

# Thermodynamics and spin-tunneling dynamics in ferric wheels with excess spin

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We study theoretically the thermodynamic properties and spin dynamics of a class of magnetic rings closely related to ferric wheels, antiferromagnetic ring systems, in which one of the Fe (III) ions has been replaced by a dopant ion to create an excess spin. Using a coherent-state spin path integral formalism, we derive an effective action for the system in the presence of a magnetic field. We calculate the functional dependence of the magnetization and tunnel splitting on the magnetic field and show that the parameters of the spin Hamiltonian can be inferred from the magnetization curve. We study the spin dynamics in these systems and show that quantum tunneling of the Néel vector also results in tunneling of the total magnetization. Hence, the spin correlation function shows a signature of Néel vector tunneling, and electron spin resonance (ESR) techniques or ac susceptibility measurements can be used to measure both the tunneling and the decoherence rate. We compare our results with exact diagonalization studies on small ring systems. Our results can be easily generalized to a wide class of nanomagnets, such as ferritin.

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## I. INTRODUCTION

Nanomagnets and molecular clusters are systems in which macroscopic quantum phenomena may be observed in the form of quantum tunneling of the magnetization.<sup>1–3</sup> Two scenarios must be carefully distinguished: incoherent macroscopic quantum tunneling (MQT) and macroscopic quantum coherence (MQC). In the latter case, tunneling between energetically degenerate spin configurations takes place at a rate  $\Delta/h$  large compared to the spin decoherence rate  $\Gamma$ . In ferromagnetic molecular clusters such as  $\text{Fe}_8$  and  $\text{Mn}_{12}$  the ground-state tunnel splitting  $\Delta$  is small compared to  $\hbar\Gamma$ .<sup>4–6</sup> However,  $\Delta$  is significantly larger in antiferromagnetic (AF) systems<sup>7,8</sup> which are promising candidates for the observation of MQC in the form of coherent tunneling of the Néel vector  $\mathbf{n}$ .

The ferric wheels (FW's)  $\text{Li:Fe}_6$ ,  $\text{Na:Fe}_6$ ,  $\text{Cs:Fe}_8$ , and  $\text{Fe}_{10}$  (Refs. 9–14) are a particularly interesting class of molecular magnets. The  $s=5/2$  Fe (III) ions are arranged on a ring, with an AF nearest-neighbor exchange coupling  $J>0$ , and a weak, easy-axis anisotropy ( $k_z$ ) directed along the ring axis  $\mathbf{e}_z$ . For  $h_x=0$ , the classical ground-state spin configuration has alternating (Néel) order with the spins pointing along  $\pm\mathbf{e}_z$ . The two states with the Néel vector  $\mathbf{n}$  along  $\pm\mathbf{e}_z$  (Fig. 1), labeled  $|\uparrow\rangle$  and  $|\downarrow\rangle$ , are energetically degenerate and separated by an energy barrier of height  $Nk_zs^2$ . However,  $|\uparrow\rangle$  and  $|\downarrow\rangle$  are not energy eigenstates. Rather, the low-energy sector of the FW consists of a ground state  $|g\rangle=(|\uparrow\rangle+|\downarrow\rangle)/\sqrt{2}$  and a first excited state  $|e\rangle=(|\uparrow\rangle-|\downarrow\rangle)/\sqrt{2}$ , separated in energy by  $\Delta$ . For weak tunneling,  $|g\rangle$  and  $|e\rangle$  are energetically well separated from all other energy eigenstates.

For  $\text{Fe}_{10}$ , the tunnel splitting  $\Delta$  can be as large as 2.18 K.<sup>14,15</sup> An estimate for the electron spin decoherence rate  $\Gamma$  in FW's can be obtained from the typical energy scales of the various interactions of the electron spins. These include nuclear dipolar interactions with  $^1\text{H}$  nuclei [0.1 mK (Ref. 16)], hyperfine interactions with  $^{57}\text{Fe}$  [1 mK (Ref. 17)], interring electron spin dipolar interactions (of order 10–50

mK), and possible interring superexchange processes, which are difficult to estimate but may be of order 100 mK. However, the tunnel splitting is sufficiently large that FW's are most promising candidates for coherent tunneling of  $\mathbf{n}$  even in the presence of intrinsic or extrinsic sources of decoherence on energy scales up to 0.5 K.

Although quantum tunneling effects in antiferromagnets are more pronounced than in ferromagnets,<sup>7,8</sup> the detection of quantum behavior is experimentally more challenging. The reason for this is that magnetization and susceptibility measurements probe only the total spin of the molecule which, by symmetry, remains unaltered upon tunneling of the Néel vector. This problem is resolved in ferrimagnets and antiferromagnets with uncompensated sublattice spins, in which  $\Delta$  is still large and tunneling of  $\mathbf{n}$  leads to large signals in the alternating-current (ac) susceptibility,<sup>18–20</sup> provided that magnetic fields are small.<sup>21–24</sup> Recent work<sup>25</sup> indicates that ferrimagnets exhibit a wealth of interesting tunnel sce-

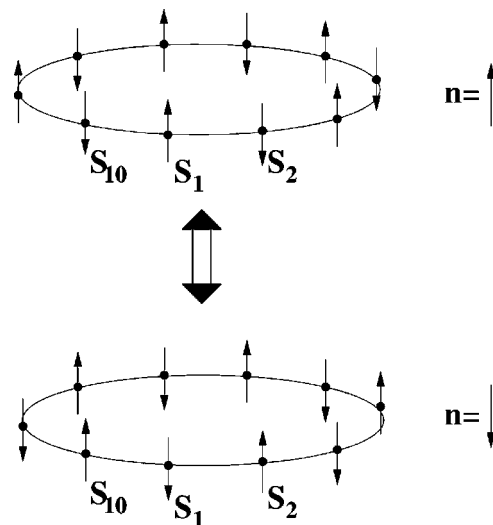


FIG. 1. The two degenerate classical ground-state spin configurations of the ferric wheel  $\text{Fe}_{10}$ .

narios also in finite magnetic fields.

In this paper we study magnetic rings closely related to the ferric wheels, in which one of the Fe (III) ions has been replaced by a Ga or Cr ion with spin  $s'=0$  or  $s'=3/2$ , respectively, to create an excess spin. Such systems have been synthesized recently.<sup>26</sup> Starting from a microscopic model Hamiltonian,

$$\hat{H} = J \sum_{i=2}^{N-1} \hat{\mathbf{s}}_i \cdot \hat{\mathbf{s}}_{i+1} + J' (\hat{\mathbf{s}}_1 \cdot \hat{\mathbf{s}}_2 + \hat{\mathbf{s}}_1 \cdot \hat{\mathbf{s}}_N) + \hbar \mathbf{h} \cdot \sum_{i=1}^N \hat{\mathbf{s}}_i - \left( k'_z \hat{s}_{1,z}^2 + k_z \sum_{i=2}^N \hat{s}_{i,z}^2 \right), \quad (1)$$

which also accounts for modified exchange ( $J'$ ) and anisotropy ( $k'_z$ ) constants due to doping, we calculate various thermodynamic quantities and spin correlation functions. In Eq. (1),  $N=10, 8$ , or  $6$ ,  $\mathbf{h} = g\mu_B \mathbf{B}/\hbar$ , with  $\mathbf{B}$  the external magnetic field, and  $g=2$  is the electron spin  $g$  factor. As we will show, the excess spin  $\delta s = s' - s$  is strongly coupled to  $\mathbf{n}$  and hence is expected to modify both the thermodynamic properties and the spin dynamics of the FW. In contrast, for an impurity spin coupled weakly to the Néel vector,<sup>27</sup> the thermodynamic properties of the wheel remain essentially unaltered. For the modified FW's discussed in the present work, Néel vector tunneling also leads to oscillations of the total spin which are in principle observable in ac susceptibility or electron spin resonance (ESR) measurements. Thermodynamic properties of AF systems with uncompensated sublattice spins by now have been studied in great detail for various anisotropy potentials and field configurations.<sup>28,29</sup> One main advantage of the small, high-symmetry modified FW studied in the present work is that the dependence of various thermodynamic quantities and spin correlation functions on the small number of microscopic parameters entering Eq. (1) can be evaluated analytically.

The outline of this paper is as follows. In Sec. II we review the theory of spin tunneling in FW's and calculate the spin correlation functions  $\chi_{\alpha\alpha}$ . In Sec. III we discuss the modified FW within a classical vector model and show that, in contrast to the FW, tunneling of  $\mathbf{n}$  now also results in oscillations of the total spin. In Sec. IV and Sec. V, we develop a semiclassical theory of the modified FW, thus generalizing earlier work on AF systems with uncompensated sublattice spins<sup>21-24</sup> to  $B_x \neq 0$ . For  $|J'/J - 1| \ll 1$ , we evaluate explicitly the tunnel splitting  $\tilde{\Delta}$  and magnetization  $M_x$  of the modified FW, and show that  $J'$  can be determined by measuring  $M_x$ . We calculate the Fourier transform of the real-time susceptibility  $\chi''_{zz}(\omega \approx \tilde{\Delta}/\hbar)$  and prove that Néel vector tunneling can be detected in ac susceptibility or ESR measurements. In Sec. VI, we discuss the modified FW for the limiting cases  $J'/J \gg 1$  and  $J'/J \ll 1$ . The relevance of the present work for experiments is discussed in Sec. VII. Finally, we indicate that our results can be easily generalized to other systems such as ferritin (Sec. VIII). We summarize our results in Sec. IX.

## II. THERMODYNAMICS AND SPIN DYNAMICS OF THE FW

### A. Thermodynamics

In this section, we give a brief review of previous work on Néel vector tunneling in FW's.<sup>14</sup> In particular, we point out that the notion of quantum tunneling applies only to  $\text{Fe}_{10}$  and  $\text{Cs:Fe}_8$  (and somewhat less to  $\text{Na:Fe}_6$ ) for large  $h_x$ , but not to  $\text{Li:Fe}_6$ .

The minimal Hamiltonian of the FW's contains only two parameters  $J$  and  $k_z$ ,

$$\hat{H}_0 = J \sum_{i=1}^N \hat{\mathbf{s}}_i \cdot \hat{\mathbf{s}}_{i+1} + \hbar \mathbf{h} \cdot \sum_{i=1}^N \hat{\mathbf{s}}_i - k_z \sum_{i=1}^N \hat{s}_{i,z}^2. \quad (2)$$

Here  $N=10, 8$ , or  $6$  and  $\hat{\mathbf{s}}_{N+1} \equiv \hat{\mathbf{s}}_1$ ,  $\mathbf{h} = g\mu_B \mathbf{B}/\hbar$ , with  $\mathbf{B}$  the external magnetic field, and  $g=2$  is the electron spin  $g$  factor. Throughout this paper we restrict our attention to  $\mathbf{B} = B_x \mathbf{e}_x$ , i.e., magnetic fields applied in the ring plane. For  $k_z=0$ , the eigenstates of the total spin  $\hat{\mathbf{S}} = \sum_{i=1}^N \hat{\mathbf{s}}_i$  are also energy eigenstates, with energy<sup>10,14</sup>  $E_{S,S_x} \approx (2J/N)S(S+1) + \hbar h_x S_x$ . For systems with weak anisotropy,  $k_z \ll 2J/(Ns)^2$ , the anisotropy can be taken into account in perturbation theory for a wide range of  $h_x$ . However, the scenario changes for large anisotropy  $k_z \gtrsim 2J/(Ns)^2$ , where mixing of different spin multiplets becomes appreciable, as is the case for  $\text{Fe}_{10}$ ,  $\text{Cs:Fe}_8$ , and  $\text{Na:Fe}_6$ .

