Magnetic properties of a helical spin chain with alternating isotropic and anisotropic spins: Magnetization plateaus and finite entropy

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We propose a model which could explain some of the unusual magnetic properties observed for the one-dimensional helical spin system $\mathrm{Co}(hfac)_2$NITPhOMe. One of these properties is that the magnetization shows some plateaus if a magnetic field is applied along the helical axis. The system consists of cobalt ions (which have easy axes which are tilted at an angle θ_i with respect to the helical axis) and organic radicals alternating with each other. We consider a model in which the tilt angles θ_i are allowed to vary with i with period three. Using the transfer matrix approach, we show that for certain patterns of θ_i, the model exhibits the magnetization plateaus mentioned above. At the ends of the plateaus, we find that the entropy is finite even at very low temperatures, while the magnetic susceptibility and specific heat also show some interesting features.

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The last several years have witnessed extensive studies of one-dimensional systems and molecular clusters with a variety of interesting magnetic properties, both static and dynamic.[1] Very recently, there have been some experimental studies of a one-dimensional molecular system $\mathrm{Co}(hfac)_2$NITPhOMe (to be called CoPhOMe henceforth) which shows some unusual behavior in the presence of a time-dependent magnetic field.[2,3] The system has a helical structure, in which cobalt ions (which are effectively spin-1/2 due to their strong anisotropy) and organic radicals (which are spin-1/2 and isotropic) alternate, with a repeat period of three cobalts for every turn of the helix; this is shown in Fig. 1. Below a certain temperature, the time scale associated with the variation of the magnetization is found to become extremely long (leading to a pronounced hysteresis) if the magnetic field is applied along the helical axis (called the c axis), but not if the field is in the plane perpendicular to that axis (called the a-b plane). It is also found that the magnetization shows some plateaus (which become more pronounced at lower temperatures) if the magnetic field points along the c axis, but not if it is in the a-b plane.

In this work, we will consider the second feature mentioned above, namely, the appearance of some plateaus with nontrivial magnetizations when the magnetic field is applied along the c axis; these plateaus are known to persist when the magnetic field is cycled, and hence have a static origin.[3] Motivated by the magnetization data, we will present a phenomenological model which can qualitatively explain this feature. Our model is a variation of the one considered in the earlier studies of this system;[2–4] for reasons explained below, the model presented in those papers is not able to explain the magnetization plateaus.

We begin by presenting the model introduced for this system in the earlier papers.[2–4] The organic radicals carry spin-1/2. The cobalt ions are effectively spin-1/2 objects due to their strong anisotropy; they have an easy axis $\mathbf{e}_i$ which is tilted by an angle θ_i with respect to the c axis. Further, the angle between the projections of $\mathbf{e}_{i+1}$ and $\mathbf{e}_i$ on the a-b plane is given by $2\pi/3$. (We assume that $\mathbf{e}_i$ is a unit vector.) If we identify the c axis with the $\mathbf{z}$ axis, the three components of $\mathbf{e}_i$ are given by $(\sin\theta_i \cos 2\pi(i-1)/3, \sin\theta_i \sin 2\pi(i-1)/3, \cos\theta_i)$. Due to the anisotropy, the cobalt spins can be described classically using Ising variables $\sigma_i = \pm 1$. The organic radicals are completely isotropic, and their spins have to be treated quantum mechanically. The earlier papers assumed the tilt angles θ_i to be the same for all the cobalts. However, we will consider a phenomenological model in which the θ_i vary with i, but with a period of three keeping the pitch of the helix the same as in the earlier models. For temperatures and magnetic fields which are much smaller than the coupling between nearest-neighbor cobalts and radicals, one can compute the thermodynamic properties of the system using the transfer matrix approach. We will show that certain patterns of the θ_i allow us to reproduce the observed magnetization plateaus.

In the ith cobalt-radical pair, let us denote the component of the cobalt spin along its easy axis by σ_i, and the spin operators of the radical by $\mathbf{T}_i$ (these are given by half the Pauli matrices). In the presence of a magnetic field $\mathbf{B}$, the Hamiltonian for this system is given by

$$H_{CR} = \sum_i \left[\frac{J}{2}\sigma_i \mathbf{e}_i \cdot (\mathbf{T}_i + \mathbf{T}_{i-1}) - \mu_B \mathbf{B} \cdot \left(\frac{1}{2} g_C \sigma_i \mathbf{e}_i + g_R \mathbf{T}_i \right) \right], \tag{1}$$

where g_C and g_R denote the gyromagnetic ratios of the cobalt and radical spins, respectively, and $\mu_B = e\hbar/(2mc)$ is the Bohr magneton. (We note that $\mu_B/k_B = 0.672$ K/Tesla.) Fits to the magnetization data at different temperatures seem to lead to somewhat different values of the various parameters. One set of parameters which has been quoted in some of the papers is as follows: $J/k_B \sim 400$ K (antiferromagnetic in sign), $g_C = 9$, $g_R = 2$, and the tilt angle θ is in the vicinity of the angle $\theta_0 = \cos^{-1}(1/\sqrt{3}) \simeq 54.74°$;[3,4] this is called the "magic angle" in the context of dipole-dipole interactions. (Large values of the effective g factor given by $g_{\mathcal{J}}\mathcal{J}$ are known to arise in high spin systems when a strong uniaxial anisotropy restricts the accessible spin states $\mathcal{J}_z$ to $\pm\mathcal{J}$ at low temperatures.[5,6])

