# Exact spin-cluster ground states in a mixed diamond chain

Ken'ichi Takano and Hidenori Suzuki*
*Toyota Technological Institute, Tenpaku-ku, Nagoya 468-8511, Japan*

Kazuo Hida
*Division of Material Science, Graduate School of Science and Engineering, Saitama University, Saitama, Saitama 338-8570, Japan*
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The mixed diamond chain is a frustrated Heisenberg chain composed of successive diamond-shaped units with two kinds of spins of magnitudes $S$ and $S/2$ ($S$: integer). Ratio $\lambda$ of two exchange parameters controls the strength of frustration. With varying $\lambda$, the Haldane state and several spin-cluster states appear as the ground state. A spin-cluster state is a tensor product of exact local eigenstates of cluster spins. We prove that a spin-cluster state is the ground state in a finite interval of $\lambda$. For $S=1$, we numerically determine the total phase diagram consisting of five phases.

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## I. INTRODUCTION

Effects of frustration under strong quantum fluctuation in low-dimensional quantum spin systems have been of great interest in condensed-matter physics. Among them, the diamond chain consisting of successive diamond-shaped units has been attracting remarked attention.

It has been rigorously shown that a ground state of the uniform spin diamond chain (UDC) is a singlet spin-cluster state with spontaneous breakdown of translational symmetry.[1] The spin-cluster state is an essentially quantum state described as a tensor product of local singlet states each consisting of several spins. For a usual gapped spin liquid, such a state is an approximation or is exact only at a single parameter value. However, in the UDC, the spins in each cluster forms an exact local singlet and the exact solution is realized over a finite parameter range.

The distorted version of this model has been also investigated theoretically.[2–5] Since its discovery in a natural mineral azurite,[6,7] this system is attracting a renewed interest. Also materials in a unfrustrated parameter region are found.[8,9]

In this paper, we report rigorous ground states including spin clusters which are not singlet. We found the cluster states for the mixed diamond chain (MDC) which has the same lattice structure as the UDC as shown in Fig. 1(a). Unlike the UDC, the MDC consists of two kinds of spins with magnitudes $S$ and $\frac{1}{2}S$ ($S$: a positive integer). The ratio of two exchange constants in this model is a parameter representing the strength of the frustration. For a weak frustration case, the ground state of the MDC is the Haldane state[10] while that of the UDC is ferrimagnetic. An interest is how the ground state changes from the Haldane state when frustration increases. We show that the MDC undergoes a series of characteristic quantum phase transitions with increasing frustration. A typical ground state is of a tensor-product form of finite-length triplet clusters and dimers in an alternating array; thus the translational symmetry is spontaneously broken. Rigorous results on the phase diagram are presented for general values of $S$. In particular, a tensor-product state is proven to be the ground state for a finite parameter range. For $S=1$, the whole phase diagram is numerically determined.

The cluster ground states of the MDC have a macroscopic degeneracy because each nonsinglet cluster degenerates with respect to the spin direction. Such macroscopic degeneracy can give birth to a rich variety of quantum phenomena in the presence of perturbation. Even within our preliminary studies, quantum ferromagnetic, unusual Haldane phases with spontaneous breakdown of translational symmetry, and infinite series of quantum phase transitions are found in the presence of lattice distortion.

This paper is organized as follows. In Sec. II, we introduce the Hamiltonian describing the MDC and consider its classical version to roughly explain the feature of this model. In Sec. III, we present rigorous results for the ground states of the MDC with general spin magnitude $S$. In Sec. IV, we incorporate numerical calculations with the rigorous results in the case of $S=1$. In particular, we present complete phase diagram of the ground states. Section V is devoted to summary and discussion.

