Numerical exact diagonalization study of triangulated kagome Heisenberg spin system

M Isoda¹, H Nakano² and T Sakai²,³

¹ Department of Physics, Faculty of Education, Kagawa University, Saiwai-cho 1-1, Takamatsu 760-8522, Japan
² Graduate School of Material Science, University of Hyogo, 3-2-1 Kouto, Kamigori-cho, Akou-gun, Hyogo 678-1297, Japan
³ Japan Atomic Energy Agency, SPring-8, Sayo 679-5148, Japan

E-mail: misoda@ed.kagawa-u.ac.jp

Abstract. The thermodynamic properties and the magnetization under magnetic field at zero temperature of the spin-1/2 Heisenberg model on triangulated kagome lattice, which composed of two sublattices, are investigated by numerical exact diagonalization method for 18 and up to 27 spin clusters, respectively. The temperature dependence of magnetic susceptibility may be reproduced qualitatively with the weak ferromagnetic intersublattice nearest neighbor exchange coupling constant $J_{AB}$ as proposed by previous studies, although it is quantitatively insufficient in comparison with the experimental result. The magnetization under magnetic field shows the 5/9 plateau for every examined values of $J_{AB}$, but 1/3 plateau, visible in the experiment, may be reproduced only for not so weak antiferromagnetic case of $J_{AB}$. This discrepancy for $J_{AB}$ in those two qualities has also been recognized in previous studies on classical spin models and is not still resolved even for the present quantum spin system.

1. Introduction

A new type of two-dimensional spin frustration system has been found, which is referred to "triangle-in-triangle" or "triangulated" kagome lattice system. Therein the small triangles are formed in every triangle forming kagome lattice. The lattice structure is realized by Cu²⁺ ions with spin-1/2 in compounds Cu₉X₂(cpa)₆‧nH₂O (cpa=carboxypentonic acid; X=F,Cl,Br)[1-3]. In the lattice structure, lattice sites occupied by Cu²⁺ ions are classified into two sublattices, a sublattice A forming smaller triangles and another sublattice B forming large triangles constructing a kagome lattice as shown in Fig.1. The unit cell of this lattice structure includes nine sites, as shown in Fig.1(a), and includes six A-sublattice sites and three B-sublattice ones.

All these compounds have a magnetic ground state, but any phase transition to long-range order has not been observed down to 1.7K[1]. The measurements of magnetic susceptibility and magnetization under magnetic field have shown the peculiar properties. On the magnetic susceptibility its inverse reveals the clear bend deviating from high temperature Curie-Weiss like behavior[1-3]. On its properties, the Weiss temperature changes from -230K at high temperature to 6K at below 50K and equivalently the slope of inverse magnetic susceptibility becomes to more than five times. On the latter, the magnetization measured under magnetic field up to 38T shows the tendency of saturation to one third of full polarization value[2,3].
Figure 1. Lattice structure of triangulated kagome lattice. The 18 site cluster used for calculations is denoted by green-broken lines (a), where the unit cell of 9 sites is also shown by enclosing by brown-solid lines. Symbols A(solid circle) and B(open circle) denote A- and B-sublattice, respectively. The 27 site cluster used for calculation is shown in (b) enclosing by green-broken lines.

On the other side, theoretically, Ising model[4,5] and Ising-Heisenberg mixed model[6,7], where Heisenberg spin is resided on A-sublattice and Ising spin on B-sublattice, are treated exactly through a mapping to the ferromagnetic Ising model on the kagome lattice. In these studies, two types of magnetic interaction are taken into account, one for A-A interactions among small triangle $J_{AA}$ and the other for nearest neighbor(nn) A-B interactions $J_{AB}$. The interaction $J_{AA}$ is believed to be strongly antiferromagnetic[1,4,5,6], but $J_{AB}$ still remains uncertainly even in its sign[5], in concern with the experiment of Cu$_9$X$_2$(cpa)$_6$·nH$_2$O. As an example, in comparison of thermodynamics of experimental results with those of Ising model, the temperature dependence of magnetic susceptibility multiplied by temperature, $\chi T$, supports a ferromagnetic coupling between A and B intersublattice nn spins $J_{AB}$[1,5], but oppositely the reproduction of 1/3 plateau in antiferromagnetic case in Ising model[2,5] might indicate the antiferromagnetic interaction of $J_{AB}$. Preceding these works, spin-1/2 quantum Heisenberg model was examined by the variational procedure based on the Bogoliubov inequality by Strečka[8]. In these theoretical investigations[6,8], the exchange coupling $J_{AB}$ has been chosen as ferromagnetic and $J_{AB}/J_{AA} \simeq -0.025$. However the determination both of sign and magnitude of $J_{AB}$ still remains without giving the consistent explanation for both experiments of magnetic susceptibility and magnetization.

