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MAGNETIC PROPERTIES OF MODIFIED DIAMOND SPIN CHAIN

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The work is devoted to the theoretical study of the energy spectrum and magnetic properties of the modified antiferromagnetic spin (1/2, s) diamond chain. This is a frustrated mixed spin system with the unit cells formed by two spin ½ and one spin s>1/2. On the base of extended Lieb theorem we proved the possibility of the appearance of quantum phase transitions mediated by ratio of coupling parameters at arbitrary nonzero value of the spin s for the above model. The results of our exact diagonalization study for some finite chain clusters with s=1 supports this conclusion. We also studied analytically and numerically magnetic properties of Heisenberg – Ising diamond mixed spin chain. The exact energy spectrum of this model is found in analytical form at arbitrary values of model parameters. On the base of this spectrum we studied the field dependence of two-particle correlators for neighbor Ising spins. It was found that at special relation between coupling parameters there is a critical value of external magnetic field for which the above correlator takes zero value (the absence of the correlation between Ising spins). For infinite spin chain model we studied field dependence of specific magnetization by means of classical transfer- matrix method and found intermediate plateau in the low-temperature magnetization profile. According to our calculations, the size of this plateau depends strongly on the relations between coupling parameters of the model. We hope this feature of our model gives new possibilities for the design of new magnetic chemo-sensors.

Keywords: mixed spin diamond chain model, intermediate magnetization plateau.

Introduction

Over the last decades, the low-dimensional geometrically frustrated spin systems have attracted considerable research interest, especially due to their extraordinary diverse behavior in the ground state [1-3]. In solid state physics the term “geometric frustration” describes a phenomenon, where interactions between crystal lattice sites compete, preventing the system from reaching the minimum energy with simple geometric ordering. In context of antiferromagnetic spin-lattice systems this term means lattices containing the cycles with odd number of sites. The geometrically frustrated spin systems demonstrate some intriguing phenomena such as quantum phase transitions and quantized plateaux in the magnetization curves for these systems. One of them is the spin-1/2 quantum Heisenberg model with diamond chain topology [4-6]. This model describes adequately unusual magnetic properties of the natural mineral azurite $Cu_3(CO_3)_2(OH)$, such as the presence of a plateau at one-third of the saturation magnetization in the magnetization curve at low temperature. Nevertheless, it should be noted that according to [4], total explanation of a wide range of experiments for the frustrated magnet azurite requires the balanced combination of density functional theory (DFT) and effective spin Hamiltonian approach. Theoretical interest focused on the diamond chain structure also supported its experimental realizations provided by other polymeric compounds of transition metals. There are also a number of exact results related to the ground state and thermodynamics of mixed spin Ising-Heisenberg diamond chain giving useful information for understanding the origin of peculiarities of the magnetic properties of quasi-one dimensional binuclear complexes of transition metals [1, 5, 6].

In our work we consider non-symmetric modification of mixed spin Heisenberg and Ising-Heisenberg diamond chains with nodal spins ½ and two different interstitial spins s =½ and $\overline{s} > 1/2$.

We will show the existence of quantum phase transitions between different spin ordering states for arbitrary values of $\overline{s} > 1/2$. In particular for model with $\overline{s} = 1$ we demonstrate the possibility of the transition between nonmagnetic and magnetic states due to the change of coupling constants describing the exchange interactions between neighboring magnetic ions of the complex. These interactions can depend strongly on the chemical surrounding of these ions, which open the promising way for the design of new magnetic chemo-sensors.

Modified Heisenberg mixed spin diamond chain model

Let us consider the non-symmetric mixed spin Heisenberg diamond chain having all site spin ½ excepting the spins located on low interstitial sites (Fig.1).

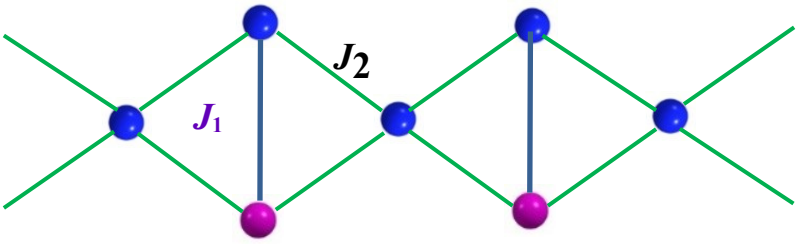

Figure 1. Modified diamond mixed spin chain. The crimson and blue spheres correspond to the spin carriers with $\overline{s} > 1/2$ and s=1/2 located at the nodes of the chain.