## II. HAMILTONIAN AND ITS CLASSICAL VERSION

The MDC consisting of $N$ diamond units is described by the Hamiltonian,

$$H_N = \sum_{i=1}^{N} \mathcal{H}_i, \tag{1}$$

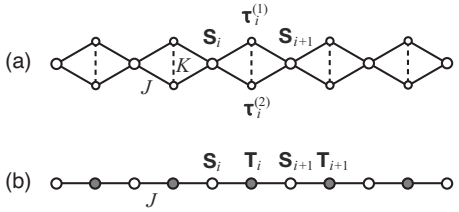


FIG. 1. (a) The MDC, where spin $\mathbf{S}_i$ has a magnitude $S$ (a positive integer) and spin $\boldsymbol{\tau}_i^{(\alpha)}$ ($\alpha=1,2$) has $\tau=\frac{1}{2}S$. The solid (dashed) line represents exchange parameter $J(K)$. (b) The equivalent lattice to the lattice in (a) for each set of $\{T_i\}$, where $T_i$ is the magnitude of $\mathbf{T}_i=\boldsymbol{\tau}_i^{(1)}+\boldsymbol{\tau}_i^{(2)}$.

 

$$\mathcal{H}_i = J(\mathbf{S}_i + \mathbf{S}_{i+1}) \cdot (\boldsymbol{\tau}_i^{(1)} + \boldsymbol{\tau}_i^{(2)}) + K\boldsymbol{\tau}_i^{(1)} \cdot \boldsymbol{\tau}_i^{(2)}. \quad (2)$$

In the $i$th unit cell, $\mathbf{S}_i$ is a spin whose magnitude $S$ is an integer, while $\boldsymbol{\tau}_i^{(\alpha)}$ $(\alpha=1,2)$ is a spin of magnitude $\tau=\frac{1}{2}S$. Below we sometimes use the notations, $\widetilde{\mathbf{S}}_i \equiv \mathbf{S}_i + \mathbf{S}_{i+1}$ and $\mathbf{T}_i \equiv \boldsymbol{\tau}_i^{(1)} + \boldsymbol{\tau}_i^{(2)}$. We assume that $J>0$. Then the ratio $\lambda \equiv K/J$ represents the strength of frustration if $K>0$.

We first examine the classical limit of $S \to \infty$ with finite $JS^2$. (i) For $\lambda \leq 2$, we write the classical version of Eq. (2) as

$$\mathcal{H}_i^{\mathrm{cl}} = \frac{1}{4}J[(2\mathbf{T}_i + \widetilde{\mathbf{S}}_i)^2 - 2(2-\lambda)\mathbf{T}_i^2 - \widetilde{\mathbf{S}}_i^2 - \lambda S^2]. \quad (3)$$

This is minimized if $|\mathbf{T}_i| = 2\tau = S$, $|\widetilde{\mathbf{S}}_i| = 2S$, and $|\mathbf{T}_i + \frac{1}{2}\widetilde{\mathbf{S}}_i| = 0$. Then all the $\mathbf{S}_i$'s ($\boldsymbol{\tau}_i^{(\alpha)}$'s) in the chain are aligned parallel (antiparallel) to a fixed axis and the ground state is antiferromagnetic. This ground state is elastic since any local modification of the spin configuration increases the energy. (ii) For $\lambda > 2$, we use the expression

$$\mathcal{H}_i^{\mathrm{cl}} = \frac{J}{4\lambda}[2(\lambda\mathbf{T}_i + \widetilde{\mathbf{S}}_i)^2 - 2\widetilde{\mathbf{S}}_i^2 - \lambda^2 S^2]. \quad (4)$$

This is minimized if $|\widetilde{\mathbf{S}}_i| = 2S$ and $|\mathbf{T}_i + \widetilde{\mathbf{S}}_i/\lambda| = 0$. Hence $\mathbf{S}_i$ and $\mathbf{S}_{i+1}$ are parallel, and $\boldsymbol{\tau}_i^{(1)}$ and $\boldsymbol{\tau}_i^{(2)}$ form a triangle with $\widetilde{\mathbf{S}}_i/\lambda$. $\boldsymbol{\tau}_i^{(1)}$ and $\boldsymbol{\tau}_i^{(2)}$ may be rotated about the axis of $\mathbf{S}_i$ and $\mathbf{S}_{i+1}$ without raising the energy. Then all the $\mathbf{S}_i$'s in the chain are aligned parallel to a fixed axis and the arbitrariness of the local rotation of $\boldsymbol{\tau}_i^{(1)}$ and $\boldsymbol{\tau}_i^{(2)}$ is not obstructed. Thus the ground state is ferrimagnetic with magnetization $(1-2/\lambda)SN$.

