Impurity effects in the quantum kagome system $ZnCu_3(OH)_6Cl_2$

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Motivated by the recent experiments on the spin half kagome compound $ZnCu_3(OH)_6Cl_2$, we study a phenomenological model of a frustrated quantum magnet. The model has a spin liquid ground state and is constructed so as to mimic the macroscopically large quasidegeneracies expected in the low-lying energy structure of a kagome system. We use numerical studies of finite size systems to investigate the static as well as the dynamical responses at finite temperatures. The results obtained using our simple model are compatible with a large number of recent experiments including neutron scattering data. Our study suggests that many of the anomalous features observed in experiments have a natural interpretation in terms of spin-$\frac{1}{2}$ defects (impurities) coupled to an underlying kagome-type spin liquid.

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The quest for spin liquids in real materials has been in the forefront of condensed matter physics since Anderson's suggestion of resonating valence bond states as a possible ground state for the antiferromagnetic insulating phase seen in high T_c superconductors. Typically, one expects spin liquid ground states in geometrically frustrated systems with a high degree of frustration like in the Heisenberg antiferromagnet on pyrochlore lattices, checkerboard lattices, and the kagome lattice.[1] The Heisenberg antiferromagnet on the kagome lattice is particularly interesting in that numerical calculations show the existence of a special kind of spin liquid ground state with a macroscopic quasidegeneracy.[2] However, not much is known about the dynamical properties of these spin liquids. Interest in the physics of kagome lattices has been boosted by the synthesis of a paratacamite compound $ZnCu_3(OH)_6Cl_2$, which is considered as a faithful realization of a spin-$\frac{1}{2}$ kagome system.[3] A spate of recent experiments[4–7] has however, generated a huge debate about whether the observations are actually due to intrinsic kagome physics or whether other aspects such as impurities or Dzyaloshinski-Moriya interactions[8] may need to be taken into account.

Motivated by the current lack of perfect stoichiometric control in the synthesis of $ZnCu_3(OH)_6Cl_2$, and its impurity-like low temperature behavior of the static magnetic susceptibility, we introduce a schematic model which toys with the idea that the anomalous features seen in experiments may arise from spinful impurities dressed by an underlying spin liquid with an energy spectrum of the kagome type. Our mean-field model explicitly mimics the principal feature of the kagome antiferromagnet: a high degree of frustration leading to a macroscopic degeneracy of the ground state. Due to its mean-field nature, our model is much easier to study than the full kagome system. We begin by considering the following Hamiltonian:

$$H = \sum_{i \neq j=1}^{N} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1)$$

where $\mathbf{S}$ represent the spin half operators and J_{ij} the antiferromagnetic interactions between two spins. Since all the spins interact with each other, the model is maximally frustrated. For $J_{ij}=J$ for all i,j, the model is exactly soluble since the Hamiltonian can be written as $H=J/2[\mathbf{S}_{tot}^2-3N/4]$ and all states with a given value of total spin S_{tot} are degenerate. For N even, the ground state is a bunch of degenerate singlets with a gap to the degenerate triplets given by $\Delta=J$. For N odd, the ground state is described by degenerate spin-$\frac{1}{2}$ states with a gap to the quadruplet spin $\frac{3}{2}$ given by $\Delta=1.5J$. In order to mimic the quasidegenerate nature of the low energy sector of the kagome spin system, we add a small disorder term to the magnetic interactions $J_{ij}=J(1+\delta_{ij})$, where $\delta_{ij} \ll 1$ are normally distributed random numbers. This small change in couplings is sufficient to lift the exact degeneracy of the states, but not large enough to destroy the energy separation between the low-lying sectors. The number of quasidegenerate states of the ground-energy sector is macroscopic and given by $A_{even} \approx 1.68^N$ for N even and $A_{odd} \approx 1.74^N$ for N odd. This resembles the scaling seen in the kagome lattice where $A_{even} \approx 1.14^N$ for N even and $A_{odd} \approx 1.16^N$ for N odd. Thus, in the N even (odd) case, both models feature a quasidegenerate and macroscopically large lowest energy sector with $S=0$ ($S=1/2$) and a first excited sector of similar characteristics with $S=1$ ($S=3/2$). We solve the model using exact diagonalization methods[9,10] and calculate the static spin susceptibility and the local dynamic susceptibility in the presence and absence of an external magnetic field. These calculations are done at finite temperatures which restrict the size of the systems that we can access numerically. Nonetheless, as we will show below, finite size effects are rather minimal. This is partly due to the mean-field nature of the model, and, also to the fact that the computed observables are obtained as direct averages over realizations of disorder.[9,10]

