Ground State Phase Transition in $S = 1$ Distorted Kagomé Heisenberg Antiferromagnets

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The ground state phase transition in the distorted $S = 1$ kagomé Heisenberg antiferromagnet (KHAF) is studied by means of the perturbational calculation and numerical exact diagonalization method. For strong $\sqrt{3}\times\sqrt{3}$ lattice distortion, the hexgonal singlet solid (HSS) ground state of the uniform KHAF is destroyed and a new singlet state, the large HSS (LHSS) state, which is globally different from the HSS state is realized. The quantum phase transition between these two singlet states is analogous to the Haldane-dimer transition in the $S = 1$ antiferromagnetic Heisenberg chain. The presence of this transition is fully consistent with the HSS picture of the ground state of the uniform $S = 1$ KHAF and supports the validity of this picture.

KEYWORDS: kagomé Heisenberg antiferromagnet, lattice distortion, hexagonal singlet solid

The kagomé Heisenberg antiferromagnet (KHAF) has been extensively studied theoretically and experimentally because of the interest in the interplay of the strong thermal and quantum fluctuation and the highly frustrated nature of the lattice structure[1-9]. To date, most attempts have been focused on the ground state and low-lying excitations of the uniform KHAF. In both $S = 1/2$ [2-7] and $S = 1$[8] cases, it is expected that the ground state is a spin singlet state and the magnetic excitation has a finite energy gap. In the $S = 1/2$ case, there are a number of singlet excitations below the first triplet excitation possibly down to zero energy in the thermodynamic limit[5]. On the other hand, the singlet excitations also have finite energy gaps in the $S = 1$ case[8].

The present author proposed the hexagonal singlet solid (HSS) picture for the ground state of $S = 1$ KHAF[8] which is analogous to the valence bond solid (VBS) picture of the ground state of the $S = 1$ antiferromagnetic Heisenberg chain (AFHC)[10,11]. In both HSS and VBS pictures, the $S = 1$ spins are decomposed into symmetrized pairs of two $S = 1/2$ spins. In the HSS state, six $S = 1/2$ spins are assigned for each hexagon and they form a six-spin singlet state around each hexagon. This is analogous to the VBS state in which these $S = 1/2$ spins form a two-spin singlet state on each bond. The HSS state was explicitly constructed in the previous paper and shown to give a good variational energy[8]. A similar physical picture has also been proposed for the $S = 1$ pyrochlore system[12].

As a real material, Wada and coworkers[13-15] have investigated the magnetic behavior of m-MPYNN·BF_4 which can be regarded as the $S = 1$ kagome antiferromagnet. Therefore, if the HSS picture of the ground state of $S = 1$ KHAF is verified, this material is the first realistic example of the VBS-like state in two-dimensional $S = 1$ magnetic systems. In this context, it is important to check the validity of the HSS picture for the ground state of the $S = 1$ KHAF from various points of view. In the present work, we investigate the stability of the ground state against the lattice distortion which *destroys* the characteristic magnetic structure of the HSS state. The obtained results are consistent with the assumption that the ground state of the undistorted $S = 1$ KHAF is the HSS state.

It should also be noted that the material m-MPYNN·BF_4 actually undergoes a structual transformation around 128K to a distorted phase with a $\sqrt{3} \times \sqrt{3}$ structure[16]. This is another motivation of the present study, although the strength of the distortion might not be strong enough to induce a ground state phase transition.

Let us consider the $S = 1\sqrt{3} \times \sqrt{3}$ distorted KHAF given by

$$\mathcal{H} = \mathcal{H}_{\rm A} + \mathcal{H}_{\rm B} + \mathcal{H}_{\rm C}, \tag{1}$$

$$\mathcal{H}_\mu = J_\mu \sum_{<i,j>\in\mu} \boldsymbol{S}_i \boldsymbol{S}_j, \tag{2}$$

where $\boldsymbol{S}_i$ is the spin operator with $S = 1$ and $\sum_{<i,j>\in\mu}$ represents the summation over the bonds around the type-μ (μ = A, B or C) hexgons, which are depicted in Fig. 1. In the following, we mainly consider the case $J_{\rm B} = J_{\rm C} = \alpha J_{\rm A}$, unless otherwise specified.

