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Field-Induced Disorder Point in Non-Collinear Ising Spin Chains

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We perform a theoretical study of a non-collinear Ising ferrimagnetic spin chain inspired by the compound Co(hfac)$_2$NITPhOME. The basic building block of its structure contains one Cobalt ion and one organic radical each with a spin 1/2. The exchange interaction is strongly anisotropic and the corresponding axes of anisotropy have a period three helical structure. We introduce and solve a model Hamiltonian for this spin chain. We show that the present compound is very close to a so-called disorder point at which there is a massive ground state degeneracy. We predict the equilibrium magnetization process and discuss the impact of the degeneracy on the dynamical properties by using arguments based on the Glauber dynamics.

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I. INTRODUCTION

Recent advances in coordination chemistry have led to the synthesis of low-dimensional magnets with unconventional magnetic properties. Some of them are spin chains that exhibit complex magnetization behavior under an applied external field. The Ising ferrimagnetic spin chain Co(hfac)$_2$NITPhOME (CoPhOME in the following) is the first quasi-1D compound in which slow dynamics of the magnetization has been directly observed. For this system it has been shown that the very long time scale required for establishment of equilibrium preclude the experimental determination of the static magnetization curve at low temperature.

This very special magnet has two kinds of spins $S=1/2$: half of them are Cobalt ions Co$^{2+}$ and the other half are organic radicals NITPhOME. They strictly alternate along the chain and have highly anisotropic exchange interactions best described by an Ising-like Hamiltonian. The chain itself describes a spiral in real space so that the local anisotropy axis have a complex pattern: see Fig. (1). The primitive cell contains three Cobalt ions alternating with three radicals. Each Cobalt is related to the other Cobalts by a 120° rotation around the c-axis and has a local anisotropy axis which makes an angle $\theta$ of approximately 50° with c. The effective $S=1/2$ spin of the Cobalt and the $S=1/2$ spin of the radical have different $g$-values and thus the chain behave as a unidimensional ferrimagnet due to non-compensation of the magnetic moments. Only part of the magnetization curve is known because the exchange energy scale is very high in terms of accessible magnetic fields. Experiments show a metamagnetic jump at low fields, much less than the value expected for full saturation.

In this paper we investigate the equilibrium, static behavior of a model Hamiltonian for CoPhOME that we believe encompasses all the main physical characteristics of this magnet. We show that this model Hamiltonian can be tuned through a so-called disorder point as a function of the direction $\theta$ of the local axes and magnitude of an applied external uniform magnetic field. In the case of CoPhOME, the angle $\theta$ is not known precisely but our estimates show that it is very close to the critical value $\theta_c \approx 55°$ expected for the disorder point ($\cos \theta_c = 1/\sqrt{3}$, the magic angle of NMR).

In a 1D Ising system with nearest and next-to-nearest neighbor exchange it is known that under certain conditions, the spin correlation function can change from a monotonic exponential decay to a damped oscillating behavior, passing through zero when the temperature has a special value called the disorder point. We find that a similar phenomenon is driven by the geometrical arrangement of anisotropic magnetic centers even in the sole presence of nearest-neighbor interactions. The Hamiltonian for CoPhOME is complicated by the fact that the eigenvectors of the $g$-tensors do not coincide with the axis of the chain so that it is not obviously diagonal. We show that it is possible to choose the quantization axis of the spins so that all the eigenvalues can be computed exactly. All thermodynamic properties as well as spin correlations may then be obtained by a transfer-matrix computation. We are then able to

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Figure 1: The helical structure of the 1D magnet CoPhOMe. Each anisotropic center has a local axis of anisotropy $\hat{z}_i$. These axes are all tilted by a common angle $\theta$ with respect to the chain axis $\underline{c}$. The angle between the projections of $\hat{z}_i$ and $\hat{z}_{i+1}$ on the plane perpendicular to $\underline{c}$ is equal to $\frac{2\pi}{3}$.

show that, in a well defined range of orientation, the correlation function can switch from a monotonic to an oscillating behavior by application of a magnetic field. The zero correlation function condition occurs at a given temperature-dependent field $h_d(T)$ (disorder field). The monotonic behavior appears when the ground state is ferrimagnetic while the oscillating behavior is related to an antiferromagnetic arrangement of the spins.

