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Thermodynamics of the Mn₁₂-ac molecule in a skew magnetic field at $T \gtrsim 21$ K

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Abstract

We derive the high-temperature expansion of the Helmholtz free energy of the quantum and classical models for the Mn₁₂-ac molecule in the presence of a skew magnetic field, including the transverse term in the Hamiltonians, for $T \gtrsim 21$ K. In this region of temperature, we show that the transverse term can give a measurable contribution to the x component of the magnetization. We obtain the specific heat per site of a powder sample of Mn₁₂-ac under a constant magnetic field. For strong skew magnetic fields ($h/D > 1$), the specific heat differs up to 20% from its value of a crystal sample under purely longitudinal magnetic fields. Finally, we obtain that in the limit $T \rightarrow \infty$, the values of the classical and quantum specific heat differ; in particular, for $\hbar = 0$ this difference is 0.96%.

1. Introduction

The Mn₁₂-ac molecule is a classical example of a single-magnetic molecule (SMM) that is expected to have nanomagnetic behavior. It was chemically synthesized by Lis in 1980 [1]. Since then, molecular chemistry has achieved designing new magnetic clusters that present nanomagnetic behavior [2]. The Mn₁₂-ac molecule is described by a spin Hamiltonian ($S = 10$) at the ground state. The properties of the Mn₁₂-ac cluster have been widely studied; in the 1980s and 1990s, its magnetic behavior at very low temperatures was described by a term proportional to $(S_+^4 + S_-^4)$ that breaks the conservation of the spin z component [3, 4]. At temperatures below 3 K it has been experimentally verified that the presence of even and odd numbers of transitions in the hysteresis curve cannot be explained by this non-conserving S_z term. In 2001 Chudnovsky and Garanin [5, 6] included the new transverse term $E(S_x^2 - S_y^2)$ in the Hamiltonian of this system. This term comes from dislocations in Mn₁₂-ac crystals. Due to this distortion, an external longitudinal magnetic field acting on the SMM induces the presence of a transverse component in the

x direction [6]. Recently Su *et al* [7] used the $S = 10$ Hamiltonian, including the E -term, to numerically reproduce the number of steps in the low-temperature stepwise hysteresis curve of Mn₁₂-ac [8].

Another interesting point about the Mn₁₂-ac molecule is that, due to the high value of spin, it is likely to behave classically.

In [9] Lascialfari *et al* affirm that the correlation effects leading to the $S = 10$ ground state of the Mn₁₂-ac happen below room temperature. They consider the high-temperature region of this SMM as $T \gtrsim 200$ K; that makes the $S = 10$ Hamiltonian an interesting model to be studied at finite temperature.

Although the thermodynamics of the $S = 10$ Hamiltonian can be solved numerically for all temperatures, it would be interesting to have a high-temperature expansion (β expansion) of its Helmholtz free energy (HFE), as a function of arbitrary values of the parameters, and in the presence of an external magnetic field with longitudinal (h_z) and transverse (h_x) components. The expansions of the thermodynamical functions derived from this analytic HFE would easily allow fitting of the experimental data, including the effects due to the transverse term. The β expansion of the HFE, as

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a function of the arbitrary values of the parameters of the Hamiltonian, opens the possibility of determining suitable ranges of values for such parameters so that some desirable behavior is achieved, when designing new magnetic clusters.

The aim of this paper is fourfold: (i) to derive the β expansion of the HFE of the quantum and the classical models of the Mn_{12} -ac molecule, including the transverse term in the Hamiltonian, for arbitrary constant magnetic field with h_x and h_z components; (ii) to check if the terms in the Hamiltonian related to the stepwise low-temperature hysteresis curve which gives a significant contribution to the thermodynamical functions at $T \gtrsim 21$ K; (iii) to calculate the average specific heat per site of a powder sample of the SMM that is uniformly distributed in the (x, z) plane; and (iv) to verify if the thermodynamic behavior of the quantum model of the SMM can be safely approximated by its classical version. We calculate the β expansion of the HFE of the quantum ($S = 10$) and the classical models of the Mn_{12} -ac up to order β^{18} and β^{19} , respectively. In section 2 we adapt the results of [10] to the one-site model and show that, for this type of non-interacting Hamiltonian, we only need to calculate the functions $H_{1,1}^{(i)}$, where $i \in \{1, 2, \dots, n\}$, when calculating the expansion of the HFE up to order β^n . In section 3 we study the thermodynamics of the Mn_{12} -ac in the region of $T \gtrsim 21$ K. In section 3.1 we present the Hamiltonian under consideration and the main features of the β expansion of the quantum and the classical HFEs; in section 3.2 we verify the importance of the C and E terms in the Hamiltonian to the magnetization and the specific heat of the quantum model; in section 3.3 we compare the specific heats of a powder sample and an SMM crystal, under longitudinal magnetic field; and in section 3.4 we verify if the magnetization and specific heat per site of the quantum model can be replaced by their respective classical versions for $T \gtrsim 21$ K, including the limit $T \rightarrow \infty$. Section 4 presents our conclusions. The β expansions of the quantum and classical models are extremely large expressions, but in appendices A and B we present them up to order $(D\beta)^3$ as functions of the parameters of their respective Hamiltonians.

2. The β expansion of the HFE of the one-site model

In [10] Rojas *et al* present a closed relation for the coefficients of the cumulant expansion of the HFE of any homogeneous chain model subject to periodic space conditions and first-neighbor interaction. The general form of the Hamiltonian is

$$\mathbf{H} = \sum_{i=1}^N \mathbf{H}_{i,i+1}, \quad (1)$$

where N is the number of sites in the chain. In this section we review the steps in [10] for calculating the β expansion of the HFE, in the thermodynamical limit ($N \rightarrow \infty$), of N homogeneously distributed non-interacting sites ($\mathbf{H}_{i,i+1} \equiv \mathbf{H}_i$).

The β expansion [11] of the thermodynamical limit of the HFE for the model (1) is

$$\begin{aligned} \mathcal{W}(\beta) &= \lim_{N \rightarrow \infty} -\frac{1}{N\beta} \ln[\mathcal{Z}(\beta)] \\ &= -\frac{1}{\beta} [\ln(\text{tr}_1(\mathbf{1}_1)) + \ln(1 + \xi(\beta))], \end{aligned} \quad (2)$$

in which $\mathcal{Z}(\beta)$ is the partition function, $\beta = \frac{1}{kT}$, k is the Boltzmann constant and T is the absolute temperature. The operator $\mathbf{1}_i$ is the identity operator of the i th site, with $i = 1, 2, \dots, m+1$, and $\text{tr}_1(\mathbf{1}_1)$ corresponds to its trace, that is, the Hilbert space dimension of each site in the chain; for a given spin S we have $\text{tr}_1(\mathbf{1}_1) = (2S + 1)$ [11].

