Antiferromagnetic spin systems on geometrically frustrated lattices show many unusual behaviors in magnetic and thermal properties. Their origin may essentially be attributed to the point that their classical ground state has a thermodynamic degeneracy with a potential instability towards various phases. Villain pointed out the possibility that thermal fluctuations drive symmetry breaking to the phase with the largest entropy. This mechanism of order by disorder is also expected for quantum fluctuations. In this paper, I study the ground state of the $S = \frac{1}{2}$ Heisenberg antiferromagnet on the pyrochlore lattice and examine the possibility of a new quantum phase.

The pyrochlore lattice is a three-dimensional (3D) network of corner-sharing tetrahedra (see Fig. 1), realized as a sublattice of many compounds including pyrochlores and spinels. Since all the elementary closed paths of spin exchange processes are triangular, antiferromagnets on the pyrochlore lattice are subject to strong frustration due to this lattice geometry. Another important character is the loose packing of the lattice, which is in contrast with the closed packing of the fcc lattice, another example of a geometrically frustrated lattice in 3D.

The combination of geometrical frustration and loose packing of the pyrochlore lattice leads to thermodynamically degenerate ground states of classical antiferromagnets on it, which was first pointed out by Anderson for the Ising model. Numerical simulations for the classical antiferromagnets indicate the absence of a finite-temperature magnetic phase transition, suggesting that thermal fluctuations cannot break symmetry.

Quantum fluctuations are another channel of lifting the classical ground-state degeneracy. This possibility for the pyrochlore lattice was first examined by Harris et al. They used a field-theoretical approach and degenerate perturbation for the spin-singlet ground-state multiplet and showed a sublattice ordering of dimerization. This was followed by Canals and Lacroix, who also started from decoupled tetrahedra and calculated the spin-spin correlation function at finite temperatures, using perturbation in the tetrahedron-tetrahedron interactions up to the second order. The result shows that the spin correlation length remains very short at the lowest temperature, and they concluded that the ground state is a quantum spin liquid with a finite spin gap, which is consistent with the claim of Harris et al. In the pyrochlore lattice, it is believed that there exist a thermodynamic number of singlet states below the spin gap. In this paper, I study the possibility of symmetry breaking in the singlet sector driven by quantum fluctuations. To this end, I follow a similar approach as those of the previous two works and start from a set of weakly interacting tetrahedra. I construct a full effective model for the spin-singlet ground-state multiplet within the third-order degenerate perturbation. I show that its mean-field solution is a partially dimerized state with a four-sublattice structure, and discuss spin and chirality correlations.

fig:fig1

Antiferromagnetically Quantum Spins on the Pyrochlore Lattice

Hirokazu TSUNETOSUGU

Institute of Materials Science, University of Tsukuba, Tsukuba 305-8573

(Received Dec. 25, 2000)

The ground state of the $S = \frac{1}{2}$ Heisenberg antiferromagnet on the pyrochlore lattice is theoretically investigated. Starting from the limit of isolated tetrahedra, I include interactions between the tetrahedra and obtain an effective model for the spin-singlet ground state multiplet by third-order perturbation. I determine its ground state using the mean-field approximation and found a dimerized state with a four-sublattice structure, which agrees with the proposal by Harris et al. I also discuss chirality correlations and spin correlations for this state.
where \((ij)\) are also the eigenfunctions of the chirality around site 1, \(\Gamma_{ij}\) since the singlets belong to the complex 1D representation \(S\), the triplets belong to the 3D representation \(T\). In Fig. 2(a) the energy of 70 states in \(S_{\text{tot}}^z = 0\) subspace, as a function of \(J'\). The degeneracy of the ground-state multiplet is 4-fold, and it is never lifted. Therefore, we have to go to the next step, and consider three neighboring type-A tetrahedra each pair of which is connected by one bond. There are two different cases. In the first case, two perturbative bonds are connected to the same site on each tetrahedra, whereas in the second case they are connected to two distinct sites. It is found that the second case lifts the degeneracy, but the first case does not. Figure 2(b) shows the energy of 924 states in the \(S_{\text{tot}}^z = 0\) subspace, for the second case. The ground-state multiplet with 8-fold degeneracy is now split into 4 levels with 1, 3, 1, and 3 fold degeneracies, respectively, in the ascending order of energy. At \(J' = J\), this energy split is 0.2468\(J\) between the lowest and highest levels, while the singlet-triplet gap is 0.5491\(J\).

