Valence Bond Glass Phase in the Diluted Kagome Antiferromagnets

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We present a theory for site dilution in the Valence Bond Crystal Phase of the Kagome Lattice Heisenberg Model. The presence of an empty site leads to strong singlet bonds across the impurity. It also creates a free spin, which delocalizes inside the unit cell. Finite concentration of quenched impurities leads to a Valence Bond Glass phase. This phase has short-range Valence Bond order, 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 delocalized over a few lattice constants. It provides a framework for a comprehensive understanding of thermodynamic, neutron, and Raman measurements in the Herbertsmithite material ZnCu$_3$(OH)$_6$Cl$_2$, including recently reported $H/T$ and $\omega/T$ 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 twenty five 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)$_6$Cl$_2$, containing structurally perfect Kagome planes,[17–23] have raised 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 non-magnetic 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 in context of Dimer series expansions.\[10, 24\] We find that dilution leads to a Valence Bond Glass phase, which has short-range Valence Bond order, no spin-gap, large spin-susceptibility, linear specific heat due to two-level systems as well as singlet and triplet excitations that decompose into kink-antikink pairs with energies spread up to approximately $2.5J$. Unlike the VBC phase, which is stabilized by higher order quantum fluctuations, with energy scales less than 0.01 J per site (energy scales that differentiate different VBC phases are only 0.001 J per site), the VBG phase is stabilized by second order perturbation theory with an energy scale of order 0.1 J per site. This VBG phase provides a novel framework for a comprehensive understanding of the Herbertsmithite materials.

A single impurity can be accommodated in the Valence Bond Crystal phase in several inequivalent positions of the 36-site unit cell with nearly equal energy. The addition of such an impurity leads to strong singlet bonds across from it, in agreement with earlier studies of Dom-mange et al.\[25\] However, contrary to the work of Dom-mange 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 six percent, which would imply on average 2 randomly placed impurities per unit cell. Combined with the singlet bonds across from the impurities, it also means 30 percent of spins are inactive. At this high impurity concentration no semblance of long range VBC order would remain. Instead, one obtains a randomly pinned Valence Bond Glass phase 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.

The dimer expansions provide a hierarchy of energy
The addition of holes lifts the degeneracy of the dimer configurations already in second order perturbation theory. For a finite concentration of holes, not having a strong bond in a triangle with a missing spin raises the energy of the dimer configuration by about 0.05 if one bond opposite the missing spin is absent and 0.1 if both bonds opposite the missing spin are absent. Given this relatively large energy scale, it is fair to assume that these impurities freeze all quantum fluctuations except those involving (i) a pair of neighboring dimers (second order perturbation), (ii) resonating hexagons and (iii) pinwheels and analogous structures. Because the pinwheels have a doubly degenerate dimer configuration, they play a vital role in the VBG phase at low impurity concentration.

We first ask the question, how would the crystal respond to a single impurity? 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 the dark bonds in Fig. 1. They are the same bonds that lead to heavy (non-mobile) triplets in the VBC phase. 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 structures are all bounded from outside by dimerized triangles, which are in their ground state. Hence, it suffices to diagonalize the pinwheels only, plus the extra triangle in case (iii).

The ground state bond energies and spin configurations for the three cases are shown in Fig. 2. Fig. 2(a) through (c) show the pattern of dimerization around the impurity. Fig. 2(d) through (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 across 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. 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 across 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. [24, 25].

In contrast to the dark bonds, if the impurity is placed on the grey bonds, the resulting free spin can delocalize through the network of grey bonds. It cannot delocalize too far because of the confining dimerizing field, but the dimerization between the weak and strong bonds connecting the empty triangles is relatively weak. 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, there will be lots of free spins created. When two of these spins meet they would bind into a singlet. The mobile spins can also wander into the pinwheel regions and form singlets with spins there. The strength of the pairing will depend on the ability of the spins to be in overlapping regions and thus would decrease 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 with a strength proportional to the impurity concentration. But, at any significant impurity concentration this strength would be reduced. We show in appendix that the assumption that these spins go into a random singlet phase with a power-law distribution of exchange constants, allows us to reproduce the H/T and ω/T scaling reported recently.

The glassy system has many potential two-level system type local excitations created by the impurities. For very dilute impurities, the pin-wheels would serve as two level systems. The random environment would produce a weak random exchange field on the pinwheels giving rise to a small splitting, between its two ground states. In a higher concentration range, as relevant for the Herbutsmithite 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, 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 upto 10 percent of J (approximately 20 K) that would lead to a density of states of 1/(720K) per copper atom. This will give rise to a linear term in specific heat of approximately 20mJ/molK² per copper atom. This is in the right ballpark of the experimental observations on the Herbutsmithite materials when the spin degrees of freedom associated with free spins in the zinc planes, are suppressed by a magnetic field.

