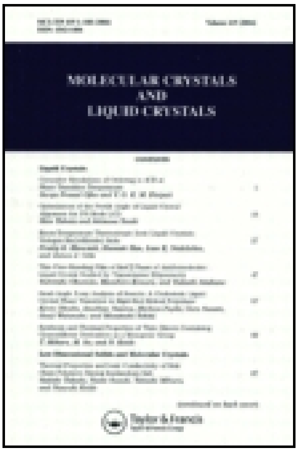

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Magnetism of Ferrimagnetic Polymer Chains

C. Vitoriano [a] , F. B. De Brito [a] , E. P. Raposo [a] & M. D. Coutinho-Filho [a]

[a] Laboratório de Física Teórica e Computacional, Departamento de Física, Universidade Federal de Pernambuco, Recife, PE, 50670-901, Brazil

Version of record first published: 29 Oct 2010

To cite this article: C. Vitoriano, F. B. De Brito, E. P. Raposo & M. D. Coutinho-Filho (2002): Magnetism of Ferrimagnetic Polymer Chains, Molecular Crystals and Liquid Crystals, 374:1, 185-190

To link to this article: http://dx.doi.org/10.1080/10587250210446

Mol. Cryst. Liq. Cryst., Vol. 374, pp. 185-190

1058-725X/02 $12.00 + .00

Magnetism of Ferrimagnetic Polymer Chains

C. VITORIANO, F. B. DE BRITO, E. P. RAPOSO
and M. D. COUTINHO-FILHO

*Laboratório de Física Teórica e Computacional,
Departamento de Física, Universidade Federal de Pernambuco,
50670-901, Recife, PE, Brazil*

Abstract We report new analytical results on AB_2 ferrimagnetic polymer chains, with experimental motivation in organic and inorganic materials. In particular, we exactly solve the Ising model on this structure and study the Heisenberg version using the spin-wave and mean-field methods in an applied magnetic field.

Keywords Magnetic Polymers; Heisenberg Model; Ferrimagnetism

1. INTRODUCTION

In previous works [1, 2], we have shown that the special AB_2 and AB_1B_2 (henceforth referred to as AB_2) chains shown in Figure 1, with experimental motivation in organic and inorganic polymeric materials [3], exhibit ferrimagnetic ground state ordering. In particular, by starting with a Hubbard Hamiltonian on the AB_2 structure, we have found [1] that Lieb's theorem [4] holds at the ground state for any value of the repulsive Coulombian coupling: the unit-cell average spin reads: $|N_B - N_A|\hbar/2 = \hbar/2$, where N_A (N_B) is the number of A (B) sites in the unit cell. Moreover, for half filling and strong-coupling limit, a mapping [2] onto the quantum AB_2 Heisenberg model and its associated quantum non-linear σ model, with extra Wess-Zumino terms due to the AB_2 topology, was found to present low-temperature (T) critical properties similar to those of the quantum AB ferromagnetic Heisenberg model, in agreement

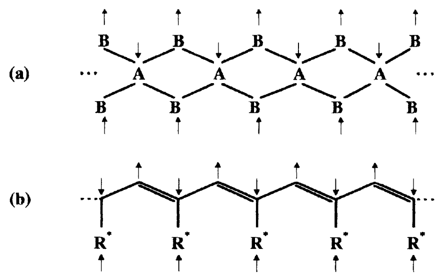

FIGURE 1 Bipartite AB_2 chain and ferrimagnetic spin configurations [1, 2]: (a) In inorganic compounds, A (B) is a metal (ligand); (b) substituted polyacetilene with lateral radical R^*.

with the data for the organic ferromagnetic chain, p-NPNN [5].

In this paper we will consider the Heisenberg and Ising models on the symmetric AB_2 chain of N sites shown in Figure 1(a):

$$\mathcal{H} = J/\hbar^2 \sum_{\langle i\alpha, j\beta\rangle} [S^z_{i\alpha} S^z_{j\beta} + \Delta(S^x_{i\alpha} S^x_{j\beta} + S^y_{i\alpha} S^y_{j\beta})] - g\mu_B H/\hbar \sum_{i\alpha} S^z_{i\alpha}, \quad (1)$$

where H is a magnetic field along the z axis, μ_B is the Böhr magneton, g is the gyromagnetic factor, Δ is the anisotropy parameter, and $J > 0$ is the antiferromagnetic exchange coupling between nearest-neighbour $A - B$ sites, indicated by $\langle i\alpha, j\beta\rangle$ ($i, j = 1, 2, \ldots, 2N/3$ and an additional label $\alpha, \beta = B_1, B_2$ for even numbers).