These behaviors are described by degenerate perturbation in \(J'\). The second order only yields a constant self-energy, \(-\frac{3}{16}J'^2/J\) per spin, and we require third-order terms to mix different chirality configurations on a tetrahedron triple. To describe chirality for the tetrahedron positioned at \(R\), I introduce spin-\(\frac{1}{2}\) pseudospin operators, \(\frac{1}{2}\mathbf{\tau}_R\), such that their \(z\)-component is a diagonal matrix in the chirality space. Using these operators, the third-order effective model is written as

\[
H_{\text{eff}}^{(3)} = \sum (\mathbf{R}, \mathbf{R}'; \mathbf{R}'') [c - b(1 - 2e(\alpha_1) \cdot \mathbf{\tau}_R)] \times (1 - 2e(\alpha_2) \cdot \mathbf{\tau}_{R'}) (1 - 2e(\alpha_3) \cdot \mathbf{\tau}_{R''})],
\]

where \(c = \frac{2J^3J'^3}{J^2}, b = \frac{1}{8}J^3J'^2, e(\alpha) = (\cos \alpha, \sin \alpha, 0)\). Type-A tetrahedra constitute the fcc arrangement, and the summation is taken over all the tetrahedra in the second case explained above. Note that the total chirality is not conserved and also that the chirality pseudospins interact only in their transverse directions. The angle \(\alpha_j\) depends on the position of not only its cor-
responding tetrahedron but also the other two in each triple. Its value is shown in Fig. 3. The one-body terms in eq. (3) are canceled out after taking the summation.

We may understand the second and third-order effective models by examining their virtual processes. It is essential to recall that the chirality of each spin-singlet eigenfunction on a tetrahedron is identical around any of its four sites. On the other hand, a spin-triplet chiral eigenstate around one site is a mixture of all the three chiral eigenstates around another site. It is also important that perturbation of a single bond conserves the chirality of each tetrahedron around the site to which the bond is connected, in both spin singlet and triplet multiplets. Therefore, as shown in Fig. 4(a), the chirality configuration on a tetrahedron pair always returns to the original one, after the second-order virtual processes, more generally in any orders, and the ground state degeneracy is not lifted. In the case of a coupled tetrahedron triple shown in Fig. 4(b), chirality is mixed up in the virtual processes including spin-triplet tetrahedra, since two bonds are connected to different sites on each tetrahedron. Therefore, any of the eight chirality configurations can undergo a transition to all of them. This is why the effective model (3) has one-, two-, and three-body interactions in the transverse components in the chirality space.

Now I discuss the ground-state configuration of a set Bragg peaks using the mean-field approach. To this end, I first determine the second- and third-order effective models of the tetrahedron, each of its vertices (j = 1–4) being a type-A tetrahedron on the pyrochlore lattice. The mean-field Hamiltonian, $E$, is simply obtained by replacing chirality operators in eq. (3) with classical unit vectors, $\tau \rightarrow (\cos \theta, \sin \theta, 0)$, and aside from a constant it is given as

$$E(\theta_1, \theta_2, \theta_3, \theta_4) = -b \left[ (1 - 2 \cos \theta_2) [(1 - 2 \cos \theta_3 + \phi)] \right.$$

$$\times \left[ (1 - 2 \cos \theta_1 + \phi) + (\theta_2, \theta_3, \theta_4 \rightarrow \theta_1, \theta_2, \theta_3) + (\theta_2, \theta_3, \theta_4 \rightarrow \theta_2, \theta_1, \theta_3) + (\theta_2, \theta_3, \theta_4 \rightarrow \theta_1, \theta_3, \theta_2) \right].$$

(4)

