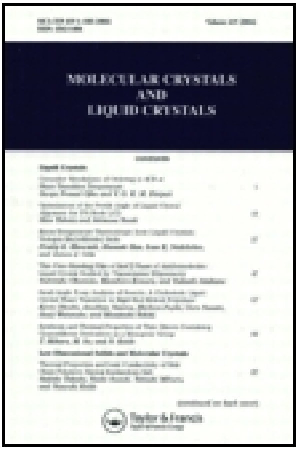

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Simulations of the Molecular—Based S = 1 Magnetic Chains

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To cite this article: Alvaro Caramico D'auria, Filippo Esposito, Ugo Esposito, Dante Gatteschi, Grzegorz Kamieniarz & Stanislaw Walcerz (1999): Simulations of the Molecular—Based S = 1 Magnetic Chains, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 335:1, 675-684

To link to this article: http://dx.doi.org/10.1080/10587259908028907

Mol. Cryst. and Liq. Cryst., 1999, Vol. 335, pp. 675-684
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Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Simulations of the Molecular – Based $S = 1$ Magnetic Chains

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A numerical quantum transfer-matrix approach to $S = 1$ macroscopic chains with single-site anisotropy and alternating bonds is worked out in the framework of statistical mechanics. A fit of the experimental susceptibility data for a number of the quasi-one-dimensional molecular magnets is performed down to the low-temperature region. New microscopic parameters for the uniform as well as the non-uniform systems are established, and the temperature behaviour of the zero-field susceptibility for different ferro–antiferro coupling ratios is presented.

Keywords: molecular magnetic chains; transfer-matrix simulations; bond-alternating interactions

INTRODUCTION

A dramatic increase in the number and in the types of one-dimensional magnetic materials has been achieved. The presence of bulky organic non-magnetic groups in the molecules results in effective shielding of the chains from one another, so that the materials containing them enable testing the theories of the thermodynamic properties of low dimensional materials. Moreover, the intrinsic low symmetry of the building blocks easily affords not only uniform chains, i.e. systems in which the nearest neighbour pairs are all identically coupled to each other[1–6], but also non-uniform chains[7–10].

The quantitative description of the uniform molecular spin $S = 1$ compounds is, however, mainly based on the Weng expansion[11,12] calculated for the high-temperature behaviour of the zero-field susceptibility. Interpretation of experiments for systems with alternating interactions becomes even more difficult. So far, a scaled theoretical approach[7] and the numerical finite-chain technique for short rings[9,10] have been available. Recently a numerical quantum transfer-matrix technique (QTM) has been developed[13] for non-uniform and anisotropic systems. The QTM method proves particularly useful. It is not subject to any statistical nor systematic errors and enables reaching the macroscopic limit $N \to \infty$.

HAMILTONIAN AND SIMULATION TECHNIQUE

The aim of this report is to apply the QTM approach to a number of the molecular-based chains described by the $S = 1$ Hamiltonian

$$\mathcal{H} = J_1 \sum_{i=1}^{N/2} S_{2i-1} \cdot S_{2i} + J_2 \sum_{i=1}^{N/2} S_{2i} \cdot S_{2i+1} + D \sum_{i=1}^{N} (S_i^z)^2 - g_\alpha \mu_B B \sum_{i=1}^{N} S_i^\alpha, \quad (1)$$

where J_1, J_2 denote the nearest-neighbour interaction constants, D stands for the anisotropy parameter, B is the external field which can be applied along the chain ($\alpha = z$) or in the perpendicular direction ($\alpha = x$). g_α is the corresponding gyromagnetic ratio and N is the size of a given chain.

In the Hamiltonian (1) the open boundary conditions are assumed and the alternation of the bond variable in the strength and sign is allowed. For the antiferromagnetic coupling, the positive values to J_i ($i = 1, 2$) are assigned. The Hamiltonian (1) can be expressed as

$$\mathcal{H} = \sum_{i=1}^{N-1} \mathcal{H}_{i,i+1},$$

where the two-site operator

$$\begin{aligned} \mathcal{H}_{i,i+1} &= J_i S_i \cdot S_{i+1} + \frac{1}{2} D \left[(S_i^z)^2 + \left(S_{i+1}^z \right)^2 \right] \\ &\quad - \frac{1}{2} g_\alpha \mu B \left(S_i^\alpha + S_{i+1}^\alpha \right) \end{aligned}$$

alternates with the site index i (J_i amounts to J_1 or J_2 for i odd or even, respectively), implying the alternation of the local transfer operator[14] $\mathcal{V}_i$ related to the exponential of $\mathcal{H}_{i,i+1}$.