2. ISING MODEL ON AB_2 CHAINS

For the highly anisotropic Ising case, $\Delta = 0$ in Eq. (1). By summing over all sites B_1, B_2 the exact partition function can be written as $\mathcal{Z} = (2f)^{N/3}\mathcal{Z}_0(N/3)$, where f is a function of T and H, and $\mathcal{Z}_0$ is the partition function of the Ising model on a linear AB chain of $N/3$ sites with effective coupling constant and applied field given by:

$$\beta J^* = -2\ln\left\{\frac{\cosh[\beta(g\mu_B H - J)/2]\cosh[\beta(g\mu_B H + J)/2]}{\cosh^2(\beta g\mu_B H/2)}\right\}, \quad (2)$$

$$\beta g\mu_B H^* = \beta g\mu_B H + 2\ln\left\{\frac{\cosh[\beta(g\mu_B H - J)/2]}{\cosh[\beta(g\mu_B H + J)/2]}\right\}, \quad (3)$$

where $\beta = 1/k_B T$. The exact magnetization is calculated using $M = -(\partial F/\partial H)_T$, with the free energy per site $F = -(1/N\beta)\ln \mathcal{Z}$. At $T = 0$ the average spin per unit cell is $\hbar/2$ up to a critical magnetic field $H_c^* = 2J/g\mu_B$, above which it suffers a discontinuity and saturates at $3\hbar/2$.

At $H = 0$ the susceptibility is found from $\chi = (\partial M/\partial H)_{H=0}$:

$$\chi = \frac{\beta(g\mu_B)^2[4\text{sech}^2\beta J/2 + (1 - 2\tanh\beta J/2)^2(1 + \cosh^2\beta J/2)]}{12(1 + \text{sech}^2\beta J/2)}. \tag{4}$$

For $\beta J \gg 1$ the asymptotic behavior $\chi \simeq 3(g\mu_B/4)^2\beta e^{\beta J}$ should be compared with that of the AB ferromagnetic Ising chain: $\chi = (g\mu_B)^2\beta e^{\beta J/2}/4$ [6]. Comparison of other thermodynamical quantities, such as the specific heat and entropy, shows that the low-T properties of the AB_2 ferrimagnetic Ising chain are similar to those of the AB ferromagnetic Ising chain, with $J \to -2J$ and modified amplitudes. This evidences that the $T = 0$ quantum phase transitions occurring in both systems belong to the same universality class.

3. HEISENBERG MODEL ON AB_2 CHAINS

Spin Waves

In this subsection we use the method of spin waves to study the quantum Heisenberg model on AB_2 chains, $\Delta = 1$ in Eq. (1). We shall limit ourselves to very low temperatures where the thermodynamics is dominated by effects due to non-interacting spin waves. We introduce the boson creation and annihilation operators, $a_{j\alpha}^+$ and $a_{j\alpha}$, through the Holstein-Primakoff transformation and define the Fourier transform: $a_{j\alpha} \equiv \sqrt{(N/3)}\sum_k e^{i(-1)^{j+1}kj}\alpha_k$, where $\alpha_k = \{A_k, B_{1k}, B_{2k}\}$ are subjected to the boson commutation rules. Here, k varies over $N/3$ wave vectors in the first Brillouin zone. Using this procedure in Eq. (1), we obtain a non-diagonal Hamiltonian form:

$$\begin{aligned}\mathcal{H} = E_{ord} - g\mu_B H \sum_k [A_k^+ A_k - B_{1k}^+ B_{1k} - B_{2k}^+ B_{2k}] \\ +(1/2)\sum_k [J(k)(A_k^+ B_{1k}^+ + A_k B_{1k} + A_k^+ B_{2k}^+ + A_k B_{2k})] \\ +(J/2)\sum_k [4A_k^+ A_k + 2B_{1k}^+ B_{1k} + 2B_{2k}^+ B_{2k}]\ ,\end{aligned} \tag{5}$$

where $J(k) = 2J\cos(ka)$, $2a$ is the unit-cell length, and E_{ord} is the

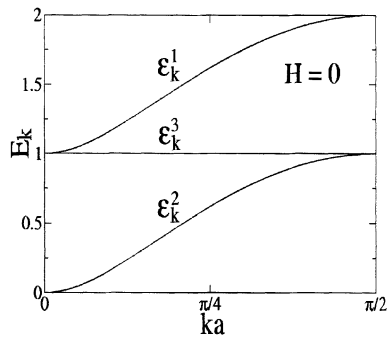

FIGURE 2 Spin wave dispersion relations in units of J: ϵ_k^3 is a non-dispersive optical mode, $\epsilon_k^{1,2}$ are dispersive optical and acoustical modes, respectively. $\epsilon_k^2 = 2J(ka)^2,\ ka \ll 1,\ H = 0$.

energy of a fully ordered ferrimagnetic state with spins at sites A (B_1, B_2) pointing down (up). Hamiltonian (5) can be diagonalized using the Bogoliubov-Tyablikov method: $\mathcal{H} = E_0 + \sum_{m=1}^{3}\sum_k \epsilon_k^m \xi_{mk}^+ \xi_{mk}$, with the new set of boson operators, ξ_{mk}, ξ_{mk}^+, $m = 1, 2, 3$, such that

$$E_0 = E_{ord} - (J/2)\sum_k [3 - \sqrt{1 + 8\sin^2(ka)}] \ , \tag{6}$$

$$\epsilon_k^{1,2} = (J/2)[\pm 1 + \sqrt{1 + 8\sin^2(ka)}] \mp g\mu_B H \ , \tag{7}$$

