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MAGNETIC PROPERTIES OF GENERALIZED POLYALLYL SPIN CHAIN

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The work is devoted to the theoretical simulation of low-temperature magnetic properties of generalized polyallyl spin chain with the antiferromagnetic coupling of the neighboring spins (GPSC) - spin model of a family of quasi-one dimensional molecular ferrimagnets. First, the exact energy spectra of Heisenberg spin Hamiltonians of the finite lattice clusters of GPSC with the spins of the main chain s=1/2 and pendant spins $\check{s}$=1 have been studied by means of the exact diagonalization method. The calculations were performed for different positive values of the coupling parameters for neighboring spins of the main chain of GPSC clusters. On the base of the above exact energy spectra and the Boltzmann distribution law the field dependencies of magnetization of finite lattice clusters are calculated numerically at different temperatures. In the result, for low temperatures the presence of intermediate plateau in field dependencies of the cluster magnetization has been shown. These calculations demonstrated the stabilization of the intermediate magnetization plateau with the growth of the spin coupling along the main chain of GPSC clusters. In addition, the numerical study of temperature dependence of zero field magnetic susceptibility of 12- spin clusters of GPSC gives the results which are similar to the 1D model of molecular ferrimagnets like necklace spin ladder.

Similar calculations of the magnetization profile were performed for infinite Heisenberg –Ising GPSC model with Ising type of the antiferromagnetic interactions between the neighboring spins of the main chain. The classical transfer- matrix method was used for this purpose. In the result, it was shown the presence of an intermediate plateau in the low-temperature magnetization profile of infinite chain model and the increase of the plateau size with increasing of the Ising coupling between the spins of the main chain.

Keywords: polyallyl spin chain, intermediate magnetization plateau.

Introduction

The polyallyl spin chain was one of the first many electron models of organic chain ferrimagnets [1]. It consists of three-centered unit cells, in each center of which is the spin s=1/2. On the other side, there is a big family of mixed-spin chain quantum ferrimagnets with two kinds of antiferromagnetically coupled spin centers [2, 3]. Recently, a new interesting model of quasi-1D mixed-spin ferrimagnets was proposed and studied [4]. This is a decorated spin chain with back side spins describing cyanide-bridged coordination compounds with pendant magnetic ions. It can be treated as a chain fragment of decorated rectangular lattice, such as can be viewed as a generalization of a polyallyl spin chain. The magnetic properties of these spin systems may be governed by an external stress—say a mechanical force or a magnetic field. Since the exchange coupling of localized spin moments of ions in polymeric complexes of transition metals is mediated by ligands, its modification due to changes in the chemical surroundings may also affect to the magnetic properties of the above complex compounds.

The purpose of our work is the numerical simulation of low-temperature magnetic properties of generalized polyallyl spin chain at different values of coupling parameters in order to study the possible effect of the variation of chemical structure of the corresponding magnet on their magnetic properties.

Isotropic spin systems

Consider the following generalized polyallyl spin chain (GPSC) shown on Fig. 1, formed by the spin-1/2 main chain and pendant spins with $\check{s}$>1/2.

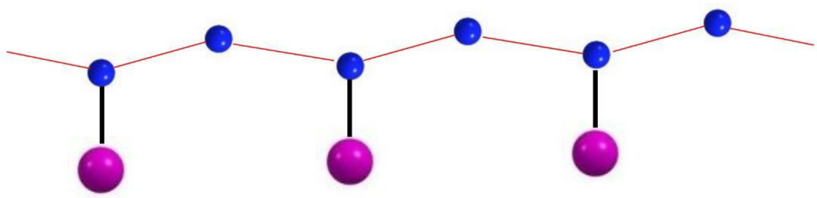

Figure 1. Fragment of GPSC lattice (big purple bolls correspond to lateral spins $\check{s}$)

In the nearest neighbors approximation the Heisenberg spin Hamiltonian of this chain has the following form:

$$\mathbf{H}_1 = \sum_{k=1}^{L} \{ \overline{\mathbf{S}}_{1,k} \mathbf{S}_{2,k} + J \mathbf{S}_{2,k} (\mathbf{S}_{3,k-1} + \mathbf{S}_{3,k}) - h(\overline{\mathbf{S}}_{1,k}^z + \mathbf{S}_{2,k}^z + \mathbf{S}_{3,k}^z) \} \tag{1}$$

where $\overline{\mathbf{S}}_{1,\check{s}}$ is the spin $\check{s}$ operator located on the first lattice site of the k-th three-site unit cell, $\mathbf{S}_{2(3),k}$ is the spin ½ operator located on the second (third) site of the same unit cell; J is the coupling parameter for the interaction of neighbor spins s=1/2 of the main chain, h is the external magnetic field in the energy units.

