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Low-energy excitations and thermodynamical properties of the quantum $(\frac{5}{2}, \frac{1}{2}, \frac{1}{2})$ ferrimagnetic chain

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Abstract

The low-energy structures of the quantum ferrimagnetic Heisenberg chain consisting of $(\frac{5}{2}, \frac{1}{2}, \frac{1}{2})$ trimers are investigated theoretically. The results of the linear spin-wave theory are compared with those from the numerical exact diagonalization calculation and the matrix product method for the lowest optical mode. The temperature behaviour of thermodynamical properties such as magnetic susceptibility, specific heat and entropy are analysed in the framework of the modified spin-wave theory. The results of the calculations are used to explain the experimental data obtained for the molecule-based heterospin magnets $[Mn(hfac)_2BNO_R]$ (R = H, F, Cl, Br) with one-dimensional chain structure.

1. Introduction

The magnetic properties of molecule-based heterospin magnets have been a subject of renewed interest in the physics of one-dimensional (1D) magnetic systems. In this respect, the compounds with a general formula $[Mn(hfac)_2BNO_R]$ (R = H, F, Cl, Br) are of special interest. These magnetic systems undergo a three-dimensional (3D) ordering at very low temperatures ($T < T_N$ or T_C) but they exhibit essentially 1D behaviour above the 3D ordering regime [1]. The magnetic properties of the compounds strongly depend on the chemical formula and spin configuration in space. In these compounds the manganese ions and diradical 5-R-1, 3-bis(*N*-*tert*-butyl-*N*-oxy-amino)benzene (BNO_R) molecules (R = H, F, Cl, Br) form 1D zigzag polymeric chains. The spins of the NO groups of the diradical are ordered ferromagnetically with a large value of the energy of the exchange coupling (figure 1). The exchange interaction between 3d electrons of the divalent Mn ion and 2p electrons of the NO group is antiferromagnetic. The 1D complexes with R = H and F are ordered antiferromagnetically below 5.5 and 5.3 K, respectively, due to a negative interchain

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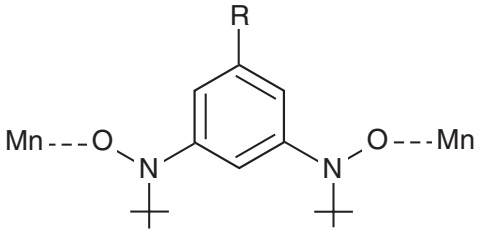

Figure 1. The schematic chain structure of $[Mn(hfac)_2BNO_R]$ compounds.

interaction, while the compounds with R = Cl, Br show ferrimagnetic order below 4.8 and 5.3 K, respectively. The compounds have three-spin periodicity along the 1D chains.

The three-spin model $(\frac{5}{2}, \frac{1}{2}, \frac{1}{2})$ with two types of exchange parameter suggested for a description of the system presents a further natural development of the theory of two-spin (S, s) ferrimagnetic chains [2]. Thus, it is interesting to see how the quantum behaviour of the model depends on the constituent spins and what features are inherited in such an expansion of the model. The existence of metal ions with the large spin $\frac{5}{2}$ makes a quantum treatment of the system a non-trivial problem. Though the correlation length of the $(\frac{5}{2}, \frac{1}{2}, \frac{1}{2})$ chain is very small [2], a numerical investigation of the system is problematic because of the large number of magnetic cell states. The chosen model of a linear spin chain is a simplified description of the real compounds with zigzag space structure. A possible exchange interaction between two NO radicals adjoining one Mn ion and a possible exchange interaction between two Mn ions are omitted in such considerations. Taking account of the interactions (equivalent to the two-leg zigzag ladder) may result in a non-collinear spin arrangement.

The main feature of 1D ferrimagnets is a long-range order with simultaneous strongly developed quantum fluctuations. Nevertheless, the spin-wave approach leads to very satisfactory results for the ground state, magnetization and low-energy excitations [3, 4]. This represents a difference between ferrimagnets and 1D antiferromagnets, where quantum fluctuations play an essential role, resulting in destruction of the long-range order, and the spin-wave theory is not appropriate.

A variational procedure based on the DMRG algorithm has been suggested also for quantum ferrimagnets [5]. As is shown, application of the approach to the three-spin ferrimagnet allows one to describe reasonably well the ground state properties from a non-interacting $(\frac{1}{2}, \frac{5}{2}, \frac{1}{2})$ trimer limit up to a situation where the model becomes equivalent to the $(\frac{5}{2}, 1)$ ferrimagnetic chain model [2].

As has been demonstrated in a number of works, there is a coexistence of ferromagnetic and antiferromagnetic features in quantum ferrimagnets. In recent studies the following scenario has been established [6]. At low temperatures the mixed-spin model behaves like a ferromagnet and at intermediate temperatures as an antiferromagnet. Both types of excitation may be observed, for example, in the thermal behaviour of the zero-field magnetic susceptibility. In the theory of two-spin (S, s) ferrimagnetic chains the non-interacting spin-wave approximation is valid for the lowest gapless mode, but it only captures qualitatively the elementary excitations of optical magnons. The quantum fluctuations have been taken into account by including a spin-wave interaction [7]. The calculation of the optical magnon dispersion results in excellent consistency with the numerical Monte Carlo and direct diagonalization results. The modified variational method has been generalized for calculations for optical magnons of the $(1, \frac{1}{2})$ chain [8].

