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ENERGY SPECTRUM AND MAGNETIC PROPERTIES OF THE DECORATED SPIN LADDER MODELS OF NANOMAGNETS ON THE BASE OF POLYMERIC TRANSITION METAL COMPOUNDS

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The work is devoted to the theoretical study of the energy spectrum and low-temperature magnetic properties of the decorated spin-ladder model with the polyacene topology and the three types of the site spins. On the base of cluster expansion technique an approximate analytical treatment of lowest part of the energy spectra of two isomeric ladder structures was given. It is shown that the ladder model with singlet ground state is more stable than its isomeric analog with the macroscopic ground state spin. In addition, the numerical study of field dependence of low-temperature magnetization of 8- spin clusters of both ladder models was performed by means of exact diagonalization method. On the base of these results, it was shown the presence of an intermediate plateau in low-temperature magnetization profile of the above spin ladder models.

Keywords: *mixed spin ladder model, intermediate magnetization plateau.*

Introduction

Low-dimensional quantum spin systems have become the subject of immense interest during the last few years, since their properties are strongly affected by quantum fluctuations. The design of highly ordered systems of paramagnetic metal centers is a current subject with the aim of providing magnetic materials exhibiting spontaneous magnetization. The most known mixed spin systems correspond to rather big family of so-called bimetallic magnets like $NiCu(pbaOH)(H_2O)_3{\cdot}2H_2O$, where pba is 1,3-propylenebis(oxamato) [1]. There are also trimetalic polymeric systems like Prussian blue analog $(Ni_x\ Mn_{1-x})_{1.5}[Cr(CN)_6]\ nH_2O$ (x~0.4). The exchange interaction of localized spin moments of metal centers in polymeric complexes is mediated by ligands [1-3]. Hence, the chemical modification of the ligands effects on the magnetic properties of these complexes. It open the way for targeted design of new magnetic materials for different technological applications. On the other side, numerous experimental realizations of mixed spin compounds motivate their study by means of different methods of solid state physics and quantum chemistry.

In this study the main attention will be given to the consideration of two isomeric decorated spin ladder systems formed by three different site spins s=1/2, 1 and 3/2. These spin systems have the topology of polyacene lattice described by effective Heisenberg spin Hamiltonians – spin formalism of well- known Valence Bond method of quantum chemistry. The exact energy spectra of these systems are unknown. For approximate evaluation of the lowest part of the energy spectra of our ladder models with the infinite number of unit cells we use simple two block cluster expansion technique [4]. In addition, in order to get information about the magnetic properties of the above spin systems, we use the exact diagonalization study for the Hamiltonians of small lattice clusters at different values of spin coupling parameters.

Heisenberg spin lattice model with three different types of the site spins

Let us start our consideration with two simple lattice systems formed by three different site spins s=1/2, 1 and 3/2 with uniform antiferromagnetic coupling of neighboring spins (Fig.1)

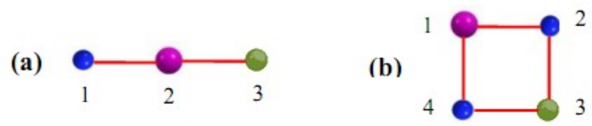

Figure 1. Three and four spin systems formed by three different types of site spins. Here crimson, green and blue balls correspond to the site spins s=3/2, 1 and 1/2, respectively.

In nearest neighbor approximation these two systems can be described by the following Heisenberg spin Hamiltonians with coupling constant $\boldsymbol{J}$=1:

$$\mathbf{H}_a = \mathbf{S}_1\mathbf{S}_2 + \mathbf{S}_2\mathbf{S}_3, \qquad \mathbf{H}_b = \mathbf{S}_1\mathbf{S}_2 + \mathbf{S}_2\mathbf{S}_3 + \mathbf{S}_3\mathbf{S}_4 + \mathbf{S}_1\mathbf{S}_4 \qquad (1)$$

These Hamiltonians can be rewritten in the scalar product of two new spin operators with obvious energy spectra:

$$\mathbf{H}_a = \mathbf{S}_2\mathbf{S}_A, \quad \mathbf{S}_A = \left(\mathbf{S}_1 + \mathbf{S}_3\right), \qquad \mathbf{H}_b = \mathbf{S}_A\mathbf{S}_B, \quad \mathbf{S}_A = \left(\mathbf{S}_1 + \mathbf{S}_3\right), \mathbf{S}_B = \left(\mathbf{S}_1 + \mathbf{S}_3\right)$$

It can be easily shown that the ground state of $\mathbf{H}_a$ is singlet (nonmagnetic) with the energy E_0=-15/4. For the Hamiltonian $\mathbf{H}_b$ the ground state spin is S_0=3/2 and the corresponding energy is E_0=-7/2. These results are in agreement with the extended Lieb theorem [5-7] for bipartite spin lattice systems.

