The Utilization of Classical Spin Monte Carlo Methods to Simulate the Magnetic Behavior of Extended Three-Dimensional Cubic Networks Incorporating M(II) Ions with an S = 5/2 Ground State Spin

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The numerical simulations of the magnetic properties of extended three-dimensional networks containing M(II) ions with an S = 5/2 ground-state spin have been carried out within the framework of the isotropic Heisenberg model. Analytical expressions fitting the numerical simulations for the primitive cubic, diamond, together with (10−3) cubic networks have all been derived. With these empirical formulas in hands, we can now extract the interaction between the magnetic ions from the experimental data for these networks. In the case of the primitive cubic network, these expressions are directly compared with those from the high-temperature expansions of the partition function. A fit of the experimental data for three complexes, namely $[(N(CH_3)_4][Mn(N_3)]$ **1**, $[Mn(CN_4)]_n$ **2**, and $[Fe^{II}(bipy)_3][Mn^{II}_2(ox)_3]$ **3**, has been carried out. The best fits were those obtained using the following parameters, $J = -3.5$ cm^{-1}, $g = 2.01$ (**1**); $J = -8.3$ cm^{-1}, $g = 1.95$ (**2**); and $J = -2.0$ cm^{-1}, $g = 1.95$ (**3**).

Introduction

In recent years, the progress made by inorganic chemists in the development of suitable methods for the self-assembly of two classes of materials, namely molecule-based networks and high nuclearity clusters, has led to major advances in the field of magnetochemistry. Both classes of compounds give rise to interesting magnetic properties, since molecule-based networks exhibit spontaneous magnetization, whereas high nuclearity clusters often display slow magnetic relaxation times and the quantum tunneling phenomena. Furthermore, the large majority of compounds falling into either one of these two classes of materials often crystallize in novel, aesthetically pleasing structural topologies, with the metal ions adopting a wide range of coordination geometries.

The large, or even infinitely large, number of possible configurations that these systems can adopt makes it impossible to calculate directly the exact value of the partition function. As a consequence, the derivation of important thermodynamic properties such as magnetic susceptibilities and specific heat capacities is also beyond our reach. To fully understand and fine-tune the physical properties of these classes of materials, it is necessary to gain as much information as possible that sheds any light on the thermodynamic properties. In this respect, approximate methods can be used to address the problem. Among the variety of approximate methods available in the literature, the Monte Carlo technique (MC) plays an important role. The relative simplicity of the method, together with the fact that the limitations of the method are well documented, allow for good control over the reliability and accuracy of the results obtained. This however, is not the case for alternative methods, where one has to be particularly careful as uncontrolled approximations may well lead to inaccurate results. Our series of studies have shown that it is possible to use Monte Carlo simulation methods based on the Metropolis algorithm to derive an empirical law for the magnetic susceptibility as a function of temperature for extended networks incorporating M(II) ions with an S = 5/2 ground-state spin. Furthermore, we have found that it is possible to use these laws to fit the real experimental magnetic data for three-dimensional systems containing Mn(II) ions. To illustrate the usefulness of this approach, we have selected three examples, all of which are three-dimensional cubic networks, as model compounds for our studies. To check the reliability of the MC method, the empirical law for the primitive three-dimensional cubic network was first derived. For this system alternative methods exist,[1] and data is thus available in the chemical literature so that direct comparisons can be made to check the accuracy of the method. As shown below, our initial calculation confirmed the high reliability of the MC method for applications to three-dimensional cubic systems. Additional studies were then carried out to derive the empirical law for both the 4-connected diamond net and the 3-connected 10-gon (10, 3) cubic networks[2], Figure 1. To the best of our knowledge, these are the first empirical laws derived for the two latter types of three-dimensional networks. Finally, we have applied these results, using the derived empirical laws, to fit real experimental data for all three classes of compounds, namely $[(NCH_3)_4][Mn(N_3)]_3$[3] **1**, $[Mn(CN)_4]_n$[4] **2**, and $[Fe^{II}(bipy)_3][Mn^{II}_2(ox)_3]$[5] **3**.

