Neutron spectra of Herbertsmithite Materials: Observation of a Valence Bond Liquid phase?

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We argue that neutron spectra in a short-range ordered Valence Bond state is dominated by two-spinon states localized in small spatial regions such as a pinwheel. These excitations lead to angle averaged dynamic structure factor that is spread over a wide frequency range up to about $2.5J$, whereas its wavevector dependence at all frequencies remains very close to that of isolated dimers. These results are in excellent agreement with recent Neutron scattering data in the Herbertsmithite materials ZnCu$_3$(OH)$_6$Cl$_2$.

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Recent experimental studies[1–6] of the Herbertsmithite material ZnCu$_3$(OH)$_6$Cl$_2$ with structurally perfect Kagome planes has brought renewed interest in the study of Quantum Spin-Liquid phases in the Kagome Lattice Heisenberg Model.[7–12] The issues of Quantum Spin-Liquid versus Valence Bond Crystal Order,[13] of a possible gap in the spin excitation spectra and of deconfinement of fractional spin excitations continue to be subjects of intense theoretical debate.[14–22] The experimental studies provide a complimentary perspective to this long standing problem.

In a recent letter de Vries et al presented neutron scattering data on these materials over a range of momentum and frequency transfers.[23] They discuss their data primarily in the context of Algebraic Spin-Liquid and other theories.[11, 12] Here, we would like to argue that the data is much better understood in terms of a Valence Bond phase[13, 16] with well developed short-ranged Valence Bond order but no long-range Valence Bond Crystal order. Such a finite temperature phase, lacking long-range quantum coherence, may appropriately be called a classical Valence Bond Liquid.

The powder-diffraction neutron data of de Vries et al covers a temperature range from 2K to 120 K, an energy transfer of up to 30 meV and the full range of momentum transfer values. Their key findings can be summarized as follows: After allowance is made for phonons as well as for some impurity spins, the magnetic behavior intrinsic to the system, is rather well described by an angle averaged q-dependent form-factor which is essentially identical to that of a single spin-dimer. However, unlike a single dimer, where such a spectrum would be strongly peaked at the singlet-triplet energy gap ($J$ for an isolated dimer), the spectral weight is spread nearly uniformly over a wide range of energies extending at least down to 4meV and up beyond 30 meV. Furthermore, this behavior is evident at 2K but persists also at 120 K. The frequency dependence makes the behavior clearly inconsistent with that of isolated dimers and the temperature dependence makes it inconsistent with a Valence Bond Crystal order (and any other quantum ground state with an ordering scale much smaller than 100K as expected in the model).

We first note that the exchange constant for the material has been estimated[2, 24, 25] to be in the range 170K-190K, which translates to about 15meV. There is increasing theoretical support for a Valence Bond Crystal (VBC) ground state of the Kagome-Lattice Heisenberg Model with a 36-site unit cell.[16, 20] One of the distinctive features of the VBC state is a pin-wheel (See Fig. 1) in each unit cell, a defect free structure of Valence-Bond containing triangles, where the bonds remain almost completely dimerized. An isolated pinwheel is an example of a Delta chain,[21, 26, 27] a system of corner sharing triangles, where the Hamiltonian is minimized by

![FIG. 1: Proposed Valence Bond Phase of the Kagome Lattice Heisenberg Model consists of a Honeycomb Lattice of resonating hexagons (H), where six hexagons surround a pinwheel (P). The pinwheels are isolated from empty triangles leading to substantially reduced quantum fluctuations on their dimer bonds. Triplets on dimers represented by black thick lines are heavy nearly immobile particles, whereas triplets on grey thick lines represent particles mobile throughout the lattice.](image-url)
FIG. 2: 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. When the two spinons are together as in Fig. (a), the kink spin can also move by going through higher energy intermediate states.

In the VBC state, there is significant quantum fluctuations. In particular, the dimerization inside the resonating hexagons is strongly reduced. But, the pinwheel region is geometrically protected against quantum fluctuations and hence remains essentially fully dimerized.

Different Valence Bond phases have energy difference of only 0.001 J per site. Thus one expects any phase transition to such a state to occur at a very low temperature. However, short-range Valence Bond order is set by $J$ and can develop at significantly higher temperatures. Once this short-range order is a few lattice constants, pin-wheel like structures should begin to form locally. Because they have extremely low local energies, they should be stable up to higher temperatures.

The triplet excitations of the pinwheel are kink-antikink pairs. In an infinite Delta chain, the kinks are immobile, whereas the antikink can hop from one triangle to another. The kink has zero excitation energy, whereas the energy of the antikink can be approximated by

$$\epsilon(k) = 5/4 - \cos k.$$  \hspace{1cm} (1)

Note that this means that excitations extend over the energy range $J/4 < \epsilon < 9J/4$. For the infinite system more detailed analytical and numerical calculations show that the lowest energy antikink is roughly at 0.219$J$, whereas the upper energy may extend up to as much as 3$J$. For the finite system, spin excitation from the ground state creates a pair of parallel spins on one of the singlet bonds of the ground state. While the kink antikink description is roughly valid, because both the kink and antikink remain in each other’s vicinity, both free spins or spinons become mobile. Fig. 2, shows the configurations that correspond to the mobile antikink. On the other hand the kink can also move by going through higher energy intermediate configuration, when the two spins are next to each other. In the $S^z = 1$ sector, assuming two free spins and the rest of the system in the ground state leads to 66 states, of which 36 states are of the kink-antikink type, where one spin is in the inner hexagon, whereas the other spin is on the outside vertices of the pinwheel. One expects the spectral weight to be primarily spread over these states, giving rise to spectral weight spread roughly over the energy range $J/4 < \epsilon < 9J/4$. 