The function $\xi(\beta)$ is defined as

$$\xi(\beta) = \sum_{n=0}^{\infty} \frac{1}{(n+1)!} \frac{\partial^n}{\partial \lambda^n} (\varphi(\lambda)^{n+1}) \Big|_{\lambda=1} \quad (3)$$

in which the auxiliary function $\varphi(\beta)$ is given by

$$\varphi(\lambda) = \sum_{m=1}^{\infty} \sum_{n=m}^{\infty} \frac{(-\beta)^n}{\lambda^m} H_{1,m}^{(n)}. \quad (4)$$

The functions $H_{1,m}^{(n)}$ correspond to the ‘connected’ strings with n operators $\mathbf{H}_{i,i+1}$ so that m of them are distinct, that is,

$$H_{1,m}^{(n)} = \sum_{\{n_i\}}^{n-m+1} \left\langle \prod_{i=1}^m \frac{\mathbf{H}_{i,i+1}^{n_i}}{n_i!} \right\rangle_g. \quad (5)$$

The notation $\sum_{\{n_i\}}^n$ stands for the summation over the indices $n_i = 1, \dots, n - m + 1$, where $i = 1, 2, \dots, m$, but under the restriction $\sum_{i=1}^m n_i = n$. The index m satisfies the condition $1 \leq m \leq n$. The g traces (generalized traces) are commuting objects defined as

$$\begin{aligned} \langle \mathbf{H}_{i_1,i_1+1}^{n_1} \mathbf{H}_{i_2,i_2+1}^{n_2} \cdots \mathbf{H}_{i_m,i_m+1}^{n_m} \rangle_g &\equiv \frac{n_1! \cdots n_m!}{n!} \\ &\times \sum_{\mathcal{P}} \langle \mathcal{P}(\mathbf{H}_{i_1,i_1+1}^{n_1}, \mathbf{H}_{i_2,i_2+1}^{n_2}, \dots, \mathbf{H}_{i_m,i_m+1}^{n_m}) \rangle, \end{aligned} \quad (6)$$

where $\sum_{i=1}^m n_i = n$ with $n_i \neq 0$, $i = 1, 2, \dots, m$, and the indices i_k , $k = 1 \cdots m$ are all distinct. By definition, $\langle \mathcal{P}(\mathbf{H}_{i_1,i_1+1}^{n_1}, \mathbf{H}_{i_2,i_2+1}^{n_2}, \dots, \mathbf{H}_{i_m,i_m+1}^{n_m}) \rangle$ represents the normalized trace of a distinct permutation \mathcal{P} of the n operators inside the parentheses, that is, traces of operators normalized by the dimension of the Hilbert space they act upon. For instance

$$\langle \mathbf{H}_{12}^{n_1} \mathbf{H}_{23}^{n_2} \cdots \mathbf{H}_{m,m+1}^{n_m} \rangle \equiv \frac{\text{tr}_{1,2,\dots,m+1} [\mathbf{H}_{12}^{n_1} \mathbf{H}_{23}^{n_2} \cdots \mathbf{H}_{m,m+1}^{n_m}]}{\text{tr}_1(\mathbf{1}_1) \cdot \text{tr}_2(\mathbf{1}_2) \cdots \text{tr}_{m+1}(\mathbf{1}_{m+1})}. \quad (7)$$

We refer the reader to [10] for further details on this approach.

The Hamiltonian (1) of a model of N non-interacting sites is rewritten as

$$\mathbf{H} = \sum_{i=1}^N \mathbf{H}_i, \quad (8)$$

with

$$[\mathbf{H}_i, \mathbf{H}_j] = 0, \quad i, j = 1, 2, \dots, N; \quad (9)$$

this is a particular case of the Hamiltonian (1). Consequently the results (2)–(7) can be applied to the calculation of the HFE for (8), independent of the particular way in which the N non-interacting sites are spatially distributed. As a consequence of

the previous commutation relation, we obtain that the g trace and the normalized trace of operators turn out to be identical:

$$\langle \mathbf{H}_{i_1, i_1+1}^{n_1} \mathbf{H}_{i_2, i_2+1}^{n_2} \cdots \mathbf{H}_{i_m, i_m+1}^{n_m} \rangle_g = \left\langle \prod_{j=1}^m \mathbf{H}_{i_j}^{n_j} \right\rangle_{i_1 \cdots i_m}. \quad (10)$$

Substituting result (10) in relation (5), we have

$$H_{1,m}^{(n)} = \sum_{\{n_i\}}^{n-m+1} \left\langle \prod_{i=1}^m \frac{\mathbf{H}_i^{n_i}}{n_i!} \right\rangle = \sum_{\{n_i\}}^n \left[\prod_{i=1}^m H_{1,1}^{(n_i)} \right] \quad (11)$$

and $H_{1,1}^{(n_i)} = \frac{1}{n_i!} \frac{\text{tr}_1(\mathbf{H}_1^{n_i})}{\text{tr}_1(\mathbf{1})}$.

In order to derive the β expansion of the HFE of both quantum and classical models in the thermodynamical limit, it suffices to calculate the functions $H_{1,1}^{(n)}$, $n = 1, 2, 3, \dots$, of the respective model. The result (11) is also valid for classical models.

3. Thermodynamics of the Mn₁₂-ac at $T \gtrsim 21$ K

3.1. The Hamiltonian of the Mn₁₂-ac

In order to reproduce the stepwise magnetic hysteresis curve of the Mn₁₂-ac molecular clusters at low temperature [12], Chudnovsky and Garanin [5, 6] proposed that local rotations of the anisotropy axes due to dislocations are responsible for odd tunneling resonances. This static deformation generates a transverse component of the magnetic field even if the cluster is in the presence of an external longitudinal magnetic field [6].

The one-site Hamiltonian that fits the experimental data of the Mn₁₂-ac molecular clusters, in the presence of a skew magnetic field, at the i th site is [13]

$$\mathbf{H}_i = -D(S_z^i)^2 - B(S_z^i)^4 - C[(S_+^i)^4 + (S_-^i)^4] + E[(S_x^i)^2 - (S_y^i)^2] - h_x S_x^i - h_z S_z^i, \quad (12)$$

where S_x^i , S_y^i and S_z^i are the spin operators for $S = 10$, at the i th site; for the creation and destruction operators we have $S_{\pm}^i \equiv \frac{1}{\sqrt{2}}(S_x^i \pm iS_y^i)$. The total Hamiltonian is $H = \sum_i^N \mathbf{H}_i$, where N is the number of Mn₁₂ molecules in the medium (we take $N \rightarrow \infty$ in the thermodynamical limit). The constant external magnetic field has components h_x and h_z , the direction z being the easy axis. We introduce a transverse component of the magnetic field in the x direction in order to mimic the transverse magnetic field due to dislocations in Mn₁₂-ac crystals. The terms proportional to the parameters C and E in (12) do not commute with S_z and are responsible for transitions among its eigenstates. The term proportional to E appears due to local rotations of the easy axis [5, 6]. We can write the components of the external magnetic field, constrained to the xz plane without loss of generality, as functions of the angle θ between the constant external magnetic field and the easy axis (z axis):

$$h_x = h \sin(\theta) \quad \text{and} \quad h_z = h \cos(\theta), \quad (13)$$

where $\theta \in [0, 2\pi]$. The magnetic field has norm h ($h = |\vec{h}|$).

