The specific heat and magnetic properties of a spin-1/2 ladder including butterfly-shaped molecular cages

Hamid Arian Zad

Young Researchers and Elite Club, Mashhad Branch, Islamic Azad University, Mashhad, Iran

Abstract

The specific heat, structural characterization, and magnetic property studies of a new spin configuration of butterfly-shaped molecular cages are reported. The model introduced here is an infinite spin ladder-type of spin-1/2 particle cages for which unit blocks consist of four pivalate ligands bridge wing-body spin centers within the butterflies, two of them bridge body-body, and two of them bridge between the butterflies. Spins on the bodies of butterflies have XXZ Heisenberg interaction with two extra spin-1/2 particles in the cage. Hence, there are six interstitial spins and four nodal spins with Ising interaction per block. To obtain the partition function of this model, we use the transfer matrix approach and investigate magnetization process as well as the specific heat. Interestingly, we see a vivid magnetization plateau in $M \approx 0.85M_s$ that is strongly dependent on the magnetic field and anisotropy. Moreover, some unexpected phenomena are observed in the low temperature limit, such as anomalous triple-peak in the specific heat function which gradually turns to a double-peak upon increasing the magnetic field and/or anisotropic Heisenberg coupling, due to the ferromagnetic phase predomination.

Keywords: Magnetization, Specific heat, Spin ladder

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1. Introduction

Obtaining a profound perception about interacting quantum many-body systems like low-dimensional magnetic materials with competing interactions or geometrical frustration have become an intriguing research object in a number of subjects such as condensed matter physics, material science and inorganic chemistry. In these particular areas many investigations concerned about quantum ferrimagnetic chains have been carried out, due to that they present a relevant combination of ferromagnetic and antiferromagnetic phases. As a result of zero and finite temperature phase transitions, these materials present various ground states and thermal properties \[1, 2, 3, 4, 5, 6, 7, 8, 9\]. Spin ladders can be counted as attractive models among these systems. The latter consist of square-shaped topological units along the ladder \[9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19\].

During the past two decades it has become possible to synthesize a large variety of compounds such as \(A_3Cu_3(PO_4)_3\) with \(A = Ca, Sr\) \[20\], \(Cu_3Cl_6(H_2O)_2 \cdot 2H_2C_4SO_2\) \[21, 22\], the ferromagnetic diamond chains in polymeric coordination compound \(Cu_3(TeO_3)_2Br_2\) \[23\] and the natural mineral azurite \((Cu_3(CO_3)_2(OH)_2)\) \[24, 25\], which can be properly introduced in terms of Heisenberg spin models. Recently, A. Baniodeh et al. verified experimentally the ground state as well as low temperature thermodynamic properties of material \([Fe_{10}Gd_{10}(Me - tea)_{10}(Me - teaH)_{10}(NO_3)_{10}] \cdot 20MeCN\) as a saw-tooth spin chain in detail \[26\]. Motivated by some compounds such as \(Bi_2Fe_4O_9\), F. C. Rodrigues et al. designed an interesting spin model for one stripe of the Cairo pentagonal Ising-Heisenberg lattice, then they investigated in detail zero-temperature phase transition for such model in Ref. \[27\].

Quantum phase transitions have been one of the most interesting topics of strongly correlated systems during the last decade. It is basically a phase transition at zero temperature where the quantum fluctuations play the dominant role \[18, 19, 28, 29, 30, 31, 32, 33\]. Further studies to investigate these quantum spin models have provided precise outcomes for the ground-state phase transition in the presence of an external magnetic field, which can be induced through
the exchange couplings [34, 35, 36, 37]. It is quite noteworthy that the ground state and thermodynamics of the spin ladders constituted by higher spins have been particularly examined as well [4, 36].

Magnetization curves of low-dimensional quantum ferromagnets/antiferromagnets are topical issue of current research interest, in order to they often exhibit intriguing features such as magnetization plateaus. The spin-1/2 quantum chain in a transverse magnetic field [38, 39], the spin-1/2 quantum spin ladder [18, 40], spin-1/2 Ising-Heisenberg diamond chain in a transverse magnetic field [2, 7, 8, 30, 31, 32] are a few exactly solved quantum spin models for which magnetization varies smoothly with rising absolute magnetic field until reaches its saturation magnetization. For the small quantum spin clusters, V. Ohanyan et al. investigated general non-commutativity features of the magnetization operator and Hamiltonian [41].

