PHYSICAL REVIEW B VOLUME 49, NUMBER 5 1 FEBRUARY 1994-I

Theory of the magnetic properties of isotropic ladder-type double chains with classical spins at the bunch-upright intersections: Application to Gd(III)-Cu(II) compounds

Roland Georges
Laboratoire de Chimie du Solide, Centre National de la Recherche Scientifique, Université de Bordeaux-I, 33405, Talence CEDEX, France

Olivier Kahn and Olivier Guillou
Laboratoire de Chimie Inorganique, Université de Paris-Sud, Bâtiment 420, 91405, Orsay, France

(Received 1 July 1993)

A general method is proposed for computing the susceptibility of a large category of regular magnetic double chains in which more or less complex quantum spin systems, occupying the uprights and the bunches, are linked through the nodes by magnetic cations. Only two conditions are required: (i) the magnetic cations at the intersections of the uprights and the bunches must exhibit large enough spin quantum numbers to allow a classical treatment and (ii) the overall zero-field Hamiltonian must be isotropic. The main applications of the model are listed. More specifically, results are given for the case where the quantum spin systems are empty, and the neighboring classical spins directly interact through Heisenberg exchange. The model is also used with particular success to interpret the observed magnetic properties of the compound $Gd_2(ox)[Cu(pba)]_3[Cu(H_2O)_5]\cdot 20H_2O$, which enters the general framework, with each quantum system reducing to a single $\frac{1}{2}$ spin. It is also applied tentatively to the related compound $Gd_2[Cu(pba)]_3\cdot 23H_2O$.

I. INTRODUCTION

The potentialities of molecular chemistry in terms of the design of exotic systems is almost limitless.[1] Three decades ago, or so, the first regular, or equally spaced, magnetic chain compounds were described.[2,3] Shortly after, the first alternating chain compounds involving a unique type of spin carrier, but with two types of exchange pathways, were reported.[4] More recently, during the 1980s, the synthesis of equally spaced bimetallic chain compounds was achieved.[5–7] Alternating bimetallic chain compounds in which there is alternation, not only of the spin carriers, but of the exchange pathways as well, have also been characterized.[8–11]

In the beginning of the study of low-dimensional magnetic materials, the compounds synthesized by the chemists were used to test models proposed by the theoretical physicists. This was, for instance, the case for the equally spaced copper(II) chains, the magnetic properties of which were successfully interpreted with the Bonner-Fisher model.[12,13] The situation was changed when the objects designed by the chemists became more and more sophisticated. The object was first described, then a theoretical model to understand quantitatively its thermodynamical properties was built. What happened as far as the bimetallic one-dimensional systems are concerned is quite characteristic in this respect.

Recently, chemists have reported even more complex low-dimensional magnetic compounds. Among them, we may mention the ladder-type compounds. For instance, two of us described several families of rare earth(III)-copper(II) molecular materials resulting from the reaction of the copper(II) precursor $[Cu(pba)]^{2-}$ shown in Fig. 1, with lanthanide(III) ions [pba stands for oxamido-bis(oxamato)].[14] Two compounds involve Gd(III) and Cu(II) ions. The former (hereafter referred to as compound 1) of formula $Gd_2(ox)[Cu(pba)]_3(Cu(H_2O)_5)\cdot 20H_2O$, with ox=oxalato, has a two-dimensional structure. $Gd_2[Cu(pba)]_3$ ladder-like motifs shown in Fig. 2 are linked together by oxalato groups forming a dianionic frame formulated as $\{Gd_2(ox)[Cu(pba)]_3\}^{2-}$. Dications $[Cu(H_2O)_5]^{2+}$ are interspersed in the gap between the layers, anchoring the slabs to each other. In addition, noncoordinated water molecules provide hydrogen bonds between the layers.[15] The zero-field magnetic susceptibility of compound 1 was investigated down to 1.3 K. The product $\chi_M T$ of the molar magnetic susceptibility by the temperature increases more and more rapidly as T is lowered, which was qualitatively interpreted as resulting from Gd(III)-Cu(II) ferromagnetic interactions through the oxamato bridges within the ladders. Indeed, it was known from the magnetic properties of $Gd(ox)_3\cdot(H_2O)_{9.5}$ that the Gd(III)-Gd(III) interaction through the oxalato bridge is very

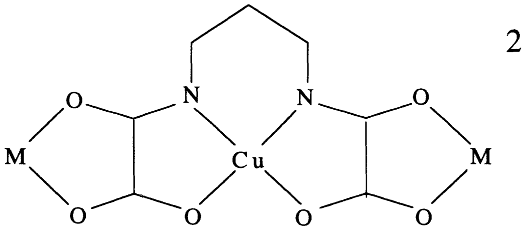

FIG. 1. View of the anionic precursor $[Cu(pba)]^{2-}$.

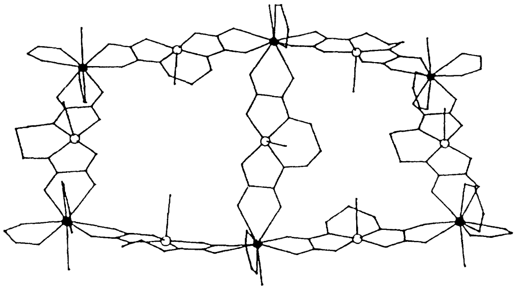

FIG. 2. View of the ladder-type motif in $Gd_2(ox)[Cu(pba)]_3[Cu(H_2O)_5]\cdot 20H_2O$ (1).

small. Finally, the magnetic contribution associated with the isolated $[Cu(H_2O)_5]^{2+}$ units may be reasonably assumed to follow a Curie law.