The data which indicates magnetization plateaus lies at a temperature of about 2 K and a magnetic field of up to 3 Tesla. Since these temperatures and magnetic fields are much smaller than the value of J/k_B and J/μ_B, respectively, we will begin by making the approximation that each radical spin is aligned in a direction which is entirely dictated by the directions of its two neighboring cobalt spins. Namely, we will assume that the expectation value of $\mathbf{T}_i$ is given by

$$\langle \mathbf{T}_i \rangle = -\frac{1}{2}\frac{\sigma_i \mathbf{e}_i + \sigma_{i+1}\mathbf{e}_{i+1}}{\sqrt{2 + 2\sigma_i\sigma_{i+1}\mathbf{e}_i \cdot \mathbf{e}_{i+1}}}. \tag{2}$$

Upon substituting this in Eq. (1), we obtain an effective Hamiltonian defined purely in terms of the cobalt Ising variables σ_i,

$$H_{1C} = \sum_i \Bigg[-\frac{J}{4}\sqrt{2 + 2\sigma_i\sigma_{i+1}\mathbf{e}_i \cdot \mathbf{e}_{i+1}} - \frac{\mu_B}{2}\mathbf{B}\cdot\mathbf{e}_i\sigma_i\Bigg(g_C - \frac{g_R}{\sqrt{2 + 2\sigma_i\sigma_{i+1}\mathbf{e}_i \cdot \mathbf{e}_{i+1}}} - \frac{g_R}{\sqrt{2 + 2\sigma_i\sigma_{i-1}\mathbf{e}_i \cdot \mathbf{e}_{i-1}}}\Bigg)\Bigg]. \tag{3}$$

As mentioned above, the experimental data indicates that the tilt angles θ_i are close to the angle θ_0. If all the θ_i were *exactly* equal to θ_0, the easy axes of neighboring cobalts would be perpendicular to each other, i.e., we would have $\mathbf{e}_i \cdot \mathbf{e}_{i+1} = 0$. Then the Hamiltonian in Eq. (3) would have no interactions between neighboring cobalts, and the (subtracted) two-spin correlations, $\langle(\sigma_i - \langle\sigma_i\rangle)(\sigma_j - \langle\sigma_j\rangle)\rangle$, would be strictly zero for $i \neq j$ at any temperature. [This is called a disorder point; it corresponds to the smaller eigenvalue of the transfer matrix (discussed below) being equal to zero.[4,7]]

Motivated by the ranges of the various experimental parameters, let us assume that $\delta\theta_i \equiv \theta_i - \theta_0$ are small numbers (in radians), so that

$$\mathbf{e}_i \cdot \mathbf{e}_{i+1} \simeq -\frac{1}{\sqrt{2}}(\delta\theta_i + \delta\theta_{i+1}) \tag{4}$$

is much less than 1 in magnitude. We also assume that $J(\delta\theta_i + \delta\theta_{i+1})$ is of the same order as (or larger than) than the magnitude of $\mu_B|\mathbf{B}|$. Then Eq. (3) can be approximately written, up to a constant, as

$$H_{2C} = \sum_i \left[J_{i,i+1}\sigma_i\sigma_{i+1} - \frac{\mu_B}{2} g_{\rm eff}\mathbf{B}\cdot\mathbf{e}_i^0\sigma_i \right],$$

$$J_{i,i+1} = \frac{J}{8}(\delta\theta_i + \delta\theta_{i+1}),$$

$$g_{\rm eff} = g_C - \sqrt{2}g_R, \tag{5}$$

and

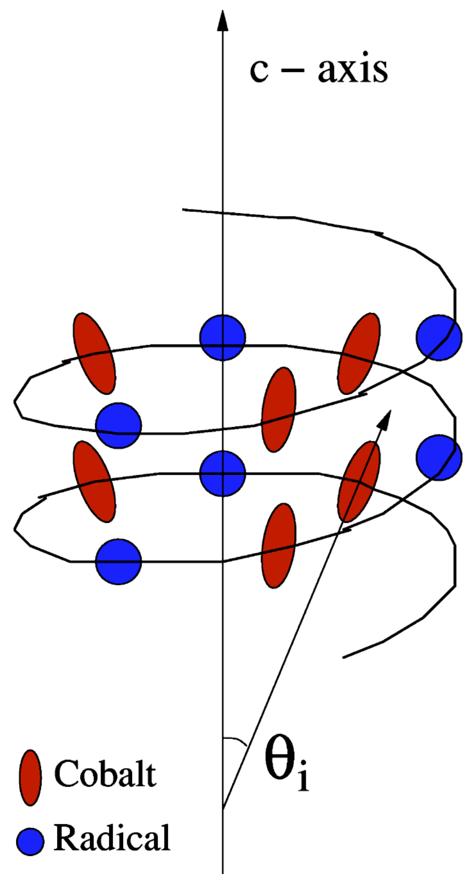

FIG. 1. (Color online) The structure of the molecular chain CoPhOMe. The cobalt spins are anisotropic with a local axis denoted by $\mathbf{e}_i$ which is tilted by an angle θ_i with respect to the helical axis c. The angle between the projections of $\mathbf{e}_{i+1}$ and $\mathbf{e}_i$ on the a-b plane is equal to $2\pi/3$. The organic radical spins are isotropic.

$$\mathbf{e}_1^0 = (\sqrt{2/3}, 0, 1/\sqrt{3}),$$

$$\mathbf{e}_2^0 = (-1/\sqrt{6}, 1/\sqrt{2}, 1/\sqrt{3}),$$

$$\mathbf{e}_3^0 = (-1/\sqrt{6}, -1/\sqrt{2}, 1/\sqrt{3}). \tag{6}$$

The effective nearest neighbor Ising interaction $J_{i,i+1}$ in Eq. (5) is ferromagnetic or antiferromagnetic depending on whether $\delta\theta_i + \delta\theta_{i+1}$ is negative or positive.