In section II we give an analytical solution to the eigenvalue problem for a ring of $N$ spins; we will show that it is possible to have a non trivial plateau in the zero temperature magnetization curve at an arbitrary small field $h_c$.

In section III we study the thermodynamics of the infinite chain obtaining the geometrical disorder condition in zero field. In section IV we discuss the consequence of our findings on the dynamical properties. Finally section V contains our conclusions.

II. ANALYTICAL SOLUTION OF THE EIGENVALUE PROBLEM

In the spin chain compound CoPhOMe $[4, 6]$ the $i$th elementary unit cell for spins consists of a pair of spins one-half, with Hamiltonian:

$$H_{i}^{\text{intracell}} = J t_i^z s_i^z - \mu_B g_{\text{iso}} B \cdot t_i - \mu_B g_{\text{ani}} (B \cdot \hat{z}_i) s_i^z. \quad (1)$$

In this equation, the $t_i$ are spin-1/2 operators describing the isotropic centers NITPhOMe and the $s_i$ describe the Cobalt $S=1/2$ anisotropic ions. For the isotropic organic radicals we have $g_{\text{iso}} = 2$. The Ising-like coupling $[12]$ takes place along the local axis of anisotropy $\hat{z}_i$. The exchange coupling between the radical and the Cobalt is strongly antiferromagnetic $[5]$. The Cobalt ions are coupled to the external field only by the spin component along the axis of anisotropy : the $\hat{z}_i$ unit vector defines this direction. The restriction to a $t_i^z s_i^z$ Ising coupling, the form of the $g$ tensors and the fact that the anisotropic centers do not interact directly allow an analytical treatment of the problem, even when the local directions of anisotropy $\hat{z}_i$ are not collinear. Our calculation is performed for the particular geometry in which the magnetic centers are arranged in a helical structure with a threefold periodicity (see figures $[6, 7]$). In the helical structure of CoPhOMe, the elementary unit cell of the crystal consists of three cells of the type described by Equation (1), with three vectors $\hat{z}_1, \hat{z}_2, \hat{z}_3$. The angle of these vectors with the chain axis $\underline{c}$ is $\theta$ and the angle between their projections in the plane perpendicular to $\underline{c}$ is $2\pi/3$ (their vector sum is along $\underline{c}$).

Since the value of the angle $\theta$ is not known precisely from experiments, we will solve the problem for arbitrary values of $\theta$ and obtain constraints in the case of CoPhOMe. From the study of a monomeric complex of formula Co(hfac)$_2$(NITPhOMe)$_2$ where the Cobalt ion coordination is practically the same as in CoPhOMe, it is known that $\theta$ is close to 50°.

The intracell Hamiltonian Eq.(1) in zero field is trivially diagonal on the basis $|m_{\text{iso}}⟩ \otimes |m_{\text{ani}}⟩$ if we take the quantization axis to be the local axis of the anisotropic center. It is important to note that this axis is a function of the site and is not fixed over the whole system. The $t_i$ spin will interact also with the other nearest neighbor $s_{i+1}$ with the same Ising Hamiltonian:

$$H_{i,i+1}^{\text{intercell}} = J t_{i}^{z_{i+1}} s_{i+1}^{z_{i+1}}. \quad (2)$$
For the sake of clarity we have labelled in (3) the two $z$ axes with the index of their respective cell. If we want to express all the operators in the same frame, we can simply choose the crystal frame. Thus $z_{\text{crystal}}$ is now the chain axis and a perpendicular direction $x_{\text{crystal}}$ can be chosen along the projection of one of the $z_i$ vectors, say $z_1$. The simplest way to pass from the local frame to the crystal frame is to rotate the tensors:

$$J = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & J \end{pmatrix}, \quad g = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & g_{ani} \end{pmatrix},$$

as ordinary 3x3 matrices. If $R(\varphi, \theta, \psi)$ is the rotation matrix parameterized by Euler angles that transforms the cartesian components of a general vector from the crystal frame to the frame of the $i$th anisotropic center, the relative $J^i$ ($g^i$) tensor is transformed according to the relation $J \rightarrow R(\varphi, \theta, \psi = 0) \ J \ R^T(\varphi, \theta, \psi = 0)$ (a diagonal matrix in which the first two terms are equal is insensitive to the $\psi$ rotation). More explicitly, the transformation corresponds to a rotation of $\varphi$ about the axis of the helix and a rotation of $\theta$ about the new $y$ axis. In our particular geometry, three successive local $z$ axes are associated to the values $\varphi = 0, \frac{2\pi}{3}, \frac{4\pi}{3}$ (see figures 1,2), in such a way that the effective magnetic cell of the chain contains six spins. The Hamiltonian expressed in the crystal frame is then:

$$\mathcal{H} = \sum_{i=1}^{N/2} t_{i-1} \cdot J^i \cdot s_i + t_i \cdot J^i \cdot s_i - \mu_B \sum_{i=1}^{N/2} g_{ani} B \cdot t_i + B \cdot g^i \cdot s_i + \mu_B g_{ani} \sigma_i (B \cdot \hat{z}_i)$$

where the rotated tensors $J^i$ and $g^i$ are periodic with period three with respect to the site index $i$. We take periodic boundary conditions: site $\frac{3}{2} + 1$ is identified to site 1. The Landé factor of the isotropic centers is insensitive to the rotation.

### A. Local basis rotation

To diagonalize the generalized Ising-like Hamiltonian, we first use the local axis $\hat{z}_i$ as quantization axis for the Cobalt spin $s_i$. Hence we can replace the spin operator $s_i^z$ by its eigenvalue $\sigma_i/2$, $\sigma_i = \pm 1$ and we set $\hbar = 1$ everywhere. This is not enough to convert the Hamiltonian to a diagonal form because the other spins $t_i$ appear through their projections on two special directions: $\hat{z}_i$ as well as $\hat{z}_{i+1}$ in Eq. (3). However, once we have used this basis we have to solve a set of decoupled two-dimensional problems since the Hamiltonian is now given by:

$$\mathcal{H}(\{\sigma_i\}) = \sum_i \frac{J_i}{2} \left[ \sigma_i t_{i+1} + \sigma_{i+1} t_{i} \right] + \frac{1}{2} \sigma_i \left( B \cdot \hat{z}_i + B \cdot \hat{z}_{i+1} \right) - \frac{1}{2} \mu_B g_{ani} \sigma_i (B \cdot \hat{z}_i)$$

It is an explicit function of the new classical spin configuration $\{\sigma_i\}$. We see now that there is an effective magnetic field acting upon the spins of the radicals but no direct interactions between them:

$$\mathcal{H}(\{\sigma_i\}) = \sum_i t_i \cdot h_{eff} - \frac{1}{2} \mu_B g_{ani} \sigma_i (B \cdot \hat{z}_i),$$
between two consecutive $\hat{\tau}$

In these equations, we have defined $h$ hence $\theta$

$\theta$ configuration in the ground state according to the value of the parameter $\tau$. From Eq.(8) we see that the ground

state spin configuration is obtained when all variables $\tau_i$ are equal to -1 for any applied field. The effective field takes only three distinct values:

\[
\begin{align*}
\mathbf{h}^{\text{eff}}_i(\sigma_i = +1, \sigma_{i+1} = +1, \mathbf{B}) & \equiv \lambda_{++} = J \sqrt{\frac{1}{2} (1 + \cos \gamma) + g_{\text{iso}}^2 \frac{h}{J} + 2 g_{\text{iso}} \frac{h}{J} \cos \theta}, \\
\mathbf{h}^{\text{eff}}_i(\sigma_i = -1, \sigma_{i+1} = -1, \mathbf{B}) & \equiv \lambda_{--} = J \sqrt{\frac{1}{2} (1 + \cos \gamma) + g_{\text{iso}}^2 \frac{h}{J} - 2 g_{\text{iso}} \frac{h}{J} \cos \theta}, \\
\mathbf{h}^{\text{eff}}_i(\sigma_i = \pm 1, \sigma_{i+1} = \mp 1, \mathbf{B}) & \equiv \lambda_{+-} = J \sqrt{\frac{1}{2} (1 - \cos \gamma) + g_{\text{iso}}^2 \frac{h}{J}^2}.
\end{align*}
\]