The latter compound (2), of formula $Gd_2[Cu(pba)]_3\cdot 23H_2O$, can be seen as the condensation of two puckered ladders together with quite an unexpected redistribution of the rungs, giving rise to an infinite tubelike motif of an essentially square section and quasi fourfold symmetry,[16] as shown in Fig. 3. Again, the magnetic properties of 2 indicate Gd(III)-Cu(II) ferromagnetic interactions within the tube motifs.

The synthesis and the investigation of the magnetic properties of the ladder-type compounds, in particular, the Gd(III)-Cu(II) systems just presented, has been a strong incitement to develop a new model, treating a more general configuration, and allowing to examine the compound 1 as a special case.

II. THEORY

Various kinds of magnetic double chains have been investigated from both experimental and theoretical points of view.[17] Most of time they were characterized by essentially anisotropic properties. Furthermore, the case of simple isotropic chains showing classical spins alternating with quantum spin or quantum spin systems have been considered in some detail.[18–20] In the compounds described in the previous part, the Gd(III) ions carry $\frac{7}{2}$ spins. This value is generally thought to be large enough to allow a classical treatment of the corresponding spin operators. Moreover, both Gd(III) and Cu(II) exhibit essentially isotropic characters. Thus, as far as (1) is concerned, we need a model for an isotropic double chain, with the nodes occupied by classical spins interacting through $\frac{1}{2}$ spins. Actually, we shall develop a much more general model in which the $\frac{1}{2}$ spins are replaced by isotropic quantum spin systems. This model will appear to be applicable to a large variety of configurations of experimental or fundamental interest.

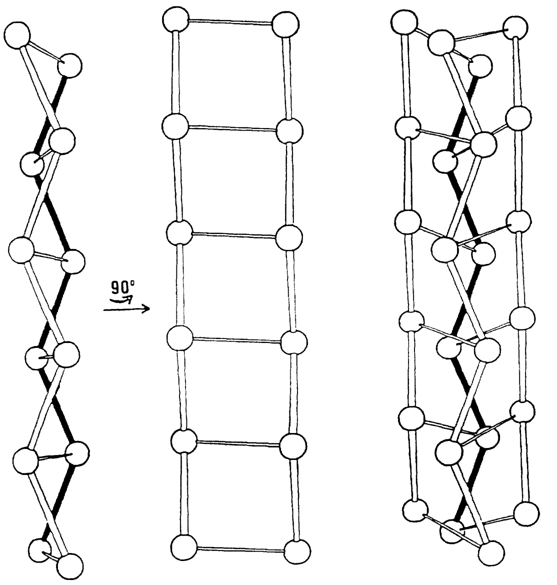

FIG. 3. Condensation of two ladder-type motifs to achieve the tubelike motif in $Gd_2[Cu(pba)]_3\cdot 23H_2O$ (2).

We consider the general chain structure schematized on Fig. 4. It is assumed to be fully isotropic in the spin space, and to present a translational symmetry for the interaction network. The unit cell i contains two classical spins $\mathbf{S}_i$ and $\mathbf{S}'_i$ and three more or less complex quantum spin systems s_i^a, s_i^b, and s_i^c. The spins $\mathbf{S}_i$ and $\mathbf{S}'_i$ are considered within the classical approximation. A weak magnetic field $\mathbf{H}$ (amplitude H) is applied to the chain and defines the z direction.

The model is based on the standard transfer matrix method. Starting from a formal expansion, on the basis of a suitable function set, for the partition function of a finite length chain, we examine the recurrent way its coefficients are affected when an extra unit cell is added. The new coefficients will appear as linear combinations of the previous ones, thus giving rise to the matrix transfer.

Let us start with the chain limited by the cells with indices 0 and N. The Hamiltonian is

$$H = \sum_{i=0,N} H_i \ , \tag{1}$$

with

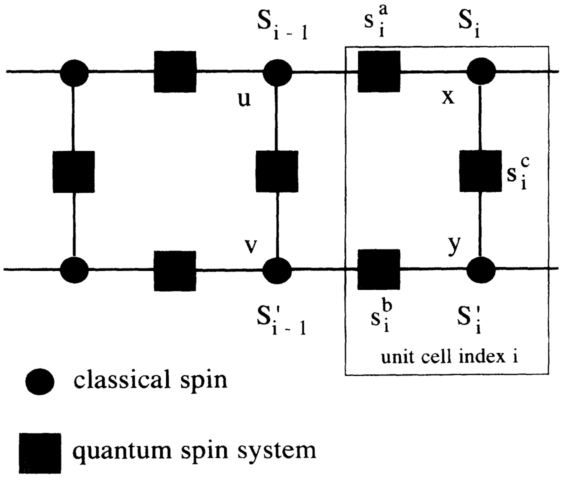

FIG. 4. General structure of the chains considered by the model.