## III. RIGOROUS RESULTS FOR GENERAL SPIN MAGNITUDE $S$

Returning to the quantum case with general $S$, the MDC has a series of conservation laws

$$[\mathbf{T}_i^2, H_N] = 0 \quad (i = 1,2,\ldots,N), \quad (5)$$

i.e., $T_i(=0,1,\ldots,S)$ of $\mathbf{T}_i^2 = T_i(T_i+1)$ for each $i$ is a good quantum number. With a fixed set $\{T_i\}$, the original problem of $3N$ spins reduces to a problem of a linear chain with $2N$ spins, where the $(2i-1)$th site is occupied by the spin $\mathbf{S}_i$ and the $2i$th by $\mathbf{T}_i$. The energy of $K$ bonds is determined solely by $\{T_i\}$. In particular, if $T_i=0$, then there is no interaction between the left and right sides of $\mathbf{T}_i$ and the whole lattice is decoupled. We denote the lowest energy of $H_N$ for a fixed set $\{T_i\}$ as $E_N(\{T_i\},\lambda)$ and sometimes drop $\{T_i\}$ and/or $\lambda$ in it. Hereafter we use an energy unit of $J=1$.

There is an equivalent lattice to the MDC for each fixed set of $\{T_i\}$ because $\mathbf{T}_i^2$'s are conserved. The equivalent lattice for set $\{T_i\}$ is a nearest-neighbor antiferromagnetic linear spin chain on $2N+1$ sites. The spin magnitudes are $S$ on all odd sites and $T_i$ on $2i$th site for all $i$, as seen in Fig. 1(b). The Hamiltonian is

$$\widetilde{H}_N = \sum_{i=1}^{N} (\mathbf{S}_i + \mathbf{S}_{i+1}) \cdot \mathbf{T}_i. \quad (6)$$

$\widetilde{H}_N$ is related to $H_N$ as

$$H_N = \widetilde{H}_N + \frac{1}{2}\lambda \sum_{i=1}^{N} \left[ T_i(T_i+1) - \frac{1}{2}S(S+2) \right]. \quad (7)$$

The ground-state energy of $\widetilde{H}_N$ is denoted by $\widetilde{E}_N(\{T_i\})$ or simply $\widetilde{E}_N$.

We begin with analyzing eigenstates of an isolated diamond unit described by $\mathcal{H}_i$. This is realized in the total system, if $T_{i-1}=T_{i+1}=0$. Using the expression,

$$\mathcal{H}_i = \frac{1}{2}\{(\mathbf{T}_i + \widetilde{\mathbf{S}}_i)^2 + (\lambda-1)\mathbf{T}_i^2 - \widetilde{\mathbf{S}}_i^2\} - \frac{\lambda}{4}S(S+2), \quad (8)$$

the lowest energy of $\mathcal{H}_i$ for a given $T_i$ is

$$E_1(T_i) = \frac{1}{2}T_i(T_i+1)[\lambda - \Lambda(T_i)] - \frac{1}{4}\lambda S(S+2), \quad (9)$$

where $\Lambda(L) \equiv 2(2S+1)/(L+1)$ for non-negative integer $L$. Then the total spin of the diamond unit is $2S-T_i$. For the whole spin chain, we have the following lemma:

*Lemma 1.* If $L \geq 1$ and $\lambda > \Lambda(L)$, then $T_i \neq L$ for any $i$ in the ground state of the MDC.