The aim of the present work is to study the excitations of the model heterospin $(\frac{5}{2}, \frac{1}{2}, \frac{1}{2})$ ferrimagnetic chain and to apply the results obtained to give an explanation of the magnetic

properties of the metal–radical complexes with a chain structure. The powder samples of the above compounds were prepared and examined as described in Inoue *et al* [9]. The magnetic susceptibility was measured between 1.8 and 350 K by using a Quantum Design SQUID magnetometer in the applied field 5000 Oe. The powder samples were placed in a Japanese pharmacopoeia gel capsule. The background data for the capsule were measured separately and subtracted from the sample-in-cell data.

The paper is organized in the following way. In section 2 the linear spin-wave treatment is developed. In section 3 the lower optical magnon branch of excitations is calculated by the matrix product method (MPM). The SW results for the quadratic gapless mode are compared with the values obtained in the real-space quantum renormalization group and exact diagonalization methods.

In section 4 the zero-field magnetic susceptibility, the specific heat and the entropy are found in the framework of the modified spin-wave theory. The agreement with the experimental data for the $[Mn(hfac)_2BNO_R]$ (R = H, Cl, Br) compounds is discussed.

2. Spin-wave calculation

We consider the model of the 1D spin chain ($\frac{5}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) described by the Hamiltonian

$$\hat{H} = J_a \sum_n \vec{S}_{1n} \cdot \vec{S}_{2n} + J_f \sum_n \vec{S}_{2n} \cdot \vec{S}_{3n} + \frac{J_a}{2}\left(\sum_n \vec{S}_{3n} \cdot \vec{S}_{1n+1} + \sum_n \vec{S}_{3n-1} \cdot \vec{S}_{1n} \right), \tag{1}$$

where $\vec{S}_{1n}$, $\vec{S}_{2n}$ and $\vec{S}_{3n}$ are respectively the spin-$\frac{5}{2}$, spin-$\frac{1}{2}$ and spin-$\frac{1}{2}$ operators of the nth elementary magnetic cell. The sum n runs over the N sites of the chain. Due to the translational invariance, the last two terms in equation (1) coincide. Only the exchange interaction between nearest neighbours is considered and all bonds between $\frac{5}{2}$ and $\frac{1}{2}$ spins ($J_a > 0$) are taken as antiferromagnetic while those between $\frac{1}{2}$ and $\frac{1}{2}$ spins ($J_f < 0$) are taken as ferromagnetic. In the limit of strong ferromagnetic exchange interaction ($|J_f| > J_a$) one can consider a spin chain ($\frac{5}{2}$, 1) instead of the spin chain ($\frac{5}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) with the Hamiltonian

$$H = J \sum_n \vec{S}_n \cdot \vec{s}_n + J \sum_n \vec{s}_n \cdot \vec{S}_{n+1} \qquad (S = 5/2,\ s = 1), \tag{2}$$

where J corresponds to the antiferromagnetic exchange coupling $J = J_a/2$.

Firstly, we obtain the spin-wave theory results giving a qualitative view of the low-energy structure. By supposing a Néel state with a magnetization $(3/2)N$ the bosonic operators for the spin deviation in each sublattice are defined as

$$\begin{aligned} &S^z_{1n} = S_1 - a^+_{1n}a_{1n}, \qquad S^+_{1n} = \sqrt{2S_1}\,a_{1n}, \qquad S^-_{1n} = a^+_{1n}\sqrt{2S_1} \\ &S^z_{in} = -S_i + a^+_{in}a_{in}, \qquad S^+_{in} = a^+_{in}\sqrt{2S_i}, \qquad S^-_{in} = \sqrt{2S_i}\,a_{in} \qquad (i = 2, 3). \end{aligned} \tag{3}$$

To obtain the dispersion relations of the spin-wave excitations, the boson Hamiltonian is treated up to quadratic order. On using the momentum representation of the bosonic operators:

$$\begin{aligned} a_{1n} &= \frac{1}{\sqrt{N}} \sum_k \mathrm{e}^{\mathrm{i}k(n-\frac{1}{3})} a_{1k}, \\ a_{2n} &= \frac{1}{\sqrt{N}} \sum_k \mathrm{e}^{-\mathrm{i}kn} a_{2k}, \\ a_{3n} &= \frac{1}{\sqrt{N}} \sum_k \mathrm{e}^{-\mathrm{i}k(n+\frac{1}{3})} a_{3k} \end{aligned} \tag{4}$$

the initial Hamiltonian takes the form

$$H = \sum_k 2J_a S_2 a_{1k}^+ a_{1k} + \sum_k \sum_{i=2,3} (J_a S_1 - J_f S_2) a_{ik}^+ a_{ik}$$
$$+ \sum_k J_a \sqrt{S_1 S_2} (\mathrm{e}^{-\mathrm{i}\frac{k}{3}} a_{1k} a_{2k} + \mathrm{e}^{\mathrm{i}\frac{k}{3}} a_{1k}^+ a_{2k}^+) + \sum_k J_f S_2 (\mathrm{e}^{-\mathrm{i}\frac{k}{3}} a_{2k}^+ a_{3k} + \mathrm{e}^{\mathrm{i}\frac{k}{3}} a_{2k} a_{3k}^+)$$
$$+ \sum_k J_a \sqrt{S_1 S_2} (\mathrm{e}^{-\mathrm{i}\frac{k}{3}} a_{3k}^+ a_{1k}^+ + \mathrm{e}^{\mathrm{i}\frac{k}{3}} a_{3k} a_{1k}) - 2N J_a S_1 S_2 + N J_f S_2^2. \tag{5}$$