This has a symmetry associated with spatial rotation: $E(\theta_1, \theta_2, \theta_3, \theta_4) = E(\theta_1 + \phi, \theta_2 + \phi, \theta_3 + \phi, \theta_4 + \phi) = E(\theta_1 + \phi, \theta_2 + \phi, \theta_1 + \phi, \theta_3 + \phi) = E(\theta_1 + \phi, \theta_2 + \phi, \theta_3 + \phi, \theta_2 + \phi) = E(\theta_1 + \phi, \theta_1 + \phi, \theta_2 + \phi, \theta_4 + \phi)$. I minimize this classical energy and find four types of ground-state configurations,

$$(\theta_1, \theta_2, \theta_3, \theta_4) = (\theta_1, \pi, \frac{1}{3} \pi, \frac{1}{3} \pi), (\pi, \theta_2, \frac{1}{3} \pi, \frac{1}{3} \pi),$$

$$\left(\frac{1}{3} \pi, \frac{1}{3} \pi, \theta_3, \pi\right), \left(\frac{1}{3} \pi, \frac{1}{3} \pi, \pi, \theta_4\right).$$

(5)

In each solution, one angle variable is still free and the classical energy is degenerate with respect to it.

I can patch up these four types of solutions for a supertetrahedron to construct a ground-state configuration on the entire fcc lattice, and the result is shown in Fig. 5. Three of the four sublattices show a long-range order. The other one remains disordered, and its residual entropy is $\frac{1}{N} \log 2$ per original spin. I emphasize here that this solution is the global energy minimum within the mean-field approximation. This is because the solution minimizes the energy for each supertetrahedron in the whole fcc lattice without any extra energy cost. The degeneracy of this state is $4 \times 2^{N/4}$, where the first factor is from the number of sublattices and the second one is from the disordered sublattice.

The long-range order contributes to the chirality structure factor by giving the pseudospin a finite expectation value of the pseudospin, $(\tau_R \cdot \tau_R) = (\cos \theta, \sin \theta, 0)$. However, its $z$-component describing spin chirality is zero, meaning that the time-reversal symmetry is not broken and dominant spin-spin correlations are collinear rather than chiral. The transverse components are finite instead, and I now discuss its physics with considering the wavefunction of four spins on an original tetrahedron.

This for the given value of angle $\theta$ is given as the eigenfunction of the operator, $(\tau \cdot \tau) = \tau^x \cos \theta + \tau^y \sin \theta$. All of the three cases, $\theta = \pi, \frac{1}{3} \pi, \frac{2}{3} \pi$, correspond to a valence bond state, i.e., a dimer pair, but with different pair combinations:

$$\theta = \pi : [12] \otimes [34], \frac{1}{3} \pi : [13] \otimes [24], \frac{2}{3} \pi : [14] \otimes [23].$$

(6)
where \([ii']\) denotes the spin singlet wavefunction of two spins, \(i\) and \(i'\) (see Fig. 1). Therefore, the mean-field ground state has a long-range order of dimerization in three of the four tetrahedron sublattices and breaks the translation, mirror, and rotation symmetries in space. However, it does not break symmetry in spin space, since the order occurs within the spin-singlet multiplet. The possibility of dimerization was first discussed by Harris et al.\textsuperscript{[6]} and the present solution agrees with their proposal.

Koga and Kawakami\textsuperscript{[9]} also discussed dimerization on the pyrochlore lattice with including additional distortion which favors the \(q = 0\) order of either a tetramer singlet or one of the dimer pairs in eq. (3), and found that these two states become degenerate as the distortion is switched off. Their solution is not continuously connected to the present solution, but this is because the distortion under consideration is limited to intra-tetrahedron modes with \(q = 0\). As the result of \(S_\sigma(Q)\) shows, the present solution has a triple-\(q\) structure with wavevectors \((2\pi,0,0)\), \((0,2\pi,0)\), and \((0,0,2\pi)\). The dimerized state resonates with the tetramer state to realize the other two dimerized states in eq. (6) with spatially modulated coefficients, and the three-body interactions in the effective model\textsuperscript{[15]} stabilize the triple-\(q\) structure with four sublattices.

To compare with the experiments, one useful quantity is the spin structure factor, \(S_\sigma(q) = (4N_A)^{-1}\sum_{r,r'}e^{iq(r-r')}(S_r \cdot S_{r'})\). This is calculated for the mean-field ground state and the result is

\[
S_\sigma(q) = \frac{1}{3} \left[ 1 + \cos \frac{q_x}{2} \cos \frac{q_x}{2} + \cos \frac{q_x}{2} \cos \frac{q_y}{2} \right].
\]