According to the ESR investigation[9], it is reported that the $g$-value of Cu$^{2+}$ in Cu$_9$X$_2$(cpa)$_6$ looks unusually isotropic. Then it is highly interested in how the magnetic susceptibility as a function of temperature and the 1/3 plateau in magnetization are varied in isotropic quantum spin model against those in the Ising and Ising-Heisenberg model.

In this study, the quantum Heisenberg model will be studied for the thermodynamics and the magnetization under magnetic field with the variation of exchange coupling constants. We perform the numerical exact diagonalization study for the clusters of the lattice of $N = 18$ for finite temperature properties and up to $N = 27$ spins for the zero temperature property with periodic boundary condition. The chosen system sizes, which are twice and three times of lattice sites of unit cell, might be too small to derive reliable results for thermodynamic limit. However,
the numerical diagonalization method may be a most trustworthy or only one numerical method for two-dimensional frustrated system, to our knowledge.

2. Numerical calculations

2.1. Thermodynamics

The present quantum spin Heisenberg model upon the underlying triangulated kagome lattice is given as

\[ \mathcal{H} = J_{AA} \sum_{<i,j>} \mathbf{S}_i^A \cdot \mathbf{S}_j^A + J_{AB} \sum_{<i,j>} \mathbf{S}_i^A \cdot \mathbf{S}_j^B - H \sum_i (\mathbf{S}_i^{z,A} + \mathbf{S}_i^{z,B}), \]

where \( J_{AA} \) is the nn coupling constant among A-sublattice spins and \( J_{AB} \) the nn one between A-sublattice spin and B-sublattice one. The summation in the first term should be performed for nn pairs of sites \( i \) and \( j \), both belonging to A-sublattice, but it in the second term for nn pairs between two spins belonging to different sublattice. The quantum spin-1/2 operator on site \( i \) of sublattice-A is depicted as \( \mathbf{S}_i^A \) and the superscript \( z \) on the spin operator denotes the \( z \)-component of its operator. \( H \) is a magnetic field applied along \( z \) direction. Through the paper, we use the conventional energy scale, \( J' \equiv J_{AB}/J_{AA} \) and \( h \equiv H/J_{AA} \), and set as \( J_{AA} = 1 \), assuming an antiferromagnetic interaction. The temperature \( T \) is also measured in this units of energy.

The eigen values for the Hamiltonian are obtained by using the TITPACK. For getting the thermodynamic quantities of magnetic susceptibility \( \chi \) and specific heat \( C \), the full spectra of the small finite number of spins of \( N = 18 \) have been derived by the Householder algorithm. Based on the obtained spectra, the specific heat and the magnetic susceptibility are calculated through the usual canonical thermal average procedure for various values of \( J' \) and the results are shown in Fig.2(a) and (b), respectively.

In Fig.2(a), the specific heat shows two or three peaks (including shoulders in the cases of weakly antiferromagnetic \( J' = 0.1,0.3 \)). Such multiple peak structure is also found in kagome and triangular lattice quantum spin systems\[10\]. The highest-temperature peaks scarcely shift on the temperature axis regardless of \( J' \). This fact has also been suggested in kagome and triangular lattice as due to a short range correlation\[10\]. The experimental specific heat measurement for \( \text{Cu}_9\text{X}_2(\text{cga})_6 \cdot n\text{H}_2\text{O} \) has not yet done as far as we know. The comparison our calculated result with experimental one has to be postponed.

In Fig.2(b), the inverse magnetic susceptibility and the magnetic susceptibility multiplied by temperature are shown. For the ferromagnetic interaction \( J_{AB}(<0) \) even for small value as \( J' = -0.025 \), the inverse magnetic susceptibility seems to vanish at \( T = 0 \) suggesting the magnetic ground state, but in antiferromagnetic cases \( \chi^{-1} \) divergently increase toward zero temperature implying the singlet ground state. A prominent character is a downturn deviation below about \( T \leq 0.5 \) from high temperature Curie-Weiss like behavior which is distinctly observed in weak intersublattice coupling cases of \( |J'| \ll 1 \). Such character has been found in Monte Carlo (MC) simulation study for Ising spin\[5\] and has also been indicated by us previously as an inherent character of triangle-based frustrated lattice system for both models of Heisenberg\[10\] and Ising\[11\]. In those references, below the temperature, where \( \chi^{-1} \) bends downward with decreasing temperature, a formation of a quantum doublet state on a triangle trimer of A-sublattice in triangulated kagome lattice might be developed as the short range correlation for weak intersublattice coupling \( |J'| \ll 1 \). This quantum trimer formation below the characteristic temperature may be represented as a classical-quantum crossover at the temperature. The higher temperature peak of specific heat at around \( T \sim 0.5 \) emerged for every cases in Fig.2(a) may be related the characteristic temperature found in magnetic susceptibility\[10,11\].