Carrying out a Bogoliubov transformation:

$$\begin{aligned} a_{1k} &= u_{11}(k)\alpha_{1k} + u_{12}(k)\alpha_{2k}^+ + u_{13}(k)\alpha_{3k}^+, \\ a_{2k} &= u_{21}(k)\alpha_{1k}^+ + u_{22}(k)\alpha_{2k} + u_{23}(k)\alpha_{3k}, \\ a_{3k} &= u_{31}(k)\alpha_{1k}^+ + u_{32}(k)\alpha_{2k} + u_{33}(k)\alpha_{3k} \end{aligned} \tag{6}$$

the diagonal Hamiltonian

$$H = E_0 - \sum_k E_{1k}\alpha_{1k}^\dagger \alpha_{1k} + \sum_k E_{2k}\alpha_{2k}^\dagger \alpha_{2k} + \sum_k E_{3k}\alpha_{3k}^\dagger \alpha_{3k} \tag{7}$$

is reached, where E_0 is a zero-frequency energy. The coefficients of the transformation may be found through equations of motion for the Green functions $G^{(1)} = \langle\langle a_{1k} | a_{1k}^+ \rangle\rangle$, $G^{(2)} = \langle\langle a_{2k}^+ | a_{1k}^+ \rangle\rangle$ and $G^{(3)} = \langle\langle a_{3k}^+ | a_{1k}^+ \rangle\rangle$:

$$\begin{pmatrix} E - A & -C_k^* & -C_k \\ C_k & E + B & D_k^* \\ C_k^* & D_k & E + B \end{pmatrix} \begin{bmatrix} G^{(1)} \\ G^{(2)} \\ G^{(3)} \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix}, \tag{8}$$

where $A = 2J_a S_2$, $B = J_a S_1 - J_f S_2$, $C_k = J_a \sqrt{S_1 S_2}\ \exp(-\mathrm{i}k/3)$, $D_k = J_f S_2 \exp(-\mathrm{i}k/3)$. The Bogoliubov transformation coefficients are given by

$$u_{11}(k) = \left[\frac{\Delta_{1k}(-E_{1k})}{(E_{1k} - E_{2k})(E_{1k} - E_{3k})} \right]^{\frac{1}{2}},$$
$$u_{12}(k) = \left[\frac{\Delta_{1k}(-E_{2k})}{(E_{1k} - E_{2k})(E_{2k} - E_{3k})} \right]^{\frac{1}{2}},$$
$$u_{13}(k) = \left[\frac{\Delta_{1k}(-E_{3k})}{(E_{1k} - E_{3k})(E_{3k} - E_{2k})} \right]^{\frac{1}{2}},$$
$$u_{21}(k) = \frac{\Delta_{2k}(-E_{1k})}{[\Delta_{1k}(-E_{1k})(E_{1k} - E_{2k})(E_{1k} - E_{3k})]^{\frac{1}{2}}},$$
$$u_{22}(k) = \frac{\Delta_{2k}(-E_{2k})}{[\Delta_{1k}(-E_{2k})(E_{1k} - E_{2k})(E_{2k} - E_{3k})]^{\frac{1}{2}}},$$
$$u_{23}(k) = \frac{\Delta_{2k}(-E_{3k})}{[\Delta_{1k}(-E_{3k})(E_{1k} - E_{3k})(E_{3k} - E_{2k})]^{\frac{1}{2}}},$$
$$u_{31}(k) = \frac{\Delta_{3k}(-E_{1k})}{[\Delta_{1k}(-E_{1k})(E_{1k} - E_{2k})(E_{1k} - E_{3k})]^{\frac{1}{2}}},$$
$$u_{32}(k) = \frac{\Delta_{3k}(-E_{2k})}{[\Delta_{1k}(-E_{2k})(E_{1k} - E_{2k})(E_{2k} - E_{3k})]^{\frac{1}{2}}},$$
$$u_{33}(k) = \frac{\Delta_{3k}(-E_{3k})}{[\Delta_{1k}(-E_{3k})(E_{1k} - E_{3k})(E_{3k} - E_{2k})]^{\frac{1}{2}}},$$

where

$$\begin{aligned} \Delta_k(E) &= (E + E_{1k})(E + E_{2k})(E + E_{3k}), \\ \Delta_{1k}(E) &= (E + B)(E + B) - D_k^* D_k, \\ \Delta_{2k}(E) &= \Delta_{3k}^*(E) = -(E + B)C_k + C_k^* D_k^*. \end{aligned}$$

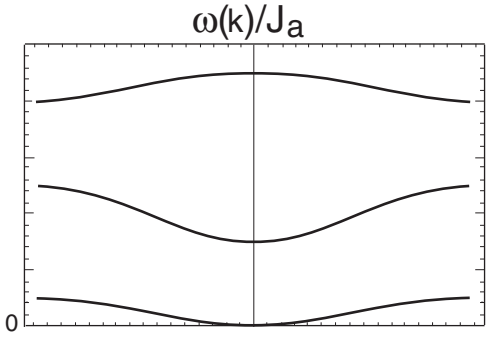

Figure 2. Spin-wave theory dispersion curves for the linear ferrimagnetic ($\frac{5}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) chain.

The energies of the elementary excitations

$$E_{ik} = -2\sqrt{-\frac{p}{3}}\cos\left(\frac{\alpha}{3} + (i-1)\frac{2\pi}{3}\right) + \frac{a}{3} \qquad (i = 1, 2, 3) \tag{9}$$

where $\alpha = \cos^{-1}(-q/2\sqrt{-(p/3)^3})$, $p = -a^2/3 + b$, $q = 2(a/3)^3 - ab/3 + c$ with

$$a = 2(J_a(S_1 - S_2) - J_f S_2), \qquad b = J_a(S_1 - 2S_2)(J_a S_1 - 2J_f S_2),$$
$$c = 4J_a^2 J_f S_1 S_2^2 \sin^2\left(\frac{k}{2}\right).$$

The calculation yields a gapless excitation from the ferrimagnetic ground state with the total magnetization $M = \sum_{i=1}^{n}(S_{1i}^z + S_{2i}^z + S_{3i}^z) = (3/2)N - 1$; the lowest optical mode corresponds to the total magnetization $M = (3/2)N + 1$, and the second branch does to $M = (3/2)N + 2$ (figure 2).

