Valence Bond Glass Phase in Dilute Kagome Antiferromagnets

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We present a theory for site dilution in the kagome lattice Heisenberg model. The presence of an empty site leads to strong singlet bonds opposite to the impurity. It also creates a free spin which delocalizes near the impurity. Finite impurity concentration leads to a valence bond glass phase with no spin gap, large spin susceptibilities, linear specific heat due to two-level systems, as well as singlet and triplet excitations that decompose into kink-antikink pairs. It provides a framework for a comprehensive understanding of thermodynamic, neutron, and Raman measurements in the herbertsmithite material $ZnCu_3(OH)_6Cl_2$, including recently reported H/T and ω/T scaling.

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The kagome lattice Heisenberg model (KLHM) is one of the most studied realistic quantum spin models where resonating valence bond (RVB) physics, first proposed by Anderson [1] more than 25 years ago, may be realized. In this model, extensive degeneracy at the classical level and in the space of valence bond configurations leads to the possibility of quantum spin liquids as well as many competing or coexisting orders [2–16].

Experimental studies of the herbertsmithite materials $ZnCu_3(OH)_6Cl_2$, containing structurally perfect kagome planes [17–23], have raised the hope of realizing RVB physics in a real material. Ideally, these materials have a pyrochlore structure, where spin-half copper atoms form kagome layers, which are separated by nonmagnetic zinc containing triangular layers. This ideal case is now known to be not true, as substitution of some fraction of zinc and copper sites leads to extra isolated spins in the zinc planes and site-dilution in the copper planes.

Here we develop a theory for site dilution in KLHM using dimer series expansions [10,24]. We find that dilution leads to a valence bond glass (VBG) phase. Unlike the valence bond crystal (VBC), which is stabilized by higher order perturbation theory, with energy scales less than 0.01 J per site (energy scales that differentiate different VBC phases are only 0.001 J per site) [10,24], the VBG phase is stabilized by second order perturbation theory with an energy scale of order 0.1 J per site.

A single impurity can be accommodated in the VBC in several inequivalent positions of the 36-site unit cell (see Fig. 1) with nearly equal energy. The addition of such an impurity leads to strong singlet bonds opposite to the impurity (see Fig. 2), in agreement with earlier studies of Dommange *et al.* [25]. However, contrary to the work of Dommange *et al.*, we find that the impurity also creates a free spin, which delocalizes inside the unit cell. The herbertsmithite materials have a large impurity concentration of order 6%, which would imply on average 2 randomly placed impurities per unit cell. At this high impurity concentration no semblance of long-range VBC order would remain. Instead, one obtains a randomly pinned VBG with only short range valence bond order. We will show that the VBG description leads to a consistent picture for thermodynamics, neutron, and Raman scattering experiments in the herbertsmithite materials.

In dimer expansions [26], one picks a nearest-neighbor dimer configuration and writes the Hamiltonian as

$$\mathcal{H} = \mathcal{H}_0 + \lambda \mathcal{H}_1, \tag{1}$$

where $\mathcal{H}_0$ consists of all exchanges corresponding to bonds in the dimer configuration and $\mathcal{H}_1$ consists of all other exchanges. Perturbation theory is carried out in powers of λ and the results are evaluated at $\lambda = 1$. For KLHM, such an expansion was done for an arbitrary dimer configuration [10]. Setting $J = 1$, a dimer configuration has energy per spin of -0.375. Including second order terms, the energy of each dimer configuration is lowered to $-0.421\,875$. At this level all dimer configurations are degenerate. On the other hand the exact ground state energy of KLHM is known from a variety of numerical studies to be approximately -0.433 [8]. Thus the entire set of higher order terms, beyond second order, changes the energy of the system by only another -0.011. The VBC

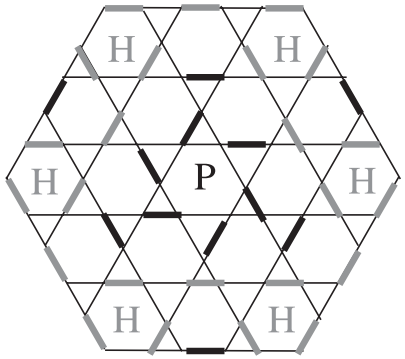

FIG. 1. Proposed valence bond crystal of the kagome lattice Heisenberg model has a 36-site unit cell that includes two resonating hexagons (H) and a pinwheel (P).