Regarding the current debate on whether the observed experimental behavior is intrinsic to the putative spin liquid state of a kagome lattice or due to impurity effects, we shall show below that many experimental observations can be naturally explained as due to strongly interacting many-body spin-$\frac{1}{2}$ states that are present only in N odd systems. We shall argue that this leads to the interpretation that low energy

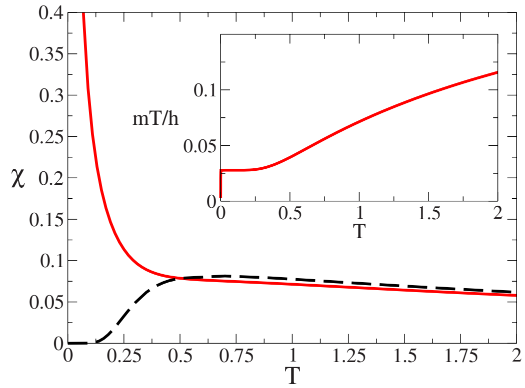

FIG. 1. (Color online) Typical behavior of the static susceptibility as a function of temperature T for N odd (full line) and N even (dashed line). The inset shows the typical temperature variation of the normalized magnetization in a field for N odd. The finite intercept and the convex shape of the curve are in qualitative agreement with the experiments of Ref. 5

features seen in current experiments on the paracatamite are controlled by impurities.

To begin with the discussion of our toy model results, we first consider the uniform static susceptibility per spin $\chi(T)$. This quantity is easily computed from the magnetic moment $m(h)$ for small fields, i.e., $\chi = m/h$, where m is the magnetic moment per spin at a temperature T and h is a small external applied field. Due to the mean-field nature and the translationally invariant spin liquid ground state of our model, the local and the global magnetic moment are the same. Consequently, the ensuing analysis holds for local as well as global susceptibilities.[5] From Fig. 1, we see that $\chi(T)$ is strongly dependent on whether the total number of spins is even or odd. This can be easily understood from the fact that even systems have a singlet ground state (with other singlets nearly degenerate with the ground state) and a well defined gap to the first triplet. This gap leads to $\chi(T) \propto \exp(-\Delta/T) \to 0$ as $T \to 0$. On the other hand, systems with N odd have a multitude of low-lying spin doublet states that are quasidegenerate with the ground state. Thus, as $T \to 0$, this results in a Curie-like behavior of the susceptibility,