The magnetic susceptibility multiplied by temperature, \( \chi T \), as a function of temperature is also shown in Fig.2(b). In the ferromagnetic intersublattice coupling, the quantity \( \chi T \) has a
Figure 2. The specific heat $C$ as a function of logarithmic temperature (a) and the inverse magnetic susceptibility $\chi^{-1}$ (referred the left side axis) and the magnetic susceptibility multiplied by temperature $\chi T$ (referred the right side axis) as a function of $T$ (b) calculated by numerical exact diagonalization method for various values of $J'$ on 18-spin cluster with periodic boundary condition. In both figures, the curves $C$ and $\chi^{-1}$ for $J' = -1, -0.1, -0.025, 0.1, 0.3, 1$ are depicted by red-square, green-diamond, blue-circle, black-reverse triangle, brown-cross and dark green-triangle, which are in order upward in (b). In (b), $\chi T$ for $J' = -0.025$ and 0.3 are depicted by a blue solid line and a brown dash-dot-dash line, respectively.

minimum and then steeply increase with decreasing temperature, but it monotonically decreases down to zero for antiferromagnetic $J_{AB}(< 0)$. This difference in the temperature dependence of $\chi T$ between two cases different in sign of $J'$ has been found for the Ising spin on the triangulated kagome lattice[5]. The experimental observation[1] shows a clear minimum well corresponding with the solid line in Fig.2(b) depicted as an example for weak ferromagnetic intersublattice coupling. The value of $J' = -0.025$ is an evaluated one from experimentally observed magnetic susceptibility[6,8]. This fact seems to support the weak ferromagnetic coupling between A and B sublattices.

2.2. Magnetization under magnetic field

In next place, we investigate the magnetization under magnetic field at zero temperature. For the purpose, we use the Lanczos algorithm for $N = 18$ and 27 spin clusters with the periodic boundary condition.

The obtained results for magnetization normalized by the full polarized value in each system size, $m$, as a function of magnetic field $h$ are devoted in Fig.3(a) and (b). An example for the case, where the 1/3 plateau is seen over a recognizable range in ratio to the field strength for full polarization $h \sim 2$ in the case of Fig.3(a), is shown in Fig.3(a) for $J' = 0.5$. The black solid line denotes the result for system size $N = 18$ and the red dash-dot-dash line for $N = 27$. In the case of $J' = 0.2$ (figure is not shown), the range of 1/3 plateau shrinks to about 0.2 sufficiently smaller than the range of 5/9 plateau of about 1.2 and the full polarization field of 1.7. As another example, the magnetization for an intermediate ferromagnetic coupling $J' = -0.5$ is shown in Fig.3(b) for the same system sizes. Other some values for weak ferro- and antiferromagnetic interactions such as $J' = \pm 0.025$ were also examined for N=18 and 27 clusters. These cases of $J' = \pm 0.025$ are carefully examined, because the ferromagnetic case $J' = -0.025$ corresponds to the value evaluated from the experiment of magnetic susceptibility and may well explain the temperature dependence of $\chi T$ qualitatively as discussed in previous subsection. For the value of $J'$, the 5/9 plateau is attained by very weak magnetic field and survives firmly up to full polarization field of about 1.5, but unfortunately 1/3 plateau does not realize over recognizable range.
Figure 3. The magnetization $m$ in units of fully polarized value under magnetic field $h$. (a) is for $J' = 0.5$ as an example of intermediate antiferromagnetic intersublattice coupling. The black solid lines depict for $N = 18$ and the red dashed lines for $N = 27$. (b) is given for $J' = -0.5$ as an example of other $J'$ values in comparison with (a).

The emergence of 5/9 plateau has been recognized for corresponding value of $J' = -0.025$ in Ref.8 for variational procedure for the same model as given in eq.(1). On the other side, the Ising spin MC simulation [5] has shown the 1/3 plateau for $J' = 0.5$. The present result well corresponds with these previous studies.