If the ground state of the $S = 1$ KHAF is the HSS state, this state should be destroyed for $J_{\rm A} >> J_{\rm B} = J_{\rm C}$, because the $S = 1$ spins around each A-hexagon form a singlet cluster as a whole and no decomposition into $S = 1/2$ spin pairs can take place in this limit. A phase transition should therefore take place at an intermediate value of α. A corresponding phenomenon has been well established for $S = 1$ AFHC, in which the VBS state is destabilized by strong dimerization[17-19]. This observation elucidated that the ground state of the uniform $S = 1$ AFHC is the VBS state which is essentially differ-

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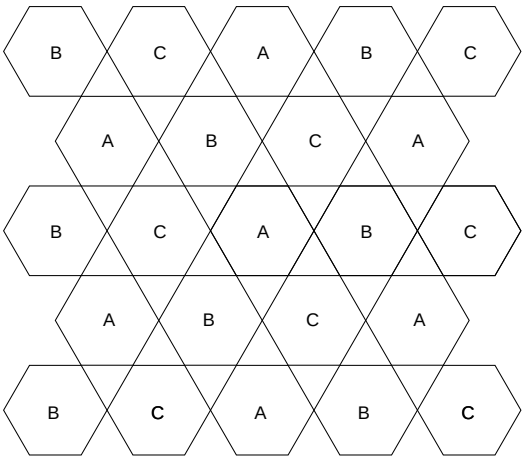

Fig. 1. $\sqrt{3} \times \sqrt{3}$ distorted kagomé lattice.

ent from the dimer phase in the dimerized $S = 1$ AFHC. Therefore, it is important to verify the presence of this transition in order to substantiate the HSS picture of the uniform $S = 1$ KHAF.

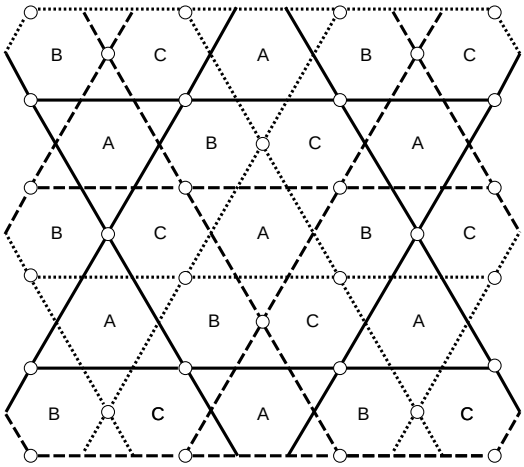

Fig. 2. Strongly distorted KHAF. Open circles represent the 'alive' spins. Strongest effective bonds for case $J_{\rm A} >> J_{\rm B} = J_{\rm C}$ are shown by thick lines.

Let us start our calculation with the strong distortion limit including the case $J_{\rm B} \neq J_{\rm C}$. As explained above, the six $S = 1$ spins around each A-hexagon approximately form a six-spin singlet state for $J_{\rm A} >> J_{\rm B}, J_{\rm C}$. The number of remaining spins is $N/3$. These $N/3$ 'alive' spins, in turn, form a larger kagomé lattice as depicted by the open circles in Fig. 2. Even in the strong distortion limit, signs of the effective interactions between 'alive' spins are not generally obvious, because there are various paths which mediate the effective interaction. We therefore explicitly carry out the perturbation calculation up to the second order in $J_{\rm B}$ and $J_{\rm C}$ to obtain the