Within the Heisenberg spin model, the energy states of the above diamond spin chain are described by the Hamiltonian

$$\mathbf{H} = \sum_{k=1}^{L} \left\{ J_1 \mathbf{S}_{1,k} \overline{\mathbf{S}}_k + J_2 \left(\mathbf{S}_{1,k} + \overline{\mathbf{S}}_k \right) \left(\mathbf{S}_{2,k-1} + \mathbf{S}_{2,k} \right) \right\}, \tag{1}$$

where index k enumerates 3-site unite cells of the model, $\mathbf{S}_{k,i}$ (i = 1, 2) is a spin operator for spins s=1/2 of k-th unit cell and $\overline{\mathbf{S}}_k$ is a spin $\overline{s}$ operators of k-th unit cell. For positive coupling parameters J_1 and J_2 we use arbitrary energy units.

Let us consider two limit cases of the above model: $J_1 >> J_2$ and $J_1 = 0$. For the first case the lowest part of the model energy spectrum can be described approximately by the Hamiltonian of linear spin chain with alternating values of neighboring spins s=1/2 and $\hat{s} = \overline{s} - 1/2$ (Fig.2).

Figure 2. Linear spin chain with alternating values of neighboring spins

The Hamiltonian of this chain in the first order of perturbation theory in the parameter $\alpha = J_2 / J_1$ has the form

$$\mathbf{H}_1 = -J_1 L \left(\overline{s} + 1 \right) / 2 + J_2 \sum_{k=1}^{L} \left(\mathbf{S}_{1,k} + \mathbf{S}_{1,k+1} \right) \hat{\mathbf{S}}_k, \tag{2}$$

where $\hat{\mathbf{S}}_k$ is an operator of spin $\hat{s}$ located on k unit cell of the chain (Fig.2).

Due to the alternating topology, the ground state of the chain is non-degenerate and, by the generalized Lieb theorem [7-9], corresponds to the total spin $S_0 = (\overline{s} - 1) L$. Hence, for $\overline{s} = 1$ and big even L we have antiferromagnetic linear spin ½ chain the with gapless energy spectrum, ground state spin $S_0 = 0$ and the corresponding energy $E_0 / L = -J_1 - (\ln 2 - 1/4) J_2$.

In the case of $J_1 = 0$ the modified diamond spin chain is transformed into a decorated necklace spin ladder model (Fig.3).

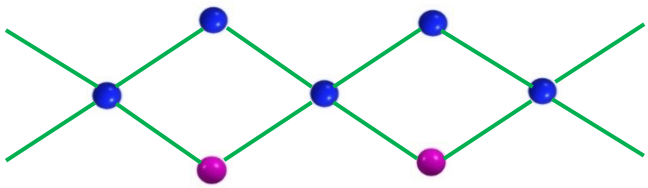

Figure 3. Decorated necklace spin ladder.

The corresponding spin system also has an alternant structure and is described by the following Hamiltonian:

$$\mathbf{H}_1 = J_2 \sum_{k=1}^{L} \left(\mathbf{S}_{1,k} + \overline{\mathbf{S}}_k \right) \left(\mathbf{S}_{2,k-1} + \mathbf{S}_{2,k} \right) \tag{3}$$

According to the generalized Lieb theorem, this Hamiltonian has a nondegenerate ground state with total spin $S_0 = \overline{s}\, L$.

Thus, increasing the ratio of coupling constants $\alpha = J_2 / J_1$ can lead to a macroscopic increase in the ground state spin of the modified diamond chain. In a particular case $\overline{S} = 1$, we have a transition from a nonmagnetic state of the diamand chain to a magnetic one.