The spin state in 5/9 plateau found in this study may be readily understood for the present case of $J' \ll 1$. Under the antiferromagnetic coupling $J_{AA}$, every A-site triangle is regarded as an effective 1/2-spin. Thus six spins in A-site per unit cell contribute a magnetization $m_A = 2/9$ under finite magnetic field. Three spins in B-site, each bonded to four A-site spins weakly by $J_{AB}$, are aligned parallel to the magnetic field, contributing $m_B = 1/3$ per unit cell. Both of these gives $m = m_A + m_B = 5/9$. While, on the 1/3 plateau, the quantum spin state can not yet be determined through the present numerical study. As giving a brief insight, an classical Ising model has been examined. It is stabilized at the magnetic field of $h \leq 2J'$ against the 5/9 plateau state only for the antiferromagnetic $J_{AB} (J' > 0)$. There the spontaneous symmetry-breaking state, where a single B-site spin in a unit cell directs antiparallel to the magnetic field and four A site spins coupled to this B-site spin are parallel to the magnetic field, maintaining $S_z = 1/2$ for every A site trimer. This estimation of the transition field between 1/3 and 5/9 plateau states seems to give a good estimation of the numerical results on quantum spins in Fig.3 (a), together with the sign of exchange coupling $J_{AB}$.

3. Conclusions and discussions

We have examined the spin-1/2 quantum Heisenberg spin model on the triangulated kagome lattice, by taking account of the intrasublattice nn interaction in A-sublattice and the intersublattice nn one, by a numerical exact diagonalization method. The specific heat and the magnetic susceptibility have been calculated as a function of temperature for cluster-size of $N = 18$ and the magnetization at zero temperature as a function of magnetic field for $N = 18$ and 27.

On the specific heat, two or more peaks have been detected and the temperature at the highest temperature peak is insensitive on the intersublattice nn coupling. The peak might give the sign of the development of short range correlation up to nearly nn distance. Such multiple peaks are also detected in kagome and triangular lattice Heisenberg systems[10]. The experimental measurement of specific heat has not been performed up to now, as far as we know, and then is highly desired.

The magnetic susceptibility shows the clear difference in the low temperature behavior
depending on the sign of intersublattice coupling constant $J_{AB}$. For ferromagnetic case ($J_{AB} < 0$), the inverse magnetic susceptibility vanishes to zero, but for antiferromagnetic case ($J_{AB} > 0$) it increases divergently as approaching zero temperature. A characteristic feature is found in the case of weak intersublattice coupling $|J'| \ll 1$, the downward deviation from high temperature Curie-Weiss like temperature dependence below about $T \simeq 0.5$. In our result, the slope of inverse magnetic susceptibility increases up to about twice for the typical case of $J' = -0.025$, which is the value proposed in some preceding issues[6,8]. However the experimental result shows larger change in slope more than four or five times[2,3], suggesting the remarkable quantitative difference. On another aspect, the magnetic susceptibility multiplied by temperature $\chi T$ for $J' = -0.025$ shows minimum and then increases as decreasing temperature, giving the qualitative consistency with the experiment[1].

The magnetization under magnetic field at zero temperature has revealed the 5/9 plateau for every examined cases of $|J'| < 1$, but the 1/3 plateau visible in the experiment[2,3] has been reproduced not so weak $J'$ under the assumption of $|J'| < 1$. The plateau ranges in both plateaus are not modified remarkably by changing the system size between $N = 18$ and 27 or by adding the small value of further neighbor interactions, although figures are not given. The elucidation of the quantum spin states of 1/3 and 5/9 plateaus should be performed in future.

The investigated quantum Heisenberg model has not suggested the qualitative difference in the temperature dependence of susceptibility and the magnetic field dependence of magnetization from the classical Ising[4,5] and the Ising-Heisenberg mixed models[6,7]. The contradiction both in its sign and magnitude of $J_{AB}$ for the interpretation of two physical quantities discussed above is not still resolved and remains as a future problem. The careful estimation of further neighbor exchange interaction by the inspection of exchange path might be required or the additional mechanism like Dzyaloshinskii-Moriya interaction might be needed[12].

According to the recent survey on the magnetic plateau in quantum spin system, the plateau in spin-1/2 Heisenberg kagome system is realized like a ramp with finite slope[13]. In the triangulated kagome system, whether the observed plateaus are real plateaus or should be called as a ramp is a future problem.

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