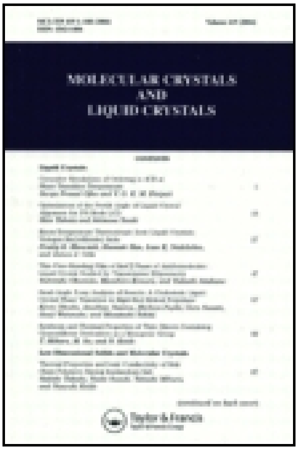

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Theoretical and Experimental Study of Alternating (Classical Spin)/(Quantum System) Isotropic Ferrimagnets

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THEORETICAL AND EXPERIMENTAL STUDY OF ALTERNATING (CLASSICAL SPIN)/(QUANTUM SYSTEM) ISOTROPIC FERRIMAGNETS

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Abstract Compounds containing well isolated complex magnetic chains are now available from inorganic and molecular chemistry. Interpreting their magnetic behavior generally requires specific models. We describe here a general analytic solution for a large class of such compounds. The model concerns isotropic chains, where a single moment which may be treated classically, alternates with a composite system of quantum spins. It is applied to to the magnetic properties the one-dimensional compound $MnCu_2(bapo)(H_2O)_4.2H_2O$, (where bapo = N,N'-bis(oxamato1,3-propylene)oxamido), within which one may observe --Mn^{II}-Cu^{II}-Cu^{II}-Mn^{II}-- sequences with nearest neighbor antiferromagnetic interactions. The results appear to be consistent with independant estimates of Mn^{II}-Cu^{II} and Cu^{II}-Cu^{II} exchange interations involving similar paths.

INTRODUCTION

The field of one-dimensional (1-d) magnetic systems has been intensively explorated for a long time, from static and dynamical points of view. In the last few years many papers have focussed on the so-called 1-d ferrimagnets, that is solid state structures exhibiting well separated magnetic chains along which two cationic species occupy alternating sites, generally with antiferromagnetic nearest neighbor coupling, thus providing the main basic conditions for ferrimagnetism. In the present time, more involved uncompensated 1-d magnetic systems are studied, since compounds containing more complex chains are currently synthetized in organic as well as inorganic solid state chemistry[1-3]. The reason for this strong interest is that, besides the general attractiveness of 1-d physics (which results from specific behaviors, but also from the opportunity of sometimes solving exactly the quantum and statistical problems), there is a great variety of predictible cationic or even topological combinations among which a number are of great appeal for solid state physicist[5-8]. Specific models have been proposed for solving various simple problems. But it appears that the methods thus introduced may often be extended to more general 1-d systems, and there is now a trend to develop general technics which apply to wider classes of chains[9]. In the present paper we describe such a model dealing with the static properties of a very large category of 1-d ferrimagnets.

THE MODEL

The model concerns chains only submitted to the following three conditions: (i) all single ion properties and exchange interactions are strictly istropic; (ii) the chain structure is characterized by an alternate sequence $\ldots \xi_{i-1}\ \zeta_i\ \xi_i\ \zeta_{i+1}\ \xi_{i+1} \ldots$ of magnetic systems, where each ζ_i reduces to a single spin (with a large enough quantum number to allow classical treatment), whereas the ξ_i's are systems involving one or more classical spins or vector operators; (iii) any ζ_i or ξ_i interacts with its nearest neighbors only.

In practice ζ_i is defined by the amplitude G_i of the moment it carries and by the direction of the unit vector $\mathbf{S}_i$ along this moment. ξ_i contains n_i spin or orbital momentum vector operators $\mathbf{s}_{i\lambda}$ ($\lambda=1, \ldots, n_i$). For practical purpose, n_i should be finite and small enough for allowing a complete analytical or computational resolution of the properties of ξ_i when submited to the influence of its neighbors ζ_i and ζ_{i+1} (which then act like external field sources). It must be underlined that the mathematical treatment we present here includes random distributions of the numerical and topological (interaction network) features of the ζ- and ξ- systems. Moreover all parameters and characteristics carrying the same i-index may be correlated.