*Proof.* The total Hamiltonian is divided as $H = \mathcal{H}_m + H'$, where $N$ of $H_N$ is omitted and $H'$ is the sum of $\mathcal{H}_i$'s with $i \neq m$. We take a state $|\Psi_0\rangle = |0_m\rangle \otimes |\Psi'\rangle$, where $|0_m\rangle$ is the singlet wave function of $\mathbf{T}_m$ and $|\Psi'\rangle$ is the lowest-energy state of the other spins. Since $\langle 0_m|\mathcal{H}_m|0_m\rangle = E_1(0)$ does not involve $\mathbf{S}_m$ and $\mathbf{S}_{m+1}$, we have $\langle\Psi_0|H|\Psi_0\rangle = E_1(0) + E'$ with $E' = \langle\Psi'|H'|\Psi'\rangle$ being the ground-state energy of $H'$. Let $|\Psi\rangle$ be any state with $T_m = L \geq 1$. Then $\langle\Psi|H|\Psi\rangle = \langle\Psi|\mathcal{H}_m|\Psi\rangle + \langle\Psi|H'|\Psi\rangle$. Clearly $\langle\Psi|\mathcal{H}_m|\Psi\rangle \geq E_1(L)$ and $\langle\Psi|H'|\Psi\rangle \geq E'$; also $E_1(L) > E_1(0)$ for $\lambda > \Lambda(L)$. Therefore $\langle\Psi|H|\Psi\rangle > \langle\Psi_0|H|\Psi_0\rangle$ and $|\Psi\rangle$ is not the ground state of $H$.

Since $\Lambda(L)$ decreases with $L$ from $\Lambda(1) = 2S+1$ to $\Lambda(S) = 2(2S+1)/(S+1)$, we obtain the following result:

*Theorem 1.* If $\lambda > 2S+1$, then $T_i = 0$ for all $i$ in the ground state.

In this ground state, all pairs of $\boldsymbol{\tau}_i^{(1)}$ and $\boldsymbol{\tau}_i^{(2)}$ form singlet dimers so that all $\mathbf{S}_i$'s are decoupled from each other and behave as free spins. Hence we call this state the *dimer-monomer* (DM) state. The DM state for $S=1$ is shown in Fig. 2(a). The picture is also the same for the DM state of a system with $S \geq 2$. The ground-state energy is $NE_1(0)$ for the lattice consisting of $N$ diamond units, where $2N$ spins with magnitude $\frac{1}{2}S$ and $N+1$ spins with magnitude $S$ are included. Due to the free spins, there is a $(2S+1)^N$-fold degeneracy in the DM state.

For $\lambda < 2S+1$, we have the following lemma:

*Lemma 2.* For $\lambda$ in $\frac{2}{3}(2S+1) < \lambda < 2S+1$, $T_i$ at any site is 0 or 1 in the ground state. Also at least one of $T_i$'s is not 0.

*Proof.* For $\tau = \frac{1}{2}$, the ground state is composed of $T_i$'s with their magnitude 0 or 1. It is true even for $\tau \geq 1$ if $\Lambda(2) < \lambda < \Lambda(1)$ because of Lemma 1; the region is rewritten as $\frac{2}{3}(2S+1) < \lambda < 2S+1$. Further for $\lambda < 2S+1$, the DM state, where $T_i=0$ for all $i$, is not a ground state because we can lower the energy by introducing an isolated $T_i=1$ in the DM state as known from Eq. (9).

Hence $\lambda_1^{\mathrm{c}} \equiv \Lambda(1) = 2S+1$ is the phase boundary of the DM phase.