3. Matrix product method

The linear spin-wave theory gives a qualitative description of the excitation spectrum. Quantitative calculation—for example, of the optical magnon branches—is of special interest due to possible magnetization plateaux appearing in the 1D system [10, 11]. A quantitative spin-wave theory must take into account spin-wave interaction to show good consistency with numerical calculations [7]. A different scheme which has proven to be very successful for the quantum ferrimagnet is the variational MPM [5]. A calculation of an optical magnon spectrum by this method has been carried out by Kolezhuk *et al* [8], where a trial wavefunction for the optical magnon with the momentum k under periodic boundary conditions is constructed as

$$|k\rangle = \sum_n \mathrm{e}^{\mathrm{i}kn}|n\rangle, \qquad |n\rangle = \mathrm{Tr}\{g_1 \dots g_{n-1}\tilde{g}_n g_{n+1} \dots g_L\}.$$

The elementary matrices g_i and $\tilde{g}_i$ are formed from the block states $|SM_S\rangle$. The energy dependences of the block states on the ratio J_f/J_a are presented in figure 3. In the previous investigation of ground state properties we retained the two lowest states $|\frac{3}{2}M\rangle$ and $|\frac{5}{2}M\rangle$ which allows us to use a g-matrix of size 2×2. The inclusion of the next upper states $|\frac{7}{2}M\rangle$ requires an expansion of the g-matrix size up to the dimension 3×3. The ground state energy per site found by the MPM with the g-matrix of size 2×2 is $-5.805J$ and it is $-5.914J$ for the size 3×3. In the latter case the g-matrix contains five independent variational parameters and

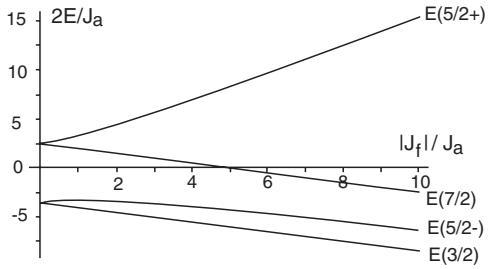

Figure 3. Energy levels of the block states. The three lowest states are taken into consideration in the matrix product approach.

the contribution of the states $|\frac{7}{2}M\rangle$ turns out to be not small. (The corresponding variational coefficient $\eta = C^{27/2}_{3/2}/C^{03/2}_{3/2} \approx 0.72$, where the notation of [5] is used.)

In the low-energy excitation study one can include the $|\frac{7}{2}M\rangle$ states in a g-matrix of size 2×2. In view of this, one may count on a sufficient quantitative accuracy of the approach presented below.

The ground state has two Affleck–Kennedy–Lieb–Tasaki (AKLT) singlet bonds [12], since a low-lying excitation may be considered qualitatively as the forming of one triplet bond in the AKLT valence-bond-solid state and $\tilde{g}$ should carry the 'hyperspin' quantum numbers $(\frac{5}{2}, \frac{5}{2})$:

$$g^{\frac{5}{2}\frac{5}{2}} = \tilde{g} = \begin{pmatrix} (u_1 - \sqrt{\frac{5}{7}}u_3)|\frac{5}{2}\frac{5}{2}\rangle - \sqrt{\frac{3}{14}}u_4|\frac{7}{2}\frac{5}{2}\rangle & \sqrt{\frac{3}{2}}u_4|\frac{7}{2}\frac{7}{2}\rangle \\ -\{\sqrt{2}u_2|\frac{3}{2}\frac{3}{2}\rangle - \frac{2}{\sqrt{7}}u_3|\frac{5}{2}\frac{3}{2}\rangle & \\ -\frac{1}{\sqrt{14}}u_4|\frac{7}{2}\frac{3}{2}\rangle\} & (u_1 + \sqrt{\frac{5}{7}}u_3)|\frac{5}{2}\frac{5}{2}\rangle + \sqrt{\frac{3}{14}}u_4|\frac{7}{2}\frac{5}{2}\rangle \end{pmatrix}, \tag{10}$$

while each g carries ground state quantum numbers $(\frac{3}{2}, \frac{3}{2})$:

$$\hat{g}^{\frac{3}{2}\frac{3}{2}} = \begin{pmatrix} (u - \sqrt{\frac{3}{5}}v)|\frac{3}{2}\frac{3}{2}\rangle - \frac{2}{\sqrt{15}}\omega|\frac{5}{2}\frac{3}{2}\rangle & \frac{2}{\sqrt{3}}\omega|\frac{5}{2}\frac{5}{2}\rangle \\ -\frac{2}{\sqrt{5}}v|\frac{3}{2}\frac{1}{2}\rangle - \sqrt{\frac{2}{15}}\omega|\frac{5}{2}\frac{1}{2}\rangle & (u + \sqrt{\frac{3}{5}}v)|\frac{3}{2}\frac{3}{2}\rangle + \frac{2}{\sqrt{15}}\omega|\frac{5}{2}\frac{3}{2}\rangle \end{pmatrix}. \tag{11}$$

In Kolezhuk *et al* [8] the set of one-magnon states $|n\rangle$ has been taken as mutually orthogonal by special choice of the variational parameters. In our calculation we used the conventional method operating with the non-orthogonal basis, when the states $|n\rangle$ are not orthogonal to each other, but are orthogonal just to the ground state. The details of the technique may be found in [13].