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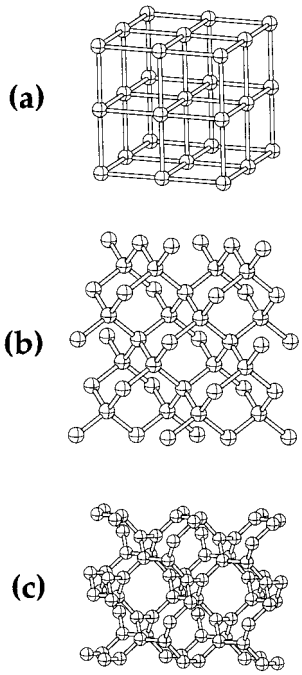

Figure 1. Cubic networks: (a)primitive cubic, (b) diamond, (c) (10, 3) net.

Experimental Section

In the canonical ensemble, the average magnetization M is defined as:

$$\langle M\rangle = \frac{\sum_{i=1}^{\infty} M_i e^{-E_i/kT}}{\sum_{i=1}^{\infty} e^{-E_i/kT}} \tag{1}$$

Since we cannot calculate the exact value of this quantity (1), an approximation to this equation is made by applying Monte Carlo methods, where the sum over all states is substituted with a partial sum based on a subset of characteristic configurations.

$$\langle M\rangle = \frac{\sum_{i=1}^{N} M_i e^{-E_i/kT}}{\sum_{i=1}^{N} e^{-E_i/kT}} \tag{2}$$

In the limit, as N $\rightarrow \infty$, the sum formula (2) equates to (1). The first possible approach involved the random selection of the configurations for the subset, i.e., to adopt the simple sampling variant of Monte Carlo simulation. This approach, however, has major drawbacks, as a rapidly varying exponential function in the Boltzmann distribution causes most of the chosen configurations to bring a negligible contribution to formula (2), since E_i is relatively large and consequently it biases the calculation of the average quantities. As a consequence, all Monte Carlo simulations were performed using the Metropolis algorithm,[6] which generates a sampling of states following the Boltzmann distribution that preferentially contains configurations that bring important contributions at temperature T in formula (2). The magnetic susceptibility, $\chi_{M,}$ is related to the fluctuations in the magnetization by the expression (3).[7]

$$\chi = 1/kT(<M^2> - <M>^2) \tag{3}$$

Where $\langle M\rangle$ and $\langle M^2\rangle$ are the mean values of M and M^2, respectively, M being the magnetization.

All simulations were performed on finite samples, thus introducing systematic errors. To minimize the edge perturbation and accelerate convergence toward the infinite lattice limit, periodic boundary conditions (PBC) were adopted.[8] To obtain reliable results, the optimal sizes of the samples were determined by carrying out simulations on a range of different sample sizes. Finally, samples with $10 \times 10 \times 10$ sites were used, which is three times larger than the minimum size that showed a finite-size effect for the studied reduced temperature range $T/|J|$. For each site 2×10^5 Monte Carlo steps were performed (MCS), and the first 2×10^4 were discarded as the initial transient stage.[8] To avoid a freezing of the spin configuration,[8] we have used a low cooling rate according to the following equation:

$$T_{i+1} = 0.98(T_i) \tag{4}$$

where T = temperature.

The numerical simulations for the primitive cubic, diamond, and (10, 3) cubic networks were fitted with a rational function, and these empirical laws were used to fit the experimental data. In all cases, a final check was carried out, i.e., Monte Carlo simulations were carried out using the best parameters suggested by the fits. For all three cases, the results were identical.

Results and Discussion

It is well established that S = 5/2 ground state spins are fairly isotropic and can be described according to the Heisenberg model (5),

$$H = \sum_{i=1,j>\mathrm{i}}^{N} -J_{ij} S_i S_j \tag{5}$$

where N spins (S_i), at lattice site i interact with their nearest neighbors j with an exchange coupling constant of J_{ij}.

As a consequence of the difficulties in finding the eigenvalues and eigenstates of the Hamiltonian (5) using quantum models, classical spin operators S_i were included in (5). This approximation for Mn(II) ions (S = 5/2) has been previously described in the chemical literature.[9,10] To compare calculated values with experimental observations, the classical spin operators are scaled according to the following factor:

$$S_i \Rightarrow \sqrt{S_i(S_i+1)} \tag{6}$$

For all simulations carried out, the reduced magnetic susceptibility curve $\chi_M|J|$ versus $\beta = T/|J|$ was fitted to the rational function β

$$\chi|J| = \frac{g^2}{4}\,\frac{a_0 + \sum_{i=1}^{k} a_i \beta^i}{1 + \sum_{j=1}^{k+1} b_j \beta^j} \tag{7}$$

The coefficients associated with the highest degree of the polynomials for both the denominator and the numerator are