$$\chi(T) \approx \frac{\alpha(N)}{4T}. \tag{2}$$

The inset of Fig. 2 shows the scaling of the Curie coefficient $\alpha(N)$. Interestingly, the finite size scaling reveals that, despite the macroscopic number of low-lying spin doublet states, $\alpha(N) = 1/N$. Thus, the strength of the divergent part of $\chi(T)$ corresponds exactly to the contribution of a single effective spin-$\frac{1}{2}$, independently of N. In other words, since $\chi(T)$ is the susceptibility per spin, our result implies that for systems of any size N (odd), the strength of the Curie-Weiss contribution of the *total* spin susceptibility $N\chi(T)$ is exactly 1. This is a clear indication of a spin-$\frac{1}{2}$ many-body state emerging in odd-N systems, which can also be thought of as a missing spin-$\frac{1}{2}$ (defect) in an otherwise $S=0$ spin liquid. The existence of this effective "dangling" spin is further clarified by the behavior of $\chi(T)$ at small finite fields h. From Fig. 2, we see that the Curie divergency observed in odd-N systems is cut off by h, and χ becomes temperature independent for $T \lesssim h$. This is in agreement with the results reported in Ref. 5, where a field of 0.2 T was applied and the saturation of $\chi(T)$ below 0.2 K was observed. At intermediate and high temperatures, $\chi(T)$ is almost the same for systems with odd and/or even-N modulo finite size scaling effects. At high enough temperatures $T > J$, we recover the usual Curie-Weiss behavior of the susceptibility $\chi(T) \propto (T + T_{\mathrm{CW}})^{-1}$. As expected for a mean-field model where every spin has $N-1$ neighbors, we find that the Curie-Weiss temperature which fixes the scale of the antiferromagnetic exchange in the system is given by $T_{\mathrm{CW}} \approx -0.3(N-1)J$, where the factor of 0.3 is due to quantum fluctuations and the inherent frustration. To compare the scale of the Curie-Weiss temperature predicted by the mean-field model with that of real experiments, we can use the experimental value of $J = 170$ K. For kagome lattices, since the number of nearest neighbors is 4, we obtain $|T_{\mathrm{CW}}| \simeq 1.2J$ (=204 K) which is of the same order as the experimental estimate of around 270–320 K.

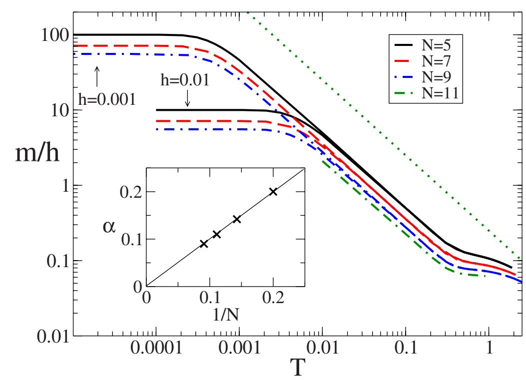

FIG. 2. (Color online) The finite size scaling for the susceptibility shows the saturation of χ as $T \to 0$ in a field. The dotted green line represents $\chi = 1/4T$. The inset shows the variation of the coefficient α defined in Eq. (2) with system size.

We now discuss the behavior of dynamical quantities. We use the following spectral decomposition to calculate the imaginary part of the dynamic susceptibility $\mathrm{Im}\,\chi \equiv \chi''$:

$$\chi''(\omega) = \frac{\pi}{ZNM} \sum_{m=1}^{M} \sum_{i=1}^{N} \sum_{\nu\mu} |\langle \mu^m | S_i^z | \nu^m \rangle|^2 \delta(\omega - E_\mu^m + E_\nu^m) \times \exp(-\beta E_\nu^m)[1 - \exp(-\beta\omega)], \tag{3}$$

where Z is the partition function and M the number of disorder realizations that are used to average χ. In Fig. 3, we plot χ'' for both even and odd systems. Note that, as already anticipated, the finite size effects on $\chi''(\omega)$ are quite weak. Both even and odd spectra show the presence of a prominent peak at a frequency of order of the gap $\Delta \propto J$ to the first excited state. Note that in the absence of disorder, these peaks are delta functions. The peak at $\omega_0 \approx J$ for even systems results from excitations between states in the $S_{tot}=0$ and $S_{tot}=1$ sectors, while in the case of odd systems, the transitions are between $S_{tot}=1/2$ and $S_{tot}=3/2$ with an

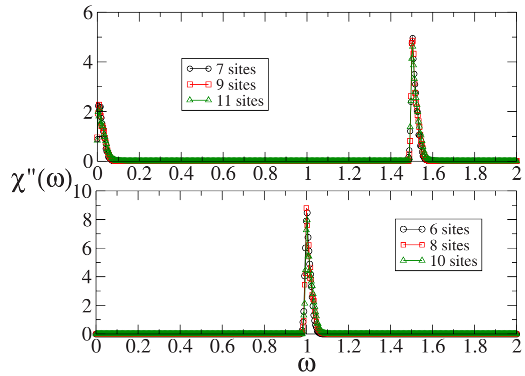

FIG. 3. (Color online) The $T=0$ dynamic susceptibility $\chi''(\omega)$ as a function of frequency ω in units of J for systems with N odd and N even.