The m-th approximant Z_m to the partition function can be evaluated[15] in terms of the global transfer matrix operator $\mathcal{W} = \mathcal{W}_1 \mathcal{W}_2$ as

$$Z_m = Tr\, \mathcal{W}^{N/2}\,, \tag{2}$$

where

$$\mathcal{W}_i = \left(P^2 V_i\right)^m P\,,\ i = 1,2\,, \tag{3}$$

and P is a unitary shift operator[14], and m is the Trotter number,

The corresponding approximant to the canonical mean value of the α component of spin at the central-site n is

$$\langle S_n^\alpha \rangle_m = \frac{1}{Z_m} Tr \mathcal{W}^{N/2} S_n^\alpha \mathcal{W}^{N/2}\,. \tag{4}$$

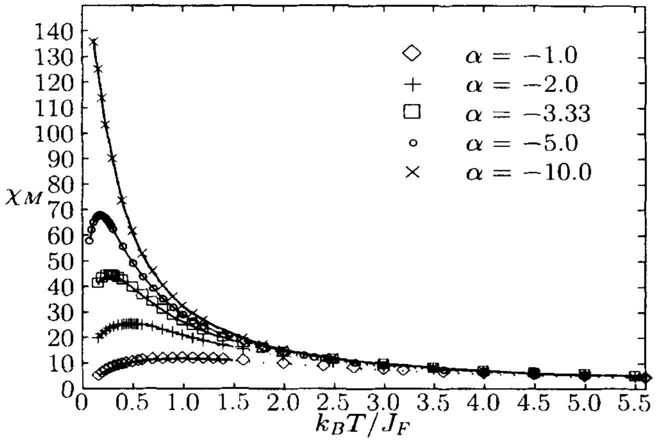

FIGURE 1 The molar susceptibility of the alternating ferro - antiferromagnetic chains in [memu/mole] as a function of k_BT/J_F for different $\alpha = J_F/J_{AF}$.

The trace operations in Eqs. (2) and (4) are over the 3^{2m}-dimensional subspace of all the configurations of the classical spin variables $S = 1$ located in the strip of the size $2m \times N$. In the macroscopic limit ($N \to \infty$), only the contributions corresponding to the largest eigenvalue of the transfer matrix

W survive, so that the calculations are much simplified. Finally, the zero-field susceptibility , needed for the characterization of our systems, follows from the numerical derivative of the magnetization (4) with respect to the external field and from the extrapolations in $1/m^2$ for $3 \leq m \leq 7$.

APPLICATIONS AND RESULTS

First, we have examined the susceptibility profiles for a number of ratios $\alpha = J_F/J_{AF}$. Assuming the fixed ferromagnetic coupling constant $J_F/k_B = 50$ K, the susceptibility curves corresponding to $\alpha = -1$, -2, -3.33, -5.0 and -10.0 are plotted in Fig. 1. The symbols show the values of susceptibility obtained from the QTM calculus, while the lines represent the least-square fit in terms of Chebyshev polynomials

$$\chi_M(x) = \sum c_n T_n(x), \tag{5}$$

where $x = k_B T/J_F$ and $T_n(x) = \cos(n \arccos x)$. Each curve is expressed by two polynomials: the first one in the interval $x \leq 1$ and the other for $x > 1$. The coefficients c_n of the fitting polynomials are collected in Table I.The results indicate a pronounced dependence of the low-temperature part of the susceptibility on the ratio α. It can be observed that the greater α the greater the slope of the curve and the higher the maximum of the susceptibility.

Next, we reanalyze a number of uniform and bond-alternating molecular-based chains reported in literature[1-10]. The first category contains: a) the compound *cis*–$[Ni(333\text{-tet})(\mu\text{-}N_3)]_n(PF_6)_n$ - denoted as **2** by Escuer *et al.*[1] and abbreviated here as $U1$; b) $[NiL_2(\mu\text{ - }N_3)]_n(ClO_4)_n$ (L = 1.2-diamino2-methylpropane) - denoted as compound **1** by Ribas *et al.*[2], and considered also by Ward *et al.*[3], abbreviated here as $U2$; c) $[NiL_2(\mu\text{ - }N_3)]_n(PF_6)_n$ (L = 1.2-diamino2-methylpropane) - denoted as compound **2** by Ribas *et al.*[2] and abbreviated here as $U3$; e) $[Ni(hfac)_2NITEt)]_2$ - considered by Caneschi *et al.*[5] and abbreviated here as $U4$; e) the compounds **1** and **2** - considered by Monfort *et al.*[6]and denoted here as $U5$ and $U6$, repectively.