Let us now consider the finite chain $\zeta_0\, \xi_0\, \zeta_1\, \xi_1 \ldots \zeta_i\, \xi_i\, \zeta_{i+1} \ldots \xi_{n-1} \zeta_n$ described by the hamiltonian

$$H_n(B) = \sum_{i=0}^{n-1} \mathcal{H}(\xi_i, \mathbf{S}_i, \mathbf{S}_{i+1}, B) - \sum_{i=0} G_i S_i^z B, \tag{1}$$

where $\mathcal{H}(\xi_i, \mathbf{S}_i, \mathbf{S}_{i+1}, B)$ is the hamiltonian of the system ξ_i submitted to the action of ζ_i and ζ_{i+1} and to a uniform magnetic field $\mathbf{B}$, with amplitude B, applied along a definite direction referred to as the z-direction. The partition function is :

$$Z_n(B) = \int d\mathbf{S}_0 U_0 \int d\mathbf{S}_1 V_0 U_1 \ldots \int d\mathbf{S}_i V_{i-1} U_i \ldots \int d\mathbf{S}_n V_{n-1} U_n. \tag{2}$$

where :

$$U_i = \exp(\beta G_i S_i^z B) \;, \quad V_i = \mathrm{Trace}(\exp(-\beta \mathcal{H}(\xi_i, \mathbf{S}_i, \mathbf{S}_{i+1}, B))). \tag{3}$$

In these expressions $\int d\mathbf{S}_i$ means integrating over all the directions available to $\mathbf{S}_i$, and β is Boltzmann's factor $1/k_BT$. The zero-field magnetic susceptibility for the whole chain is then given by:

$$\chi_{0n} = \sum_i \left[(U_i'') + (V_i'') + 2\sum_{j>i} [(U_i', U_j') + (V_i', V_j')] + 2\sum_j (U_i', V_j') \right] . \qquad (4)$$

The current braket $(W_r^{\nu_r}, \ldots, W_s^{\nu_s})$, with W = U or V, is obtained by calculating the integral (2) with $W_r, \ldots, W_s$ replaced by their zero-field $\nu_r{}^{th}, \ldots, \nu_s{}^{th}$ derivatives with respect to B, then dividing the result by $-\beta Z_n(0)$. The U-derivations of interest are easily performed and expressed in terms of the spherical functions $Y_\ell^0(\mathbf{S}_i)$ and $Y_\ell^0(\mathbf{S}_{i+1})$ (where ℓ = 0,1,2, and $\mathbf{S}_i$ is written in place of its azimuthal angles θ_i and ϕ_i with respect to a cartesian coordinate system involving the z-axis).

For the V-derivatives, we first notice that except for pathological couplings, we can develop the current eigenvalue $E_{i,u}(B)$ of $H_i(\xi_i, \mathbf{S}_i, \mathbf{S}_{i+1}, B)$ as a power series of the field components :

$$E_{i,u}(\mathbf{B}) = E_{i,u,0} + \sum_\delta B_\delta (\partial E_{i,u}(\mathbf{B})/\partial B_\delta)_0 + {}^1/_2 \sum_{\delta\delta'} B_\delta B_{\delta'} (\partial^2 E_{i,u}(\mathbf{B})/\partial B_\delta \partial B_{\delta'})_0 . \qquad (5)$$

The first order term involves the amplitude $E_{i,u,g}$ of the zero-field gradient of $E_{i,u}(\mathbf{B})$ and the corresponding unit vector $\mathbf{e}_{i,u,g}$. The second order one may be expressed in terms of the eigenvalues $E_{i,u,\alpha}$ (α=1,2,3) of the laplacian tensor and the corresponding unit eigenvectors $\mathbf{e}_{i,u,\alpha}$. Due to isotropy, the $E_{i,u,\alpha}$'s (α=1,2,3,g) only depend on the angle ψ_i between $\mathbf{S}_i$ and $\mathbf{S}_{i+1}$. Similarly, $\mathbf{e}_{i,u,g}$ and, say, $\mathbf{e}_{i,u,1}$ and $\mathbf{e}_{i,u,2}$ are linear functions of these vectors with coefficients depending on $\cos\psi_i$ only. Let us call $c_{i,u,\alpha}$ the director cosine of $\mathbf{e}_{i,u,\alpha}$ with respect to the z-direction. For α = g, 1 or 2, these cosines are linear functions of $Y_1^0(\mathbf{S}_i)$ and $Y_1^0(\mathbf{S}_{i+1})$, with ψ_i-dependant coefficients. On the other hand, we only need the sqarre of $c_{i,u,3}$ which is immediately derived from $c_{i,u,1}$ and $c_{i,u,2}$. We assume that the various functions of the angle ψ_i, may be developed in terms of Legendre polynomials, and then of spherical function products $Y_\ell^m(\mathbf{S}_i)\ Y_\ell^{-m}(\mathbf{S}_{i+1})$. Now introducing the resulting expressions into Eq. (4), we get a very cumbersome integral, which due to the orthonormality of the spherical harmonics, reduces to :