$\omega_0 \approx 3J/2$.[11] However, we note that there is a fundamental difference between N even and odd in that the latter has significant low frequency spectral weight. In the rest of this Brief Report, we shall discuss the behavior of this low frequency feature in the context of recent neutron scattering experiments on $ZnCu_3(OH)_6Cl_2$.[4]

The qualitative difference between the low energy spectra of even and odd systems can be readily understood. This spectrum corresponds to transitions within the lowest energy sector that contains a macroscopic number of quasidegenerate states [i.e., within energy $O(\delta J)$ from the ground state]. This sector has $S_{tot}=0$ for even systems and $S_{tot}=1/2$ for odd systems. Since the spin susceptibility induces transitions between states which differ in one unit of the z component of the spin, these are forbidden between the singlets of even size systems, but are perfectly possible between the low-lying doublets of odd systems. Based on this argument, the low frequency feature in $\chi''(\omega)$ seen in odd systems should have a characteristic width of order δJ as is verified by Figs. 3 and 4. Thus, the physics of the low frequency contribution to the dynamical susceptibility is also due to the same effective spin-$\frac{1}{2}$ degree of freedom that was previously responsible for the low temperature contribution to $\chi(T)$.

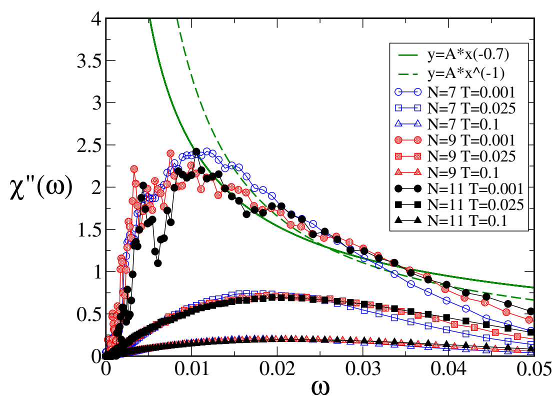

FIG. 4. (Color online) The low frequency peak in $\chi''(\omega)$ as a function of frequency ω in units of J for different temperatures $T=0.001J$, $0.025J$ and $0.1J$. Taking $J=170$ K, our data approximately correspond to the same experimental window reported in Ref. 4. The solid and dashed lines represent the power law fits proposed in that experimental study.

We now focus on the temperature dependence of this low frequency peak. As one increases T from $10^{-3}J$ to $10^{-1}J$, which is roughly the same range as that studied in the experiments of Ref. 4, we observe the following: first, the height and intensity of the peak diminish dramatically and second, the peak shifts to higher frequencies. These behaviors are qualitatively similar to those seen in neutron experiments.[4] At smallest T, there is a strong enhancement of $\chi''(\omega)$ toward lower frequencies. However, eventually, the susceptibility vanishes as $\omega \to 0$ at the very low frequency end of the spectra. The curves for the three different system sizes shown in the figure demonstrate that even in this low frequency regime, the finite size effects are rather small. As argued before, the width of the peak is controlled by the disorder distribution δ which is a phenomenological parameter in our model. Since $J=170$ K, we adjust the disorder strength to the value $\delta=0.01$ to fit the experimental neutron data. The frequency range shown in Fig. 4 corresponds to the experimental range of the reported neutron scattering,[4] and we clearly see that taking into account the experimental error bars, our results are indeed compatible with the observed data. For comparison, the power law fits suggested by the experiments are also shown in this figure. However, our results do not predict a divergence of $\chi''(\omega)$ for $\omega \to 0$. Therefore, our study suggests that the putative divergence observed may be merely due to rather large error bars of the lowest frequency data, which is the region where the experiment suffers from largest uncertainty. Moreover, the lack of finite size effects permits us to obtain a rather reliable estimate of the integrated intensity of the low frequency feature, and we find that it amounts to about 25% of the total spectral weight. This value is compatible with the reported 20% estimated from the neutron experiments.