According to the method, one needs to calculate: the norm of the states $|k\rangle$; the expectation value $\langle k|\hat{H}_B|k\rangle$ of the block Hamiltonian

$$\hat{H}_B = \sum_n J_a \vec{S}_{1n} \cdot \vec{S}_{2n} + J_f \vec{S}_{2n} \cdot \vec{S}_{3n}, \tag{12}$$

including the intrablock interactions; and the expectation value $\langle k|\hat{H}_{BB}|k\rangle$ of the interblock interactions

$$\hat{H}_{BB} = J_a \sum_n \vec{S}_{3n} \cdot \vec{S}_{1n+1}. \tag{13}$$

As a result, one obtain the energy functional in the form

$$E = LE_{\rm gr} + \omega(k),$$

with the energy of the ground state

$$E_{\rm gr} = \lim_{L\to\infty} \frac{\langle k|H^{(1)}_B|k\rangle + \langle k|H^{(1)}_{BB}|k\rangle}{\langle k|k\rangle},$$

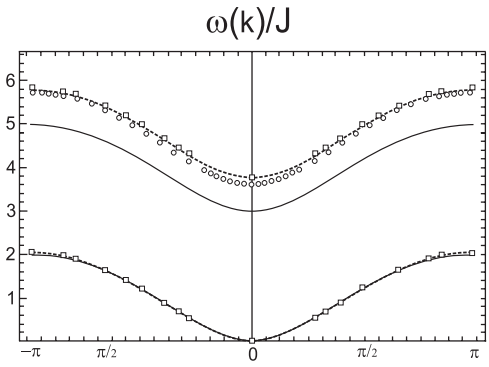

Figure 4. Dispersion relations for the ferromagnetic and lower antiferromagnetic elementary excitations. The non-interacting and interacting spin-wave calculations are shown by solid and dotted curves respectively, whereas ◯ represents the matrix product and □ the exact diagonalization results (up to $N = 7$). The ground state energy is supposed to be zero.

and the excitation energy

$$\omega(k) = \lim_{L\to\infty} \frac{\langle k|H_B^{(0)}|k\rangle + \langle k|H_{BB}^{(0)}|k\rangle}{\langle k|k\rangle}. \tag{14}$$

The upper index (1) denotes the terms in the expectation values which are proportional to L and (0) those which are proportional to 1. Minimization of the ground state energy $E_{\rm gr}$ gives the coefficients u, v, w. The excitation spectrum is obtained by minimizing the excitation energy $\omega(k)$ for each k with the u, v, w found and the result is presented in figure 4, where strong ferromagnetic coupling is assumed. This provides a satisfactory agreement with the spin-wave calculation for the two-spin (S, s) ferrimagnetic model with account taken of the spin-wave interaction $\tilde{\omega}_k^{\pm} = \omega_k^{\pm} \pm \delta\omega_k^{\pm}$ [7], where

$$\begin{aligned}
&\omega_k^{\pm} = \omega_k \pm (S - s), \qquad \omega_k = \sqrt{(S-s)^2 + 4Ss\sin^2 k},\\
&\delta\omega_k^{\pm} = 2(S+s)\Gamma_1\frac{\sin^2 k}{\omega_k} + \frac{\Gamma_2}{\sqrt{Ss}}\omega_k^{\pm},\\
&\Gamma_1 = \frac{1}{2N}\sum_k\left(\frac{S+s}{\omega_k} - 1\right), \qquad \Gamma_2 = -\frac{1}{N}\sum_k \frac{\sqrt{Ss}}{\omega_k}\cos^2 k,
\end{aligned} \tag{15}$$

and one has to use $S = 5/2$, $s = 1$. Since, in its turn, an account of the spin-wave interaction gives a good agreement with the numerical Monte Carlo and exact diagonalization calculations, one may suggest that the variational procedure developed describes both the ground state properties and the antiferromagnetic branch of elementary excitations well, quantitatively.

To control our g-matrix choice, one needs to calculate the value of the full spin chain magnetization $S^z = (1/L)\sum_i S_{1i}^z + S_{2i}^z + S_{3i}^z$ in the Bloch state:

$$\langle S^z\rangle = \lim_{L\to\infty} \frac{\langle k|S^z|k\rangle}{\langle k|k\rangle}. \tag{16}$$

For the antiferromagnet branch this may be evaluated for the set of variational parameters found. It turns out to be $(3/2)L + 1$ in full accordance with the qualitative reasoning presented above.

The small-momentum ferromagnetic excitations must dominate the low-temperature thermodynamics. Previously, the quantum ferrimagnetic chain has been considered by the quantum renormalization method in real space [2] and as a result of this effective description

the gapless ferromagnetic mode can be obtained by using the dispersion relation of the $S = 3/2$ Heisenberg ferromagnet with renormalized exchange coupling $\tilde{J} = -(14/25)J$. The curvature for quadratic dispersion $2\tilde{J}S(1 - \cos k)$ is $v \approx 0.84J$. For comparison, the spin-wave theory of the 1D quantum (S, s) ferrimagnetic chain yields to the following result: $v = (Ss/[2(S - s)])J \approx 0.83J$.