To the second category belong the alternating chains: a) the compound trans-$[Ni(333\text{-tet})(\mu\text{-}N_3)]_n(ClO_4)_n$ - denoted as **1** by Escuer *et al.*[1] and ab-

TABLE I The Chebyshev coefficients c_n for the alternating ferro-antiferromagnetic couplings.

n	$\alpha = -1.0$		$\alpha = -2.0$		$\alpha = -3.33$	
1	9.8219	7.6936	23.0459	9.9904	36.2039	11.2647
2	3.0450	-3.9301	-0.1739	-7.5509	-9.0872	-9.4148
3	-1.1734	0.6251	-2.3579	2.6053	-1.6882	3.7284
4	0.3185	0.0851	0.7530	-0.7977	1.5226	-1.3863
5	-0.1281	-0.1311	-0.1221	0.2042	-0.6366	0.4889
6	0.0497	0.0728	0.0027	-0.0325	0.2085	-0.1678
n	$\alpha = -5.0$		$\alpha = -10.0$			
1	48.1884	11.9403	69.9736	12.6591		
2	-19.5235	-10.4483	-48.5362	-11.5143		
3	-1.2479	4.3565	14.3019	5.0473		
4	3.6561	-1.7384	-3.4681	-2.1058		
5	-2.4545	0.6682	0.3398	0.8561		
6	1.2246	-0.2454		-0.3453		

breviated here as $A1$; b) $[FeON_8C_{26}H_{14}]_n$ - considered by Hiller *et al.*[7] and abbreviated here as $A2$; c) the compounds **1** and **2** - considered by Ribas *et al.*[8] and abbreviated here as $A3$ and $A4$, respectively; d) $[Ni(N_3)_2(tmeda)]_n$ - considered by Ribas *et al.*[9] and abbreviated here as $A5$. e) $Ni_2(EDTA)\cdot 6H_2O$ considered by Borras – Almenar *et al.*[10] and abbreviated here as $A6$:

Our global QTM numerical calculations confirm the selection of parameters found previously for the uniform systems. Using our best-fit parameters from the second and the third column of Table II (where the error bars for

TABLE II Estimates of the best-fit exchange couplings J_1 and J_2 (or J if $J_1 = J_2$) and the g factor for the compounds listed in the first and the fourth column.

Un	J	g	Al	$J_1/k_B[K]$	$J_2/k_B[K]$	g
$U1$	26.6 ± 1.0	2.29	$A1$	99.5 ± 2.0	63.5 ± 2.0	2.38 ± 0.02
$U2^*$	24.0 ± 1.0	2.13	$A2$	408.0 ± 10.0	90.0 ± 15	2.33 ± 0.02
$U3$	4.68 ± 0.1	2.24	$A3$	225 ± 5.0	-25.0 ± 5.0	2.45 ± 0.03
$U4$	2.8 ± 0.1	2.47	$A4$	40 ± 1.0	25.0 ± 5.0	2.39 ± 0.02
$U5$	27.9 ± 1.0	2.16	$A5$	43.0 ± 1.0	13 ± 0.5	2.35 ± 0.02
$U6$	80.0 ± 2.0	2.29	$A6^{**}$	10.6 ± 1.0	3.3 ± 0.5	2.20 ± 0.02

* for $U2$ the anisotropy constant $D = 6 \pm 1$;

** for $A6$ the anisotropy constant $D = 5 \pm 1$.

g amount to ±0.02), the susceptibility estimates coincide with experimental findings within $2 \div 3$ % in the low temperature region. An example is shown in Fig. 2 for the compound $U6$, where the experimental susceptibility is plotted by the the diamonds and our QTM estimates - by the dotted line. The parameters displayed in the legend coincide with those of Monfort *et al.*[6] and describe $U6$ in the *entire* temperature region.

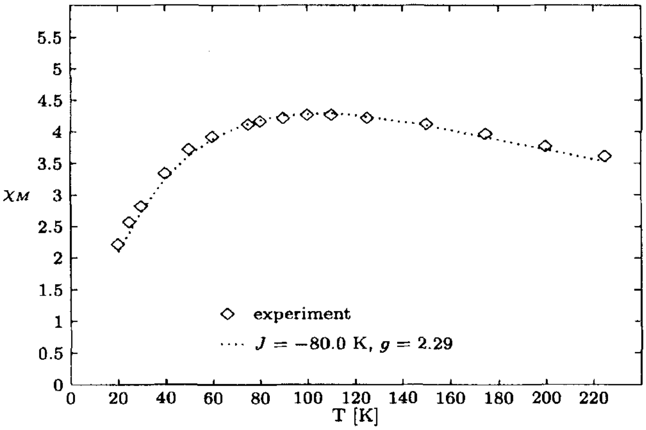

FIGURE 2 The molar susceptibility χ in [memu/mole] versus temperature for $U6$.