We finally consider the effect of a magnetic field on the dynamical susceptibility. In the presence of an external field $\mathbf{h}=h\mathbf{z}$, χ is the longitudinal susceptibility, whereas for fields aligned along the x direction, χ represents the transverse susceptibility. We plot the temperature evolution of $\chi''(\omega)$ for applied fields with different orientations. The strength of the magnetic field is set to $h=0.067J$ so as to match the experimental value of 11.5 T used in Ref. 4. Our results show that h has a strong effect on $\chi''(\omega)$ at both high and low frequencies. For an applied field in the z direction, the longitudinal susceptibility χ'' (bottom panels in Fig. 5) remains essentially unchanged since a longitudinal field does not produce spin flips. For a transverse field, the computed $\chi''(\omega)$ now corresponds to the transverse susceptibility and as expected, the high frequency feature at $\omega_0=3/2J$ shows the usual Zeeman splitting $\omega_0 \pm h$ (top right panel). This splitting corresponds to excitations from states with $S^z_{tot}=\pm 1/2$ to states with $S^z_{tot}=\pm 3/2$. Interestingly, we also see a shift of the low energy part of the spectrum toward a higher frequency $\omega \sim h$. A single spin-$\frac{1}{2}$ would give a sharp peak at the Larmor frequency h. However, in the present case, in addition to a sharp peak, we also find a broad asymmetric contribution. This anomalous behavior is due to the quasidegeneracy of the low-lying states and the many-body nature of the remnant

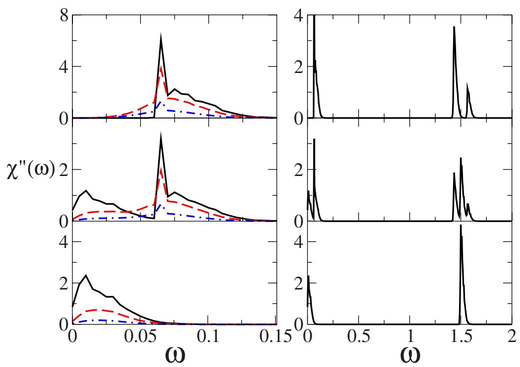

FIG. 5. (Color online) $\chi''(\omega)$ as a function of frequency ω. An external magnetic field is applied along the transverse x axis (top), the longitudinal z axis (bottom), and a tilted axis in the x-z plane (middle). To match the experimental value, we set $h=0.067J$ and $T=0.001J$, $0.025J$, and $0.1J$ (top, middle, and bottom curves in each left panel). The left column panels show a detailed of the low energy region, and the corresponding full spectra are shown in the right column (only the lowest T is plotted).

spin-$\frac{1}{2}$ degree of freedom present in odd systems. Interestingly, a similar broad anomalous feature was also seen in the reported neutron data.[4] For fields applied in the tilted (1,0,1), direction (central panels), the resulting response can be easily interpreted as the superposition of the transverse and longitudinal responses. Thus, the high energy feature splits into three peaks centered around ω_0 and $\omega_0 \pm h$, and a similar analysis is also valid for low frequencies. The response in a tilted field can be considered as a generic case and is also more likely to be closer to the experiments which were performed on powder samples.

We believe that the accord we find between our mean-field toy model results and experiments may provide useful guidance, especially, with regards to the current debate on whether the low energy behavior seen in experiments is dominated by impurity effects. In fact, odd systems can be viewed as even systems with a spin defect (i.e., an impurity), or, alternatively, as a single (impurity) spin dressed by the coupling to an $S_{tot}=0$ (even) spin liquid. Thus, our results for odd systems naturally lead to the interpretation of the anomalies observed in current experiments as arising from impurities and/or defects which may originate from the lack of precise stoichiometric control in currently available samples. Once a chemical handle is found for the synthesis of the compounds, a systematic study of the dependence with Zn-Cu substitution may help disentangle the impurity and intrinsic contributions and eventually validate our proposed scenario for this fascinating quantum magnet system.

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[11] The fact that these excitation energies do not converge with even and odd N as $N \to \infty$ is a peculiarity of the model which is irrelevant for the discussion of the present work.