Magnetic tetrastability in a spin chain

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Bistability in magnetism is extensively used, in particular for information storage. Here an alternative approach using tetrastable magnetic domains in one-dimensional (1D) spin systems is presented. Using numerical and analytical calculations, we show that a spin chain with a canting angle of $\pi/4$ possesses four energy-equivalent states. We discuss the static properties of this canted 1D system such as the profile and the energy of the domain walls as they govern the dynamics of the magnetization. The realization of this $\pi/4$ canted spin chain could enable the encoding of the information on four bits, which is a potential alternative toward the increase of storage density.

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I. INTRODUCTION

Spintronics using magnetic materials in electronic devices has made considerable progress from fundamental studies to practical applications [1]. This technology is based on the discovery of magnetoresistive effects, such as the giant magnetoresistance in ferromagnetic conductors. Nowadays these properties are mainly used for reading information encoded in the magnetic domains of a hard drive disk [2]. Depending on the relative magnetization orientation of the domains (either up or down), a drastic change of the electrical resistance is observed in the read head. The constant reduction of the domain size, which slightly approaches the domain wall thickness, has almost reached its limit in standard inorganic magnetic materials. Moreover, as the domain size reduces, the anisotropy and therefore the bistability of these systems decreases [3]. Hence, the challenge resides in finding new ways to store information on magnetic media. One of the approaches consists in using an alternative magnetic object such as molecular nanomagnets [4,5] or single atoms [6], which are the smallest magnetic domains that one can create.

Here, going beyond the traditional bistable storage of magnetic information, a strategy relying on spin chains exhibiting a magnetic tetrastability is presented. This approach allows the encoding of information on four states and thus offers an unprecedented opportunity to extend the storage density. Numerical and analytical calculations demonstrate that the so-called $\pi/4$ canted spin chain presents four stable magnetic domains with orthogonal magnetizations separated by $\pi/2$ domain walls. The profile of these domain walls in the weak and strong anisotropy limits is reported emphasizing the finite energy of the domain walls, that should prevent their nucleation at low temperature (and thus the relaxation of the magnetization, i.e., loss of information) and therefore preserve the encoded information.

Among the variety of low dimensional magnets, single-chain magnets (SCMs) [7,8] have been extensively studied as they present a slow relaxation of magnetization, promising for information storage [7–11]. SCMs are generally made by assembling together molecular building blocks [9–11] that own a strong uniaxial anisotropy [12]. A SCM can be simply described by a chain of spins, as depicted in Fig. 1(a), with the following parameters: S is the amplitude of each spin, D is the on-site magnetic anisotropy, α is the canting angle between the local easy direction of magnetization and the normal to the chain axis, J is the exchange interaction between two neighboring spins, and θ_n and ϕ_n are the orientation of two consecutive spins at the site n with canting angle $+\alpha$ and $-\alpha$. We consider here only a uniaxial anisotropy [$D > 0$ in the convention of Hamiltonian (1)] that is the most common case in SCM systems for which the transverse anisotropy term is usually negligible [9,10,13].

In the simple case where the anisotropy axis of different sites are collinear ($\alpha = 0$), the SCM presents a classical magnetic bistability: two kinds of magnetic domains exist with the same energy but opposite magnetizations [see Fig. 1(b)] [9,10]. These magnetic domains are constituted of a given number of spins, which align along the unique easy axis of magnetization of the system [8–10]. Therefore, the domains are separated by domain walls (DWs) in which the magnetization is rotated by π, and are quoted as π DWs [14,15]. It is important to note that the width of these DWs depends on the ratio D/J. The spin chains can be treated considering classical anisotropic spins in the following Heisenberg Hamiltonian [9]:

$$H_{\alpha=0} = -2JS^2 \sum_{-\infty}^{+\infty} \vec{u}_n \cdot \vec{u}_{n+1} - DS^2 \sum_{-\infty}^{+\infty} u_{n,z}^2, \qquad (1)$$

where $\vec{u}_n$ is the unitary vector that gives the orientation of the nth spin of the chain and z is the direction of the anisotropy axis ($\alpha = 0$). As shown by Barbara using this spin Hamiltonian, the DWs become strictly narrow for $D/J > 4/3$ (a DW is located between two antiparallel spins) [14]. This case corresponds to the so-called Ising limit.