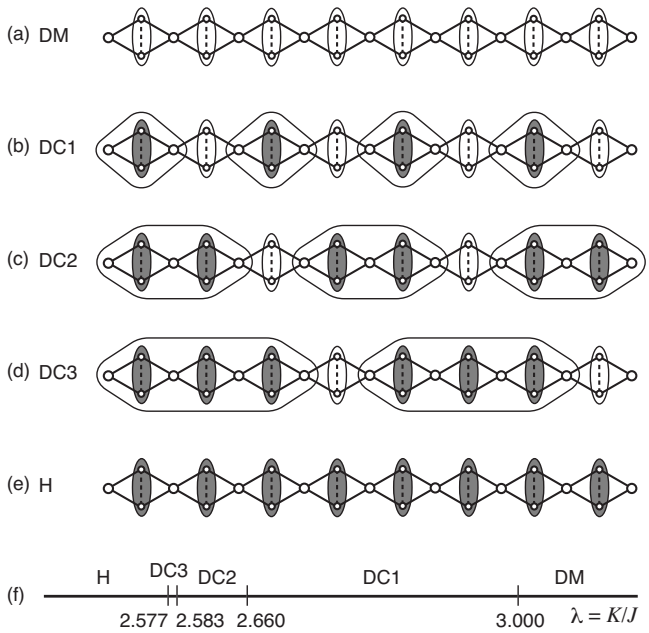


FIG. 2. The ground states for the MDC in the case of $S=1$ and $\tau=\frac{1}{2}$: (a) The DM state. An unshaded oval represents a singlet dimer ($T_i=0$). There are free spins (monomers) on the sites not enclosed by ovals. (b) The DC1 state. A shaded oval represents a triplet pair ($T_i=1$). A loop including a diamond unit is a cluster 1 whose spin magnitude is unity. (c) The DC2 state. A loop including two diamond unit is a cluster 2 whose spin magnitude is unity. (d) The DC3 state. A loop including a diamond unit is a cluster 3 whose spin magnitude is unity. (e) The Haldane (H) state. (f) The ground-state phase diagram.

For $\frac{2}{3}(2S+1)<\lambda<2S+1$, the ground state consists of an appropriate array of $T_i=0$ and 1. For further arguments, we define the *cluster n* as the local ground state of a successive $n$ diamond units in the case that $T_i$'s are all unity in the $n$ diamond units and both $T_i$'s just outsides of it are zero; the cluster $n$ is a state of $n+1$ $\mathbf{S}_i$'s, $n$ $\boldsymbol{\tau}_i^{(1)}$'s, and $n$ $\boldsymbol{\tau}_i^{(2)}$'s. The magnetization of the cluster $n$ is $(n+1)S-n$ due to the Lieb-Mattis theorem.[11] In particular, for $S=1$, the cluster $n$ is the Haldane state of a finite Haldane chain with $2n+1$ sites and is a triplet state. Denoting the energy of the cluster $n$ by $E_n$, we define the energy per diamond unit for a cluster $n$ measured from the DM state as

$$e_n(\lambda)=\frac{1}{n+1}[E_n-nE_1(0)]. \tag{10}$$

We have divided it by $n+1$ and not by $n$ since a cluster $n$ is accompanied with the neighboring $T_i=0$'s and it is convenient to include the effect of one of them. If $e_n(\lambda)$ is the minimum at a single value of $n$, then the ground state in the thermodynamic limit ($N\to\infty$) is realized by an alternating array of cluster $n$'s with $T_i=1$ and dimers with $T_i=0$. We call the state the *dimer-cluster-n* (DC$n$) state. The DC$n$ states with $n=1$, 2, and 3 for $S=1$ are illustrated in Figs. 2(b)–2(d), respectively. The DC$n$ state has spatial periodicity $n+1$ and the translational symmetry is spontaneously broken. The degeneracy is $(n+1)3^{N/(n+1)}$ for large $N$.

To investigate the ground state of the MDC in the region of $T_i=0$ or 1 for all $i$, we need the following lemma for small equivalent lattices:

*Lemma 3.* $\tilde{E}_2>2\tilde{E}_1$, if $T_i=1$ for all $i$.

