J Low Temp Phys (2016) 185:564–570
DOI 10.1007/s10909-015-1457-9

Quantum Theory of Strongly Anisotropic Two- and Four-Sublattice Single-Chain Magnets

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Received: 24 June 2015 / Accepted: 28 December 2015 / Published online: 19 January 2016

Abstract We have developed the spin wave theory of Heisenberg magnets with strong single-ion anisotropy of arbitrary symmetry with two and more sublattices. Using this approach, the low-temperature magnetic properties of the single-chain magnet catena-$[Fe^{II}(ClO_4)_2Fe^{III}(bpca)_2](ClO_4)$ with four sublattices and twisting mutually orthogonal easy plane have been calculated. It has been shown that the modulation of the easy planes directions creates on the one hand the low-temperature excitation spectrum similar to the one of the Ising models, and on the other hand strong spin fluctuations.

Keywords Quantum magnets · Spin wave theory · Strong single-ion anisotropy

1 Introduction

Recently, the organic single-chain magnets (SCMs) with strong single-ion anisotropy and several magnetic sublattices have attracted significant interest [1]. Practically, the main desired properties of these compounds are connected with the possibility of excitation of the microscopic domains with sharp domain walls under external stimulus like light irradiation [1–4]. The lifetime of these excited states can be as long as several

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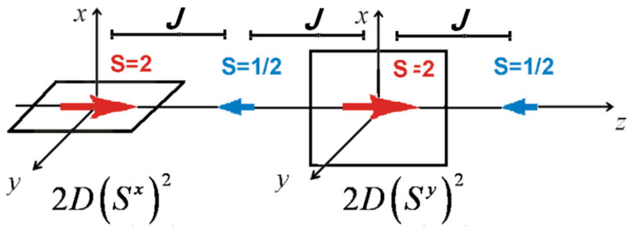

Fig. 1 The magnetic structure of the single-chain magnet catena-[$Fe^{II}(ClO_4)_2Fe^{III}(bpca)_2](ClO_4)$ (Color figure online)

hours [1,2]. Due to this property, the SCMs are considered to be the perspective elemental base of spintronics and memory devices. From a fundamental point of view, the SCMs are of interest as low-dimensional magnetic materials in which the spin and charge fluctuations could contribute much to low-temperature magnetic properties of the ones [5–9]. In terms of the magnetic structure and optical properties, one of the most interesting SCMs is the catena-[$Fe^{II}(ClO_4)_2Fe^{III}(bpca)_2](ClO_4)$ (below SCM-catena) [10,11]. From the magnetic point of view, the SCM-catena is a four-sublattices Heisenberg ferrimagnetic chain with twisting and mutually orthogonal easy planes (Fig. 1). Due to different orientations of the above easy planes, the effective easy axis along the chain direction is induced and microscopic magnetic domains with sharp domain walls are created. On the other hand, the presence of the easy-plane single-ion anisotropy induces strong spin fluctuations [12,13] which have to be taken into account for consecutive analysis of experimental data [10]. In this work, we have developed a spin wave approach for the description of Heisenberg magnets with single-ion and exchange anisotropy. The exactly considered single-ion anisotropy of arbitrary symmetry is involved in the single-ion Hamiltonian. Using this approach, the low-temperature properties of the SCM-catena have been calculated.

2 General Approach for Description of Two Sublattice Anisotropic Heisenberg Magnets

Let us consider an anisotropic two-sublattices Heisenberg magnet. Assuming the presence of non-zero averages of magnetization on the A and B sublattices: $\langle \mathbf{S}_A \rangle$, $\langle \mathbf{S}_B \rangle$, the Hamiltonian of the model can be written in the form

