Randomness-induced quantum spin liquid behavior in the $s=1/2$ bond-random Heisenberg antiferromagnet on the pyrochlore lattice

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We investigate the zero- and finite-temperature properties of the bond-random $s=1/2$ Heisenberg antiferromagnet on the pyrochlore lattice by the exact diagonalization and the Hams–de Raedt methods. We find that the randomness induces the gapless quantum spin liquid (QSL) state, the random-singlet state. Implications to recent experiments on the mixed-anion pyrochlore-lattice antiferromagnet Lu$_2$Mo$_2$O$_7$$_2$ exhibiting gapless QSL behaviors are discussed.

The quantum spin liquid (QSL) state has attracted much attention as an exotic state of matter, where any magnetic long-range order (LRO) or a spontaneous symmetry breaking is absent down to low temperatures due to strong quantum fluctuations. In the quest for the QSL state, geometrical frustration has been examined quite extensively as a key ingredient. In the last decade, a variety of QSL candidates were experimentally reported in geometrically frustrated quantum magnets in two dimensions (2D), e.g., $s=1/2$ organic salts on the triangular lattice-like $\kappa$-(ET)$_2$Cu$_2$(CN)$_3$ $^{1–5}$, EtMe$_2$Sb[Pd(dmit)$_2$]$_2$ $^{6, 7}$, $\kappa$-H$_3$(Cat-EDT-TTF)$_2$ $^{8, 9}$, and $s=1/2$ inorganic kagome antiferromagnet herbertsmithite CuZn$_3$[OH]$_6$Cl$_2$ $^{10, 11}$. Most of these QSL magnets are $s=1/2$ Heisenberg magnets exhibiting gapless (or nearly gapless) QSL behaviors with the $T$-linear low-temperature ($T$) specific heat. Gapless QSL behaviors have been observed not only for geometrically frustrated lattices, but also for geometrically unfrustrated lattices such as square and honeycomb lattices.

In the latter, frustration is borne by, e.g., the competition between the nearest- and next-nearest-neighbor interactions, $J_1$ and $J_2$. Examples might be a square-lattice magnet Sr$_2$Cu[Te$_{1–x}$W$_x$]O$_6$ $^{18–20}$ and a honeycomb-lattice magnet 6HB-Ba$_3$Ni$_2$O$_6$ $^{21, 22}$. In this way, there are now considerable number of experimental realizations of gapless QSL in 2D. The true physical origin of such gapless QSL behaviors, however, still remains controversial.

One promising scenario might be that the randomness or inhomogeneity, either of extrinsic or intrinsic origin, induces the gapless QSL-like state. $^{23–27}$ The present authors and collaborators have demonstrated that such a randomness-induced gapless QSL-like state, called the “random-singlet state”, is stabilized for various 2D frustrated $s=1/2$ Heisenberg models, including the triangular $^{23–27}$, kagome $^{24, 25}$, $J_1–J_2$ square $^{27}$ and $J_1–J_2$ honeycomb $^{26}$ magnets, as long as the randomness is moderately strong. The origin of such (effective) randomness could be of variety, e.g., the intrinsic ones like the dynamical freezing of the charge (dielectric) degrees of freedom in case of $\kappa$-ET and dmit salts and the slowing down of the proton motion in case of Cat salt, or the extrinsic ones like the possible Jahn-Teller distortion accompanied by the the random substitution of Zn$^{2+}$ by Cu$^{2+}$ in case of herbertsmithite and the random occupation of Te/W, in case of Sr$_2$Cu[Te$_{1–x}$W$_x$]O$_6$. The role of randomness on the possible QSL-like behavior was also studied recently by other groups for various 2D Heisenberg models $^{28–31}$.

The next question might be whether the QSL state is ever possible in 3D, whatever its physical origin. Generally, 3D magnets tend to be subject to less fluctuation and to stronger ordering tendency than in 2D even on frustrated lattices. In this connection, the pyrochlore lattice, known to be a highly frustrated 3D lattice, might provide a promising stage.