However, the magnetic topology of SCMs is generally more complex than the $\alpha = 0$ regular case. Indeed, a large number of synthesized SCMs possess two anisotropic axes with different orientations, which alternate along the spin chain

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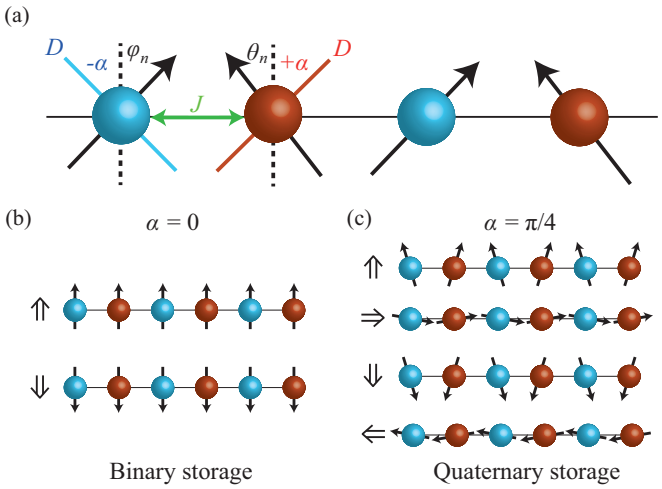

FIG. 1. Scheme of principle for information storage in a spin chain. (a) Representation of the spin orientations θ and ϕ associated to the easy axis, $+\alpha$ and $-\alpha$ (red and blue lines). The θ_n and ϕ_n angles measure the orientation of the θ and ϕ spins relatively to the normal to the chain axis (dashed line). The J and D parameters describe, respectively, the magnetic interaction between two neighboring spins and the magnetic anisotropy of a given spin. (b) Representation of the two energy-equivalent domains in the classical SCM with $\alpha = 0$. (c) Representation of the four energy-equivalent domains for an $\alpha = \pi/4$ canted SCM for a finite θ_e.

[16–20]. These one-dimensional (1D) systems, possessing a finite angle α, are called canted SCMs. In these chains, due to a competition between the exchange interaction and the magnetic anisotropy, the equilibrium spin configuration in the magnetic domains (for which the chain energy is minimum) is different from the $\alpha = 0$ case [10]. In the case of canted SCMs, the corresponding Hamiltonian is

$$H_{\alpha\neq 0} = -2JS^2 \sum_{-\infty}^{+\infty} \cos(\phi_n - \theta_n) + \cos(\theta_n - \phi_{n+1}) + DS^2 \sum_{-\infty}^{+\infty} \sin^2(\phi_n + \alpha) + \sin^2(\theta_n - \alpha), \quad (2)$$

where θ_n and ϕ_n are the spin orientation associated to the easy axis at $+\alpha$ and $-\alpha$. If several references already described the static properties of canted SCMs [16,21–25], the theoretical study of a chain in the particular case of a $\pi/4$ canting angle has never been reported so far. However, its promising magnetic properties described below should motivate chemists to rationally synthesize this novel kind of SCM.

II. RESULTS AND DISCUSSION

Using Eq. (2) in the particular case of $\alpha = \pi/4$, the energy of the chain is given by Eq. (3) (see Appendix A):

$$\frac{E}{2JS^2} = \sum_{-\infty}^{+\infty} -\cos(\phi_n - \theta_n) - \cos(\theta_n - \phi_{n+1}) + \frac{D}{4J} \sum_{-\infty}^{+\infty} 2 + \sin(2\phi_n) - \sin(2\theta_n). \quad (3)$$

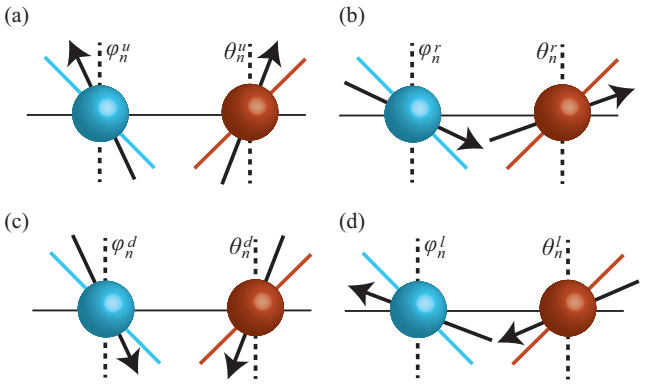

FIG. 2. Scheme of the four equilibrium configurations in the magnetic domains for a D/J finite value. Configuration of the (a) "up", (b) "right", (c) "down," and (d) "left" magnetization.

In order to find the spin configuration along the chain at the equilibrium, the derivative of the chain energy with respect to θ_n and ϕ_n must be calculated leading to a system of angular equations:

$$\frac{\partial E}{\partial \theta_n} = \sin(\theta_n - \phi_n) + \sin(\theta_n - \phi_{n+1}) - \frac{D}{2J}\cos(2\theta_n) = 0,$$
$$\frac{\partial E}{\partial \phi_n} = \sin(\phi_n - \theta_n) + \sin(\phi_n - \theta_{n-1}) + \frac{D}{2J}\cos(2\phi_n) = 0. \quad (4)$$