The very low energy magnetic response will depend on the DM interactions which are not considered here. For example, the NMR spectra has already been addressed by Rousochatzakis et al in context of frozen dimers and it requires non-zero DM interactions in addition to impurities. 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 of the materials by deVries et al 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 that the kinks are gapless and anti-kink energy can be approximated by

$$\epsilon(k) = \frac{5}{4} - \cos k,$$

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 percent 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 spread over a wide energy range yet have angle integrated spectral weight essentially that of isolated dimers, in agreement with experiments.

The presence of dilution also provides a simple explanation for the absence of large peaks at low energy in the Raman spectra that were found in exact diagonalization studies of finite clusters. The pinning of dimers destroys the low energy singlets, by making any long-range rearrangement of dimers energetically costly. Light scattering should produce two antiparallel triplet excitations on neighboring dimers. Two of these spins can combine into a singlet to leave a kink-antikink pair or two anti-kinks 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 2.5\(J\). Indeed, the exact diagonalization results of Laechli 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. Hao and Tchernyshyov have shown\[15\] that these excitations have fermionic statistics. The minimum excitation energy is reduced when one does not have perfect pin-wheel structures. These features are, indeed, consistent with the experiments.\[37\]

Since the disordered glass phase breaks no symmetry, there should be no phase transition in the system and only a gradual crossover from the high temperature paramagnet to the VBG phase. The temperature scale for the freezing is set by 0.1\(J\), but some strong bonds may freeze at temperatures approaching \(J\) giving one a broad crossover region. Indeed the neutron scattering measurements suggest that Dimer correlations persist beyond \(T = J/2\). On the other hand the Raman spectra show a clear development of a quasi-elastic peak at low energies as the temperature is raised from 5\(K\) to 295\(K\).\[37\] This is suggestive of a gradual melting of the Valence Bond Glass into a classical Valence Bond Liquid as the frozen dimers are freed up, giving rise to lots of low energy overdamped singlet excitations. Details of the Raman spectra, including dependence on polarization\[38\] 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 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 that delocalize over a local network of corner sharing triangles. This phase provides a consistent picture of thermodynamic, neutron and Raman measurements in the Herbersmithite materials. Significantly reduced concentration of impurities can help provide clearer signatures for the Valence Bond Crystal phase in the Kagome Lattice Heisenberg Model.

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**APPENDIX**

In this appendix, we address the recently reported Neutron scattering data on the Herbersmithite materials by Helton et al.\[27\] We make the assumptions that the large number of free spins created by the impurities go into a random singlet phase, where the spins are coupled by a renormalized distribution of exchange constants, which has a power-law behavior \(P(J) = CJ^{-\alpha}\). With this the magnetization of the system as a function of field is given by

\[
M(H,T)/T^{1-\alpha} = \int dxx^{-\alpha}f_1(y,x).
\]

with \(y = gb/T\) with \(h = \mu_B H\), and

\[
f_1(y,x) = \frac{2 \sinh y}{e^x + 1 + 2 \cosh y}
\]

The susceptibility in a field is given by

\[
\chi(H,T)T^{\alpha} = \int dxx^{-\alpha}f_2(y,x)
\]

with

\[
f_2(y,x) = \frac{2 \cosh y(e^x + 1) + 4}{(e^x + 1 + 2 \cosh y)^2}
\]

Also, the imaginary part of the dynamic susceptibility for \(\omega > 0\) is given by

\[
\chi''(\omega,T)T^{\alpha} = \left(\frac{\omega}{\omega'}\right)\frac{e^{\omega/T} - 1}{e^{\omega/T} + 3}
\]

Motivated by the experimental observation, we will take \(\alpha = 0.66\). We also take \(g = 2.2\). With these the plots for \(M(H,T)\), \(\chi(H,T)\) and \(\chi''\) are shown in Figures. They appear remarkably similar to the experiments.
With this assumption, theses spins will contribute $T^{1-\alpha}$ to the specific heat. That combined with a linear specific heat coming from the singlet degrees of freedom, can explain the observation of an apparent power-law specific heat with an exponent in the range 0.5 to 0.66.\cite{18}

Experiments show that these power law have a wide range of validity in the Herbertsmithite materials.

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