Both the tunnel splitting  $\Delta$  and the magnetization  $M_x$  of the FW can be obtained from the partition function  $Z_0[h_x]$  which we evaluate using spin path integrals. Introducing spin coherent states, we decompose the local spin fields  $\mathbf{s}_i$  (Ref. 30)

$$\mathbf{s}_i = (-1)^{i+1} s \mathbf{n} + \mathbf{l} \quad (3)$$

into a Néel ordered field  $\pm s \mathbf{n}$  ( $n^2=1$ ) and fluctuations  $\mathbf{l} \perp \mathbf{n}$  around it. For small systems containing six, eight, or ten spins, spatial fluctuations of the fields  $\mathbf{n}$  and  $\mathbf{l}$  are frozen out at low temperature  $T$ . Carrying out the Gaussian integral over  $\mathbf{l}$ , we obtain  $Z_0 = \int \mathcal{D}\mathbf{n} \exp\{-\int_0^{\beta\hbar} d\tau L_0(\mathbf{n})/\hbar\}$  with a Euclidean Lagrangian depending only on  $\mathbf{n}$ ,

$$L_0[\mathbf{n}] = \frac{N\hbar^2}{8J} [-(i\mathbf{n} \times \dot{\mathbf{n}} - \mathbf{h})^2 + (\mathbf{h} \cdot \mathbf{n})^2 - \omega_0^2 n_z^2], \quad (4)$$

where  $\omega_0 = s\sqrt{8Jk_z}/\hbar$ .

In contrast to the classical description of the states  $|\uparrow\rangle$  and  $|\downarrow\rangle$  used in Sec. I, in a quantum mechanical treatment  $\mathbf{n}$  always exhibits quantum fluctuations around its classical minima. The notion of quantum tunneling, however, is only applicable if  $\mathbf{n}$  is well localized in the states  $|\uparrow\rangle$  and  $|\downarrow\rangle$ , i.e., if  $1 - \langle \uparrow | n_z^2 | \uparrow \rangle \ll 1$ . The quantum fluctuations of  $\mathbf{n}$  can be estimated from Eq. (4). For  $\mathbf{h}=0$ ,  $L_0$  describes two independent harmonic oscillators of frequency  $\omega_0$ , corresponding to fluctuations of  $\mathbf{n}$  in the direction of  $\mathbf{e}_x$  and  $\mathbf{e}_y$ . If the amplitude of the fluctuations is small, we can evaluate the mean deviation of the Néel vector from  $\mathbf{e}_z$ ,  $1 - \langle n_z^2 \rangle \approx 2/(\mathcal{S}_0/\hbar)$ , where  $\mathcal{S}_0/\hbar = Ns\sqrt{2k_z}/J$  is the classical tunnel action. Hence,  $\mathbf{n}$  is well localized along  $\mathbf{e}_z$  only if  $\mathcal{S}_0/\hbar \gg 2$  or,

TABLE I.  $\mathcal{S}_0/\hbar = Ns\sqrt{2k_z/J}$  and  $\hbar\omega_0/2\mu_B$  for Fe<sub>10</sub>, Cs:Fe<sub>8</sub>, Na:Fe<sub>6</sub>, and Li:Fe<sub>6</sub>.

	$\mathcal{S}_0/\hbar$	$\hbar\omega_0/2\mu_B$
Fe <sub>10</sub>	3.32	7.68 T
Cs:Fe <sub>8</sub>	3.91	16.37 T
Na:Fe <sub>6</sub>	2.47	20.11 T
Li:Fe <sub>6</sub>	1.54	7.98 T

equivalently, if the ground-state energy  $2\omega_0/2$  is small compared to the potential barrier  $Nk_z s^2$ . The scenario changes if a strong magnetic field  $\mathbf{h} = h_x \mathbf{e}_x$ ,  $h_x \gg \omega_0$ , is applied in the ring plane. Then, the mode of  $\mathbf{n}$  along  $\mathbf{e}_x$  is frozen out, such that  $1 - \langle n_z^2 \rangle \approx 1/(\mathcal{S}_0/\hbar)$ , and the FW can exhibit quantum tunneling if  $\mathcal{S}_0/\hbar \gg 1$ . Note that for large tunnel action  $\mathcal{S}_0/\hbar \gtrsim 10$ , the tunnel splitting becomes small, which would make the system under consideration a less favorable candidate for the observation of MQC.

The FW's Li:Fe<sub>6</sub>, Na:Fe<sub>6</sub>, Cs:Fe<sub>8</sub>, and Fe<sub>10</sub> have been well characterized.<sup>10–13,15,31</sup> For Fe<sub>10</sub>,  $J = 15.56$  K and  $k_z = 0.0088J$ . For Cs:Fe<sub>8</sub>,  $J = 22.5$  K and  $k_z = 0.0191J$ .<sup>13</sup> For Fe<sub>6</sub>,  $J$  and  $k_z$  vary appreciably depending on the central alkali-metal ion and ligands: for Na:Fe<sub>6</sub>,  $J = 32.77$  K and  $k_z = 0.0136J$ , whereas for Li:Fe<sub>6</sub>,  $J = 20.83$  K and  $k_z = 0.0053J$ .<sup>31,15</sup> In Table I,  $\mathcal{S}_0/\hbar$  and  $\hbar\omega_0/2\mu_B$  are given for Fe<sub>10</sub>, Cs:Fe<sub>8</sub>, Na:Fe<sub>6</sub>, and Li:Fe<sub>6</sub>. As is obvious from these values, for none of the molecular rings  $\mathcal{S}_0/\hbar$  is sufficiently large to assure that a tunnel scenario is rigorously applicable if  $h_x \lesssim \omega_0$ . In Na:Fe<sub>6</sub>, even at large  $B_x \gg 20$  T,  $\mathbf{n}$  is far less well localized along  $\mathbf{e}_z$  than in Fe<sub>10</sub>, which hence remains the most favorable candidate for the observation of quantum tunneling. Note, however, that even in Fe<sub>10</sub> and Cs:Fe<sub>8</sub>,  $\mathcal{S}_0/\hbar$  is so small that corrections to the instanton techniques used below may become large.<sup>32</sup>

For  $h_x \gg \omega_0$ , the magnetic field  $\mathbf{B}$  strongly confines  $\mathbf{n}$  to the  $(y, z)$  plane and thus determines the tunnel path of the electron spins. This allows one to evaluate  $Z_0$ . We parametrize

$$\mathbf{n} = (\cos \theta, \sin \theta \cos \phi, \sin \theta \sin \phi) \quad (5)$$

and expand  $L_0$  to second order in  $\vartheta = \theta - \pi/2$ ,

$$L_0[\mathbf{n}] = \frac{N\hbar^2}{8J} [-(h_x - i\dot{\phi})^2 - \omega_0^2 \sin^2 \phi] + \frac{1}{2} \vartheta G^{-1}[\phi] \vartheta, \quad (6)$$

where  $G^{-1}[\phi] = (N\hbar^2/4J)[-\partial_\tau^2 + (h_x - i\dot{\phi})^2 + \omega_0^2 \sin^2 \phi]$ ,  $\dot{\phi} = \partial_\tau \phi$ , and  $\omega_0 = s\sqrt{8Jk_z}/\hbar$  as defined above. The typical energy scales for the dynamics of  $\phi$  and  $\vartheta$  are  $\omega_0$  and  $h_x$ , respectively. Due to this separation of energy scales, we can use an adiabatic approximation, in which  $\vartheta$  oscillates rapidly in a quasistatic harmonic potential<sup>33</sup>  $(N\hbar^2/8J)(h_x^2 - 2ih_x\dot{\phi})$ . Integrating out  $\vartheta$ , we obtain an expression for  $L_0$  depending only on  $\phi$ .<sup>14</sup> For  $k_B T/\hbar \ll \omega_0 \ll h_x$ , we find

$$L_0[\phi] \approx \frac{N\hbar^2}{8J} [-(h_x - i\dot{\phi})^2 - \omega_0^2 \sin^2 \phi] + \hbar \frac{h_x - i\dot{\phi}}{2} + \mathcal{O}(\omega_0^2/h_x), \quad (7)$$

where the term  $\hbar(h_x - i\dot{\phi})/2$  arises from the  $\vartheta$  fluctuation determinant. The two saddle points of Eq. (7),  $\phi \equiv \pi/2$  and  $\phi \equiv 3\pi/2$ , correspond to the two classical spin configurations sketched in Fig. 1. If tunneling is weak,  $\mathcal{S}_0/\hbar \gg 1$ , the remaining path integral over  $\phi$  is straightforward.<sup>34,14</sup> Summing all multi-instanton solutions, one finds

$$Z_0 = \exp \left[ \beta \left( \frac{N\hbar^2}{8J} h_x^2 - \hbar \frac{h_x + \omega_0}{2} \right) \right] \cosh \left( \frac{\beta \Delta(h_x)}{2} \right), \quad (8)$$

with the tunnel splitting

$$\Delta(h_x) = \Delta_0 \left| \sin \left( \pi \frac{N\hbar}{4J} h_x \right) \right|, \quad (9)$$

where  $\beta = 1/k_B T$ ,  $\Delta_0 = 8\hbar\omega_0\sqrt{\mathcal{S}_0/2\pi\hbar} \exp[-\mathcal{S}_0/\hbar]$ , and  $\mathcal{S}_0/\hbar = Ns\sqrt{2k_z/J}$ . In particular,  $\Delta$  is periodic as a function of  $h_x$ . Differentiating with respect to  $B_x$ , we obtain the magnetization<sup>14</sup>

$$M_x = (g\mu_B) \left[ \frac{N\hbar}{4J} h_x - \frac{1}{2} + \frac{1}{2\hbar} \frac{\partial \Delta}{\partial h_x} \tanh \left( \frac{\beta \Delta}{2} \right) \right]. \quad (10)$$

Because  $\partial \Delta / \partial h_x$  is discontinuous at the zeros of  $\Delta$ ,  $M_x$  exhibits steps at  $B_{c,n} = n4J/Ng\mu_B$ , where  $n = 1, 2, \dots, Ns$ . From

$$M_\alpha = (g\mu_B) \frac{N\hbar}{4J} \frac{1}{Z} \int \mathcal{D}\mathbf{n} [h_\alpha - i(\mathbf{n} \times \dot{\mathbf{n}})_\alpha - n_\alpha \mathbf{h} \cdot \mathbf{n}] \times \exp \left( - \int_0^{\beta\hbar} d\tau L_0[\mathbf{n}]/\hbar \right), \quad (11)$$

it also follows that, for arbitrary  $h_x$ ,  $M_\alpha = 0$  for  $h_\alpha = 0$ ,  $\alpha = y, z$ , which is a result of the invariance of  $\hat{H}_0$  under rotation around  $\mathbf{B}$  by  $\pi$ .<sup>35</sup>

## B. Spin dynamics

We show now that the tunneling dynamics of  $\mathbf{n}$  does not enter the susceptibility of the FW, i.e., that the imaginary part of the susceptibility,  $\chi''_{\alpha\alpha}(\omega)$ , has no absorption peak  $\delta(\omega - \Delta/\hbar)$ . To prove this, we calculate the susceptibility of the total spin,  $\hat{\mathbf{S}} = \sum_{i=1}^N \hat{\mathbf{s}}_i$ , in Matsubara representation,

$$\chi_{\alpha\alpha}(i\omega_n) = (g\mu_B)^2 \int_0^{\beta\hbar} d\tau e^{i\omega_n \tau} \times [\langle T_\tau \hat{S}_\alpha(\tau) \hat{S}_\alpha(0) \rangle - \langle \hat{S}_\alpha \rangle^2], \quad (12)$$

where  $\alpha = x, y, z$ . As we will show below,  $\chi_{\alpha\alpha}(i\omega_n)$  contains *no* terms proportional to  $1/(i\omega_n - \Delta/\hbar)$ . This implies that ac susceptibility or ESR measurements cannot be used to detect Néel vector tunneling in FW's described by  $\hat{H}_0$ .