$$H_i = H_i^a + H_i^b + H_i^c \; . \tag{2}$$

In these expressions H_i^a (H_i^b, H_i^c) refers to the quantum system s_i^a (s_i^b, s_i^c), submitted to the exchange field of the neighboring classical vectors $\mathbf{S}_{i-1}$ and $\mathbf{S}_i$ ($\mathbf{S}'_{i-1}$ and $\mathbf{S}'_i$, $\mathbf{S}_i$ and $\mathbf{S}'_i$) and to the applied field $\mathbf{H}$. H_i^c also includes the Zeeman energy term for the classical spins $\mathbf{S}_i$ and $\mathbf{S}'_i$, carrying magnetic moments of amplitudes γ and γ', respectively. Due to the classical approximation and the resulting commutation properties, the partition function of the partial chain is given by

$$\begin{aligned} Z_N(H,T) = \int d\mathbf{S}_0 \int d\mathbf{S}'_0 Z(-\beta H_0^a) Z(-\beta H_0^b) Z(-\beta H_0^c) \cdots \\ \times \int d\mathbf{S}_i \int d\mathbf{S}'_i Z(-\beta H_i^a) Z(-\beta H_i^b) Z(-\beta H_i^c) \cdots \\ \times \int d\mathbf{S}_N \int d\mathbf{S}'_N Z(-\beta H_N^a) Z(-\beta H_N^b) Z(-\beta H_N^c) \; , \end{aligned} \tag{3}$$

where β is Boltzmann's factor $1/k_B T$ and $Z(-\beta X)$ stands for the trace of the operator $\exp(-\beta X)$. In order to obtain the zero-field magnetic susceptibility of the chain, we only require the expansion of $Z_N(H,T)$ up to second order with respect to H.

Let us focus on the ith cell. For simplicity we introduce the unit vectors $\mathbf{u}$, $\mathbf{v}$, $\mathbf{x}$, and $\mathbf{y}$ along $\mathbf{S}_{i-1}$, $\mathbf{S}'_{i-1}$, $\mathbf{S}_i$, and $\mathbf{S}'_i$, respectively. It has been shown[20] that, due to the isotropic properties of H_i^a, we have

$$Z(-\beta H_i^a) = \sum_{m=0,2} \sum_{n=0,\infty} \sum_{0 \le q+r \le m}^{*} \zeta^a_{n,m,q,r} H^m P_n(\mathbf{u}\cdot\mathbf{x}) P_q(u) P_r(v) \; , \tag{4}$$

where u (v) is the component of $\mathbf{u}$ ($\mathbf{v}$) along the z direction. P_s refers to the Legendre polynomial of degree s. The coefficients $\zeta^a_{n,m,q,r}$ depend on the detailed structure of H_i^a, i.e., on the quantum system s_i^a itself and the coupling of the quantum spins it involves with $\mathbf{S}_{i-1}$ and $\mathbf{S}_i$. Their determination is straightforward, but may be quite tedious if s_i^a is a complex system.[20] Due to the assumed translational symmetry, they do not explicitly depend on i. Moreover, from physical considerations, it appears that the integral of $Z(-\beta H_i^a)$ over all of the available directions of the neighboring classical spins must be even with respect to applied field reversal. Then, the index sum $m+q+r$ must also be even. In the present approach, since we are looking for the zero-field magnetic susceptibility, it will be restricted to the values 0 and 2. In this respect, we shall use the notation $\sum^{*}_{i \le j \le k}$ which indicates that the current index j keeps the same parity as its limiting values i and k. Of course, similar considerations hold for $Z(-\beta H_i^b)$ and $Z(-\beta H_i^c)$.

The partition function $Z_N(H,T)$ may then be written in the partly integrated form:

$$Z_N(H,T) = \int d\mathbf{x} \int d\mathbf{y}\, z_N(\mathbf{x},\mathbf{y}) \; , \tag{5}$$

where the unit vectors $\mathbf{x}$ and $\mathbf{y}$ now refer to the spins $\mathbf{S}_N$ and $\mathbf{S}'_N$, and $z_N(\mathbf{x},\mathbf{y})$ presents the same symmetry properties as $Z(-\beta H_i^f)$ ($f=a,b,c$). Thus, we may write

$$z_N(\mathbf{x},\mathbf{y}) = \sum_{n \ge 0} \sum_{m=0,2} H^m \sum_{0 \le q+r \le m}^{*} z_{N,n,m,q,r} P_n(\mathbf{x}\cdot\mathbf{y}) \times P_q(x) P_r(y) \; . \tag{6}$$

Clearly, $z_N(\mathbf{x},\mathbf{y})$ is linked to $z_{N-1}(\mathbf{u},\mathbf{v})$ ($\mathbf{u}$ and $\mathbf{v}$ refer to $\mathbf{S}_{N-1}$ and $\mathbf{S}'_{N-1}$) by the recurrence relation

$$z_N(\mathbf{x},\mathbf{y}) = \int d\mathbf{u} \int d\mathbf{v}\, Z(-\beta H_N^a) Z(-\beta H_N^b) Z(-\beta H_N^c) \times z_{N-1}(\mathbf{u},\mathbf{v}) \; . \tag{7}$$

