

THE DYNAMIC SUSCEPTIBILITY OF A QUASI-ONE-DIMENSIONAL Mn PORPHYRIN-BASED HYBRID MAGNET: COLE-COLE ANALYSIS

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The dynamic response of a quasi-one-dimensional hybrid organic-inorganic manganese porphyrin-based magnet, $[\text{MnTPP}][\text{TCNE}] \cdot x(o\text{-DCB})$ (TPP = meso-tetraphenylporphyrinato, TCNE = tetracyano-ethylene, and *o*-DCB = ortho-dichlorobenzene), is studied using Cole-Cole analysis. The frequency dependence of the linear susceptibility suggests cluster glass-like behavior (at the limit of superparamagnetism). It is proposed that the unusual magnetic properties of these compounds reflect one-dimensional ferrimagnetic clusters interacting weakly through dipole-dipole interactions to form three-dimensional domains.

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1. Introduction

The design of molecule-based magnets has been an area of increasing interest and remarkable results [1]. In many of the approaches used to obtain molecule-based magnets a common trend has been to use chains or layers of radicals (spins) with strong magnetic coupling (even antiferromagnetic) as first steps in building three-dimensional (3D) magnets. The challenge is, then, to order the resulting spins ferromagnetically by controlling the structural packing of the low-dimensional constituents. In this paper we discuss the nature of the low-temperature 3D magnetic ordering of a quasi-one-dimensional (1D) ferrimagnetic system.

Alternating metalloporphyrin-acceptor systems provide a laboratory for study of quasi-one-dimensional magnetic phenomena, because it offers a wide range of controlling factors, including the choice of cyanocarbon bridges connecting the adjacent porphyrins, substituent groups at the periphery of the porphyrin, and various solvents. These choices result in a family of related crystal structures and can also introduce different degrees of disorder.

Recent studies have uncovered a wide range of magnetic phenomena in these materials, including spin- and lattice-dimensionality crossovers [2,3,4] and cluster-glass formation [5,6]. Progress has been made in understanding the role of the different building blocks forming these materials [7]. We have shown that the different cyanocarbon bridges used as acceptors, (TCNE = tetracyanoethylene, and HCBBD = hexacyanobutadiene) led to similar antiferromagnetic coupling within the chains, causing high temperature one-dimensional ferrimagnetic behavior. The organic constituents attached to the porphyrin play an essential role in determining the 3D ordering by keeping the chains further apart and/or providing exchange pathways [7]. In the case of $[\text{MnOEP}][\text{HCBBD}]$ (where OEP = octaethylporphyrinato), evidence has been found for antiferromagnetic coupling between chains [2,3], while in the TPP (*meso*-tetraphenylporphyrinato) based compounds, $[\text{MnTPP}][\text{TCNE}] \cdot (\text{solvent})$, weak ferromagnetic behavior has been observed [7]. Finally, no glassy behavior has been noticed in the system without solvent, $[\text{MnOEP}][\text{HCBBD}]$ [2,3], while the presence of different solvents (like PhMe, toluene, *o*-Xy, *ortho*-xylene, and *o*-DCB, *ortho*-dichlorobenzene) in $[\text{MnTPP}][\text{TCNE}]$ (solvent) has

been correlated with different degrees of disorder and cluster glass-like behavior [5, 6].

In this paper we discuss in more detail the glassy behavior of the [MnTPP][TCNE][solvent] system, extending the results published earlier [5, 6]. We focus on the transition from the one-dimensional ferrimagnetism to the three-dimensional magnetic state presenting both weak ferromagnetic and cluster glass-like characteristics. The term cluster glass is used here not in the traditional sense of system with high concentration of magnetic ions, intermediate between a spin glass and a ferromagnet [8], but as an intermediate between a spin glass and a superparamagnet.

2. Experimental

The manganese-porphyrin systems are electron transfer salts consisting of alternating chains, ...D⁺A⁻D⁺A⁻..., of electron donors (D = [MnOEP], [MnTPP], etc.) bound by cyanocarbon acceptors (A = [TCNE] or [HCBD]). The adjacent spins along these chain alternate, S = 2 on the donor and S = 1/2 on the acceptor. The first member of the manganeseporphyrin family to be synthesized and studied was [MnTPPP][TCNE] × z(PhMe), z ≈ 2 [9]. [MnTPP][TCNE] × x(o-Xy) and [MnTPP][TCNE] × y(o-DCB) are related compounds, obtained using different solvents [10]. The maximum amount of solvent incorporated into the structure is 3, as obtained from an X-ray structural determination. The actual amount of solvent, as determined by thermogravimetric analysis, is generally less than the maximum values and x ≈ 1 for the samples reported here.