$\chi_{xx}(i\omega_n)$  can be calculated from the generating functional  $Z[\delta h_x(\tau)]$ , where  $\delta h_x(\tau)$  is a small probing field added to

the static field  $h_x \gg \omega_0$ . Because we are only interested in the low-frequency response of the FW,  $\omega_n \lesssim \Delta/\hbar \ll \omega_0$ , we may restrict our attention to a slowly varying field  $\delta h_x$  whose Fourier components vanish for  $\omega_n \gtrsim \Delta/\hbar$ . The typical time scale for the dynamics of  $\phi$ ,  $1/\omega_0$ , is short compared to the time scale on which  $\delta h_x$  varies. In particular, approximating  $\delta h_x(\tau)$  by a constant during instanton passage, we find

$$Z[\delta h_x(\tau)] \approx \exp \left[ \int_0^{\beta\hbar} d\tau \left( \frac{N\hbar^2}{8J} [h_x + \delta h_x(\tau)]^2 - \hbar \frac{h_x + \delta h_x(\tau) + \omega_0}{2} \right) \right] \times \cosh \left[ \int_0^{\beta\hbar} d\tau \frac{\Delta [h_x + \delta h_x(\tau)]}{2} \right]. \quad (13)$$

Differentiating twice and setting  $\delta h_x \rightarrow 0$ , for  $\omega_n \lesssim \Delta/\hbar$ ,

$$\chi_{xx}(i\omega_n) = (g\mu_B)^2 \left[ \frac{N\hbar}{4J} + \frac{1}{2\hbar} \frac{\partial^2 \Delta}{\partial h_x^2} \tanh(\beta\Delta/2) + \frac{\beta}{\hbar} \left( \frac{1}{2} \frac{\partial \Delta}{\partial h_x} \right)^2 \cosh^{-2}(\beta\Delta/2) \delta_{\omega_n,0} \right]. \quad (14)$$

The transverse susceptibilities can be evaluated directly from  $\delta^2 Z / \delta h_\alpha(\tau) \delta h_\alpha(0)$ ,  $\alpha = y, z$ . Using the parametrization in Eq. (5),  $\vartheta = \theta - \pi/2$  can be integrated out in the path-integral expression for  $\chi_{\alpha\alpha}$ . After lengthy calculation (Appendix A), we obtain for  $\omega_n \ll h_x$

$$\chi_{yy}(i\omega_n) \approx (g\mu_B)^2 \frac{N\hbar}{4J},$$

$$\chi_{zz}(i\omega_n) \approx (g\mu_B)^2 \frac{N\hbar}{4J}. \quad (15)$$

From Eqs. (14) and (15) it is evident that none of the susceptibilities  $\chi_{\alpha\alpha}(i\omega_n)$  contains a term proportional to  $1/(i\omega_n \pm \Delta/\hbar)$ . In the tunneling regime discussed here,  $|g\rangle$  and  $|e\rangle$  are energetically well separated from all other states. Then, Eq. (15) and the spectral representation

$$\chi_{\alpha\alpha}(i\omega_n) = \sum_{i,j} \frac{e^{-\beta E_i}}{Z} |\langle i | \hat{S}_\alpha | j \rangle|^2 \left( \frac{1}{i\omega_n - (E_i - E_j)/\hbar} - \frac{1}{i\omega_n + (E_i - E_j)/\hbar} \right) - \beta\hbar \delta_{\omega_n,0} \langle \hat{S}_\alpha \rangle^2, \quad (16)$$

where  $|i\rangle$  and  $|j\rangle$  label energy eigenstates, imply that  $\langle e | \hat{S}_\alpha | g \rangle = 0$  ( $\alpha = x, y, z$ ). Although for the parameters of Fe<sub>10</sub>, Cs:Fe<sub>8</sub>, and Na:Fe<sub>6</sub> tunnel corrections to  $\chi_{\alpha\alpha}$  neglected in Eq. (15) can be significant, the main conclusion of our calculation—that coherent tunneling of  $\mathbf{n}$  does not enter the susceptibilities  $\chi_{\alpha\alpha}$ —remains valid.

Indeed,  $\langle e | \hat{S}_\alpha | g \rangle = 0$  is a direct consequence of the invariance of  $\hat{H}_0$  as  $i \rightarrow i+1$ , i.e., the exchange of the two sublattices

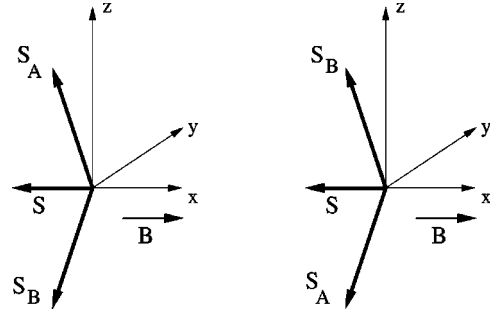


FIG. 2. Sublattice spins and total spin of the FW in magnetic fields.

of the bipartite AF ring. In order to clarify this point, we introduce the sublattice spin operators

$$\hat{\mathbf{S}}_A = \sum_{i=\text{odd}} \hat{\mathbf{s}}_i, \quad \hat{\mathbf{S}}_B = \sum_{i=\text{even}} \hat{\mathbf{s}}_i, \quad (17)$$

with  $\hat{\mathbf{S}} = \hat{\mathbf{S}}_A + \hat{\mathbf{S}}_B$ . In a semiclassical description of the FW, spins of one sublattice couple ferromagnetically to each other. The classical spin fields<sup>30</sup>  $\mathbf{s}_i$  then obey  $\mathbf{s}_i = \mathbf{S}_A/(N/2)$  for odd  $i$  and  $\mathbf{s}_i = \mathbf{S}_B/(N/2)$  for even  $i$ . This amounts to treating  $\mathbf{S}_A$  and  $\mathbf{S}_B$  as single large spins<sup>7,8,22</sup> with spin quantum number  $Ns/2$ , and  $\hat{H}_0$  reduces to

$$\hat{H}_{0,\text{subl}} = \frac{4J}{N} \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B + \hbar \mathbf{h} \cdot (\hat{\mathbf{S}}_A + \hat{\mathbf{S}}_B) - \frac{2k_z}{N} (\hat{S}_{A,z}^2 + \hat{S}_{B,z}^2). \quad (18)$$

Similar to the nonlinear sigma model (NLSM) formalism used above,  $\hat{H}_{0,\text{subl}}$  provides an appropriate description of the low-energy physics of the FW.

In Fig. 2, the two classical ground-state spin configurations of  $\hat{H}_{0,\text{subl}}$  are shown. A finite magnetic field  $\mathbf{B}$  tilts the sublattice spins away from the direction of  $\mathbf{B}$  such that  $\mathbf{S} = \mathbf{S}_A + \mathbf{S}_B$  is parallel to  $\mathbf{B}$ . During tunneling of  $\mathbf{n}$ , the sublattice spins retain their position relative to each other and rotate jointly around  $\mathbf{e}_x$ . The total spin vector  $\mathbf{S}$ , however, remains invariant during tunneling such that the real-time spin correlation function does not contain terms proportional to  $e^{i\Delta t/\hbar}$  or, equivalently,  $\langle e | \hat{S}_\alpha | g \rangle = 0$ .

### III. PHENOMENOLOGICAL MODEL FOR THE MODIFIED FW

The fact that the susceptibilities  $\chi_{\alpha\alpha}$  of the FW show no signature of the tunneling of  $\mathbf{n}$  is a consequence of the symmetry of  $\hat{H}_{0,\text{subl}}$  under  $\hat{\mathbf{S}}_A \leftrightarrow \hat{\mathbf{S}}_B$ . In the modified FW's [Eq. (1)] this symmetry is broken, which makes them much more suitable for the observation of tunneling of  $\mathbf{n}$ . In this section we discuss the saddle-point, i.e., classical, properties of the phenomenological sublattice model for the modified FW. We generalize earlier work<sup>21-24</sup> to finite magnetic fields and show that, in contrast to systems with easy-plane anisotropy,<sup>25</sup> in molecular rings with easy-axis anisotropy and finite excess spin,  $\mathbf{S}$  oscillates as  $\mathbf{n}$  tunnels.

Following Sec. II B, we introduce  $\hat{\mathbf{S}}_A$  and  $\hat{\mathbf{S}}_B$  as defined in

Eq. (17). The Hamiltonian  $\hat{H}$  of the modified FW can thus be mapped onto a simpler version in terms of sublattice spins,

$$\hat{H}_{\text{subl}} = \frac{4[(N-2)Js^2 + 2J's's']}{(Ns + 2\delta s)Ns} \hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B + \hbar \mathbf{h} \cdot (\hat{\mathbf{S}}_A + \hat{\mathbf{S}}_B) - \frac{2k_z}{N} \left[ \frac{1 + 2(k'_z s'^2 - k_z s^2)/(Nk_z s^2)}{(1 + 2\delta s/Ns)^2} \hat{S}_{A,z}^2 + \hat{S}_{B,z}^2 \right], \quad (19)$$

where  $\delta s = s' - s$ ,  $S_A = (N/2 - 1)s + s' = Ns/2 + \delta s$ , and  $S_B = Ns/2$ . Throughout this paper we assume the following inequalities:

$$|\delta s| \ll Ns, \quad (20)$$

$$|k'_z s'^2 - k_z s^2| \ll Nk_z s^2/2, Js, \quad (21)$$

$$2J's' \ll NJs, \quad (22)$$

where  $J, J' > 0$ . Equation (20) guarantees that the modified FW is an AF system with small excess spin, to which the theory of Néel vector tunneling applies. For both Cr and Ga dopant ions ( $|\delta s| = 1$  and  $5/2$ , respectively), Eq. (20) is well satisfied. Equation (21) will allow us to treat the difference in sublattice anisotropies ( $k'_z s'^2 - k_z s^2$ ) in perturbation theory. Typical values of  $k'_z$  and  $k_z$  are on the order of only  $0.01J$ , such that this condition holds for most systems of interest. Finally, Eq. (22) together with Eq. (20) assures that the ‘‘bulk’’ parameters of a FW are only slightly altered by exchanging one single spin, such that the parameters of the undoped FW (Table I) still determine whether the modified FW is in a quantum-tunneling regime. However, as will be shown below, the excess spin  $\delta s \neq 0$  leads to qualitative changes in both thermodynamic and dynamic quantities. We further assume

$$k_B T \ll \hbar \omega_0, \quad (23)$$

which allows us to restrict our attention to the low-energy sector of the FW, which consists of two tunnel-split states only.

We first discuss the classical vector model of Eq. (19) for  $k_z = k'_z = 0$ , but finite  $h_x$ . For an AF system with equal sublattice spins, the spins would lie close to the plane perpendicular to the field  $h_x$ . As sketched in Fig. 2, tilting of the spins leads to a gain in energy  $N\hbar^2 h_x^2/8J$ . However, for uncompensated sublattices, the configuration sketched in Fig. 3(a) provides an energy gain  $|\delta s|\hbar h_x$  and hence is favorable for  $\hbar h_x \ll |\delta s|8J/N = \hbar h_c$ . Only for  $h_x \gg h_c$  is the classical ground-state spin configuration as sketched in Fig. 3(b). The energy is minimized if the projections of  $\mathbf{S}_A$  and  $\mathbf{S}_B$  onto the  $(y, z)$  plane are antiparallel, such that  $\mathbf{S} = \mathbf{S}_A + \mathbf{S}_B$  is parallel to  $\mathbf{B}$ . This picture remains valid for a system with easy-plane anisotropy and  $\mathbf{B}$  applied in the easy plane.<sup>25</sup>

The scenario changes for easy-axis ( $\mathbf{e}_z$ ) anisotropy and a magnetic field  $\mathbf{B}$  perpendicular to  $\mathbf{e}_z$ . First, the anisotropy favors the spin configuration sketched in Fig. 3(b) over that in Fig. 3(a). The true classical ground-state spin configura-

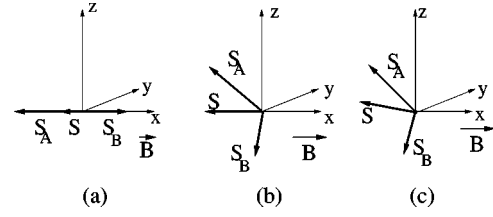


FIG. 3. Classical ground-state spin configurations (schematically) of an AF system with excess spin in a magnetic field. (a)  $k_z = k'_z = 0$  and  $h_x < h_c = |\delta s|8J/N\hbar$ . (b)  $h_x > h_c$  and  $k_z = k'_z = 0$ . (c)  $h_x > h_c$ . Now, the finite anisotropies  $k_z, k'_z \neq 0$  lead to a finite component  $S_z$  perpendicular to the magnetic field  $\mathbf{B}$ .

tion depends on the ratio  $k_z/\hbar h_x$ . More importantly, even for  $h_x \gg h_c$ ,  $\mathbf{S}$  now has a component perpendicular to  $\mathbf{B}$ . The reason for this is that for  $\delta s \neq 0$  or  $k'_z s'^2 - k_z s^2 \neq 0$ , Eq. (19) is no longer invariant under exchange of  $\mathbf{S}_A$  and  $\mathbf{S}_B$  if  $k_z \neq 0$ . Due to Eq. (21) and (22), the components  $S_y$  and  $S_z$  of the total spin can be evaluated perturbatively. With the polar angle  $\phi$  parametrizing the projection of  $\mathbf{S}_A$  onto the  $(y, z)$  plane, to leading order in  $\delta s$  and  $(k'_z s'^2 - k_z s^2)/2Js$  we obtain

$$\begin{pmatrix} S_y \\ S_z \end{pmatrix} \approx \begin{pmatrix} \omega_0^2 \\ \delta s \frac{\omega_0^2}{h_x^2} + \frac{k'_z s'^2 - k_z s^2}{2Js} \end{pmatrix} \sin^2 \phi \begin{pmatrix} \cos \phi \\ \sin \phi \end{pmatrix}. \quad (24)$$

As is evident from Eq. (24), finite  $S_y$  or  $S_z$  can be due to  $\delta s \neq 0$  or  $k'_z s'^2 - k_z s^2 \neq 0$ , i.e., excess spin or unequal effective anisotropies for  $\mathbf{S}_A$  and  $\mathbf{S}_B$ .