In these equations, we have defined $h = |\mu_B|B$, $\theta$ is the angle between the $z$-axis and the vectors $\hat{\tau}_i$ and $\gamma$ is the angle between two consecutive $\hat{\tau}_i$ vectors. In the umbrella structure of CoPhOMe, one has $\cos \gamma = \frac{1}{4} \cos^2 \theta - \frac{1}{2}$. To get the ground state we can equivalently consider the simplified energy:

\[
\hat{E}(\{\sigma_i\}) = \frac{1}{2} \sum_i \{-\mathbf{h}^{\text{eff}}_i(\sigma_i, \sigma_{i+1}, \mathbf{B}) - \mu_B g_{\text{ani}} \sigma_i (\mathbf{B} \cdot \hat{\tau}_i)\}.
\]

With only three values for the effective field it can be written as:

\[
\hat{E}(\{\sigma_i\}) = -J \text{eff} \sum_i \sigma_i \sigma_{i+1} - B \text{eff} \sum_i \sigma_i + \text{Cst},
\]

where:

\[
J \text{eff} = \frac{1}{4} \{\lambda_{++} + \lambda_{--} - 2 \lambda_{+-}\} \quad \text{and} \quad B \text{eff} = \frac{1}{2} \mu_B g_{\text{ani}} B \cos \theta + \frac{1}{3}(\lambda_{++} - \lambda_{--}).
\]

From these equation it is now clear that the Cobalt spins will adopt a ferromagnetic (F) or antiferromagnetic (AF) configuration in the ground state according to the value of the parameter $J \text{eff}$. If the ground state is AF in zero field, increasing the applied field will ultimately turn the system to a F state. Comparing energies, we find that this happens for the following condition:

\[
\lambda_{+-} - \lambda_{--} = |\mu_B| g_{\text{ani}} B \cos \theta.
\]

(We use conventions for which $\mu_B < 0$ and the F state at large field has all $\sigma_i = -1$).

In zero field, the ground state is ferromagnetic for $\theta < \theta_c$, where $\theta_c$ the value of $\theta$ for which $\cos \gamma = 0$: $\cos \theta_c = 1/\sqrt{3}$ hence $\theta_c \approx 55^\circ$. It is AF for larger values of $\theta$. Geometrically at the critical angle $\theta_c$, the units vectors $\hat{\tau}_i$ are all perpendicular and $\cos \gamma = 0$: this is the configuration called the "magic angle" in NMR. If we have a zero-field AF ground state and apply a field then at some point it will be replaced by the F state: this will happen with a jump of the magnetization since the levels do simply cross. The location of the critical field as a function of the applied field and the angle $\theta$ is displayed in Fig.(3)

For $\theta = \theta_c$ we have a $2\theta_c^\circ$ degenerate ground state for all configurations of the Cobalt spins.
Figure 3: The critical field between F and AF ground states as a function of the angle $\theta$ for $g_{\text{iso}} = 2$ and $g_{\text{ani}} = 9.5, 9, 8.5, 8, 7.5, 7$ from bottom to top.

Figure 4: Ground state magnetization curve for $\theta = 50^\circ, 55^\circ, 60^\circ, 65^\circ$. We use $g_{\text{ani}} = 9$ and $g_{\text{iso}} = 2$ as appropriate for CoPhOME.

B. The $T = 0$ Magnetization Curve

We now discuss the magnetization curve at zero temperature of the previous model. From the ingredients of the previous section, it is straightforward to derive simple expressions for the magnetization. In the ground state we have the sum of the contribution of the Cobalt spins that are always completely polarized along their local anisotropy axis and the contribution from the radical spins that always follow exactly the local field:

$$\langle M \rangle = \sum_i \frac{1}{2} \mu_B g_{\text{ani}} \sigma_i \hat{z}_i - \frac{1}{2} \mu_B g_{\text{iso}} \frac{h_{\text{eff}}^i}{\| h_{\text{eff}}^i \|}.$$  \hspace{1cm} (16)

This expression is valid for an arbitrary spin configuration. In the F state the magnetization is nonzero only along the $z$ axis and equal to:

$$\frac{2}{N} \langle M^z \rangle = -\frac{1}{2} \mu_B g_{\text{ani}} \cos \theta + \frac{1}{2} \mu_B g_{\text{iso}} \frac{J \cos \theta + \mu_B g_{\text{iso}} B}{\lambda_{--}},$$  \hspace{1cm} (17)
N is the total number of spins Cobalt + radical. In the AF state, the magnetization from Eq.(16) is zero in zero applied field and again only along z in nonzero field. We find then:

\[
\frac{2}{N} \langle M^z \rangle = \frac{1}{2} \mu_B^2 g_{anis}^2 \frac{B}{\Lambda_+}.
\]  

(18)

Sample curves are displayed in Fig.(4). For F ground states the magnetization process is smooth and converges to a saturation value \((g_{anis} \cos \theta + g_{iso} |\mu_B|/2)\) which is reached however only at \(B \to \infty\). In the AF case, for \(\theta\) large enough there is a jump of the magnetization when the spins reorient themselves into the ferromagnetic state.