At the equilibrium, the θ_n and ϕ_n angles are independent of the site number, n, and are labeled θ_e and ϕ_e. In these conditions, the summation of the equations given in Eq. (4) leads to the relation $\cos(2\theta_e) = \cos(2\phi_e)$. Four solutions of lowest energy to this equation are found inducing the presence of four domain orientations described as follows:

$$\theta_n^u = \theta_e, \quad \phi_n^u = -\theta_e,$$
$$\theta_n^r = \pi/2 - \theta_e, \quad \phi_n^r = \pi/2 + \theta_e,$$
$$\theta_n^d = \pi + \theta_e, \quad \phi_n^d = \pi - \theta_e,$$
$$\theta_n^l = -\pi/2 - \theta_e, \quad \phi_n^l = -\pi/2 + \theta_e. \quad (5)$$

The equilibrium angle, θ_e, can be deduced from Eqs. (4), allowing direct access to a solution of Eq. (5):

$$\tan(2\theta_e) = \frac{D}{4J}. \quad (6)$$

These four configurations correspond to four domains with the same energy but different magnetizations, "up," "down," "right," and "left" as described in Fig. 2. Therefore, the $\alpha = \pi/4$ canted spin chain can be viewed as a four-state system where each state corresponds to a magnetic domain with a specific magnetization orientation [Fig. 1(c)]. In the following, we will describe the $\pi/2$ DW that separates two of these magnetic domains with orthogonal magnetization (e.g., "right" and "up"), as their profile and energy govern the static [26,27] and dynamic [28,29] properties of SCMs.

For any value of the D/J ratio, the profile of this $\pi/2$ DW can be obtained numerically by solving Eq. (4) using a Newton-Raphson refinement [30]. The convergence of the refinement is reached when the energy of the DW [as defined

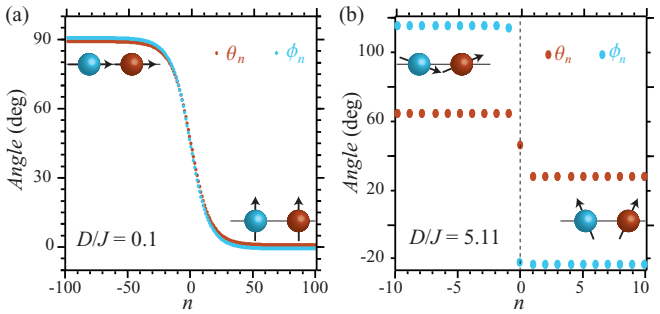

FIG. 3. Profiles of a $\pi/2$ domain wall in the broad [$D < J$; (a)] and sharp [$D > J$; (b)] limits for the $\alpha = \pi/4$ canted spin chain. The insets represent the "right" and "up" magnetization domains linked by the DW. The dashed line in (b) shows that the $\pi/2$ DW center is pinned on a single spin.

in Eq. (7)] is minimized (see Appendix A).

$$\frac{\Delta E}{2JS^2} = \sum_{-\infty}^{+\infty} 2\cos(2\theta_e) - \cos(\phi_n - \theta_n) - \cos(\theta_n - \phi_{n+1}) + \frac{D}{4J}\sum_{-\infty}^{+\infty} 2\sin(2\theta_e) + \sin(2\phi_n) - \sin(2\theta_n). \quad (7)$$

Figures 3(a) and 3(b) show typical $\pi/2$ DW profiles for $D < J$ and $D > J$, respectively.

In both cases, the DW links the "right" and "up" magnetization domains. Its center is pinned on a θ site and corresponds to a spin perfectly aligned with its easy axis ($\theta_0 = \pi/4$). The DWs are broad in the $D < J$ limit as described in the $\alpha = 0$ case [9,10]. However, for increasing D/J ratio, the DW thickness decreases but stays always greater than the distance between two sites. As a consequence, and in contrast with the $\alpha = 0$ case, strictly sharp DWs (i.e., Ising-like) are forbidden even in the $D \gg J$ limit.

In order to complete these numerical results, the DW profile was derived analytically using Eq. (4) and the DW energy [Eq. (7)] in the two limit cases. In the broad profile case ($D < J$), neighboring spins inside a DW possess very close orientations. This fact leads us to introduce a continuous description of the DW profile, by defining the variables ω_n and γ_n:

$$\omega_n = \frac{\phi_n + \theta_n}{2}, \quad \gamma_n = \frac{\phi_n - \theta_n}{2}. \quad (8)$$

Thanks to these new variables, the continuous calculation of Eq. (7) can be carried out and the profile can be expressed as a function of the ratio D/J (see Appendix B):

$$\tan[\omega(u)] = \exp\left(-u\frac{D}{J}\right),$$
$$\gamma(u) = \frac{D}{8J}\frac{\left[1 + \exp\left(-u\frac{D}{J}\right)\right]}{\cosh\left(u\frac{D}{J}\right)} - \theta_e \quad (9)$$

with u being the continuous variable describing the distance to the DW's center. In the sharp profile case ($D > J$), the orientations of the spins inside the DW are very close to their equilibrium values due to the dominant magnetic anisotropy.

