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The modification of low-temperature magnetic properties of the Fe-based double-zigzag single-chain magnet under irradiation

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ABSTRACT

An exact solution for a generalized Ising model describing single-chain magnet $[Fe^{III}(Tp^*)(CN)_3]_2Fe^{II}(bpmh)\}\cdot 2H_2O$ with alternating high-spin and low-spin iron ions and double-zigzag magnetic topology has been calculated making use of the transfer-matrix technique. The introduction of a statistical ensemble taking into account the presence of iron ions with high-spin (HS) and low-spin (LS) states made it possible to describe the modification of magnetic susceptibility under optical irradiation. It has been shown that joint implementation of iron ions with photoinduced magnetic states and non-magnetic intersite repulsion ions of these states is caused by the difference of the ionic radii of HS Fe^{II} and LS Fe^{II} leads to the quantum phase transitions in the system.

1. Introduction

Single-chain magnets (SCM) are the objects in which magnetic carriers such as metal ions are surrounded by large organic ligands [1]. On the one hand, the presence of such ligands leads to the screening of magnetic interactions in two spatial dimensions. On the other hand, it shows strong single-ion anisotropy. Among the synthesized SCMs there are the ones are able to change own magnetic states under optical irradiation [2,3]. From fundamental point of view the SCMs are interest as the low dimensional magnetic materials with strong single-ion anisotropy and photoinduced magnetic states [2–8].

Due to the quasi one-dimensional magnetic structure and strong easy-axis single ion anisotropy, SCMs are would possess bistable states capable of interchanging between two magnetic polarization directions without a 3D magnetic ordering [2,4]. These states are characterized by nanoscale sizes and long life-times (about several hours). As a result, SCMs demonstrating magnetic bistable states attract a great deal of attention, because these bistable states can act as elementary binary units (bits) used for information storage, providing potential applications in high-density information storage and spintronics [2].

Peculiarities of temperature dependence of static magnetic susceptibility $\chi(T)$ and relaxation time $\tau(T)$ contain basic information on magnetic interactions in SCMs. The basic models describing these features of SCMs are several generalizations of the 1D Ising model and the Glauder model [6,9].

Recently, SCM $\{[Fe^{III}(Tp^*)(CN)_3]_2Fe^{II}(bpmh)\}\cdot 2H_2O$ (hereafter SCM-zigzag) supporting light-induced modification of magnetic states has been synthesized [3]. Its magnetic structure is formed by alternating Fe^{II} spin-crossover (SCO) units and paramagnetic $LS\ Fe^{III}$ ($\sigma = 1/2$) ions that are embedded into a well-isolated double-zigzag chain (Fig. 1). Experimental studies of SCM-zigzag show that magnetic susceptibility exhibits strong modification under optical irradiation. This phenomenon has been interpreted on the basis of the assumption of light-induced SCO of the iron ions located on the nodal sites of double-zigzag chain from the low-spin (LS, $S = 0$) non-magnetic states to the hight-spin (HS, $S = 2$) magnetic states. A magnetic state of nodal iron ions imply the exchange bonds and the formation of finite spin-chains of various lengths. According to magnetization vs magnetic field data, the ligand environment of $HS\ Fe^{II}$ ions produces strong easy-axis single-ion anisotropy.

In this paper the low-temperature thermodynamics of SCM-zigzag has been calculated and the change of its magnetic susceptibility under optical irradiation has been explained using the transfer-matrix method [10,11]. Based on the assumption that $HS\ Fe^{II}$ ions form the annealed type of magnetic disorder and that there is an intersite non-magnetic repulsion caused by the difference between $HS\ Fe^{II}$ and $LS\ Fe^{II}$ iron radii [12,13] a possibility of quantum phase transitions (QPTs) in the system has been demonstrated.