From the shape of the known magnetization curve of CoPhOMe, we find that we need an angle \(\theta\) which is close to the critical value. From the saturation value we get an estimate of the \(g\)-factor of the Cobalt ions once we assume that the \(g\) of the radical is extremely close to 2. Considering present experimental data \([6]\), the preferred values are \(g_{anis} \approx 9\) and \(\theta \approx 54^\circ\).

III. FINITE TEMPERATURE PROPERTIES

The formula \([3]\) we have found for the eigenvalues of the closed ring can be used to obtain the finite temperature properties, in the thermodynamic limit, with the transfer matrix method. The analytical treatment will be given only for the field applied along the chain axis; in this case two successive anisotropic spins experience the same field and the magnetic unit cell consists of one isotropic-anisotropic pair.

A. The \(\sigma-\sigma\) Transfer Matrix

If we explicitly sum over the \(\tau\) coordinates we can define the \(\sigma-\sigma\) transfer matrix:

\[
T_{\sigma,\sigma'} = \exp \left[ -\frac{1}{4} \beta g_{anis} h \cos \theta (\sigma + \sigma') \right] \sum_{\tau=\pm 1} \exp \left[ \frac{1}{2} \beta \tau h^{eff}(\sigma, \sigma', B) \right],
\]  

(19)

and obtain the well known expression for the partition function of the problem:

\[
\mathcal{Z} = Tr \left[ T_{\sigma,\sigma'}^N \right] = \Lambda_+ N^2 + \Lambda_- N^2
\]  

(20)

where \(\Lambda_+\) and \(\Lambda_-\) are the eigenvalues of the matrix \(T_{\sigma,\sigma'}\). In the thermodynamic limit the largest eigenvalue dominates and \(\mathcal{Z} = \Lambda_+^N\). The spin correlation function for \(N \to \infty\) is given by:

\[
\langle \sigma_k \sigma_l \rangle = |\langle \phi^+ | \sigma | \phi^+ \rangle|^2 + |\langle \phi^+ | \sigma | \phi^- \rangle|^2 \left( \frac{\Lambda_-}{\Lambda_+} \right)^{|k-l|},
\]  

(21)

where the \(|\phi^\pm\rangle\) are the two eigenvectors of the transfer matrix \([19]\).

B. The Zero-Field Spin Correlation Function

The first term in \([21]\) is simply the square expectation value of each anisotropic spin and it is different from zero only in non zero field. In zero field the solution to the eigenvalues problem gives:

\[
\Lambda_\pm = 2[\cosh(\nu_{\pm\pm}) \pm \cosh(\nu_{\pm\perp})] \quad \text{and} \quad |\phi^\pm\rangle = \frac{1}{\sqrt{2}} \left( \frac{1}{\pm 1} \right),
\]  

(22)

where:

\[
\nu_{\pm\pm} = \frac{1}{2} \beta \lambda_{++}, \quad \nu_{\pm\perp} = \frac{1}{2} \beta \lambda_{+-}, \quad \nu_{\perp\perp} = \frac{1}{2} \beta \lambda_{--},
\]  

(23)

and in zero field \(\nu_{\parallel\parallel} = \nu_{\parallel\perp}\). The \(\sigma-\sigma\) correlation function is:

\[
\langle \sigma_k \sigma_l \rangle = \left[ \frac{\cosh(\nu_{\parallel\parallel}) - \cosh(\nu_{\parallel\perp})}{\cosh(\nu_{\parallel\parallel}) + \cosh(\nu_{\parallel\perp})} \right]^{|k-l|},
\]  

(24)
that decays exponentially with increasing spin separation for every non zero temperature.