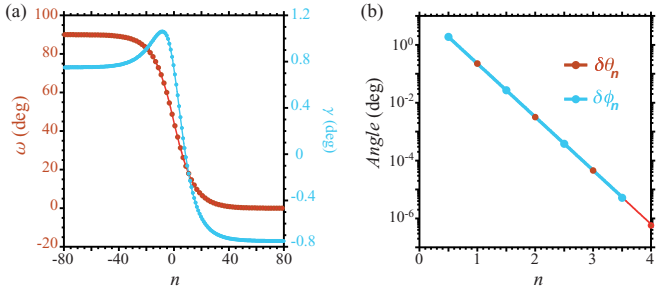

FIG. 4. Comparison of the analytical expressions, Eqs. (9) and (11), with the numerical profile of the $\pi/2$ domain walls presented in Fig. 3 in the broad [$D < J$; (a)] and sharp [$D > J$; (b)] limits. The dots are the numerical values of the profile variables and the lines are the fits of the same data with the analytical profile expressions. The analytical profile (a) leads to a D/J value of 0.104 735 in good agreement with the value obtained numerically of 0.104 737. Similarly, the fit of DW profile (b) gives a D/J value of 5.103 in good agreement with the numerical value of 5.111.

Therefore, the equation system (4) can be linearized with respect to the angles $\delta\theta_n$ and $\delta\phi_n$:

$$\delta\theta_n = \theta_n - \theta_e\,, \quad \delta\phi_n = \phi_n + \theta_e. \quad (10)$$

Considering a $\pi/2$ DW between "right" and "up" domains for which the spin orientation θ_0 is exactly equal to $\pi/4$, the profile can be calculated as an exponential decrease from the first spin after the DW's center (see Appendix C):

$$\delta\theta_n = \delta\phi_1 \exp\left[-\left(n - \tfrac{1}{2}\right)\psi\right],$$
$$\delta\phi_n = \delta\phi_1 \exp[-(n-1)\psi] \quad (11)$$

with ψ the parameter defined by $\cosh(\psi/2) = D^2/8J^2 + 1$.

Figures 4(a) and 4(b) present the numerical calculation of DW profiles in the broad and sharp limits, respectively, fitted with the analytical expressions, Eq. (9) and Eq. (11). For both broad and sharp limits, the fitting of the variables, ω_n, γ_n and $\delta\theta_n$, $\delta\phi_n$, respectively, are in good agreement with the values extracted from numerical computation.

The perfect agreement between the numerical profiles and their analytical expressions in the two limits confirms the validity of our numerical method. As a consequence, this numerical approach appears perfectly reliable to extrapolate the DW profiles between the two limits.

Following the description of the spin profile, the DW energy, which is also the energy barrier that separates two orthogonal ground states, has been determined. Indeed, if the DW has no energetic cost, its nucleation will relax the total magnetization of the SCM and therefore the encoded information will be lost. Using the DW profile obtained from the Newton-Raphson refinement and Eq. (7), the energy of the $\pi/2$ DW has been calculated as shown in Fig. 5.

In both $D < J$ and $D > J$ limits, the normalized energy follows simple power laws of the ratio D/J:

$$\frac{\Delta E_{D \ll J, \alpha = \pi/4}}{4JS^2} = \frac{D}{8J}, \quad (12)$$
$$\frac{\Delta E_{D \gg J, \alpha = \pi/4}}{4JS^2} = \frac{J}{D}. \quad (13)$$

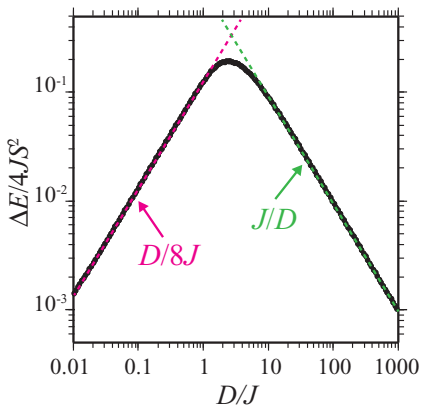

FIG. 5. Energy of a $\pi/2$ domain wall as a function of the D/J ratio. The dashed line represents the analytical limits of the normalized DW energy in the broad and sharp limits.

Using the analytical profile expression obtained previously [Eqs. (9) and (11)], these two expressions can also be obtained analytically by solving Eq. (7) in the continuous limit for $D \ll J$ (see Appendix B), and using its Landau development for $D \gg J$ (see Appendix C). Between these two limits, the normalized DW energy exhibits a maximum of the order of JS^2. As a consequence, the DW has a finite energy which precludes its nucleation at sufficiently low temperature.