As shown by the expansion (4) [and the corresponding ones for $Z(-\beta H_N^b)$ and $Z(-\beta H_N^c)$], and due to the properties of the Legendre polynomials, the integrand in (7) reduces to a sum of spherical function products. Each product involves functions of arguments $\mathbf{x}$, $\mathbf{y}$, $\mathbf{u}$, and/or $\mathbf{v}$. On integration, taking advantage of the orthonormality properties of the $\mathbf{u}$- and $\mathbf{v}$-dependent ones, the expansion coefficients of $z_N(\mathbf{x},\mathbf{y})$ in (6) will appear as linear functions of the corresponding ones for $z_{N-1}(\mathbf{u},\mathbf{v})$, thus leading to the transfer matrix terms. Using Eq. (4), we first get

$$\begin{aligned} z_N(\mathbf{x},\mathbf{y}) = \sum_{n,n',n'',n''' \ge 0} \; \sum_{0 \le m+m'+m''+m''' \le 2}^{*} H^{m+m'+m''+m'''} \\ \times \sum_{0 \le q+r \le m}^{*} \; \sum_{0 \le q'+r' \le m'}^{*} \; \sum_{0 \ge q''+r'' \le m''}^{*} \; \sum_{0 \le q'''+r''' \le m'''}^{*} z_{N-1,n,m,q,r} \zeta^a_{n',m',q',r'} \zeta^b_{n'',m'',q'',r''} \zeta^c_{n''',m''',q''',r'''} \\ \times I_{nn'n''qq'rr''}(\mathbf{x},\mathbf{y}) P_{n'''}(\mathbf{x}\cdot\mathbf{y}) P_{r'}(x) P_{q'''}(x) P_{r''}(y) P_{r'''}(y) \; , \end{aligned} \tag{8}$$

where $I_{nn'n''qq'rr''}(\mathbf{x},\mathbf{y})$ is given by

$$I_{nn'n''qq'rr''}(\mathbf{x},\mathbf{y})=\int d\mathbf{u}\int d\mathbf{v}\, P_n(\mathbf{u}\cdot\mathbf{v})P_{n'}(\mathbf{u}\cdot\mathbf{x})P_{n''}(\mathbf{v}\cdot\mathbf{y}) \times P_q(u)P_{q'}(u)P_r(v)P_{q''}(v) \ . \tag{9}$$

Expanding $P_n(\mathbf{u}\cdot\mathbf{v})$ in terms of the spherical functions[21] $Y_n^p(\mathbf{u})$ and $Y_n^{p'}(\mathbf{v})$, we readily get

$$I_{nn'n''qq'rq''}(\mathbf{x},\mathbf{y})=\sum_p(-)^p J^p_{nn'n''qq'rq''}Y^p_{n'}(\mathbf{x})Y^{-p}_{n''}(\mathbf{y}) \ , \tag{10}$$

with

$$J^p_{nn'n''qq'rq''}=(4\pi)^3 A_{nn'n''}K^p_{nn'qq'}K^p_{n''nrq''} \ , \tag{11}$$

$$A_{nn'n''}=[(2n+1)(2n'+1)(2n''+1)]^{-1} \ , \tag{12}$$

$$K^p_{nn'qq'}=\int d\mathbf{u}\, Y^p_n(\mathbf{u})Y^{-p}_{n'}(\mathbf{u})P_q(u)P_{q'}(u) \ . \tag{13}$$

Expanding now $P_q(u)$ in terms of $Y^0_q(\mathbf{u})$, using the Clebsh-Jordan coefficients[21]

$$L^p_{qq'Q}=L^p_{q'qQ}=\int d\mathbf{u}\, Y^p_q(\mathbf{u})Y^{-p}_{q'}(\mathbf{u})Y^0_Q(\mathbf{u}) \ , \tag{14}$$

which vanish for odd $q+q'+Q$ values, the product $P_q(u)P_{q'}(u)$ in $K^p_{n,n',q,q'}$ may be written as the linear combination of spherical functions

$$P_q(u)P_{q'}(u)=4\pi B_{qq'}\sum^*_{|q-q'|\leq Q\leq q+q'} L^0_{qq'Q}Y^0_Q(\mathbf{u}) \ , \tag{15}$$

with

$$B_{qq'}=[(2q+1)(2q'+1)]^{-1/2} \ . \tag{16}$$

Due to the orthonormality of the spherical functions, $K^p_{nn'qq'}$ reduces to

$$K^p_{nn'qq'}=4\pi B_{qq'}\sum^*_{|q-q|\leq Q\leq q+q'} L^0_{qq'Q}L^p_{nn'Q} \ . \tag{17}$$

It appears that $K^p_{nn'qq'}$ vanishes unless $q+q'$ and $n+n'$ have the same parity, and the domains $(|q-q'|,q+q')$ and $(|n-n'|,n+n')$ have a nonempty intersection. Thus

$$I_{nn'n''qq'rq''}(\mathbf{x},\mathbf{y})=(4\pi)^5 A_{nn'n''}\sum^*_{|q-q'|\leq Q\leq q+q'}\ \sum^*_{|r-q''|\leq Q'\leq r+q''} B_{qq'}L^0_{q,q'Q}B_{rq''}L^0_{rq''Q'}\sum_p(-)^p L^p_{n,n',Q}L^p_{n''nQ'}Y^p_{n'}(\mathbf{x})Y^{-p}_{n''}(\mathbf{y}) \ , \tag{18}$$