In the earlier papers,[2–4] θ_i had been assumed to take the same value θ for all i. Then the effective Ising interaction is given by

$$J_{i,i+1} = \frac{J}{4}\delta\theta. \tag{7}$$

The thermodynamic properties of this model can be calculated easily using the transfer matrix method. If $g_{\rm eff} > 0$, and the magnetic field is large compared to $J\delta\theta$ (but much smaller than J), then Eq. (5) implies that the magnetization per cobalt-radical pair will take a value given by

$$M_S = \frac{\mu_B}{6} g_{\rm eff} \sum_{i=1}^{3} |\hat{B} \cdot \mathbf{e}_i^0|,$$

$$\hat{B} = \frac{\mathbf{B}}{|\mathbf{B}|}. \tag{8}$$

We will henceforth refer to M_S as the saturation magnetization. [We should emphasize here that this only corresponds to a partial (ferrimagnetic) saturation of the magnetization, since each radical points in the direction opposite to the sum of its two neighboring cobalt spins. If the magnetic field becomes much larger than J/μ_B, i.e., about 600 Tesla, then the original Hamiltonian in Eq. (1) implies that the magnetization will reach the final saturation value of $(\mu_B/6)(g_C \Sigma_i |\hat{B} \cdot \mathbf{e}_i^0| + 3g_R)$ where all the radicals also point in the same direction. But this kind of field strength is not experimentally accessible at present; we will therefore not be interested in this fully saturated state.]

Let us now consider the case of very low temperatures and a magnetic field applied along the c axis; then all the cobalt spins experience the same magnetic field strength $\mathbf{B} \cdot \mathbf{e}_i^0 = |\mathbf{B}|/\sqrt{3}$. The magnetization will show a plateau at $M = 0$ if the effective interaction in Eq. (7) is positive (antiferromagnetic), but not if it is negative (ferromagnetic). For large fields, the magnetization will saturate at $M = M_S = \mu_B g_{\rm eff}/(2\sqrt{3})$. We thus see that there is no magnetization plateau at fractional values of M_S (such as $M_S/3$) regardless of what the sign of $\delta\theta$ in Eq. (7) is; namely, states with magnetization equal to $M_S/3$ are not the lowest energy states for any value of the field.

We therefore require a slightly different model in order to obtain magnetization plateaus at both $M=0$ and $M=M_S/3$ as the experimental data seems to suggest.[3] We considered several possible variations of the basic model; these included

(i) dipole-dipole interactions, both between two cobalts and between two radicals (including interactions between pairs of sites which are third neighbors, and therefore lie one above the other on two successive turns of the helix; the dipole-dipole interaction between two third-neighbor cobalts vanishes because the orientation of their easy axes with respect to the c axis corresponds to the "magic angle"), and

(ii) transverse couplings between a cobalt and its neighboring radicals, i.e., couplings between the components of a cobalt spin which are perpendicular to its easy axis and the corresponding components of its neighboring radicals.

Based on numerical studies (exact diagonalization of small systems with up to six cobalt and six radical spins), we concluded that these two variants do not help to explain the experimentally observed magnetization plateaus. Finally, we discovered that the following variation works. We assume that all the cobalt spins in a single molecular chain do not have the same angle of tilt with respect to the c axis. We further assume that the angles θ_i take three different values θ_1, θ_2, and θ_3 for three successive cobalts, and that they repeat periodically thereafter. (This assumption is consistent with the helical structure of the system which repeats after every three cobalts.) The periodicity of three makes it plausible that there could be a magnetization plateau at $M_S/3$ (corresponding to a state with σ_i repeating as 1, 1, −1, i.e., a ↑↑↓ spin alignment). However, it turns out that θ_1, θ_2, and θ_3 need to satisfy some additional conditions as we will now discuss.

Since the θ_i's repeat with period three, the thermodynamic properties of the system can again be found using the transfer matrix method. If the number of cobalt-radical pairs is denoted by N, and we use periodic boundary conditions (taking N to be a multiple of 3), then the partition function can be written as

$$Z = \mathrm{Tr}(A_1 A_2 A_3)^{N/3}, \tag{9}$$

where the matrix elements of the 2×2 matrices A_i are given by

$$(A_i)_{11} = \exp\left[-\beta J_{i,i+1} + \frac{\beta \mu_B g_{\rm eff}}{4} \mathbf{B} \cdot (\mathbf{e}_i^0 + \mathbf{e}_{i+1}^0) \right],$$

$$(A_i)_{12} = \exp\left[\beta J_{i,i+1} + \frac{\beta \mu_B g_{\rm eff}}{4} \mathbf{B} \cdot (\mathbf{e}_i^0 - \mathbf{e}_{i+1}^0) \right],$$

$$(A_i)_{21} = \exp\left[\beta J_{i,i+1} + \frac{\beta \mu_B g_{\rm eff}}{4} \mathbf{B} \cdot (-\mathbf{e}_i^0 + \mathbf{e}_{i+1}^0) \right],$$

$$(A_i)_{22} = \exp\left[-\beta J_{i,i+1} + \frac{\beta \mu_B g_{\rm eff}}{4} \mathbf{B} \cdot (-\mathbf{e}_i^0 - \mathbf{e}_{i+1}^0) \right], \tag{10}$$

with $\beta = 1/(k_B T)$. The magnetization per cobalt-radical pair is then given by the derivative of $\ln Z$ with respect to $|\mathbf{B}|$,

$$M = -\frac{k_B T}{NZ} \frac{dZ}{d|\mathbf{B}|}. \tag{11}$$

(We must eventually take the limit $N \to \infty$.)