For \( \nu_{1+} > \nu_{1-} (\theta < \theta_c) \) the decay of (24) is monotonic whereas for \( \nu_{1+} < \nu_{1-} (\theta > \theta_c) \) it is oscillatory with sign \((-1)^{|k-l|}\). For \( \theta = \theta_c \) the expression (24) vanishes at any temperature; this is related to the fact that the energies (5) do not depend on the \( \sigma \) coordinates. The thermal fluctuations lead to the same behavior in the Ising ferromagnet with an antiferromagnetic next-to-nearest neighbor interaction, but not strong enough to destroy the ferromagnetic structure of the ground state [7, 8]. Here it is the \( \theta \) angle which is the tuning parameter instead of the temperature that makes the system pass through a disorder point at \( \theta = \theta_c \). From the Eq.(24) we can also obtain an expression for the zero-field correlation length:

\[
\xi^{-1} = -\frac{1}{2} \ln \left| \frac{\cosh(\nu_{1+}) - \cosh(\nu_{1-})}{\cosh(\nu_{1+}) + \cosh(\nu_{1-})} \right|.
\]  

The factor one half comes from the fact that the correlation function Eq.(24) corresponds to an actual separation of \(2|k-l|\) magnetic centers.

The Eq.(25) gives back the Ising model correlation length when \( \theta = 0 \). From figure (5) we observe that at any temperature while increasing \( \theta \) the correlation length decreases until it reaches \( \theta_c \). When \( \theta > \theta_c \) it increases again, but in this case the effective coupling between the \( s_i \) spins is antiferromagnetic. For \( \theta = \theta_c \) it vanishes, as well as the correlation function, at all temperatures.

C. Field dependence of the critical point

It is straightforward to wonder if it is possible to have a vanishing correlation length for \( \theta \neq \theta_c \) using the external field as a tunable parameter. This happens when the smallest eigenvalue of the transfer matrix is zero (see equation (11)). The eigenvalues in presence of the field are:

\[
\Lambda_\pm = X \cosh(\nu_{1+}) + X^{-1} \cosh(\nu_{1-}) \pm \sqrt{[X \cosh(\nu_{1+}) - X^{-1} \cosh(\nu_{1-})]^2 + 4 \cosh^2(\nu_{1+})},
\]  

where:

\[
X = \exp\left(-\frac{\beta}{2} g_{ani} h \cos \theta \right)
\]  

The \( \Lambda_- = 0 \) condition is fulfilled when:

\[
\cosh(\nu_{1+}) \cosh(\nu_{1-}) = \cosh^2(\nu_{1-}).
\]  

This equation can be solved numerically for any \( \theta \) in order to obtain what we call the disorder field \( h = h_d \) for which:

\[
\langle \sigma_k \sigma_l \rangle - \langle \sigma_k \rangle^2 = \exp\left[-\frac{2|k-l|}{\xi} \right] = 0.
\]
A numerical analysis shows that the Eq. (28) has a solution only for $0 < \theta \leq \theta_c$. In the Ising limit ($\theta = 0$) the equation (28) reduces to:

$$\cosh^2(2\beta J) - \tanh^2(\beta g_{iso} h/2) \sinh^2(2\beta J) = 1,$$

(30)

that has no solution for any $h < \infty$. On the other hand we know that for $\theta = \theta_c$ the disorder field is $h_d = 0$. Moreover the Eq. (28) is symmetric in the exchange $h \leftrightarrow -h$. Since there is no physical reason to think the $h_d$ dependence on $\theta$ to be discontinuous this means that the disorder field already takes all the allowed values in the range $0 < \theta \leq \theta_c$, leaving no solution to the Eq. (28) for $\theta > \theta_c$. This is in agreement with the numerical results.

In figure (6) the disorder field dependence on the temperature is shown for different values of $\theta$. This dependence is less strong for $\theta$ approaching $\theta_c$. For $\theta = \theta_c$, we find a line lying on the zero-field axis.

In figure (7) we note that the critical point appears as cusp in the correlation length $\xi$ vs field plot. If we consider
In this case we see that the ratio \( W = \frac{\Delta}{E} \) of the energy gap between the magnetic and the non-magnetic state can be arbitrarily small for the quantity \( \Delta \) to vanish for any \( \theta \). This behavior is closely related to the presence of a disorder point of the magnetic axis, where all eigenvalues can be determined analytically if the applied field is along the axis of the chain. As a consequence, the correlation length and the slowest time scale are usually related by a dynamical critical exponent. Thus, we can easily imagine this system to show a very rich scenario in the long-time scale dynamics too. In this section, we investigate the implications of detailed balance on the transition functions \( W(\sigma_k) \) and \( W(\tau_k) \) involved in a Glauber-like approach [13]. The Eq. (8) in zero field can be written as:

\[
\beta E(\sigma, \tau) = \sum_{i=1}^{N/2} \tau_i \left[ \frac{\nu_{i\uparrow} + \nu_{i\downarrow}}{2} + \tau_{i+1} \frac{\nu_{i\uparrow} - \nu_{i\downarrow}}{2} \right].
\] (31)

