Ground State Properties of an $S=1/2$ Distorted Diamond Chain

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We investigate the ground state properties of an $S=1/2$ distorted diamond chain described by the Hamiltonian $H = J_1 \sum_{\ell=1}^{N/3} \left( \vec{S}_{3\ell-1} \cdot \vec{S}_3 + \vec{S}_3 \cdot \vec{S}_{3\ell+1} \right) + J_2 \sum_{\ell=1}^{N/3} \left( \vec{S}_{3\ell-2} \cdot \vec{S}_{3\ell-1} + \vec{S}_{3\ell-1} \cdot \vec{S}_{3\ell-2} + \vec{S}_{3\ell+1} \cdot \vec{S}_{3\ell+2} - 2 \vec{S}_3 \cdot \vec{S}_{3\ell+2} \right)$ $(J_1, J_2, J_3 \geq 0)$, which models well a trimerized $S=1/2$ spin chain system Cu3Cl6(H2O)2·2H6C4SO2. Using an exact diagonalization method by means of the Lanczos technique, we determine the ground state phase diagram in the $H = 0$ case, composed of the dimerized, spin fluid, and ferrimagnetic phases. Performing a degenerate perturbation calculation, we analyze the phase boundary line between the latter two phases in the $J_2, J_3 \ll J_1$ limit, the result of which is in good agreement with the numerical result. We calculate, by the use of the density matrix renormalization group method, the ground state magnetization curve for the case (a) where $J_1 = 1.0$, $J_2 = 0.8$, and $J_3 = 0.5$, and the case (b) where $J_1 = 1.0$, $J_2 = 0.8$, and $J_3 = 0.3$. We find that in the case (b) the 2/3-plateau appears in addition to the 1/3-plateau which also appears in the case (a). The translational symmetry of the Hamiltonian $H$ is spontaneously broken in the 2/3-plateau state as well as in the dimerized state.

KEYWORDS: $S=1/2$ distorted diamond chain, Cu3Cl6(H2O)2·2H6C4SO2, ground state phase diagram, dimerized phase, spin fluid phase, ferrimagnetic phase, ground state magnetization curve, magnetization plateau, spontaneous symmetry breaking, exact diagonalization method, density matrix renormalization group method, method of level spectroscopy

§1. Introduction

In the past years a great deal of work has been devoted to the study of quantum spin systems with competing interactions. This has stemmed largely from their being systems which include two phenomena of great interest, frustration and quantum fluctuation. Recently, magnetic properties of a trimerized $S = 1/2$ spin chain system Cu3Cl6(H2O)2·2H6C4SO2 have been experimentally studied by Ishii, Tanaka, Hori, Uekusa, Ohashi, Tatani, Narumi, and Kindo.1) (See below for the discussion on the competition of the exchange interactions in this system.) They have measured the temperature dependence of the magnetic susceptibility and also the magnetization curve at sufficiently low temperatures. Their results clearly demonstrate that the ground state of this system is nonmagnetic and that there exists the energy gap with the magnitude of about 3.9 T or 5.2 K between the ground state and a first exited magnetic state. Furthermore, the result for the magnetization measurement shows that the so-called 1/3-plateau in the magnetization curve may start from about 58T.

As has been discussed by Ishii et al.,1) the magnetic properties of Cu3Cl6(H2O)2·2H6C4SO2 can be well described by the following Hamiltonian $H$, which is a sum of the exchange interaction term $H_{ex}$ and the Zeeman term $H_Z$:

$$H = H_{ex} + H_Z,$$ (1.1a)

$$H_{ex} = J_1 \sum_{\ell=1}^{N/3} \left( \vec{S}_{3\ell-1} \cdot \vec{S}_3 + \vec{S}_3 \cdot \vec{S}_{3\ell+1} \right) + J_2 \sum_{\ell=1}^{N/3} \left( \vec{S}_{3\ell-2} \cdot \vec{S}_{3\ell-1} + \vec{S}_{3\ell-1} \cdot \vec{S}_{3\ell-2} + \vec{S}_{3\ell+1} \cdot \vec{S}_{3\ell+2} - 2 \vec{S}_3 \cdot \vec{S}_{3\ell+2} \right),$$ (1.1b)

$$H_Z = -H \sum_{\ell=1}^{N} \vec{S}_3^2,$$ (1.1c)