⁵ The definition of these operators differs from that used in previous articles on the subject. In Hamiltonian (12) we have: $C = -4 C_{\text{Mertes}}$.

Using the results of section 2, we calculate the high-temperature expansion of the HFE of Hamiltonian (12), for arbitrary values of the parameters, up to order $(D\beta)^{18}$ for the quantum model (see equation (A.1)) and up to order $(D\beta)^{19}$ for the classical model (see equation (B.4)). The parameter $(D\beta)$ is dimensionless. In appendices A and B we present these results up to order $(D\beta)^3$. Regarding these expressions, we observe that:

- (1) each coefficient of $(D\beta)^i$, $i = 1, 2, \dots, n$, in the expansions (A.1) ($n = 18$) and (B.4) ($n = 19$) is exact;
- (2) the HFE of both models are even functions of h_x and h_z ;
- (3) if $E = 0$ (i.e. no distortion) and $h_x = 0$ (no transverse component of the magnetic field) the HFE (either classical or quantum) is an even function of the parameter C , whereas for $E \neq 0$ or $h_y \neq 0$ this parity is destroyed;
- (4) the zero-field static magnetic susceptibility tensor has non-null diagonal elements $\chi_{xx}(\beta)$ and $\chi_{zz}(\beta)$ for the quantum and classical models;
- (5) the \mathcal{M}_x component of the magnetization vector is an even function of h_z and an odd function of h_x ; the \mathcal{M}_z component is an even function of h_x and an odd function of h_z .

In order to study the thermodynamics of the Mn₁₂-ac molecular cluster for $T \gtrsim 21$ K, we use the values of [13] for the parameters in Hamiltonian (12):

$$\frac{D}{k} = +0.548(3) \text{ K};$$

$$\frac{B}{k} = 1.173(4) 10^{-3} \text{ K} \quad \text{and} \quad \frac{C}{k} = \mp 1.16 10^{-4} \text{ K}, \quad (14)$$

k being the Boltzmann constant, and replace them in the expansions (A.1) and (B.4).

More recently, Su, Shen and Tao [7] proposed a Gaussian distribution

$$P(E) = \frac{1}{\sqrt{2\pi}} \frac{1}{\sigma} e^{-\frac{(E-E_0)^2}{2\sigma^2}}, \quad (15)$$

for the parameter $E \in (-\infty, \infty)$.

The numerical analysis performed in [7] for the experimental values (14) of parameters gives

$$\frac{E_0}{k} = +0.018 \text{ K} \quad \text{and} \quad \frac{\sigma}{k} = 0.006 \text{ K}. \quad (16)$$

3.2. The contribution of the non-diagonal terms at $T \gtrsim 21$ K

From the β expansions of the HFE of the quantum (see equation (A.1)) and the classical (see equation (B.4)) versions of Hamiltonian (12), it is simple to calculate the high-temperature expansion of some thermodynamical functions since they are functions of arbitrary values of the parameters in the Hamiltonian. We will restrict our discussion to the impact of the non-diagonal terms on the magnetization and on the specific heat per site for several values of the angle θ , and for $T \gtrsim 21$ K. Instead of considering a definite value for the parameter E , we will average over the Gaussian distribution (15).

In what follows we present the steps to calculating the contribution of the distortion term to any thermodynamical function \mathcal{G} . The β expansion of \mathcal{G} in the dimensionless parameter $(D\beta)$ can be written as

$$\mathcal{G}(D, B, C, E, h_x, h_z; \beta) = (D)^{l_0} \sum_{n=0}^{n_0} g_n(\tilde{B}, \tilde{C}, \tilde{E}, \tilde{h}_x, \tilde{h}_z)(D\beta)^n, \quad (17)$$

where $\tilde{B} \equiv B/D$, $\tilde{C} \equiv C/D$, $\tilde{E} \equiv E/D$, $\tilde{h}_x \equiv h_x/D$ and $\tilde{h}_z \equiv h_z/D$. The values of n_0 and l_0 depend on the particular thermodynamical function under consideration. The coefficients $g_n(\tilde{B}, \tilde{C}, \tilde{E}, \tilde{h}_x, \tilde{h}_z)$ are obtained from a suitable derivative of the high-temperature expansion of either the quantum or the classical HFE—equations (A.1) and (B.4), respectively.

The average of \mathcal{G} over E is

$$\langle \mathcal{G} \rangle_E \equiv \int_{-\infty}^{\infty} dE P(E) \mathcal{G}(D, B, C, E, h_x, h_z; \beta), \quad (18)$$

where $P(E)$ is an experimental probability distribution of the parameter E . The expansion (17) is a power function in E . For any distribution $P(E)$, it is simple to use algebraic software to calculate the integral on the rhs of equation (18). In the present paper, we use the Gaussian distribution (15) for $P(E)$.

Substituting expressions (15) and (17) in relation (18), we obtain the high-temperature expansion of $\langle \mathcal{G} \rangle_E$:

$$\langle \mathcal{G} \rangle_E = \frac{(D)^{l_0}}{\sqrt{2\pi}} \sum_{n=0}^{n_0} \left[\frac{(D\beta)^n}{\tilde{\sigma}} \times \int_{-\infty}^{\infty} d\tilde{E} g_n(\tilde{B}, \tilde{C}, \tilde{E}, \tilde{h}_x, \tilde{h}_z) e^{-\frac{(\tilde{E}-\tilde{E}_0)^2}{2\tilde{\sigma}^2}} \right], \quad (19)$$

where $\tilde{E}_0 \equiv E_0/D$ and $\tilde{\sigma} \equiv \sigma/D$.

We begin by studying the averaged components of the magnetization $\langle \mathcal{M}_i \rangle_E = -\frac{\partial \langle W \rangle_E}{\partial h_i}$, $i \in \{x, z\}$, where $\langle W \rangle_E$ is the Gaussian average expansion when (A.1) or (B.4) are substituted in equation (19) with the set of parameters (14) and (16).

From the manipulation of the β expansions of the quantum and classical $\langle \mathcal{M}_x \rangle_E$ we verify that the convergence region of these expansions decreases as θ vanishes (the limit of a purely longitudinal magnetic field). In order to determine the range of validity of the β expansion of \mathcal{M}_x , as a function of $(D\beta)$, we impose that in the interval $\theta \in [\pi/3, \pi/2]$, the contribution of the term of order $(D\beta)^{18}$ in this expansion is $\lesssim 0.3\%$.