FIG. 3: Angle averaged dynamic structure factor versus frequency of the Pinwheel state at $T = 0$ with small broadening.

FIG. 4: Angle averaged dynamic structure factor versus frequency of the Pinwheel state at $T = 0$ with larger broadening.
that the lowest triplet state has an excitation energy of of the 12-site Heisenberg model on a pinwheel. One finds wavenumber compared with results of a single dimer.  

This can be easily confirmed by exact diagonalization of the 12-site Heisenberg model on a pinwheel. One finds that the lowest triplet state has an excitation energy of 0.260 J. The spectral weight is spread over a large number of states. The highest spectral weight of any one single state is only about 5 percent. The states with the highest 36 spectral weights are spread over the energy range 0.260 J < $\epsilon$ < 2.039 J and they contribute above 80 percent to the spectral weight. If we look at total spectral weight up to some energy, roughly 95.5 percent of the weight extends up to an energy of 2.25 J, 97.7 percent of the weight extends up to an energy of 2.5 J and roughly 99.7 percent of the weight extends up to an energy of 3 J. This strongly confirms that the dominant spectral contributions come from the kink-antikink states.

In the Valence Bond Crystal state, these triplets can ultimately decay to still lower lying light triplets, \cite{29} though those decay times are likely to be very long, because the pinwheels are surrounded by dimerized triangles and have no empty triangles in their immediate vicinity, which strongly reduces quantum fluctuations. In the liquid phase, these excitations should have a shorter finite lifetime, which one could represent by a Lorentzian broadening. The frequency dependence of the angle averaged dynamic structure factor, for several q-values, at a small Lorentzian broadening (0.01 J) is shown in Fig 3, where as at a larger broadening (0.10 J) it is shown in Fig. 4. The latter may be more representative of the liquid state. One finds that at higher broadening one has a spectral weight that is spread roughly continuously up to an energy of about 3J.

For any pair of spins at a distance $r$, the angle averaged value of $\exp(i\mathbf{q} \cdot \mathbf{r})$ is given by $\sin (qr)/qr$. This can be used to calculate the angle averaged dynamic structure factor for any given $q$. For all frequencies, the structure factor as a function of wavenumber shows dependence, which is very close to that of an isolated dimer (See Fig. 5). In an isolated pinwheel, the equal-time correlation function is strictly that of a dimer, but excitations are extended over the full pin-wheel. Thus the energy integrated structure factor is strictly that of an isolated dimer, but not the spectral weight at a given energy. However, what the calculations show is that while the spectral weight is spread out over a wide range of frequencies, the q-dependence is always near that of an isolated dimer. Since delta chains are likely to be ubiquitous in the short-range Valence Bond ordered phase of the Kagome Lattice Heisenberg model, \cite{21} this spectral feature may persist up to energy comparable to J, that is, as long as the system has short range Valence Bond order.

This picture implies that the equal-time spin-spin correlations in the system are essentially only nearest neighbor. However, the arrangement of dimerized triangles makes any triplet excitation break into a kink-antikink pairs. These lead to spectral weight spread over a wide frequency range.

In fact, the spectra obtained by exact-diagonalization of 24, 30 and 36-site clusters by Lauchli and Lhuillier \cite{19} show very similar frequency dependence, where much of the spectral weight is nearly uniformly spread between $J/4$ to about 2.5J. The finite size system has only short-range Valence bond order. This is further evidence that almost all states with short range Valence Bond order have these features.

One also knows that the Herbertsmithite materials have a small Dzyaloshinski-Moria anisotropy. \cite{30,32} These anisotropies would strongly influence the low energy spectra and the nature of long-range order without significantly altering the high energy spectral properties. In the experiments, the reduction in spectral weight at low temperatures below an energy of 4 meV may well be related to the DM anisotropy which would cause the low energy spectral weight to move to even lower energies.

Furthermore, the true signature of long-range VBC order, would be the observation of low energy light triplets, which live on the perfect hexagon and bridging dimers. \cite{17,29} In the VBC phase these provide an extended network for the triplets to move around, whereas the pinwheels form isolated pristine regions which are nearly protected from quantum fluctuations, and have only localized triplets. The honeycomb VBC state has 50 percent of the spectral weight in the non-fluctuating dimer-like heavy excitations and the rest of the 50 percent of the spectral weight in the light mobile triplets, which with long-range VBC order have an energy gap of order $J/20$. \cite{14,15}

In conclusion, we have argued that the observation of dimer-like q-dependence combined with a spectral weight
spread over a wide frequency range and remaining nearly
temperature independent over a wide range of temper-

ture is strongly suggestive of a Valence Bond Liquid
phase, with short-range Valence Bond Order exceeding a
couple of lattice constants. These excitations can be
regarded as a kink-antikink pair or two spinons, which are
confined in a very small spatial region. They extend up
to fairly high temperatures of order $J$, where such excita-
tions are necessarily broadened by the underlying classi-
cal liquid environment. Whether at low enough tempera-
tures, the development of long-range quantum coherence
leads to truly delocalized spinons as in algebraic quan-
tum spin-liquid phases or to the development of much
sharper localized and extended triplet excitations as in a
Valence Bond Crystal remains to be seen.

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