FINITE TEMPERATURE SIMULATIONS OF THE FRUSTRATED $S = 1/2$ CHAINS*

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Thermodynamical properties of the one-dimensional $S = 1/2$ Heisenberg model with dimerized nearest and uniform next-nearest neighbors interactions, applicable to $CuGeO_3$ and $Pb[Cu(SO_4)(OH)_2]$ compounds, are studied by the numerically exact quantum transfer-matrix method. Suzuki–Trotter formula is used to obtain a classical system with spin σ=3/2 and effective interactions between nearest neighbors only. Magnetic specific heat and magnetic susceptibility curves are calculated and compared with experimental results in a wide temperature range giving estimates of the coupling parameters in the model proposed for $CuGeO_3$ and $Pb[Cu(SO_4)(OH)_2]$.

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1. Introduction

Low-dimensional spin systems with antiferromagnetic interactions have received much attention in recent years. We studied $S = 1/2$ one-dimensional Heisenberg model with nearest neighbors (nn) and next-nearest neighbors (nnn) interactions described by the Hamiltonian

$$H = -J \sum_{i=1}^{N} (S_i S_{i+1} + \alpha S_i S_{i+2}) , \tag{1}$$

where N denotes the size of the chain, J and α are the nn exchange integral and the ratio of the nnn exchange integral to the nn one, respectively.

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It was proved in 1995 [1–3], that after addition of the following term

$$H_\delta = \sum_{i=1}^{N} (-1)^i \delta S_i S_{i+1} \,, \tag{2}$$

model (1) corresponds to the best known 1D Hamiltonian for the famous Spin–Peierls (SP) system $CuGeO_3$. In this case the parameter δ, which depends on T, describes progressive dimerization below the critical temperature $T_{SP} = 14.3\,K$, where the alternation of J has to be taken into consideration. Additionally, it can be shown that model (1) is applicable to $Pb[Cu(SO_4)(OH)_2]$.

In this report we use the modified Quantum Transfer Matrix (QTM) technique to calculate the thermodynamical properties of $CuGeO_3$ and $Pb[Cu(SO_4)(OH)_2]$ and to estimate the best-fit values for J and α.

2. QTM technique

The standard QTM algorithm based on the Trotter formula fails for $\alpha \neq 0$. In order to perform calculations for a macroscopic chain (infinite N value), we need to reverse the transfer from the chain to the Trotter direction. It can be accomplished in two steps.

Firstly, we divide the Hamiltonian (1) into two parts $H = H_A + H_B$

$$\begin{aligned} H_A &= H_{1,4} + H_{5,8} + H_{9,12} + \dots \,, \\ H_B &= H_{3,6} + H_{7,10} + H_{11,14} + \dots \,, \end{aligned} \tag{3}$$

in which $H_{i,i+3}$ describes the interactions inside the four-spin block beginning at the i-th site of the quantum chain. Then we used the Trotter expansion to obtain the m-th classical approximation Z_m of the partition function Z

$$Z_m = \sum_{\{S_{r,i}\}} \prod_{r=1}^{m} \prod_{i=1}^{N/4} L_{2r-1,4i-3}(S)\, L_{2r,4i-1}(S) \,, \tag{4}$$

where

$$L_{r,i}(S) = \langle S_{r,i} \dots S_{r,i+3}|\, \mathrm{e}^{-\beta H_{i,i+3}/m} |S_{r+1,i} \dots S_{r+1,i+3}\rangle \,. \tag{5}$$

Z_m is now the partition function of the classical system of $2m \times N$ spins, with the effective interactions grouped into eight-spin blocks. For this system, we define a global transfer matrix between the r-th and $(r+1)$-th rows and expand it in the product of four-spin local transfer matrices $L_{r,i}(S)$.

Secondly, we introduce an effective classical spin $\sigma = 3/2$ and we replace each pair of $S = 1/2$ spins, distributed along a given row r, by the spin σ

$$(S_{r,i}, S_{r,i+1}) \longrightarrow \sigma_{r,j}\,, \quad \text{where} \quad j = 1 \ldots N/2\,. \tag{6}$$

At the same time, the local transfer matrix $L_{r,i}(S)$ can be expressed as $L_{r,j}(\sigma)$, *i.e.* can be rewritten in the basis of σ. Now, we can reverse the transfer direction by defining a new local transfer matrix $V_{r,r+1}$

$$\begin{gathered} \langle \sigma_{r,j}\sigma_{r+1,j}|V_{r,r+1}|\sigma_{r,j+1}\sigma_{r+1,j+1}\rangle \\ || \\ \langle \sigma_{r,j}\sigma_{r,j+1}|\,\mathrm{e}^{-\beta H_{j,j+1}/m}|\sigma_{r+1,j}\sigma_{r+1,j+1}\rangle\,. \end{gathered} \tag{7}$$

The global transfer matrices W_1 and W_2 (for odd and even columns of spins, respectively) can be expressed by the corresponding products of $V_{r,r+1}$. Finally, the m-th classical approach to the partition function of (1) can be written in the form

$$Z_m = \ \mathrm{Trace}\,[W_1 W_2]^{N/4}\,. \tag{8}$$

For an infinite system (*i.e.* when $N \to \infty$) the free energy per spin is simply given by the maximum eigenvalue $\lambda_{\max}(m)$ of the transfer matrix $W_1 W_2$

$$f_m = -k_{\mathrm{B}} T \log \lambda_{\max}(m)\,. \tag{9}$$

The free energy of the initial quantum system can be found from f_m by extrapolation to $m \to \infty$, according to the formula

$$f_m = \sum_{n=1}^{\infty} \frac{a_n}{m^{2n}} + f_\infty\,. \tag{10}$$

For this reason, we have calculated the maximum eigenvalues $\lambda_{\max}(m)$ using the iteration method. We were able to calculate the approximants f_m up to $m = 6$, which took 15 minutes on Cray J916. Then we calculated the thermodynamical properties by numerical differentiation of the free energy f_m and we extrapolated their values to infinite Trotter number m according to the formula (10).