An intensively studied example might be Tb$_2$Ti$_2$O$_7$ $^{32, 33}$. Earlier muon studies indicated no spin ordering nor the spin freezing down to 70mK $^{32}$, and this material has widely been regarded as a quantum analog of the classical spin ice, i.e., quantum spin ice. Indeed, the so-called “pinch point”, a characteristic neutron-scattering signal of the “2-in, 2-out” or “divergence-free” spin-ice state, was observed at $T \lesssim 20$K, suggestive of the formation of the quantum spin-ice state $^{32}$. A possibility of the $U(1)$ QSL has been discussed $^{32}$. Meanwhile, it turns out that even a minute amount of off-stoichiometry induces a sharp specific-heat peak at $T_c \approx 400$mK signaling a thermodynamic phase transition $^{32}$. Furthermore, in samples both with and without a sharp specific-heat peak, “quasi-Bragg” peaks associated with the antiferromagnetic (AF) spin-ice order were observed by neutron scattering at $T \lesssim 275$mK $^{34}$, accompanied by the onset of the glass-like spin freezing $^{34, 35}$. Thus, the true situation for Tb$_2$Ti$_2$O$_7$ at low enough temperature still remains elusive. In any case, Tb$_2$Ti$_2$O$_7$ possesses a modest amount of Ising-like (111) anisotropy so that the underlying physics would be that of the anisotropic spin ice.

One may then ask what is the situation in more isotropic Heisenberg-like pyrochlore magnets. Recently, an interesting Heisenberg-like pyrochlore magnet exhibiting the QSL behavior down to the low temperature of
0.5K was reported in the mixed-anion antiferromagnet Lu$_2$Mo$_2$O$_5$N$_2$ [37]. In this oxynitride, magnetism is borne by $s = 1/2$ spins of Mo$^{5+}$ and $d^1$, in contrast to its precursor oxide Lu$_2$Mo$_2$O$_7$ where the magnetism is borne by $s = 1$ spins of Mo$^{4+}$ and $d^2$. The oxynitride Lu$_2$Mo$_2$O$_5$N$_2$ was observed to exhibit gapless QSL behaviors characterized by the $T$-linear specific heat and the broad dynamical structure factor, in contrast to the oxide Lu$_2$Mo$_2$O$_7$ which exhibits a spin-glass (SG) freezing and the low-$T$ specific heat proportional to $T^2$. An interesting observation here is that the oxynitride exhibiting the gapless QSL behavior inevitably contains a significant amount of quenched disorder derived from the random occupation of O$^2−$ and N$^3−$ anions. Hence, somewhat counter-intuitively, the introduction of randomness into the nominally disorder-free SG state apparently induces the QSL state [37]. Lu$_2$Mo$_2$O$_5$N$_2$ was recently investigated theoretically by means of the density functional theory and the pseudofermion functional renormalization group method, while the analysis was basically that of the homogeneous system and the effect of O/N randomness was not considered explicitly [38].

Under such circumstances, we wish to investigate in the present Letter the role of randomness in the quantum Heisenberg antiferromagnet on the 3D pyrochlore lattice. We consider the bond-random $s = 1/2$ isotropic Heisenberg model on the pyrochlore lattice with the AF nearest-neighbor (NN) interaction. The Hamiltonian is given by

$$ \mathcal{H} = J \sum_{\langle i, j \rangle} j_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1) $$

where $\mathbf{S}_i = (\mathbf{S}^x_i, \mathbf{S}^y_i, \mathbf{S}^z_i)$ is an $s = 1/2$ spin operator at the $i$-th site, and the sum $\langle i, j \rangle$ is taken over all NN pairs on the lattice, while $j_{ij} \geq 0$ is the random variable obeying the bond-independent uniform distribution between $[1 - \Delta, 1 + \Delta]$ with $0 \leq \Delta \leq 1$. We consider the NN interaction only just for simplicity, and put $J = 1$ as the energy unit. The parameter $\Delta$ represents the extent of the randomness: $\Delta = 0$ corresponds to the regular case and $\Delta = 1$ to the maximally random case when the interaction is to be kept AF.

The corresponding regular model with $\Delta = 0$ has been studied extensively by various numerical methods. There is a consensus that the system remains disordered even at $T = 0$ without any spin LRO, while the nature of the nonmagnetic ground state still remains unclear [39]. Whether the ground state is gapped or gapless also remains controversial, though the bulk of the numerical calculations seem to suggest a nonzero spin gap. By contrast, there has been no systematic numerical study of the corresponding random model with $\Delta > 0$.

