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Energy spectrum and thermodynamics of quasi-one-dimensional ferrimagnets on the basis of transition metal compounds

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The study of energy spectrum of necklace spin ladder modelling magnetic properties of a number of quasi-one-dimensional ferrimagnetics containing ions of transition metals, was carried out. It was shown that the excitations without decrease of total spin are separated from ground state by finite energy gap, and the excitations with decrease of total spin are gapless. Temperature dependence of magnetic susceptibility, agreed with known experimental data for quasi-one-dimensional Cu-Ni bimetallic ferrimagnets and analytical formula for Ising model of NL, was built on the base of exact energy spectra of small ladder clusters.

Проведено изучение энергетического спектра диагональной спиновой лестницы типа "ожерелье", моделирующей магнитные свойства ряда квазиодномерных ферримагнетиков, содержащих ионы переходных металлов. Показано, что возбуждения без уменьшения полного спина отделены от основного состояния конечной энергетической щелью, а возбуждения с уменьшением полного спина - безщелевые. На основе точного энергетического спектра малых лестничных кластеров построена температурная зависимость магнитной восприимчивости, согласующаяся с известными экспериментальными данными для квазиодномерных Cu-Ni биметаллических ферримагнетиков и аналитической формулой, полученной в рамках соответствующей модели Изинга.

In spite of intensive study during last decades, the low-dimensional magnetic systems offer permanently new challenges to researches by exhibiting a wide variety of exotic physical phenomena. Many of these interesting and novel phenomena were first predicted from theoretical studies on one-dimensional spin systems [1-4]. These predictions motivated a number of experimental efforts in field of synthesis and study of quasi-one-dimensional magnetic systems with spin chains and ladders. The search for molecular ferromagnets is among the important challenges in this area and it has been already resulted in discovery of many interesting magnetic systems. Those include a simplest representative of diagonal ladders, a necklace spin ladder (NL) with antiferromagnetic exchange coupling between nearest neighbor only (Fig. 1). This system describes adequately magnetic properties of $(IPA)_2CuCl_4$ crystals (IPA is isopropylammonium) [5-8]. The main difference between NL and ordinary rectangular lattice having the same unit cells is a macroscopic ground state spin of NL. The reason is as follows: although NL is bipartite system, the number of sites in each sublattice is different. This unbalance between the numbers of sites in each sublattice is responsible for the ferrimagnetism exhibited in NL. Another interesting systems are quasi-one-dimensional bimetallic

molecular magnets containing two transition metal ions per unit cell and having the general formula ACu(pbaOH)$(H_2O)_3 \cdot 2H_2O$ with pbaOH = 2-hydroxo-1,3- propylene-bis(oxamato) and A = Mn, Fe, Co, Ni. These magnets belong to the alternating spin chain family which exhibit ferrimagnetic behavior.

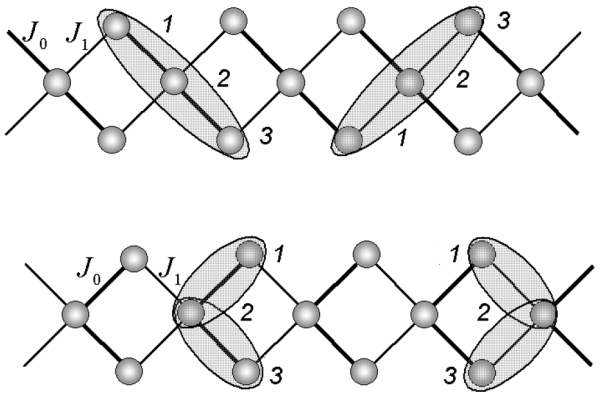

Fig.1. The unit cell selection for an NL with periodic boundary conditions.

The parameters of the corresponding spin models are sensitive to changes in chemical structure of ferrimagnets. Therefore, the theoretical study of these spin models in a wide region of coupling parameters is of direct interest in designing of new quasi-one-dimensional ferromagnetic materials. This study deals with the energy spectrum and low-temperature thermodynamics of necklace ladder. Because of the similarity of low-temperature thermodynamics of NL and of a spin chain with alternate spin-1 and spin-1/2 sites, the results of this study are also applicable to some bimetallic molecular magnets.