where $\vec{S}_3$ is the spin operator with the magnitude $S = 1/2$ for the Cu$^{2+}$ ion located at the $\ell$th site, and periodic boundary conditions $(\vec{S}_{N+1} = \vec{S}_1, \vec{S}_{N+2} = \vec{S}_2)$ are imposed. In the following discussions, the total number $N$ of spins is assumed to be a multiple of six. From the crystal structure and the lattice parameters of Cu3Cl6(H2O)2·2H6C4SO2, Ishii et al.,1) have inferred that three exchange constants, $J_1$, $J_2$, and $J_3$ are all antiferromagnetic (positive). Thus, the three interactions compete with each other. They have also inferred that...
$J_1$ is larger than $J_2$ and $J_3$. This means that the spins $S_{3\ell-1}$, $S_{3\ell}$, and $S_{3\ell+1}$ form a trimer; $J_1$ is the intratramer exchange constant, and $J_2$ and $J_3$ are the intertrimer ones. Schematical representations of the Hamiltonian $\mathcal{H}_{\text{ex}}$ are given in Figs. 1(a) and 1(b). Referring to Fig. 1(a), we may call this model the ‘distorted diamond chain model’.  

Fig. 1. (a) and (b) Two ways of representing schematically the Hamiltonian $\mathcal{H}_{\text{ex}}$. (c) and (d) The two-fold degenerate dimerized (D) states. In (a) - (d), the open circles stand for the $S=1/2$ spins, and the solid, wavy, and dotted lines correspond to the $J_1$, $J_2$, and $J_3$ interactions, respectively. Two spins surrounded by an ellipse in (c) and (d) form a singlet dimer.

In the present paper, we explore the ground-state properties of the distorted diamond chain, performing mainly numerical calculations based on the Lanczos method as well as the density matrix renormalization group (DMRG) method. We focus our attention upon the ground state phase diagram in the case of zero external magnetic field ($H=0$) and the ground state magnetization curve. We treat the case where $J_1 \geq J_3$ and $J_2 \geq 0$, noting that the $J_1 < J_3$ case is equivalent to the $J_1 > J_3$ case by interchanging the role of $J_1$ and $J_3$.

Let us now discuss three special cases where $H=0$ is assumed. First, when $J_3=0$, we can readily show by the use of the Lieb-Mattis theorem that the ground state is a ferrimagnetic (FRI) state where the magnitude $S_{\text{tot}}$ of the total spin $S_{\text{tot}} = \sum_{\ell=1}^{N} S_{\ell} \left( S_{\text{tot}} = S_{\text{tot}}(S_{\text{tot}} + 1) \right)$ is given by $S_{\text{tot}} = N/6$. We note that this value is one third of that of the maximum (ferromagnetic) value, $N/2$. Second, when $J_3=0$, the system is reduced to the $J_1$-$J_1$-$J_2$ trimerized $S=1/2$ antiferromagnetic chain; in particular, if $J_1 = J_2$, the $S=1/2$ uniform antiferromagnetic chain is obtained. Thus, the ground state is the spin fluid (SF) state with $S_{\text{tot}} = 0$, which has no excitation energy gap. Third, the case where $J_1 = J_3$ has already been investigated by Takano, Kubo, and Sakamoto. They have shown that the ground state is the FRI state with $S_{\text{tot}} = N/6$, the tetramer-dimer (TD) state with $S_{\text{tot}} = 0$, or the dimer-monomer (DM) state with $S_{\text{tot}} = 0$, depending on whether $J_2/J_1 < 0.909$, $0.909 < J_2/J_1 < 2$, $2 < J_2/J_1$. In the TD state, quadruplets $S_{3\ell-3}$, $S_{3\ell-2}$, $S_{3\ell-1}$, and $S_{3\ell}$ (or $S_{3\ell}$, $S_{3\ell+1}$, $S_{3\ell+2}$, and $S_{3\ell+3}$) of spins form singlet tetramers, and pairs $S_{3\ell+1}$ and $S_{3\ell+2}$ ($S_{3\ell+4}$ and $S_{3\ell+5}$) of spins, which we call $J_2$-pairs, singlet dimers. Thus, the TD state is two-fold degenerate. In the DM state, on the other hand, the $J_2$-pairs form singlet dimers, and the remaining monomer spins $S_{3\ell}$ are free, which leads to $2N/3$-fold degeneracy. These are schematically illustrated in Fig. 1 in ref. 6. The explicit expressions of the eigenfunctions and some physical quantities for both the TD and the DM state are given in Appendix. As has been shown by Takano et al., the commutation relation $[\mathcal{H}_{\text{ex}}, (S_{3\ell+1}^3 + S_{3\ell+2}^3)] = 0$ holds in the $J_1 = J_3$ case. Therefore, each $J_2$-pair forms a singlet or a triplet. It is interesting to note that in the DM and FRI states, all the $J_2$-pairs form the singlets and the triplets, respectively, while in the TD state the singlet and triplet $J_2$-pairs are arranged alternatively.