and, finally

$$\begin{aligned} z_N(\mathbf{x},\mathbf{y})={}&(4\pi)^5\sum^*_{0\leq m+m'+m''+m'''\leq 2} H^{m+m'+m''+m'''}\sum_{n,n',n'',n'''\geq 0} A_{nn'n''}\sum^*_{0\leq q+r\leq m}\ \sum^*_{0\leq q'+r'\leq m'}\\ &\times\sum^*_{0\leq q''+r''\leq m''}\ \sum^*_{0\leq q'''+r'''\leq m'''} z_{N-1,n,m,q,r}\zeta^a_{n',m',q',r'}\zeta^b_{n'',m'',q'',r''}\\ &\times\zeta^c_{n''',m''',q''',r'''}B_{qq'}B_{rq''}\left[\sum^*_{Q=|q-q'|,q+q'}\ \sum^*_{Q'=|r-q''|,r+q''} L^0_{q,q',Q}L^0_{rq''Q'}S^0_{nn'n''QQ'}\right]P_{n'''}(\mathbf{x}\cdot\mathbf{y})P_{r'}(x)P_{q'''}(x)P_{r''}(y)P_{r'''}(y), \end{aligned} \tag{19}$$

with

$$S_{nn'n''QQ'}(\mathbf{x},\mathbf{y})=\sum_m(-)^m L^m_{nn'Q}L^m_{n''nQ'}Y^m_{n'}(\mathbf{x})Y^{-m}_{n''}(\mathbf{y}) \ . \tag{20}$$

Due to the various selection rules, only the following nine $(nn'n''QQ')$ index sets are relevant: $(n,n,n,0,0)$, $(n,n+1,n,1,0)$, $(n,n-1,n,1,0)$, $(n,n+2,n,2,0)$, $(n,n,n,2,0)$, $(n,n-2,n,2,0)$, $(n,n+1,n+1,1,1)$, $(n,n+1,n-1,1,1)$, and $(n,n-1,n-1,1,1)$.

Now we introduce the expression of $Y^m_n(\mathbf{u})$ in terms of the Legendre functions $P^m_n(\cos\theta_u)$[21] and the complex exponentials $e^{im\phi_t}$ (θ_t and ϕ_t are the spherical angles for the unit vector $\mathbf{t}$). Using the standard recurrence relation[22] between the P^m_n's and the values of the Clebsh-Jordan coefficients, these sums may be given for more practical forms. In order to avoid a tedious presentation, we only examine with some details the second sum $S_{n,n+1,n,1,0}(\mathbf{x},\mathbf{y})$. We successively obtain

$$S_{n,n+1,n,1,0}(\mathbf{x},\mathbf{y})=3^{1/2}\sum_m(-)^m(n+1-m)P^m_{n+1}(\cos\theta_x) \times P^{-m}_n(\cos\theta_y)e^{im(\phi_x-\phi_y)} \ , \tag{21}$$

and the recurrent relation

$$S_{n,n+1,n,1,0}(\mathbf{x},\mathbf{y})=3^{1/2}(2n+1)\cos\theta_x P_n(\mathbf{x}\cdot\mathbf{y}) -S_{n-1,n,n-1,1,0}(\mathbf{x},\mathbf{y}) \ . \tag{22}$$

As a result,

$$S_{n,n+1,n,1,0}(\mathbf{x},\mathbf{y})=(4\pi)^{1/2}\left[\sum_{k=n,n-2,\ldots\geq 0}(2k+1)P_1(x)P_k(\mathbf{x}\cdot\mathbf{y})-\sum_{k=n-1,n-3,\ldots\geq 0}(2k+1)P_1(y)P_k(\mathbf{x}\cdot\mathbf{y})\right] \ . \tag{23}$$

The same process applies to the various sums appearing in $z_N(\mathbf{x},\mathbf{y})$, and analogous expressions are obtained. It may be checked by direct inspection that the factor of $S_{n,n+1,n,1,0}(\mathbf{x},\mathbf{y})$ in $z_N(\mathbf{x},\mathbf{y})$ is

$$\begin{aligned}C_{n,n+1,n,1,0}=(4\pi)^5H^2\sum_{n'=0,\infty}P_{n'}(\mathbf{x}\cdot\mathbf{y})[&(z_{N-1,n,000}\zeta^a_{n+1,211}\zeta^b_{n,000}\zeta^c_{n',000}+z_{N-1,n,110}\zeta^a_{n+1,101}\zeta^b_{n,000}\zeta^c_{n',000}\\&+z_{N-1,n,110}\zeta^a_{n+1,000}\zeta^b_{n,000}\zeta^c_{n',110}+z_{N-1,n,000}\zeta^a_{n+1,110}\zeta^b_{n,000}\zeta^c_{n',110})P_1(x)\\&+(z_{N-1,n,110}\zeta^a_{n+1,000}\zeta^b_{n,101}\zeta^c_{n',000}+z_{N-1,n,110}\zeta^a_{n+1,000}\zeta^b_{n,000}\zeta^c_{n',101}\\&+z_{N-1,n,000}\zeta^a_{n+1,110}\zeta^b_{n,101}\zeta^c_{n',000}+z_{N-1,n,000}\zeta^a_{n+1,110}\zeta^b_{n,000}\zeta^c_{n',101})P_1(y)]\ .\end{aligned}\tag{24}$$

