Figure 3 that an applied magnetic field of 5 and 14 Teslas is enough to significantly reduce $S(t)$ for $t \lesssim 0.06$. Such fields are low in comparison to J but of the order of the estimated coupling between the impurities. The difference between the curves at 0 and 5 (or 14) Teslas may thus provide a rough estimate of the contribution of the impurities. Note that $S(t)$ at 5 Teslas become closer to the $S(t)$ computed by the entropy method with $\alpha = 2$. The experimental value $\alpha < 1$ could be due to the impurities and the actual value of α for the kagome spins could be larger than 1. In any case, at $t = 0.06 (\simeq 11$ K), the experimental entropy ($\simeq 0.2 \ln 2$) is thus at *least* 7% of $\ln 2$ below the theoretical estimates ($0.27 \ln 2$). This seems a rather robust indication that some additional interactions play some role in this energy range, by freezing some degrees of freedom of the spins in the kagome planes and pushing the corresponding entropy to higher energies. We may mention in particular DM interactions [27], non-magnetic impurities in the kagome planes ("dilution") [20] and interactions between impurities and the kagome spins. We conclude that $15 \sim 20$ K is a minimal temperature for a kagome lattice Heisenberg model description of $ZnCu_3(OH)_6Cl_2$ to be valid.

We are grateful to C. Lhuillier for many discussions and comments about the manuscript. We also thank P. Mendels and F. Bert for useful discussions. GM also thanks Y.S. Lee and J. Helton for discussions and for providing their data as well as P.A. Lee, Y. Ran, T. Senthil, X.-G. Wen for discussions on related topics.

Note added:

After the first submission of this manuscript, two preprints [20,25] (neutron scattering) confirmed the importance of magnetic impurities (from 6% to 10%) in $ZnCu_3(OH)_6Cl_2$. The smaller value found here could be due to our simplified model to fit the magnetic susceptibility.

References

1. V. Elser, Phys. Rev. Lett. **62**, 2405 (1989)
2. C. Zeng, V. Elser, Phys. Rev. B **42**, 8436 (1990)
3. J.T. Chalker, J.F.G. Eastmond, Phys. Rev. B **46**, 14201 (1992)
4. R.R.P. Singh, D.A. Huse, Phys. Rev. Lett. **68** 1766, (1992)
5. P.W. Leung, V. Elser, Phys. Rev. B **47**, 5459 (1993)
6. T. Nakamura, S. Miyashita, Phys. Rev. B **52**, 9174 (1995)
7. P. Lecheminant, B. Bernu, C. Lhuillier, L. Pierre, P. Sindzingre, Phys. Rev. B **56**, 2521 (1997)
8. C. Waldtmann, H.U. Everts, B. Bernu, C. Lhuillier, P. Sindzingre, P. Lecheminant, L. Pierre, Eur. Phys. J. B **2**, 501 (1998)
9. S. Sachdev, Phys. Rev. B **45**, 12 377 (1992)
10. Fa Wang, A. Vishwanath, Phys. Rev. B **74**, 174423 (2006)
11. J.B. Marston, C. Zeng, J. Appl. Phys. **69**, 5962 (1991)

[5] This is due to the finite order in the high-temperature expansion. Still, for a given value of α, we believe that this method gives a qualitatively correct picture for $c_v(T)$, even at low T.

12. M.B. Hastings, Phys. Rev. B **63**, 014413 (2000)
13. P. Nikolic, T. Senthil, Phys. Rev. B **68**, 214415 (2003)
14. R. Budnik, A. Auerbach, Phys. Rev. Lett. **93**, 187205 (2004)
15. Y. Ran, M. Hermele, P.A. Lee, X.-G. Wen, Phys. Rev. Lett. **98**, 117205 (2007)
16. J.S. Helton, K. Matan, M.P. Shores, E.A. Nytko, B.M. Bartlett, Y. Yoshida, Y. Takano, A. Suslov, Y. Qiu, J.-H. Chung, D.G. Nocera, Y.S. Lee,
17. P. Mendels, F. Bert, M.A. de Vries, A. Olariu, A. Harrison, F. Duc, J.C. Trombe, J.S. Lord, A. Amato, C. Baines Phys. Rev. Lett. **98**, 077204 (2007)
18. O. Ofer, A. Keren, E.A. Nytko, M.P. Shores, B.M. Bartlett, D.G. Nocera, C. Baines, A. Amato, e-print `arXiv:cond-mat/0610540`
19. T. Imai, E.A. Nytko, B.M. Bartlett, M.P. Shores, D.G. Nocera, e-print `arXiv:cond-mat/0703141`
20. M.A. de Vries, K.V. Kamenev, W.A. Kockelmann, J. Sanchez-Beniteza, A. Harrison, e-print `arXiv:0705.0654`
21. P.W. Anderson, Mater. Res. Bull. **8**, 153 (1973)
22. G. Misguich, C. Lhuillier, in *Frustrated Spin Systems*, edited by H.T. Diep (World Scientific, Singapore, 2005) e-print `arXiv:cond-mat/0310405`
23. N. Elstner, A.P. Young, Phys. Rev. B **50**, 6871 (1994)
24. G. Misguich, B. Bernu, Phys. Rev. B **71**, 014417 (2005)
25. S.-H. Lee, H. Kikuchi, Y. Qiu, B. Lake, Q. Huang, K. Habicht, K. Kiefer, e-print `arXiv:0705.2279`
26. P. Sindzingre, G. Misguich, C. Lhuillier, B. Bernu, L. Pierre, C. Waldtmann, H.U. Everts, Phys. Rev. Lett. **84**, 2953 (2000)
27. M. Rigol, R.R.P. Singh, Phys. Rev. Lett. **98**, 207204 (2007)
28. B. Bernu, G. Misguich, Phys. Rev. B **63**, 134409 (2001)