Theoretical investigation of topological ferrimagnetic intertwining double chain

M. Benhammou[a], M.Belaïche[a*], M. Bakhache[a], M. Soufiaoui[b], A. Benyoussef [c*] and E. H Saïdi[d*]

[a] *Laboratoire de Magnétisme, Matériaux magnétiques, Micro-ondes et Céramique. ENS Takaddoum, Rabat, Morocco.*
[b] *Laboratoire de Chimie des plantes, Synthèse organique et Bioorganique. Faculté des Sciences, B.P. 1014, Rabat, Morocco.*
[c] *Laboratoire de Magnétisme et de Physique des Hautes Energies, Faculté des Sciences, B.P. 1014, Rabat, Morocco.*
[d] *Laboratoire de Physique des Hautes Energies, Faculté des Sciences, B.P. 1014, Rabat, Morocco*
[*] *Hassan II Academy of Science and Technology, Rabat, Morocco*

In this paper, a novel trimeric chain approach to organometallic ferrimagnetics is proposed. The inter and intratrimer exchange interaction has been determined to be antiferromagnetic from a theoretical model magnetic susceptibility.
The Curie law observed at very low temperature (θ = 5.764 K l0) contrasts with significant ferromagnetic behaviour. The magnetic data were fitted with the IDC model. The compounds interestingly exhibit ferrimagnetic interactions with g_{Cu1} =1.81, g_{Cu2} =2.04 and g_{Cu3} =2.43;
J_1 =-89.93K and J_2 = -2.68 K
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* Corresponding author, M. Belaïche
E-mail address: mbelaiche@ hotmail.com

I. Introduction

In the last few years studies on self-assembled coordination polymers with specific network topologies have attracted much attention. Molecular-based ferro-or ferrimagnets, synthetic – metal conductors, non linear optical materials and electronic materials are some of their applications [1]. Many types of interesting network ferrimagnetic one dimensional (1D) system [2] exhibits original physical properties, which are characterised by a minimum of the magnetic susceptibility at intermediate temperature, which depends on the strength of exchange interactions and magnetic anisotropy and the divergence of the susceptibility at lower temperature [3]. The inorganic-organic hybrid strategy present a rich magnetic behavior including ferrimagnetic compounds [4,5], mono-spin chains can be ferrimagnetic with polymerised exchange interactions [6]. The trimetric intertwining double-chain compound is another solution to homometallic one dimensional ferrimagnets, where the noncompensation of two sublattice magnetisations is of topological origin [7,8]. Only few results have been reported on the magnetic properties of $Cu_4[CH_3C(OH)(PO_3)_2]_2(C_4H_4N_2)(H_2O)_4$ from susceptibility [9], it has been shown that this compound exhibit an antiferromagnetic transition at T= 4.7K . In the present paper, we report the applicability of one dimensional statistical model to describe the thermodynamic properties and the conditions for stabilizing a ferrimagnetic material.

II. Description of the structure

Thecompound $Cu_4[CH_3C(OH)(PO_3)_2]_2(C_4H_4N_2)(H_2O)_4$ was synthesized by Ping yin and al [9]. It's crystallize in triclinic structure with the space group P_{-1}, the lattice parameters are a = 6.248 ; b = 8.035 ; c 11.014 ; α = 86.035 ; β = 87.88 ; γ = 82.809. The structure may be described as the non linear stacking of the metal ions. There are two copper sites. The Cu [1] site has a square planar surrounding, while the other two occupy irregular polyhedra of five oxygen atoms. The compounds may be described as infinite ribbons of [Cu3] trimers stacked in such a way that Cu [1] is connected to four Cu [2] in two different fashions. Thus the nearest neighbour interactions between copper ions involve one bridging species (PO_4) in elementary trimers, and two bridging species between Cu [1] and Cu [2] of the adjacent trimers.