In solid state physics and Material science, most of the theoretical treatments are based on numerical techniques. Hence, an analytical approach to describe the ground state, magnetic and thermodynamic properties of the quantum spin systems such as the magnetization and specific heat, is definitely required. A promising method is the transfer-matrix formalism which has widely been applied to a number of strongly correlated systems at zero temperature as well as low temperature for studying the ground and low-lying state properties of spin models. In the present paper we rigorously describe how the transfer matrix method may be used to calculate the thermodynamic properties of a new spacial spin-1/2 ladder with Ising-Heisenberg interactions.

The specific heat of magnetic materials usually exhibits a remarkably temperature dependence, the reason is that the overall thermal behavior is the result of various specific factors such as lattice vibrations, magnetic excitations and etc. Such a parameter can be typically approximated under a certain thermodynamic condition by the Schottky theory [9, 42]. The associated round maximum of the specific heat, the so-called Schottky peak, has been experimentally detected in various magnetic compounds [43, 44, 45].

In the present work, we are going to examine the magnetization and the
specific heat for the interstitial half-spins of a spin ladder-type of decanuclear spin-1/2 particle cages in the presence of an external magnetic field at low temperature. The considered ladder with periodic boundary conditions is shown in Fig. 1. Heretofore, the structural characterization, synthesis and magnetic properties of transition metal (M = Co, Ni) phosphonate based cages have been reported in Ref. [46] (and some references therein). Indeed, they investigated single molecular magnetic materials containing phosphorus. The unit blocks of our favorite spin-1/2 model is similar to the model used for spin-1 Ni compound-4 in Ref. [46]. The great motivation to consider such a particular spin ladder with analytical Hamiltonian is to investigate theoretically some thermodynamic parameters like magnetization and specific heat of a so close spin model to real magnetic materials in terms of spin configuration that exhibits stimulating behaviors against magnetic field at low temperature.

The paper is organized as follows. In Sec. 2 we introduce the exactly solvable model. In Sec. 3 we present the thermodynamic solution of the model with in the transfer-matrix formalism. In this section, we also numerically discuss
the magnetization and specific heat of the model in the presence of an external
homogeneous magnetic field. Some conclusions and future outlooks are briefly
mentioned in Sec. 4.

2. Model and exact solution within the transfer matrix formalism

The Hamiltonian of the spin model shown in Fig. 1 can be expressed as

\[ H = \sum_{i=1}^{N} J_{Is}(S_{1,i}^z S_{2,i}^z + S_{5,i}^z S_{6,i}^z) + \sum_{j=1}^{4} J_{H}(S_{j,i} \cdot S_{j+2,i})\Delta + 
\]

\[ J_{Is} \left[ (\sigma_{1,i}^z + \sigma_{1,i+1}^z)(S_{1,i}^z + S_{2,i}^z) + (\sigma_{2,i}^z + \sigma_{2,i+1}^z)(S_{5,i}^z + S_{6,i}^z) + 
\]

\[ \sigma_{1,i}^z \sigma_{2,i}^z + \sigma_{2,i}^z \sigma_{2,i+1}^z \right] - g \mu_B B_z \left( \sum_{j=1}^{6} S_{j,i}^z + \frac{1}{2} \sum_{j=1}^{4} \sigma_{j,i}^z \right), \]

where \( N \) is the number of blocks and

\[ (S_{j,i} \cdot S_{j+2,i})\Delta = S_{j,i}^x S_{j+2,i}^x + S_{j,i}^y S_{j+2,i}^y + \Delta S_{j,i}^z S_{j+2,i}^z, \]

(2)
corresponds to the interstitial anisotropic Heisenberg spins coupling \( J_{H} \) and \( \Delta \),
while the nodal spins localized on the \( i \)-th rung are representing by Ising-type
exchanges \( J_{Is} \). \( 2S^\alpha = \sigma^\alpha \) for which \( \sigma^\alpha = \{ \sigma^x, \sigma^y, \sigma^z \} \) are Pauli operators (with
\( \hbar = 1 \)). \( B_z \) is applied homogeneous magnetic field in the \( z \)-direction. The
gyromagnetic ratio is taken to be \( g = 2.42 \) (\( \mu_B = 1 \)) in the plots drawn in this
paper.