In a recent paper, Okamoto, Tonegawa, Takahashi, and Kaburagi have studied the ground state of the distorted diamond chain in the case of $H=0$, employing analytical methods based mainly on the bosonization technique and doing physical considerations. According to them, a tetramer in Takano et al.’s TD state is very peculiar to the $J_1 = J_3$ case, and when $J_1 > J_3$, the tetramer consisting of the spins, $S_{3\ell-3}$, $S_{3\ell-2}$, $S_{3\ell-1}$, and $S_{3\ell}$ is decomposed into two dimers, one of which consists of $S_{3\ell-3}$ and $S_{3\ell-2}$, and the other of $S_{3\ell-2}$ and $S_{3\ell-1}$. Thus, the TD state is a special case of the two-fold degenerate dimerized (D) state with $S_{\text{tot}} = 0$, shown in Figs. 1(c) and 1(d). The DM state is also peculiar to the $J_1 = J_3$ case. When $J_1 > J_3$, the monomer is no longer free and interacts with neighboring monomers through the dimer between them. Thus, the DM state is a special case of the SF state with $S_{\text{tot}} = 0$.

Summarizing these, Okamoto et al. have concluded that the ground state phase diagram of the distorted diamond chain is composed of the D and SF phases plus the FRI phase which is stable at least when $J_2$ is sufficiently smaller than $J_1$ and $J_3$. They have also shown that the transition between the D and SF phases is of the Berezinskii-Kostelitz-Thouless (BKT) type, as in the case of the $S=1/2$ antiferromagnetic chain with uniform nearest and next-nearest neighbor interactions, and have presented the ground state phase diagram determined numerically. In the region where the D state is the ground state, there exists a finite gap between the two-fold degenerate ground state and a first exited state. As can be seen from Figs. 1(c) and 1(d), the period of the translational symmetry of the D state is six, which is twice as large as that of the Hamiltonian $\mathcal{H}_{\text{ex}}$. Thus, the
spontaneous symmetry breaking occurs in the D ground state. This is consistent with the necessary condition for the appearance of the plateau in the ground state magnetization curve,

\[ n(S - m) = \text{integer}, \]  

(1.2)

obtained by Oshikawa, Yamanaka, and Affleck. Here, \( n \) and \( m \) are, respectively, the period of translational symmetry of the plateau state and the average magnetization per site in the plateau, and \( S \) is the magnitude of spins in the system. (Note that \( n = 6, S = 1/2 \) and \( m = 0 \) for the present ground D state in the \( H = 0 \) case.)

In the present paper, we discuss the derivation of the ground state phase diagram in more detail. Furthermore, we discuss the ground state magnetization curve, as mentioned before.

\section{Ground State Phase Diagram in the \( H = 0 \) Case}

Let us denote, respectively, by \( E^{(0)}(S_{\text{tot}}; N) \) and \( E^{(1)}(S_{\text{tot}}; N) \) the lowest and second-lowest energy eigenvalues for a given set of \( S_{\text{tot}} \) and \( N \) of the Hamiltonian \( \mathcal{H}_{\text{ex}} \). We have calculated numerically these eigenvalues for finite size systems with \( N = 6, 12, 18, \) and 24, employing the computer program package KOBEPACK/S10 coded by one of the present authors (M. K.) by means of the Lanczos technique. Our calculation shows that, depending on the values of \( J_1, J_2, \) and \( J_3 \), only \( E^{(0)}(0; N) \) or \( E^{(0)}(N/6; N) \) becomes minimum among \( E^{(0)}(S_{\text{tot}}; N) \)'s for all values of \( S_{\text{tot}} = 0, 1, \ldots, N/2 \). This is consistent with the fact that the ground state phase diagram is composed of the D, SF, and FRI phases, as discussed in \$1.\)

The ground state phase is the FRI phase when \( E^{(0)}(N/6; \infty) < E^{(0)}(0; \infty) \), and it is the D or the SF phase when \( E^{(0)}(N/6; \infty) > E^{(0)}(0; \infty) \). We estimate the critical value \( J_{\text{c},i}^{\text{FRI}} \) of \( J_i (i = 12, 3) \) between the former phase and one of the latter phases for a given set of the other two \( J \)'s in the following way. We first calculate numerically the value \( J_{\text{c},i}^{\text{FRI}}(N) \) which satisfies

\[ E^{(0)}(N/6; N) = E^{(0)}(0; N). \]

Then, we estimate \( J_{\text{c},i}^{\text{FRI}} \) by fitting \( J_{\text{c},i}^{\text{FRI}}(N) \)'s with 12, 18, and 24 to a quadratic function of \( 1/N^2 \), that is,

\[ J_{\text{c},i}^{\text{FRI}}(N) = J_{\text{c},i}^{\text{FRI}} + \frac{a}{N^2} + \frac{b}{N^4}, \]

(2.2)

where \( a \) and \( b \) are numerical constants.