Let us consider a general structure of the exact energy spectrum of NL with isotropic exchange interaction in the absence of external magnetic field. If all interactions between spins inside of unit cell of the ladder with periodic boundaries are equal, this cell can be chosen by four different means. (Fig.1).

In case of "linear" unit cells, the spin Hamiltonian of the ladder can be written in two different forms:

$$\mathbf{H} = J_0 \sum_{\alpha=1}^{2} \sum_{n=1}^{L} \mathbf{S}_{\alpha,n} \mathbf{S}_{\alpha+1,n} + J_1 \sum_{n=1}^{L} \left(\mathbf{S}_{2,n} \mathbf{S}_{1,n+1} + \mathbf{S}_{3,n} \mathbf{S}_{2,n+1} \right), \tag{1}$$

$$\mathbf{H} = J_1 \sum_{\alpha=1}^{2} \sum_{n=1}^{L} \mathbf{S}_{\alpha,n} \mathbf{S}_{\alpha+1,n} + J_0 \sum_{n=1}^{L} \left(\mathbf{S}_{2,n} \mathbf{S}_{1,n+1} + \mathbf{S}_{3,n} \mathbf{S}_{2,n+1} \right). \tag{2}$$

Thus, the exact energy spectrum of NL with periodic boundaries obeys the conditions

$$E_k(J_0, J_1) = E_k(J_1, J_0). \tag{3}$$

The "corner " unit cells can be treated in absolutely similar manner. The corresponding lattice Hamiltonian has a form

$$\mathbf{H} = J_1 \sum_{\alpha=1}^{2} \sum_{n=1}^{L} \mathbf{S}_{\alpha,n} \mathbf{S}_{\alpha+1,n} + J_0 \sum_{n=1}^{L} \left(\mathbf{S}_{1,n} + \mathbf{S}_{3,n} \right) \mathbf{S}_{2,n+1}. \tag{4}$$

The exact energy spectrum of (4) also obeys the condition (3) and does not coincide with the spectra of the Hamiltonians (1, 2) at $J_1 \neq J_0$. Besides, similar to the case $J_1 = J_0$ considered in [7], the Hamiltonian (4) satisfies the condition

$$\mathbf{H} \left(\mathbf{S}_{1,n} + \mathbf{S}_{3,n} \right)^2 = \left(\mathbf{S}_{1,n} + \mathbf{S}_{3,n} \right)^2 \mathbf{H}. \tag{5}$$

This means that upper and lower spins of each unit cell form a pure singlet or triplet. Let this composed spin to be equal to 1 for all unit cells. In this case, the corresponding part of the exact en-

ergy spectrum (4) is described by the Hamiltonian of a linear chain with alternating spins: $s = 1/2$ and $s = 1$

$$\mathbf{H} = \sum_{n=1}^{L} \left(J_1 \mathbf{T}_n \mathbf{S}_n + J_0 \mathbf{S}_n \mathbf{T}_{n+1} \right). \tag{6}$$

If the composite spin of an arbitrary cell is zero, this cell does not interact with its surrounding and cyclic chain is transformed to the linear chain having $L-1$ unit cells. This consideration can be easily generalized to the case of an arbitrary number of composite spins. As a result, similar to [7], the exact energy spectrum of (4) is reproduced by the set of the Hamiltonians of the type (6) for cyclic chain, linear chains of different length, and the corresponding set of isolated spins $s = 1/2$. Therefore, the thermodynamics of NL with "corner" unit cell and linear chain with alternating spins can be supposed to be quite similar at low temperatures.