For the compund $U2$, there are available the powder[2] and the single crystal[3] susceptibility data. The later are given by the symbols in Fig. 3. The low-temperature anisotropy may be attributed to the non-negligible value of D. The fit shown in Fig. 3 is found for $D/k_B = 6 \pm 1$ K and the remaining parameters listed in Table II. Our present estimates are somewhat different from those calculated previously[15] when fitting the powder data.

We have also reanalyzed the experimental data for the bond-alternating molecular-based chains $A1$ - $A6$ reported in literature[1,7-10]. As an example, in Fig. 4 we draw the susceptibility results for $[Ni(N_3)_2(tmeda)]_n$ (the compound denoted here as $A5$): experimental ones by the diamonds, our QTM estimates for the parameters selected previously[9] by the dotted line and those for the parameters from Table II by the full line. For the sake of

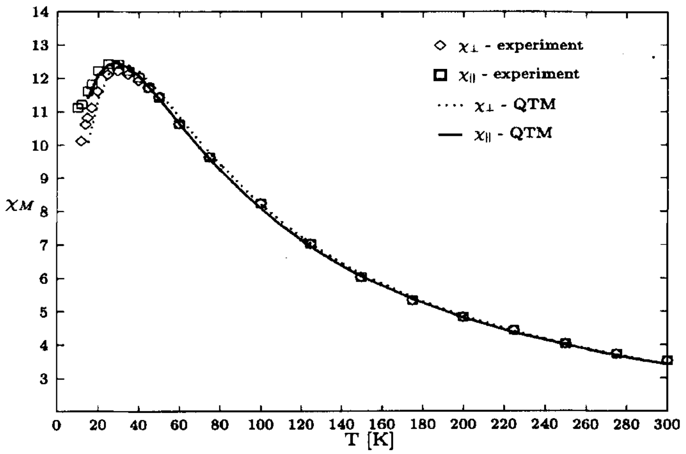

FIGURE 3 The molar susceptibility χ_M in [memu/mole] versus temperature for $U2$.

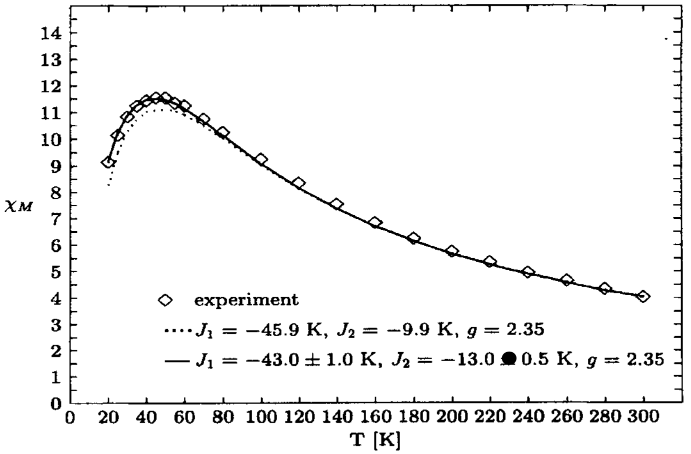

FIGURE 4 The molar susceptibility χ_M in [memu/mole] versus temperature for $A5$. The best QTM fit is drawn with the full line.

clarity, the corresponding parameters are also defined in the legend. The curves demonstrate some discrepancies between theory and experiment for the previous estimates of the parameters. Similar discrepancies are encountered for other systems. Our accurate QTM simulations for the compounds $A1$ – $A6$ and the subsequent fitting analyses lead to the values for the best-fit parameters listed in the last three columns of Table II.