According to Eq. (20), the modified FW is an AF system with small excess spin which is expected to exhibit spin tunnel dynamics qualitatively similar to the FW, as indicated by the close formal analogy between Eqs. (18) and (19). For magnetic fields

$$\max[\hbar \omega_0, |\delta s|8J/N] \ll \hbar h_x \ll 4Js, \quad (25)$$

the sublattice spin vectors  $\mathbf{S}_A$  and  $\mathbf{S}_B$  lie close to the  $(y, z)$  plane. Due to the easy-axis anisotropy, configurations with  $\mathbf{S}_A$  and  $\mathbf{S}_B$  close to the  $z$  axis are energetically favorable. It is noteworthy that the condition  $h_x \gg \omega_0$  is not indispensable for quantum tunneling of  $\mathbf{n}$ , but only assures that a tunnel scenario remains applicable for a wider range of  $k_z$  (Sec. II A). In contrast,  $\hbar h_x \gg |\delta s|8J/N$  guarantees that there are two energetically degenerate, macroscopically distinct spin configurations between which spin tunneling may take place<sup>25</sup> and hence, in general, will shift the range of magnetic fields in which a tunneling scenario as discussed in the present context (Fig. 1) is valid. Henceforth, we will always assume that  $B_x$  is large enough to satisfy Eq. (25). For sufficiently large  $k_z$ , the two-state model for the low-energy sector of the system outlined in Sec. I then still applies. As Eq. (24) indicates, the modified FW exhibits one important novel feature: as  $\mathbf{n}$  tunnels between  $\mathbf{e}_z$  and  $-\mathbf{e}_z$  ( $\phi = \pi/2$  and  $\phi = 3\pi/2$ , respectively), the  $z$  component of the total spin,  $S_z$ , oscillates between  $S_0 = [\delta s \omega_0^2/h_x^2 + (k'_z s'^2 - k_z s^2)/2Js]$  and  $-S_0$ .

#### IV. THERMODYNAMICS OF THE MODIFIED FW

In order to quantify the statements on Néel vector tunneling in modified FW's (Sec. III), we now develop a semiclassical theory of the modified FW. In this section, we discuss thermodynamic quantities such as the magnetization  $M_x$  and specific heat  $c_v$ . While our theory treats the spins semiclassically, we give the explicit dependence on the microscopic parameters of  $\hat{H}$  [Eq. (1)]. To this end we evaluate the partition function  $Z$ , thus generalizing the procedure reviewed in Sec. II A to systems with  $k'_z \neq k_z$ ,  $J' \neq J$ , and  $\delta s \neq 0$ . The most significant change is that, for  $\delta s \neq 0$ , the staggering [Eq. (3)] must be modified in order to account for  $\mathbf{s}_1^2 = s'^2$ . The ansatz

$$\mathbf{s}_1 = s' \mathbf{n} + \frac{s'}{s} \mathbf{l},$$

$$\mathbf{s}_i = (-1)^{i+1} s \mathbf{n} + \mathbf{l} \quad \forall i \neq 1 \quad (26)$$

is equivalent to the assumption that spins within sublattices  $A$  and  $B$  are ferromagnetically coupled.<sup>7,8,21–24</sup> The results for the magnetization  $M_x$  and susceptibilities obtained from this ansatz turn out to be in good agreement with those obtained from numerical exact diagonalization (ED) (see below and Sec. V) as long as  $|J'/J - 1| \ll 1$ . We restrict ourselves to this case first and discuss further limiting cases  $J' \ll J$  and  $J' \gg J$  in Sec. VI.

As for the FW,<sup>14</sup> at low temperatures spatial variations of the Néel field  $\mathbf{n}$ , and the fluctuations  $\mathbf{l}$  around it, are suppressed in small ring system. With the coherent spin states defined in Eq. (26),<sup>36</sup>

$$Z = \int \mathcal{D}\mathbf{n} \mathcal{D}\mathbf{l} \delta(\mathbf{n} \cdot \mathbf{l}) e^{-S[\mathbf{n}, \mathbf{l}]/\hbar}, \quad (27)$$

where

$$S[\mathbf{n}, \mathbf{l}] = -i\hbar \left( s' \omega \left[ \mathbf{n} + \frac{1}{s} \mathbf{l} \right] + s \sum_{i=2}^N \omega \left[ (-1)^{i+1} \mathbf{n} + \frac{1}{s} \mathbf{l} \right] \right) + \int_0^{\beta\hbar} d\tau H[\mathbf{n}, \mathbf{l}]. \quad (28)$$

Here,

$$H[\mathbf{n}, \mathbf{l}] = 2 \left[ (N-2)J + 2 \frac{s'}{s} J' \right] \mathbf{l}^2 + \hbar \left( N + \frac{\delta s}{s} \right) \mathbf{h} \cdot \mathbf{l} - [(N-1)k_z s^2 + k'_z s'^2] n_z^2 + \frac{2}{s} (k_z s^2 - k'_z s'^2) n_z l_z + \delta s \hbar \mathbf{h} \cdot \mathbf{n} \quad (29)$$

is the classical energy of a given spin configuration. The small term  $[(N-1)k_z + k'_z] l_z^2$  has already been neglected. The first term in Eq. (28) is the Berry-phase term, where  $\omega[\Omega]$  denotes the area traced out by some vector  $\Omega(\tau)$  on the unit sphere. Here, we use the south pole gauge (i.e.,  $\omega[\Omega(\tau) \equiv -\mathbf{e}_x] = 0$ ). Expanding the Berry-phase term to leading order in  $\mathbf{l}$  with the parametrization Eq. (5) yields

$$- \int_0^{\beta\hbar} d\tau \left[ i \delta s \dot{\phi} (1 + \cos \theta) + i \left( N + \frac{\delta s}{s} \right) (\mathbf{n} \times \dot{\mathbf{n}}) \cdot \mathbf{l} \right]. \quad (30)$$

The first term is due to the fact that, for  $\delta s \neq 0$ , the Berry-phase terms of the AF-ordered components  $s' \omega[\mathbf{n}] + s \sum_{i=2}^N \omega[(-1)^{i+1} \mathbf{n}] = \int d\tau [Ns \dot{\phi} + \delta s \dot{\phi} (1 + \cos \theta)]$  do not add to an integer multiple of  $2\pi$ .<sup>37,38</sup>

Carrying out the Gaussian integral over  $\mathbf{l}$  we obtain  $Z = \int \mathcal{D}\mathbf{n} \exp\{-\int_0^{\beta\hbar} d\tau L[\mathbf{n}]/\hbar\}$ , with a Euclidean Lagrangian

$$L[\mathbf{n}] = \frac{N\hbar^2}{8\tilde{J}} \left\{ -(\mathbf{h} + h_A n_z \mathbf{e}_z - i\mathbf{n} \times \dot{\mathbf{n}})^2 + [(\mathbf{h} + h_A n_z \mathbf{e}_z) \cdot \mathbf{n}]^2 - \tilde{\omega}_0^2 n_z^2 \right\} + \delta s \hbar [\mathbf{h} \cdot \mathbf{n} - i \dot{\phi} (1 + \cos \theta)], \quad (31)$$

where

$$\frac{\tilde{J}}{N} = \frac{(N-2)J + 2s'J'/s}{(N + \delta s/s)^2},$$

$$h_A = \frac{2(k_z s^2 - k'_z s'^2)}{(N + \delta s/s)s\hbar},$$

$$\tilde{\omega}_0^2 = \frac{8\tilde{J}}{N} [(N-1)k_z s^2 + k'_z s'^2]. \quad (32)$$

Equation (31) is the analog of Eq. (4) for the FW. A finite excess spin  $\delta s$  of the modified FW leads to two significant changes in  $L[\mathbf{n}]$ : first, the typical energy scales of the system are slightly renormalized,  $J \rightarrow \tilde{J}$  and  $\omega_0 \rightarrow \tilde{\omega}_0$ , even for  $J' = J$  and  $k'_z = k_z$ . More importantly,  $L$  acquires an additional term due to the Zeeman energy and Berry phase of the uncompensated spin  $\delta s \mathbf{n}$ . For all cases of experimental interest, due to Eq. (21), we have  $h_A \ll \tilde{\omega}_0 \ll h_x$ . The  $h_A$ -dependent terms in Eq. (31) hence lead only to minor modifications of the thermodynamic properties of the modified FW compared to the FW, but feature in the dynamics.

We will show now that, for  $h_x \neq 0$ ,  $\mathbf{n}$  and hence the excess spin no longer trace a tunneling path in the  $(y, z)$  plane. As can be seen from

$$L[\phi, \theta] \approx \frac{N\hbar^2}{8\tilde{J}} \left[ -(h_x - i\dot{\phi})^2 - \tilde{\omega}_0^2 \sin^2 \phi \right] - i\hbar \delta s \dot{\phi} + \frac{N\hbar^2}{8\tilde{J}} \left[ \dot{\theta}^2 + \cos^2 \theta ((h_x - i\dot{\phi})^2 + \tilde{\omega}_0^2 \sin^2 \phi) \right] + 2 \cos \theta (h_x - i\dot{\phi}) \left( \delta s \frac{4\tilde{J}}{N\hbar} + h_A \sin^2 \theta \sin^2 \phi \right), \quad (33)$$

the time scales for the dynamics of  $\phi$  and  $\theta$  separate due to Eq. (25), and we can again invoke the adiabatic approximation used in Sec. II B. Here  $\theta$  oscillates in a slowly varying harmonic potential with the potential minimum at  $\theta_0$ , where

$$\cos \theta_0 = -\frac{h_x - i\phi}{(h_x - i\phi)^2 + \tilde{\omega}_0^2 \sin^2 \phi} \left( \frac{4\tilde{J}}{N\hbar} \delta s + h_A \sin^2 \phi \right). \quad (34)$$

Corrections to the adiabatic approximation are beyond the order of the present calculation. Equation (34) shows that finite  $\delta s \neq 0$  or  $h_A \neq 0$  leads to a shift in the saddle points of the Lagrangian  $L[\phi, \theta]$  away from  $\theta_0 = \pi/2$ , which is due to the fact that then  $\mathbf{S}_A - \mathbf{S}_B$  no longer lies in the  $(y, z)$  plane [Fig. 3(c)]. Expanding Eq. (33) to second order in  $\vartheta = \theta - \theta_0$  and carrying out the Gaussian integral over  $\vartheta$ , we obtain a  $\phi$ -dependent effective Lagrangian

$$L[\phi] = \frac{N\hbar^2}{8\tilde{J}} \left[ -(h_x - i\phi)^2 - \tilde{\omega}_0^2 \sin^2 \phi \right] - i\hbar \left( \delta s + \frac{1}{2} \right) \dot{\phi} + \hbar \frac{h_x}{2} + \mathcal{O}(\tilde{\omega}_0^2/h_x, Nh_A \tilde{\omega}_0/8\tilde{J}). \quad (35)$$

Comparison with the corresponding Lagrangian for  $\delta s = 0$  [Eq. (7)] shows that, to leading order in the excess spin  $\delta s$  and anisotropy field  $h_A$ , the only effect of an excess spin is to introduce an additional topological phase  $-i\delta s \dot{\phi}$ . In particular, in contrast to the case  $h_x = 0$  discussed in earlier work on tunneling in ferrimagnets,<sup>21–24</sup> the potential barrier and hence the real part of the tunnel action are only slightly altered by the excess spin. This is due to the fact<sup>25</sup> that, for  $\hbar h_x > |\delta s| 8J/N$  [Eq. (25)], the system is in the AF regime in which the tunnel splitting is only slightly modified by the excess spin. Note that Eq. (35) is formally identical to Eq. (7), which provides a rigorous proof of the statement that the modified FW also may exhibit tunneling of  $\mathbf{n}$  for sufficiently large anisotropy, as already claimed on basis of physical arguments at the end of Sec. III.