The dc magnetic data were recorded using a MPMS-5 Quantum Design SQUID magnetometer and the dc susceptibility was calculated as the ratio of the magnetization, M, and field, H, $\chi_{dc} = M/H$ (assuming a linear response of M on H). The magnetic ac susceptibility was measured with a Lake Shore 7225 ac susceptometer - dc magneto-meter at various driving frequencies and amplitudes. A lock-in amplifier allowed phase sensitive detection and both in-phase (χ') and out-of-phase (χ'') susceptibilities were measured. Powder samples were handled and weighed in an argon environment to avoid exposure to air, and sealed in quartz sample holders, after being evacuated to 10⁻⁵ mbar. The diamagnetism of the sample holders was measured in situ. The susceptibility results have been corrected for both core and sample holder diamagnetism.

3. Results

The [MnTPP][TCNE](solvent) compounds have been synthesized using a variety of solvents (PhMe, o-Xy, o-DCB, etc.) [9,10]. Here we concentrate our attention on the o-DCB system. The compound shows one-dimensional ferrimagnetic behavior at high temperatures, as evidenced by the good fit to Seiden's model [11] for alternating classical and quantum spin chains. Seiden's expression for the product of the magnetic susceptibility and temperature, χT , as a function of T, allowed the fit of the experimental data, the fitting parameters being the intrachain exchange coupling J_{intra} and the Landé g-factor. While the g-factor affects the high temperature behavior ($T > 300$ K), the exchange constant influences the curvature of the data at lower T [7]. The intrachain exchange obtained was $J/k_B = -140$ K, for [MnTPP][TCNE] × x(o-DCB). At temperatures below 50 K the χT product was found to deviate above the prediction for 1D behavior, indicating ferromagnetic correlations between the chains [7]. Based on the absence of obvious interchain exchange pathways in these systems we proposed [7] that the interchain interactions are dipolar in origin. Moreover, preliminary calculations of the critical temperature, T_c obtained using estimations for the strength of the dipolar interaction, gave values of T_c in qualitatively good agreement with the experimental values [7]. Also, the low temperature limit of the in-phase ac susceptibility data at $T < 4$ K was found to be a nonzero constant, suggesting spin canting [4].

The ac susceptibility measurement allowed the determination of the critical temperature ($T_c \approx 8$ K), based on the value of the low-frequency peak temperature of the in-phase component of the susceptibility. The frequency dependence of the low temperature ac susceptibility data of

[MnTPP][TCNE]·*x*(*o*-DCB) is shown in Figs. 1 and 2. The data were taken on warming such that at each temperature an ac field of amplitude 1 Oe was applied in a sequence of increasing frequencies.

Striking in these figures is the frequency dependence of the peak temperature in both the in-phase and the out-of-phase susceptibility, indicating slow-relaxation times and suggesting the presence of disorder. The values of the relative variation of the peak temperature per decade of frequency, $(\Delta T_p/T_p)/\Delta(\log f) \approx 0.19$ places this compound somewhere between canonical spin glasses and superparamagnets (which have typical values [8] of 0.005-0.02 and 0.28, respectively), suggesting a picture of weakly interacting clusters. We note that the value of $(\Delta T_p/T_p)/\Delta(\log f)$ depends on the sample preparation conditions, presumably due to the change in solvent content, *x*.

The frequency dependence of the ac susceptibility indicates long relaxation times. Detailed analysis of these relaxation times and their temperature dependence can be made using the phenomenological description proposed by Cole and Cole [12, 13], which involves a modeling of the susceptibility (χ_{CC}) dynamic at a given temperature onto a distribution of relaxation times that is symmetric on the logarithmic time scale.