An analysis of these data can be achieved by considering infinite intertwining double chains of copper (II) ions connected through Cu [1] kinks, two different exchange interactions are expected to occur in the double; one within trimer units [J2], the other between adjacent trimers (J1), as sketched in figure 1.

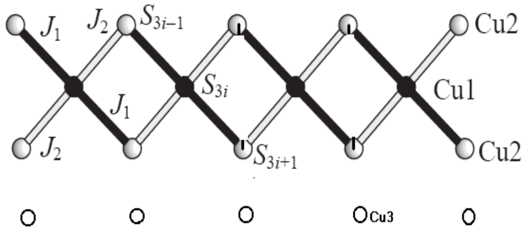

Figure 1: Illustration of the trimeric chain. Solid lines represent the inter-trimer coupling J_1 and solid double lines the intra-trimer coupling J_2.

III. Magnetic properties of $Cu_4[CH_3C(OH)(PO_3)_2]_2(C_4H_4N_2)(H_2O)_4$:

Temperature dependencies of the magnetic susceptibility of $Cu_4[CH_3C(OH)(PO_3)_2]_2(C_4H_4N_2)(H_2O)_4$ was measured in the temperature range 2 - 300 K, it is plotted in figure 2 as $\chi T = f(T)$ which is more better adopted than χ to analysis such a coupled system χT vs T exhibits three many features:

i) The high temperatures limit $(\chi T)_{HT}$ of χT is equal to the sum of the contributions of the isolated ions, hence

$$(\chi T)_{HT} = \frac{N\mu_B^2}{3K}\left(2g^2_{(Cu2)} + g^2_{(Cu1)} + g^2_{(Cu3)}\right)S(S+1)$$

$$(\chi T)_{HT} = \frac{N\mu_B^2}{4K}\left(2g^2_{(Cu2)} + g^2_{(Cu1)} + g^2_{(Cu3)}\right)$$

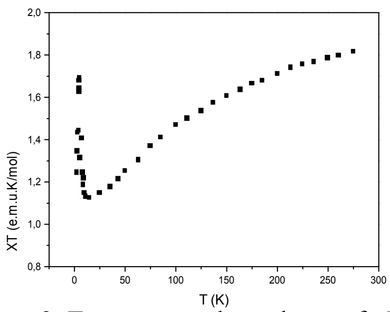

Figure 2: Temperature dependence of χT product.

This high temperature limit is close to 1.5 emu $K.mol^{-1}$ (for $g_{(Cu1)} = g_{(Cu2)} = g_{(Cu3)} = 2$). We remark that the regular decrease of χT, upon cooling down, from 1.76 emu (at 285K) to 1.15emu (at 20K); the asymptotic behavior of χT at higher temperature agrees with the expect Curie constant for uncoupled ions (χT = 1.75 emu).

ii) The minimum corresponds to a short-range order state where the copper spins nearest neighbor are antiparallel, when temperature decreases, the correlation length in the chain increases, leading to a ferrimagnetic short- range order.

iii) The sharp maximum at 4.7K suggesting a three dimensional ordering (3D) as a consequence of antiferromagnetic coupling between the chains.

The χ_m^{-1} Vs T curve exhibits a curvature near 30 K. Between 100 and 300 K, the χ_m^{-1} Vs T curve is fitted the Curie Weiss equation $\chi_m = \frac{C}{T-\theta}$. The Curie constant, C, 0,438 e.m.u.K/mol, and the Weiss constant, θ, of -2,39 K. These value shows that each Cu ion has spin ½ and these interact antiferromagnetically with each other. Between 8 and 25 K, the fitting gave C = 2.001 e.m.u/Cu/mol and θ = 5,764 K. The ratio between the Curie constant at the high and low temperature regions C_{HT}/C_{LT} is 4,56.

The exchange interaction between copper ions will be estimated by the following after the theoretical treatment.