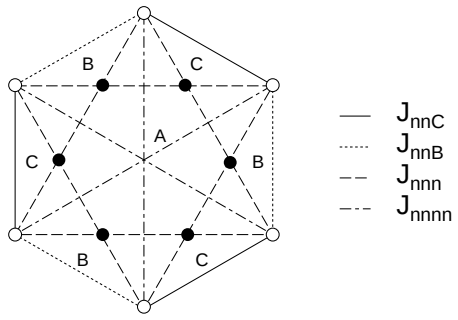

Fig. 3. Effective exchange coupling constants between 'alive' spins (open circles). Filled circles represent 'dead' spins connected by A-bonds.

effective Hamiltonian for the 'alive' spins as

$$\begin{aligned}\mathcal{H}_{\rm eff} = & J_{\rm nnB} \sum_{<{\rm nnB}>} \boldsymbol{S}_i \boldsymbol{S}_j \\ & + J_{\rm nnC} \sum_{<{\rm nnC}>} \boldsymbol{S}_i \boldsymbol{S}_j \\ & + J_{\rm nnn} \sum_{<{\rm nnn}>} \boldsymbol{S}_i \boldsymbol{S}_j \\ & + J_{\rm nnnn} \sum_{<{\rm nnnn}>} \boldsymbol{S}_i \boldsymbol{S}_j, \end{aligned} \tag{3}$$

where $\boldsymbol{S}_i$ is the spin operator with $S = 1$ and the summations $\sum_{<{\rm nnB}>}$, $\sum_{<{\rm nnC}>}$, $\sum_{<{\rm nnn}>}$ and $\sum_{<{\rm nnnn}>}$ are taken over the nearest neighbour pairs within B-hexagons, those within C-hexagons, next nearest neighbour pairs and next to next nearest neighbour pairs of 'alive' sites, respectively, as depicted in Fig. 3.

Using the numerically obtained eigenvalues and eigenstates of the six-spin hexagon cluster, the effective exchange couplings are calculated as

$$\begin{aligned} J_{\rm nnB} &= 1.190573 J_{\rm B} J_{\rm C} - 0.669519 J_{\rm B}^2 - 0.519357 J_{\rm C}^2, \\ J_{\rm nnC} &= 1.190573 J_{\rm B} J_{\rm C} - 0.519357 J_{\rm B}^2 - 0.669519 J_{\rm C}^2, \\ J_{\rm nnn} &= 1.112947 J_{\rm B} J_{\rm C} - 0.519357 (J_{\rm B}^2 + J_{\rm C}^2), \\ J_{\rm nnnn} &= 1.035321 J_{\rm B} J_{\rm C} - 0.519357 (J_{\rm B}^2 + J_{\rm C}^2), \end{aligned} \tag{4}$$

up to the second order in $J_{\rm B}$ and $J_{\rm C}$. Here, we have set $J_{\rm A} = 1$.

If we set $J_{\rm B} = J_{\rm C} = \alpha$, we have $J_{\rm nnB} = J_{\rm nnC} = 0.001697\alpha^2$, $J_{\rm nnn} = 0.074233\alpha^2$, $J_{\rm nnnn} = -0.003394\alpha^2$. In this case, the strongest effective interaction is the next nearest neighbour interaction. If we neglect other interactions, the entire lattice of 'alive' spins is decomposed into three equivalent sublattices of kagomé type which are depicted by thick solid lines, thick dotted lines and thick broken lines in Fig. 2. If the ground state of the uniform $S = 1$ KHAF is the HSS state, the alive spins again form three HSS states on large hexagons which are three times larger than the original kagomé lattice. Thus, the ground state for small α is a tensorial product of three large HSS states constructed from 'alive' $S = 1$

spins and almost isolated singlet clusters of six $S = 1$ spins around A-hexagons. We call this state the 'large hexagonal singlet solid' (LHSS) state. As explained earlier, this state is an analog of the dimer phase of the $S = 1$ dimerized AFHC in which none of the $S = 1$ spins are decomposed into $S = 1/2$ spins but paired into a local singlet state on the strong bonds as a whole. In contrast to the latter, however, the 'alive' spins in the LHSS state are again decomposed into two $S = 1/2$ spins and form a six-spin singlet state on enlarged sublattices. Thus, the LHSS state is a singlet state whose structure is globally different from the HSS state of the undistorted kagomé lattice.