$$\widehat{\mathscr{H}} = \sum_{f\in A}\left[\mathscr{H}_a^A(\mathbf{S}_f) - \mathbf{H}^A\mathbf{S}_f^A\right] + \sum_{g\in B}\left[\mathscr{H}_a^B(\mathbf{S}_g) - \mathbf{H}^B\mathbf{S}_g^B\right] + \\ + \sum_{ff'}\left(\Delta\mathbf{S}_f, \hat{I}_{ff'}\cdot\Delta\mathbf{S}_{f'}\right) + \sum_{gg'}\left(\Delta\mathbf{S}_g, \hat{K}_{gg'}\cdot\Delta\mathbf{S}_{g'}\right) + \sum_{fg}\left(\Delta\mathbf{S}_f, \hat{J}_{fg}\cdot\Delta\mathbf{S}_g\right). \quad (1)$$

where $\mathbf{S}_f$ and $\mathbf{S}_g$ are the vector operators of the spin moments of the sites f and g connected with A and B sublattices, respectively. $\Delta\mathbf{S}_f = \mathbf{S}_f - \langle \mathbf{S}_A \rangle$, $\Delta\mathbf{S}_g = \mathbf{S}_g - \langle \mathbf{S}_B \rangle$; $\mathbf{H}^A = g_A\mathbf{H} + \hat{I}_0\langle \mathbf{S_A} \rangle + \hat{J}_0\langle \mathbf{S_B} \rangle$ and $\mathbf{H}^B = g_B\mathbf{H} + \hat{K}_0\langle \mathbf{S_B} \rangle + \hat{J}_0\langle \mathbf{S_A} \rangle$ are the effective magnetic fields and g_A and g_B are the g-factors of the A and B

magnetic ions, respectively. H is the external magnetic field, and $\hat{I}_0$, $\hat{K}_0$, $\hat{J}_0$ are the Fourier-transforms of matrices at the zero quasimomentum: $\hat{I}_0 = \sum_f \hat{I}_{ff'}$, $\hat{K}_0 = \sum_g \hat{K}_{gg'}$ $\hat{J}_0 = \sum_g \hat{J}_{fg}$. The three-dimensional matrices $\hat{I}_{ff'}$, $\hat{K}_{gg'}$ and $\hat{J}_{fg}$ have the diagonal form with arbitrary diagonal elements and describe the anisotropy of the exchange interaction. The single-ion anisotropy of the ions on the A and B sublattices are described by operators $\mathscr{H}_a^A(\mathbf{S}_f)$ and $\mathscr{H}_a^B(\mathbf{S}_g)$, respectively.

We use the ideology of atomic representation [14]. This allows us to consider strong single-ion anisotropy correctly. The atomic representation assumes a diagonalization of the single sites operators of the Hamiltonian (2). Let us introduce the Hubbard operators [15] $X_{fj}^{pq} = |\Psi_{fj}^p\rangle\langle\Psi_{fj}^q|$ based on the eigenstates $\{|\Psi_{fj}^p\rangle\}$ of the single-ion operators of the A and B sublattices. In this representation, the spin operators have the form $S_{fj}^{z(+)} = \sum_\alpha \gamma_{\parallel(\perp),j}(\alpha) X_{fj}^\alpha + \sum_p \Gamma_{\parallel(\perp),j}(p) h_{fj}^p$; where $j = A, B$; $h_j^p \equiv X_j^{pp}$; $\gamma_{\parallel(\perp)}(\alpha)$, $\Gamma_{\parallel(\perp)}(\alpha)$ are the parameters of the representation of the spin operators in terms of the Hubbard operators. The sum over α is the sum over the root vectors $\boldsymbol{\alpha} = \boldsymbol{\alpha}(p, q)$ for which $X_j^{pq} \equiv X_j^{\alpha(p,q)}$. The Hamiltonian of the system (2) in the atomic representation has the form:

$$\widehat{\mathscr{H}} = \widehat{\mathscr{H}_0} + \widehat{\mathscr{H}_{\text{exch}}}; \qquad \widehat{\mathscr{H}_0} = \sum_f \sum_n \Big[E_{A,n} h_{fA}^n + E_{B,n} h_{fB}^n \Big];$$