We remind that the term proportional to E in Hamiltonian (12) is introduced to explain the stepwise magnetic hysteresis curve at very low temperatures [5, 6]. Figure 1(a) shows the contribution of this term to the thermodynamics of the SMM for $T \gtrsim 17.8$ K by plotting the per cent difference of the quantum \mathcal{M}_x in its presence ($E \neq 0$) and in its absence ($E = 0$), as a function of $(D\beta)$ and θ , for $D\beta \in [0, 0.031]$, $\theta \in \{\pi/3, \pi/4, \pi/2\}$ at $h/D = 3.7$. The per cent difference is defined as

$$\Delta_E \mathcal{M}_x(\beta) \equiv 100\% \times \left| \frac{\langle \mathcal{M}_x(E_0, \sigma; \beta) \rangle_E - \mathcal{M}_x(E = 0; \beta)}{\mathcal{M}_x(E = 0; \beta)} \right|. \quad (20)$$

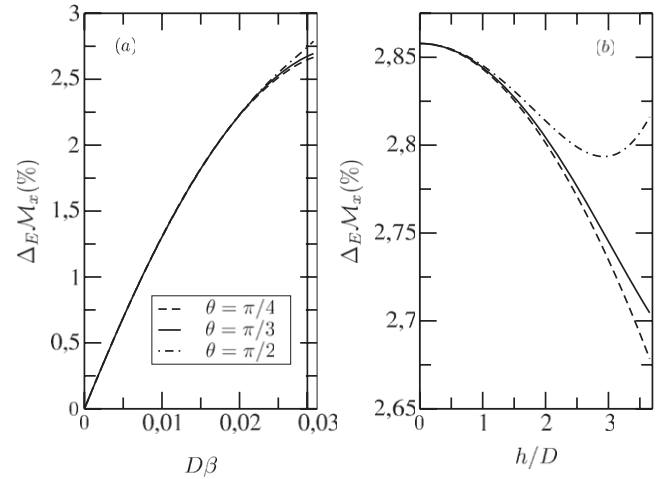


Figure 1. The per cent difference $\Delta_E \mathcal{M}_x(\%)$ at $\theta = \pi/3$ (solid line), $\pi/4$ (dashed line) and $\pi/2$ (dotted–dashed line). Panel (a) shows $\Delta_E \mathcal{M}_x$ versus $(D\beta)$ in which $(D\beta) \in [0, 0.031]$ (i.e. $T \gtrsim 18.1$ K) and at $h/D = 3.7$; in (b) this per cent difference is plotted as a function of h/D , in which $h/D \in [0, 3.7]$ and $T = 18.9$ K.

In figure 1, we use the set of parameters (14) and (16) for the constants in the Hamiltonian (12). In writing equation (20), we calculate the average (19) over all possible values of E .

In figure 1(b) this difference (20) is plotted as a function of h/D for $\theta \in \{\pi/3, \pi/4, \pi/2\}$ at $T = 18.9$ K. From the analysis of these curves, we verify that $\Delta_E \mathcal{M}_x$ can be larger than 2% even in the region of $T \gtrsim 17.8$ K.

The unexpected behavior in figure 1(b) is that the per cent difference (20) is a decreasing function of h/D .

Depending on the experimental precision of data about the x component of the magnetization, the contribution of the distortion term proportional to E must be taken into account in calculating $\mathcal{M}_x(T)$ for temperatures up to 32 K, since $\Delta_E \mathcal{M}_x(\beta)$ is larger than 2%.

The term proportional to the parameter C in (12) is also responsible for the stepwise magnetic hysteresis curve at low temperatures (we call it the C term). In order to verify if this term gives a significant contribution to the quantum \mathcal{M}_x , we define the per cent difference $\Delta_C \mathcal{M}_x(\beta)$:

$$\Delta_C \mathcal{M}_x(\beta) \equiv 100\% \times \left| \frac{\langle \mathcal{M}_x(E_0, \sigma, C; \beta) \rangle_E - \langle \mathcal{M}_x(E_0, \sigma, C = 0; \beta) \rangle_E}{\langle \mathcal{M}_x(E_0, \sigma, C = 0; \beta) \rangle_E} \right|. \quad (21)$$

We obtain that the highest value of (21), for $T \gtrsim 18.3$ K and for $h/D \in [0, 3.7]$, occurs when the external magnetic field is almost aligned with the easy axis z ($\theta \ll 1$) and the magnetic field is near zero. Under those conditions we have $\Delta_C \mathcal{M}_x \lesssim 0.025\%$.

We point out that [6] shows that, in the presence of a longitudinal magnetic field, the dislocations in the crystal induce a transverse x component of the magnetic field.

For the z component of the magnetization of the quantum model of SMM, we define per cent differences similar to (20) and (21) in order to verify the contributions of the E and C

terms to $\langle \mathcal{M}_z \rangle_E$ for $T \gtrsim 18.3$ K. Again, for $h/D \neq 0$, the highest contribution of the E term happens for $\theta \rightarrow \pi/2$, although $\langle \mathcal{M}_z(\theta = \pi/2) \rangle_E = 0$. For $(D\beta) \in [0, 0.03]$ and $h/D \in (0, 3.7]$ we obtain that $\Delta_E \mathcal{M}_z(\beta) \lesssim 0.014\%$ whereas $\Delta_C \mathcal{M}_z(\beta) \lesssim 0.003\%$.

In the region of temperature $T \gtrsim 18.3$ K, the xz element of the magnetic susceptibility tensor ($\chi_{i,j} = -\frac{\partial^2 W}{\partial h_i \partial h_j}$, where $i, j \in \{x, z\}$) is at least one order of magnitude smaller than the xx and zz elements of this tensor for $\theta \in [0, \pi/2]$ and $h/D \in [0, 3.7]$. In these intervals, the value of χ_{zz} is at least twice as large as the value of χ_{xx} . We point out that χ_{xx} and χ_{zz} are non-null at $\theta = 0$ and $\theta = \pi/2$, respectively.

The effective Curie constant of χ_{zz} (that is, $C_{zz} \equiv T \chi_{zz}$), T being the absolute temperature, shows the same behavior as shown in figure 1 of [9] for $h/D = 0.245$. From the high-temperature expansion of χ_{zz} we obtain that $\chi_{zz} = 40.9$ at $T = 20$ K and that $\chi_{zz} = 24.2$ at $T = 100$ K; consequently, the same decrease of χ_{zz} by almost a factor of 2 is exhibited, when the temperature increases from 20 to 100 K, as mentioned in [9].

Although the value of χ_{xz} is one order of magnitude lower than that of the diagonal elements of the magnetic susceptibility tensor, defining a per cent difference analogous to equation (20) yields $\Delta_E \chi_{xz}(\beta)$ to be larger than 4% for $\theta \sim \pi/2$, $T \gtrsim 21.9$ K and $h/D \neq 0$.

Similarly to the z component of the magnetization, the per cent difference of the specific heat per site $\mathcal{C}(\beta)$ ($\mathcal{C}(\beta) = -\beta^2 \frac{\partial^2 \langle \beta W \rangle}{\partial \beta^2}$) of the quantum models (with and without crystal dislocations) for $(D\beta) \in [0, 0.026]$ ($T \gtrsim 21.1$ K) and $h/D \in [0, 3.0]$ is smaller than 0.02%. (An analogous definition to equation (20) has been applied for the specific heat.) For a fixed norm h of the external magnetic field, the highest value of this per cent difference occurs at $\theta = \pi/2$. We also verify the contribution of the C term in (12) to the specific heat by defining a per cent difference analogous to (21). For $(D\beta) \in [0, 0.026]$ and $h/D \in [0, 3.0]$, this difference is $\lesssim 0.02\%$, and for $T \gtrsim 46$ K and $h/D \in [0, 3.0]$, this difference is almost insensitive to the value of the angle θ .