The cornerstone of our further calculations is based on the commutation
relation between different block Hamiltonians \([h_i, h_j] = 0\), which will allow us
to characterize the partition function of the ladder under consideration and rep-
resent it as a product over block partition functions

\[ Z = Tr \left[ \prod_{i=1}^{N} \exp(-\beta h_i) \right], \]

where \( \beta = \frac{1}{k_B T} \), \( k_B \) is the Boltzmann’s constant and \( T \) is the temperature. In the
two qubit standard eigenbasis of the composite spin operators \( \{ \sigma_{1,i}^\alpha, \sigma_{2,i}^\alpha, \sigma_{1,i+1}^\alpha, \sigma_{2,i+1}^\alpha \} \)
of the two consecutive rungs of the block \( i \), we can consider the following matrix
representation to formulate partition function \( Z \) as

\[ Z = Tr \left[ (\sigma_{1,i,1}^\alpha \sigma_{2,i,1}^\alpha | T | \sigma_{1,i,2}^\alpha \sigma_{2,i,2}^\alpha) \cdots (\sigma_{1,N}^\alpha \sigma_{N,N}^\alpha | T | \sigma_{2,N+1}^\alpha \sigma_{2,N+1}^\alpha) \right], \]

(3)
where $\sigma^z_{j,i} = \pm 1$, and under the periodic boundary conditions we have $\sigma_{j,N+1} = \sigma_{j,1}$. We can figure out the $4 \times 4$ transfer matrix $T$ as follows

$$T(i) = \langle \sigma^z_1,i \sigma^z_i \vert \exp(-\beta h_i) \vert \sigma^z_1,i+1 \sigma^z_i \rangle = \sum_{k=1}^{64} \exp \left[ -\beta \mathcal{E}_k(\sigma^z_1,i,\sigma^z_i,\sigma^z_{i+1},\sigma^z_{i+1}) \right].$$

(4)

$\mathcal{E}_k$ denotes eigenvalues of the unit block Hamiltonian. Since we seek eigenvalues of the transfer matrix in the thermodynamic limit $N \to \infty$, the largest eigenvalue $\Lambda_{\text{max}}$ has the most effect on the thermodynamic properties of the system, whereas other three smaller eigenvalues are almost effect less and their contribution can be completely neglected. Hence, the free energy per block can be obtained from the largest eigenvalue of the transfer matrix (4) as

$$f = -\frac{1}{\beta} \lim_{N \to \infty} \ln \frac{1}{N} Z = -\frac{1}{\beta} \ln \Lambda_{\text{max}}.$$

(5)

3. Thermodynamic parameters

Now one can utilize the thermodynamic relations to evaluate various quantities that would be investigated. Specific heat, entropy, and magnetization per block can be defined as

$$M = -\left( \frac{\partial f}{\partial B} \right)_T, \quad S = -\left( \frac{\partial f}{\partial T} \right)_B, \quad C = -T \left( \frac{\partial^2 f}{\partial T^2} \right)_B.$$

(6)