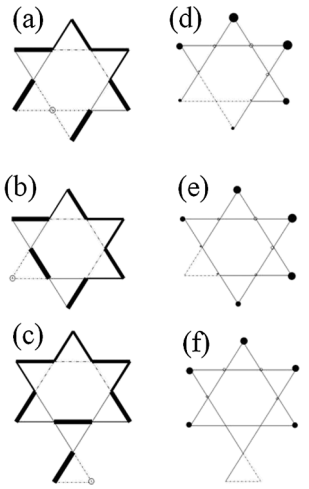

FIG. 2. Dimer configurations around the impurity, when the impurity is placed (i) in the inner hexagon, (ii) on the outer vertices, and (iii) in the bond neighboring the pinwheel. (a)–(c) show the dimerization pattern, with the thickness of the lines showing the strength of the singlet bonds. Note the strong dimer bond opposite to the impurity. The other side of the impurity in (b) and (c) is a nonfluctuating singlet bond (not shown). (d)–(f) show the distribution of free spins. The filled circles show the positive spin expectation values, whereas empty circles show negative values. The size of the circle represents the size of the spin.

configuration, found to have lowest energy by dimer expansions, is shown in Fig. 1. We note that the same VBC configuration has been obtained in an unbiased tensor-network based variational study by Evenbly and Vidal [14].

The removal of magnetic sites lifts the degeneracy of dimer configurations already in second order. Only bonds neighboring empty triangles [10] can contribute in second order. Not having a dimer bond opposite to a missing spin amounts to placing the missing spin at the vertex of an empty triangle. Hence, some second order contribution is lost. The energy of the dimer configuration is raised by about 0.05 if one bond opposite to the missing spin is absent and 0.1 if both bonds opposite to the missing spin are absent. This strongly favors having singlet bonds present opposite to the impurity.

We first study the single impurity case in more detail for our VBC in Fig. 1. Given the many inequivalent sites, the crystal is free to adjust itself to place the impurity at any site. Second order perturbation theory tells us that the impurity will prefer to go to one of the bonds that do not touch any empty triangles. These are shown as dark bonds in Fig. 1. To a high numerical approximation, there are three inequivalent sites where the missing spin can go. These are (i) the inside hexagon of the pinwheel, (ii) the outside vertices of the pinwheel, and (iii) on one of the dark bonds that are not part of the pinwheel. The pinwheels are all bounded from outside by dimerized triangles. Hence, neglecting higher order fluctuations, it suffices to diagonalize the pinwheels only, plus the extra triangle in case (iii), to obtain the spin and dimer patterns around the impurity.

The ground state bond energies and spin configurations for the three cases, obtained by exact diagonalization, are shown in Fig. 2. Figures 2(a)–2(c) show the pattern of dimerization around the impurity. Figures 2(d)–2(f) show how the free spin is delocalized over the pinwheel. In all cases, the energy cost of removing a spin is not 0.75 as for an isolated dimer but rather approximately 0.25. The system chooses to put a strong singlet bond opposite to the impurity, which gets back the lost 0.75 of energy. Instead, an antikink develops in the pinwheel, which is known to have a minimum energy of approximately 0.25 [27,28]. The actual energy cost in the three examples is found by exact diagonalization to be approximately 0.2764, 0.2632, and 0.2468 in cases (i), (ii), and (iii), respectively. The singlet bond opposite to the impurity has strength -0.725, -0.716, and -0.731, respectively. The bond patterns have a clear resemblance to the study of Dommange *et al.* [25].

In contrast to the dark bonds, if the impurity falls on the gray bonds, the resulting free spin can delocalize through the network of gray bonds. It cannot delocalize to arbitrarily large distance because of the confining dimerizing field, but the dimerization between the weak and strong bonds connecting the empty triangles is relatively weak [24]. This implies that the confining potential is weak and the spin can delocalize over several unit cells.