We should note here that when we actually do the transfer matrix calculations (on which Figs. 2–7 are based), we have not used the assumption made in Eqs. (3) and (5) that each radical spin is aligned in a direction which is determined only by the neighboring cobalt spins. Rather, we solve for the two eigenvalues of the Hamiltonian of each radical spin which is interacting both with its neighboring cobalt spins *and* with the applied magnetic field. We then take only the lower eigenvalue into account when we integrate out that particular radical spin; the justification for this is that the two eigenvalues are separated by an energy of order J, and the temperatures of interest are much smaller than J/k_B.

While considering the magnetization as a function of the magnetic field, one can think of various possible patterns of signs and magnitudes of the parameters $\delta\theta_1$, $\delta\theta_2$, and $\delta\theta_3$. One pattern which leads to magnetization plateaus at 0 and $M_S/3$, for a magnetic field applied along the c axis, is given by the conditions

$$\text{(i)}\ \delta\theta_1 + \delta\theta_2,\ \delta\theta_1 + \delta\theta_3,\ \delta\theta_2 + \delta\theta_3 > 0,$$

$$\text{(ii)}\ \delta\theta_1 \geqslant \delta\theta_2,\ \delta\theta_3, \text{ and } 2\delta\theta_1 > \delta\theta_2 + \delta\theta_3. \tag{12}$$

[Condition (i) in Eqs. (12) corresponds to antiferromagnetic interactions $J_{i,i+1}$ between neighboring cobalt spins.] At zero temperature, we then find that there is a magnetization pla-

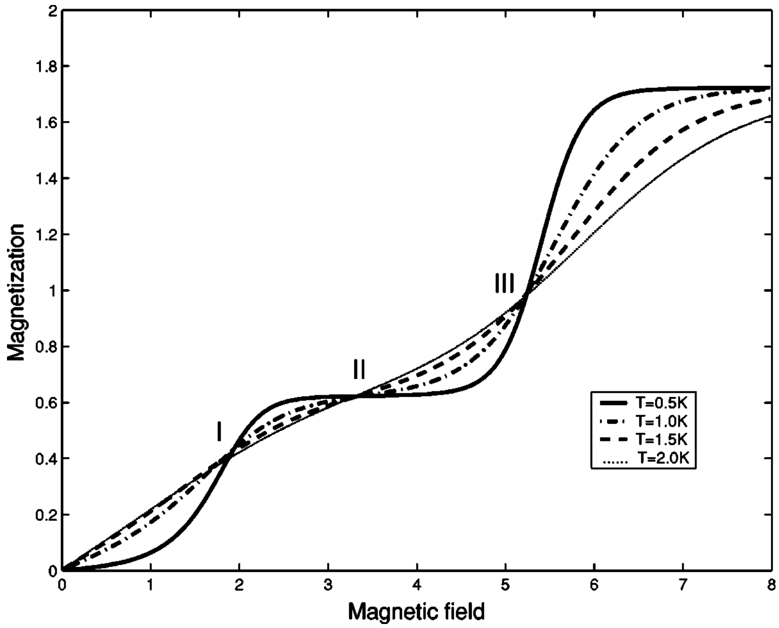

FIG. 2. Magnetization (in units of μ_B) per cobalt-radical pair versus the magnetic field (in Tesla) applied along the c axis, for various temperatures. The crossing points I, II, and III are discussed in the text. (We have taken J/k_B =400 K, g_C=9, g_R=2, $\delta\theta_1=\delta\theta_2$=2.64°, and $\delta\theta_3$ =−1.32°.)

teau at $M=0$ if the strength of the field lies in the range $0<B<B_1$, where

$$B_1 = \frac{\sqrt{3}}{2}\frac{\delta\theta_2 + \delta\theta_3}{g_{\text{eff}}}\frac{J}{\mu_B}, \tag{13}$$

a plateau at $M=M_S/3$ if the field lies in the range $B_1<B<B_2$, where

$$B_2 = \frac{\sqrt{3}}{4}\frac{2\delta\theta_1 + \delta\theta_2 + \delta\theta_3}{g_{\text{eff}}}\frac{J}{\mu_B}, \tag{14}$$

and a saturation plateau at $M=M_S$ if $B>B_2$. [Note that the condition $2\delta\theta_1>\delta\theta_2+\delta\theta_3$ in Eqs. (12) is needed in order to have $B_2>B_1$; otherwise the intermediate plateau at $M=M_S/3$ will not exist.] As we raise the temperature, the plateaus will gradually disappear.

In Fig. 2, we show the magnetization as a function of a magnetic field applied along the c axis, for one particular choice of the parameters $\delta\theta_i$ which satisfies the conditions in Eqs. (12), and different temperatures. For the various parameters given in the caption of Fig. 2 and using Eqs. (8), (13), and (14), we find that B_1=1.92 Tesla, B_2=4.81 Tesla, and M_S/μ_B=1.78. The locations of the plateaus in Fig. 2 at the lowest temperature of 0.5 K are consistent with these numbers. We have chosen the parameters $\delta\theta_i$ in such a way that the locations of the plateaus and their temperature dependences are in rough agreement with the data presented in Ref. 3; the agreement can be improved by changing the value of g_C, but we will not do that here.