On the other hand, in order to estimate the critical value \( J_{\text{c},i}^{\text{D}-\text{SF}} \) between the D and SF phases, we employ the method of level spectroscopy, which has been successfully applied to estimate numerically the BKT critical points in many cases. The procedure of the method is as follows. (For the physical interpretation of this procedure the reader is referred, for example, to ref. 7.) First, we introduce the singlet-singlet energy gap \( \Delta_{ss}(N) \) and the singlet-triplet energy gap \( \Delta_{st}(N) \) for the finite-\( N \) system defined by

\[ \Delta_{ss}(N) = E^{(1)}(0; N) - E^{(0)}(0; N), \]

(2.3a)

\[ \Delta_{st}(N) = E^{(0)}(1; N) - E^{(0)}(0; N), \]

(2.3b)

where \( E^{(0)}(0; N) \) is nothing but the ground state energy. Then, we calculate the value \( J_{\text{c},i}^{\text{D}-\text{SF}}(N) \) satisfying

\[ \Delta_{ss}(N) = \Delta_{st}(N). \]

(2.4)

Finally, we extrapolate the results \( J_{\text{c},i}^{\text{D}-\text{SF}}(N) \)'s to \( N \to \infty \) by the use of a polynomial of \( 1/N^2 \) to estimate \( J_{\text{c},i}^{\text{D}-\text{SF}} \).

In the practical calculations we have performed this extrapolation by using the values of \( J_{\text{c},i}^{\text{D}-\text{SF}}(N) \)'s with 12, 18, and 24 and the formula,

\[ J_{\text{c},i}^{\text{D}-\text{SF}}(N) = J_{\text{c},i}^{\text{D}-\text{SF}} + \frac{a'}{N^2} + \frac{b'}{N^4}, \]

(2.5)

with numerical constants \( a' \) and \( b' \).

We can obtain the ground state phase diagram on a exchange constant parameter plane by plotting the estimated critical points and by connecting them as smoothly as possible. The results are depicted in Figs. 2(a) and 2(b), which show, respectively, the phase diagram on the \( J_1 \) versus \( J_2 \) plane with \( J_1 \) fixed at \( J_1 = 1 \) and that on the \( J_3 \) versus \( J_1 \) plane with \( J_1 = 1 \); note that the former is a replot of Fig. 9 in ref. 7. In these phase diagrams the case where \( J_1 < J_3 \) is included to make them more complete.

The phase transition between the FRI phase and the D or the SF phase is, of course, of first order. Furthermore, when \( J_1 = J_3 \), the transition between the D and SF phases, or equivalently, that between Takano et al.'s TD and DM phases, at \( J_2/J_1 = 2 \) is also of first order. As is shown in Appendix, the ground state energy \( \varepsilon_g(N) \) per site for \( 0.99 < J_2/J_1 < 2 \) and that for the \( 2 < J_2/J_1 \) case are, respectively, given by \( \varepsilon_g(N) = E_{\text{TD}}(N)/N = -(4J_1 + J_2)/12 \) and \( \varepsilon_g(N) = E_{\text{DM}}(N)/N = -J_2/4 \), and therefore, plotting \( \partial \varepsilon_g(N)/\partial J_1 \) as a function of \( J_1 \), we have a discontinuity at \( J_1 = J_2/2 \).
neighbor interaction [see Fig.1(d)] which never lifts a two-fold degeneracy in the D ground state. Thus, no first order transition occurs in the ground state of the present chain, except for the two peculiar cases stated above.

In order to supplement the above reason discussed physically, we have calculated numerically the $J_1$-dependence of $\partial \varepsilon_s(N)/\partial J_1$ with $N = 6, 12, 18$, and 24 for the $J_2=1$ and $J_3/J_1=0.999$ case, for which the D-SF critical point is given by $J^\text{cSF}_1 \approx 0.5002$ according to the phase diagram shown in Fig. 2(b). The result is plotted in Fig. 3, together with that for the $J_2=1$ and $J_3/J_1=1$ case mentioned above. This figure demonstrates clearly that $\partial \varepsilon_s(N)/\partial J_1$ for the $J_2=1$ and $J_3/J_1=0.999$ case have no anomaly around $J_1 = 0.5$. This result suggests that we have no first order transition in the $J_1 < J_3$ case (and also in the $J_1 > J_3$ case) except for the FRI-D transition.

Fig. 3. Plot versus $J_1$ of $\partial \varepsilon_s(N)/\partial J_1$ with $N = 6$ (closed circles), 12 (open circles), 18 (pluses), and 24 (crosses) for $J_2 = 1$ and $J_3/J_1 = 0.999$, together with that (solid lines) for $J_2 = 1$ and $J_3/J_1 = 1$.