*Proof.* We define three-spin Hamiltonians $\tilde{H}_{1L}=(\mathbf{S}_1+\mathbf{S}_2)\cdot\mathbf{T}_1$ and $\tilde{H}_{1R}=(\mathbf{S}_2+\mathbf{S}_3)\cdot\mathbf{T}_2$. The five-spin Hamiltonian for $\mathbf{S}_1$, $\mathbf{T}_1$, $\mathbf{S}_2$, $\mathbf{T}_2$, and $\mathbf{S}_3$ is written as

$$\tilde{H}_2=\tilde{H}_{1L}\otimes I_{T_2,S_3}+I_{T_1,S_1}\otimes\tilde{H}_{1R}, \tag{11}$$

where $I_{T,S}$ is an identity operator in the subspace of spins $\mathbf{T}$ and $\mathbf{S}$. The ground states of $\tilde{H}_{1L}$, $\tilde{H}_{1R}$, and $\tilde{H}_2$ are denoted by $|\psi_{3L}\rangle$, $|\psi_{3R}\rangle$, and $|\psi_5\rangle$, respectively. From variational consideration, the following inequality holds:

$$\tilde{E}_2=\langle\psi_5|\tilde{H}_2|\psi_5\rangle\geq\langle\psi_{3L}|\tilde{H}_{1L}|\psi_{3L}\rangle+\langle\psi_{3R}|\tilde{H}_{1R}|\psi_{3R}\rangle=2\tilde{E}_1. \tag{12}$$

We now deduce a contradiction by assuming $\tilde{E}_2=2\tilde{E}_1$. This is valid only if $|\psi_5\rangle$ is also the ground state of both $\tilde{H}_{1L}\otimes I_{T_2,S_3}$ and $I_{T_1,S_1}\otimes\tilde{H}_{1R}$. The Lieb-Mattis theorem[11] applied to $\tilde{H}_{1L}$ says that the magnitude of the total spin $\mathbf{S}_1+\mathbf{T}_1+\mathbf{S}_2$ must be $2S-1$ in $|\psi_{3L}\rangle$. Therefore $|\psi_{3L}\rangle$ contains only the states with $S_1^z+T_1^z+S_2^z\leq 2S-1$. Applying the Lieb-Mattis theorem to $\tilde{H}_2$, however, the ground state $|\psi_5\rangle$ has total spin $3S-2$ and contains all the $S^z$-diagonal states $|S_1^z,T_1^z,S_2^z,T_2^z,S_3^z\rangle$ with total spin $3S-2$. This implies that $|\psi_5\rangle$ contains the state with $S_1^z+T_1^z+S_2^z=2S$ such as $|S,0,S,-1,S-1\rangle$ with finite amplitude. This is a contradiction and therefore we have $\tilde{E}_2>2\tilde{E}_1$.

Based on Lemma 3, we have the following proposition on the ground state in a region just below $\lambda_1^c=2S+1$:

*Theorem 2.* There exists a positive number $\delta$ such that the DC1 state is the ground state for $\lambda_1^c-\delta<\lambda<\lambda_1^c$ in the thermodynamic limit.

*Proof.* Due to Lemma 2, we only have spin magnitudes 0 or 1 for $\mathbf{T}_i$'s for $\frac{2}{3}(2S+1)<\lambda<2S+1$. We consider a segment of $n$ diamond units between two 0's. The equivalent lattice is described by Eq. (6) with $N=n$ and $T_i=1$ for all $i$. By using the ground-state energy $\tilde{E}_n$, we have $E_n-nE_1(0)=\tilde{E}_n+n\lambda$. We adopt $\delta\equiv\tilde{E}_2-2\tilde{E}_1(>0)$ if it is smaller than $\frac{1}{3}(2S+1)$ and show that $\delta$ satisfies the condition of Theorem 2.

If $n$ is even, the Hamiltonian for $\tilde{E}_n$ is divided into $\frac{n}{2}$ sub-Hamiltonians, each equivalent to that for $\tilde{E}_2$. A variational argument gives

$$\tilde{E}_n\geq\frac{1}{2}n\tilde{E}_2=n\tilde{E}_1+\frac{1}{2}n\delta \tag{13}$$

for even $n$ and

$$\tilde{E}_n\geq\frac{1}{2}(n-1)\tilde{E}_2+\tilde{E}_1=n\tilde{E}_1+\frac{1}{2}(n-1)\delta \tag{14}$$

for odd $n$. Since $e_1=(\tilde{E}_1+\lambda)/2=(\lambda-\lambda_1^c)/2$, a lower bound on $e_n-e_1$ is given as

$$\frac{n-1}{2(n+1)}(\lambda-\lambda_1^c+\delta), \tag{15}$$

which is positive for $\lambda>\lambda_1^c-\delta$ and $n\geq 2$.