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Table 1: Coefficients of the Rational Functions Giving the Thermal Variation of the Reduced Magnetic Susceptibilty $\chi_M|J|$ in Function of $\beta = T/|J|$ for Primitive Cubic, Diamond, and (10, 3) Cubic Networks (J in Kelvin)

	simple cubic	diamond	10−3
a_0	0.0815865	0.116	0.156
b_0	1	1	1
a_1	0	0	0
b_1	0	0	0
a_2	$1.22599\ 10^{-5}$	1.85958	$1.20777\ 10^{-4}$
b_2	$-2.78782\ 10^{-3}$	11.7921	$5.11803\ 10^{-5}$
a_3	0	0	0
b_3	0	0	0
a_4	$-5.34657\ 10^{-7}$	324.872	$6.12417\ 10^{-4}$
b_4	$9.71169\ 10^{-6}$	2795.33	$-2.47313\ 10^{-4}$
a_5	0	0	0
b_5	0	0	0
a_6	$3.56382\ 10^{-8}$	2.50121	$-1.0435\ 10^{-6}$
b_6	$1.37954\ 10^{-7}$	18.033	$-2.32108\ 10^{-4}$
a_7	0	0	0
b_7	$8.14585\ 10^{-9}$	0	0
a_8	0	0.264794	$3.99986\ 10^{6}$
b_8	0	0.816704	$8.05117\ 10^{-6}$
a_9	0	0	0
b_9	0	0.0605244	$9.14253\ 10^{-7}$

set so that they converge to the Curie law at high temperatures ($\chi_M T = 4.375$ cm^3 K mol^{-1}, for $g = 2$). Furthermore, the constant terms in the numerator are fixed so that they converge at low temperature with the finite values of $\chi_M|J|$ obtained by the simulations. Empirical laws were obtained, with β values in the range 0.5−200. The exact numerical coefficients associated with the empirical laws derived for the three classes of cubic networks are given in Table 1.

The results are presented in Figure 2 , and a comparison is made with the high-temperature series expansion of the partition function (HTE) for primitive cubic network by Rushbrook and Wood,[11] (solid line, Figure 2). As expected, the antiferromagnetic ordering temperature $T_N/|J|$ (maximum value of $\chi_M|J|$) is displaced toward a lower temperature when the connectivity between the magnetic ions decreases. This maximum is observed at 13.6, 8.6, and 5.8, for the primitive cubic (connectivity 6), diamond (connectivity 4), and (10, 3) (connectivity 3) networks, respectively. In correlation terms, the maximum value of $\chi_M|J|$ increases from 0.119 cm^3 mol^{-1} K for the primitive cubic network, to 0.174 cm^3 mol^{-1} K for the diamond network, and finally reaches a value of 0.22 cm^3 mol^{-1} K for the (10,3) network. In the case of the primitive cubic network, for high β values, the agreement between the MC simulation and the HTE approach is excellent, as depicted in Figure 2. MC and HTE methods do not, however, provide a maximum at the same $T/|J|$ value, with MC methods giving a maximum at 13.8 whereas using the HTE approach a maximum at 11 is obtained. Hence, below the maximum value of $\chi_M|J|$, there is a discrepancy between the MC simulation and the HTE approach due to inadequacy of the HTE method in the ordered phase. Below $T_N/|J|$ our results could be compared to the less accurate mean field approximation. In this approach, the expected limit of the $\chi_M|J|$ value at $T/|J| = 0$ is equal to $(2/3)\chi_M|J|_{max}$. The results obtained by the Monte Carlo simulation are along this line, with $\chi_M|J|$ values at $T/|J| = 0$ equal to $0.136(0.62\ \chi_M|J|_{max})$, $0.116(0.667\chi_M|J|_{max})$, and $0.0816(0.69\chi_M|J|_{max})$ for the 10,3, diamond, and primitive cubic networks, respectively. The Monte Carlo simulation has proved to be the only method able to yield the ordering temperature $T_N/|J|$ and to reproduce the physical behavior in the paramagnetic and the ordered phase, while the HTE is limited to the paramagnetic region. In principle, the mean field approximation can be applied in the paramagnetic region and in the ordered phase; however, this method leads to a large overestimation of the ordering temperature.[12]

To check the validity of MC approach, the empirical law was derived from the MC simulation of a primitive cubic network, and this was used to fit the data for one compound in this class, namely $[N(CH_3)_4][Mn(N_3)]$ **1**.[3] Compound **1** adopts a distorted perovskite structure, where the Mn(II) ions located at the corners of a cube are connected through a μ-1,3-azido ligand (or μ-end-to-end (EE)). It is well-known that the EE azido-bridges give rise to antiferromagnetic coupling interactions, whereas the EO bridges (μ-end-to-on or μ-1,1) lead to ferromagnetic interactions between metal ions, and these observations hold even for Mn(II) ions with a high S = 5/2 ground-state spin.[3,13−21] Results from this approach and those obtained by the HT method are presented in Figure 3.