The ratio of the two equilibrium probabilities corresponding to the configurations \((\sigma_1, \tau_1, \ldots, \sigma_k, \tau_k, \sigma_{k+1}, \ldots, \tau_{N/2})\) and \((\sigma_1, \tau_1, \ldots, \sigma_k, \tau_k, \sigma_{k+1}, \ldots, \sigma_N, \tau_N)\) is:

\[
\frac{P_{eq}(\sigma_k)}{P_{eq}(\tau_k)} = \frac{\exp\left(\frac{\tau_k (\nu_{i\uparrow} + \nu_{i\downarrow})}{2}\right)}{\exp\left(-\tau_k (\nu_{i\uparrow} + \nu_{i\downarrow})/2\right)} \frac{1 + \tau_k \sigma_{k+1} \tanh\left(\frac{\nu_{i\uparrow} - \nu_{i\downarrow}}{2}\right)}{1 - \tau_k \sigma_{k+1} \tanh\left(\frac{\nu_{i\uparrow} - \nu_{i\downarrow}}{2}\right)}.
\] (32)

which must be equal, for the detailed balance condition to be satisfied, to the ratio \( \frac{W(\tau_k)}{W(\sigma_k)} \). The (32) tells us that even if the energy gap between the magnetic and the non-magnetic state can be arbitrarily small for \( \theta \sim \theta_c \) \((\nu_{i\uparrow} \sim \nu_{i\downarrow})\), the energy barrier appearing in the transition probability \( W(\tau_k) \) will always be \( \Delta E \simeq \frac{1}{2}(\nu_{i\uparrow} + \nu_{i\downarrow}) \), that does not vanish for any \( \theta \).

For the sake of completeness, we write the equivalent of the (32) for the Cobalt spins:

\[
\frac{P_{eq}(\sigma_k)}{P_{eq}(\tau_k)} = \frac{1 + \frac{1}{2} \sigma_k (\tau_k \sigma_{k+1} + \tau_{k-1} \sigma_{k-1}) \tanh(\nu_{i\uparrow} - \nu_{i\downarrow})}{1 - \frac{1}{2} \sigma_k (\tau_k \sigma_{k+1} + \tau_{k-1} \sigma_{k-1}) \tanh(\nu_{i\uparrow} - \nu_{i\downarrow})}.
\] (33)

In this case we see that the ratio \( \frac{P_{eq}(\sigma_k)}{P_{eq}(\tau_k)} \rightarrow 1 \) for \( \theta \rightarrow \theta_c \).

Even if we do not have so far a rigorous treatment for the dynamics of this system, it seems reasonable to relate the quantity \( \Delta E \) to the activation energy of the relaxation process. For our purpose it is enough to observe that the presence of a jump in the \( T = 0 \) magnetization curve, occurring at relatively small fields, and the presence of a tunable disorder point is consistent with the observation of the slow decay of the macroscopic magnetization.

**V. CONCLUSION**

We have introduced a magnetic Hamiltonian suited to the description of the Ising-like spin chain CoPhOMe. This model contains two kinds of spins with very different \( g \)-factors. We have shown that by a careful choice of quantization axis all eigenvalues can be determined analytically if the applied field is along the axis of the chain. As a consequence, we have obtained the magnetization curve. This curve displays a metamagnetic jump at some critical value of the external applied field. The position of the jump is closely related to the presence of a disorder point of the magnetic...
model. This disorder point can be reached theoretically by tuning the angle of the Cobalt anisotropy axis with the chain axis. All experimental data indicate that the real chain CoPhOMe is very close to this critical value. Right at this disorder point there is extensive ground state degeneracy. By using ideas taken from the Glauber dynamics we show that this is likely to be related to the very long relaxation times observed when performing magnetization measurements on this chain. There is still the problem of developing a realistic model of the dynamical properties of this spin chain.