In order to obtain more detailed information about the energy spectrum of the Hamiltonian (1), we have performed numerical calculations of the exact energy spectra of finite chains for some values of the model parameters. For this purpose, we used the basis of spin configurations (4), which have the form of direct products of the eigenfunctions of z-components of site spin operators. All these spin configurations are the eigenfunctions of the operator of z-projection of the diamond chain total spin *M*:

$$\Phi_{\{s,m\}}(M) = \prod_{k=1}^{N} \Omega(s_k, m_k) \tag{4}$$

where *N* is the total number of lattice sites; the multi-index {s, m} lists all possible combinations of the quantum numbers of the sites (s_k, m_k). $\Omega(s_k, m_k)$ is the eigenfunction of the spin operator $\mathbf{S}_k^z$ with given values of *s* and its z-projection *m*.

We used the exact diagonalization method to get the energy spectra of finite clasters of modified diamond chain formed by one and two unit cells with $\overline{S} = 1$. Due to the scalar nature of the spin Hamiltonian (1), comparing the energy levels for each subspace with a given value of M allows us to obtain the lowest energy levels with a fixed value of the total spin S. The results of these numerical calculations are presented below on Fig. 4 and Fig.5

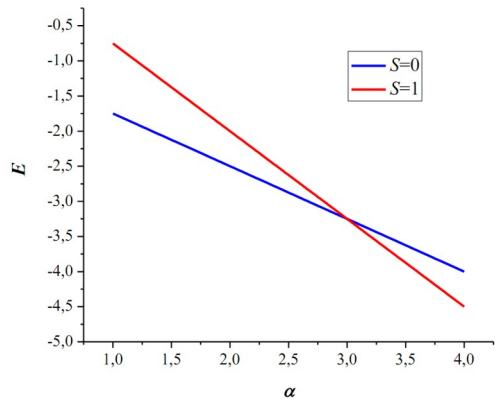

Figure 4. The dependence of the lowest energy levels of the unit cell (in units of J_1) in the spaces with $S = 0$ (blue curve) and $S = 1$ (red curve) on the frustration parameter $\alpha = J_2 / J_1$.

According to these calculations, the unit cell of the modified diamond chain changes the ground state spin from 0 to 1 at the point $\alpha = 3$.

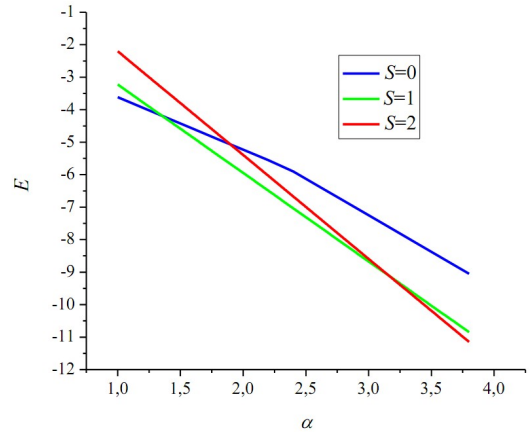

Figure 5. The dependence of the lowest energy levels in units of J_1 for 6-spin cluster (two unit cells) in the spaces with $S = 0$ (blue curve) and $S = 1$ (green curve) and $S = 2$ (red curve) on the frustration parameter α.

Here the transition between lowest energy levels with $S=0$ and $S=2$ occurs gradually through an intermediate state with $S=1$. The chain fragment acquires the value of the ground state spin $S=3$ when the parameter $\alpha>3,2$.

We also performed numerical simulation of the field dependence of magnetization of the cluster of modified diamond chain formed by 3 unit cells. For this purpose we used exact energy spectrum of the cluster and Boltzmann`s distribution (5).

$$m(h,T)=\sum_i M_i \exp(-(E_i-hM_i)/k_BT)/\left(L\sum_i \exp(-(E_i-hM_i)/k_BT)\right), \quad (5)$$

Here, for simplicity, we consider equal g-factors for all lattice spins and presented the results of our calculations for specific spin moment $m=M/L$; T is the temperature and k_B is the Boltzmann`s constant. Also we used the external magnetic field h in energy units.

The results of the corresponding calculations are shown in Fig.6 for two different values of the frustration parameter α, which correspond to the nonmagnetic and magnetic ground states of the chain. It is easy to see the radical change in the magnetization profile driven by the frustration parameter α.