2. Model and method

Let us study single-chain magnet SCM-zigzag using the model of magnetic structure shown in Fig. 2. At low temperatures and without irradiation, this compound (from the magnetic point of view) consists

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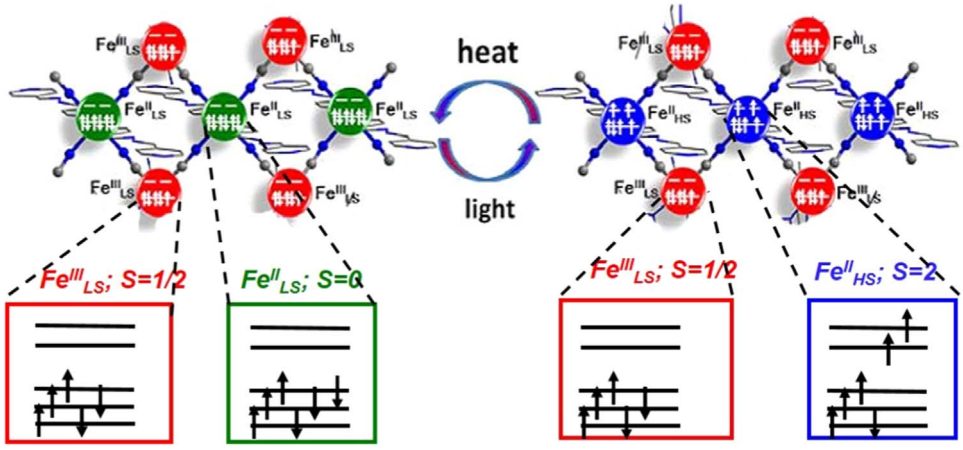

Fig. 1. Modification of magnetic structure of SCM-zigzag under irradiation. The divalent Fe^{II} ions (the nodal sites of double-zigzag) undergo the light induced spin-crossover from the low-spin *LS* Fe^{II} (S=0) non-magnetic states to the high-spin *HS* Fe^{II} (S=2) magnetic states [3].

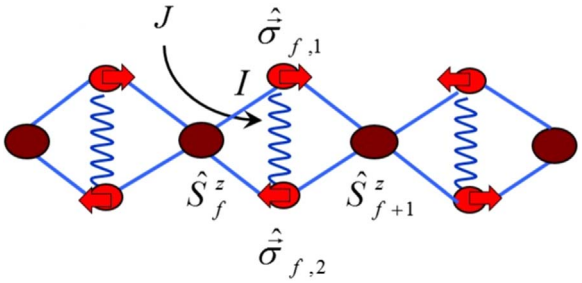

Fig. 2. Magnetic structure of SCM-zigzag. The large circles mark divalent Fe^{II} iron ions (S=0 before irradiation; S=2 after irradiation), small circles denote Fe^{III} ($\sigma_{1,2}$ = 1/2) ions. The exchange interactions of Heisenberg and Ising types are depicted by wavy curves and straight lines, accordingly.

of non-interacting spin dimers consisting of *LS* Fe^{III} (σ = 1/2) ions. After optical irradiation, some of LS Fe^{II} ions shows the light-induced spin-crossover into the HS (S=2) state with strong easy-axis single-ion anisotropy. At the limit of high-intensity irradiation, the system, in terms of magnetic viewpoint, consists of alternating spin dimers and the Ising centers with the spin S=2, incorporated into double-zigzag chain. Here we consider the Hamiltonian describing the low-temperature properties of the compound under irradiation in the form:

$$\widehat{\mathcal{H}} = \sum_f \widehat{\mathcal{H}}_f; \widehat{\mathcal{H}}_f = J\vec{\hat{\sigma}}_{f1}\vec{\hat{\sigma}}_{f2} + V\hat{n}_f\hat{n}_{f+1} - \frac{g_2 h}{2}(\hat{S}^z_f + \hat{S}^z_{f+1}) - ([g_1 h - I(\hat{S}^z_f + \hat{S}^z_{f+1})](\hat{\sigma}^z_{f1} + \hat{\sigma}^z_{f2})) - \frac{\mu}{2}(\hat{n}_f + \hat{n}_{f+1}) \quad (1)$$