By analogy with the ferromagnetic chain, we can conclude that the relaxation time of the magnetization will be large as soon as the DW energy becomes much larger than k_BT. In this temperature range, the $\alpha = \pi/4$ canted chain will be operational for information storage. According to our numerical and analytical results, the tetrastability of the $\alpha = \pi/4$ canted spin chain is realized for $k_BT \ll DS^2/2$ and $k_BT \ll 4J^2S^2/D$ in the $D \ll J$ and $D \gg J$ limits, respectively. Finally, when the D/J ratio is of the order of 1, the energy barrier between orthogonal ground states reaches its maximum and is of the order of $4JS^2/5$. This is the optimum situation for information storage as soon as $k_BT \ll JS^2$.

III. CONCLUDING REMARKS

In this work, the existence of four energy-equivalent states has been demonstrated and theoretically studied in an $\alpha = \pi/4$ canted spin chain. These magnetic states are associated to four kinds of magnetic domains, which bear magnetization with different orientations along the chain. This unique property reinforces the potential interest of SCMs for data storage applications with the possibility to code information on these four states. At the same time, we emphasized the fact that these magnetic domains are linked by $\pi/2$ DWs instead of the more traditional π DWs usually described in the $\alpha \neq \pi/4$ case. The physical ingredients that describe the crossover from π to $\pi/2$ DWs when the canting angle gets close to $\pi/4$ are currently being investigated and will be described elsewhere. Moreover, the spin profile and energy of the $\pi/2$ DWs have been described thanks to combined numerical and analytical approaches. These theoretical results establish that the highest DW energy is obtained when the D/J ratio ranges between 1 and 10. Overall, the remarkable properties of the $\alpha = \pi/4$ canted SCMs predicted in this work should encourage chemists in the fields of coordination chemistry and molecular magnetism to obtain experimental $\alpha = \pi/4$ canted SCM materials and to verify their applicability toward storage devices.

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APPENDIX A: CHAIN AND DOMAIN WALL ENERGIES

In order to calculate the energies of spin chain and domain wall, we use a classical Heisenberg Hamiltonian composed of spin-exchange interaction and anisotropic terms. These two components can be expressed with angles describing the spin orientations (Fig. 1):

$$H_{\text{exchange}} = -2JS^2 \sum_{-\infty}^{+\infty} \vec{u}_{n,\phi} \cdot \vec{u}_{n,\theta} + \vec{u}_{n,\theta} \cdot \vec{u}_{n+1,\phi}$$
$$= -2JS^2 \sum_{-\infty}^{+\infty} \cos(\phi_n - \theta_n) + \cos(\theta_n - \phi_{n+1}), \quad \text{(A1)}$$

$$H_{\text{anisotropy}} = -DS^2 \sum_{-\infty}^{+\infty} u^2_{n,z,\phi/-\alpha} + u^2_{n,z,\theta/+\alpha}$$
$$\equiv DS^2 \sum_{-\infty}^{+\infty} \sin^2(\phi_n + \alpha) + \sin^2(\theta_n - \alpha), \quad \text{(A2)}$$

where $\vec{u}_{n,\phi}$ and $\vec{u}_{n,\theta}$ are the unitary vectors describing the orientation of the nth spins, and $u_{n,z,\phi/-\alpha}$ and $u_{n,z,\theta/+\alpha}$ are their projection amplitude along their respective easy axis. Thus the energy of the spin chain can be deduced from the total Hamiltonian $H_{\text{total}} = H_{\text{exchange}} + H_{\text{anisotropy}}$. In the $\alpha = \pi/4$ case, the chain energy is written as follows [using $\sin^2(x \pm \pi/4) = 1/2[1 \pm \sin(2x)]$:

$$\frac{E}{2JS^2} = \sum_{-\infty}^{+\infty} -\cos(\phi_n - \theta_n) - \cos(\theta_n - \phi_{n+1})$$
$$+ \frac{D}{4J} \sum_{-\infty}^{+\infty} 2 + \sin(2\phi_n) - \sin(2\theta_n). \quad \text{(A3)}$$

At the equilibrium, i.e., for an infinite chain without any domain wall, θ_n and ϕ_n angles are equal to their equilibrium values θ_e and ϕ_e. As an illustration and for simplicity, we consider here the case where the chain at equilibrium is in its "up" configuration leading to $\phi_e = -\theta_e$. Therefore, the energy of the infinite chain at equilibrium E_{eq} can be deduced from Eq. (A3):

$$\frac{E_{\text{eq}}}{2JS^2} = \sum_{-\infty}^{+\infty} -2\cos(2\theta_e) + \frac{D}{4J} \sum_{-\infty}^{+\infty} 2 - 2\sin(2\theta_e). \quad \text{(A4)}$$

Finally, the energy ΔE of a domain wall is defined as the difference between the chain energy [Eq. (A3)] and the

equilibrium energy [Eq. (A4)]:

$$\frac{\Delta E}{2JS^2} = \sum_{-\infty}^{+\infty} 2\cos(2\theta_e) - \cos(\phi_n - \theta_n) - \cos(\theta_n - \phi_{n+1}) + \frac{D}{4J}\sum_{-\infty}^{+\infty} 2\sin(2\theta_e) + \sin(2\phi_n) - \sin(2\theta_n). \tag{A5}$$