§3. Ground State Magnetization Curve

We have calculated the ground state magnetization curve of the present system, using the DMRG method proposed originally by White. Here, we describe briefly the procedure for our DMRG calculation. We employ the finite system algorithm as improved by White, which reduces substantially the required computational time. The maximum number of block states we keep in the calculation is $n_{\text{max}} = 100$, which leads to the truncation error of the order of $10^{-8}$. Comparing the calculated results for the cases where $m = 70$ and $m = 100$ block states are kept, we may conclude that the results for $m = 100$ are within an accuracy of roughly $10^{-8} \sim 10^{-5}$. Thus, we adopt these results as our final results without carrying out any $m$-extrapolation. We assume open boundary conditions for the Hamiltonian $\mathcal{H}_{\text{ext}}$, subtracting the two terms, $J_1 \vec{S}_N \cdot \vec{S}_{N+1} (\equiv J_1 \vec{S}_N \cdot \vec{S}_1)$ and $J_3 \vec{S}_N \cdot \vec{S}_{N+2} (\equiv J_3 \vec{S}_N \cdot \vec{S}_2)$, from the expression of eq. (1.1b). This is because, as is well known, open boundary conditions make the DMRG method work more effectively. It should be noted that these boundary conditions lead to an open chain which has no inversion symmetry with respect to its center.

For finite size systems with up to $N = 96$ spins, we have calculated the lowest energy eigenvalue $E^{(0)}(M; N)$ of $\mathcal{H}_{\text{ext}}$ within the subspace determined by the value $M$ of the $z$-component of $\vec{S}_{\text{tot}}$. Once the values of $E^{(0)}(M; N)$ for nonnegative $M$’s (i.e., $M = 0, 1, \cdots, N/2$) are known, the ground state magnetization curve can be obtained by plotting as a function of $H$ the average magnetization
m(N)=M/N per site determined from
\[
m(N) = \begin{cases} 
0 & \text{when } \Delta E_q^{(0)}(M, M - q; N) > H, \\
\max_N & \text{(otherwise)}, 
\end{cases} 
\]
with \(M = 1, 2, \cdots, N/2\), and \(q = 1, 2, \cdots, M\), where
\[
\Delta E_q^{(0)}(M, M - q; N) = \frac{E^{(0)}(M; N) - E^{(0)}(M - q; N)}{q}. 
\]

It is noted that \(m(N) = 0\) when \(0 \leq H \leq H_0(N)\), where \(H_0(N) = \min\{\Delta E_q^{(0)}(q, 0; N)\}\), and the saturation field \(H_s(N)\) is given by \(H_s(N) = \max\{\Delta E_q^{(0)}(N, N - q; N)\}\). The resulting magnetization curve is a stepwisely increasing function of \(H\). In particular, when the ground state in the case of \(H = 0\) is the \(S_m = 0\) state and the competition among the three interactions is not too strong, the magnetization curve has \(N/2\) steps, starting from \(m(N) = 0\) and ending at \(m(N) = 1/2\); at each step \(m(N)\) increases by \(1/N\).\(^{16}\)

Then, \(H_0(N) = \Delta E_1^{(0)}(1, 1; N) = \Delta s(1, N), \) and \(H_s(N) = \Delta E_1^{(0)}(M, M - 1; N)\). Following Bonner and Fisher’s pioneering work,\(^ {17}\) we may obtain, except for plateau regions, a satisfactorily good approximation to the magnetization curve in the thermodynamic \((N \to \infty)\) limit by drawing a smooth curve through the midpoints of the steps in the finite size results.

| \(H_0(N)\) | \(H_1/3,1(N)\) | \(H_{1/3,1}(N)\) | \(H_{1/3,1}(N)\) |
|-------------|----------------|----------------|----------------|
| 0.024525    | 0.160260       | 0.702154       |
| 0.016736    | 0.161043       | 0.699845       |
| 0.012795    | 0.160143       | 0.699090       |
| 0.00335     | 0.161210       | 0.698291       |

(a) the case (a) where \(J_1 = 1.0, J_2 = 0.8\), and \(J_3 = 0.5\).

(b) the case (b) where \(J_1 = 1.0, J_2 = 0.8\), and \(J_3 = 0.3\).