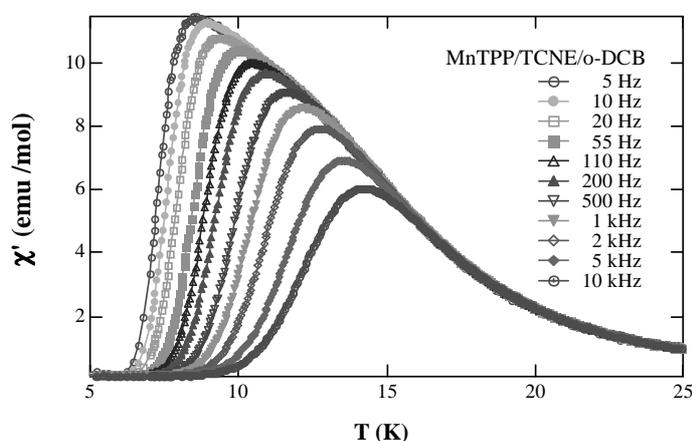


Fig. 1. Temperature dependence of real (in-phase) magnetic susceptibility for [MnTPP][TCNE]·*x*(*o*-DCB), measured in an ac field with an amplitude of 1 Oe (zero dc field) at selected frequencies between 10 and 10000 Hz.

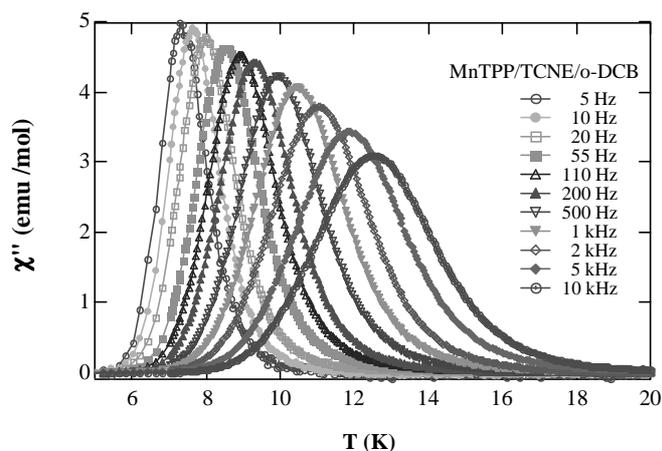


Fig. 2. Temperature dependence of imaginary (out-of-phase) magnetic susceptibility of [MnTPP][TCNE]·*x*(*o*-DCB), measured in an ac field with an amplitude of 1 Oe (zero dc field) at selected frequencies between 10 and 10000 Hz.

The Cole-Cole formalism introduces a parameter $0 < \alpha < 1$, which determines the width of the distribution of relaxation times, $g(\ln \tau)$, around the median relaxation time, τ_c .

$$\chi_{CC} = \chi(\infty) + \frac{\chi(0) - \chi(\infty)}{1 - (i\omega\tau_c)^{1-\alpha}} \quad (1)$$

$$g(\ln \tau) = \frac{1}{2\pi} \frac{\sin(\alpha\pi)}{\cosh[(1-\alpha) \ln(\tau / \tau_c)] - \cos(\alpha\pi)} \quad (2)$$

Based on the Cole-Cole equation one can determine an expression for χ'' as a function of χ' , which allows the fit of the experimental data [13]. Such fits (with α , τ_c , and $\chi(\infty)$ as parameters) are displayed along with the data in the Argand plot (Fig. 3). The phenomenological Cole-Cole model leads to a $\chi''(\chi')$ dependence that follows circular arcs of size $(1-\alpha)\pi$ cutting the χ' axis at $\chi(0)$ and $\chi(\infty)$, with a maximum at $\omega\tau_c = 1$.

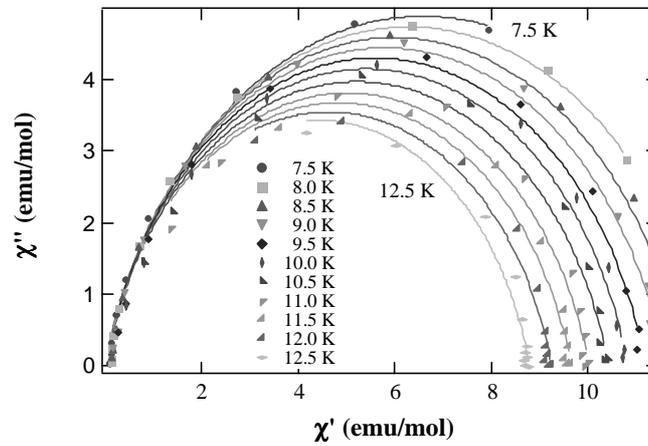


Fig. 3. Argand plot of the magnetic susceptibility data (shown in Figs. 1 and 2) of $[\text{MnTPP}][\text{TCNE}] \cdot x(o\text{-DCB})$. The experimental points represent $\chi''(\chi')$ for $7.5 \leq T \leq 12.5$ K. The lines represent the fits according to the Cole-Cole analysis.