APPENDIX B: THE $D \ll J$ LIMIT

The DW profile in the $D \ll J$ limit is broad, meaning that neighboring spins have close orientations. Therefore, the spin profile is given by the ω_n and γ_n variables:

$$\omega_n = \frac{\phi_n + \theta_n}{2} = \frac{\delta\phi_n + \delta\theta_n}{2}, \quad \gamma_n = \frac{\phi_n - \theta_n}{2} = \frac{\delta\phi_n - \delta\theta_n}{2} - \theta_e = \bar{\gamma}_n - \theta_e. \tag{B1}$$

With these new variables, the DW profile and energy determination can be achieved through the continuous approximation. In this approach, each term of the DW energy [Eq. (7)] is expressed with the ω_n and γ_n variables at the third order in ψ [this parameter is defined by $\cosh(\psi/2) = D^2/8J^2 + 1$]:

$$\cos(\phi_n - \theta_n) = \cos(2\theta_e)(1 - 2\bar{\gamma}^2) + \sin(2\theta_e)2\bar{\gamma}, \tag{B2}$$

$$\begin{aligned}\cos(\theta_n - \phi_{n+1}) &= \cos(\omega_n - \bar{\gamma}_n - \bar{\gamma}_{n+1} - \omega_{n+1} + 2\theta_e) \\ &= \cos(2\theta_e)\left\{1 - \frac{1}{2}\left[\left(\frac{d\omega}{du} + 2\bar{\gamma}\right)^2 + \left(\frac{d^2\omega}{du^2} + 2\frac{d\bar{\gamma}}{du}\right)\left(\frac{d\omega}{du} + 2\bar{\gamma}\right)\right]\right\} + \sin(2\theta_e)\left(\frac{d\omega}{du} + 2\bar{\gamma}\right),\end{aligned} \tag{B3}$$

$$\sin(2\phi_n) - \sin(2\theta_n) = -2\sin(2\theta_e) + 4\sin(2\theta_e)\sin^2(\omega) + 4\cos(2\theta_e)\bar{\gamma}[1 - 2\sin^2(\omega)] \tag{B4}$$

with u being the continuous variable describing the distance to the DW center. Therefore, the DW energy [Eq. (7)] can be written as integrals over the DW size:

$$\begin{aligned}\frac{\overline{\overline{\Delta E}}}{4JS^2\cos(2\theta_e)} &= \int\left\{\bar{\gamma}^2 + \left(\frac{1}{2}\frac{d\omega}{du} + \bar{\gamma}\right)^2 + \left(\frac{1}{2}\frac{d^2\omega}{du^2} + \frac{d\bar{\gamma}}{du}\right)\left(\frac{1}{2}\frac{d\omega}{du} + \bar{\gamma}\right)\right\}du \\ &\quad + 2\sinh^2\left(\frac{\psi}{4}\right)\int\{\sin^2\omega\}du - \tan(2\theta_e)\int\left\{4\bar{\gamma}\sin^2\omega + \frac{1}{2}\frac{d\omega}{du}\right\}du.\end{aligned} \tag{B5}$$

Two integrals can be directly evaluated considering a $\pi/2$ DW between "right" and "up" domains as represented in Fig. 3(a):

$$\begin{aligned}\int\frac{d\omega}{du}du &= [\omega]_{u=-\infty}^{u=+\infty} = -\frac{\pi}{2}, \\ \int\left(\frac{1}{2}\frac{d^2\omega}{du^2} + \frac{d\bar{\gamma}}{du}\right)\left(\frac{1}{2}\frac{d\omega}{du} + \bar{\gamma}\right)du &= \left[\frac{1}{2}\left(\frac{1}{2}\frac{d\omega}{du} + \bar{\gamma}\right)^2\right]_{u=-\infty}^{u=+\infty} = -2{\theta_e}^2.\end{aligned} \tag{B6}$$

Then, the DW energy in the continuous approximation can be simplified:

$$\begin{aligned}\frac{\overline{\overline{\Delta E}}}{4JS^2\cos(2\theta_e)} &= \int\left\{\bar{\gamma}^2 + \left(\frac{1}{2}\frac{d\omega}{du} + \bar{\gamma}\right)^2\right\}du + \frac{D^2}{8J^2}\int\{\sin^2\omega\}du \\ &\quad - \frac{D}{J}\int\{\bar{\gamma}\sin^2\omega\}du - 2{\theta_e}^2 + \frac{D}{4J}\frac{\pi}{4}.\end{aligned} \tag{B7}$$