A good approximation for the HFE of the quantum and classical versions of the Mn_{12} -ac crystals for $T \gtrsim 46$ K, except for the calculation of the transverse component of the magnetization, is obtained by substituting the parameters (14) in expansions (A.1) and (B.4) and taking $C = 0$ and $E = 0$. The expansion of the HFE of the quantum model of Mn_{12} -ac, up to order $\mathcal{O}(T^{-3})$, is

$$\begin{aligned} W_{\text{quant}}(T)/k &= -\ln(21)T - 22.923\,391\,33 \\ &+ \left(-\frac{55\bar{h}_z^2}{3} - 231.632\,4426 - \frac{55\bar{h}_x^2}{3} \right) \frac{1}{T} \\ &+ (-1234.567\,484 + 175.658\,2714\bar{h}_x^2 \\ &- 351.316\,5430\bar{h}_z^2) \frac{1}{T^2} + \left(-2651.710\,866\bar{h}_z^2 \right. \\ &+ 1384.084\,800\bar{h}_x^2 + 6426.167\,002 + \frac{2431}{36}\bar{h}_x^4 \\ &+ \left. \frac{2431}{18}\bar{h}_z^2\bar{h}_x^2 + \frac{2431}{36}\bar{h}_z^4 \right) \frac{1}{T^3} + \mathcal{O}\left(\frac{1}{T^4}\right), \end{aligned} \quad (22)$$

and of its classical version, is

$$\begin{aligned} W_{\text{class}}(T)/k &= -\ln(4\pi)T - 22.931\,993\,33 \\ &+ \left(-233.845\,9236 - \frac{55\bar{h}_x^2}{3} - \frac{55\bar{h}_z^2}{3} \right) \frac{1}{T} \\ &+ (177.089\,4540\bar{h}_x^2 - 1296.587\,019 \\ &- 354.178\,9079\bar{h}_z^2) \frac{1}{T^2} \\ &+ \left(-2777.549\,329\bar{h}_z^2 + 1388.774\,664\bar{h}_x^2 \right. \\ &+ 5761.517\,828 + \frac{605}{9}\bar{h}_x^4 \\ &+ \left. \frac{1210}{9}\bar{h}_z^2\bar{h}_x^2 + \frac{605}{9}\bar{h}_z^4 \right) \frac{1}{T^3} + \mathcal{O}\left(\frac{1}{T^4}\right). \end{aligned} \quad (23)$$

In equations (22) and (23), we use the notation: $\bar{h}_x \equiv \frac{h_x}{k}$ and $\bar{h}_z \equiv \frac{h_z}{k}$. The terms in expansions (22) and (23) are in K (kelvin).

We should say a word of caution about comparing the thermodynamical functions derived from the HFEs (22) and (23) (and the results in appendices A and B) with the experimental data. At the intermediate range of temperature where our results are valid, other factors like the thermal population of excited spin states can also influence the thermodynamics of the Mn_{12} -ac crystals.

3.3. The specific heat in a powder sample of Mn_{12} -ac

In a powder sample of Mn_{12} -ac molecules, the angle θ between the easy axis (z axis) and the constant external magnetic field \bar{h} (constrained to the xz plane, without loss of generality) varies in the interval $[0, 2\pi]$. The high-temperature expansion of the quantum and classical specific heat per site $\mathcal{C}(h, \theta; \beta)$ up to order $(D\beta)^{19}$ and $(D\beta)^{20}$ are derived from expansions (A.1) and (B.4), respectively. This thermodynamical function is even in h_x and h_z . The average specific heat (with respect to the orientation of the chain to the external constant magnetic field) of the powder sample of the Mn_{12} -ac is given by

$$\bar{\mathcal{C}}(\beta) = \int_0^{\pi/2} \mathcal{C}(h, \theta; \beta) P(\theta) d\theta, \quad (24)$$

where $P(\theta) d\theta$ is the probability of finding an angle between θ and $\theta + d\theta$ between the easy axis of the SMM and the external magnetic field. This distribution of probability depends on the experimental arrangement. Since our expansions of the quantum and classical specific heat are continuous functions of θ , they can be used in the calculation of $\bar{\mathcal{C}}(\beta)$ for any particular distribution $P(\theta)$.

Assuming a homogeneous probability distribution of chain orientations $P(\theta) = \frac{2}{\pi}$, for $\theta \in [0, \pi/2]$ we calculate $\bar{\mathcal{C}}(\beta)$. We call $\mathcal{C}_{\text{long}}(\beta)$ the specific heat per site of a chain of Mn_{12} -ac molecules under the action of an external longitudinal magnetic field. In order to investigate the behavior of this averaged thermodynamical function in a powder sample, we use the per cent difference

$$\Delta \bar{\mathcal{C}}(\beta) \equiv 100\% \times \left| \frac{\bar{\mathcal{C}}(\beta) - \mathcal{C}_{\text{long}}(\beta)}{\bar{\mathcal{C}}(\beta)} \right|. \quad (25)$$

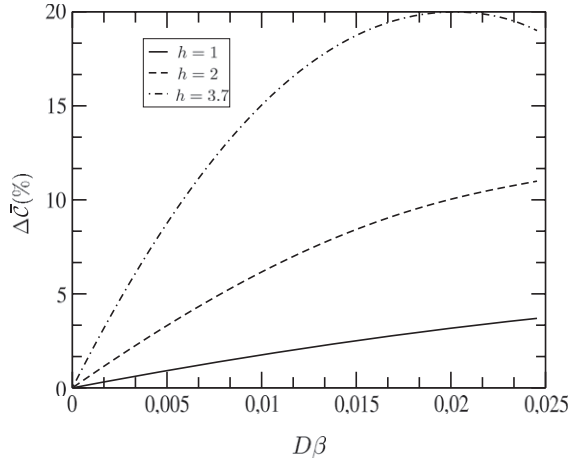


Figure 2. The per cent difference of the specific heat, averaged over all orientations of the magnetic field and the specific heat for a longitudinal (parallel to the easy axis) external magnetic field of the chain, as a function of $(D\beta)$, plotted for $h = 1$ (solid line), $h = 2$ (dashed line) and $h = 3.7$ (dotted–dashed line).

Figure 2 shows $\Delta\bar{C}$ versus $(D\beta)$ at $h/D = 1, 2,$ and 3.7 . We obtain that the per cent difference between the specific heat function in a powder sample and that of a crystal, in the presence of a longitudinal magnetic field, is an increasing function of the norm of the external magnetic field, and it can be as high as 20% for $h/D = 3.7$ and $T \gtrsim 21.1$ K. We point out that the contributions of terms of order $(D\beta)^{19}$ in the β expansions of the longitudinal and the average specific heat to the values of these functions, in the interval $(D\beta) \in [0, 0.025]$, is smaller than 0.17% for $h/D = 1$, 0.16% for $h/D = 2$ and 2.8% for $h/D = 3.7$.