At J=h=0 the above chain transforms into a set of L non-interacting two-center fragments with the ground state spin s_0=$\check{s}$-1/2 and the energy ε_0=-($\check{s}$+1)/2, and a set of L isolated spins s=1/2. At J>0 according to the generalized Lieb - Mattis theorem [5, 6], the ground state of this Hamiltonian is nondegenerate and corresponds to the full spin S_0=$L\,\check{s}$. Therefore, in thermodynamic limit at J>0 the Hamiltonian (1) has a macroscopic ground state spin. Also, we can expect that the Hamiltonian (1) has no gap in the exact energy spectrum at $L\rightarrow\infty$. For nonzero values of J the exact energy spectrum of the Hamiltonian (1) is unknown. Therefore, a detailed study of the magnetic properties of this model can be performed in modified spin wave approximation like work [7] or by numerical approaches like the exact diagonalization study for finite lattice clusters and the density matrix renormalization group theory [8]. In our work, we used exact diagonalization method to estimate the field dependences of the magnetization of linear lattice clusters consisting of 12 spins with pendant spins $\check{s}$=1 at different values of the coupling parameter J. The results of our calculations are shown in Fig.2 and Fig.3 for two different values of the temperature T.

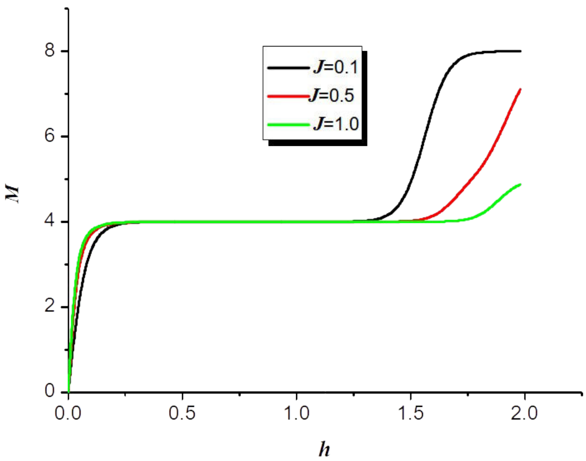

Figure 2. Field dependence of GPSC cluster magnetic susceptibility at three different values of coupling J and temperature $k_B T$=0.05.

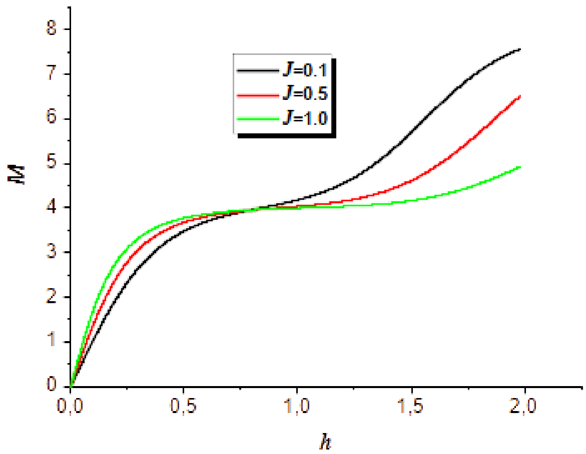

Figure 3. Field dependence of GPSC cluster magnetic susceptibility at three different values of coupling J and temperature $k_B T$=0.2.

According to our simulation (Fig.2 and Fig.3), at different values of coupling 0.1< J <1 there is an intermediate plateau in magnetization profile which corresponds to the maximum value of z projection of the ground state spin in the absence of an external magnetic field. The appearance of such a plateau can be explained by a gap in the exact excitation spectrum in the sector with total spin S>S_0. The increase of temperature leads to partial destruction of intermediate magnetization plateaus.