This is a linear combination of $P_1(x)\sum_{n'}P_{n'}(\mathbf{x}\cdot\mathbf{y})$ and $P_1(y)\sum_{n'}P_{n'}(\mathbf{x}\cdot\mathbf{y})$, the coefficients of which are, to their turn, linear combinations of the $z_{N-1,n,mqr}$'s. Since a two-Legendre polynomial product may be expanded as a finite sum of such polynomials,

$$P_{n'}(t)P_k(t)=\sum_{1=|n'-k|,n'+k}R_{n'k1}P_1(t)\ ,\tag{25}$$

we have, for instance,

$$\begin{aligned}P_1(y)\sum_{n'}P_{n'}(\mathbf{x}\cdot\mathbf{y})S_{n,n+1,n,1,0}(\mathbf{x},\mathbf{y})=(4\pi)^{1/2}\Bigg[&\frac{1}{3}\sum_{k=n,n-2,\ldots\geq 0}(2k+1)[2P_2(x)+P_0(x)]\sum_{1=|n'-k|,n'+k}R_{n'k1}P_1(\mathbf{x}\cdot\mathbf{y})\\&-\sum_{k=n-1,n-3,\ldots\geq 0}(2k+1)P_1(y)P_1(y)\sum_{1=|n'-k|,n'+k}R_{n'k1}P_1(\mathbf{x}\cdot\mathbf{y})\Bigg]\ .\end{aligned}\tag{26}$$

As could have been expected from physical and symmetry considerations, this expression which contributes to $z_N(\mathbf{x},\mathbf{y})$ has the same structure as $z_{N-1}(\mathbf{u},\mathbf{v})$. This result is valid for all such contributions. Moreover, the related coefficients are linear combinations of the parameters $z_{N-1,nmpq}$. Thus, the expansion coefficients for $z_N(\mathbf{x},\mathbf{y})$ in (19) are deduced from the corresponding ones for $z_{N-1}(\mathbf{u},\mathbf{v})$ by a linear transformation. The associated matrix is the so-called transfer matrix. Its largest eigenvalue may be considered as the infinite chain partition function Z_{cell} referred to the unit cell. By convenient partial derivations, various thermodynamical functions may be deduced. In the present case, the applied field **H** has been taken into account up to the H^2 terms, and we may obtain the unit cell zero-field susceptibility $\chi_{\text{cell}}(T)$ given by the usual expression

$$\chi_0(T)=\left[\frac{T}{Z_{\text{cell}}}\frac{\partial^2 Z_{\text{cell}}}{\partial H^2}\right]_{H=0}\ .\tag{27}$$

III. APPLICATIONS

The present model, dealing with ladder-type systems, assumes one may compute the elements of the transfer matrix associated with the unit cell. In principle, their number is infinite, since the partition function expansion requires an infinite set of Legendre polynomials. Moreover, except maybe in particularly simple configurations of the quantum systems, it is hopeless to get an analytical expression for the largest eigenvalue. Thus, the expansions will be necessarily truncated, and we shall not avoid some computational work. Truncating is essentially critical in the low-temperature range, where, in the classical description, the spins are almost frozen in parallel directions, a situation which requires a large set of Legendre polynomials to be accounted for. Actually, we observed that for k_BT of the order of one tenth of the exchange energy parameters, neglecting the Legendre polynomials above the fourth order introduces relative errors on the susceptibility that are less than 10^{-4}.

Since the only basis conditions of the model are the isotropy of the spin Hamiltonian and the translational periodicity of the magnetic network, it applies to a very large set of interesting situations. It may be noticed that the larger spin values often concern half-filled shell cations [Mn(II), Fe(III), Eu(II), Gd(III),. . .], showing convenient isotropic properties. Moreover, in a number of molecular compounds, isotropic $\frac{1}{2}$ spins cations (Cu^{++}) or organic radicals (nitronyl nitroxide) are inserted between them in order to convert the generally antiferromagnetic nearest-neighbor coupling into a next nearest-neighbor ferromagnetic tendency, without significant overall magnetization reduction.

Among the possible ladder conformations compatible with the present model one may point out the following ones. The ladder may have nonequivalent uprights and/or not symmetrical rungs. The unit cell may involve a sequence of nonidentical elements on the model of those described in Fig. 4. In such a case, the various element contributing to the composite unit cell gives rise to distinct matrices, and the partition function is the largest eigenvalue of their conveniently ordered product. In particular, doubling the unit cell permits us to consider various kinds of exchange alternance along the uprights, or to eliminate one rung over two. Also, part of the quantum systems may be empty, being replaced by a direct interaction between the neighboring classical spins. In that case, if one considers a double cell, and alternatively lets one of the Heisenberg couplings become infinite, one deals with the classical chain made of triangles sharing sides, which has been discussed in the z-z coupling framework only.[20]

We leave to a future article a detailed examination of most of the various interesting situations that the flexibility of the present model allows to treat. Here, we shall restrict ourselves to two particular problems.

The first one deals with the simplest situation: the quantum systems s^a, s^b, and s^c are empty, and the corresponding parts of the Hamiltonian reduce to direct Heisenberg couplings between the neighboring classical spins. Moreover, we assume that they carry the same magnetic moment ($\gamma'=\gamma$), and that all the coupling constants have the same value J. Thus, following the general prescriptions,

$$\begin{aligned} &H_i^a=J\mathbf{S}_{i-1}\cdot\mathbf{S}_i,\quad H_i^b=J\mathbf{S}'_{i-1}\cdot\mathbf{S}'_i,\\ &H_i^c=J\mathbf{S}_i\cdot\mathbf{S}'_i-\gamma H(u_i+u'_i)\ . \end{aligned} \tag{28}$$

Compounds showing such ladder-type exchange networks have already been mentioned in the literature[17] and have given rise to several models. But none of them was conveniently described by a classical isotropic Hamiltonian and the corresponding theory has not yet been developed. The present analysis thus completes this field.