One can diagonalize the Hamiltonian (2) of the finite (S, s) chain with periodic boundary conditions using the Lanczos algorithm [14, 15]. The exact diagonalization results are reliable for the system under consideration because of the small correlation length, comparable with the lattice unit. To obtain the acoustic and lower optical branches we calculate the ferromagnetic and antiferromagnetic dynamic structure factors [16]:

$$S^{-+}(k, \omega) = \sum_n |\langle n|S_k^- + s_k^-|0\rangle|^2 \delta(\omega - (E_n - E_0)),$$
$$S^{+-}(k, \omega) = \sum_n |\langle n|S_k^+ + s_k^+|0\rangle|^2 \delta(\omega - (E_n - E_0)),$$

respectively, where $|n\rangle$ denotes an eigenstate of the Hamiltonian with the energy E_n and E_0 is ground state energy with spin $(S - s)N$. Since the total magnetization $M = \sum_j S_j^z + s_j^z$ is a conserved quantity, one can diagonalize the Hamiltonian (2) in each subspace with a given M. The dynamic structure factor is expressed through the Green function

$$S^{\sigma\bar{\sigma}}(k, \omega) = -\frac{1}{\pi} \operatorname{Im} G^{\sigma\bar{\sigma}}(k, \omega),$$

where $\sigma = \pm 1$ and $\bar{\sigma} = -\sigma$, which is determined as a continued fraction:

$$G^{\sigma\bar{\sigma}}(k, \omega) = \frac{\langle 0|(S_{-k}^{\bar{\sigma}} + s_{-k}^{\bar{\sigma}})(s_k^{\sigma} + S_k^{\sigma})|0\rangle}{\omega - a_0 - b_1^2/\omega - a_1 - \frac{b_2^2}{\omega - a_2 - \cdots}},$$

where the coefficients $a_n = \langle f_n|H|f_n\rangle/\langle f_n|f_n\rangle$, $b_n^2 = \langle f_n|f_n\rangle/\langle f_{n-1}|f_{n-1}\rangle$, $b_0 = 0$ are determined by a set of orthogonal states

$$|f_{n+1}\rangle = H|f_n\rangle - a_n|f_n\rangle - b_n^2|f_{n-1}\rangle, \qquad |f_0\rangle = (s_k^{\sigma} + S_k^{\sigma})|0\rangle.$$

The initial state is taken as the lowest energy state with $M = N(S - s)$ and the Fourier transforms of the spin operators defined as $S_k^{\pm} = N^{-1/2} \sum_j e^{ik(j-1/4)} S_j^{\pm}$, $s_k^{\pm} = N^{-1/2} \sum_j e^{ik(j+1/4)} s_j^{\pm}$. The exact diagonalization results are presented in figure 4 up to the chain length $N = 7$. They show good consistency with the spin-wave theory calculation even for the small chain length. The ground state energy per site is $E_0/N \approx -5.916J$, obtained for $N = 7$.

4. Magnetic susceptibility and heat capacity

The thermodynamical properties can be conveniently considered in terms of the modified spin-wave theory with an additional constraint on the magnetization [17]. The low-temperature thermodynamics will determined by the dispersion relation of the gapless ferromagnetic branch, whereas the gapped antiferromagnetic modes will be displayed at intermediate temperatures. The occupation numbers of three branches of spin excitations:

$$\tilde{n}_{1k} = \{\exp[(-E_{1k} - \mu(-|u_{11}(k)|^2 + |u_{12}(k)|^2 + |u_{13}(k)|^2))/(k_B T)] - 1\}^{-1}, \tag{17}$$
$$\tilde{n}_{ik} = \{\exp[(E_{ik} - \mu(-|u_{i1}(k)|^2 + |u_{i2}(k)|^2 + |u_{i3}(k)|^2))/(k_B T)] - 1\}^{-1} \qquad (i = 2, 3)$$

depend on the chemical potential μ. According to modified spin-wave theory [18] it controls the boson numbers if one imposes the requirement that the full magnetization of the cell must be zero [19]:

$$\frac{1}{N}\left\langle \sum_i S_{1i}^z + S_{2i}^z + S_{3i}^z \right\rangle = (S_1 - 2S_2) + (-n_1 + n_2 + n_3) = 0, \tag{18}$$

where

$$n_i = \frac{1}{N}\sum_k \langle a_{ik}^+ a_{ik}\rangle = \frac{1}{N}\sum_k n_{ik} \qquad (i = 1, 2, 3). \tag{19}$$

The constraint introduced above is appropriate at high temperatures, since at low temperatures the system considered is unstable against 3D arrangement.

The susceptibility $\chi = [1/(3T)]\sum_m \langle (S_0^z - \langle S^z\rangle)(S_m^z - \langle S^z\rangle)\rangle$ may be written as

$$\chi = \frac{1}{3T}\sum_m [-(S_1 - 2S_2)^2 + \langle a_0^+ a_0 a_m^+ a_m\rangle - \langle a_0^+ a_0 b_m^+ b_m\rangle - \langle a_0^+ a_0 c_m^+ c_m\rangle - \langle b_0^+ b_0 a_m^+ a_m\rangle + \langle b_0^+ b_0 b_m^+ b_m\rangle + \langle b_0^+ b_0 c_m^+ c_m\rangle - \langle c_0^+ c_0 a_m^+ a_m\rangle + \langle c_0^+ c_0 b_m^+ b_m\rangle + \langle c_0^+ c_0 c_m^+ c_m\rangle], \tag{20}$$

where the correlation functions involved in equation (20) are calculated through Wick's theorem:

$$\begin{aligned}
&\langle a_{i0}^+ a_{i0} a_{im}^+ a_{im}\rangle = 2n_i^2 + n_i \qquad (i = 1, 2, 3),\\
&\langle a_{30}^+ a_{30} a_{2m}^+ a_{2m}\rangle = n_3 n_2 + \left(\frac{1}{N}\sum_k \langle a_{3k}^+ a_{2k}\rangle\right)\left(\frac{1}{N}\sum_{\acute{k}} \langle a_{3\acute{k}} a_{2\acute{k}}^+\rangle\right),\\
&\langle a_{20}^+ a_{20} a_{3m}^+ a_{3m}\rangle = n_2 n_3 + \left(\frac{1}{N}\sum_k \langle a_{2k}^+ a_{3k}\rangle\right)\left(\frac{1}{N}\sum_{\acute{k}} \langle a_{2\acute{k}} a_{3\acute{k}}^+\rangle\right),\\
&\langle a_{10}^+ a_{10} a_{jm}^+ a_{jm}\rangle = n_1 n_j \qquad (j = 2, 3),
\end{aligned}$$

where

$$\begin{aligned}
&n_{1k} = |u_{11}(k)|^2\,\tilde{n}_{1k} + |u_{12}(k)|^2(1 + \tilde{n}_{2k}) + |u_{13}(k)|^2(1 + \tilde{n}_{3k}),\\
&n_{ik} = |u_{i1}(k)|^2(1 + \tilde{n}_{1k}) + |u_{i2}(k)|^2\tilde{n}_{2k} + |u_{i3}(k)|^2\,\tilde{n}_{3k}, \qquad (i = 2, 3)\\
&\langle a_{2k}^+ a_{3k}\rangle = u_{21}^*(k)u_{31}(k)(1 + \tilde{n}_{1k}) + u_{22}^*(k)u_{32}(k)\tilde{n}_{2k} + u_{23}^*(k)u_{33}(k)\tilde{n}_{3k},\\
&\langle a_{2k} a_{3k}^+\rangle = u_{21}(k)u_{31}^*(k)\tilde{n}_{1k} + u_{22}(k)u_{32}^*(k)(1 + \tilde{n}_{2k}) + u_{32}(k)u_{33}^*(k)(1 + \tilde{n}_{3k}).
\end{aligned} \tag{21}$$

An example of the model calculation fitting $(N_A(g\mu_0)^2/k_B)\chi$ to the experimental data is shown in figure 5 for a different relationship of the exchange parameters. The experimental data for the compounds $[Mn(hfac)_2BNO_R]$ with different ions R = H, Cl, Br differ weakly from each other above the 3D transition temperature. The spin-wave calculation captures qualitatively the temperature behaviour of the magnetic susceptibility. It has been demonstrated previously in the investigation of the elementary excitation spectrum in two-spin ferrimagnetic chains that numerical quantum Monte Carlo estimates result in a more rapid decrease of the magnetic susceptibility with temperature increase. One has to use a more precise value for the gyromagnetic ratio, which is taken as 2, for simplicity. The relationship of the exchange parameters $|J_f| > J_a$ gives a better accordance with the low-temperature data, but gives values higher than those data at high temperatures. With further increase of the temperature the antiferromagnetic branch of the elementary excitations is displayed as a steady susceptibility, increasing from the temperature corresponding to the antiferromagnet gap. One may conclude that the temperature behaviour of the magnetic susceptibility is insensitive to the relationship of the exchange parameters. The curves of magnetic susceptibility are the same for the different sets of J_a and J_f at $T < 350$ K (figure 5). The difference in temperature behaviour becomes visible above the temperature corresponding to the lowest antiferromagnetic gap. Judging by the available experimental data, it occurs at temperatures far exceeding temperatures where the compound is still stable.

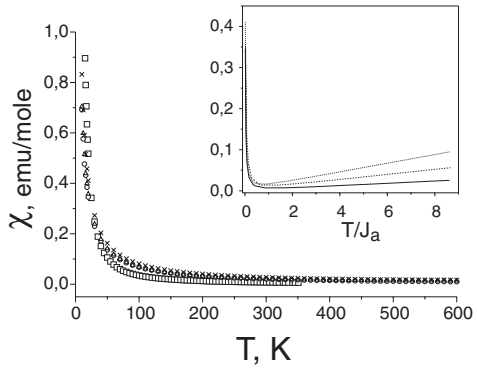

Figure 5. The temperature dependence of the zero-field susceptibility. The open squares are the experimental data, while the open circles ($J_a = 1160$ and $J_f = -2321$ K), the triangles ($J_a = 696$ and $J_f = -696$ K) and the crosses ($J_a = 1160$ and $J_f = -23$ K) are the results of the modified spin-wave calculation. In the inset the same results, measured in units of J_a, are shown for a wider temperature range.

It should be noted that the magnetization measurements of a single-crystalline sample of $[Mn(hfac)_2BNO_H]$ in the ordered state (at $T < 5.5$ K) have revealed the presence of an anisotropy of the critical transition field that suggests a non-collinear arrangement of magnetic moments [20]. Such a non-collinear antiferromagnetic structure may be a result of the influence of the next-nearest-neighbour exchange interaction. Bearing in mind the zigzag form of the chains in $[Mn(hfac)_2BNO_R]$, the suggestion looks quite reasonable. It requires an account of the next-nearest-neighbour exchange in our model that we hope will allow improvement of the agreement between the experimental data and theory in the low-temperature region. As to the interchain interaction, it seems to be rather small to bias the magnetic susceptibility well above the ordering temperature, since the critical field needed to overcome the antiferromagnetic exchange between chains in $[Mn(hfac)_2BNO_H]$ is found to be 200–400 Oe at $T = 1.8$ K [20].