We observe three special points labeled I, II, and III in Fig. 2 where the curves for different temperatures seem to cross, particularly at low temperatures. In terms of the mag-

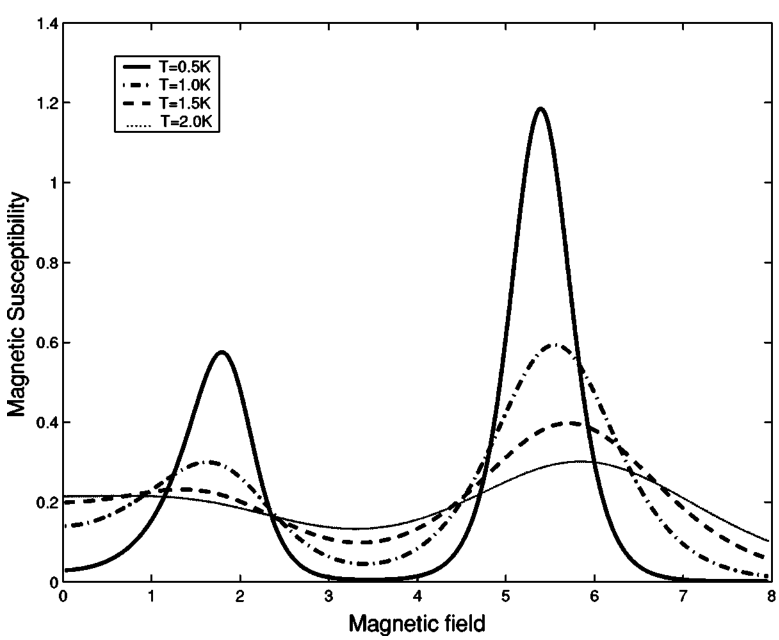

FIG. 3. Magnetic susceptibility (in units of μ_B/Tesla) per cobalt-radical pair versus the magnetic field (in Tesla) applied along the c axis, for various temperatures. (J/k_B=400 K, g_C=9, g_R=2, $\delta\theta_1=\delta\theta_2$=2.64°, and $\delta\theta_3$=−1.32°.)

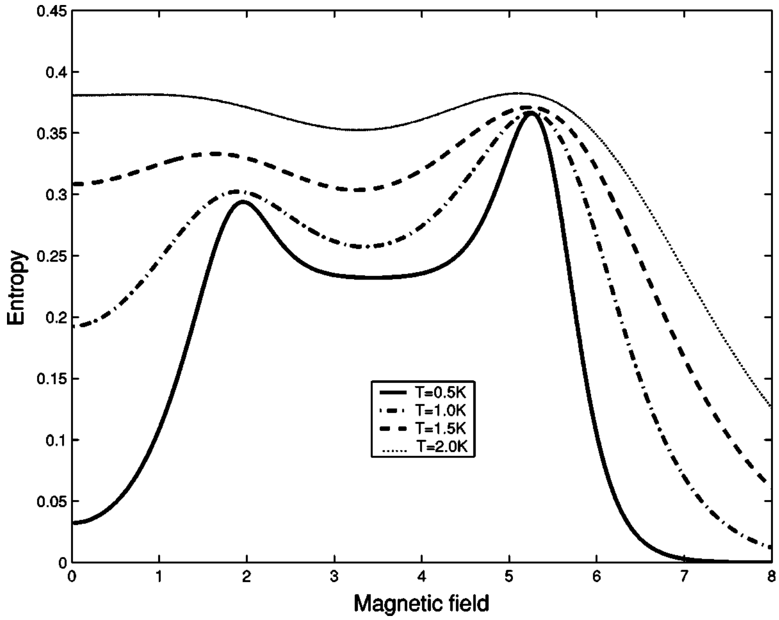

FIG. 4. Entropy (in units of k_B) per cobalt-radical pair versus the magnetic field (in Tesla) applied along the c axis, for various temperatures. (J/k_B=400 K, g_C=9, g_R=2, $\delta\theta_1=\delta\theta_2$=2.64°, and $\delta\theta_3$=−1.32°.)

netic field (in Tesla) and magnetization (in units of μ_B), we find numerically that these crossing points lie at I =(1.94,0.44), II=(3.38,0.62), and III=(5.26,1.00). We will now provide an analytical understanding of these points based on the transfer matrix method in the limit of zero temperature.

In the limit $T \to 0$, we find that the matrix $A_1A_2A_3$ has, up to some factors which do not affect the entropy, the eigenvalues ± 1 for $B < B_1$, $1 \pm \sqrt{2}$ for $B = B_1$, 2 and 0 for $B_1 < B < B_2$, 3 and 0 for $B = B_2$, and 1 and 0 for $B > B_2$. Hence, for $B_1 \leqslant B \leqslant B_2$, we find that there is an exponentially large number of degenerate ground states, giving rise to a finite entropy per cobalt-radical pair at $T=0$. In the limit $N \to \infty$, the zero temperature entropy (in units of k_B) per cobalt-radical pair is given by

$$\begin{aligned} \frac{S}{Nk_B} &= \frac{1}{3}\ln(\sqrt{2}+1) \quad \text{for } B = B_1, \\ &= \frac{1}{3}\ln 2 \quad \text{for } B_1 < B < B_2, \\ &= \frac{1}{3}\ln 3 \quad \text{for } B = B_2, \\ &= 0 \quad \text{for } B < B_1 \text{ and } B > B_2. \end{aligned} \tag{15}$$