3.4. Comparison of the quantum and classical models of the Mn_{12} -ac

The $S = 10$ Hamiltonian (12) is likely to exhibit classical behavior, in view of its high spin value. In its classical version, we consider a spin with norm equal to $\sqrt{110}$ and the angle θ between the z component of the classical spin and the easy axis varying continuously in the interval $[0, \pi]$. In appendix B we present the main steps to derive the HFE of the classical model and its expansion up to order $(D\beta)^3$. The high-temperature expansion of the classical specific heat per site is obtained from (B.4).

In order to compare the specific heat of the quantum ($C_{\text{quant}}(\beta)$) and the classical ($C_{\text{class}}(\beta)$) models, including the C and E terms in Hamiltonian (12), we define

$$\Delta_{C,Q}C(\beta) \equiv 100\% \times \left| \frac{C_{\text{class}}(\beta) - C_{\text{quant}}(\beta)}{C_{\text{quant}}(\beta)} \right|. \quad (26)$$

In figure 3 we present the curve $\Delta_{C,Q}C(\beta) \times (D\beta)$ at $h/D = 0$ for $D\beta \in [0, 0.025]$ ($T \gtrsim 21.1$ K). The interval in the variable $(D\beta)$ is chosen such that the terms of order $(D\beta)^{19}$ in C_{class} and C_{quant} contribute by less than 0.13% to the values of these functions at $h/D = 0$ and $(D\beta) \in [0, 0.025]$. This per cent difference $\Delta_{C,Q}C(\beta)$ goes up to 4.84% within this interval of temperature. From figure 3 we verify that $C_{\text{class}} \neq C_{\text{quant}}$ at

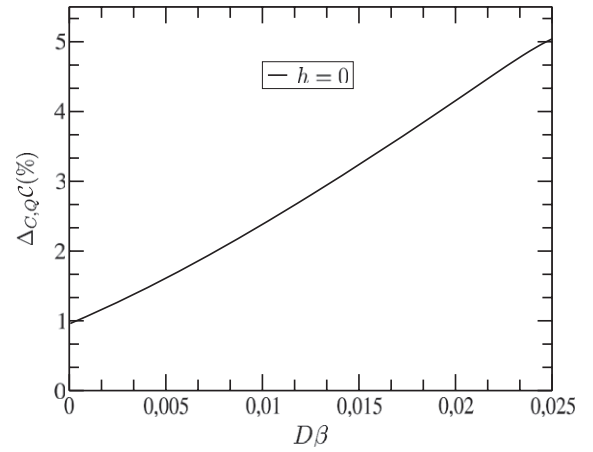


Figure 3. The per cent difference between the classical and the quantum specific heat as a function of $(D\beta)$ at $h/D = 0$.

$\beta = 0$ ($T \rightarrow \infty$) and $h/D = 0$ ($\Delta_{C,Q}C(0) = 0.96\%$). For $h/D \neq 0$, we have

$$\lim_{\beta \rightarrow 0} \Delta_{C,Q}C(\beta) = \frac{0.444}{0.464 + 0.110 \times 10^{-1} \left(\frac{h}{D}\right)^2}, \quad (27)$$

which shows that the quantum and classical models have the same value for the specific heat per site at $\beta = 0$ only in the presence of a very strong external magnetic field.

For $T \gtrsim 21.1$ K, $h/D \in [0, 3]$, and $\theta \in [0, \pi/2]$ the per cent difference of the quantum and classical x and z components of the magnetization is smaller than 1.4%. At $\beta = 0$ the value of the quantum and classical $\langle \mathcal{M}_x(\beta) \rangle_E / \langle \mathcal{M}_z(\beta) \rangle_E$ is equal.

4. Conclusions

The $S = 10$ Hamiltonian has been used to fit the experimental data of the Mn_{12} -ac molecule at finite temperatures. In 2001 Chudnovsky and Garanin [5, 6] included a transverse term in the Hamiltonian of this SMM in order to explain the even and odd number of magnetic transitions presented in the hysteresis curve for $T < 3$ K. We obtain the β expansion of the HFE of the quantum and classical models of the Mn_{12} -ac up to order $(D\beta)^{18}$ and $(D\beta)^{19}$, respectively. The range of validity of each β expansion depends on the particular thermodynamical function, but we can say that they are all valid at least for $T \gtrsim 21$ K. (The expansion of the magnetization is valid for $T \gtrsim 17.8$ K.) We show that in the interval $17.8 \text{ K} \lesssim T \lesssim 32 \text{ K}$ the presence of the transverse term in the Hamiltonian (12) can give a contribution larger than 2% to the x component of the magnetization, whereas the contribution of the C term is much smaller ($\lesssim 0.028\%$).

The contributions of the C and E terms to the z component of the magnetization and the specific heat per site are $\lesssim 0.014\%$ and $\lesssim 0.02\%$, respectively.

We obtain that the non-diagonal element of the magnetic susceptibility tensor (χ_{xz}) is one order of magnitude lower than χ_{xx} and χ_{zz} . For $T \gtrsim 21.9$ K we have $\chi_{xx} < \chi_{zz}$. We also have a qualitative agreement with the curves $\chi_{zz}(T)$ and the

effective Curie constant versus T for $T \gtrsim 21$ K, as shown in figure 1 of [9].

In the regime of strong magnetic fields ($h/D > 1$), the average specific heat (24) can be 20% larger than the specific heat in the presence of a longitudinal magnetic field at $T \sim 21.1$ K and $h/D = 3.7$.

Finally we obtain that the magnetization of the $S = 10$ Hamiltonian can be replaced by its classical version with a precision smaller than 1.4%, whereas the specific heat per site does not agree with the classical value even at $\beta = 0$ ($T \rightarrow \infty$). The per cent difference between the quantum and classical specific heat goes up to 4.84% for $T \gtrsim 21.9$ K and $h/D = 0$.

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Appendix A. The high-temperature expansion of the quantum $S = 10$ model