Figure 4 shows the magnetization curves calculated for \(N = 96\): Figs. 4(a) and 4(b) are, respectively, for the case (a) where \(J_1 = 1.0, J_2 = 0.8\), and \(J_3 = 0.5\), and for the case (b) where \(J_1 = 1.0, J_2 = 0.8\), and \(J_3 = 0.3\). In each case, we have a 1/3-plateau, and moreover, in the case (b), we have a 2/3-plateau in addition to this. We denote the highest and lowest values of \(H\) giving the \(p\)-plateau \((p = 1/3, 2/3)\) by \(H_{p,h}(N)\) and \(H_{p,l}(N)\), respectively. We have calculated these as well as \(H_0(N)\) and \(H_s(N)\) also for \(N = 72\) and 48 in the cases (a) and (b), and have extrapolated the results to \(N \to \infty\) to estimate the values in the thermodynamic limit. The results are tabulated in Table I. We see from this Table that, except for \(H_0(N)\), the finite size results for \(N = 96\) give good approximations to the results in the thermodynamic limit.

The 1/3-plateau state is essentially the same as the ferromagnetic state which becomes the ground state when \(J_3 > J_3^{PR} < 0.813\) in the \(J_1 = 1.0, J_2 = 0.8, \) and \(H = 0\) case. On the other hand, we see from eq. (1.2) that the periodicity \(n\) of the 2/3-plateau state should be a multiple of six, since \(S_m = 1/2\) and \(M = 1/3\). In order to check this fact, we have calculated, by means of the DMRG method, the \(\ell\)-dependence of the expectation value \(m(\ell, N)\) of \(S_\ell^z\) for the 2/3-plateau state in the case (b). The results for \(N = 96\) depicted in Fig. 5 clearly demonstrates that \(n = 6\) for this state, which means that the translational symmetry is spontaneously broken also.
in this state as in the D state. Thus, the mechanism for the appearance of the 2/3-plateau in the present case is considered to be the same as that, which has been clarified by Totsuka,\textsuperscript{18} for the appearance of the 1/2-plateau in the ground state magnetization curve of the $S = 1/2$ antiferromagnetic chain with bond alternating nearest and uniform next-nearest neighbor interactions.\textsuperscript{19} Based on this mechanism, we can use, by the method of level spectroscopy,\textsuperscript{8,11} the region, where the 2/3-plateau appears, of $J_3$ for a given set of the other two $J_i$. Leaving the details of this investigation for a forthcoming paper, we only mention here that, according to our preliminary result, the 2/3-plateau appears when $0.169 \lesssim J_3 \lesssim 0.375$ in the $J_1 = 1.0$ and $J_2 = 0.8$ case.

\section*{§4. Concluding Remarks and Discussion}

We have explored the ground state properties of an $S = 1/2$ distorted diamond chain described by the Hamiltonian $\mathcal{H}$ [see eqs. (1.1a)-(1.1c)], which models well a trimerized $S = 1/2$ spin chain system Cu$_3$Cl$_6$(H$_2$O)$_2$·2H$_2$C$_6$H$_{14}$SO$_4$. Using an exact diagonalization method by means of the Lanczos technique, we have determined the ground state phase diagram in the $H = 0$ case [Figs. 2(a) and 2(b)], composed of the D, SF, and FRI phases. As has been mentioned in §1, the ground state of Cu$_3$Cl$_6$(H$_2$O)$_2$·2H$_2$C$_6$H$_{14}$SO$_4$ is nonmagnetic with a relatively small but finite energy gap. Furthermore, the three exchange constants, $J_1$, $J_2$, and $J_3$, in this system satisfy $J_1 > J_2$, $J_1 > J_3$. From these facts together with the obtained phase diagram shown in Figs. 2(a), we may anticipate that in Cu$_3$Cl$_6$(H$_2$O)$_2$·2H$_2$C$_6$H$_{14}$SO$_4$ the values of $J_3/J_1$ and $J_3/J_2$ are in the region of $0.7 \lesssim J_3/J_1 \lesssim 0.9$ and $0.45 \lesssim J_3/J_2 \lesssim 0.65$. We have also calculated, by the use of the density matrix renormalization group method, the ground state magnetization curve for the case (a) where $J_1 = 1.0$, $J_2 = 0.8$, and $J_3 = 0.5$ [Fig. 4(a)], and the case (b) where $J_1 = 1.0$, $J_2 = 0.8$, and $J_3 = 0.3$ [Fig. 4(b)]. We have found that in the case (b) the 2/3-plateau appears in addition to the 1/3-plateau which also appears in the case (a), and have clarified that the translational symmetry of the Hamiltonian $\mathcal{H}_{\text{ex}}$ is spontaneously broken in the 2/3-plateau state.