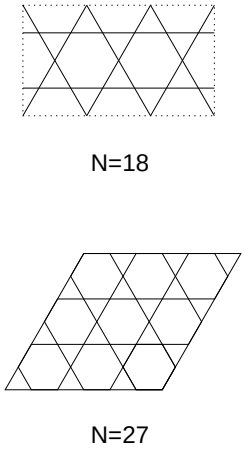

Fig. 4. Clusters used for numerical diagonalization.

To confirm that the ground state of the uniform $S = 1$ KHAF is destroyed by the lattice distortion with $J_{\rm B} = J_{\rm C} = \alpha J_{\rm A}$, a numerical diagonalization calculation is carried out for the finite-size cluster with $N = 18$ shown in the upper half of Fig. 4 using the original Hamiltonian (1). Unfortunately, this size of cluster is not sufficiently large to support the LHSS structure. The minimum cluster size to support the LHSS structure is $N = 54$ which is far from tractable by the presently available computers. However, the HSS structure itself can be constructed on the $N = 18$ cluster. Therefore, the limit of stability of the HSS state can be analyzed using the cluster of this size.

Actually, the α-dependence of the singlet-triplet gap ΔE plotted in Fig. 5(a) shows a minimum $\Delta E \simeq 0.016 J_A$ around $\alpha \simeq 0.50$. Although we cannot analyze the system size dependence of the gap due to the limitation of size, this result indicates that the ground state at $\alpha = 1$ is destroyed around $\alpha \simeq 0.5$ by distortion. This fragility of the ground state of the undistorted $S = 1$ KHAF is consistent with the HSS picture. Taking into account that the HSS picture is also supported by the variational calculation[8], it is highly plausible that the ground state of the undistorted $S = 1$ KHAF is the HSS state, although there is no final proof. Furthermore, if this picture is valid, the ground state of the strongly distorted KHAF is the LHSS state and the HSS-LHSS phase transition is expected at $\alpha = \alpha_{\rm c} \sim 0.5$ in the thermodynamic limit.

Just for comparison, we calculated the magnetic excitation gap of the $S = 1/2$ KHAF for $N = 18$ and 27 with the clusters shown in Fig. 4. As shown in Fig. 5(b), the phase transition is not observed in the $S = 1/2$ case. This is also consistent with our senario because neither HSS nor LHSS states can be constructed for the $S = 1/2$ case.

For the $S = 1$ case, the energy gap with $N = 18$ shows a maximum around $\alpha \simeq 0.41$. This is due to the level crossing of the first excited state. We expect that this behavior persists in the thermodynamic limit in the following way. In the LHSS phase, there are two different types of singlet clusters. One is the cluster composed of six $S = 1$ spins around A-hexagons. The other is the large hexagon cluster of six $S = 1/2$ spins which are generated by decompostion of the $S = 1$ 'alive' spins. Even in the LHSS phase, it is convenient to discuss this problem in terms of the decomposed $S = 1/2$ spins for all spins. Among twelve $S = 1/2$ spins around A-hexagons, only six spins participate the formation of the HSS-type clusters around A-hexagons in the HSS phase. The remaining six $S = 1/2$ spins belong to the HSS-type clusters around B- or C-hexagons. They come into the $S = 1$ A-hexagon cluster in the LHSS phase. For $\alpha \lesssim \alpha_{\rm c}$, however, these spins are bound to A-hexagons only weakly. Thus, the excitation energy required to break up such a singlet cluster is small and gives the lowest excitation gap. This gap vanishes as α reaches $\alpha_{\rm c}$. For $\alpha << \alpha_{\rm c}$, the $S = 1$ spins around A-hexagons are tightly bound, so that the lowest energy gap is that of the large HSS cluster of 'alive' spins. Therefore, the level crossing between these two types of excitations takes place within the LHSS phase. However, this does not cause the global change of the ground state structure and the intermediate phase is not expected between the HSS and LHSS phases. For the $N = 18$ cluster also, the numerically found crossover behavior is understood as the level crossing between the excitation around A-hexagons and that of the cluster of 'alive' spins, even though the latter does not form the complete LHSS state.