If $\delta=\tilde{E}_2-2\tilde{E}_1>\frac{1}{3}(2S+1)$, we use $\delta'\equiv\frac{1}{3}(2S+1)$ instead of $\delta$. Then $\lambda_1^c-\delta'$ is the lower bound of Lemma 2 where spin magnitudes of $\mathbf{T}_i$'s are 0 or 1. The argument of the last paragraph stand still for $\delta'$ replacing $\delta$ since $0<\delta'<\delta$.

For $\lambda\leq 1$, we show that the ground state of the MDC is equivalent to that of the uniform linear spin chain with spin magnitude $S$.

*Theorem 3.* If $\lambda\leq 1$, then $T_i=S$ for all $i$ in the ground state.

*Proof.* We divide the total lattice into two sublattices $A$ and $B$, where $\mathbf{S}_i$'s are on the $A$ sublattice and $\boldsymbol{\tau}_i^{(\alpha)}$'s on the $B$ sublattice. For $\lambda\leq 1$, we have $K\leq J$ for interaction $J(>0)$ between spins on the different sublattices and interaction $K$ between spins on the same $B$ sublattice. This suits to the condition for the Lieb-Mattis theorem.[11] Hence the total spin of the ground state is given as $|(N+1)S-NS|=S$ for the lattice consisting of $N$ diamond units.

We also apply the Lieb-Mattis theorem to the ground state of the equivalent lattice with $\{T_i\}$. Then the total spin of the ground state is given as $|(N+1)S-\Sigma_{i=1}^N T_i|$. This must be the same value $S$ as the total spin of the ground state of the MDC. This is possible only if $T_i=S$ for all $i$.

Thus, at least for $\lambda\leq 1$, the MDC is equivalent to a uniform linear chain with integer spin magnitude $S$. The ground state of an integer spin chain is the Haldane state.[10] The picture of the Haldane state for the MDC with $S=1$ is shown in Fig. 2(e).

## IV. GROUND STATES FOR $S=1$

For $S=1$, the DC$n$ ground state is resolved into the ground states of spin clusters equivalent to finite-length spin-1 chains. Therefore we can precisely determine the phase boundaries by the exact numerical diagonalization for the finite chains. Equation (10) becomes

$$e_n(\lambda)=\frac{\tilde{E}_n-\lambda}{n+1}+\lambda, \tag{16}$$

where $\tilde{E}_n$ is the ground-state energy of the spin-1 chain with length $2n+1$. Typical values are

$$\tilde{E}_0=0,\quad \tilde{E}_1=-3,$$

$$\tilde{E}_2=-5.8302125227708,$$

$$\tilde{E}_3=-8.6345319827062. \tag{17}$$

If $T_i=1$ for all $i$, the ground-state energy per unit cell is given by $e_\infty(\lambda)=2\tilde{\epsilon}_\infty+\lambda$, where $\tilde{\epsilon}_\infty\simeq-1.401484038971$ (Ref. 12) is the ground-state energy of an infinite spin-1 chain per unit cell. The phase transition between the DC$(n-1)$ and DC$n$ phases takes place at $\lambda=\lambda_n^c$ with

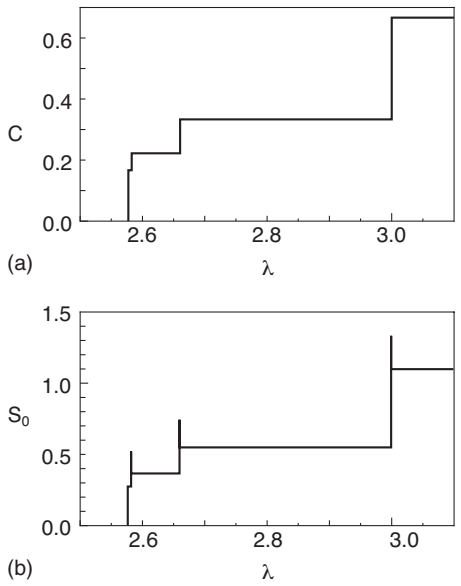


FIG. 3. λ dependence of the (a) Curie constant and (b) residual entropy for the MDC with $S=1$.