With a finite concentration of randomly placed impurities, a macroscopically large number of ''free'' spins are created. When two of the aforementioned delocalized spins meet, they bind into a singlet [15]. The mobile spins can also wander into the pinwheel regions and form singlets with spins there. The strength of the pairing depends on the ability of the spins to find overlapping regions and thus decreases rapidly with separation of impurities. In a thermodynamic system of randomly placed impurities, most of the spins would be paired into singlets at T near zero. Only very rare regions with isolated impurities will have a free spin. This implies a zero spin gap for the system. At infinitesimally small impurity concentration there would be a $1/T$ susceptibility. It will be shown elsewhere [29] that assuming these ''free'' spins form a random singlet phase [30] with a renormalized power-law distribution of exchange constants, recently reported [31] H/T and ω/T scaling, together with earlier reported sublinear ($T^{1-\alpha}$) zero-field specific heat [18] can be reproduced.

We should note here that the full low-energy magnetic response will depend on the Dzyaloshinski-Moria (DM) interactions [32–34], which are not considered here. For example, the NMR spectra was investigated by Rousochatzakis *et al.* and its low temperature behavior was shown to require nonzero DM interactions in addition to impurities [35,36].

A typical glassy system has many potential two-level system type local excitations created by the impurities

[37]. For the KLHM, at very dilute impurities the pinwheels naturally serve as two-level systems. The random environment produces a weak random exchange giving rise to a small splitting, between its two ground states. In a higher concentration range, as relevant for the herbertsmithite materials, very few intact pinwheels are likely to remain. Instead, at larger impurity concentration, the two-level systems would be a network of corner sharing triangles, where the valence bonds can switch between alternate dimer configurations, with very little energy cost. These would resemble delta chains or Husimi trees [15,27,28], a pinwheel being just one special case. If we assume one two-level system per 36 sites and further assume that their splitting can range up to 10% of J (approximately 20 K) that would lead to a density of states of $1/720$ K per copper atom. This will give rise to a linear term in specific heat of approximately 20 $\mathrm{mJ/mol\,K^2}$ per copper atom. This is in the right ballpark of the experimental observations on the herbertsmithite materials when the low-energy spin degrees of freedom are quenched by a magnetic field [38].

The VBG phase also provides a natural explanation for the observed neutron spectra in the materials. One of the key observations of recent powder diffraction neutron measurement by de Vries *et al.* [39] is that the spectra is spread over a large frequency range and its angle averaged behavior is very close to that of isolated dimers. This is exactly what one expects for pinwheels or Delta chains, as we show below.

Because the ground state of a pinwheel is fully dimerized, the equal-time correlation function is strictly nearest neighbor only, that is, it is that of isolated dimers. However, the triplet excitations in these systems decompose into a kink-antikink pair as shown in Fig. 3. Hence the dynamic correlations are not strictly nearest neighbor only and, unlike a single dimer, they extend over a wide energy range. It is known [27,28] that the kinks are gapless and antikink energy can be approximated by

$$\epsilon(k) = 5/4 - \cos k,$$

so that the kink-antikink pair energy ranges approximately from about $1/4$ to $9/4$. Indeed, we have found by exact diagonalization that 98% of the spectral weight of the pinwheel is spread over the energy 0.26 to 2.50. Also, as shown in Fig. 4, the angle-integrated spectra at every energy has q dependence that is very close to that of isolated dimers. This shows that Delta chains have spectra that spread over a wide energy range, yet have angle-integrated spectral weight essentially that of isolated dimers, in agreement with experiments [39].