where I is the parameter of the Ising-type exchange interaction between the nodal sites of the chain and nearest spin dimers, g_1 and g_2 are g factors of LS Fe^{III} and HS Fe^{II} ions, accordingly. h describes the external magnetic field; μ is the Lagrange multiplier that allows us to control the average number of HS Fe^{II} ions (see Eq. (6)); $\vec{\hat{\sigma}}_{f1,2}$ is the vector-operator of the Pauli matrices, describing the magnetic states of the dimers belonging to magnetic cell f; J is the parameter of exchange interaction between two iron ions belonging to one dimer. The parameter V describes the effective intersite repulsion between the nearest HS Fe^{II} ions. The physical meaning of parameter V will be discussed below. The matrices $\hat{S}^z_f$ and $\hat{n}_f$ characterize a projection of magnetization of HS Fe^{II} ions belonging to the nodal site f on the quantization axis z and number of the same ions on the nodal site f, accordingly. In terms of the eigenstates of the Ising sites these matrices have the form:

$$\hat{S}^z = S\cdot diag(0, 1, -1); \hat{n} = diag(0, 1, 1). \quad (2)$$

Such form of $\hat{S}^z_f$ and $\hat{n}_f$ implies the possibility of the Fe^{II} ions interchange spin states.

The statistical sum and magnetic averages for the ensemble of chains introduced (1) is calculated by the transfer-matrix approach [10,11]. We suggest that the Hamiltonians describing the different sites are commute $[\widehat{\mathcal{H}}_f, \widehat{\mathcal{H}}_g] = 0$. Then the expressions for single-site averages can be written as follows

$$<S^z_f>_N = \frac{1}{\Xi}\sum_{m=1}^{3}\langle u_m|\hat{S}^z|u_m\rangle\lambda_m^N;$$

$$<\sigma^{x,y,z}_{f;1,2}>_N = \frac{1}{\Xi}\sum_{m=1}^{3}\langle u_m|\hat{\Sigma}^{x,y,z}_{1,2}|u_m\rangle\lambda_m^{N-1};$$

$$\hat{\Sigma}^{x,y,z}_{1,2}(S^z_f, S^z_{f+1}) = Sp_{\{Q_f\}}(\hat{\sigma}^{x,y,z}_{f;1,2}\cdot e^{-\beta\widehat{\mathcal{H}}_f(S^z_f, S^z_{f+1})}). \quad (3)$$

Here index Q_f describes quantum states of the spin dimer belonging to magnetic cell f; values S_f are diagonal elements of the matrices (2) and describe magnetic states of nodal sites f. $\Xi = \lambda_1^N + \lambda_2^N + \lambda_3^N$, where λ_m, are the eigenvalues of the transfer-matrix of the system, which takes the form

$$\hat{T}(S^z_f, S^z_{f+1}) = 2e^{\beta\cdot[h/2(S^z_f+S^z_{f+1})+\mu/2(n_f+n_{f+1})-Vn_fn_{f+1}]\cdot} (e^{\beta J/4}\cosh(\beta J/2) + e^{-\beta J/4}\cosh(\beta|I(S^z_f + S^z_{f+1})| - h)). \quad (4)$$

3. Modification of magnetic susceptibility under irradiation

Molar susceptibility of the SCM-zigzag for a given intensity of irradiation has been calculated by the formula

$$\chi_m(T) = N_A\mu_B^2\frac{\partial}{\partial h}\sum_N\frac{\overline{N}e^{-\overline{N}}}{N!}\langle g_1 S^z_f + g_2(\sigma_{f1} + \sigma_{f2})\rangle_N. \quad (5)$$

We take into account the impurities and defects of natural origin with life-times much greater than the characteristic times of the dynamics of magnetic subsystem. It has been assumed that these inclusions are distributed uniformly over the chain and are not correlated and that the detection probability of a chain with the number of sites N in a sample obeys the Poisson statistics.