Therefore, the DW energy is minimized with respect to ω and $\bar{\gamma}$:

$$\bar{\gamma} = -\frac{1}{4}\frac{d\omega}{du} + \frac{D}{4J}\sin^2(\omega), \quad \frac{d^2\omega}{du^2} = \frac{D^2}{2J^2}\sin(2\omega) - \frac{D^2}{J^2}\sin^2(\omega)\sin(2\omega) \tag{B8}$$

and the solution of this system gives the DW profile described by the ω and $\bar{\gamma}$ variables:

$$\tan(\omega) = \exp\left(-u\frac{D}{J}\right), \quad \bar{\gamma} = \frac{D}{8J}\frac{\left[1 + \exp\left(-u\frac{D}{J}\right)\right]}{\cosh\left(u\frac{D}{J}\right)}. \tag{B9}$$

With these profile equations, the DW energy [Eq. (B7)] is written as an integral over ω:

$$\frac{\overline{\overline{\Delta E}}}{4JS^2\cos(2\theta_e)} = \frac{D^2}{4J^2}\int_{-\infty}^{+\infty}\{\sin^2\omega - \sin^4\omega - \sin^3\omega\cos\omega\}du - 2{\theta_e}^2 + \frac{D}{4J}\frac{\pi}{4} \tag{B10}$$

and then, the energy can be evaluated as a function of the ratio D/J and the θ_e angle:

$$\frac{\overline{\overline{\Delta E}}}{4JS^2\cos(2\theta_e)} = \frac{D}{8J} - 2\theta_e^2. \tag{B11}$$

Finally, the DW energy in the asymptotic limit $D \ll J$ is deduced neglecting θ_e:

$$\frac{\Delta E_{D\ll J,\alpha=\pi/4}}{4JS^2} = \frac{D}{8J}. \tag{B12}$$

APPENDIX C: THE $D \gg J$ LIMIT

The system of angular equation [Eq. (4)] can be linearized in the $D \gg J$ limit with respect to the $\delta\theta_n$ and $\delta\phi_n$ angles ($\delta\theta_n = \theta_n - \theta_e,\ \delta\phi_n = \phi_n + \theta_e$):

$$\left[\frac{D^2}{4J^2} + 2\right]\delta\theta_n = \delta\phi_n + \delta\phi_{n+1}, \quad \left[\frac{D^2}{4J^2} + 2\right]\delta\phi_n = \delta\theta_n + \delta\theta_{n-1}. \tag{C1}$$

By symmetry argument, the spin at the DW center is aligned with its associated easy axis. Then, the spin profile satisfying the Eq. (C1) is described by an exponential decrease of the $\delta\theta_n$ and $\delta\phi_n$ values starting from the first spin after the DW center. Considering the DW between the "right" and "up" domains, the center angle is then $\theta_0 = \pi/4$ and the DW profile can be described only by the $\delta\phi_1$ angle and the ψ parameter [$\cosh(\psi/2) = D^2/8J^2 + 1$]:

$$\delta\theta_n = \delta\phi_1 \exp\left[-\left(n - \frac{1}{2}\right)\psi\right], \quad \delta\phi_n = \delta\phi_1 \exp\left[-(n-1)\psi\right]. \tag{C2}$$

From this profile, the DW energy can be written at the second order with respect to $\delta\phi_1$:

$$\begin{aligned}\frac{\overline{\Delta E}}{4JS^2} = &\left\{\cos(2\theta_e) - \frac{\sqrt{2}}{2}[\cos(\theta_e) - \sin(\theta_e)] + \frac{D}{8J}[\sin(2\theta_e) - 1]\right\} - \delta\phi_1\left\{\frac{\sqrt{2}}{2}[\cos(\theta_e) + \sin(\theta_e)] - \sin(2\theta_e)\right\} \\ &+ \frac{{\delta\phi_1}^2}{2}\left\{\frac{\sqrt{2}}{2}[\cos(\theta_e) - \sin(\theta_e)] + \cos(2\theta_e)\tanh\left(\frac{\psi}{4}\right)\left[1 + \exp\left(\frac{\psi}{2}\right)\right]\right\}\end{aligned} \tag{C3}$$

with the three terms enclosed in square brackets being positive. The $\delta\phi_1$ value is estimated from the minimization of the DW energy [Eq. (7)] . $\overline{\delta\phi_1}$ does not cancel exactly for a given D/J ratio, indicating that there is no strictly sharp DWs in the $\alpha = \pi/4$ case:

$$\overline{\delta\phi_1} = \frac{\frac{\sqrt{2}}{2}[\cos(\theta_e) + \sin(\theta_e)] - \sin(2\theta_e)}{\frac{\sqrt{2}}{2}[\cos(\theta_e) - \sin(\theta_e)] + \cos(2\theta_e)\tanh\left(\frac{\psi}{4}\right)(1 + e^{\psi/2})}. \tag{C4}$$