The calculations have been performed on the basis of Hamiltonian (28) for both ferromagnetic and antiferromagnetic Heisenberg coupling. The main results are given on Fig. 5 which shows the thermal behavior of the product $(\chi T)_n$ normalized to the infinite temperature value for the double chain as well as for the simple one as a reference. In the ferromagnetic case, the susceptibility is known to behave like $M\xi^2$, where M is the magnetic moment per unit cell, and ξ the correlation length. Since the product χT^2 appears to have a finite limit at absolute zero (Fig. 6) the correlation length is shown to diverge like T^{-1} for both types of chain, the front coefficient being larger as the interchain coupling increases. For antiferromagnetic coupling, in the low-temperature limit, the computation results agree with elementary energy considerations, which gives the absolute zero initial susceptibility (per spin)

$$\chi_{T=0}=M^2/3zJ\ , \tag{29}$$

where z is the number of neighbors with which a spin interacts through J. The main features of the low-temperature susceptibility behavior in both the ferromagnetic and antiferromagnetic cases are thus similar within multiplicative factors, whatever the nature (simple or double) of the classical isotropic chain is.[23]

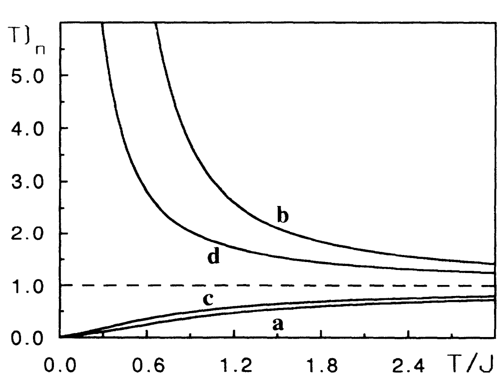

FIG. 5. Behavior of the normalized $[\chi T]_n$ product (see text) for the purely classical chains, with a common value J for all nearest-neighbor exchange interactions [Hamiltonian (28)]. (a) double chain, antiferromagnetic coupling; (b) double chain, ferromagnetic coupling; (c) simple chain, antiferromagnetic coupling; (d) simple chain, ferromagnetic coupling.

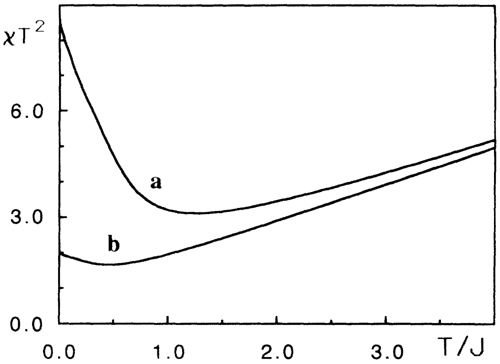

FIG. 6. Thermal behavior of the product χT^2 for the purely classical ferromagnetic chains, with a common value J for all nearest-neighbor exchange interactions [Hamiltonian (28)]. (a) double chain; (b) simple chain.

The next illustration we shall present deals with the compound (1) described in the Introduction. As indicated, its chain structure enters the present framework, with each quantum spin system reducing to a single $\frac{1}{2}$ spin, carried by the Cu(II) of each $[\mathrm{Cu(pba)}]_3$ unit. The $\frac{7}{2}$ spin vector operators belonging to the Gd(III) are treated classically. Finally, the intervening cations are compatible with an isotropic Hamiltonian. We have noticed that the extra paramagnetic contribution to the magnetic susceptibility arising from the moments on the isolated Cu(II) belonging to the $[\mathrm{Cu(H_2O)_5}]^{2+}$ units follows a Curie law.

We have analyzed the experimental results concerning the thermal behavior of the χT product. The same Landé factor $g=2.00$, determined in the high-temperature limit, has been attributed to all cations. As suggested by the detailed structure of the exchange pathways, a unique coupling constant J has been introduced for all the Cu(II)-Gd(III) interactions. We have thus used the Hamitonians

$$H_i^a=J\sigma_i^a\cdot(\mathbf{S}_{i-1}+\mathbf{S}_i)-g(\sigma_i^a)^zH\ , \tag{30a}$$

$$H_i^b=J\sigma_i^b\cdot(\mathbf{S}'_{i-1}+\mathbf{S}'_i)-g(\sigma_i^b)^zH\ , \tag{30b}$$

$$H_i^c=J\sigma_i^c\cdot(\mathbf{S}_i+\mathbf{S}'_i)-g(\sigma_i^c)^zH-g(u_i+u'_i)\tfrac{7}{2}H\ , \tag{30c}$$

where $\sigma_i^f(f=a,b,c)$ is the $\frac{1}{2}$ spin operator to which the subsystem s_i^f reduces. The best fitting of the experimental results in the range 1.3–21 K has been obtained for $J=-0.40$ K (Fig. 7). It must be noticed that the remarkable agreement between the experimental data and the computed curve has been obtained using J as the single fitting parameter. Within our conventions, the negative J value refers to a ferromagnetic exchange coupling, in agreement with the positive paramagnetic Curie temperature $\Theta_P=0.08$ K.[15] However, this temperature cor-

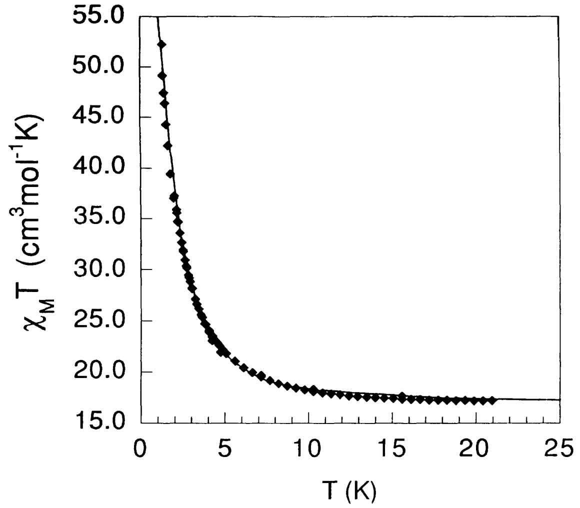

FIG. 7. Fitting of the experimental χT product behavior for the compound $Gd_2(ox)[Cu(pba)]_3[Cu(H_2O)_5]\cdot 20\ H_2O$.