At $J_1 = 0$, the ladder has a form of a collection of isolated segments (unit cells) and its energy spectrum is a set of different combinations of isolated cell energies. In zero magnetic field, these energies are equal to

$$\varepsilon_1 = -J_0, \quad \varepsilon_2 = 0, \quad \varepsilon_3 = \frac{J_0}{2}. \tag{7}$$

The corresponding wave functions of three-site unit cells have a form:

$$\varphi_1\left(\frac{1}{2}, i\right) = \frac{1}{\sqrt{6}}\left(\mathbf{S}^-_{1,1} - 2\mathbf{S}^-_{2,1} + \mathbf{S}^-_{3,1}\right)|0\rangle, \; \varphi_2\left(\frac{1}{2}, i\right) = \frac{1}{\sqrt{2}}\left(\mathbf{S}^-_{3,1} - \mathbf{S}^-_{1,1}\right)|0\rangle,$$

$$\varphi_3\left(\frac{1}{2}, i\right) = \frac{1}{\sqrt{3}}\left(\mathbf{S}^-_{1,1} + \mathbf{S}^-_{2,1} + \mathbf{S}^-_{3,1}\right)|0\rangle, \tag{8}$$

where $|0\rangle$ is the unit cell wave function with maximal value of spin momentum $m = \frac{3}{2}$ and energy ε_3.

Obviously, in the absence of magnetic field, the ladder ground state is 2^N fold degenerate and can possess any value of z-projection of total spin M from the interval $(-N/2, N/2)$. The degenerate ground state wave functions of the ladder are direct product of unit cell eigenfunctions of the energy ε_1

$$\Psi_0(M) = \prod_{i=1}^{N} \varphi_1(m_i, i), \quad m_i = \pm\frac{1}{2}, \; M = \sum_{i=1}^{N} m_i \,, \tag{9}$$

where $\varphi_1(m_i, i)$ is the ground state eigenfunction of i -th unit cell having z-projection of cell spin m_i .

Weak interaction between cells eliminates the degeneracy in first order of perturbation theory (PT) in coupling J_1 . When considering the corresponding matrix elements of this interaction, it can be shown that in first PT order the lowest part of the energy spectra of rectangular and diagonal ladders are described by effective Heisenberg spin Hamiltonians of the following form:

$$\mathbf{H}_R = N\varepsilon_1 + J_1 \sum_{i=1}^{N} \mathbf{S}_i \mathbf{S}_{i+1} \,, \tag{10}$$

$$\mathbf{H}_{NL} = N\varepsilon_1 - \frac{4J_1}{9} \sum_{i=1}^{N} \mathbf{S}_i \mathbf{S}_{i+1} \,. \tag{11}$$

Thus, the ground state of rectangular ladder formed by three chains corresponds to minimal value of total spin ($S_0 = 0,\ 1/2$), whereas for diagonal ladder, $S_0 = N/2$, which is in agreement

Table. Exact lowest excitation energies for NL lineal segments containing 4-7 unit cells; (*) the results of numerical simulation by DMRG method.
J_0=2J_1=1; $\Delta_1 = E_0(S_0+1) - E_0(S_0)$, $\Delta_2 = E_1(S_0) - E_0(S_0)$, $\Delta_3 = E_0(S_0) - E_0(S_0-1)$

	4	5	6	7	1002*
D_1	1.4727	1.4717	1.4710	1.4705	1.4676
D_2	1.1544	1.1557	1.1562	1.1563	1.1565
D_3	0.1072	0.0742	0.0538	0.0406	0.34×10^{-6}

with Lieb theorem [9]. Besides, the excitations of the rectangular ladder with the spin S_0 should be gapless, similar to uniform Heisenberg spin chain.

In case of diagonal ladder (NL) there is only one state of spin $S_0 = N/2$ in first PT order in J_1. Therefore, to create the ladder excited states with total spin S_0, we should use the cell states φ_2 and φ_3. It can be shown easily that these excitations are separated from the ground state by the finite energy gap $\Delta E \sim J_0$. A similar conclusion can be done for the excitations with total spin $S > S_0$. The excitations with a decrease of total spin are described by the Hamiltonian (11) and thus should be gapless in agreement with the theorem from [10]. This character of NL energy spectrum results, within the limit of weak interaction between cells, in a plateau in field dependence of magnetization at $M = L/2$. It should be noted that in contrast to magnetization plateau of rectangular ladder formed by three spin chains [2], the plateau for NL appears at zero value of magnetic field.