3. Results

In order to estimate the values J and α for $CuGeO_3$ we calculated the magnetic susceptibility along the c crystal direction and compared them to the very well calibrated results obtained for a single crystal [4]. We

chose the Landé factor g_c equal to 2.07. The experimental values for the a and b crystal directions can be inferred from our results by simple rescaling according to the law $\chi_x/\chi_c = (g_x/g_c)^2$, where $x = a, b$.

We obtained the best fit for the following set of parameters:

$$J = -166\,\mathrm{K}, \qquad \alpha = 0.36, \qquad \delta(0) = 0.022. \tag{11}$$

Our values are consistent with the parameters estimated by Riera and Dobry [2] who used the exact diagonalization technique and the latest density matrix renormalization group calculations of Klümper *et al.* [5]. The results

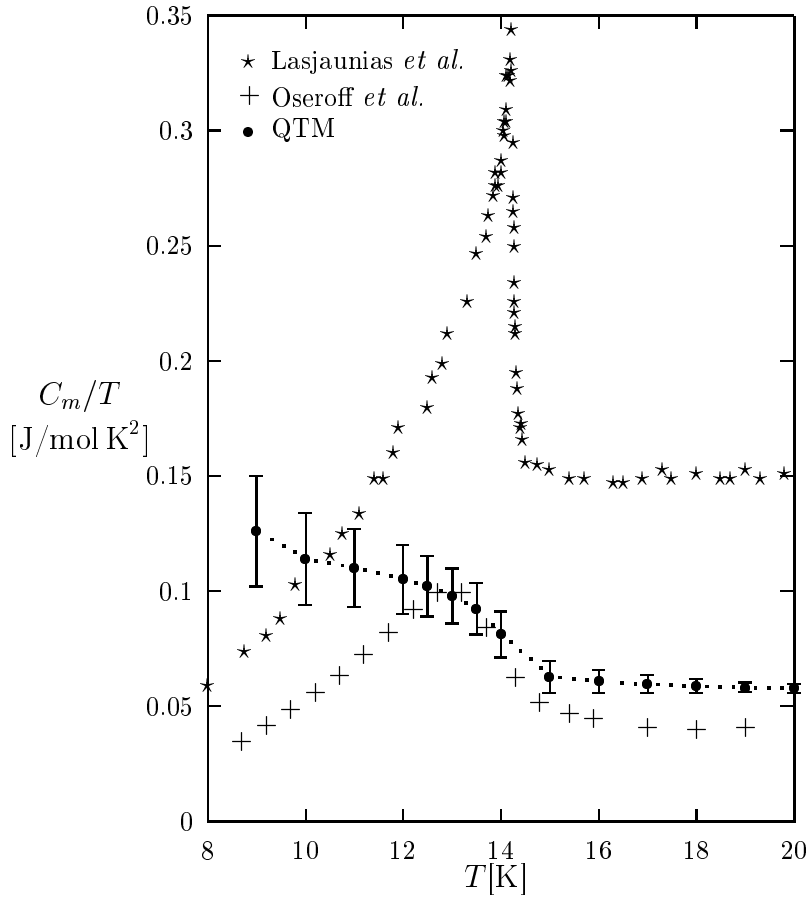

Fig. 1. Magnetic specific heat of $CuGeO_3$. Symbols $\star$ and $+$ correspond to the experimental results. Full circles mark the values obtained from the quantum transfer-matrix calculations for $J = -166\,\mathrm{K}$ and $\alpha = 0.36$.

obtained are in a very good agreement with the experimental data down to the low-temperature region [4], which confirms the appearance of frustration in the spin model proposed for $CuGeO_3$. The estimated value of $\alpha = 0.36$ is significantly greater than the critical value $\alpha_c = 0.2411$ [3].

Subsequently, we performed the calculations of magnetic susceptibility of $Pb[Cu(SO_4)(OH)_2]$ along all three main crystal directions and compared them with experiment carried out on the mono-crystal sample [6]. For g factors we estimated the values $g_a = 2.00$, $g_b = 2.19$ and $g_c = 2.30$. Our best fit results lead to the following set of the exchange parameters

$$J = -30\,\mathrm{K} \quad \text{and} \quad \alpha = -0.5\,. \tag{12}$$

Finally we calculated magnetic specific heat of $CuGeO_3$ for the exchange integral values (11) extracted from susceptibility calculations. Our results plotted by full circles are compared to estimates found from experiment [7,8] in Fig. 1. Above T_{SP} the numerical curve can be described by the well-known equation $C_m = \gamma/T$ for $\gamma = 0.58\mathrm{J/mol\,K}$ which is close to that of Oseroff *et al.* [8]. In the low temperature region we do not recover the decrease of the experimental data. We do not know if this drawback follows from the deficiency of the model or simply from the weak convergence of our approximants. The error bars increase with decreasing temperature and the last point in Fig. 1 is at the edge of applicability of our approach.

4. Conclusions

We have shown that the modified QTM technique can be successfully used for calculation of the thermodynamical properties of frustrated $S = 1/2$ antiferromagnetic quantum chains. The application of this method to $Pb[Cu(SO_4)(OH)_2]$ and the spin–Peierls $CuGeO_3$ gives numerical results fully consistent with the latest experimental data and the best-fit values of the exchange integrals in the spin model proposed for both compounds.

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