Let us now consider more complicated two-leg spin-1/2 ladder model with the legs decorated by two different site-spins s=1 and s=3/2, as it is shown below on Fig.2.

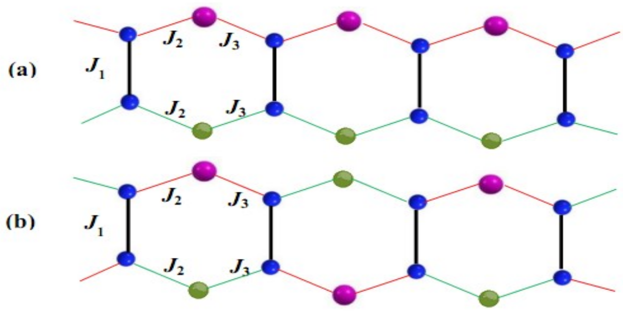

Figure 2. Two isomeric mixed spin ladder systems.

The above two spin ladder systems are described by Heisenberg spin Hamiltonian with antiferromagnetic coupling of neighbor site spins (J_1 - J_3>0). For example, the Hamiltonian of the system 2(a) with periodic boundaries has the form

$$\mathbf{H}_a = \sum_{l=1}^{L}\left[J_1\mathbf{S}_{2,l}\mathbf{S}_{3,l} + \mathbf{S}_{1,l}\left(J_2\mathbf{S}_{2,l} + J_3\mathbf{S}_{2,l+1}\right) + \mathbf{S}_{4,l}\left(J_2\mathbf{S}_{3,l} + J_3\mathbf{S}_{3,l+1}\right)\right] \qquad (2)$$

where L is the total number of 4-spin unit cells and all spins are enumerated along the unit cells; $\mathbf{S}_{2,i}$-is the spin-1/2 operator, located on l-th unit cell of the ladder; $\mathbf{S}_{1,i}$ and $\mathbf{S}_{3,i}$ - are the operators of spin s=3/2 and s=1, respectively.

The spin ladder systems 2(a) and 2(b) have bipartite symmetry and, according to the generalized Lieb theorem, the corresponding Heisenberg Hamiltonian have nondegenerate ground state with total spin S_0=L/2 for model 2(a), and S_0=0 for model 2(b) with even number of 4-spin structural units (unit cells in the case of model 1(a)). In addition, according to [7, 8] the ground state of the model 2(a) should have ferrimagnetic spin ordering. Note also, that for the model 1(a) similar to the perturbative treatment from [9, 10], we may expect an appearance of intermediate plateau in field dependence of magnetization at least in the case of the weak interaction between unit cells(J_3<<J_2).

In order to get more information about the lowest energy states of the above spin ladder models 2(a) and 2(b), we performed numerical calculations of the exact energy spectra of finite ladder clusters formed by 8 site spins (two unit cells for model 2(a)) at some values of model parameters. For this purpose we used basis of spin configurations (3) having the form of direct products of eigenfunctions of the site spins. It can be easily shown, that these functions are the eigenfunctions of the operator of z-projection of the ladder total spin M:

$$\Phi_{\{s,m\}}(M)=\prod_{k=1}^{N}\Omega(s_k,m_k) \tag{3}$$

where N is a total number of site spins; multiindex $\{s, m\}$ enumerates all possible combinations of site quantum numbers (s_k, m_k). $\Omega(s_k, m_k)$ is the eigenfunction of the site spin operator $\mathbf{S}_k^z$ with the specified values of spin s and its z-projection m.

For example:

$$\Omega(1/2,1/2)=\alpha \qquad \Omega(3/2,1/2)=\frac{1}{\sqrt{3}}(\alpha\alpha\beta+\alpha\beta\alpha+\beta\alpha\alpha)$$

where for site spin s=1/2 $\mathbf{S}_k^z\alpha=1/2\alpha$, $\mathbf{S}_k^Z\beta=-1/2\beta$.

The exact diagonalization study was performed for all fixed values of quantum number M separately. Due to the scalar character of the ladder Hamiltonians, the comparison of the energy levels for each subspace with specified value of M permits us to obtain the lowest energy levels with fixed value of total spin S. We also used the result of our analytical consideration of the three-spin clusters (Fig.1) for testing of the above numerical scheme.

Some results of the exact diagonalization study of the ladder clusters for model 2(a) with J_1=J_2=1 are presented on Table 1.

Table 1. The lowest energies of the 8-spin clusters of the ladder models 2(a).