Also, it would be appropriate here to mention two assumptions important in derivation of the formula (5). First, it has been taken into account that the experimental investigation of the optical impact on SCM-zigzag was performed after prolonged irradiation lasting several hours. We have assumed that Fe^{II} ions undergo a photoinduced spin-crossover between low (S=0) and high (S=2) spin states once or twice during this period. The irradiation intensity has been simulated by changing photon concentration $n_{hv} = \langle n\rangle$ inducing such spin-cross-

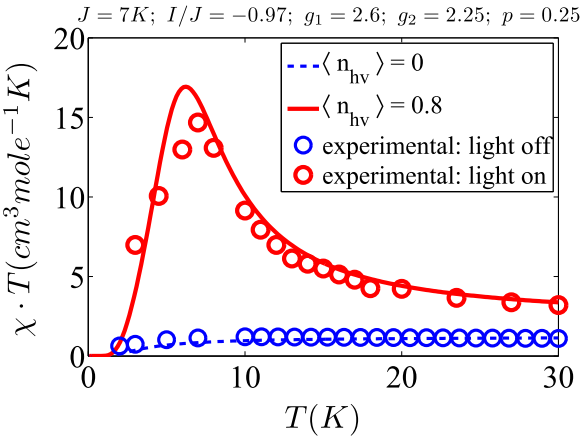

Fig. 3. Modification of the temperature dependence of the magnetic susceptibility of SCM-zigzag in the absence of radiation (theory (solid blue curve) and experiment (blue circles)) and under irradiation (theory (dotted red curve) and experiment (red circles)). The experimental data are borrowed from [3], and calculation parameters of the model are defined by relations (7). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

overs. Accordingly, the averages were calculated from Eq. (3) with simultaneous solution of the equation for Lagrange multiplier

$$\langle n \rangle_N (\mu) = n_{hv}. \tag{6}$$

The formula for the average $\langle n \rangle_N$ can be obtained from the Eq. (3) by the replacement: $\hat{n} \to \hat{S}^z$. We also suggested that V=0.

The second suggestion is connected with measuring of magnetic properties of SCM-zigzag in powder form. After irradiation the compound become strongly-anisotropic and there are grains with non-collinear to magnetic field quantization axes. Accordingly, absolute value of magnetic susceptibility $\chi(T)$ for the powder compound would be less than $\chi(T)$ for the monocrystal system. In this work, such property has been taken into account by introducing factor $p < 1$ for the system after irradiation. Before irradiation SCM-zigzag is isotropic in terms of magnetic point of view and factor p has not been introduced.

The results of the theoretical calculations of modification of the molar susceptibility $\chi(T) \equiv \chi_m(T)$ under irradiation of SCM-zigzag are demonstrated in Fig. 3 by the lines. The experimental data are depicted in Fig. 3 by the circles. It turns out that the following set of parameters (7) of the effective model (1) are the best from the viewpoint of agreement between theoretical results and experimental data:

$$J = 7\ \text{K};\ I = -6.8\ \text{K};\ p = 0.25;\ N = 100$$
$$g_1 = 2.6;\ g_2 = 2.25;\ H = 1000\ \text{Oe}. \tag{7}$$

Here g factors have been determined from behavior of high-temperature (100 K < T < 200 K, T > 200 K) magnetic susceptibility.

4. Photoinduced change of Fe^{II} ion radius. Quantum phase transition

It is known that spin-crossover from LS Fe^{II} to HS Fe^{II} states is accompanied by increase of the iron ion radius [11–13]. This effect leads to the change of potential energy of interaction between the ions and neighbouring ones. Taking into account SCM-zigzag the inequality of ion radii of Fe^{II} ions in different spin states can lead to the increase of potential energy of states with two neighbouring HS Fe^{II} ions compared to the states where these ions are not nearest neighbors. Description of the energy inequality has been achieved by introducing terms $V\hat{n}_f\hat{n}_{f+1}$ with $V > 0$ into the Hamiltonian (1).