The DW energy in the $D \gg J$ limit can be deduced from the term independent of $\delta\phi_1$ thanks to the linearization of $\cos(2\theta_e)$ and $\sin(2\theta_e)$:

$$\begin{aligned}\cos(2\theta_e) &= \frac{1}{\sqrt{1 + \tan^2(2\theta_e)}} = \frac{1}{\sqrt{1 + \frac{D^2}{16J^2}}} \approx \frac{4J}{D}, \\ \sin(2\theta_e) &= \frac{\tan(2\theta_e)}{\sqrt{1 + \tan^2(2\theta_e)}} = \frac{1}{\sqrt{1 + \frac{16J^2}{D^2}}} \approx 1 - \frac{8J^2}{D^2}.\end{aligned} \tag{C5}$$

Therefore, the asymptotical limit of the DW energy at the zeroth order with respect to $\delta\phi_1$ is obtained:

$$\frac{\Delta E_{D\gg J,\alpha=\pi/4}}{4JS^2} = \frac{J}{D}. \tag{C6}$$

[1] A. Fert, Rev. Mod. Phys. **80**, 1517 (2008).
[2] C. Chappert, A. Fert, and F. N. Van Dau, Nat. Mater. **6**, 813 (2007).
[3] L. Néel, Adv. Phys. **4**, 191 (1955).
[4] A. Caneschi, D. Gatteschi, R. Sessoli, A. L. Barra, L. C. Brunel, and M. Guillot, J. Am. Chem. Soc. **113**, 5873 (1991).
[5] R. Sessoli, D. Gatteschi, A. Caneschi, and M. A. Novak, Nature (London) **365**, 141 (1993).
[6] S. Loth, S. Baumann, C. P. Lutz, D. M. Eigler, and A. J. Heinrich, Science **335**, 196 (2012).
[7] A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M. G. Pini, and M. A. Novak, Angew. Chem., Int. Ed. **40**, 1760 (2001).
[8] R. Clérac, H. Miyasaka, M. Yamashita, and C. Coulon, J. Am. Chem. Soc. **124**, 12837 (2002).
[9] C. Coulon, H. Miyasaka, and R. Clérac, Struct. Bonding (Berlin) **122**, 163 (2006).
[10] C. Coulon, V. Pianet, M. Urdampilleta, and R. Clérac, Struct. Bonding (Berlin) **164**, 143 (2015).
[11] K. S. Pedersen, J. Bendix, and R. Clérac, Chem. Commun. **50**, 4396 (2014)
[12] M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer, K. Nakata, K.-i. Sugiura, M. Yamashita, C. Coulon, and R. Clérac, J. Am. Chem. Soc. **127**, 3090 (2005).
[13] W. Werndorfer, R. Clérac, C. Coulon, L. Lecren, and H. Miyasaka, Phys. Rev. Lett. **95**, 237203 (2005).
[14] B. Barbara, J. Phys. **34**, 1039 (1973).
[15] B. Barbara, J. Magn. Magn. Mater. **129**, 79 (1994).
[16] B. Barbara, C. Becle, R. Lemaire, and D. Paccard, J. Physique Colloque **32**, C1-299 (1971).
[17] K. Bernot, J. Luzon, R. Sessoli, A. Vindigni, J. Thion, S. Richeter, D. Leclercq, J. Larionova, and A. Van Der Lee, J. Am. Chem. Soc. **130**, 1619 (2008).
[18] I. Bhowmick, E. A. Hillard, P. Dechambenoit, C. Coulon, T. D. Harris, and R. Clérac, Chem. Commun. **48**, 9717 (2012).
[19] W.-X. Zhang, R. Ishikawa, B. Breedlove, and M. Yamashita, RSC Adv. **3**, 3772 (2013).
[20] H.-L. Sun, Z.-M. Wang, and S. Gao, Coord. Chem. Rev. **254**, 1081 (2010).
[21] K. Bernot, J. Luzon, A. Caneschi, D. Gatteschi, R. Sessoli, L. Bogani, A. Vindigni, A. Rettori, and M. G. Pini, Phys. Rev. B **79**, 134419 (2009).
[22] R. Pandit and C. Tannous, Phys. Rev. B **28**, 281 (1983).
[23] S. Sahoo, J.-P. Sutter, and S. Ramasesha, J. Stat. Phys. **147**, 181 (2012).
[24] P. Sobczak, A. Barasinski, G. Kamieniarz, and A. Drzewinski, Phys. Rev. B **84**, 224431 (2011).
[25] A. Barasinski, G. Kamieniarz, and A. Drzewinski, Phys. Rev. B **86**, 214412 (2012).
[26] K. Nakamura and T. Sasada, Solid State Commun. **21**, 891 (1977).
[27] K. Nakamura and T. Sasada, J. Phys. C: Solid State Phys. **11**, 331 (1978).
[28] R. J. Glauber, J. Math. Phys. **4**, 294 (1963).
[29] O. V. Billoni, V. Pianet, D. Pescia, and A. Vindigni, Phys. Rev. B **84**, 064415 (2011).
[30] W. Press, S. Teukolsky, W. Vetterling, and B. Flannery, *Numerical Recipes* (Cambridge University Press, New York, 2007).