$$\epsilon_k^3 = J + g\mu_B H \ , \tag{8}$$

as shown in Figure 2. In particular, the ferrimagnetic structure at $T = 0$ is unstable for $H > H_c = J/g\mu_B$. Moreover, it is also affected by quantum fluctuations. We observe that Eqs. (7) and (8) are exact results and correct previous ones [2] derived using only half of the available Hilbert states. The zero-T average site spins read:

$$\frac{\langle S_A^z \rangle}{\hbar} = -\frac{1}{2} + \frac{1}{N/3}\sum_k \sinh^2 \delta_k, \frac{\langle S_{B_1,B_2}^z \rangle}{\hbar} = \frac{1}{2} - \frac{1}{2N/3}\sum_k \sinh^2 \delta_k, \tag{9}$$

in which $(3/N)\sum_k \sinh^2 \delta_k \approx 0.2$. Notice that the unit-cell average spin remains $\hbar/2$, in agreement with Lieb's theorem.

The low-T specific heat per unit cell reads:

$$C/k_B \simeq [3\zeta(3/2)/(4\sqrt{2\pi})](k_B T/J)^{1/2} \ , \tag{10}$$

where ζ is the Riemann function. Eq. (10) also applies to the quantum AB Heisenberg ferromagnetic chain [5]. The factor 2 of difference between their low-k dispersion relations of the acoustical mode is compensated by the distinction between the Brillouin zones.

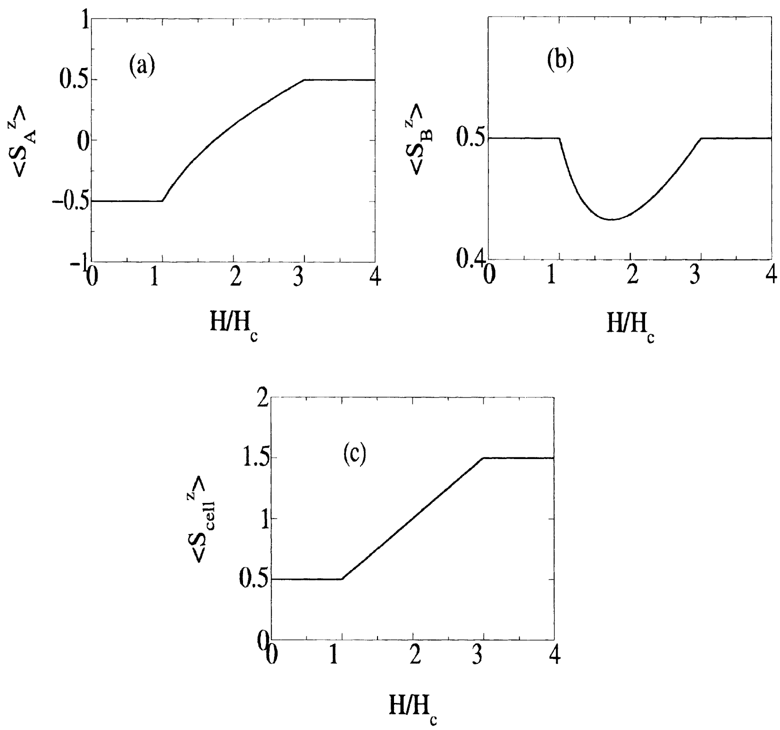

FIGURE 3 H-dependence of the average site [(a) and (b)] and unit-cell spins (c) (in units of $\hbar$).

Transition in an Applied Field: Mean-Field Approach

In this subsection we describe the field-induced ferrimagnetic-paramagnetic transition at $T = 0$ using the mean-field approach. Due to the lack of space, we present the results for the field dependence of the average site [Figures 3(a) and 3(b)] and unit-cell [Figure 3(c)] spins. As seen from the figures, for $0 \leq H < H_c$ the field alignes the spins in the z direction, with zero average values of the transversal components, while the ferrimagnetic structure is sustained. For $H_c \leq H < 3H_c$ the average spin at sites A continuously rotates seeking a full alignement with the field. This effect is accompanied by a rotation of the spins at sites B, such that for each value of H the transversal components at sites A and B are cancelled. To achieve this cancellation the spins at sites B rotates in the opposite direction up to a maximum angle $\theta = 30^o$ and then rotates back. The final result is that the unit-cell average spin increases linearly with H for $H_c \leq H < 3H_c$. For $H \geq 3H_c$ the system saturates. These features are corroborated by the result of the Gibbs free energy, which is quadratic in H for $H_c \leq H < 3H_c$ due to the contribution of the transversal components, and linear otherwise (z components only).

4. CONCLUSIONS

In conclusion, we have shown that the low-T properties of the AB_2 ferrimagnetic Ising chain are similar to those of the AB ferromagnetic Ising chain. For the AB_2 Heisenberg case, at $T = 0$ ferrimagnetism is sustained under quantum fluctuations, although the average site spins are reduced. Also, for $H > H_c$ and before saturation, the spins continuously rotate, such that their transversal components cancel and the unit-cell average spin increases linearly with H.

Work supported by CNPq, CAPES, FINEP, and FACEPE.

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