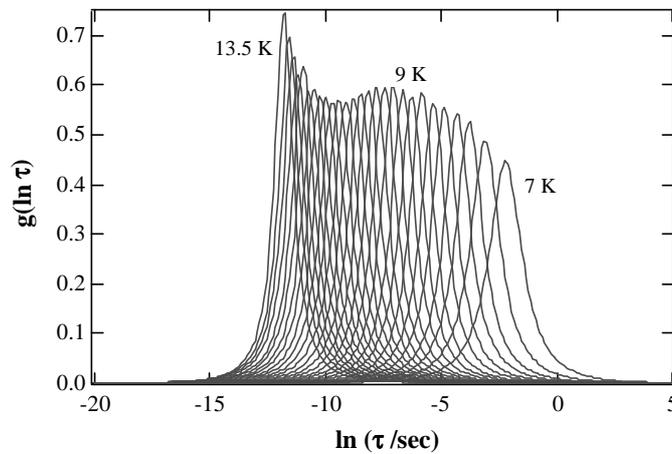


Fig. 4. Distribution of relaxation times for $[\text{MnTPP}][\text{TCNE}] \cdot x(o\text{-DCB})$ at temperatures between 7 and 13.5 K, with intervals of 0.2 K, obtained by Cole-Cole analysis of the ac susceptibility data shown in Figs. 1 and 2.

Noteworthy in Fig. 3 is the shift of the data points from a nearly adiabatic susceptibility at 12.5 K to a nearly isothermal susceptibility at 7.5 K.

The distribution of relaxation times obtained with the parameters α , τ_c , provided by the Cole-Cole analysis is displayed in Fig. 4. As the temperature is decreased from 13.5 to 7 K, the median relaxation time increases about three orders of magnitude, which indicates the growth of the correlation length of the system of spins, as expected for a system near a phase transition [8]. The width of the relaxation time distribution, however, has an unusual evolution with temperature. On cooling a canonical spin glass toward the freezing temperature and below, the parameter α is expected [8] to increase monotonically, reflecting the fact that the distribution of cluster sizes broadens. For [MnTPP][TCNE] \cdot $x(o$ -DCB), however, although overall α increases with decreasing temperature, there is a range of temperatures around 9 K at which the expected trend is reversed. While the overall widening of the distribution of relaxation times at low T was expected, the unusual feature around 9 K has no immediate explanation.

Given the $\tau_c(T)$ obtained through Cole-Cole analysis, one can determine the critical dynamics by fitting to the Arrhenius, Vogel-Fulcher or generalized Vogel-Fulcher laws, listed respectively below [8]:

$$\tau(T) = \tau_o \exp[E/k_B T] \quad (3)$$

$$\tau(T) = \tau_o \exp[E/k_B(T - T_o)] \quad (4)$$

$$\tau(T) = \tau_o \exp[E/k_B(T - T_o)^{z_V}] \quad (5)$$

The Arrhenius law is typical for superparamagnets, for which the relaxation time has an activated dependence on temperature. The energy barrier E corresponds to the flipping of all the spins within a cluster, and is due to the magnetic anisotropy of the magnetic ions. The Vogel-Fulcher law comes from real glasses, where it describes the viscosity of supercooled liquids. With three parameters the fitting will always be better, but the question that remains regards the physical meaning of the new parameter, T_o . The generalized Vogel-Fulcher law introduces yet another parameter, the critical exponent, and, in the limit of $T_o \rightarrow 0$ it becomes relevant for the systems with a 0 K phase transition.