$$\widehat{\mathscr{H}_{\text{exch}}} = \sum_{j,j'=A,B} \; \sum_{f\in j;\; g\in j'} \; \sum_{\lambda\lambda'} \big(\mathbf{c}_j(\lambda), \hat{V}_{fg}^{jj'} \cdot \mathbf{c}_{j'}(\lambda')\big) \Delta R_f^\lambda \Delta R_g^{\lambda'}; \tag{2}$$

where

$$R_f^\lambda = \begin{cases} X_f^\alpha, \; \lambda = \alpha; \\ h_f^n, \; \lambda = n; \end{cases} \quad \mathbf{c}_j(\lambda) = \begin{cases} [\gamma_{\parallel;j}(\alpha), \gamma_{\perp;j}(\alpha), \gamma_{\parallel;j}(-\alpha)], \; \lambda = \alpha; \\ [\Gamma_{\parallel;j}(n), \Gamma_{\perp;j}(n), \Gamma_{\parallel;j}(n)], \quad \lambda = n. \end{cases} \tag{3}$$

Matrices $\hat{V}^{jj'}$ are $\hat{V}_{fg}^{AB} = \hat{a}\hat{J}_{fg}\hat{\bar{a}}$; $\hat{V}_{fg}^{AA} = \hat{a}\hat{I}_{fg}\hat{\bar{a}}$; $\hat{V}_{fg}^{BB} = \hat{a}\hat{K}_{fg}\hat{\bar{a}}$, where the matrix $\hat{a}$ has the components: $\hat{a} = 0.5 \cdot [0,\ 0,\ 2;\ 1,\ -i,\ 0;\ 1,\ i,\ 0]$. For studying the formulated model (2) let us introduce the two-time retarded Green functions [16]:

$$G_{jj'}^{\alpha\beta}(f - f'; t - t') \equiv \langle\langle X_{fj}^\alpha(t) | X_{f'j'}^{-\beta}(t')\rangle\rangle = -i\theta(t - t')\langle[X_{fj}^\alpha(t), X_{f'j'}^{-\beta}(t')]\rangle, \tag{4}$$

where $X_{fj}^\alpha(t)$ are the Hubbard operators in the Heisenberg representation. Using the Hubbard I approximation [15]: $\langle[X_{fj}^\alpha(t), X_{f'j'}^{-\beta}(t')]\rangle = \delta_{ff'}\delta_{jj'}\delta_{\alpha\beta} b_{j\alpha}$, the Green functions in the frequency-momentum representation have been obtained:

$$G_{jj'}^{\alpha\beta}(q, \omega) = \Big(b_{j\alpha} D_{j\alpha}(\omega) \mathbf{c}_j(-\alpha), \hat{V}_q^{jA} \mathbf{A}_{j'\beta} + \hat{V}_q^{jB} \mathbf{B}_{j'\beta}\Big) + \delta_{j\alpha;j'\beta} b_{j\alpha} D_{j\alpha}(\omega). \tag{5}$$

Here, $b_{j\alpha(p,q)} = N_{jp} - N_{jq}$; $D_{j\alpha(p,q)}(\omega) = [\omega + \varepsilon_{j\alpha(p,q)}]^{-1} \equiv [\omega + E_{jp} - E_{jq}]^{-1}$. N_{jp} and E_{jp} are the occupation numbers and the energies of the single-ion eigenstates

$|\Psi^{p}_{fj}\rangle$ with sublattice $j = A, B$, accordingly. The two three-dimensional vectors $\mathbf{A}_{j\beta}$ and $\mathbf{B}_{j\beta}$ are determined by a system of six equations:

$$\begin{pmatrix} \hat{1} - \hat{L}^{AA} \cdot \hat{V}^{AA}_{q} & \hat{L}^{AA} \cdot \hat{V}^{AB}_{q} \\ \hat{L}^{BB} \cdot \hat{V}^{BA}_{q} & \hat{1} - \hat{L}^{BB} \cdot \hat{V}^{BB}_{q} \end{pmatrix} \begin{pmatrix} \mathbf{A}_j \\ \mathbf{B}_j \end{pmatrix} = b_{j\beta} D_{j\beta}(\omega) \begin{pmatrix} \delta_{jA}\mathbf{c}_A \\ \delta_{jB}\mathbf{c}_B \end{pmatrix};$$
$$\mathbf{A}_{j\beta}(q,\omega) = \sum_{\alpha} \mathbf{c}_A(\alpha) G^{\alpha\beta}_{Aj}(q,\omega); \quad \mathbf{B}_{j\beta}(q,\omega) = \sum_{\alpha} \mathbf{c}_B(\alpha) G^{\alpha\beta}_{Bj}(q,\omega). \quad (6)$$

There $\hat{1}$ is the three-dimensional unit matrix, $\hat{V}^{jj'}_{q}$ are the Fourier-transforms of the matrices $\hat{V}^{jj'}_{fg}$. The n and m elements of the three-dimensional matrix $\hat{L}^{jj}$ are $(\hat{L}^{jj})_{nm} = \sum_{\alpha} D_{j\alpha} b_{j\alpha} (c_j(-\alpha))_n (c_j(\alpha))_m$. The Green functions (4), the low-temperature spectral and thermodynamic properties of the anisotropic two-sublattices Heisenberg magnets can be calculated using the Eqs. (5–6). The generalization of the submitted approach for anisotropic magnets with more sublattices is clear.

3 Low-Temperature Properties of the Single-Chain Magnet catena-[$Fe^{II}(ClO_4)_2Fe^{III}(bpca)_2$]($ClO_4$)

Let us consider the single-chain magnet SCM-catena [10,11] with the magnetic structure depicted in Fig. 1. Let us also take into account the presence of the experimentally observed short range ferrimagnetic ordering in the system along z-axis (Fig. 1). Generalized, the submitted approach for the case of four sublattices the Hamiltonian of the SCM-catena can be written in the following form:

$$\widehat{\mathscr{H}_G} = \sum_{j=1} \sum_{f,n} E_{jn} h^{n}_{fj} + J \sum_{j=1}^{4} \sum_{\langle f_j f_{j+1} \rangle} \sum_{\lambda,\lambda'} \left(\mathbf{c}_j(\lambda),\ \widehat{V} \cdot \mathbf{c}_{j+1}(\lambda') \right) \Delta R^{\lambda}_{fi} \Delta R^{\lambda'}_{f,j+1}. \quad (7)$$

The single-ion energy levels E_{jn} have been calculated in the self-consistent mean-field approximation. In these calculations, we restricted ourself to isotropic nearest-neighbour exchange interaction by intensity J. The modulation of the directions of the easy-plane single-ion anisotropy by intensity $2D$ (Fig. 1) has also been taken into account. Using the Hubbard I approximation one obtains:

$$G^{\alpha\beta}_{Aj}(q;\omega) = \delta_{Aj}\delta_{\alpha\beta} D_{A\alpha}(\omega) + J D_{A\alpha}(\omega) b_{A\alpha} \left(\mathbf{c}_A(-\alpha), \widehat{V} \cdot \left(\mathbf{D}_j e^{-4iq} + \mathbf{B}_j \right) \right);$$
$$G^{\alpha\beta}_{Bj}(q;\omega) = \delta_{Bj}\delta_{\alpha\beta} D_{B\alpha}(\omega) + J D_{B\alpha}(i\omega) b_{B\alpha} \left(\mathbf{c}_B(-\alpha), \widehat{V} \cdot \left(\mathbf{A}_j + \mathbf{C}_j \right) \right). \quad (8)$$