We also calculated the temperature dependence of the magnetic susceptibility of the GPSC fragment consisting of 4 unit cells (12 spins). Below there are the results of these study for the temperature dependence of the product of the magnetic susceptibility per one unit cell and temperature (Fig. 4).

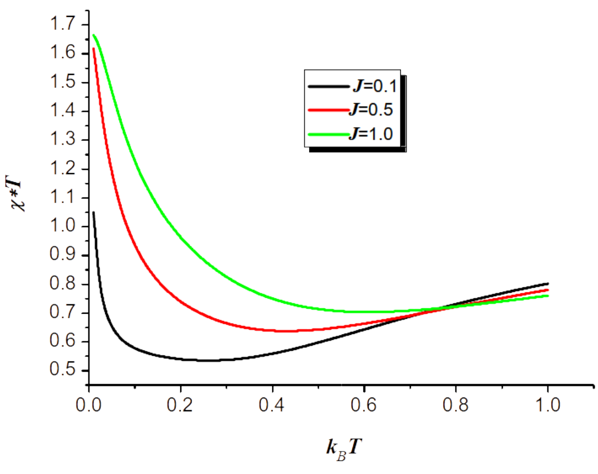

Figure 4. Temperature dependence of product χ*T at different values of coupling J.

These numerical results are in agreement with the similar temperature dependences of the magnetic susceptibility of another 1D ferrimagnet - necklace spin ladder [9].

Anisotropic GPSC

The study of anisotropic analogs of GPSC may have a big interest for different practical applications. Therefore, in our work we carried out a theoretical modeling of the magnetic properties of the anisotropic analog of the Hamiltonian (1), for which the interactions along the main GPSC chain are described by the Ising Hamiltonian. This corresponds to the absence of quantum fluctuations in the main spin chain. Due to this, the spin operators s=1/2 localized on the third sites of the unit cells can be replaced by quantum numbers $\sigma_k=\pm 1/2$ and write the corresponding anisotropic analog of the Hamiltonian (1) as follows:

$$\mathbf{H}_2 = \sum_{k=1}^{L} \{\bar{\mathbf{S}}_{1,k}\mathbf{S}_{2,k} + J\mathbf{S}^z_{2,k}(\sigma_{k-1}+\sigma_k) - h(\bar{\mathbf{S}}^z_{1,k} + \mathbf{S}^z_{2,k} + \sigma_k)\} \tag{2}$$

Here, for simplicity, we consider the case of equal g-factors for all the spins of GPSC.

Using the Peron-Frobenius theorem, similarly to [5], we can show that at h=0 the ground state of the Hamiltonian (2) belongs to the subspace of states with a full spin projection on the axis z: $S^z=L\,\check{s}$.

The algebraic structure of the Hamiltonian (2) allows to calculate of the energy spectrum and thermodynamic characteristics of this model for any number of unit cells. Thus, we can show that the ground state energy of the Hamiltonian (2) at small positive values of the external magnetic field is described by the formula $E_0=L\varepsilon_0$, where ε_0 is the ground state energy of the Hamiltonian.

$$\mathbf{H}_3 = \bar{\mathbf{S}}_1\mathbf{S}_2 + J\mathbf{S}^z_2 - h\bar{s} \tag{3}$$

At large values of the external magnetic field, the ground state is characterized by the ferromagnetic ordering of all spins and corresponds to the energy $E_0=L[\check{s}+J - 2(\check{s}+1)h]/2$.

To calculate the magnetic characteristics of the model (2) at arbitrary values of the field h and nonzero temperature, we used the classical transfer matrix approach of the magnetism theory [10]. The technical details of the corresponding numerical calculations are similar to the works [11, 12]. The transfer matrix of the model (2) can be built on the basis of the exact energy spectrum of the next Hamiltonian:

$$\mathbf{H}(\sigma_1,\sigma_2) = \bar{\mathbf{S}}_1\mathbf{S}_2 + J\mathbf{S}^z_2(\sigma_1+\sigma_2) - h(\bar{\mathbf{S}}^z_1 + \mathbf{S}^z_2 + \sigma_1/2 + \sigma_2/2) \tag{4}$$

The symmetric transfer matrix $\mathbf{T}(h)$ for the Hamiltonian (2) has the size 2×2 and at $L\to\infty$ its maximal eigenvalue $\lambda(h)$ determines the statistical sum of our model. The model magnetization can be found numerically as a field derivative of $\lambda(h)$. The results of the calculations of the field dependence of the specific magnetization of GPSC are shown in Fig. 5. These calculations demonstrate the presence of the intermediate magnetization plateau similarly to the calculations for finite clusters of the isotropic model and the increase of the size of this plateau with increasing of spin coupling in the main chain of GPSC.

