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Characterization of the $S=1$ molecular magnetic chains

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A numerical quantum transfer-matrix approach for the $S=1$ macroscopic chains with the single-site anisotropy and alternating bonds is worked out and a fit of the susceptibility data for the quasi-one-dimensional molecular magnets $[\mathrm{Ni}(dmen)(\mu-N_3)_2]_n$ and $[\mathrm{Ni}(aep)(\mu-N_3)_2]_n$ is performed in the region above the observed low-temperature minima. [S0163-1829(98)02313-3]

In recent years a number of new quasi-one-dimensional molecular-based magnets has been synthesized in order to understand the mechanisms of magnetic interactions between paramagnetic ions. These compounds are characterized not only by uniform antiferromagnetic (AF) but also by nonuniform alternating-bond interactions.[1–8] A quantitative description of the molecular spin $S=1$ compounds suffers, however, from a lack of reliable theoretical techniques. The Weng expansion,[9,10] usually resorted to, and its extension towards lower temperatures,[11] have their applicability limited to systems with uniform and isotropic interactions. The standard expansion enables only the fit of the high-temperature behavior of the zero-field susceptibility which is less sensitive to the choice of parameters than its low-temperature counterpart. Interpretation of experiments for alternating systems becomes even more difficult as only a scaled theoretical approach[6] and the numerical finite-chain technique for short rings[8] can be applied in this case.

In this communication we aim at formulating a numerical transfer-matrix method applicable to a large class of molecular magnetic chains described by the $S=1$ Hamiltonian

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

where J_1, J_2 denote the nearest-neighbor interaction constants, D stands for the anisotropy parameter, B is the external magnetic 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) we assume the open boundary conditions and allow the alternation of the bond variable to change in strength and sign. We assign positive values to J_1 and J_2 for the antiferromagnetic couplings. We also characterize the two polynuclear complexes $[\mathrm{Ni}(dmen)(\mu-N_3)_2]_n$ (denoted as 1, $dmen=N,N$-dimethylethylenediamine) and $[\mathrm{Ni}(aep)(\mu-N_3)_2]_n$ (denoted as 2, $aep=2$-aminoethylpyridine) which are the first examples of the ferromagnetic or antiferromagnetic chains[7] of $\mathrm{Ni}^{\mathrm{II}}$.

Our numerical approach is a variant of the quantum transfer-matrix (QTM) approach proposed by Delica *et al.*[12] and applied later to a class of the uniform soliton-bearing[13] and Haldane-gap[11,14] systems. In the framework of the QTM method, the canonical partition function is calculated by mapping the original quantum model (1) onto a classical four-spin counterpart defined on the square lattice consisting of $N\times 2m$ Ising spins $S=1$, where m is an integer referred to as the Trotter number. The most appealing features of the QTM technique are the absence of statistical errors and no restrictions on the size N of the chains which may become macroscopic.

The approach is based on the definition of the thermal expectation value of the self-adjoint operator $\mathcal{A}$

$$\langle\mathcal{A}\rangle=\frac{1}{Z}\mathrm{Tr}\mathcal{A}e^{-\beta\mathcal{H}},$$

where the canonical partition function Z is defined by $Z=\mathrm{Tr}e^{-\beta\mathcal{H}}$. In the real-space decomposition scheme[12] and the large N limit, the Hamiltonian (1) can be expressed as

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

where the two-site operator

$$\mathcal{H}_{i,i+1}=J_i\, S_iS_{i+1}+\frac{1}{2}D[(S_i^z)^2+(S_{i+1}^z)^2] -\frac{1}{2}g_\alpha\mu B(S_i^\alpha+S_{i+1}^\alpha)$$