In order to get more information about the energy spectrum of NL at arbitrary value of the interaction between unit cells, we have calculated numerically the lowest energy levels of finite lattice fragments. The linear and cyclic fragments formed by 4-7 unit cells were studied using the Davidson method [11]. We also applied the density matrix renormalization group method (DMRG) [12] (an algorithm for "infinite" systems) using C_2 symmetry of NL similar to "reflection symmetry" of uniform spin chain [13]. In DMRG calculations, 500 iterations were performed and up to 32 optimized states were kept to reach proper convergence (Table 1.). The energy gap Δ_1 between the ground state and lowest state with $M = N/2+1$ agrees with our PT analysis of the excitations with $S > S_0$. The gaped character of the excitations should cause plateau in field dependence of ladder magnetization with increasing M.

To determine the first excitation state of spin S_0, a standard scheme for density matrix construction basing on two eigenfunctions of superblock matrix was used. Note that for standard DMRG method, it is difficult to determine total spin of excitations, because the basic functions of a preset M subspace are superposition of eigenfunction of $\mathbf{S}^2$ with different values of S. In case of NL, the distance Δ_2 between first two energy levels of subspace $M = S_0$ is less than gap Δ_1. Hence, the second state with $M = S_0$ should also have the spin S_0. A similar approach was used to find the lowest energy state with spin $S = S_0 - 1$.

The study of NL thermodynamic characteristics such as temperature dependence of magnetic susceptibility can be done in general numerically only. Nevertheless it is of interest first to perform the analytical study of the thermodynamics of NL described by the following Ising Hamiltonian:

$$\mathbf{H} = J_0 \sum_{\alpha=1}^{2} \sum_{n=1}^{L} \mathbf{S}^z_{\alpha,n} \mathbf{S}^z_{\alpha+1,n} + J_1 \sum_{n=1}^{L} \left(\mathbf{S}^z_{2,n} \mathbf{S}^z_{1,n+1} + \mathbf{S}^z_{3,n} \mathbf{S}^z_{2,n+1} \right). \qquad (12)$$

According to transfer-matrix method, the free energy per unit cell of infinite ladder model (12)

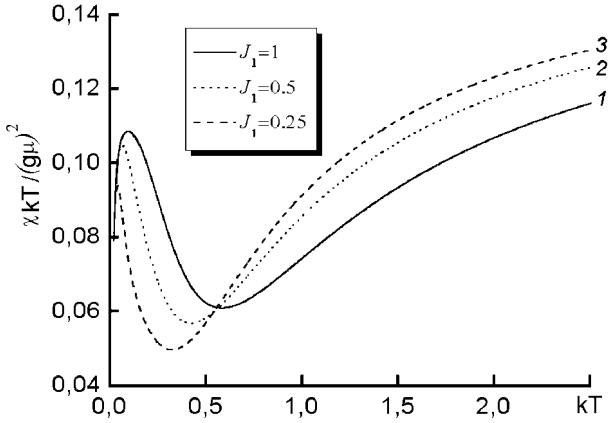

Fig. 2. Temperature dependences of quantity $\chi \times T$ for NL cyclic fragment formed by 5 unit cells at different values of J_1 ($J_0 = 1$).

has the form $f = -kT \ln \lambda$, where k is Boltzmann constant; T, temperature; λ, maximal eigenvalue of transfer-matrix $\mathbf{R}$ for the Hamiltonian (12). In the presence of magnetic field H, $\mathbf{R}$ is a symmetric 2×2 matrix with matrix elements

$$R_{11} = 2\exp(\beta h/2)\left\{\cosh\left[\beta(J_0 + J_1 - 2h)/2\right] + 1\right\}, \; R_{22}(h) = R_{11}(-h),$$

$$R_{12} = 2\left\{\cosh(\beta h) + \cosh\left[\beta(J_0 - J_1)/2\right]\right\},$$

where $\beta^{-1} = kT$; h, external magnetic field in energy units ($h = g\mu H$, g is g-factor of transition metal ions forming the magnetic sublattice; μ, Bohr magneton). The ladder free energy per unit cell has a simple form at $h = 0$:

$$f = -kT\left\{2\ln 2 + \ln\left[1 + \cosh(\beta J_0/2)\cosh(\beta J_1/2)\right]\right\}. \qquad (13)$$