The actual components of the $\mathbf{A}_j$, $\mathbf{B}_j$, $\mathbf{C}_j$, and $\mathbf{D}_j$ can be obtained by the following system of equations:

$$\begin{pmatrix} \mathbf{P}^{+}_{j} \\ \mathbf{P}^{-}_{j} \end{pmatrix} = \begin{pmatrix} \hat{\Phi}(q,\omega) & \hat{W}(q,\omega) \\ \hat{W}(q,\omega) & \hat{\Phi}(q,-\omega) \end{pmatrix} \begin{pmatrix} \mathbf{P}^{+}_{j} \\ \mathbf{P}^{-}_{j} \end{pmatrix} + \begin{pmatrix} \mathbf{y}_{j\perp}(\beta,\omega) \\ \mathbf{y}_{j\perp}(-\beta,-\omega), \end{pmatrix}; \quad (9)$$

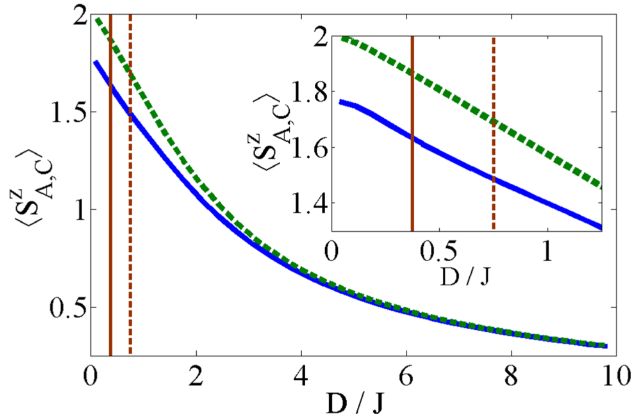

Fig. 2 The magnetization of the A, C sublattices $\langle S^z_{A,C} \rangle$ versus anisotropy D dependencies. *Solid lines* correspond to the spin-wave approximation calculations, *dotted lines*—mean-field approximation. The *vertical solid* and *dotted lines* mark the values of anisotropy $D/J = 3/8$ and $D/J = 6/8$, accordingly (Color figure online)

where $\mathbf{P}_j^{+(-)} = \{\mathbf{A}_j^{2(3)};\ \mathbf{B}_j^{2(3)};\ \mathbf{C}_j^{2(3)};\ \mathbf{D}_j^{2(3)}\}$. $\mathbf{y}_{\perp j}(\beta, \omega)$ are the four-dimensional vectors with components $y^i_{j\perp}(\beta, \omega) = \delta_{ij}\gamma_{\perp j}(\beta) D_{j\beta}(\omega))$ where $i, j = A, B, C, D$. Matrices $\hat{\Phi}$ and $\hat{W}$ have the form:

$$\hat{\Phi} = \frac{J}{2}\begin{pmatrix} -1 & z_A & 0 & z_A e^{-4iq} \\ z_B & -1 & z_B & 0 \\ 0 & z_A & -1 & z_A \\ z_B e^{4iq} & 0 & z_B & -1 \end{pmatrix}; \quad \hat{W} = \frac{J}{2}\begin{pmatrix} 0 & w & 0 & w e^{-4iq} \\ 0 & 0 & 0 & 0 \\ 0 & -w & 0 & -w \\ 0 & 0 & 0 & 0 \end{pmatrix}. \tag{10}$$

The denominator of the Green functions (8) has the form:

$$\begin{aligned} \Delta_\perp(q, \omega) &= \tilde{\Delta}_\perp\Big(q, \omega\Big)\tilde{\Delta}_\perp\left(q + \frac{\pi}{2}, \omega\right) - \frac{J}{2} z_B(\omega) z_B(-\omega) w^2(\omega)\big(1 + \cos(4q)\big); \\ \tilde{\Delta}_\perp(q, \omega) &= \Big[1 - 0.25 \cdot J_q^2 z_A(i\omega) z_B(i\omega)\Big]\Big[1 - 0.25 \cdot J_q^2 z_A(-\omega) z_B(-\omega)\Big] + \\ &\quad + \left(\frac{J_q}{2}\right)^4 z_B(\omega) z_B(-\omega) w^2(\omega), \end{aligned} \tag{11}$$

where $J_q = 2J\cos(q)$, $z_{A,B}(\omega) = (L^{AA(BB)})_{22}$, $w(\omega) = (L^{AA})_{23}$.