$$\chi_{cell} = \overline{\chi_{VV}} + (3\beta)^{-1}\ (\ \overline{G^2} + \overline{M^2} + 2(1-\overline{P})^{-1}(\overline{GP}.\overline{G} - (\overline{G} + \overline{GP})\overline{Q} - \overline{GR} + \overline{R}.\overline{Q})\ ) \qquad (6)$$

Actually, χ_{cell} is the zero-field magnetic susceptibility referred to the unit cell defined as the current entity (ζ_i, ξ_i). It is obtained by taking the large-n limit of the quantity χ_{0n}/n. It is expected that, for finite T, and with the exception of unrealistic couplings, this limit is well defined. Furthermore, the notation $\overline{F}$ reffers to the average value of the assumed randomly distributed quantity F_i. Except for $\overline{\chi_{VV}}$, Eq. (11) looks like previous ones obtained by the authors and co-workers in several contexts [6,8,9]. However the various terms now carry much wider meanings. $\overline{G^2}$ is the mean squarred magnetic moment carried by the ζ_i's. Similarly, $\overline{M^2}$ and $\overline{\chi_{VV}}$ are related to the average squarred thermodynamical mean amplitude of the gradient, and to the average thermodynamical mean trace of the laplacian tensor, respectively. They are nothing but the paramagnetic and Van Vleck contributions to the magnetic susceptibility of the ξ_i's, each one being submitted to its thermally fluctuating neighbors ζ_i and ζ_{i+1}. The last part takes into account the correlations through the (ζ-ξ) nearest neighbor couplings. P_i denotes the ratio V_i^1/V_i^0 of the first two coefficients in the Legendre polynomial development of V_i , and is merely the correlation $\langle \mathbf{S}_i.\mathbf{S}_{i+1} \rangle$. It tends to unity at absolute zero whenever the lowest (ψ_i-dependant) eigenvalue $E_{i,u,0}$, is minimized for parallel arrangement of $\mathbf{S}_i$ and $\mathbf{S}_{i+1}$. Thus, $(1-\overline{P})^{-1}$ diverges in the same limit if this condition is fulfilled all along the chain. Except for accidental vanishing in the same limit of the corresponding factor, this is the condition for the product $T.\chi_{cell}$ to diverge at low temperature, i-e for dealing with a true 1-d ferrimagnet. The last terms are easily related to the average correlations between moments belonging to neighboring ξ- and ζ- systems (i-e $\overline{G}.\overline{Q}$, $\overline{GP}.\overline{Q}$, $\overline{GR}$) or next nearest neighbor ζ-ζ ones ($\overline{GP}.\overline{G}$), or ξ-ξ ones ($\overline{Q}.\overline{R}$). It must be noticed that the complete treatment only requires the computation of the first and second coefficients in the Legendre polynomial developments of the various functions of $\cos\psi_i$.