When $h \neq 0$, the corresponding formula for f is cumbersome and is not presented here. In the case of weak magnetic field, the analytical study becomes simpler. In particular, the temperature dependence of zero field magnetic susceptibility has a following form:

$$\chi \times T = \frac{R(p,q)(g\mu)^2}{4k\left(2 + \cosh(p) + \cosh(q)\right)}, \qquad (14)$$

$$R(p,q) = 5 + \cosh(p) + 4\exp(-p) + \frac{\left(1 + 2\exp(-p) - \cosh(p)\right)^2}{1 + \cosh(q)},$$

$$p = 0.5\beta(J_0 + J_1), \; q = 0.5\beta(J_0 - J_1).$$

Numerical calculations using formula (14) show that the temperature dependence of the quantity $\chi \times T$ has a wide minimum. At $J_0 = J_1$ this minimum appears at temperature $T = 0.67J_0/k$.

To determine similar dependence for Heisenberg NL, let us use the exact energy spectrum of finite lattice clusters formed by 5 unit cells and well-known spectral formula for magnetic susceptibility. To reduce the computational work, the spin space symmetry was taken into account by means of branching diagram technique [14]. The corresponding temperature dependences of $\chi \times T$ at different values of coupling between unit cells are shown on Fig.2.

These dependences include rounded minima. At $J_1 = J_0$, the minimum corresponds to the $T_{\min} = 0.59J_0/k$, which is quite close to similar estimation for Ising model (12). As mentioned above, at $J_1 = J_0$, the low-temperature thermodynamics of NL and linear chain with alternating spins $s = 1/2$ and $s = 1$ should be similar. The DMRG calculations of temperature dependence of $\chi \times T$ for this chain show a rounded minimum at $T_{\min} = (0.5 \pm 0.1)J_0/k$ [15]. At the same

time, this spin chain simulates adequately the magnetic properties of quasi-one-dimensional ferrimagnet $NiCu(pbaOH)(H_2O)_3 \cdot 2H_2O$ [16]. If we take coupling parameter $J_0 = 94cm^{-1}$, our value $T_{\min} = 0.59J_0/k$ corresponds to experimental data ($T_{\min} = 80K$). Note that there are two independent estimations of this parameter: $J_0 = 81cm^{-1}$ [16] and $J_0 = 100cm^{-1}$ [15].

To conclude, it was shown that in an infinite NL, the excitations without decrease of total spin are separated from ground state by a finite energy gap, and the excitations with decrease of total spin are gapless. Temperature dependence of magnetic susceptibility, agreed with known experimental data for quasi-one-dimensional *Cu-Ni* bimetallic ferrimagnets and analytical formula for Ising model of NL, was built on the base of exact energy spectra of small ladder clusters.

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Енергетичний спектр і термодинаміка квазиодновимірних ферімагнетиків на основі сполук перехідних металів

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Проведено вивчення енергетичного спектру діагональної спінової драбини типу "намисто", що моделює магнітні властивості деяких квазіодновимірних феромагнетиків на основі сполук перехідних металів. Показано, що збудження без зменшення повного спіну відокремлені від основного стану скінченою енергетичною щілиною, а збудження із зменшенням повного спіну не мають такої щілини. На основі точного енергетичного спектру малих драбинних кластерів побудована температурна залежність магнітної сприятливості що погодиться з відомими експериментальними даними для квазіодновимірних Cu-Ni біметалевих ферімагнетиків та аналітичною формулою, що отримана в рамках відповідної моделі Ізінга.