We then study the ground-state properties of the model by means of the exact diagonalization (ED) Lanczos method. We treat finite-size clusters with the total number of spins $N$ up to $N \leq 36$ ($N$ is taken to be a multiple of 4 with $8 \leq N \leq 36$), periodic boundary conditions applied in all directions. The clusters of $N = 16$ and $N = 32$ possess the cubic symmetry of the bulk pyrochlore lattice. The numbers of independent bond realizations $N_s$ used in the sample average are for the order parameter, the spin gap, and the static spin structure factor $N_s = 100$ and 5 for $N = 8-32$ and 36, respectively, whereas for the dynamical spin structure factor $N_s = 100$ and 50 for $N = 16$ and 32, respectively. Error bars are estimated from sample-to-sample fluctuations. The finite-temperature properties are computed by the Hams-de Raedt method [40]. The computation is performed for the size $N = 32$, where the averaging is made over 10 initial vectors and 10 independent bond realizations. Error bars of physical quantities are estimated from the scattering over both samples and initial states by using the bootstrap method.

We first investigate the existence or nonexistence of the magnetic LRO by computing the spin freezing parameter $\bar{q}$ defined by

$$ \bar{q}^2 = \frac{1}{N^2} \sum_{i,j} \langle (\mathbf{S}_i \cdot \mathbf{S}_j)^2 \rangle_j, \quad (2) $$

where $\langle \cdots \rangle_j$ denotes the average over the disorder or samples. This quantity can detect the static spin order of any type, even including the random one like the SG order. The computed $\bar{q}$ is plotted versus $N^{-1/3}$ in Fig. (a) for various values of randomness $\Delta$, in which the spin-wave form $\bar{q}_\infty \approx \bar{q}_\infty + cN^{-1/3}$ is borne in mind. As can be seen from the figure, $\bar{q}$ is extrapolated to zero , indicating the absence of spin LRO for any $\Delta$, even including the SG one.

In Fig. (b), we show the size dependence of the spin-gap energy $\Delta E$. For smaller $\Delta < \Delta_c \approx 0.6$, $\Delta E$ tends to be extrapolated to a nonzero value suggestive of a gapped behavior, whereas, for larger $\Delta > \Delta_c$, it is extrapolated to zero within the error bar suggestive of a gapped behavior. The changeover observed between the gapless and gapped behaviors suggests the occurrence of a randomness-induced phase transition between the two distinct types of nonmagnetic states. The gapless nonmagnetic phase stabilized at $\Delta > \Delta_c$ is likely to be the random-singlet state.

Such a transition can also be detected via the ratio $R$ of the number of samples with triplet ground states. All the samples we have studied possess either singlet or triplet ground states, and $R$ represents the fraction of the triplet-ground-state samples. As can be seen from Fig. (c), $R$ vanishes for $\Delta < \Delta_c \sim 0.6$, while it grows taking nonzero values beyond $\Delta_c$. This observation is consistent with a gapped-gapless transition observed in Fig. (b), which strengthens our conclusion of a phase transition occurring between the randomness-irrelevant gapped QSL state and the randomness-relevant gapless QSL state.
for various values of $\Delta$ plotted versus $\frac{1}{N}$ are linear fits of all the data, while the dashed lines are linear fits of the data for the cubic-symmetric clusters, $N = 16$ and $32$. Error bars are represented by the width of the data curves.

FIG. 1. (Color online) (a) The spin freezing parameter $\bar{q}$ plotted versus $1/N^{1/3}$ for various values of $\Delta$. Lines are quadratic fits of the data for $N \geq 16$. (b) The mean spin-gap energy $\Delta E$ for various values of $\Delta$ plotted versus $1/N$. The solid lines are linear fits of all the data, while the dashed lines are linear fits of the data for the cubic symmetric clusters, $N = 16$ and $32$. (c) The ratio of the samples with triplet ground states plotted versus $\Delta$.

In order to probe the properties of magnetic excitations, we also compute the dynamical structure factor $S_q(\omega)$ given by [25, 41]

$$S_q(\omega) = -\lim_{\eta \to 0} \frac{1}{\pi} \text{Im} \left( \frac{1}{\omega + E_0 + i\eta - \mathcal{H}^q} \right),$$

where $E_0$ is the ground-state energy, and $\eta$ is a phenomenological damping factor taking a sufficiently small positive value. We employ the continued fraction method to compute $S_q(\omega)$ [41], putting $\eta = 0.02$. The $\omega$-dependence of the computed $S_q(\omega)$ in the random-singlet state averaged over the $q$-points $(2,0,0)$, $(0,2,0)$ and $(0,0,2)$, given in units of $2\pi/a$ where $a$ is the linear size of the cubic unit cell, is shown in Fig. 2 at the maximal randomness of $\Delta = 1$, in comparison with the corresponding data for the regular model of $\Delta = 0$. (The information of the static spin structure factor $S(\mathbf{q})$ is given in Fig. S1 of Supplemental Material, which has very broad features extended over the $q$-space with relatively high intensities at $(0,0,2)$, etc [42].) As can be seen from Fig. 2, the computed $S_q(\omega)$ exhibits broad features in $\omega$ without any clear peak, accompanied by a long tail extending to larger $\omega$. In fact, such a feature is also common with the random-singlet states in 2D [24, 27]. In the small-$\omega$ region, $S_q(\omega)$ diminishes somewhat toward $\omega \to 0$, though it still stays gapless as can be confirmed from its system-size dependence, in sharp contrast to the gapped behavior observed for $\Delta = 0$.