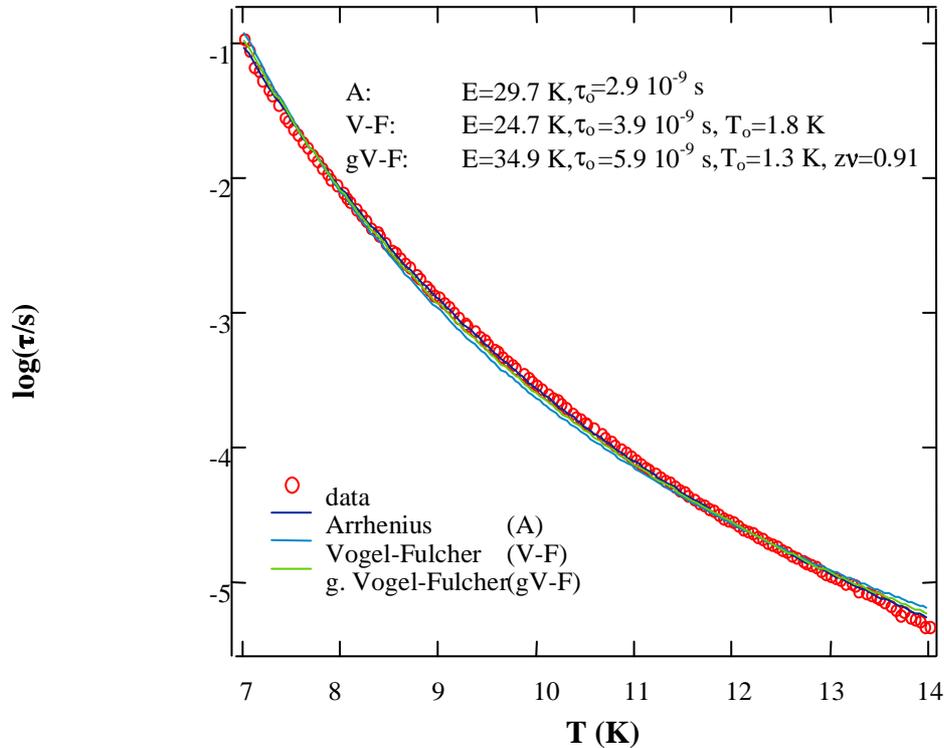


Fig. 5. Temperature dependence of the mean relaxation times of [MnTPP][TCNE] \cdot $x(o$ -DCB) obtained by Cole-Cole analysis of the ac susceptibility data shown in Figs. 1 and 2. The solid lines represent fits to Arrhenius, Vogel-Fulcher and generalized Vogel-Fulcher laws.

The best fit was obtained with the Arrhenius law, followed by the Vogel-Fulcher and the generalized Vogel-Fulcher laws, despite the larger number of fitting parameters of the last two equations. Moreover, the relatively close values for the fitting parameters E and τ_0 in all three cases, the small value of T_0 and the almost unitary value of the exponent $z\nu$, suggest that the Arrhenius law describes best the dynamics of the system. Therefore, the results of the Cole-Cole analysis and the fitting of the mean relaxation time versus T indicate a magnetic behavior similar to superparamagnets but with suggestion of presence of weakly interacting clusters. The conclusion drawn from the relative variation of the peak temperature per decade of frequency is consistent with the results of the fit.

Although the Cole-Cole analysis has its own limitations, being only a phenomenological model without very solid microscopic grounds, the picture of weakly interacting clusters obtained for the dynamic susceptibility of $[\text{MnTPP}][\text{TCNE}] \cdot x(o\text{-DCB})$ is convincing, as it is consistent with other results [4, 5, 6, 7]. For instance, the cluster glass-like behavior, suggested by the strong frequency dependence of the linear ac susceptibility data, is consistent with the presence of irreversibilities in the field-cooled/zero-field-cooled magnetization data [6]. The nonlinear ac susceptibility data (second and third harmonics) display [5], at the transition, along with the peak in the third harmonic, a peak in the second harmonic, indicating the presence of a spontaneous moment [14].

4. Discussion

In summary, based on the analysis of the dynamic susceptibility data, we report, for a manganese porphyrin – based compound, a transition from a high-temperature one-dimensional ferrimagnetic state [4, 7] to a three-dimensional state with cluster glass-like behavior (intermediate between a spin glass and a superparamagnet) [5, 6]. As the low temperature phase also has weak ferromagnetic characteristics [5], the nature of the ground state is unusual.