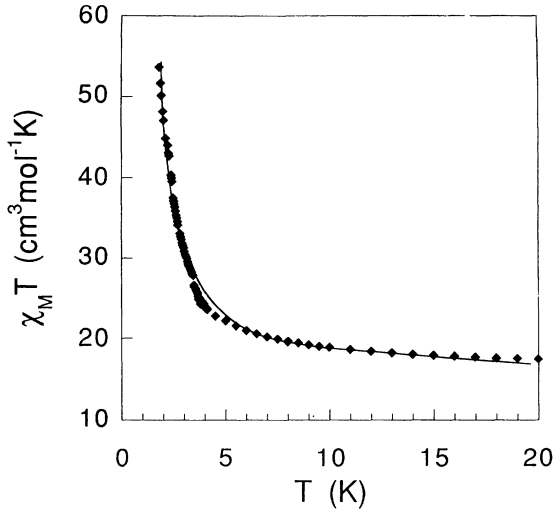

FIG. 8. Fittings of the experimental χT product behavior for the compound $Gd_2[Cu(pba)]_3\cdot 23H_2O$.

responds to a much weaker exchange value ($J=-0.06$ K). Actually, Θ_P is obtained by extrapolation from high-temperature measurements. Such an extrapolation may be questionable for several reasons, including the incidence of the phonons on the exchange parameters.[24]

We have also tentatively fitted the experimental results obtained for the compound (2),[16] using the same starting Hamiltonians (36a)–(36c). Indeed, despite the fact that this compound exhibits a more complex one-dimensional structure, it must be noticed that the Cu(II)-Gd(III) links are redistributed in such a way that, as for (1), each Gd(III) has three neighboring Cu(II), and each Cu(II) has two neighboring Gd(III) (Fig. 3). No isolated Cu(II) is present in the structure. The best fitting is shown on Fig. 8. The agreement is rather satisfactory, although, as could be predicted, not as good as previously. The largest value obtained for the exchange coupling ($J=-0.53$ K), which actually deals with the same interaction pathways, thus appears as an artifact which accounts for the more intricate magnetic connection network at intermediate distances.

IV. CONCLUSION

In the present paper, we have developed a model for analyzing the magnetic properties of ladder-type double chains, the uprights of which are characterized by the alternance of quantum spin systems with classical spins, the latter being linked by quantum spin systems forming the bunches. The only symmetry conditions are the isotropy of the overall spin Hamiltonian and the translational periodicity of the magnetic network, the unit cell involving possibly several bunches. This results in a considerable flexibility of the model which allows the handling of a very large variety of practical situations which may merge in the literature. Only two particularly simple examples have been considered. One deals with the fundamental case of the ladder-type chain involving only classical spins. At low temperature, the thermal behavior of the susceptibility in both the ferromagnetic or antiferromagnetic coupling cases follows the same power laws as for the simple classical chains, with modifications of the front coefficients. The second situation deals with the compound $Gd_2(ox)[Cu(pba)]_3[Cu(H_2O)_5]\cdot 20H_2O$, which exhibits the general structure described in Fig. 4, with each quantum system reducing to a single $\frac{1}{2}$ spin. The fitting of the experimental results is remarkably good despite only one fitting parameter, namely the Cu(II)-Gd(III) exchange coupling, has been used. Incidentally, the compound $Gd_2[Cu(pba)]_3\cdot 23H_2O$, exhibiting quadruple chains, was shown to give a surprisingly good agreement with the double chain model, probably due to the short-range similarities of the exchange networks. However, the best fitting was obtained for a slightly too large exchange value, which was interpreted as an artifact accounting for the doubling of the chain.

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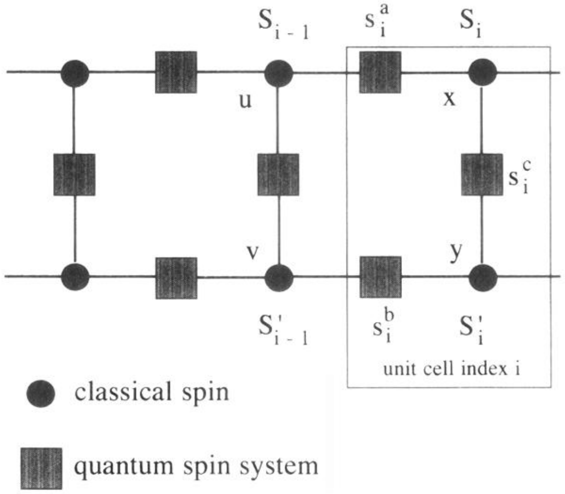

FIG. 4. General structure of the chains considered by the model.