One must now underline that the initial basic three conditions for Eq. (6) to be valid, define a wide application field. First of all, it is generally admitted that for $S \geq 5/2$ the spins may be treated as classical vectors; such an approximation is currently introduced for Mn^{II} or Fe^{III} cations[10]. Moreover, the thermodynamical properties of a number of non strictly isotropic 1-d magnetic systems may be conveniently analyzed merely on the basis of Heisenberg coupling, so long as the anisotropic to isotropic energy term ratio is sufficiently small[11]. Thus, the general expression for χ_{cell} would be of great help for analysing the magnetic properties of a number of existing or predictible 1-d ferrimagnets. For instance the model

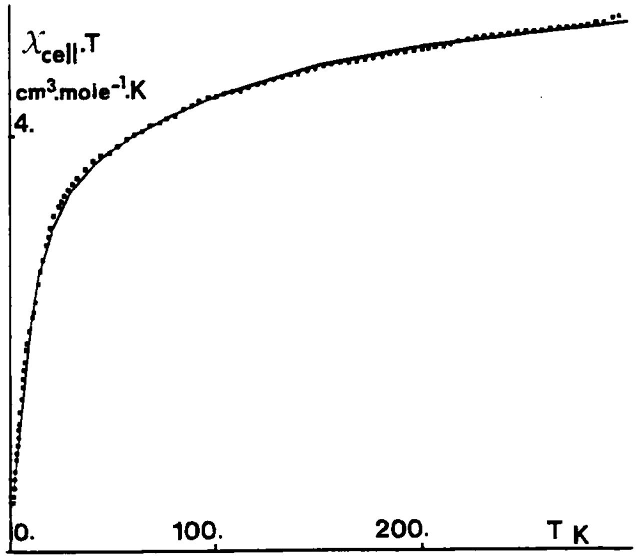

FIGURE 1. Experimental results (dotted line) and theoretical curve for the suceptibility of the compound MnCu(bapo)$(H_2O)_4.2H_2O$

applies to the compound MnCu(bapo)$(H_2O)_4.2H_2O$ which exhibits regular MnCuCu sequences with antiferromagnetic Mn^{II}-Cu^{II} and Cu^{II}-Cu^{II} nearest neighbor exchange interactions[12]. The best fitting for the thermal variation of the $\chi_{cell}.T$ product is given on Figure 2. The corresponding exchange parameters are J_{Cu-Cu} = 50.1K and J_{Mn-Cu}=100.0K, with a g-factor slightly larger than 2. for Cu^{II} only (2.1).

Recently, a new compound containing well separated linear Mn^{II}-Cu^{II}-Cu^{II}-Mn^{II} tetramers, has been synthetized[13]. The exchange interaction paths are very similar to the corresponding ones in MnCu(bapo)$(H_2O)_4.2H_2O$. A preliminary examination of its magnetic properties, also indicates a very strong Cu^{II}-Cu^{II} exchange interaction compared to the Cu^{II}-Mn^{II} ones.

REFERENCES

1. O. Kahn, Structure and Bonding, 68, 89 (1987).
2. J. Darriet, Xu Qiang, A. Tressaud, R. Georges and J.L. Soubeyroux, Phase Transitions , 13, 49 (1988).
3. J. Renaudin, G. Ferey, M. Zemirli, F. Varret, A. de Kozak and M. Drillon, Organic and Inorganic Low Dimensional Crystalline Materials, NATO-ASI Series, edited by P. Delhaes and M. Drillon, p149 (1987).
4. C.P. Landee, ibid., p75, and references therein.
5. M. Verdaguer, A. Gleizes, J.P. Renard and J. Seiden, Phys. Rev. B29, 5144 (1984).
6. M. Drillon, E. Coronado, D. Beltran, J. Curély, R. Georges, P.R. Nugteren, J.L. de Jongh and J.L. Génicon, J. Mag. Mag. Mat., 54-57, 1507 (1986).
7. Y. Pei, M. Verdaguer, O. Kahn, J. Sletten and J.P. Renard, Inorg. Chem., 26, 138 (1987).
8. R. Georges, J. Curély, J.C. Gianduzzo, X. Qiang, O. Kahn and Y. Pei, Physica B, 153, 77 (1988).
9. Xu Qiang, J. Darriet and R. Georges, J. Mag. Mag. Mat, 73, 379 (1988).
10. M. Drillon, E. Coranodo, D. Beltran and R. Georges, Chem. Phys. 79, 449 (1983).
11. M. Verdaguer, M. Julve, A. Michalowicz and O. Kahn, Inorg. Chem. 22, 2624 (1983).
12. Y. Pei, J. Sletten, and O. Kahn, J. Am. Chem. Soc. 106, 3727 (1984).
13. O. Kahn, to be published.