$$\lambda_n^c\equiv(n+1)\tilde{E}_{n-1}-n\tilde{E}_n, \tag{18}$$

which is the solution of $e_{n-1}(\lambda_n^c)=e_n(\lambda_n^c)$. However the DC$n$ phases with $n\geq 4$ do not appear[13] and a phase transition takes place directly from the DC3 phase to the Haldane (DC$\infty$) phase at $\lambda_\infty^c=\tilde{E}_3-8\tilde{\epsilon}_\infty$, which is the solution of $e_3(\lambda_\infty^c)=e_\infty(\lambda_\infty^c)$. The critical values of λ are estimated as

$$\lambda_1^c=2S+1=3,$$

$$\lambda_2^c=2.660425045542,$$

$$\lambda_3^c=2.58274585704,$$

$$\lambda_\infty^c=2.5773403291. \tag{19}$$

Thus we have the ground-state phase diagram for $S=1$ in Fig. 2(f).

Magnetically, each phase for $S=1$ is characterized by the number of alive spins; it equals the number $N/(n+1)$ of triplet clusters in the DC$n$ ground state. Consequently, as an experimentally measurable quantity, the Curie constant given by

$$C=\frac{2}{3(n+1)} \tag{20}$$

shows a stepwise λ dependence as shown in Fig. 3(a). Also, the residual entropy per unit length is given by

$$S_0=\frac{\ln 3}{n+1} \tag{21}$$

in the DC$n$ phase. At the phase boundary between the DC$n$ and DC$(n+1)$ phases, the mixing of cluster $n$ and cluster $(n+1)$ remarkably enhances the entropy, which is estimated by combinatory argument as 1.333, 0.744, and 0.522 for $n=0$, 1, and 2, respectively.[15] Thus $S_0$ has spikelike structures

as shown in Fig. 3(b). Similar structures are also reported in the diamond hierarchical Ising model.[14]

## V. SUMMARY AND DISCUSSION

Summarizing, we investigated the ground states of the MDC. We proved that the DM, DC1, and Haldane phases exist for an arbitrary integer $S$, where the system consists of spins with magnitudes $S$ and $S/2$. For $S=1$, we numerically determined all the phase boundaries of the full phase diagram, which consists of the DM, DC1, DC2, DC3, and Haldane phases.

Since each spin cluster with spin magnitude $S$ has $2S+1$ degrees of freedom, the total ground state is massively degenerate. If this degeneracy is lifted by appropriate perturbations such as distortions in the exchange constants, a variety of exotic phases are expected. Our preliminary study on systems with distortion suggests the presence of exotic phases and phase transitions, quantized and partial ferrimagnetic phases, Haldane phases with broken translational symmetry, and infinite series of quantum phase transitions, depending on the kind of distortion.

The investigation of the effect of distortion is also desired to relate the present study with the experiments on real materials. As for the UDC, the natural mineral azurite in which Cu ions carry spin-1/2 degrees of freedom[7] is a distorted version of the spin-1/2 UDC as well as other unfrustrated materials.[8,9] Although no real material described by the MDC model has been known so far, these facts encourage the search for materials described by the distorted version of the MDC.

As for finite temperature properties of the MDC, we formulated statistical mechanics for the $S=1$ case. The low-temperature limits of the Curie constant and residual entropy are reduced to Eqs. (3) and (21). These are reported in a separate paper.[15]

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*Present address: Department of Physics, College of Humanities and Sciences, Nihon University, Setagaya-ku, Tokyo 156-8550, Japan.

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