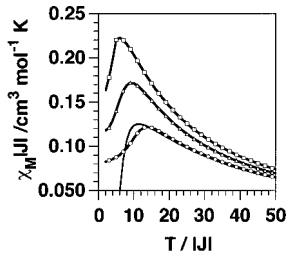

Figure 2. Reduced magnetic susceptibility $\chi_M|J|$ versus $\beta = T/|J|$ calculated with the empirical laws for the primitive cubic (bold line with circles), diamond (bold line with triangles), and (10, 3) (bold line with squares) networks. For comparison, results from the HTE method for a simple cubic net are shown by a solid line.

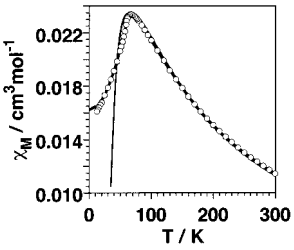

Figure 3. χ_M versus T plot for **1**. The bold line is calculated with the empirical law for the primitive cubic network together with the relevant parameters given in the text. The solid line is calculated with the HTE method and the published parameters.[3]

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In the case of compound **1**, antiferromagnetic behavior was expected, and indeed, χ_M vs. T possesses a sharp maximum at 65 K, see Figure 3, which is characteristic of antiferromagnetic three-dimensional ordering. The best agreement is obtained using the following parameters: $g = 2.025$, and $J = -3.6$ cm^{-1}. The goodness of fit parameter F defined as $\sum[(\chi_M)_{obsd} - (\chi_M)_{calcd}]^2/\sum[(\chi_M)_{obsd}]^2$ is then equal to 6.2×10^{-5}. This result is in agreement with a previous fit using the HTE approach[3] for which the following parameters were used, $g = 2.01$, and $J = -3.5$ cm^{-1}. The advantage of the MC approach is that, in contrast to the previous HTE approach, it is able to reproduce the experimental data in the low-temperature regime, below the maximum, Figure 3. It is also possible to evaluate the J value from the ordering temperature by using the mean field theory $T_N = zJS(S + 1)/3k$. The maximum observed at 65 K corresponds to $J = -2.4$ cm^{-1}. However, for a given T_N value, the mean field approximation underestimate the interaction. In fact, the improved mean field Bethe approach[22] gives a J value of -4.0 cm^{-1} closer to the one found by MC simulation. From this initial study, we have demonstrated the reliability of the MC methods for the derivation of empirical laws. Furthermore, this approach is an improvement on the high-temperature expansion of the partition function at low temperature, and as a consequence, this has enabled us to move forward and fit the experimental magnetic data with the empirical laws for both the diamond and the (10, 3) cubic networks.

Powder X-ray diffraction experiments carried out on samples of $[Mn(CN)_4]_n$ **2**[4] confirm that this compound adopts an interpenetrating diamond-like lattice in the solid-state. To the best of our knowledge, this is the only experimental example of a diamond network containing local ground-state spins of S = 5/2. In this compound, each Mn(II) ion is surrounded by four Mn(II) ions which form the vertexes of a regular tetrahedron. The Mn(II) ions are connected via cyanide bridges, implying two types of metal centers, the first bonded to four carbon atoms and the second bonded to four nitrogens. The Mn(II) ions are coupled antiferromagnetically, and the plot of χ_M vs. T shows a broad maximum around 80 K due to three-dimensional antiferromagnetic ordering. The presence of spin impurities prevent a detailed analysis of the magnetic data. It is, however, possible to obtain a reasonable fit of the published data in the 300−50 K temperature range, using the following parameters, $g = 1.95$, $J = -8.3 \pm 2$ cm^{-1}, $\rho = 11.5\%$, and $F = 7.3 \times 10^{-4}$, where ρ is the percentage of paramagnetic impurities. For the fit, the possible interaction between the two interpenetrating nets has not been taken into account. The high value found for the paramagnetic impurity is comparable to the one already published.[4]