It appears that a combination of photoinduced magnetic states of iron ions in SCM-zigzag and the effective intersite repulsion due to the difference of ionic radii can lead to quantum phase transitions in the system (see Fig. 4). Without losing the generality of subsequent results, for the sake of simplicity we consider the case of $n_{hv} = 0.5$. At $V \to 0$ and $J < 4|I| + g_1 h$ the ground state of the system is formed with microscopic separation of phases from the double-zigzag spin subchains and non-interacting spin dimers Fig. 4a. After increasing V and obtaining quantum critical point $V = V_c$ we have:

$$V_c = \begin{cases} J - g_1 h;\ 2|I| + g_1 h > J \\ 4|I| + g_1 h - J;\ 2|I| + g_1 h < J < 4|I| + g_1 h \end{cases} \tag{8}$$

and the system undergoes QPT into the state in which all of HS are not

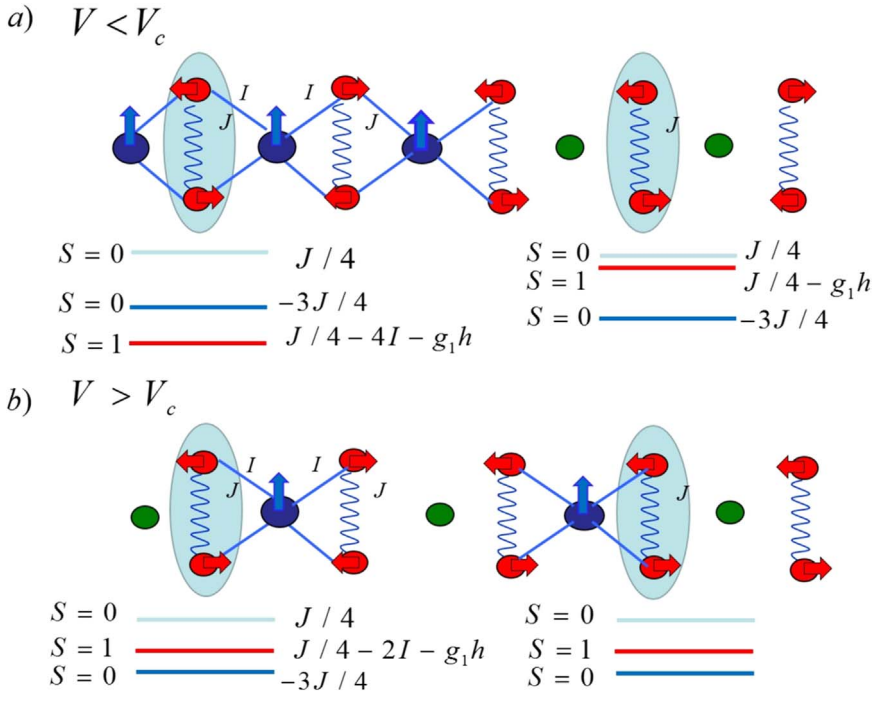

Fig. 4. Types of magnetic structure of SCM-zigzag at $n_{hv} = 0.5$ and a) $V < V_c$, b) $V > V_c$. The quantum critical point V_c is defined in Eq. (8). Small circles with arrows, single small circles and large circles with arrows mark LS Fe^{III} (S = 1/2), LS Fe^{II} (S=0) and HS Fe^{II} (S=2) iron ions, accordingly.

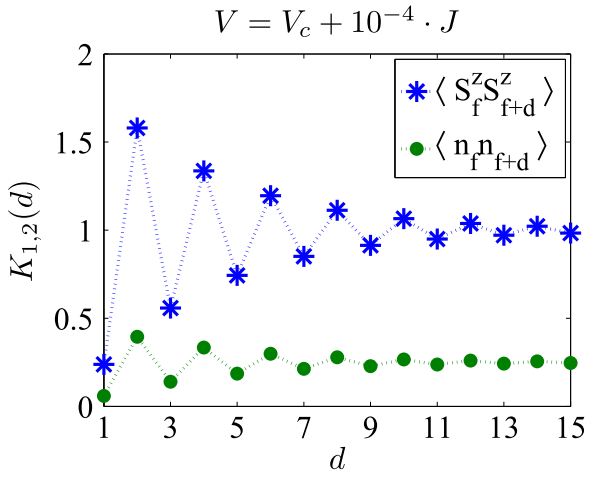

Fig. 5. Dependences of magnetic correlators $\langle S^z_f S^z_{f+d} \rangle$ and $\langle n_f n_{f+d} \rangle$ on the distance between magnetic cells d in the proximity of quantum critical point (8). They correspond to the state with strongly suppressed correlation length against to the correlation length in the absence of the intersite repulsion.

the nearest neighbors Fig. 4b. At $J > 4|I| + g_1 h$ the states of the last type are the ground states without reference to value of V. It should be noted, that values of irradiation intensity parameters $n_{h\nu} \neq 0.5$ can correspond to different QPTs.