We should note here that the discussion in the previous paragraph is valid only for our particular choice of the $\delta\theta_i$, with two of them being equal ($\delta\theta_1 = \delta\theta_2$) and larger than the

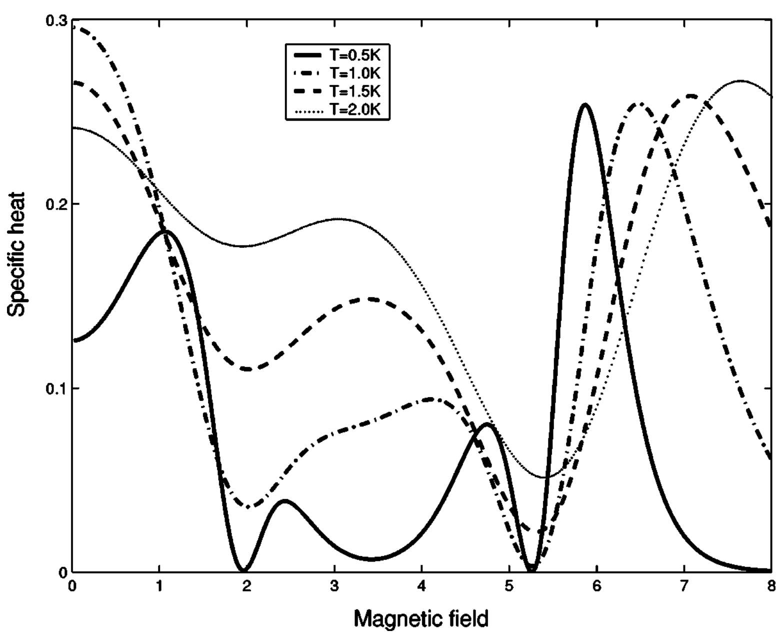

FIG. 5. Specific heat (in units of k_B) per cobalt-radical pair versus the magnetic field (in Tesla) applied along the c axis, for various temperatures. (J/k_B=400 K, g_C=9, g_R=2, $\delta\theta_1=\delta\theta_2$ =2.64°, and $\delta\theta_3$=−1.32°.)

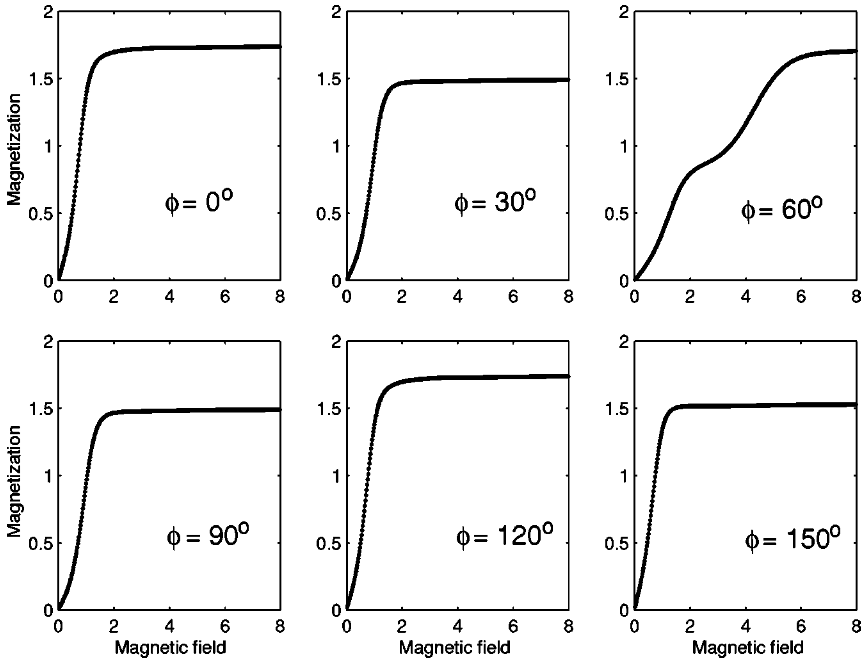

FIG. 6. Magnetization (in units of μ_B) per cobalt-radical pair versus the magnetic field (in Tesla) applied along six different directions in the *a*-*b* plane, for a temperature of 1 K. (J/k_B=400 K, g_C=9, g_R=2, $\delta\theta_1=\delta\theta_2$=2.64°, and $\delta\theta_3$=−1.32°).

third ($\delta\theta_3$). If we had made a more general choice with $\delta\theta_1 > \delta\theta_2 > \delta\theta_3$ [along with condition (i) in Eqs. (12)], the entropy at zero temperature would be finite only for $B=B_1$ and $B=B_2$; we would then get

$$\frac{S}{Nk_B} = \frac{1}{3}\ln\left(\frac{\sqrt{5}+1}{2}\right) \quad \text{for } B = B_1,$$

$$= \frac{1}{3}\ln 2 \quad \text{for } B = B_2,$$

$$= 0 \quad \text{otherwise}. \tag{16}$$

Let us now return to our model with $\delta\theta_1 = \delta\theta_2 > \delta\theta_3$. For $B_1 \leqslant B \leqslant B_2$, the magnetization at $T=0$ can be obtained by averaging over all the degenerate ground states. The calculation is hardest for $B=B_1$; we then find, up to some unimportant factors, that

$$A_1A_2A_3 = \begin{pmatrix} 1 & 1 \\ 2 & 1 \end{pmatrix}, \tag{17}$$

whose eigenvalues are given by $1\pm\sqrt{2}$ as mentioned above. In the thermodynamic limit, we find that the magnetization is given by