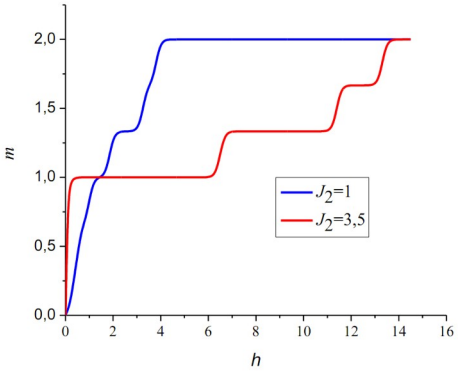

Figure 6. Magnetization profile of 9 spin fragment of modified diamond chain at J_1=1 and K_Bt=0.1.

Heisenberg-Ising mixed spin diamond chain model

In order to study the magnetic properties of our modification of mixed spin diamond chain let us consider simplified version of the model Hamiltonian (1) - mixed spin-(s,1/2) Ising–Heisenberg diamond chain. The Hamiltonian of this chain formed by L unit cells in the presence of an external magnetic field h, reads

$$\mathbf{H}=\sum_{l=1}^{L}\left[J_1\mathbf{S}_{1,l}\overline{\mathbf{S}}_l+J_2\mathbf{S}_{2,l}^z\left(\mathbf{S}_{1,l}^z+\mathbf{S}_{1,l+1}^z+\overline{\mathbf{S}}_l^z+\overline{\mathbf{S}}_{l+1}^z\right)-h\left(\mathbf{S}_{1,l}^z+\mathbf{S}_{2,l}^z+\overline{\mathbf{S}}_l^z\right)\right], \quad (6)$$

where $S_{1(2),l}^z$ -are the operators of z-projections of the corresponding spins s=1/2 of the l-th unit cell of the ladder; $S_{1,L+1}^z=S_{1,1}^z$, $\overline{S}_{L+1}^z=\overline{S}_1^z$. The last term determines the energy of the nodal spins and interstitial spins in the external magnetic field h.

Due to the commutation relation $\left[\mathbf{H},S_{2,n}^z\right]=0$, $n=1,..,L$, we can substitute the operators $S_{2,n}^z$ by their eigenvalues $\sigma_n=\pm1/2$ and rewrite the Hamiltonian (4) in the following block form:

$$\mathbf{H}=\sum_{n=1}^{L}\mathbf{H}(\sigma_n,\sigma_{n+1});$$

$$\mathbf{H}(\sigma_n,\sigma_{n+1})=(\sigma_n+\sigma_{n+1})\left[J_2\left(S_{1,n}^z+\overline{S}_n^z\right)-\frac{h}{2}\right] \quad (7)$$

$$+J_1S_{1,n}\overline{S}_n-h\left(S_{1,n}^z+\overline{S}_n^z\right).$$

The exact energy spectrum of the Hamiltonian (7) is a sum of eigenvalues of block Hamiltonians $\mathbf{H}(\sigma_n,\sigma_{n+1})$, which can be found analytically for arbitrary values of model parameters. In particular, for $J_1\gg J_2$ there is a critical value of magnetic field $h_1=2(\overline{s}-1/2)J_2$ for which the ground state energy of (7) does not depend on the set of quantities (σ_n,σ_{n+1})

$$E_0 / L = -J_1\left(\overline{s}+1\right)/2 - 2\left(\overline{s}-1/2\right)^2 J_2 \tag{8}$$

As the result, at critical field h_1 the ground state of (7) is 4-times degenerate. In this case spin-spin correlators $\langle \sigma_n \sigma_{n+1} \rangle$ should take zero values. We may also suppose that at critical field the above correlators should be close to zero at low temperatures similar to Heisenberg–Ising spin model from [2].