IV. Theory

The magnetic behavior is characteristic of ferrimagnetic trimeric chains with a magnetic ordering in the temperature range explored. The Hamiltonian of trimeric chain is giving by:

$H = H_1 + H_2$ with

$H_1 = -J_1\Sigma\, S_{3i}\,(S_{3i-3} + S_{3i+2}) - J_2\Sigma S_{3i}\,(S_{3i-1} + S_{3i+1})$ and

$H_2 = -\mu_B\, H\, \Sigma\{g_a S_{3i} + g_b\,(S_{3i-1} + S_{3i+1})\}$

Where S is the S = ½ spin, g_i is the Landé's factor and μ_{Bi} is the Bohr magneton. J_1 and J_2 the intra and inter trimers coupling constants respectively, and H is the applied magnetic field.

Using the transfer matrix technique, it may be shown the magnetic susceptibility reduces to the expression [7]:

$\chi_{chain} = N\mu^2_B\, g^2/4kT\ (A/B)$

With:

$A = (2g_a + g_b)\, 2\cosh(j_+) - (4g_a g_b\, a^{-1}b^{-1} + g_a^2)\,(\cosh(j_+) + (\cosh(j_-) + 2)$
$\quad - 4\, g_b^2\,(\cosh((j_+) + 2\cosh(j_+)\, a^{-1}b^{-1} - a^{-2}b^{-2} - (\cosh(j_-) - 1)$

$B = (\cosh(j_+) + \cosh(j_-) + 2)\,(\cosh(j-) + 1)$

Where: $J_\pm = (J_1 \pm j_2)/2KT$; $a = \exp(j_1/2KT)$; $b = \exp(J_2/2KT)$

Therefore, in the range 5 - 250 K, we have neglected any interunit coupling and supposing the two trimeric of adjacent chains [Cu (2) Cu (1) Cu [2]] and Cu [3] units were independent, we have taken the magnetic behavior as the sum of pure chain contribution and an isolated ion, it may be shown that the magnetic susceptibility reduces to the following expression:

$$\chi = \chi_{chain} + \chi_{Cu(3)}\,(unit)$$

The monomeric copper susceptibility is given by the well- known Curie low for S = ½ systems:

$\chi_{Cu(3)}(unit) = N\mu^2_B\, g_c^2/4kT$

The fit of the high temperature susceptibility data with the sum of two molecular susceptibility contributions provides the following parameters:

J_1 = -89.93 K ; J_2 = -2.68 K ; g_a = 1.81 ; g_b = 2.04 and g_c = 2.43

The fit between experimental and theoretical results, using these values, is shown in figure 3. Agreement between the two curves is surprisingly good. The two results prove we are dealing with strong intratrimer interaction and weak intertrimer interaction which play a major role at low temperature, effectively the absence of intertrimer interaction leads product χT tends towards 0.375 when approaching absolute zero, value corresponding to an uncompensated spin S = ½ per isolated trimeric unit.

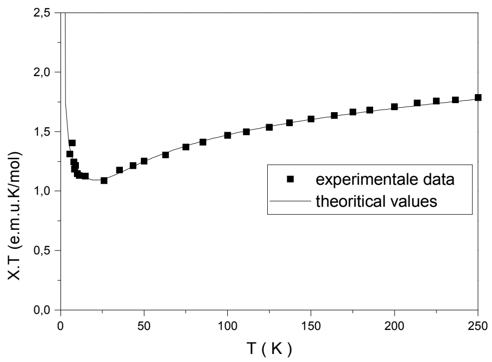

Figure 3: A plot of temperature dependence of the χT product vs. T; the solid line represents the calculated curve and solid squares represent the experimental data.

V. Summary

The statistical Ising model have been applied to the quasi one dimensional ferromagnetic chain system $Cu_4[CH_3C(OH)(PO_3)_2]_2(C_4H_4N_2)(H_2O)_4$The effect of intra and inter trimer interaction are calculated. In spite of that we are dealing with poor J_2 interactions, they play a crucial role at very low temperatures, leading to the ferrimagnetic behavior.

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