Since this state is a spin singlet with no magnetic long range order, the spin structure factor has no Bragg peak and continuously changes with the wavevector. It has a maximum value at \(q\)'s where one of \(\frac{q_x}{2}\) is \(+1\) and another one is \(-1\), e.g., \(Q_1=(4\pi,4\pi,0)\) and \(Q_2=(\pi,2\pi,0)\). Therefore, these \(q\)'s form three orthogonal sets of parallel lines, reflecting strong geometrical frustration. This result is qualitatively similar to the result, Fig. 4, of Canals and Lacroix\textsuperscript{[16]} but the maximum position is shifted as for \(Q_1\) in their calculation. On the one hand, this may be because spins on different tetrahedra have no correlations within the present approach. On the other hand, Canals and Lacroix used the second-order perturbation in the inter-tetrahedron interaction \(J'\). As I pointed out above, up to the second order, the \(J'\)-term induces no spin-spin correlations between different tetrahedra for the singlet ground-state multiplet. Therefore, the finite shift from \(Q_1\) in their result is due to the contribution of excited-state multiplets at finite temperatures, and it will vanish with the temperature approaching zero. We could improve the present result by also including perturbation for the wavefunction, but it is beyond the scope of this paper.

In this paper, I have examined the ground state of the \(S=\frac{1}{2}\) Heisenberg antiferromagnet on the pyrochlore lattice. Assuming the ground state is a spin liquid, I obtained the effective model for a thermodynamic number of spin-singlet states below the spin gap and examined symmetry breaking, based on the third-order degenerate perturbation starting from decoupled tetrahedra. I determined its ground state using the mean-field approximation. The result is a long-range order of spin-singlet dimers with a triple-\(q\) structure, and three of the four constituent tetrahedron sublattices have a ordered dimer-pair pattern. Therefore, spin-triplet excitations have a finite energy gap, whereas spin-singlet excitations exist within the spin gap. These singlet excitations are oscillations of the dimerization pattern in the ordered sublattices. One tetrahedron sublattice remains disordered, and it is randomly dimerized, tetramerized, even chiral, or any superposition of these. We expect that this sublattice will ultimately show a long-range order once quantum fluctuations are taken into account beyond the present approach. In a separate paper, I will discuss this problem both for spin and chirality degrees of freedom.

I have investigated in the present study the lift of thermodynamic degeneracy driven by spin exchange processes, but there may exist other types of instability. Recently, Yamashita and Ueda\textsuperscript{[11]} found that a Jahn-Teller lattice distortion lifts this degeneracy for the \(S=1\) antiferromagnet, and they proposed that this is a mechanism of a structural phase transition observed in \(\text{ZnV}_2\text{O}_4\)\textsuperscript{[8]}. This compound also undergoes a magnetic phase transition at a lower temperature. To explain its magnetic order, theoretical approaches limited to the spin singlet multiplet are not sufficient and we must include finite-spin multiplets not only in the virtual processes but also in the real processes. This problem is left for a future project.

I thank Frederic Mila for valuable discussions. This work was supported by a Grant-in-Aid from the Ministry of Education, Science, Sports and Culture and also by University of Tsukuba Research Projects.

\[1\] R. Liebmann: \textit{Statistical Mechanics of Periodic Frustrated Ising Systems}, (Springer, Berlin, 1986).
\[2\] A. P. Ramirez: “Geometrical Frustration” in \textit{Handbook of Magnetic Materials}, (to be published).
\[3\] J. Villain: Z. Physik B \textbf{33} (1979) 31.
\[4\] P. W. Anderson: Phys. Rev. \textbf{102} (1956) 1008.
\[5\] For example, T. Nikuni and H. Shiba: J. Phys. Soc. Jpn. \textbf{62} (1993) 3268.
\[6\] A. B. Harris, J. Berlinsky and C. Bruder: J. Appl. Phys. \textbf{69} (1991) 5200.
\[7\] B. Canals and C. Lacroix: Phys. Rev. Lett. \textbf{80} (1998) 2933.
\[8\] Harris et al. obtained in ref.\textsuperscript{[16]} the two-body part. They also discussed the three-body part, but did not give its explicit expression.
\[9\] A. Koga and N. Kawakami: cond-mat/0010128.
\[10\] Y. Yamashita and K. Ueda: Phys. Rev. Lett. \textbf{85} (2000) 4960.
\[11\] Y. Ueda, N. Fujiwara and H. Yasuoka: J. Phys. Soc. Jpn. \textbf{66} (1997) 778.