In order to study thermodynamics of the above Heisenberg–Ising spin model we applied standard transfer matrix technique. The partition function of the system (6) $Z_L(T,h)$ for given values of temperature T and external magnetic field h can be written through the 2×2 transfer matrix $\mathbf{T}(\sigma_1,\sigma_2,T,h)$ for the block Hamiltonian (7).

$$\mathbf{T}(\sigma_1,\sigma_2,T,h) = \exp\left[-\beta \mathbf{H}_1\left(\sigma_1,\sigma_2\right)\right], \quad \beta = \left(k_B T\right)^{-1} \tag{9}$$

According to transfer-matrix approach, the statistical sum for the above Hamiltonian has the form:

$$Z = \mathrm{Tr}\left[\mathbf{T}(\sigma_1,\sigma_2,T,h)\right]^L, \tag{10}$$

In the thermodynamic limit, statistical sum Z and a number of properties of the model considered are determined by the maximal eigenvalue $\lambda_{\max}$ of the transfer matrix $\mathbf{T}$. We will use it for numerical calculation of the magnetization profile of our Heisenberg-Ising spin ladder model by means of known formula

$$m = \frac{d\ln\left(\lambda_{\max}\right)}{\beta dh} \tag{11}$$

Some results of this study are presented on Fig.7

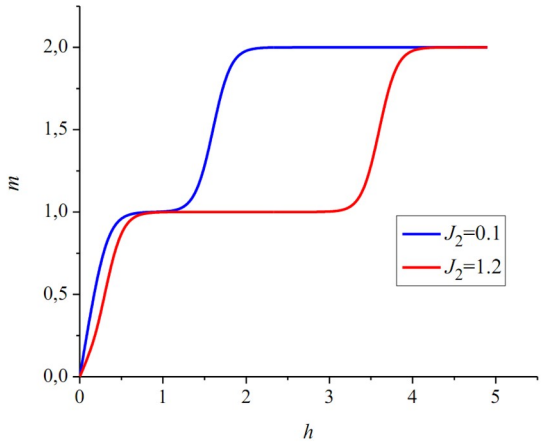

Figure 7. Field dependence of specific magnetization m of the infinite Heisenberg-Izing modified mixed spin diamond chain (6) at J_1=1, and k_BT=0.1.

Thus, the Heisenberg-Izing analog of modified diamond mixed spin chain has intermediate magnetization plateau.

Conclusion

For a model nanomagnet with a modified diamond chain structure, energy spectrum and magnetization profile calculations were performed. The existence of a transition between nonmagnetic and magnetic states, which is controlled by a change in the frustration parameter due to external stress like a change in the chemical surrounding, is shown. For infinite Heisenberg-Izing analog of modified mixed spin diamond chain the intermediate plateau in the low-temperature magnetization profile of the chain and nontrivial field dependence of two particle correlators for neighbor Ising spins were found.

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В.О. Чарновський В.В. Малярчук. Магнітні властивості модифікованого діамантового спінового ланцюжка.

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Робота присвячена теоретичному дослідженню енергетичного спектру та магнітних властивостей модифікованого антиферомагнітного спінового (1/2, s) алмазного ланцюга. Це фрустрована змішана спінова система з елементарними комірками, утвореними двома спінами ½ та одним спіном s>1/2. На основі розширеної теореми Ліба ми довели можливість виникнення квантових фазових переходів, опосередкованих співвідношенням параметрів зв'язку при довільному ненульовому значенні спіну s для вищезгаданої моделі. Результати нашого дослідження точної діагоналізації для деяких кластерів скінченних ланцюгів з s=1 підтверджують цей висновок. Ми також аналітично та чисельно вивчали магнітні властивості алмазного змішаного спінового ланцюга Гейзенберга-Ізінга. Точний енергетичний спектр цієї моделі знайдено в аналітичній формі при довільних значеннях параметрів моделі. На основі цього спектру ми вивчали польову залежність двочастинкових кореляторів для сусідніх спінів Ізінга. Було виявлено, що при спеціальному співвідношенні між параметрами зв'язку існує критичне значення зовнішнього магнітного поля, для якого вищезгаданий корелятор приймає нульове значення (відсутність кореляції між спінами Ізінга). Для моделі нескінченного спінового ланцюга ми досліджували залежність питомої намагніченості від поля за допомогою класичного методу матриці переносу та виявили проміжне плато у профілі низькотемпературної намагніченості. Згідно з нашими розрахунками, розмір цього плато сильно залежить від співвідношень між параметрами зв'язку моделі. Ми сподіваємося, що ця особливість нашої моделі надасть нові можливості для проектування нових магнітних хемосенсорів.

Ключові слова: *модель алмазного ланцюга зі змішаним спіном, проміжне плато намагніченості.*

Конфлікт інтересів: автори повідомляють про відсутність конфлікту інтересів.

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