Using the same techniques as for the FW, we find

$$Z = \exp \left[ \beta \left( \frac{N\hbar^2}{8\tilde{J}} h_x^2 - \hbar \frac{h_x + \tilde{\omega}_0}{2} \right) \right] \cosh \left( \frac{\beta \tilde{\Delta}}{2} \right), \quad (36)$$

with the tunnel splitting

$$\tilde{\Delta}(h_x) = \tilde{\Delta}_0 \left| \sin \pi \left( \frac{N\hbar}{4\tilde{J}} h_x + \delta s \right) \right|, \quad (37)$$

where  $\tilde{S}/\hbar = N\tilde{\omega}_0/2\tilde{J}$  and  $\tilde{\Delta}_0 = 8\hbar\tilde{\omega}_0 \sqrt{\tilde{S}/2\pi\hbar} \exp[-\tilde{S}/\hbar]$ . From Eq. (36) it is also straightforward to derive all thermodynamic quantities of interest. In particular, for the free energy  $F$ , the magnetization  $M_x$ , and the specific heat  $c_v$  we obtain

$$F = \hbar \frac{\tilde{\omega}_0 + h_x}{2} - \frac{N\hbar^2}{8\tilde{J}} h_x^2 - \frac{1}{\beta} \ln \cosh \left( \frac{\beta \tilde{\Delta}}{2} \right), \quad (38)$$

$$M_x = (g\mu_B) \left[ \frac{N\hbar h_x}{4\tilde{J}} - \frac{1}{2} + \frac{1}{2\hbar} \frac{\partial \tilde{\Delta}}{\partial h_x} \tanh \left( \frac{\beta \tilde{\Delta}}{2} \right) \right], \quad (39)$$

$$c_v = k_B \left( \frac{\beta \tilde{\Delta}}{2} \right)^2 \cosh^{-2} \left( \frac{\beta \tilde{\Delta}}{2} \right). \quad (40)$$

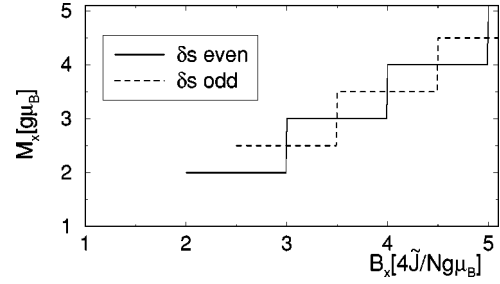


FIG. 4. Schematic plot of the ground-state magnetization of a modified FW with integer (solid line) and half-integer (dashed line)  $\delta s$ , respectively.

The most significant change in the thermodynamic properties of the modified FW is that, for half-integer  $\delta s$ , the zeros of  $\tilde{\Delta}$  and hence the magnetization steps are shifted by a magnetic field  $2\tilde{J}/Ng\mu_B$ , i.e., half of a magnetization plateau, compared to the unmodified wheel (Fig. 4). The magnetization plateaus then lie at half-integer spin values. At low  $T$ , the specific heat  $c_v$  should exhibit a characteristic Schottky anomaly, with a peak at  $T_0 \approx 0.4\tilde{\Delta}/k_B$ . So far,  $c_v$  has been measured only for  $B_x = 0$  in Fe<sub>10</sub> and Fe<sub>6</sub> samples.<sup>39</sup> Measurements of  $T_0$  in  $c_v(T)$  for various  $h_x \gg \tilde{\omega}_0$  would in principle allow one to observe the characteristic sinusoidal variation of  $\tilde{\Delta}$  as function of  $h_x$ .

The width of the magnetization plateaus,  $\delta B_{c,n} = B_{c,n+1} - B_{c,n} = 4\tilde{J}/Ng\mu_B$ , where  $B_{c,n}$  is the field at which the magnetization  $M_x$  exhibits the  $n$ th step, is a quantity which is accessible in experiments and from which  $J'$  can be inferred. Our theory predicts

$$\delta B_{c,n}(J') - \delta B_{c,n}(J' = J) = 8 \frac{s'/s}{(N + \delta s/s)^2} \frac{(J' - J)}{g\mu_B}. \quad (41)$$

In Fig. 5 we compare the functional dependence predicted by Eq. (41) with the results of ED on small rings,  $N = 4$ ,  $s = 2$ ,  $s' = 3/2$  (upper panel), and  $s' = 1$  (lower panel), respec-

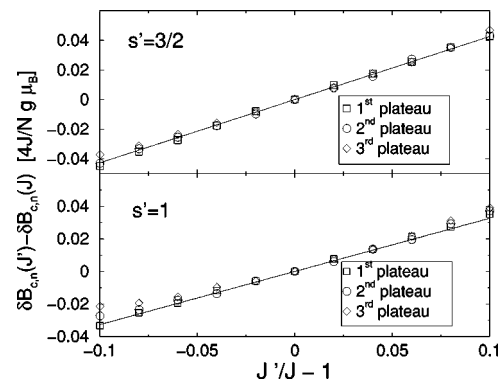


FIG. 5. Comparison of ED (symbols) and analytical (solid line) results for the difference in plateau width,  $\delta B_{c,n}(J') - \delta B_{c,n}(J' = J)$  as function of  $J' - J$  for  $\delta s = -1/2$  (upper panel) and  $\delta s = -1$  (lower panel).  $N = 4$ ,  $s = 2$ ,  $k_z = k'_z = 0.1J$ . The numerical error of the data points  $\pm 0.002 \times 4J/Ng\mu_B$  is smaller than the symbol size.

tively, for  $|J'/J-1| \leq 0.1$ .<sup>40</sup> The ED results are in good agreement with the analytical result. The deviations for  $|J'/J-1| \geq 0.1$  signal the breakdown of our ansatz in Eq. (26) for  $J'$  significantly different from  $J$  (see Sec. VI below).

We show now that although, for a given direction of  $\mathbf{n}$ , the total spin  $\mathbf{S}$  acquires a component perpendicular to the field  $\mathbf{B}$ , the magnetization  $M_\alpha=0$  still vanishes for  $\alpha=y,z$ . We define the fields  $m_\alpha(\tau) = \delta \int d\tau L[\mathbf{n}] / \delta(\hbar h_\alpha(\tau))|_{h_\alpha=0}$  such that  $M_\alpha = -(g\mu_B) \int \mathcal{D}\mathbf{n} m_\alpha(\tau) \exp(-\int d\tau L[\mathbf{n}]/\hbar) / Z$ . Using Eq. (33), we obtain

$$\begin{aligned} m_z &= \frac{N\hbar}{4\tilde{J}} [-h_A n_z (1-n_z^2) + h_x n_x n_z + i(\mathbf{n} \times \dot{\mathbf{n}})_z] + \delta s n_z \\ &\simeq -\frac{N\hbar}{4\tilde{J}} h_A \sin \phi + \delta s \frac{\tilde{\omega}_0^2}{(h_x - i\dot{\phi})^2} \sin^3 \phi \\ &\quad + i \frac{N\hbar}{4\tilde{J}} \theta_0 \cos \phi + \mathcal{O}(\vartheta), \end{aligned} \quad (42)$$

with  $\theta_0$  defined in Eq. (34).<sup>41</sup> As follows from the invariance of  $\hat{H}$  under rotation around  $\mathbf{B}$  by  $\pi$ ,  $M_y = M_z = 0$  for arbitrary  $h_x$ . In particular, at  $T=0$ ,  $M_z=0$  indicates that the ground state is not a state with definite direction of  $\mathbf{n}$ , but rather a coherent superposition of such states,  $(|\uparrow\rangle + |\downarrow\rangle)/\sqrt{2}$ , as expected for a system which shows coherent Néel vector tunneling.

## V. DYNAMICS OF THE MODIFIED FW

As we have shown above, the effective action  $L[\phi]$  of the modified FW [Eq. (35)] is formally identical to that of the FW [Eq. (7)]. In particular, for large anisotropy  $k_z$ , such that  $\tilde{\mathcal{S}}/\hbar \gg 1$ , the modified FW is in the quantum tunneling regime (Sec. II A). In this section, we evaluate explicitly the spin susceptibility  $\chi_{zz}(\tau)$  for the modified FW.

In order to motivate this, we first calculate  $\chi_{zz}$  using the results of the classical vector model (Sec. III). For  $\mathbf{n}$  along  $\mathbf{e}_z$  or  $-\mathbf{e}_z$ , the  $z$  component of the total spin vector is finite,  $S_z = \pm S_0$ , where  $S_0 = \delta s \omega_0^2 / h_x^2 + (k'_z s'^2 - k_z s^2) / 2J_s$ . For  $\mathbf{n}(t=0) = \mathbf{e}_z$ , the coherent tunneling of  $\mathbf{n}$  then results in an oscillating  $S_z(t) = S_0 \cos(\tilde{\Delta}t/\hbar)$ , such that the Fourier transform of the (real-time) susceptibility exhibits an absorption pole  $\chi''_{zz}(\omega \simeq \tilde{\Delta}/\hbar) = \pi |S_0|^2 \tanh(\beta\tilde{\Delta}/2) \delta(\omega - \tilde{\Delta}/\hbar)$ .

Generalizing the procedure for the FW (Appendix A) to  $\delta s \neq 0$ , we calculate the quantum corrections to this result from<sup>42</sup>

$$\begin{aligned} \chi_{zz}(\tau) &= (g\mu_B)^2 \frac{N\hbar}{4\tilde{J}} (1 - \langle \sin^2 \phi \rangle) \delta(\tau) + (g\mu_B)^2 \frac{1}{Z} \\ &\quad \times \int \mathcal{D}\mathbf{n} \exp\left(-\int_0^{\beta\hbar} d\tau L[\mathbf{n}]/\hbar\right) m_z(\tau) m_z(0), \end{aligned} \quad (43)$$

with  $m_z(\tau)$  given in Eq. (42). As for the undoped FW, the correlations of the  $\vartheta$  terms in  $m_z(\tau)$  give rise to a strongly peaked term  $(g\mu_B)^2 N\hbar \delta(\tau) \langle \sin^2 \phi \rangle / 4\tilde{J}$ . We hence find<sup>43</sup>

$$\begin{aligned} \chi_{zz}(\tau) &= (g\mu_B)^2 \frac{N\hbar}{4\tilde{J}} \delta(\tau) + (g\mu_B)^2 \frac{1}{Z} \\ &\quad \times \int \mathcal{D}\phi \exp\left(-\int_0^{\beta\hbar} d\tau L[\phi]/\hbar\right) \\ &\quad \times \left(-\frac{N\hbar h_A}{4\tilde{J}} \sin \phi(\tau) + \delta s \frac{\tilde{\omega}_0^2}{h_x^2} \sin^3 \phi(\tau)\right) \\ &\quad \times \left(-\frac{N\hbar h_A}{4\tilde{J}} \sin \phi + \delta s \frac{\tilde{\omega}_0^2}{h_x^2} \sin^3 \phi\right). \end{aligned} \quad (44)$$

In stark contrast to the undoped FW, the path integral in Eq. (44) gives rise to terms proportional to  $\exp[\pm \tilde{\Delta}|\tau/\hbar]$  such that, upon Fourier transform, the susceptibility in Matsubara representation contains terms  $1/(i\omega_n \pm \tilde{\Delta}/\hbar)$ . The path integral is most easily evaluated in a Hamiltonian description. We quantize the field  $\phi$  and use an effective two-state Hamiltonian to evaluate the matrix elements. Inserting the expression for  $h_A$ , we find (Appendix B)

$$\begin{aligned} |\langle e | \hat{S}_z | g \rangle| &= \left| \frac{N(k'_z s'^2 - k_z s^2)}{2\tilde{J}_s(N + \delta s/s)} \left(1 - \frac{\tilde{J}}{N\hbar \tilde{\omega}_0}\right) \right. \\ &\quad \left. + \delta s \frac{\tilde{\omega}_0^2}{h_x^2} \left(1 - 3 \frac{\tilde{J}}{N\hbar \tilde{\omega}_0}\right) \right|, \end{aligned} \quad (45)$$

$$\chi''_{zz}(\omega \simeq \tilde{\Delta}/\hbar) = \pi (g\mu_B)^2 |\langle e | \hat{S}_z | g \rangle|^2 \tanh\left(\frac{\beta\tilde{\Delta}}{2}\right) \delta(\omega - \tilde{\Delta}/\hbar). \quad (46)$$

Equations (45) and (46) are the main results of this section. For  $\delta s = -5/2$  or  $-1$  (for Ga and Cr dopants, respectively),  $|\langle e | \hat{S}_z | g \rangle|$  can be of order 0.1 even for  $h_x \gtrsim 3\tilde{\omega}_0$ . For  $k_B T \lesssim \tilde{\Delta}$  the susceptibility of the modified FW then exhibits a resonance at  $\omega = \pm \tilde{\Delta}/\hbar$  which is accessible in ac susceptibility or ESR measurements. The terms  $\tilde{J}/N\hbar \tilde{\omega}_0 = 1/(2\tilde{\mathcal{S}}/\hbar)$  in  $|\langle e | \hat{S}_z | g \rangle|$  are quantum corrections to the classical result derived at the beginning of this section.