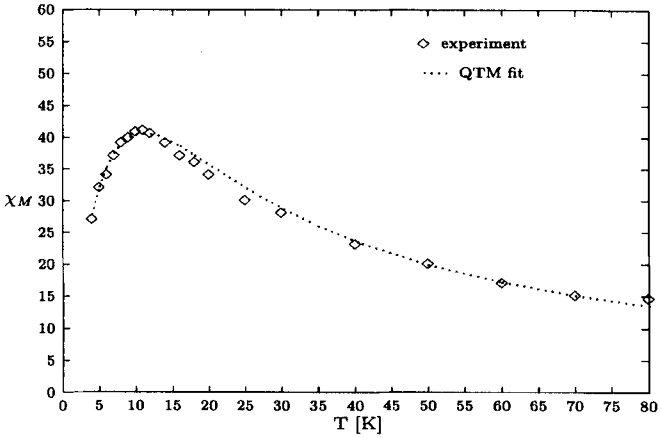

FIGURE 5 The molar susceptibility χ_M in [memu/mole] versus temperature for $A6$. The best QTM fit is drawn with the dotted line.

The pronounced anisotropy was found for $A6$[10] from the analysis of the zero-field susceptibility and specific heat. Our results for $A6$ are presented in Figs. 5 and 6 for the temperature dependence of the molar susceptibility in [memu/mole] and the specific heat, respectively. The measured values are plotted with the diamonds and the best QTM fit is drawn with the dotted line.

As far as the susceptibility is concerned, for all the alternating chains the agreement between experiment and theory is within $3 \div 4$ %. As demonstrated in Fig. 7, this is fulfilled even for the systems $A3$ and $A4$ which develop some low-temperature anomalies[8]. In this case, our results for the alternating ferro- and antiferromagnetic couplings verify quantitatively the empirical predictions[8] based on the relationship between the co-ordination

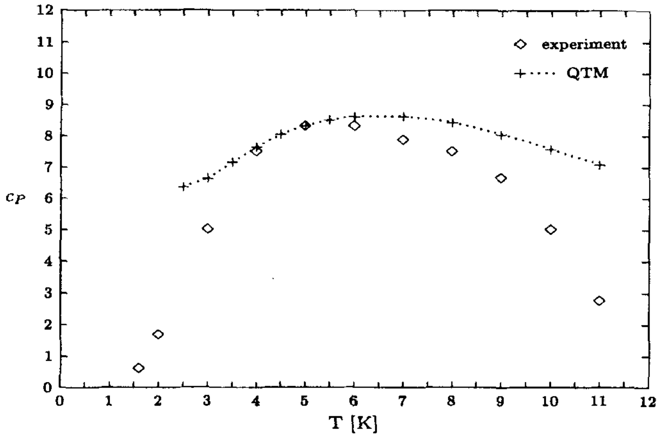

FIGURE 6 The temperature behaviour of the specific heat of $A6$.

mode and the magnetic behaviour of the polynuclear compounds of Ni^{II}.

In conclusion, we have worked out the QTM approach to the molecular systems with the bond alternation and we have carried out the first large-scale simulations obtaining high resolution data for the $S = 1$ alternating chains $A1 \div A6$ down to low temperatures. The corresponding microscopic parameters have been established as the best sets describing the susceptibility measurements for the compounds in question. Our QTM technique is applicable in the whole region of the microscopic parameters in (1) and for temperatures down to $k_BT/J \simeq 0.1$ so that the $S = 1$ molecular-based chains may be reliably characterized.

Acknowledgements

We would like to thank Dr. Andrea Caneschi for helpful discussions and Mr. R. Matysiak for the technical assistance. This work was suported in part by Committee for Scientific Research under the KBN grant No. 2 P03B 058 14. Numerical calculations were mainly carried out on the platforms of the Supercomputing and Networking Center in Poznań.

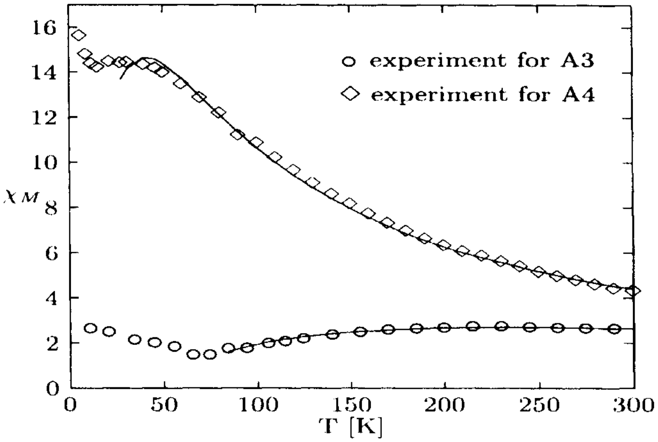

FIGURE 7 The temperature dependence of the molar susceptibility χ in [memu/mole] for the compounds $A3$ and $A4$. The QTM estimates are drawn by the lines and the experimental data are given as the symbols.

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