	S=0	S=1	S=2	S=3	S=4
J_3=1	-5.385	-5.959	-5.854	-5.664	-4.681
J_3=0.5	-4.889	-5.238	-5.130	-4.943	-3.911
J_3=0.1	-4.781	-4.856	-4.753	-4.617	-3.491

According this study the ground state of the cluster 2(a) corresponds to the total spin S=1 in agreement with the extended Lieb theorem. Let $E_{\min}(1)$ and $E_{\min}(0)$ are the corresponding exact energies of the triplet ground state and lowest singlet excited state. Similar to [9, 10], we can suppose that these two lowest energy states can be described by the following effective spin s=1/2 Hamiltonian:

$$\mathbf{H}_2=J_{eff}\mathbf{S}_1\mathbf{S}_2+R+2\varepsilon_0 \tag{4}$$

where ε_0 is the ground state energy of the 4-spin unit cell. The parameters J_{eff} and R can be estimated from the obvious system of linear equations

$$\begin{cases} E_{\min}(1)=2\varepsilon_0+R+J_{eff}/4 \\ E_{\min}(0)=2\varepsilon_0+R-3J_{eff}/4 \end{cases} \tag{5}$$

In the result, we obtain:

$$J_{eff}=E_{min}(1)-E_{min}(0)<0\ ,\quad R=(3E_{min}(1)+E_{min}(0)-8\varepsilon_0)/4 \tag{6}$$

The results of the corresponding exact diagonalization study for 8 –spin cluster of the ladder model 2(b) at J_1=J_2=1 are presented below on Table 2.

According to these results, J_{eff} = $E_{\min}(1)$ - $E_{\min}(0)$ > 0, which is in accordance with the extended Lieb theorem. Similar to the above analysis it can be shown that the lowest part of the energy spectrum of ladder model 2(b) can be described by the effective spin s=1/2 Hamiltonian of the form (6) with antiferromagnetic coupling.

This means that the mixed spin ladder model 2(a) and 2(b) should have gapless energy spectrum in the thermodynamic limit $L\to\infty$ and different types of the ground states with S=L and S=0, respectively.

Table 2. The lowest energies of the 8-spin clusters of the ladder models 2(b)

	S=0	S=1	S=2	S=3	S=4
$\boldsymbol{J}_3$=1	-5.986	-5.938	-5.833	-5.645	-4.640
$\boldsymbol{J}_3$=0.5	-5.259	-5.211	-5.106	-4.925	-3.873
$\boldsymbol{J}_3$=0.1	-4.867	-4.836	-4.742	-4.609	-3.478

It is of interest, that the ground state energy of the triplet cluster (ladder 2(a)) is bigger than the ground state energy of singlet cluster (ladder 2(b)) at all the values of parameter $\boldsymbol{J}_3$ studied. This result may be treated as a bigger chemical stability of the singlet ladder cluster in comparison with isomeric triplet cluster of our mixed spin ladder. Moreover we can estimate relative stability of the infinite spin ladder systems 2(a) and 2(b) using formulas (5) and (6). For this purpose let us estimate the difference in the corresponding ground state energies E_0^a and E_0^b per 4-spin structural unit. After simple manipulation we have:

$$\Delta E = E_0^a - E_0^b = E_{\min}^a(1) - E_{\min}^b(1) + \left(E_{\min}^b(1) - E_{\min}^b(0)\right)\ln 2 \quad (7)$$

where $E_{\min}^a(1), E_{\min}^b(1), E_{\min}^b(0)$ are the lowest triplet and singlet energies of 8-spin clusters of the spin ladders 2(a) and 2(b), respectively. These energies are presented in Table1 and Table2. In the result, for example, for $J_1=J_2=J_3=1$ $\Delta E\sim 0.0123>0$. This means that for this set of coupling parameters the infinite spin ladder (2b) is more stable than the isomeric ladder structure (2a).

We also used exact diagonalization approach for the study of low-temperature magnetization profiles of 8- spin clusters of the ladder models 2(a) and 2(b). For this purpose we used simplified version of the models with equal *g*-factors for each type of site-spins. In the result, for each energy state of the ladder, the projection of total spin on the direction of the external magnetic field is a good quantum number. Therefore, external magnetic field change the energy of the state with specified value of z-projection of total spin M by the quantity $\Delta E=-hM$, where h is a strength of magnetic field in energy units. Using standard Boltzmann distribution we have the following expression for ladder magnetization per 4-spin structural unit:

$$\bar{M}(h,T) = \sum_i M_i \exp(-(E_i - hM_i)/k_B T) / \sum_i \exp(-(E_i - hM_i)/k_B T) \quad (8)$$

where k_B –is a Boltzmann constant.