So far we have ignored decoherence of the spin tunneling, which is crucial for the notion of MQC. The condition  $\Gamma \simeq \tilde{\Delta}/\hbar$ , where  $\Gamma$  is the electron spin decoherence rate, marks the transition from coherent to incoherent tunneling dynamics. As is evident from the classical vector model discussed in Sec. III,  $S_z$  follows the tunneling dynamics of  $\mathbf{n}$ . In particular, for a single modified FW, the decay rate of  $|\langle n_z(t) n_z \rangle|$ ,  $\Gamma$ , is also the decay rate of the component of  $|\langle S_z(t) S_z \rangle|$  oscillating at frequency  $\tilde{\Delta}/\hbar$ . For  $\Gamma \neq 0$ , the  $\delta$  peak in Eq. (46) is then broadened into a Lorentzian of width  $\Gamma$ . In experiments carried out on an ensemble of modified FW's, inhomogeneous broadening (e.g., due to crystal defects or nuclear spins) adds to the width of the resonance peaks. The experimentally determined linewidth of the absorption and emission peaks provides an upper limit for  $\Gamma$ . This should



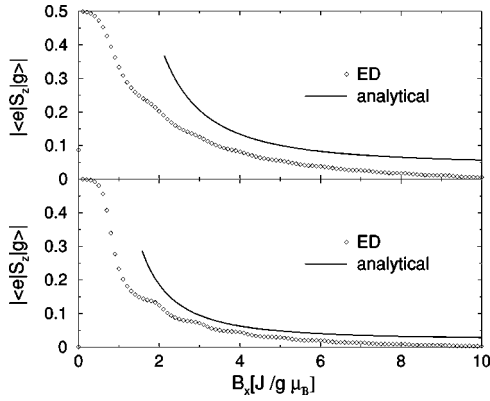


FIG. 6. Transition matrix element  $|\langle e|S_z|g\rangle|$  for small rings,  $N=4$  with  $J'=J$ ,  $s=5/2$ ,  $s'=2$ . In the upper panel,  $k_z=k'_z=0.1$ . In the lower panel,  $k_z=k'_z=0.055J$  is chosen such that  $\tilde{S}/\hbar \approx 3.3$  as for  $\text{Fe}_{10}$ . The analytical result (solid line) is shown for  $\max[\hbar\tilde{\omega}_0, |\delta s|8J/N] < \hbar h_x < 4Js$ . Due to Eq. (25), our theory is rigorously valid only for fields much larger than  $\max[\hbar\tilde{\omega}_0, |\delta s|8J/N]$  and much smaller than  $4Js$ .

allow one to settle the experimentally unresolved problem of whether true quantum coherence is established in ferric wheels.

Finally we compare our result for the transition matrix element  $|\langle e|S_z|g\rangle|$  entering Eq. (46) with results obtained from ED on small rings for a wide range of parameters (Figs. 6–8). For simplicity, we assume  $J'=J$ . In the range of validity of our theory [Eq. (25)], for  $\delta s \neq 0$  (Figs. 6 and 8), the agreement of ED ( $\diamond$ ) with analytic results (—) is both qualitatively and quantitatively convincing.<sup>44</sup> The small oscillating features seen in the exact results are due to tunneling corrections  $\mathcal{O}(\exp[-\tilde{S}/\hbar])$  to  $|\langle e|S_z|g\rangle|$ , which were neglected in Eq. (45). For Fig. 7, where  $\delta s=0$ , our theory makes the correct qualitative prediction that  $|\langle e|S_z|g\rangle|$  depends only weakly on  $h_x$ , but overestimates the matrix element. However, due to the smallness of the matrix element for  $\delta s=0$ , the discrepancy can be due to terms neglected in the derivation of Eq. (35). The significantly different qualitative features of Fig. 7 compared to Figs. 6 and 8 arise from the fact that  $\delta s=0$  in Fig. 7. The different functional dependence of  $|\langle e|S_z|g\rangle|$  on  $h_x$  for the two cases  $\delta s \neq 0$  and  $\delta s$

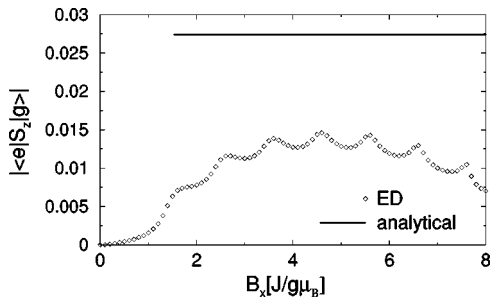


FIG. 7. Transition matrix element  $|\langle e|S_z|g\rangle|$  for a small ring  $N=4$  with  $J'=J$ ,  $s=s'=2$ , i.e.,  $\delta s=0$ , but  $k'_z=1.5k_z$  and hence  $h_A \neq 0$ . Again,  $k_z=0.0655J$  is chosen such that  $\tilde{S}/\hbar \approx 3.3$ , as for  $\text{Fe}_{10}$ . The analytical result (solid line) is shown for  $\max[\hbar\tilde{\omega}_0, |\delta s|8J/N] < \hbar h_x < 4Js$ . See also caption of Fig. 6.

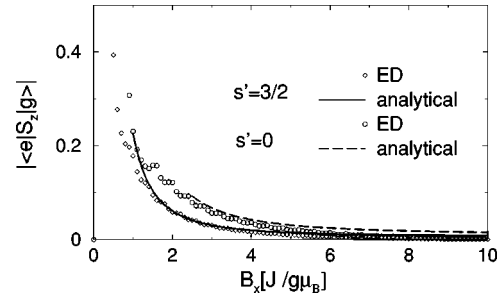


FIG. 8. Transition matrix element  $|\langle e|S_z|g\rangle|$  obtained with the phenomenological sublattice Hamiltonian [Eq. (19)] for  $\text{Fe}_{10}$  with one  $s=5/2$  substituted by (a) a dopant with  $s'=3/2$  (e.g., Cr) [numerical data ( $\diamond$ ), analytical prediction (solid line)] and (b) a dopant with  $s'=0$  (e.g., Ga) [numerical data ( $\circ$ ), analytical prediction (dashed line)]. Note that, in this case, the numerical data is not obtained from ED of Eq. (1), but rather of Eq. (19). For simplicity, we assumed  $J'=J$  and  $k'_z=k_z=0.0088J$ . The analytical results (solid and dashed lines) are shown for  $\max[\hbar\tilde{\omega}_0, |\delta s|8J/N] < \hbar h_x < 4Js$ . See also caption of Fig. 6.

$=0$  is well understood within the theoretical framework presented here [Eq. (45)]. The very large difference in matrix element magnitude illustrates the importance of looking at doped rings in experiment.

We conclude this section by remarking that, for finite excess spin  $\delta s$ , the second transverse susceptibility  $\chi''_{yy}(\omega)$  also has an absorption pole at  $\omega=\tilde{\Delta}/\hbar$ . However, since  $\mathbf{e}_y$  is a hard axis, the spectral weight of this pole is significantly smaller than that of  $\chi''_{zz}(\omega)$ , such that Néel vector tunneling in the modified FW's can be more easily detected by probing the latter quantity.

## VI. THERMODYNAMICS AND SPIN DYNAMICS FOR $J'/J \gg 1$ AND $J'/J \ll 1$

The deviations of the ED results from our theoretical predictions shown in Fig. 5 indicate that, for  $J'/J \ll 1$  or  $J'/J \gg 1$ , the theory developed in Sec. IV is no longer immediately applicable. Indeed, results obtained by ED for the ground-state magnetization  $M_x$  in small rings ( $N=4$ ,  $s=2$ , and  $s'=3/2$ ) (Fig. 9) indicate that one of the main results of Sec. IV—that  $M_x$  exhibits a series of equally spaced magnetization steps—does not hold anymore. As we will show below, this is due to the fact that our ansatz, Eq. (26), needs to be modified for  $J'$  significantly different from  $J$ . In this section we show that, for the limiting cases of  $J' \gg J$  or  $J' \ll J$ , the modified FW can be mapped onto the problem discussed in the preceding sections. We discuss the qualitative features of  $M_x$  for these systems and show that coherent tunneling of  $\mathbf{n}$  also results in coherent oscillations of the total spin.

$J' \ll J$ . In this limit,  $\mathbf{s}_1$  decouples from all other spins and aligns antiparallel to  $\mathbf{B}$  for  $\hbar h_x \geq J's$ . The remaining spins  $\mathbf{s}_2, \mathbf{s}_3, \dots, \mathbf{s}_N$  form an open spin chain, as sketched in Fig. 10(a). As shown in Appendix C, the Lagrangian of an open spin chain with an odd number of spins can also be mapped onto Eq. (35), with  $\delta s=s$  and slightly renormalized  $\tilde{J}$

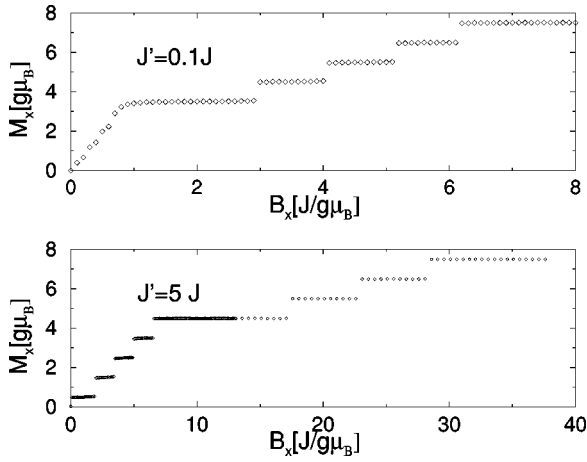


FIG. 9.  $M_x(B_x)$  at  $T=0$  for a small system with  $J' \ll J$  (upper panel) or  $J' \gg J$  (lower panel). Here,  $N=4$ ,  $s=2$ ,  $s'=3/2$ ,  $k_z=k'_z=0.1$ .

$=JN(N-2)/(N-1)^2$ . We predict that  $M_x$  has the following features.

(i)  $M_x \gtrsim g \mu_B (s' + s)$  for  $2J's \ll \hbar h_x$ .

(ii) For  $\max[\hbar \tilde{\omega}_0, s8\tilde{J}/N] \ll \hbar h_x \ll 4\tilde{J}s$ ,  $M_x$  exhibits a series of equally spaced magnetization steps with plateau width  $\delta B_{c,n} = 4\tilde{J}/Ng \mu_B$ . Depending on whether  $\delta s$  is half-integer or integer, the plateaus correspond to states with half-integer or integer total spin, respectively.