By applying the results of section 2 to the $S = 10$ Hamiltonian (12), for arbitrary values of the parameters D, B, C, E, h_x and h_z , we obtain the expansion of the HFE of the quantum model up to order $(D\beta)^{18}$. Up to order $(D\beta)^3$, it is⁶

$$\begin{aligned}
 W_{\text{quant}}(D\beta) = & -\ln(21) (D\beta)^{-1} + \left(-\frac{110}{3} - \frac{7238 \tilde{B}}{3} \right) \\
 & + \left(-\frac{55 \tilde{h}_z^2}{3} - \frac{24\,515\,700 \tilde{C}^2}{7} - \frac{55 \tilde{h}_x^2}{3} - \frac{6297\,170 \tilde{B}}{63} \right. \\
 & \left. - \frac{45\,690\,535 \tilde{B}^2}{9} - \frac{4807 \tilde{E}^2}{3} - \frac{4807}{9} \right) (D\beta) \\
 & + \left(\frac{47\,719\,438\,600 \tilde{C}^2 \tilde{B}}{7} + \frac{3148\,585 \tilde{h}_x^2 \tilde{B}}{126} \right. \\
 & \left. - \frac{4756\,974\,425 \tilde{B}^2}{27} - \frac{4034\,825\,367\,815 \tilde{B}^3}{567} \right. \\
 & \left. + \frac{569\,061\,400 \tilde{C}^2}{7} + \frac{2042\,975 \tilde{E}^2}{63} - \frac{3148\,585 \tilde{h}_z^2 \tilde{B}}{63} \right. \\
 & \left. + \frac{4807 \tilde{h}_x^2 \tilde{E}}{6} - \frac{24\,515\,700 \tilde{E}^2 \tilde{C}}{7} + \frac{4807 \tilde{h}_x^2}{18} \right. \\
 & \left. - \frac{266\,812\,535 \tilde{B}}{189} - \frac{2042\,975}{567} + \frac{178\,556\,015 \tilde{E}^2 \tilde{B}}{63} \right. \\
 & \left. - \frac{4807 \tilde{h}_z^2}{9} \right) (D\beta)^2 + \left(\frac{98\,673\,289 \tilde{E}^4}{252} \right.
 \end{aligned}$$

$$\begin{aligned}
 & - \frac{7400\,778\,485\,375 \tilde{B}^3}{567} + \frac{98\,673\,289 \tilde{E}^2}{378} \\
 & + \frac{17\,217\,417\,625 \tilde{h}_x^2 \tilde{B}^2}{378} + \frac{98\,673\,289}{2268} \\
 & - \frac{4756\,974\,425 \tilde{h}_z^2 \tilde{B}^2}{54} + 45\,316\,900 \tilde{h}_z^2 \tilde{C}^2 \\
 & + \frac{2431 \tilde{h}_z^2 \tilde{h}_x^2}{18} + \frac{2431 \tilde{h}_x^4}{36} + \frac{79\,039\,355\,548\,500 \tilde{C}^4}{49} \\
 & - \frac{17\,396\,489\,300 \tilde{E}^2 \tilde{C}^2}{7} + \frac{601\,749\,000 \tilde{E}^2 \tilde{C}}{7} \\
 & + 7100\,638\,200 \tilde{E}^2 \tilde{C} \tilde{B} + \frac{19\,732\,735 \tilde{h}_x^2 \tilde{B}}{27} \\
 & + \frac{12\,257\,850 \tilde{h}_x^2 \tilde{E} \tilde{C}}{7} - 1442\,100 \tilde{h}_x^2 \tilde{E} \tilde{B} \\
 & + \frac{204\,911\,349\,835\,900 \tilde{C}^2 \tilde{B}^2}{21} - \frac{1004\,663 \tilde{h}_x^2 \tilde{E}^2}{126} \\
 & - \frac{665\,362\,842\,293\,105 \tilde{B}^4}{324} + \frac{2431 \tilde{h}_z^4}{36} - \frac{2042\,975 \tilde{h}_z^2}{378} \\
 & + \frac{6447\,762\,385 \tilde{B}}{567} + \frac{2110\,273 \tilde{h}_z^2 \tilde{E}^2}{126} \\
 & + \frac{20\,677\,338\,62\,095 \tilde{B}^2}{2646} + \frac{22\,339\,848\,420\,200 \tilde{C}^2 \tilde{B}}{147} \\
 & + \frac{18\,495\,21\,655 \tilde{E}^2 \tilde{B}}{27} - \frac{266\,812\,535 \tilde{h}_z^2 \tilde{B}}{189} \\
 & - \frac{115\,368 \tilde{h}_x^2 \tilde{E}}{7} + \frac{10\,71\,961 \tilde{h}_x^2}{378} - \frac{138\,179\,400 \tilde{h}_x^2 \tilde{C}^2}{7} \\
 & + \frac{1651\,467\,646\,105 \tilde{E}^2 \tilde{B}^2}{378} \\
 & + \frac{12\,690\,960\,700 \tilde{C}^2}{21} \Big) (D\beta)^3 + \mathcal{O}((D\beta)^4), \tag{A.1}
 \end{aligned}$$

where we use the notation: $\tilde{B} \equiv B/D$, $\tilde{C} \equiv C/D$, $\tilde{E} \equiv E/D$, $\tilde{h}_x \equiv h_x/D$ and $\tilde{h}_z \equiv h_z/D$ and $W_{\text{quant}}(D\beta) = W_{\text{quant}}(\beta)/D$.

The quantum $S = 10$ tetrahedral symmetry case can be obtained from (A.1) by setting $E = 0$.

Since (A.1) is a function of the arbitrary parameters in (12), we are allowed to derive the β expansion of the following one-site thermal averages: $\langle S_z^2 \rangle$, $\langle S_z^4 \rangle$, $\langle S_x^2 - S_y^2 \rangle$, the x and z components of the magnetization ($\mathcal{M}_i, i \in \{x, z\}$) and the elements of the magnetic susceptibility tensor χ_{ij} , $i, j \in \{x, z\}$.

The $S = 10$ case with external magnetic field on the yz plane is obtained from the expansion (A.1) by replacing $E \rightarrow -E$ and $h_x \rightarrow h_y$.

Appendix B. The β expansion of the HFE of the classical Mn_{12} -ac model

In the classical version of the $S = 10$ Mn_{12} -ac molecule we have a classical spin with norm $\|\mathbf{S}\| = \sqrt{S(S+1)} = \sqrt{110}$

⁶ The reader is welcome to request from the authors the lengthy expansion up to higher orders.

with components

$$S_x = \sqrt{110} \sin(\theta) \cos(\phi),$$

$$S_y = \sqrt{110} \sin(\theta) \sin(\phi) \quad \text{and} \quad S_z = \sqrt{110} \cos(\theta), \quad (\text{B.1})$$

with $\theta \in [0, \pi]$ and $\phi \in [0, 2\pi]$. The relations (B.1) are replaced in Hamiltonian (12) in order to derive its classical version $H^{\text{class}}(\theta, \phi)$. The results derived in section 2 are also valid for the classical one-site models. The functions $H_{1,1}^{(n)}$ of the classical model are

$$H_{1,1}^{(n)} = \frac{1}{4\pi} \frac{1}{n!} \int_0^\pi \sin(\theta) d\theta \int_0^{2\pi} d\phi [H^{\text{class}}]^n, \quad n = 1, 2, 3, \dots \quad (\text{B.2})$$

A useful formula for evaluating this integral is [14]

$$\begin{aligned} I_\theta^{(m,n)} &\equiv \int_0^\pi d\theta (\sin\theta)^m (\cos\theta)^n \\ &= \frac{1}{4} (1 + (-1)^m)(1 + (-1)^n) \frac{\Gamma(\frac{m+1}{2})\Gamma(\frac{n+1}{2})}{\Gamma(\frac{m+n+2}{2})} \\ &\quad + \frac{1}{2} (1 - (-1)^m) \frac{(1 + (-1)^n)}{n+1} \frac{\Gamma(\frac{n+3}{2})\Gamma(\frac{m+1}{2})}{\Gamma(\frac{m+n+2}{2})}. \end{aligned} \quad (\text{B.3})$$