In summary, we have found that the ground state of the undistorted $S = 1$ KHAF is destroyed by $\sqrt{3} \times \sqrt{3}$ lattice distortion with $J_{\rm B} = J_{\rm C} < J_{\rm A}$ at an intermediate strength of distortion. The fragility of the uniform ground state against this type of lattice distortion reinforces the HSS picture of the uniform ground state which has been proposed on the basis of the variational argument in ref. 8. Of course, the present calculation is far from the complete proof of the HSS picture, so that further efforts to substantiate this picture from various aspects are necessary in future studies.

Based on the perturbational calculation, the structure of the strongly distorted phase is shown to be the LHSS state which is globally different from the HSS ground state of the undistorted $S = 1$ KHAF. Therefore, the HSS-LHSS phase transition is expected in the thermodynamic limit. This transition corresponds to the Haldane-dimer phase transition in the $S = 1$ AFHC[17-19].

In this paper, we have discussed the ground state phase

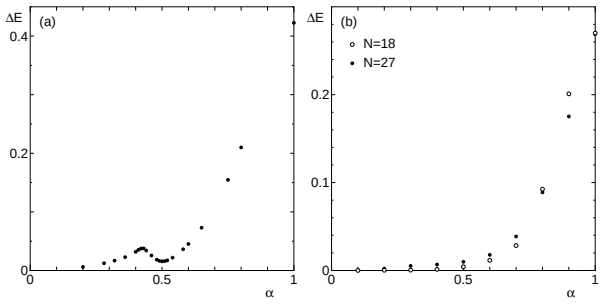

Fig. 5. α-dependence of the gap of the magnetic excitation for distorted KHAF with $J_{\rm A}=1$, $J_{\rm B}=J_{\rm C}=\alpha$ for (a) $S=1, N=18$ and (b) $S=1/2$, $N=18$, 27. For $N=18$, the ground state has total spin 0 and the excited state has total spin 1. For $N=27$ and $S=1/2$, the ground state has total spin 1/2 and the excited state has total spin 3/2.

transition in detail only for the case $J_{\rm A}>J_{\rm B}=J_{\rm C}$, because this is the simplest case in which the ground state remains singlet even in the strong distortion limit. There remains, however, the possibility of many other kinds of ground states for a general choice of $J_{\rm A}, J_{\rm B}$ and $J_{\rm C}$. Even in the strong distortion limit, the expressions of the effective coupling constants (4) show that there is strong competition between the contributions from different interaction paths. Therefore, we may expect a rich variety of ground state phases for the distorted KHAF.

For example, if we set $J_{\rm A}=1$, $J_{\rm B}=\alpha$ and $J_{\rm C}=0$, we have $J_{\rm nnB}=-0.669519\alpha^2$, $J_{\rm nnC}=-0.519357\alpha^2$, $J_{\rm nnn}=-0.519357\alpha^2$ and $J_{\rm nnnn}=-0.519357\alpha^2$. Therefore, all effective bonds are ferromagnetic and the ground state is ferrimagnetic with 1/3 of full magnetization. It is numerically verified that the ground state is always the ferrimagnetic state with the same value of magnetization for $J_{\rm A}=1, J_{\rm B}=\alpha$ and $J_{\rm C}=0$ with $0<\alpha<1$ by exact diagonalization of clusters with $N=18$ for the original Hamiltonian (1).[9] The determination of the ground state phase diagram in the entire parameter plane is an interesting issue although it requires a huge computational effort.

The numerical calculation is performed using the HITAC SR8000 at the Supercomputer Center, Institute for Solid State Physics, the University of Tokyo and the HITAC SR8000 at the Information Processing Center, Saitama University. The numerical diagonalization program is based on the TITPACK ver.2 coded by H. Nishimori and KOBEPACK/1 coded by T. Tonegawa, M. Kaburagi and T. Nishino. This work is supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology.

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