Figure 2(a) demonstrates that the boundary line between FRI and SF phases in the limit of $0 \leq J_3 \ll J_1$ and $0 \leq J_3 \ll J_1$ is approximately given by $J_2 = J_3$. This can be understood analytically by performing a degenerate perturbation calculation around the truncation point $J_2 = J_3 = 0$ in the following way. The unperturbed Hamiltonian $\mathcal{H}_0$ is given by the sum of the Hamiltonian $h_\ell$ for the th\textsuperscript{th} trimer consisting of $S_{3\ell-1}$, $S_{3\ell}$, and $S_{3\ell+1}$:

\begin{equation}
\mathcal{H}_0 = \sum_{\ell=1}^{N/3} h_\ell, \tag{4.1a}
\end{equation}

\begin{equation}
h_\ell = S_{3\ell-1}^z S_{3\ell} + S_{3\ell}^z S_{3\ell+1}, \tag{4.1b}
\end{equation}

where the value of $J_1$ is taken to be $J_1 = 1.0$ as the unit of energy. The eigenfunctions, $\phi_\ell^{(1)}$ and $\phi_\ell^{(2)}$, of the lowest energy states of $h_\ell$, which are two-fold degenerate, are expressed, by the use of $\alpha_\ell$ and $\beta_\ell$ representing, respectively, the $S_{3\ell}^z = 1/2$ and $S_{3\ell}^z = -1/2$ single spin states, as

\begin{equation}
\phi_\ell^{(1)} = \frac{1}{\sqrt{6}} \left\{ |\alpha_{3\ell-1} \alpha_{3\ell} \beta_{3\ell+1} | - 2 |\alpha_{3\ell-1} \beta_{3\ell} \alpha_{3\ell+1} | \right\}, \tag{4.2a}
\end{equation}

\begin{equation}
\phi_\ell^{(2)} = \frac{1}{\sqrt{6}} \left\{ |\beta_{3\ell-1} \alpha_{3\ell} \alpha_{3\ell+1} | - 2 |\beta_{3\ell-1} \beta_{3\ell} \beta_{3\ell+1} | \right\}. \tag{4.2b}
\end{equation}

Restricting only to these two eigenfunctions, we can represent $S_{3\ell-1}^z$, $S_{3\ell}^z$, and $S_{3\ell+1}^z$ in terms of the pseudo $S = 1/2$ operator $\vec{T}_\ell$ associated with the th\textsuperscript{th} trimer:

\begin{equation}
S_{3\ell-1}^z = -\frac{2}{3} T_\ell^z, \quad S_{3\ell}^z = \frac{2}{3} T_\ell^z, \quad S_{3\ell+1}^z = \frac{2}{3} T_{\ell+1}^z, \tag{4.3a}
\end{equation}

\begin{equation}
S_{3\ell}^z = \frac{1}{3} T_\ell^z, \quad S_{3\ell}^z = -\frac{1}{3} T_\ell^z, \quad S_{3\ell+1}^z = \frac{1}{3} T_{\ell+1}^z, \tag{4.3b}
\end{equation}

\begin{equation}
S_{3\ell+1}^z = \frac{2}{3} T_\ell^z, \quad S_{3\ell+1}^z = \frac{2}{3} T_{\ell+1}^z, \tag{4.3c}
\end{equation}

where the $T_\ell^z = 1/2$ and $T_\ell^z = -1/2$ states correspond to $\phi_\ell^{(1)}$ and $\phi_\ell^{(2)}$, respectively. Substituting eqs. (4.3a)-(4.3c) into the second ($J_2$) and third ($J_3$) terms in the right-hand side of eq. (1.1b) leads to the following effective Hamiltonian $\mathcal{H}_{\text{eff}}$:

\begin{equation}
\mathcal{H}_{\text{eff}} = \frac{4}{9} (J_2 - J_3) \sum_{\ell=1}^{N/3} \vec{T}_\ell \cdot \vec{T}_{\ell+1} \tag{4.4}
\end{equation}

with $\vec{T}_{(N/3)+1} = \vec{T}_1$. We see from this equation that the ground state of the pseudo $\vec{T}_\ell$ spin system is the ferromagnetic or the SF state depending upon whether $J_2 > J_3$ or $J_2 < J_3$, the former and the latter corresponding, respectively, to the FRI and SF states in the original $\vec{S}_\ell$ spin system. Thus, it is shown that the $J_2 = J_3$ line yields the boundary line between FRI and SF phases in the limit of $0 \leq J_2 \ll J_1$ and $0 \leq J_3 \ll J_1$. 