Figure 2 illustrates the magnetic field dependences of magnetization in the unit of its saturation. Figure 2(a) demonstrates the magnetization per block against the magnetic field at low temperature, and Figs. 2(b) and 2(c) display this quantity versus the magnetic field at higher temperatures. It is quite obvious that the magnetization curve shows a plateau at $M \approx 0.85 M_s$ ($M_s$ is saturation magnetization). The plateau gets wider upon increasing the coupling constant $\Delta$, namely, for higher values of $\Delta$, magnetization jumping from the plateau $M \approx 0.85 M_s$ to the saturation occurs at higher absolute values of the magnetic field. Interestingly, as the temperature increases the plateau gradually disappears until at high temperature the magnetization behaves as a smooth logarithmic curve without plateau. It is also noteworthy that with increase of
Figure 2: Magnetization $M$ as a function of dimensionless external magnetic field $B$ for fixed values of $J_s = -4$, $J_H = 6$ and three different dimensionless coupling constant $\Delta = 0.2$, 1 and 2, at (a) low temperature $T = 0.2$, (b) $T = 1.0$, and (c) $T = 5.0$. 
Figure 3: The specific heat of the introduced spin ladder as a function of the temperature for various fixed values of the magnetic field $B = 0.1, 1$ and $2$, where other parameters are taken as $\Delta = 2$, $J_{Is} = -4$ and $J_H = 6$. The inset displays the temperature dependence of specific heat in the presence of a weak magnetic field for three different dimensionless coupling constant $\Delta = 0.2, 1$ and $2$.

the temperature the magnetization curves coincide together, in this situation the coupling constant $\Delta$ acts as a resistance factor of this coincidence.

Now we are going to examine the exchange coupling $\Delta$ and the magnetic field variations of the specific heat versus the temperature. To this end, we display in Fig. 3 the temperature dependence of the specific heat for the model under consideration for the several fixed values of the magnetic field. When the temperature growths from zero the specific heat increases till a small peak arises ($T < 1$) in weak magnetic field (red curve). By inspecting Figs. 2 and 3 and a precise comparing, one can realize that this peak arises when the magnetization plateau appears. With further increase of the temperature, this thermodynamic quantity exhibits a steep increase where second peak is created, and in turn third peak appears that is the largest one rather than other. The latter peak becomes inferior upon increasing the magnetic field. With further increase of the mag-
netic field the value of such a peak gradually decreases until becomes smaller than second peak and moves toward higher temperatures. This phenomenon is in accordance with the ferromagnetic-antiferromagnetic quantum phase transition. As an outstanding result, here the specific heat shows three separated peaks that are strongly dependent on the magnetic field. Besides, first and second peaks undergo considerable changes under magnetic field variations, as a matter of fact, they merge together upon increasing magnetic field.

The inset shows the temperature dependence of the specific heat for various fixed values of the coupling constant $\Delta$ in the vicinity of a weak magnetic field ($B = 0.2$). Obviously, the specific heat curves coincide at high temperature when a weak magnetic field is applied. At low temperature, this quantity depicts different behavior with respect to the coupling constant $\Delta$ changes. To clarify this point, one can see that when $\Delta$ decreases the specific heat loses its smallest peak, whereas keeps other two peaks. This adventure indicates that the system undergoes one another quantum phase transition that may occur under this specific thermodynamic condition. At high temperature the specific heat decreases and gradually goes to zero.

4. Conclusions

In this paper, we have theoretically investigated thermodynamic properties of a new spin ladder-type consisting of spin-1/2 particle cages for which unit blocks include four pivalate ligands bridge wing-body spin centers within the butterflies. We consider two extra interstitial half-spins in each cage which have XXZ Heisenberg interaction with spins localized on the bodies of butterflies. To do so, we have examined the magnetization process and specific heat of this model by means of solution within the transfer-matrix formalism.

In terms of numerical investigations, we understood that the magnetization has a plateau at $M \approx 0.85M_s$. This plateau rigorously depends on the temperature and $\Delta$. Furthermore, it has been demonstrated that in the weak magnetic field, the specific heat has three separated peaks. Magnetic field variations can
remarkably alter the shape of these peaks as well as the coupling constant $\Delta$ changes. Namely, the magnetic field increment ($\Delta$ decrease) leads to vanishing the smallest peak, hence the specific heat has just a double-peak. The thermal excitation of low-lying energy causes this anomalous double-peak. Thus, changes of the specific heat may exhibit ferromagnetic-antiferromagnetic phase transition.

Further applications of the method discussed in this paper pave the way to set and interpret the numerical and analytical expressions for utilizing transfer matrix formalism in realistic scenarios and comparison of the results with the experimental data obtained from investigating novel magnetic materials with the similar spin configuration, which can play an important role in the understanding of complicated magnetic materials and their thermodynamic properties.

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