One can suggest that the behaviour of the specific heat and the entropy at low temperatures will be more informative as regards the $|J_f|/J_a$ ratio in the chain. As an example, the specific heat $C_V = N\,\partial\bar{E}/\partial T$, $\bar{E} = E_{gr} + (1/N)\sum_{\alpha=1}^{3}\sum_k E_{k\alpha}\tilde{n}_{\alpha k}$ for the chosen set of parameters is shown in figure 6(a). The decrease of the ferromagnetic exchange parameter up to a regime of non-interacting trimers is accomplished by a narrowing of the acoustic branch of magnon excitations that is displayed as a shaping of the Schottky-like peak in C_V at low temperatures. It is seen also as a transition in the entropy (S) behaviour with temperature increase from a smoothly increasing ($J_a \leqslant |J_f|$) to a steplike curve ($J_a \gg |J_f|$) (figure 6(b)). Thus, the temperature behaviour of the entropy seems to provide a more convenient way of determining the exchange interaction features in the systems.

Finally, we discuss the possibility of measuring the lowest antiferromagnetic gap experimentally in strong magnetic fields. From the experimental point of view, magnetization plateaux may appear in the compounds. According to the Lieb–Schultz–Mattis theorem extended to systems in a magnetic field, the appearance of a plateau with magnetization M may occur at $S_{max}(1 - M) \in \mathbb{Z}$, where the S_{max} is the maximal spin in the unit cell ($S_{max} = 7/2$) and the magnetization M is normalized to saturation values ± 1. Thus, one may expect the magnetization plateaux at $M = 3/7$ corresponding to the ground state, at $M = 5/7$ (partially polarized state) and $M = 1$ (fully polarized state). The lowest antiferromagnetic gap is determined by the critical magnetic field H_c of the transition from the ground state

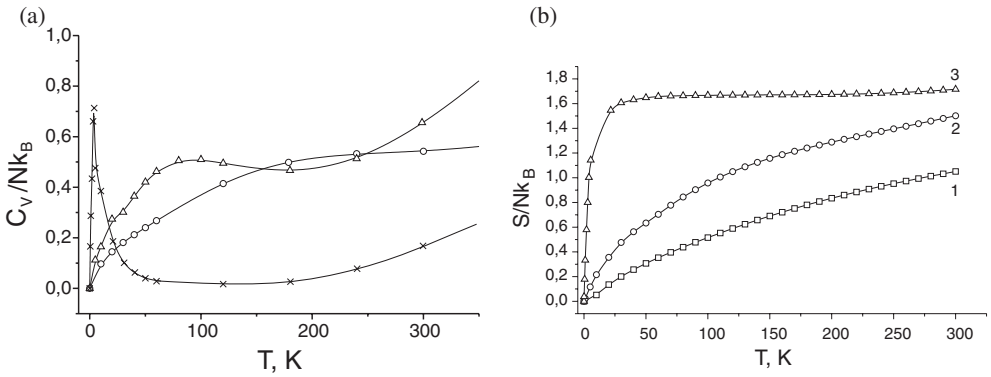

Figure 6. The temperature dependence of the specific heat (a) and entropy (b). The exchange parameters are taken as in figure 5.

magnetization plateau to steady magnetization growth. However, the plateaux might be smeared by the 3D arrangement at low temperatures. High-field magnetization measurements (up to 40 T) of the $[Mn(hfac)_2BNO_H]$ compound performed at $T = 1.6$ K, i.e. below the 3D ordering temperature, have shown that the saturation magnetization reaches a value of about 3 μ_B, which corresponds to the ground ferrimagnetic state [21]. This fact may serve as additional evidence of the large antiferromagnetic exchange interaction between 3d electrons of the Mn ions and 2p electrons of the NO groups. The field 40 T is not enough to destroy antiferromagnetic coupling in the chains. In order to observe the ground state magnetization plateau above the 3D ordering temperature, one may suggest that higher magnetic fields are needed.

5. Conclusions

The 1D quantum $(\frac{5}{2}, \frac{1}{2}, \frac{1}{2})$ ferrimagnet model is a promising candidate for describing thermodynamical properties of the molecule-based heterospin magnet with 1D chain structure and with the general formula $[Mn(hfac)_2BNO_R]$. In the current work the low-energy magnon spectrum of the model is investigated. The linear spin-wave calculation yields a gapless acoustic branch with the magnetization $(3/2)N - 1$ and two optical branches with the magnetizations $(3/2)N + 1$ and $(3/2)N + 2$. The calculation of the lowest magnon branches is compared with the results from the exact diagonalization method for strong ferromagnetic exchange between the trimers. The numerical method reveals a rapid convergence even for short chains and gives an excellent agreement with SW results.

Calculation of the lower antiferromagnetic branch is carried out by the MPM. The very satisfactory consistency between the matrix product results with the strong trimer ferromagnetic coupling and the SW theory taking into account spin-wave interactions shows that the first approach includes such interactions effectively.

Using the modified spin-wave theory, the temperature dependence of the magnetic susceptibility of the organic compounds $[Mn(hfac)_2BNO_R]$ (R = H, F, Cl, Br) is investigated. It has been found that the ratio of the ferromagnetic and antiferromagnetic exchange interactions in the chain essentially does not influence the change in susceptibility at temperatures up to 350 K. A discrepancy between calculations and the experimental data may be attributed to the influence of the next-nearest-neighbour exchange interaction.

In view of this, experiments on other thermodynamical properties such as a specific heat and entropy are encouraged. The theoretical consideration shows that the weakening

of the ferromagnetic exchange between the trimers is accompanied by a Schottky peak in the specific heat or a steplike behaviour in the entropy. The possibility of observing the lower antiferromagnetic gap in a strong magnetic field has been discussed also. The analysis presented permits us to conclude that, like in the case of the two-spin ferrimagnet, the model considered exhibits ferromagnetic and antiferromagnet aspects in the thermodynamical behaviour.

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