The results of this numerical simulation for model 2(a) are presented below (Fig.3).

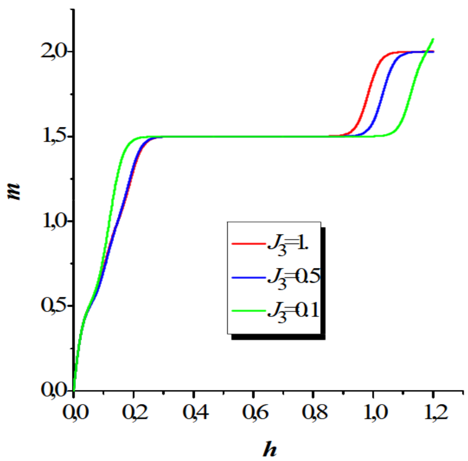

Figure 3. Field dependence of magnetization per 4 spin unit cell m of the cluster 2(a) at $J_1=J_2=1$, k_BT=0.02.

According to these calculations the low temperature magnetization profile of 8-spin cluster of model 2(a) has intermediate magnetization plateau at m=1.5. The appearance of this plateau can be explained by relatively big energy gap between states with S=3 and lowest state with S=4. The size of this plateau is increased with the decrease of the interaction between unit cells (coupling constant J_3). We have also small peculiarity in behavior of the magnetization profile near the point m=0.5 which can be explained by the triplet ground state of the ladder cluster studied.

Finally, in the result of our approximate analytical consideration and numerical simulation we may suppose that the ladder model 2(a) has intermediate plateau in low-temperature magnetization profile at arbitrary values of coupling parameter J_3 from the interval (0, J_2).

The results of similar numerical study of magnetization profile of the ladder cluster of the model 2(b) are presented below on Fig.4.

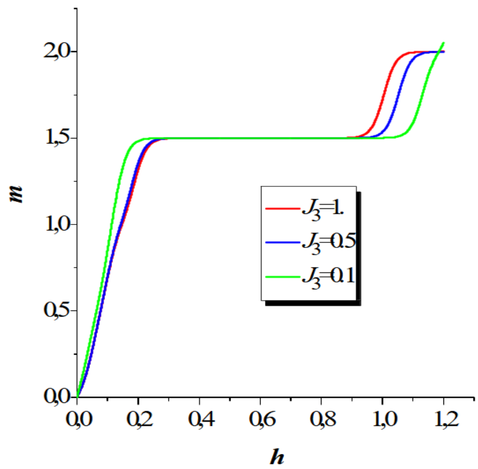

Figure 4. Field dependence of magnetization m per 4 spin structural unit of the cluster 2(b) at J_1= J_2=1, k_BT=0.1.

According to this simulation, the magnetization profile of the ladder cluster 2(b) has also intermediate magnetization plateau at m=1.5. In contrast to the cluster 2(a) there are not magnetization peculiarities at m=0.5. On the other side, according to our two block cluster expansion analyses, the initial part of the low-temperature magnetization profile of infinite ladder model 2(b) should be close to the magnetization profile of antiferromagnetic Heisenberg spin-1/2 chain without magnetization plateau.

Conclusions

The exact diagonalization study of the energy spectra and low –temperature magnetic properties of the two isomeric mixed tree-spin ladder models of polyacene topology was performed for 8-spin lattice clusters. On the base of this study we derived simple two block cluster expansion technique and showed that that the ladder model with the singlet ground state is more stable than its isomeric analog with the macroscopic ground state spin. We also found the presence of an intermediate plateaus in the low temperature magnetization profiles of the above spin ladder models.

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В.О. Черановський, В.В. Мухомодярова. Енергетичний спектр і магнітні властивості декорованих спінових сходових моделей наномагнетиків на основі полімерних сполук перехідних металів.

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Робота присвячена теоретичному дослідженню енергетичного спектру та низькотемпературних магнітних властивостей декорованої спін-сходової моделі з поліаценовою топологією та трьома типами вузлових спінів. На основі методу кластерного розширення проведено наближену аналітичну обробку нижньої частини енергетичних спектрів двох ізомерних сходових структур. Показано, що сходова модель із синглетним основним станом більш стабільна, ніж її ізомерний аналог із макроскопічним спіном основного стану. Крім того, методом точної діагоналізації проведено чисельне дослідження польової залежності низькотемпературної намагніченості 8-спінових кластерів обох сходових моделей. На основі цих результатів було показано наявність проміжного плато в низькотемпературному профілі намагніченості наведених вище моделей спінових сходів.

Ключові слова: змішана спінова сходова модель, проміжне плато намагніченості.

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