![Figure 5](image-url) Fig. 5. Plot versus $\ell$ of $m(\ell, N)$ with $N = 96$ for the 2/3-plateau state in the case (b) where $J_1 = 1.0$, $J_2 = 0.8$, and $J_3 = 0.3$. Solid lines are guides to the eye.
Ground State Properties of an $S=1/2$ Distorted Diamond Chain

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Appendix

Here, we discuss the $J_1=J_3$ case.\(^6\) Let us introduce the following states:

$$[\ell, \ell + 1, \ell + 2, \ell + 3] = \frac{1}{\sqrt{12}} \{ |\alpha\ell\beta\ell+1\beta\ell+2\beta\ell+3\rangle + |\beta\ell\beta\ell+1\alpha\ell+2\alpha\ell+3\rangle + |\alpha\ell\beta\ell+1\alpha\ell+2\beta\ell+3\rangle + |\beta\ell\beta\ell+1\alpha\ell+2\alpha\ell+3\rangle - 2 |\alpha\ell\beta\ell+1\beta\ell+2\alpha\ell+3\rangle - 2 |\beta\ell\beta\ell+1\alpha\ell+2\beta\ell+3\rangle \}, \quad (A.1a)$$

$$[\ell, \ell + 1] = \frac{1}{\sqrt{2}} \{ |\alpha\ell\beta\ell+1\rangle - |\beta\ell\alpha\ell+1\rangle \}, \quad (A.1b)$$

$$|\ell\rangle = |\alpha\ell\rangle \quad \text{or} \quad |\beta\ell\rangle. \quad \quad (A.1c)$$

Then, the eigenfunctions $\Phi_{TD}^{\pm}(N)$ of the TD state for the finite-$N$ system is given by

$$\Phi_{TD}^{\pm}(N) = \frac{1}{\sqrt{2}} \{ \Phi_{TD}^{(1)}(N) \pm \Phi_{TD}^{(2)}(N) \} \quad (A.2)$$

with

$$\Phi_{TD}^{(1)}(N) = [1, 2] [3, 4, 5, 6] \cdots [N-5, N-4] [N-3, N-2, N-1, N], \quad (A.3a)$$

$$\Phi_{TD}^{(2)}(N) = [N, 1, 2, 3] [4, 5] \cdots [N-6, N-5] [N-4, N-3, N-2, N-1]. \quad (A.3b)$$

Note here that $\langle \Phi_{TD}^{(1)}(N)|\Phi_{TD}^{(2)}(N)\rangle = 0$. On the other hand, the eigenfunction $\Phi_{DM}(N)$ of the DM state for the finite-$N$ system is

$$\Phi_{DM}(N) = [1, 2] [3] \cdots [N-3, N-2] [N]. \quad (A.4)$$

It is easy to show that the energies of the TD and DM states for the finite-$N$ system are given, respectively, by $E_{TD}(N) = -\frac{N}{12}(4J_1 + J_2)$ and $E_{DM}(N) = -\frac{N}{6}J_2$. We note that $E_{DM}(N)$ is the total energy of $\frac{N}{6}$ independent singlet dimers mentioned in §1, while $E_{TD}(N)$ is the total energy of $\frac{N}{6}$ independent singlet dimers plus that of $\frac{N}{6}$ independent singlet dimers. Furthermore, it is also straightforward to calculate the spin pair correlation functions in the TD and DM states, defined, respectively, by

$$\omega_{TD}(\ell, \ell'; N) = \langle \Phi_{TD}^{\pm}(N)|\vec{S}_{\ell} \cdot \vec{S}_{\ell'}|\Phi_{TD}^{\pm}(N)\rangle, \quad (A.5a)$$

$$\omega_{DM}(\ell, \ell'; N) = \langle \Phi_{DM}(N)|\vec{S}_{\ell} \cdot \vec{S}_{\ell'}|\Phi_{DM}(N)\rangle. \quad (A.5b)$$

When $N = 12, 18, \cdots$, the function $\omega_{TD}(\ell, \ell'; N)$ for $\ell \leq \ell^{20}$ takes nonzero values independently of $N$ only in the following cases:

$$\omega_{TD}(\ell, \ell; N) = \frac{3}{4}, \quad (A.6a)$$

$$\omega_{TD}(3\ell - 2, 3\ell; N) = \omega_{TD}(3\ell, 3\ell + 2; N) = -\frac{1}{12}, \quad (A.6b)$$

$$\omega_{TD}(3\ell - 1, 3\ell; N) = \omega_{TD}(3\ell, 3\ell + 1; N) = -\frac{1}{12}, \quad (A.6c)$$

$$\omega_{TD}(3\ell + 1, 3\ell + 2; N) = -\frac{1}{12}, \quad (A.6d)$$

$$\omega_{TD}(3\ell, 3\ell + 3; N) = \frac{1}{24}. \quad (A.6e)$$

On the other hand, the nonzero values of $\omega_{DM}(\ell, \ell'; N)$ for $\ell \leq \ell^{20}$ are

$$\omega_{DM}(\ell, \ell; N) = \frac{3}{4}, \quad (A.7a)$$

$$\omega_{DM}(3\ell + 1, 3\ell + 2; N) = -\frac{3}{4}, \quad (A.7b)$$

which are independent of $N (=6, 12, 18, \cdots)$.

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