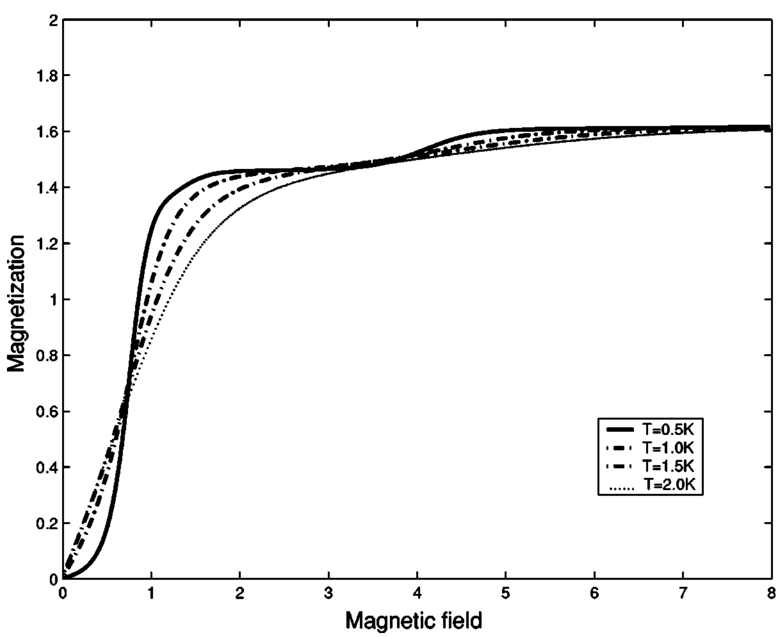

FIG. 7. Magnetization (in units of μ_B) per cobalt-radical pair versus the magnetic field (in Tesla) averaged over the six different directions shown in Fig. 2, for various temperatures. (J/k_B =400 K, g_C=9, g_R=2, $\delta\theta_1=\delta\theta_2$=2.64°, and $\delta\theta_3$ =−1.32°.)

$$M = \frac{M_S}{3} \lim_{N\to\infty} \frac{1}{(\sqrt{2}+1)^{N/3}} \mathrm{Tr}\begin{pmatrix} 1 & 1 \\ 2 & 1 \end{pmatrix}^{N/3-1}\begin{pmatrix} 1 & 0 \\ 2 & 1 \end{pmatrix} = \frac{M_S}{3\sqrt{2}}. \tag{18}$$

We thus see that for $B = B_1 = 1.92$ Tesla, $M \simeq 0.42$ (in units of μ_B). These analytical values agree well with the numerical values of the location of the crossing point I mentioned above. (For $B = B_1$ and B_2, we note that the excited states are separated from the ground states by finite gaps; hence they do not affect the locations of the crossing points I and III at very low temperatures.)

For $B = B_2 = 4.81$ Tesla, the degeneracy of $3^{N/3}$ arises because the Ising spins in each group of three successive cobalts can independently take the orientations $\uparrow\downarrow\uparrow$, $\downarrow\uparrow\uparrow$ or $\uparrow\uparrow\uparrow$; the average magnetization is therefore given by $5M_S/9 = 0.99$ which agrees well with the location of the crossing point III. However, the numerically obtained value of the magnetic field at this point does not agree so well with the analytically obtained value.

For $B_1 < B < B_2$, we can see why there is a degeneracy of $2^{N/3}$. In each group of three successive cobalts, the Ising spins $(\sigma_1, \sigma_2, \sigma_3)$ can take the orientations $\uparrow\downarrow\uparrow$ or $\downarrow\uparrow\uparrow$; different groups of three cobalts can take either of these two orientations independently of each other. The magnetization of all these states is given by $M_S/3 = 0.59$; this roughly agrees with the location of the crossing point II in Fig. 2. We will now see why this crossing point occurs at a magnetic field value of 3.36 Tesla.[8] Let us consider the lowest excitations lying above the two degenerate configurations mentioned above. There are two kinds of excitations: (i) a cobalt spin can flip from down to up, i.e., a group of three cobalts can become $\uparrow\uparrow\uparrow$, and (ii) a cobalt spin labeled σ_3 whose neighbors are pointing up can flip from up to down, i.e., a group of six cobalts can change from $\downarrow\uparrow\uparrow\uparrow\downarrow\uparrow$ to $\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow$. The first kind of excitation costs an energy

$$E_+ = \frac{J}{4}(\delta\theta_1 + 2\delta\theta_2 + \delta\theta_3) - \mu_B g_{\mathrm{eff}} \frac{B}{\sqrt{3}}, \tag{19}$$

and increases the total magnetization by $\mu_B g_{\mathrm{eff}}/\sqrt{3}$. The second kind of excitation costs an energy

$$E_- = -\frac{J}{4}(\delta\theta_1 + \delta\theta_2 + 2\delta\theta_3) + \mu_B g_{\mathrm{eff}} \frac{B}{\sqrt{3}}, \tag{20}$$

and decreases the total magnetization by $\mu_B g_{\mathrm{eff}}/\sqrt{3}$. The energy costs of the two excitations are equal at a magnetic field given by $B_0 = (B_1 + B_2)/2 = 3.36$ Tesla, where we have used Eqs. (13) and (14). At this value of the magnetic field, and at very low temperatures, the concentrations of the two kinds of excitations will be small and equal; hence the magnetization will lie at its plateau value of $M_S/3$. This explains why the different plots in Fig. 2 cross at this value of the magnetic field and magnetization.