The final compound we have studied is that of stoichiometry $[Fe^{II}(bipy)_3][Mn^{II}_2(ox)_3]$ **3**, where bipy = 2,2′bipyridine, and ox = oxalate. As previously described by Decurtins et al.,[5] the Mn(II) ions are connected via oxalate bridging ligands to build up a three-dimensional 3-connected 10-gon network (Figure 4) with the diamagnetic $[Fe^{II}(bipy)_3]^{2+}$ cations occupying the cavities in the network. An antiferromagnetic interaction is expected between the Mn(II) ions[23−29] for this type of three-dimensional structural topology. The thermal variation of the magnetic properties of **3** in the form of a χ_M vs T plot are depicted in Figure 5. The magnetic susceptibility χ_M increases with decreasing temperature, reaching a maximum value at around 16 K, before it decreases upon additional cooling. For $T < 10$ K, χ_M shows a field dependency, reaching a minimum around 4.5 K and finally increases again due to the presence of impurities. Using the empirical law for the (10, 3) network topology and allowing for the presence of impurities, the values of g, J, and ρ were determined by minimizing F in the temperature range between 300 and 30 K. The best values obtained for these parameters are as follows; $g = 1.95$, $J = -2.01$ cm^{-1}, $\rho = 2.3$, and $F = 2.97 \times 10^{-4}$. These values are in reasonable agreement with those found in the literature for other dinuclear complexes[23] and regular chains[24−28,29] incorporating oxalate molecules as bridging ligands. It is worthy to note that the mean field approach does not give a good value for the interaction through an oxalato bridge ($J = -1.3$ cm^{-1}).

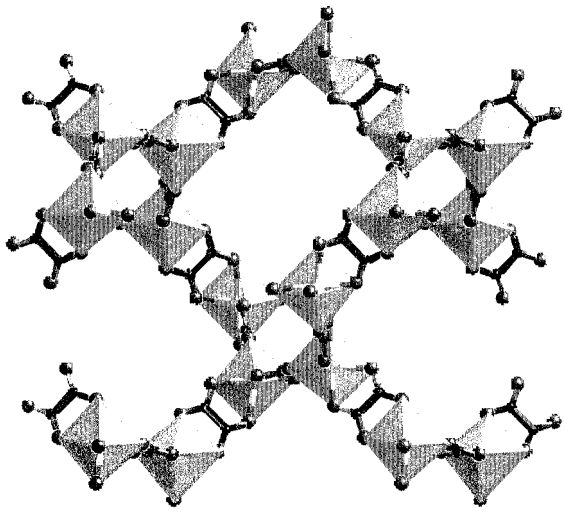

Figure 4. Representation of the structure of the polymeric $[Mn^{II}_2(ox)_3]_n^{2n-}$ network for the isostructural compound of stoichiometry $[Ni^{II}(bipy)_3][Mn^{II}_2(ox)_3]$.[5]

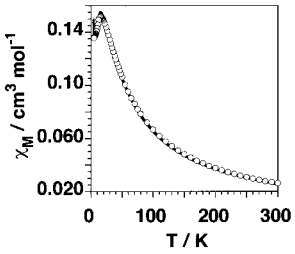

Figure 5. χ_M *vs.* T plot for **3**. The solid line is calculated using the empirical law for the (10, 3) network together with the relevant parameters given in the text.

Conclusion

During the course of these studies, we have shown that the method of Monte Carlo simulations using classical spins is well adapted to interpret the experimental magnetic data of extended three-dimensional networks containing metal ions with a local spin of S = 5/2. This method is excellent and gives good agreement when compared to results from alternative approaches based on different hypotheses, or when compared to results found in the scientific literature for discrete systems containing the same type of bridging ligand. In general, we have found

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that Monte Carlo calculations give a better fit of the real experimental observations in the low-temperature region, resulting in more reliable results. Furthermore, it is possible to use the Monte Carlo approach to treat other classes of three-dimensional extended systems and to indeed extend this method to deal with more complex systems allowing for several *J* (anti or ferromagnetic) interactions between magnetic ions.[19,30] The present limitations of the Monte Carlo method using classical spins restrict us to the study of systems with spin values $S \geq 2$. We are, however, currently working to address the problem of magnetic anisotropy, and our aim is to extend this methodology to include systems with spins $S < 2$ by applying quantum Monte Carlo techniques.

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