Replacing (B.2) for $n = 1, 2, 3, \dots, 20$ in equation (11) yields the high-temperature expansion of the classical HFE up to order $(D\beta)^{19}$. In what follows we present this expansion up to order $(D\beta)^3$ for arbitrary values of the parameter in the classical Hamiltonian, that is⁷

$$\begin{aligned} W_{\text{class}}(D\beta) &= -\ln(4\pi) (D\beta)^{-1} + \left(-2420 \tilde{B} - \frac{110}{3} \right) \\ &\quad + \left(-\frac{46851200 \tilde{B}^2}{9} - \frac{4840 \tilde{E}^2}{3} - \frac{4840}{9} - \frac{55 \tilde{h}_x^2}{3} \right. \\ &\quad \left. - \frac{234256000 \tilde{C}^2}{63} - \frac{55 \tilde{h}_z^2}{3} - \frac{2129600 \tilde{B}}{21} \right) (D\beta) \\ &\quad + \left(\frac{2420 \tilde{h}_x^2}{9} - \frac{907039232000 \tilde{B}^3}{117} - \frac{35606912000 \tilde{B}^2}{189} \right. \\ &\quad + \frac{2420 \tilde{h}_x^2 \tilde{E}}{3} + \frac{18740480000 \tilde{C}^2}{189} - \frac{234256000 \tilde{E}^2 \tilde{C}}{63} \\ &\quad - \frac{2129600}{567} + \frac{532400 \tilde{h}_x^2 \tilde{B}}{21} + \frac{6596648960000 \tilde{C}^2 \tilde{B}}{819} \\ &\quad + \frac{2129600 \tilde{E}^2}{63} - \frac{1064800 \tilde{h}_z^2 \tilde{B}}{21} - \frac{93702400 \tilde{B}}{63} \\ &\quad \left. - \frac{4840 \tilde{h}_z^2}{9} + \frac{187404800 \tilde{E}^2 \tilde{B}}{63} \right) (D\beta)^2 \\ &\quad + \left(\frac{1874048000 \tilde{B}}{189} + \frac{23425600 \tilde{E}^4}{63} - \frac{1064800 \tilde{h}_z^2}{189} \right. \\ &\quad + \frac{412290560000 \tilde{C}^2}{1053} + \frac{532400 \tilde{h}_x^2}{189} \\ &\quad \left. + \frac{21727712512000 \tilde{B}^2}{51597} + \frac{46851200 \tilde{E}^2}{189} \right) (D\beta)^3 \\ &\quad + \mathcal{O}((D\beta)^4) \end{aligned} \quad (\text{B.4})$$

⁷ The reader is welcome to request from the authors the lengthy expansion up to higher orders.

$$\begin{aligned} &+ \frac{8901728000 \tilde{h}_x^2 \tilde{B}^2}{189} - \frac{1064800 \tilde{h}_x^2 \tilde{E}}{63} \\ &- \frac{17803456000 \tilde{h}_z^2 \tilde{B}^2}{189} + \frac{937024000 \tilde{h}_z^2 \tilde{C}^2}{189} \\ &+ \frac{1210 \tilde{h}_z^2 \tilde{h}_x^2}{9} + \frac{605 \tilde{h}_x^4}{9} + \frac{56372488268800000 \tilde{C}^4}{877149} \\ &- \frac{8451956480000 \tilde{E}^2 \tilde{C}^2}{2457} + \frac{6596648960000 \tilde{E}^2 \tilde{C} \tilde{B}}{819} \\ &+ \frac{117128000 \tilde{h}_x^2 \tilde{E} \tilde{C}}{63} - \frac{93702400 \tilde{h}_x^2 \tilde{E} \tilde{B}}{63} \\ &+ \frac{124917443031040000 \tilde{C}^2 \tilde{B}^2}{125307} - \frac{532400 \tilde{h}_x^2 \tilde{E}^2}{63} \\ &- \frac{63656013301760000 \tilde{B}^4}{17901} + \frac{605 \tilde{h}_z^4}{9} \\ &- \frac{93702400 \tilde{h}_z^2 \tilde{B}}{63} - \frac{18140784640000 \tilde{B}^3}{351} \\ &+ \frac{18140784640000 \tilde{C}^2 \tilde{B}}{1323} + \frac{1064800 \tilde{h}_z^2 \tilde{E}^2}{63} \\ &+ \frac{18740480000 \tilde{E}^2 \tilde{C}}{189} + \frac{1874048000 \tilde{E}^2 \tilde{B}}{27} \\ &+ \frac{46851200 \tilde{h}_x^2 \tilde{B}}{63} - \frac{4685120000 \tilde{h}_x^2 \tilde{C}^2}{189} \\ &+ \frac{11173074176000 \tilde{E}^2 \tilde{B}^2}{2457} + \frac{23425600}{567} \Big) (D\beta)^3 \\ &+ \mathcal{O}((D\beta)^4) \end{aligned} \quad (\text{B.4})$$

where we keep the notation: $\tilde{B} \equiv B/D$, $\tilde{C} \equiv C/D$, $\tilde{E} \equiv E/D$, $\tilde{h}_x \equiv h_x/D$ and $\tilde{h}_z \equiv h_z/D$, and $W_{\text{class}}(D\beta) = W_{\text{class}}(\beta)/D$.

The classical case with external magnetic field in the yz plane is obtained by replacing $E \rightarrow -E$ and $h_x \rightarrow h_y$ in (B.4).

References

- [1] Lis T 1980 *Acta Crystallogr. B* **36** 2042
- [2] Ni Z-H *et al* 2007 *Inorg. Chem.* **46** 6029 and references therein
- [3] Barra A L, Gatteschi D and Sessoli R 1997 *Phys. Rev. B* **56** 8192
- [4] Gomes A M *et al* 1998 *Phys. Rev. B* **57** 5021
- [5] Chudnovsky E M and Garanin D A 2001 *Phys. Rev. Lett.* **87** 187203
- [6] Garanin D A and Chudnovsky E M 2002 *Phys. Rev. B* **65** 094423
- [7] Su Y-C, Shen S-Q and Tao R-B 2006 *J. Magn. Magn. Mater.* **299** 376
- [8] Chiorescu I *et al* 2000 *Phys. Rev. Lett.* **85** 4807
- [9] Lascialfari A *et al* 1998 *Phys. Rev. B* **57** 514
- [10] Rojas O, de Souza S M and Thomaz M T 2002 *J. Math. Phys.* **43** 1390
- [11] Rojas O, de Souza S M, Corrêa Silva E V and Thomaz M T 2003 *J. Phys.: Condens. Matter* **15** 8527
- [12] Friedman J R *et al* 1996 *Phys. Rev. Lett.* **76** 3830
- [13] Mertes K M *et al* 2001 *Phys. Rev. Lett.* **87** 227205
- [14] Corrêa Silva E V, Rojas O, Skea James E F, de Souza S M and Thomaz M T 2007 *Physique A* **375** 185