In Fig. 3, we present the magnetic susceptibility $\chi = (\partial M/\partial B)_T$ as a function of the magnetic field for different temperatures; these plots are just given by the derivatives of the plots in Fig. 2. At the lowest temperature of 0.5 K, we see peaks at the ends of the magnetization plateaus, i.e., at $B = B_1$ and $B = B_2$. The peaks get washed out with increasing temperature.

In Fig. 4, we show the entropy versus the magnetic field for the same values of parameters and same temperatures as in Fig. 2. We see that at the lowest temperature of 0.5 K, the entropy has a substantial value in the range $B_1 < B < B_2$, has peaks at B_1 and B_2, and is quite small for $B < B_1$ and $B > B_2$; the values of the entropy at B_1 and B_2 and on the plateau in between are in agreement with Eq. (15). As the temperature is raised, the entropy increases in such a way as to wash out these features; this is consistent with the disappearance of the magnetization plateaus in Fig. 2.

Figure 5 shows the specific heat $C_V = T(\partial S/\partial T)_B$ as a function of magnetic field at different temperatures. An interesting feature to note is that at the lowest temperature of 0.5 K, the specific heat vanishes with a parabolic shape at the ends of magnetization plateaus shown in Fig. 2, i.e., at $B = B_1$ and B_2. This can be understood as follows. If ΔE denotes the energy of a state with respect to the ground state, the contribution of that state to the specific heat is proportional to

$$\frac{C_V}{k_B} \sim \left(\frac{\Delta E}{k_B T}\right)^2 e^{-\Delta E/k_B T}. \tag{21}$$

At the lowest temperature and at $B = B_1$ and B_2, it turns out that all the states either have $\Delta E \gg k_B T$ (hence their contributions to the specific heat are exponentially small and can be ignored), or $\Delta E \ll k_B T$. For the latter states, one can show that ΔE vanishes near $B = B_1$ and B_2 as $(\mu_B g_{\mathrm{eff}}/\sqrt{3})|B - B_1|$ and $(\mu_B g_{\mathrm{eff}}/\sqrt{3})|B - B_2|$, respectively. From Eq. (21), we see that the contributions of these states to the specific heat go as $(B - B_1)^2/T^2$ and $(B - B_2)^2/T^2$, respectively. This explains the behavior of the specific heat in Fig. 5 near $B = B_1$ and B_2.

In Fig. 6, we show the magnetization versus the magnetic field applied in the *a*-*b* plane for six possible directions (parameterized by the angle ϕ with respect to the projection of $\mathbf{e}_1$ on that plane), for the same values of parameters used in Fig. 2, and a temperature of 1 K. The six directions were chosen with equiangular spacing to cover the full range of possible directions from 0° to 180°; we recall that the behavior of an Ising model does not change if the sign of the magnetic field is reversed, i.e., if $\phi \to \phi + 180°$. (The projections of the easy axes of the three cobalts on the *a*-*b* plane are given by 0°, 120°, and 240°. Since we have chosen $\delta\theta_1 = \delta\theta_2$, we also have a symmetry under $\phi \to 120° - \phi$. This explains why the plots for $\phi = 30°$ and 90° are identical, as are the plots for $\phi = 0°$ and 120°.) We see in Fig. 6 that there is a plateau at intermediate values of the magnetization only for a magnetic field direction given by 60°; even that plateau is much weaker than the plateau seen in Fig. 2 at the same temperature.

Figure 7 shows the magnetization versus the magnetic field applied in the *a*-*b* plane, averaged over the six directions indicated in Fig. 6, for various temperatures. We see that there is no discernible plateau at intermediate magnetization even at the lowest temperature of 0.5 K. This may explain why no plateau is observed experimentally when a magnetic field is applied in the *a*-*b* plane. Since the system consists of several molecular chains, and these may happen to be rotated with respect to each other by various amounts in the *a*-*b* plane, it is possible that the behavior observed experimentally is an average of the different directions of the magnetic field in that plane.

Another pattern of signs and magnitudes of the parameters $\delta\theta_1$, $\delta\theta_2$, and $\delta\theta_3$ which leads to magnetization plateaus at 0 and $M_S/3$, for a magnetic field applied along the *c* axis, is given by the conditions

$$\text{(i)}\ \delta\theta_1 + \delta\theta_2 > 0,\ \delta\theta_1 + \delta\theta_3 < 0,\ \delta\theta_2 + \delta\theta_3 < 0,$$

$$\text{(ii)}\ \delta\theta_2 \geqslant \delta\theta_1,\ \text{and}\ \delta\theta_1 + 4\delta\theta_2 + 3\delta\theta_3 > 0. \qquad (22)$$

We will not discuss the details of this case since the analysis and magnetization plots obtained are similar to the case of Eqs. (12) considered above.

To summarize, we have presented a model for CoPhOMe in which the tilt angles of the easy axes of the cobalt spins with respect to the *c* axis vary with period three. We have shown that for certain patterns of these tilt angles, the magnetization at low temperatures exhibits plateaus at nontrivial values if a magnetic field is applied along the *c* axis, but not if it is applied in the *a*-*b* plane. It would be interesting to study dynamical effects (arising from the time-dependence of the magnetic field) for the magnetization; such effects have been discussed earlier for the model in which all the angles θ_i are equal and a magnetic field is applied along the *c* axis.[3,4]

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