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[12] $\mathcal{V}_i$ related to the exponential of $\mathcal{H}_{i,i+1}$. Introducing two transfer operators

$$\mathcal{W}_i=(P^2\mathcal{V}_i)^mP, \quad i=1,2, \qquad (2)$$

where P is a unitary shift operator[12] and m is the Trotter number, the mth approximant Z_m to the partition function can be finally evaluated in terms of the global transfer matrix operator $\mathcal{W}=\mathcal{W}_1\mathcal{W}_2$ as

$$Z_m=\mathrm{Tr}\mathcal{W}^{N/2}.$$

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

$$\langle S_n^\alpha\rangle_m=\frac{1}{Z_m}\mathrm{Tr}\mathcal{W}^{N/2}S_n^\alpha\mathcal{W}^{N/2}. \tag{3}$$

Then the zero-field susceptibility follows from the numerical derivative of the magnetization (3). The specific heat data may be also computed, taking the second derivative of the free energy or the first derivative of the internal energy related to the nearest-neighbor spin-spin correlation function.

In the present approach the macroscopic limit implies that only contributions from the left and the right eigenvectors, corresponding to the largest eigenvalue of the transfer matrix $\mathcal{W}$, survive under the trace operations. Then the estimates of the thermodynamical quantities are found from the extrapolations in $1/m^2$ for $3\leqslant m\leqslant 7$. We have checked that the presence of the alternation in the model (1) does not affect the convergence of the approximants. Typical variation of the finite-m data is similar to that reported for the uniform chains[11,13] and allows linear extrapolations with an accuracy better than 5% down to temperatures $k_BT/J\simeq 0.1$.

To characterize the susceptibility measurements[7] performed on the compounds 1 and 2, we have applied the fitting procedure. We have established that in the region above the low-temperature minima the following sets of parameters describe, with an accuracy of better than 4%, the experimental findings:[7]

$$J_1/k_B=225\pm 5\ \ \mathrm{K},\quad J_2/k_B=-25\pm 5\ \ \mathrm{K},$$

$$g=2.45\pm 0.03 \tag{4}$$

and

$$J_1/k_B=40\pm 1\ \ \mathrm{K},\quad J_2/k_B=7\pm 3\ \ \mathrm{K},\quad g=2.39\pm 0.02 \tag{5}$$

for the compounds 1 and 2, respectively. A comparison between theory and experiment is shown in Fig. 1. Our results for the ferromagnetic couplings verify quantitatively the empirical predictions[7] based on the relationship between the coordination mode and magnetic behavior of the polynuclear compounds of $\mathrm{Ni^{II}}$.

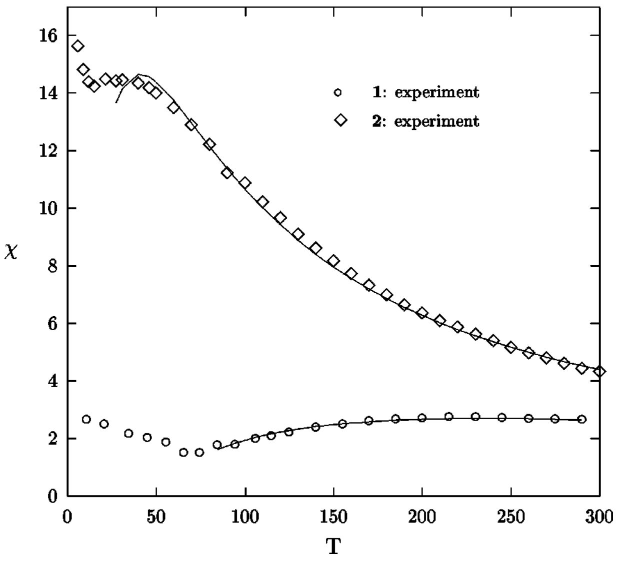

FIG. 1. The temperature dependence of the molar susceptibility χ in [emu/mole] for the compounds 1 and 2. The QTM estimates are drawn by the lines and the experimental data are plotted by the symbols.

In conclusion, we have extended the QTM approach to the systems with the bond alternation and we have carried out large-scale simulations obtaining high resolution data for the $S=1$ ferromagnetic or antiferromagnetic alternating chains 1 and 2 down to low-temperature minima attributed to some canting effects.[7] The parameters (4) and (5) 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 Eq. (1) and for temperatures down to $k_BT/J\simeq 0.1$ so that other $S=1$ molecular-based chains may be characterized as well.

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