Given the strong intra-chain antiferromagnetic interactions (~ 100 K) [7], upon cooling these systems from room temperature, one-dimensional ferrimagnetic correlations build up one-dimensional clusters. Upon cooling further the single ion anisotropy (~ 1 K) [7] on the Mn sites starts to play a role leading to preferred directions of the spins. Frustration may be caused by the weak interchain interaction (< 0.01 K) [7] because of the long range and more complex dependence on spin orientation of the dipole-dipole interaction. The presence of the weak anisotropy and of the interchain dipole-dipole interaction is likely to lead to canting and the formation of three-dimensional domains (consisting of quasi-aligned one-dimensional clusters) that present a spontaneous magnetic moment (Fig. 6).

A viable explanation of the glassy behavior in these compounds requires the identification of the sources of disorder and frustration. We proposed that the sources of disorder are, most likely, solvent vacancies and/or solvent misorientations, and the different bonding patterns of the bridging TCNE molecule (which in turn may be related to the solvent vacancy) [5]. These different orientations of the TCNE molecule have been detected in a similar compound, where it was found that about 15% of the TCNE molecules are rotated by 175° about the Mn-Mn axis. The structural disorder is likely to cause random intra- and interchain interaction strengths, possibly even competing interactions, which constitute one of the necessary conditions for glassiness.

A more careful analysis of the values obtained for the fitting parameters would require an explanation of the large value of the activation energy (the time constant being reasonable for typical microscopic relaxation times), which, expressed in units of temperature was found to be $E = 29.7$ K. In the case of superparamagnets the energy required to flip the spins is needed to overcome the anisotropy of the magnetic cluster. For weakly interacting clusters in $[\text{MnTPP}][\text{TCNE}] \cdot x(o\text{-DCB})$ the flipping of the spin clusters requires less energy, in the case of clusters with strong interactions. Therefore, the large value of E remains an open question at this moment.

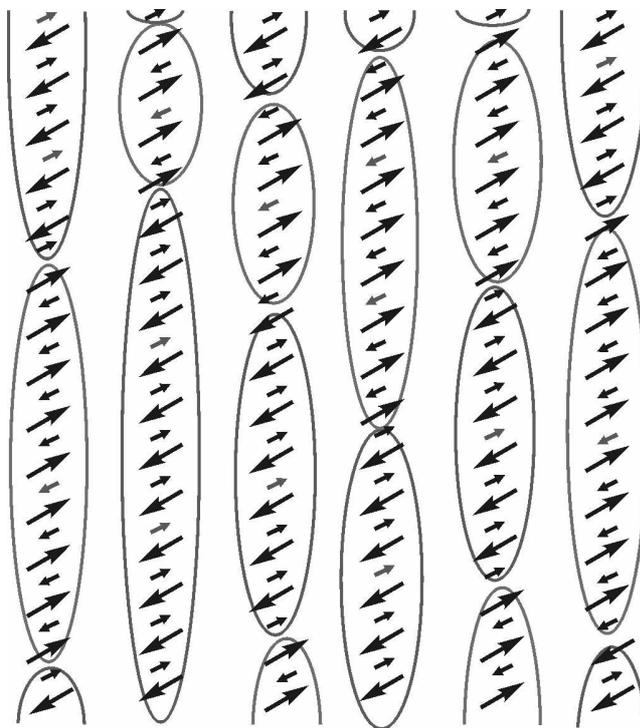


Fig. 6. Schematic drawing of weakly interacting one-dimensional ferrimagnetic clusters. The disorder causing finite sizes of the clusters is due to the different possible configurations of the TCNE molecule s well as to the solvent vacancies and/or misorientations. The interactions between chains are three - dimensional but the drawing is two - dimensional, for clarity.

5. Conclusions

The nature of the low temperature ground state in the $[\text{MnTPP}][\text{TCNE}] \cdot x(o\text{-DCB})$ compound is interesting due to the mixture of weak ferromagnetic and cluster glass-like properties. These properties are consistent with the picture of one-dimensional clusters with strong intra-cluster exchange and weak inter-cluster interaction. The structural disorder, which may be induced by the solvents and enhanced by the possibility of the bridging TCNE molecule to rotate, may limit the length of the regions of correlated spins along the chain, leading to the formation of clusters. The interchain interaction, given its dependence on the orientations of the spins, may cant the spins and lead to weak ferromagnetism. Moreover, if disorder is present, the interchain interaction could cause frustration and the glassy behavior.

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