$J' \gg J$ . In this limit, the spins  $\mathbf{s}_N$ ,  $\mathbf{s}_1$ , and  $\mathbf{s}_2$  are strongly coupled. In a semiclassical picture,  $\mathbf{s}_1$  aligns antiparallel to  $\mathbf{s}_N$  and  $\mathbf{s}_2$  and the three spins act as one single spin  $|2s - s'|$  coupled to  $\mathbf{s}_3$  and  $\mathbf{s}_{N-2}$  with exchange constant  $J$  [Fig. 10(b)]. For simplicity we assume  $s' < 2s$ . Then, for  $\hbar h_x \ll J'(s - \delta s + 1)$ ,  $\hat{H}$  can be mapped onto a Hamiltonian of the form of Eq. (1) with  $N \rightarrow N-2$ ,  $J' \rightarrow J$ ,  $k'_z \rightarrow (k'_z s'^2 + 2k_z s^2)/(2s - s')^2$ , and  $s' \rightarrow 2s - s' = s - \delta s$ . Because all  $N-2$  exchange couplings in the new Hamiltonian are identical, the theory developed in Secs. IV and V remains applicable. In particular, for the ground-state magnetization  $M_x$  we make the following predictions.

(i) For  $\max[\hbar \tilde{\omega}_0, |\delta s|8J/(N-2)] \ll \hbar h_x \ll 4Js$ ,  $M_x$  exhibits a series of equally spaced magnetization steps with  $\delta B_{c,n} \approx 4J/(N-2)g \mu_B$ . Depending on whether  $\delta s$  is half-integer or integer, the plateaus correspond to states with half-integer or integer total spin, respectively.

(ii) For  $\hbar h_x \gtrsim J'(s - \delta s + 1)$ , the Zeeman energy is sufficiently large to destroy the AF configuration of  $\mathbf{s}_N$ ,  $\mathbf{s}_1$ , and  $\mathbf{s}_2$ . This results in a series of additional magnetization steps with spacing  $J'$ .

Note that a similar argument also applies if  $J' < 0$ . In this case, the three spins  $\mathbf{s}_N$ ,  $\mathbf{s}_1$ , and  $\mathbf{s}_2$  are ferromagnetically coupled and align parallel. Again, the system can be mapped onto a smaller ring [as in Fig. 10(b)], where now  $s' \rightarrow 2s + s'$ . The magnetization curve resembles the one shown in the upper panel of Fig. 9. In Fig. 9, ED results for small rings with  $N=4$ ,  $s=2$ ,  $s'=3/2$  are displayed. The qualitative features agree with all the above predictions.

We conclude that even the qualitative features of  $M_x$  allow one to estimate the parameter  $J'$  of a modified FW. Even

more importantly, as we have shown, also for  $J' \ll J$  and  $J' \gg J$  the modified FW can be mapped onto the Lagrangian [Eq. (31)] of a system which exhibits quantum tunneling of  $\mathbf{n}$ . In all cases discussed above, the quantum tunneling of  $\mathbf{n}$  leads to coherent oscillations of the total spin  $\mathbf{S}$  and thus can be observed in ac susceptibility or ESR measurements.

## VII. DISCUSSION

The theory described in Secs. IV, V, and VI allowed us to derive explicit expressions for both thermodynamic quantities [Eqs. (39) and (40)] and the susceptibility  $\chi''_{zz}$  [Eqs. (45) and (46)] of modified FW's. In order to establish a connection with experimental issues, we now outline the steps necessary to detect coherent Néel vector tunneling. For simplicity we restrict our considerations to  $\text{Fe}_{10}$  with Ga ( $\delta s = -5/2$ ) or Cr ( $\delta s = -1$ ) impurity ions and assume  $J' \approx J$ .

For finite excess spin  $\delta s$ , the two energetically degenerate spin configurations (Fig. 1) required for coherent spin tunneling as discussed in the present work certainly exist if  $\hbar h_x \gg |\delta s|8J/N$  [Eq. (25)]. This tunneling regime is well within experimental reach for Cr dopants ( $B_x \gg 9$  T), but not for Ga dopants ( $B_x \gg 23$  T).<sup>45</sup> For Cr dopants ( $s' \neq 0$ ), however, the two new parameters  $J'$  and  $k'_z$  introduced in  $\hat{H}$  [Eq. (1)] must first be determined in order to characterize the ring system.

Both  $J'$  and  $k'_z$  can be obtained from the measurement of two independent thermodynamic quantities, such as the ground-state magnetization and tunnel splitting. A schematic plot of the ground-state magnetization for integer  $\delta s$  (○) is shown in Fig. 4. Although the magnetization steps are smeared out at finite temperature, for  $T \lesssim 1$  K, the magnetization step spacing  $\delta B_{c,n}$  still can be obtained with high accuracy.<sup>10</sup> With  $\delta B_{c,n} = 4\tilde{J}/Ng \mu_B$  and Eq. (32), this allows one to determine  $J'$ . The on-site anisotropy  $k'_z$  can be obtained from  $\tilde{\Delta}$ , which depends sensitively on the tunnel action  $\tilde{S} \propto \sqrt{(N-1)k_z s^2 + k'_z s'^2}$  and hence on  $k'_z$ . The tunnel splitting  $\tilde{\Delta}$  (and hence  $k'_z$ ) is accessible either in ac susceptibility or ESR measurements [Eq. (46)] or in measurements of thermodynamic quantities, such as  $c_p$ . Torque magnetometry is another experimental technique which has been used to determine the anisotropy constant with quasispectroscopic accuracy.<sup>31</sup>

Once  $J'$  and  $k'_z$  are known, Eq. (46) determines both the position and the spectral weight of the resonance in  $\chi''_{zz}(\omega)$  which arises from coherent quantum tunneling of  $\mathbf{n}$ . The characteristic functional dependence of  $\tilde{\Delta}$  [Eq. (37)] and  $|\langle e|S_z|g \rangle|^2$  [Eq. (45)] on  $h_x$  predicted by our theory can be checked experimentally. Finally, it is noteworthy that, although  $\tilde{\Delta}$  can be determined from thermodynamic quantities, the key problem of MQC is the measurement of the decoherence rate  $\Gamma$  which is accessible only in dynamic quantities, such as ac susceptibilities.

Throughout the current work, we have considered FW's with only one dopant ion. As we have shown in the preceding sections, thermodynamic and dynamic quantities of doped FW's may differ significantly from those of undoped FW's. In the large samples investigated experimentally, dop-

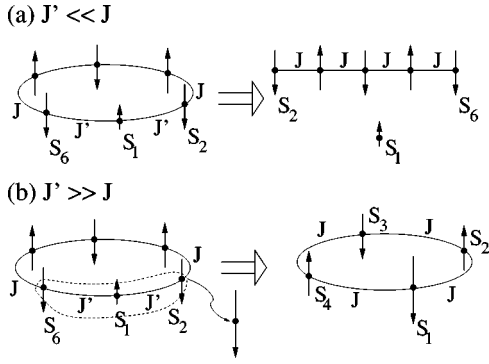


FIG. 10. (a) For  $J' \ll J$ ,  $s_1$  decouples from all other spins and the modified FW can be mapped onto an open spin chain excluding  $s_1$ . (b) For  $J' \gg J$ ,  $s_N$ ,  $s_1$ , and  $s_2$  are strongly coupled such that they can be described as one single large spin. The Hamiltonian of the ring then maps onto that of a modified FW with  $J' = J$ .

ing will lead to a random distribution both of the number of dopant ions and of their position relative to the direction of the magnetic field. We defer a detailed analysis of these issues to a future publication. Here we note only that the random distribution of impurities does not invalidate the above considerations and stress the qualitative features which ensure this. The choice of a low impurity concentration results in a large majority of the FW's containing no dopants or having only one dopant ion, which allows one to extract the system parameters of the singly doped FW's. When intraring dipolar interactions make a significant contribution to the effective uniaxial anisotropy  $k_z$ , doping with only one ion changes the effective anisotropy from uniaxial to biaxial. The theoretical framework presented in this paper can be readily extended to account for biaxial anisotropies. Because the original uniaxial anisotropy dominates the biaxial correction, the altered tunnel splittings  $\tilde{\Delta}_i$  in a singly doped FW have a magnitude similar to  $\tilde{\Delta}$  for the undoped FW and a separation which is small by comparison. Thus ac susceptibility or ESR measurements can be expected to observe signals corresponding to reversals of the total spin accompanying Néel vector tunneling and governed by the frequencies  $\tilde{\Delta}_i$ .

### VIII. SPIN QUANTUM TUNNELING IN FERRITIN

The theoretical framework developed in this work is quite general and applies to other systems besides AF ring systems. In particular, the results of the classical sublattice model (Sec. III) can be easily extended to different systems. In order to illustrate this point, we now discuss natural horse-spleen ferritin and artificial magnetoferritin, in which spin quantum tunneling has already been studied experimentally<sup>18–20</sup> and theoretically.<sup>22–25,46</sup> The experiments were carried out in the presence of small static magnetic fields ( $B_x \leq 10^{-6}$  T). In this regime,  $B_x \neq 0$  leads to an energy bias between the states  $|\uparrow\rangle$  and  $|\downarrow\rangle$ , and tunneling is suppressed for increasing  $B_x$ .

Recently it was shown<sup>25</sup> that, for sufficiently large field, i.e.,  $\hbar h_x \sim |\delta s| 8J/N$ , there are again two energetically degenerate spin configurations between which spin quantum

tunneling may take place. In natural horse-spleen ferritin,<sup>46</sup>  $J \approx 200$  K and  $\delta s/N \approx 0.05$ . For a system with uniaxial hard axis anisotropy  $\hat{H}_{an,z} = k_z \sum_i \hat{s}_{i,z}^2$ , the tunnel barrier and hence the tunnel action can be effectively controlled over a wide range of parameters by varying the magnetic field  $B_x$  applied in the easy plane.<sup>25</sup> Tunneling in the plane perpendicular to  $\mathbf{B}$  gives rise to a topological phase acquired by the spins.<sup>47,48,6</sup> A drawback of the setup considered in Ref. 25 is that, for uniaxial hard axis anisotropy, spin tunneling leaves the total spin  $\mathbf{S}$  invariant if  $\mathbf{B}$  is applied perpendicular to the hard axis. As for the FW with equal sublattice spins, spin tunneling cannot be observed in ac susceptibility measurements.

However, experiments indicate that, in addition to the strong hard-axis anisotropy, ferritin also exhibits a second weak hard-axis anisotropy  $\hat{H}_{an,y} = k_y \sum_i \hat{s}_{i,y}^2$ , where<sup>46</sup>  $k_y/k_z \approx 10^{-3}$ . In self-sustaining films of natural horse-spleen ferritin, the hard axis  $\mathbf{e}_z$  is perpendicular to the film.<sup>20</sup> In the simplest experimental setup, interference of different spin tunnel paths then could be explored if a field  $\mathbf{B} = B_z \mathbf{e}_z$  is applied along the hard axis. As long as  $\hbar h_z \ll N k_z s^2 / \delta s$  ( $\approx 10$  K for horse-spleen ferritin), due to the large anisotropy energy the spins remain confined to the film plane such that there are again two energetically degenerate spin configurations similar to Fig. 1. Tunneling takes place in the plane perpendicular to  $\mathbf{B}$ , with a tunnel splitting

$$\Delta = \Delta_0 \left| \cos \pi \left( S_{\text{tot}} + \frac{N\hbar}{4J} h_z \right) \right|, \quad (47)$$

where  $\Delta_0 \approx 5 \times 10^{-5}$  K and the total staggered spin is  $S_{\text{tot}} \approx 2.5 \times 4500$  for natural horse-spleen ferritin.  $\Delta$  is periodic as a function of  $B_z$ , with a period  $\delta B_z = 4J/Ng\mu_B$  ( $\approx 0.13$  T for natural horse-spleen ferritin). The advantage of this tunnel scenario is that quantum tunneling of  $\mathbf{n}$  also results in a tunneling of the excess spin  $\delta s$  and hence leads to a large resonance peak in the susceptibility per ferritin molecule, i.e.,

$$\chi''_{xx}(\omega \approx \Delta/\hbar) \approx \frac{1}{2} \pi (\delta s)^2 \tanh\left(\frac{\beta\Delta}{2}\right) \delta(\omega - \Delta/\hbar). \quad (48)$$

The factor 1/2 takes into account the random distribution of easy axes in the film plane. Due to the spread in particle number, the total staggered spin of the system can be either integer or half-integer. Hence, one will observe two different tunnel splittings varying with  $h_z$  as  $\Delta = \Delta_0 |\cos(\pi N \hbar h_z / 4J)|$  and  $\Delta = \Delta_0 |\sin(\pi N \hbar h_z / 4J)|$ . An experimental confirmation of this behavior would provide further strong evidence that the resonance observed in ac susceptibility measurements in ferritin<sup>18–20</sup> is due to macroscopic spin tunneling. In particular, the period of the oscillations of  $\Delta$  as function of the applied field  $B_z$  would allow one to estimate the total number of tunneling spins.