Note also that at the certain parameters of the system (1) QPT implies that not only LS and HS Fe^{II} ions change mutual arrangement, but the spin dimers can also change spin states. At $n_{h\nu} = 0.5$ ($J < 4|I| + g_1 h$), if some spin dimers have magnetic state at $V < V_c$, they would cross over to non-magnetic state at $V > V_c$. Such a transition is caused by modification of exchange fields acting on dimers under QPT. Also the QPT leads to the change of magnetic susceptibility $\chi(T)$. The last change is similar to modification of $\chi(T)$ considered in Ref. [14].

The next property of the system manifesting itself in the proximity of the quantum critical point is a frustration against two types of ground states. This frustration leads to a magnetic structure of the system mediated against the structures at $V < V_c$ and at $V > V_c$. The magnetic structure of the system has been analyzed by calculating the correlators

$$<S^z_f S^z_{f+d}>_N = \frac{1}{\Xi} Sp\,(\tilde{S}^z_f \cdot \Lambda^d \cdot \tilde{S}^z_{f+d} \cdot \Lambda^{N-d});$$
$$<n_f n_{f+d}>_N = \frac{1}{\Xi} Sp\,(\tilde{n}_f \cdot \Lambda^d \cdot \tilde{n}_{f+d} \cdot \Lambda^{N-d}), \quad (9)$$

where $\Lambda = diag\,(\lambda_1, \lambda_2, \lambda_3)$ is the transfer-matrix (4) written in basis of own eigenvectors, $\tilde{S}^z_f$ and $\tilde{n}_f$ matrices (2) in such basis. The spatial dependence of correlators (9) (d denotes the number of magnetic cell) in small proximity of QCP calculated using the formula (6) is shown in Fig. 5. The value of the irradiation intensity parameter $n_{h\nu} = 0.5$ has been chosen. Set of the model parameters (7) corresponds to Fig. 3.

At $V < V_c$ the ground state with microscopic separation in phases from double-zigzag spin subchains and non-interacting spin dimers is formed (see Fig. 4a). In this case, the correlators $\langle S^z_f S^z_{f+d} \rangle = 2$ and $\langle n_f n_{f+d} \rangle = 0.5$ do not depend on d (formula (9) is valid for chains closed in loop). At $V > V_c$, the ground state is formed by non-interacting five-spin clusters (Fig. 4b) and the correlators $\langle S^z_f S^z_{f+d} \rangle = 2$; $\langle n_f n_{f+d} \rangle = 0.5$ in case of odd d and equal to zero in case of even d. In small proximity of quantum critical point, a mediate spatial dependence of (9) is implemented (Fig. 5). It can be seen that at $V \to V_c$ the system is characterized by the phase with short-range magnetic and has no long-range correlations for arbitrary small temperatures.

5. Conclusions

The model describing the low-temperature magnetic behavior of single-chain magnet $\{[Fe^{III}(Tp^*)(CN)_3]_2 Fe^{II}(bpmh)\}\cdot 2H_2O$ (SCM-zig-zag) exposed to optical irradiation was formulated. The system under irradiation, from the magnetic viewpoint, consists of well isolated double-zigzag spin chains with the nodal sites having pseudo-spin value S=1. An exact solution for this model with the use of the transfer-matrix method was obtained for investigation of the thermodynamic properties and correlation functions of the compound. In particular, this approach allowed us describe the experimentally observed strong modification of magnetic susceptibility of SCM-zigzag under optical irradiation. It is shown that a quantum phase transition can occur in the system due to joint implementation of iron ions with photoinduced magnetic states and non-magnetic intersite repulsion between such ions. This interaction could be caused by the difference of ionic radii of initial *LS* Fe^{II} and photoinduced *HS* Fe^{II} states of iron ions. In the proximity of the quantum critical points a correlation length of the system is strongly suppressed.

Acknowledgments

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