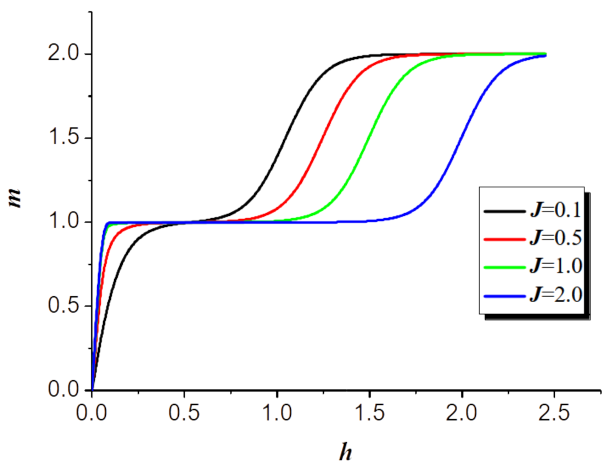

Figure 5. Field dependencies of the magnetization per the unit cell of the GPSC at different values of the spin coupling parameter for the main chain J and temperature k_BT=0.1.

Conclusions

The exact diagonalization study of the low –temperature magnetic properties of the generalized polyallyl spin chain was performed on the base of the of exact diagonalization calculations for the finite chain clusters. It is shown the presence of an intermediate plateau in the chain magnetization profile and the increase of the plateau size with increasing of the spin coupling in the main chain of the model.

The transfer matrix method is used to obtain the magnetization profile of an infinite anisotropic GPSC described by the Heisenberg-Ising model and to show the existence of an intermediate magnetization plateau which depends on the spin coupling in the main chain similar to the results of our simulation for isotropic model.

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М.А.Похмура, В.О.Черановський. Магнітні властивості узагальненого поліалільного спинового ланцюжка.

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Робота присвячена теоретичному моделюванню низькотемпературних магнітних властивостей узагальненого поліалільного спінового ланцюжка з антиферомагнітним зв'язком сусідніх спінів (УПСЛ) - спінової моделі сімейства квазіодновимірних молекулярних ферімагнетиків. Спочатку методом точної діагоналізації досліджено точні енергетичні спектри спінових гамільтоніанів Гейзенберга скінченних решіткових кластерів GPSC зі спінами *s*=1/2 головного ланцюжка та підвісними спінами *š*=1. Розрахунки виконано для різних позитивних значень параметрів зв'язку для сусідніх спінів основного ланцюга кластерів УПСЛ. На основі наведених точних енергетичних спектрів та закону розподілу Больцмана чисельно розраховані польові залежності намагніченості кластерів кінцевої решітки при різних температурах. У результаті для низьких температур показано наявність проміжного плато в польових залежностях намагніченості кластера. Ці розрахунки продемонстрували стабілізацію проміжного плато намагніченості із зростанням спінового зв'язку вздовж основного ланцюга кластерів УПСЛ. Крім того, чисельне дослідження температурної залежності магнітної сприйнятливості нульового поля 12-спінових кластерів УПСЛ дає результати, подібні до одновимірної моделі молекулярних ферімагнетиків на зразок спінової драбини- намиста.

Аналогічні розрахунки профілю намагніченості виконано для нескінченної моделі Гейзенберга-Ізінга УПСЛ із ізінгівським типом антиферомагнітних взаємодій між сусідніми спінами основного ланцюжка. Для цього було використано класичний метод трансфер-матриці. У результаті було показано наявність проміжного плато в низькотемпературному профілі намагніченості моделі нескінченного ланцюжка та збільшення розміру плато зі збільшенням ізінговського зв'язку між спінами основного ланцюжка.

Ключові слова: поліалільний спіновий ланцюжок, проміжне плато намагніченості.

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