We next move to the finite-$T$ properties. In Fig. 3 we show the temperature dependence of (a) the specific heat per spin, and of (b) the susceptibility per spin. As can be seen from Fig. 3(a), while the specific heat exhibits a double-peak structure for vanishing and weaker randomness $\Delta$, such a structure is gone in the random-singlet state at $\Delta \gtrsim 0.6$, exhibiting at lower temperatures a $T$-linear behavior, $C \sim \gamma T$, as generically observed in the random-singlet states in 2D [23, 24, 26, 27]. Such a change of behavior is also consistent with the occurrence of a phase transition within the nonmagnetic state at $\Delta = \Delta_c \approx 0.6$ argued above. Likewise, as can be seen from Fig. 3(b), in the region of the random-singlet state of $\Delta \geq \Delta_c$ the susceptibility tends to exhibit a gapless
from the experimental Curie-Weiss temperature, we get a γ-value deduced from our result, which deviates considerably from the experimental value $\gamma \sim 10 \text{ mJ/molK}^2$.

One sees from our present results that the properties of the randomness-induced QSL state, i.e., the random-field-induced Griffith Coulomb QSL, was recently proposed for anisotropic spin-ice magnets Ho$_2$Ti$_2$O$_7$ and Pr$_2$Zr$_2$O$_7$.[33, 34] While this state is also the randomness-induced QSL-like state, it derives from the highly anisotropic spin-ice state whose nature is different from the random-singlet state as studied here.

In summary, we studied both the $T = 0$ and $T > 0$ properties of the bond-random $s = 1/2$ NN Heisenberg model on the 3D pyrochlore lattice, and found that the randomness-induced gapless QSL state, the randomness-induced gapless QSL state, is stabilized as long as the system possesses a modest amount of randomness, frustration and quantum fluctuations, staying quite robust at the qualitative level against other details of the system.

We finally note that still another type of the randomness-induced QSL-like state, i.e., the randomness-induced QSL-like state, the random-singlet state is stabilized as long as the system possesses a modest amount of randomness, frustration and quantum fluctuations, staying quite robust at the qualitative level against other details of the system.

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**FIG. 3.** (Color online) The temperature dependence of (a) the specific heat per spin $C$, and of (b) the uniform susceptibility per spin $\chi$, for various values of $\Delta$.

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Supplemental Material: Randomness-induced quantum spin liquid behavior in the $s=1/2$ bond-random Heisenberg antiferromagnet on the pyrochlore lattice

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FIG. 1. (Color online) Upper row: Static spin structure factor $S_q$ for the regular case of $\Delta = 0$ in the (a) $(h, h, l)$ and (b) $(h, k, 0)$ plane. Lower row: Static spin structure factor $S_q$ for the maximally random case of $\Delta = 1$ in the (c) $(h, h, l)$ and (d) $(h, k, 0)$ plane.

STATIC SPIN STRUCTURE FACTOR

The computed ground-state spin structure factor $S_q$ is defined by

$$S_q = \frac{1}{N} \left[ \langle |S_q|^2 \rangle \right]_J$$

where $S_q = \sum_j S_j e^{i q \cdot r_j}$ is the Fourier transform of the spin operator, $r_j$ is the position vector at the site $j$, $q$ is the wave vector, $a$ is the nearest-neighbor distance of the pyrochlore lattice, while $\langle \cdots \rangle$ and $[\cdots]_J$ represent the ground-state expectation value (or the thermal average at finite temperatures) and the configurational average over $J_{ij}$ realizations.

In Fig. 1 the static spin structure factor for the regular case of $\Delta = 0$ is shown in the upper row, while the maximally random case of $\Delta = 1$ is in the lower row. The left side of Fig. 1 is the intensity plot in the $(h, h, l)$ plane, while the right side is in the $(h, k, 0)$ plane. As can be seen from these figures, there are no sharp peaks in all of Fig. 1 indicating the absence of the magnetic long-range order. The difference between the upper and the lower rows turns out to be minor so that the introduction of randomness has little effect on the static spin structure factor.