The presence of dilution also provides an explanation for the absence of large peaks at low energy in the Raman spectra [40] that were found in exact diagonalization studies of finite clusters [13]. The pinning of dimers destroys low-energy singlets, by making long-range rearrangement of dimers energetically costly. Going back to a pinwheel, light scattering should produce triplet excitations with antiparallel orientation on neighboring dimers. Two of the four spins can combine into a singlet to leave a kink-antikink pair or two antikinks one of which is trapped in a triangle with a valence bond. In either case, this leads to energy spread over the same range as the triplets, i.e., roughly up to $2.5J$. Indeed, the exact diagonalization results of Laeuchli and Lhuillier [13] show that once the low-energy peaks are removed from the spectra the frequency dependence of the neutron and Raman scattering profiles are very similar. It supports the idea of two weakly interacting spinons which can form singlets or triplets [15]. The minimum excitation energy is reduced when one does not have perfect pinwheel structures and the absence of spin gap means that Raman scattering extends down to zero energy. These features are, indeed, consistent with the experiments [40].

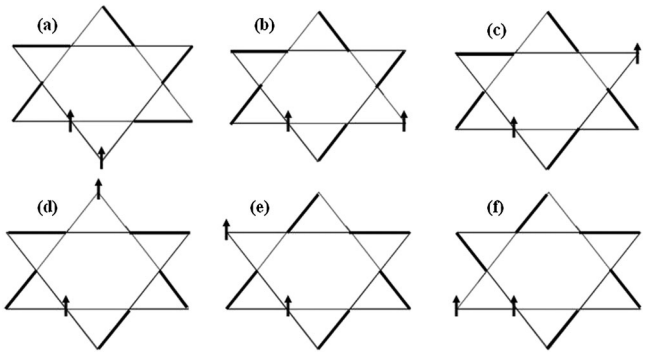

FIG. 3. Kink-antikink or 2-spinon states for the pinwheel. A triplet excitation is created by breaking a singlet bond in the ground state. The kink spinon lies on the inner hexagon, while the more mobile antikink spinon can move on the outside vertices of the pinwheel through states (a) through (f) shown in the figure.

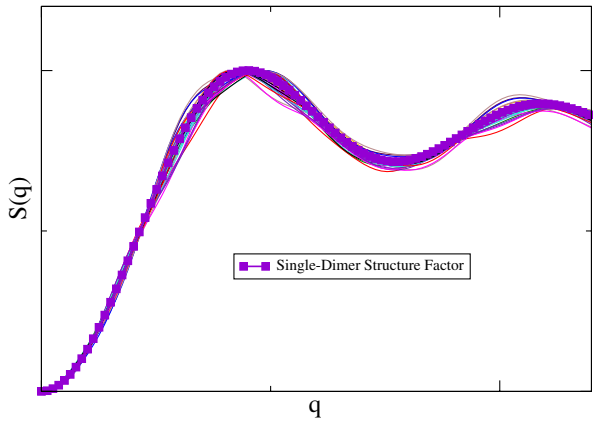

FIG. 4 (color online). Exact diagonalization results for angle averaged dynamic structure factor for a pinwheel, at different frequencies, scaled to have the same maximum, compared with results of a single dimer.

The VBG phase with random singlets should show a crossover to the high temperature paramagnetic phase, with a temperature scale of about $0.1J$. But some strong bonds may remain frozen up to $T \approx J$ giving one a broad crossover region. Indeed neutron measurements suggest that dimer correlations persist beyond $T = J/2$. Also, Raman spectra show development of a quasielastic peak at low energies as the temperature is raised from 5 to 295 K [40]. This is suggestive of a gradual melting of the VBG as the frozen dimers are freed up, giving rise to low-energy overdamped singlet excitations. Details of the Raman spectra, including dependence on polarization [41], deserve further theoretical attention.

In conclusion, we have developed a picture for the valence bond glass phase when the kagome lattice Heisenberg model is randomly site diluted. We have argued that this phase has no spin gap, and supports local two-level system excitations as well as singlet and triplet excitations that decompose into kink-antikink pairs. Free spins are created around impurities that can then form a random singlet phase. This picture provides a comprehensive framework for understanding thermodynamic, neutron and Raman measurements in the herbertsmithite materials. Experimental observation of real space structures shown in Figs. 2 and 3 would provide further confirmation for this theory. The availability of samples with significantly reduced concentration of impurities would help provide clearer signatures for the valence bond crystal phase in the kagome lattice Heisenberg model.

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