The solutions of equation $\Delta_\perp\big(q, \omega\big) = 0$ determine the elementary excitation spectrum of the SCM-catena. The magnetic averages of the sublattices can be calculated by calculations of the single-ion occupation numbers of magnetic states of sublattices. The latest has been extracted from Green functions $G^{\alpha\alpha}_{jj}(f = f'; t = t')$ (4) using the spectral theorem [16].

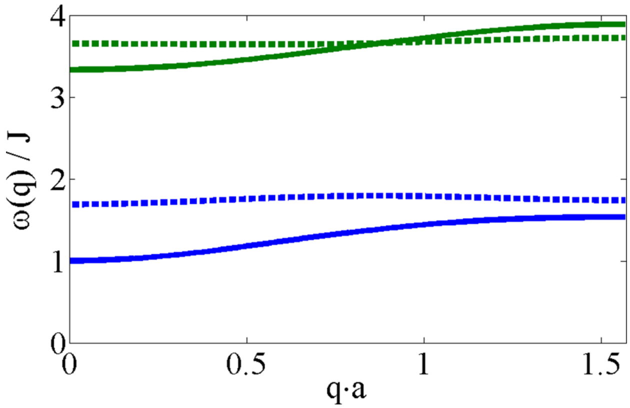

Fig. 3 The quasimomentum dependence of the two low energies branches of the excitation spectrum of SCM-catena with $D/J = 3/8$ (*solid lines*) and $D/J = 6/8$ (*dotted lines*) (Color figure online)

4 Results and Conclusions

The dependencies of $\langle S^z_{A,C}\rangle$ for HS iron ions ($S = 2$; A and C sublattices) versus anisotropy D are shown in Fig. 2. Solid lines correspond to calculations in the spin-wave approximation; dotted lines—in the mean-field approximation. The vertical solid and dotted lines mark the values of anisotropy $D/J = 3/8$ (experimentally evaluated for SCM-catena) and $D/J = 6/8$, accordingly. It is seen that the average value of the z-spin projection of the HS iron ions with $S = 2$ decreases to $\langle S^z_{A,C}\rangle \approx 1.63$ for $D/J = 3/8$ and to $\langle S^z_{A,C}\rangle \approx 3/2$ for $D/J = 6/8$. Moreover, in both cases more than one-half of the magnetization change is created by spin wave fluctuations. It is worth noting that in our notations the parameters of the single-ion anisotropy $D = D'/2$ and the exchange $J = 2J'$ are renormalized compared with the same parameters $D' = 15\ K$, $J' = 7\ K$ evaluated in the work [10]. The presence of these strong spin fluctuations would be taken into account during analysis of experimental data of static [12,13] and dynamic [17–19] magnetic properties of the material [1,10].

The results of the numerical solution of Eq. (11) are shown in Fig. 3. Solid lines represent the quasimomentum dependence of the two low energies branches of the excitation spectrum of the SCM-catena with $D/J = 3/8$. Dotted lines are the quasimomentum dependence of the similar spectrum branches for $D/J = 6/8$. In both cases, the excitation spectrum has a characteristic gap of width $\Delta \sim J$ and a low (relative to Δ) dispersion of the main excitation branches. This means that on a qualitative level, the energy structure of the SCM-catena coincides with the single-particle excitation spectrum of a ferrimagnetic Ising chain for which $\Delta = 2JS_1S_2$ and there is no dispersion of branches. These properties fulfil oneself with $D/J = 6/8$. These results explain the experimental data for the SCM-catena family compounds which display properties typical for magnets with the easy-axis type of anisotropy [10,11].

Acknowledgments This study was supported by the Presidium of the Russian Academy of Sciences, program "Actual problems of low temperature physics"; the Russian Foundation for Basic Research, Projects Nos. 13-02-00523, 14-02-31280 and 15-42-04372.

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