### IX. CONCLUSION

The AF ring systems discussed here, modified ferric wheels which are already available to experimentalists, combine the advantages of AF and ferromagnetic molecular mag-

nets. The tunnel splitting  $\tilde{\Delta}$  is sufficiently large that quantum coherence between macroscopically different states is established. Tunneling of the Néel vector  $\mathbf{n}$  also leads to a tunneling of the total spin  $\mathbf{S}$ , thus making the spin dynamics in modified FW's accessible to experiment. We have considered the simplest realistic model Hamiltonian  $\hat{H}$  [Eq. (1)] for a system in which, for example, one of the Fe ions is exchanged by Cr or Ga. We showed that the additional parameters entering  $\hat{H}$  can be inferred from equilibrium quantities such as the magnetization. Moreover, for a wide range of parameters, the system still exhibits MQC in the form of coherent tunneling of  $\mathbf{n}$ . Finally, we calculated spin correlation functions of the modified FW and showed that tunneling of  $\mathbf{n}$  can indeed be observed in ac susceptibility or ESR experiments, which allow one to measure both the tunnel splitting  $\tilde{\Delta}$  and an upper bound for the spin decoherence rate  $\Gamma$ . Hence they should be appropriate to verify experimentally that Néel vector tunneling in FW's is coherent.

Throughout this work we have used spin coherent-state path integrals leading to a NLSM description for the modified FW. The main advantage of this technique over ED is that thermodynamic and dynamic quantities can be evaluated for a realistic system size. In addition, an intuitive physical understanding of the spin dynamics (quantum tunneling of  $\mathbf{n}$ ) can be obtained. A drawback of the analytical approach chosen in the present work is that it naturally requires approximations. Corrections to our results, in particular  $1/s$  corrections, may become appreciable for the parameters of the FW's. However, our analytical results for  $|\langle e|\hat{S}_z|g\rangle|$  agree well with ED results obtained for small systems. For the parameter range explored in ED, deviations from our theoretical predictions become significant mainly if  $s'$  is small ( $s' = 1/2$  or  $1$ ), where the ansatz, Eq. (26), fails due to large quantum fluctuations of  $\hat{\mathbf{s}}_1$ . Although numerical work on rings with  $N=6, 8$ , and  $10$  is challenging, some results have been obtained for the ground-state magnetization and torque.<sup>15</sup> A detailed numerical study also of spin correlation functions would provide clearer evidence for the range of validity of the present approach and could explore its limitations. For example, as is well known, the sublattice Hamiltonian, Eq. (18), is exact for  $N=4$ . For increasing  $N$ , however, ED results<sup>49</sup> show that there are small deviations from  $\hat{H}_{0,\text{subl}}$ .

Note that our work also has important implications for undoped ferric wheels. Recent torque,<sup>50</sup>  $c_v$ ,<sup>50</sup> and proton  $1/T_1$  measurements<sup>51</sup> on single crystals of various  $\text{Fe}_6$  compounds indicate that these FW's could exhibit physics beyond the Hamiltonian, Eq. (2). One important future step in explaining the new experimental data will be to clarify to which extent the observed phenomena can be attributed to inhomogeneous level broadening. The theoretical framework presented here allows one to calculate analytically the inhomogeneous level broadening resulting from a random distribution of single exchange couplings  $J'$  and on-site anisotropies  $k'_z$  which could be a consequence of lattice defects in  $\text{Fe}_6$  crystals. Indeed, recent work on  $\text{Mn}_{12}$  suggests that lattice distortions<sup>52</sup> and a distribution of anisotropy energies

and  $g$  factors<sup>53,54</sup> could account for the observed broad distribution of tunneling rates in  $\text{Mn}_{12}$ .

Finally, we stress once more that the Hamiltonian  $\hat{H}$  [Eq. (1)] discussed in this paper is a simple model Hamiltonian, which still leads to fascinating novel features in the physical properties of the modified FW's. However, as discussed in Sec. VII, realistic systems might require modification of Eq. (1). Generalization of the present approach to more complicated anisotropies is, however, straightforward.

## ACKNOWLEDGMENTS

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## APPENDIX A: SUSCEPTIBILITIES

In this appendix, we sketch how the transverse susceptibilities  $\chi_{\alpha\alpha}(i\omega_n)$ ,  $\alpha=y,z$ , can be evaluated for the FW with Hamiltonian  $\hat{H}_0$  [Eq. (2)]. With  $M_y = M_z = 0$ ,<sup>42</sup>

$$\begin{aligned} \chi_{\alpha\alpha}(\tau) = & (g\mu_B)^2 \frac{N\hbar}{4J} \delta(\tau) (1 - \langle n_\alpha^2 \rangle) + (g\mu_B)^2 \left( \frac{N\hbar}{4J} \right)^2 \frac{1}{Z} \\ & \times \int \mathcal{D}\mathbf{n} [i(\mathbf{n} \times \dot{\mathbf{n}})_\alpha + n_\alpha h_x n_x]_\tau [i(\mathbf{n} \times \dot{\mathbf{n}})_\alpha \\ & + n_\alpha h_x n_x]_0 \exp\left(-\int_0^{\beta\hbar} d\tau L_0[\mathbf{n}]/\hbar\right), \end{aligned} \quad (\text{A1})$$

where the first (second) square bracket is evaluated at  $\tau(0)$ . Using the parametrization in Eq. (5) and expanding to second order in  $\vartheta = \theta - \pi/2$ , for  $\alpha=y$  the terms in square brackets read

$$i(\mathbf{n} \times \dot{\mathbf{n}})_y + n_y h_x n_x = -(h_x - i\dot{\phi})\vartheta \cos\phi - i\dot{\vartheta} \sin\phi. \quad (\text{A2})$$

The corresponding expression for  $\alpha=z$  can be obtained by setting  $\phi \rightarrow \phi - \pi/2$ . Integrating  $\vartheta$ , we obtain

$$\begin{aligned} \chi_{yy}(\tau) = & (g\mu_B)^2 \frac{N\hbar}{4J} (1 - \langle \cos^2\phi \rangle) \delta(\tau) + \left( \frac{N\hbar}{4J} \right)^2 \frac{1}{Z} \\ & \times \int \mathcal{D}\phi \exp\left(-\int_0^{\beta\hbar} d\tau L_0[\phi]/\hbar\right) \\ & \times \{G_{\vartheta\vartheta}(\tau) [h_x - i\dot{\phi}(\tau)] \cos\phi(\tau) (h_x - i\dot{\phi}) \cos\phi \\ & + iG_{\vartheta\dot{\vartheta}}(\tau) [h_x - i\dot{\phi}(\tau)] \cos\phi(\tau) \sin\phi \\ & + iG_{\dot{\vartheta}\vartheta}(\tau) \sin\phi(\tau) (h_x - i\dot{\phi}) \cos\phi \\ & + i^2 G_{\dot{\vartheta}\dot{\vartheta}}(\tau) \sin\phi(\tau) \sin\phi\}. \end{aligned} \quad (\text{A3})$$

The Green functions are defined by  $G_{\vartheta\vartheta}(\tau) = \langle T_\tau \vartheta(\tau) \vartheta \rangle - \langle \vartheta \rangle^2$ . In the high-field limit  $h_x \gg \omega_0$ , all Green functions

are strongly peaked at  $\tau=0$ . Using the adiabatic approximation outlined in Sec. II A, we find from  $L_0[\mathbf{n}]$  [Eq. (6)] [up to  $\mathcal{O}(\omega_0^2/h_x^2)$ ]

$$G_{\vartheta\vartheta}(\tau) \simeq \frac{2J}{N\hbar(h_x - i\dot{\phi})} e^{-(h_x - i\dot{\phi})|\tau|}, \quad (\text{A4})$$

$$G_{\vartheta\dot{\vartheta}}(\tau) \simeq \frac{2J}{N\hbar} \text{sgn}(\tau) e^{-(h_x - i\dot{\phi})|\tau|}, \quad (\text{A5})$$

$$G_{\dot{\vartheta}\dot{\vartheta}}(\tau) \simeq \frac{4J}{N\hbar} \delta(\tau) - \frac{2J(h_x - i\dot{\phi})}{N\hbar} e^{-(h_x - i\dot{\phi})|\tau|}, \quad (\text{A6})$$

where  $\dot{\phi} = \dot{\phi}(0)$ . Along the classical path, the field  $\phi$  varies on a time scale  $1/\omega_0$ , i.e., slowly on the time scale over which the Green functions vanish, which allows us to set  $\exp[-(h_x - i\dot{\phi})|\tau|] \rightarrow [2/(h_x - i\dot{\phi})] \delta(\tau)$  in  $G_{\vartheta\vartheta}$  and  $G_{\dot{\vartheta}\dot{\vartheta}}$ . Because  $G_{\vartheta\dot{\vartheta}} = -G_{\dot{\vartheta}\vartheta}$  the second and third terms in Eq. (A3) cancel. To leading order in  $\omega_0/h_x$  we then obtain

$$\begin{aligned} \chi_{yy}(\tau) &\simeq (g\mu_B)^2 \frac{N\hbar}{4J} \\ &\times \left[ (1 - \langle \cos^2 \phi + \sin^2 \phi \rangle) \delta(\tau) + \frac{h_x}{2} e^{-h_x|\tau|} \right] \\ &= (g\mu_B)^2 \frac{N\hbar h_x}{8J} e^{-h_x|\tau|} \simeq (g\mu_B)^2 \frac{N\hbar}{4J} \delta(\tau) \end{aligned} \quad (\text{A7})$$

and

$$\chi_{zz}(\tau) \simeq (g\mu_B)^2 \frac{N\hbar h_x}{8J} e^{-h_x|\tau|} \simeq (g\mu_B)^2 \frac{N\hbar}{4J} \delta(\tau). \quad (\text{A8})$$

### APPENDIX B: TWO-STATE MODEL OF THE MODIFIED FW

As shown in Secs. I and II, for weak tunneling  $\tilde{S}/\hbar \gg 1$ , the low-energy sector of the (modified) FW can be described as a two-state model with basis  $|\uparrow\rangle$  and  $|\downarrow\rangle$ . In this approximation,  $\hat{H} = -(\tilde{\Delta}/2)[|\uparrow\rangle\langle\downarrow| + |\downarrow\rangle\langle\uparrow|]$ , where the parameters of the original microscopic Hamiltonian enter  $\tilde{\Delta}$ .

For any operator  $\hat{O}$ , the transition matrix element between  $|g\rangle$  and  $|e\rangle$  can be evaluated from

$$\langle e|\hat{O}|g\rangle = \frac{1}{2} (\langle\uparrow|\hat{O}|\uparrow\rangle - \langle\downarrow|\hat{O}|\downarrow\rangle + \langle\uparrow|\hat{O}|\downarrow\rangle - \langle\downarrow|\hat{O}|\uparrow\rangle). \quad (\text{B1})$$

For  $h_x \gg \tilde{\omega}_0$  the state  $|\uparrow\rangle$  describes a Gaussian probability distribution for  $\mathbf{n}$  in the plane  $\perp \mathbf{B}$  with variance  $\langle\uparrow|\cos^2\phi|\uparrow\rangle = 2\tilde{J}/N\hbar\tilde{\omega}_0 = 1/(\tilde{S}/\hbar)$  (Sec. II A). Expanding  $\sin\phi \simeq \pm(1 - \cos^2\phi/2)$  for  $\phi \simeq \pi/2$  and  $\phi \simeq 3\pi/2$ , respectively, we obtain

$$|\langle e|\sin\phi|g\rangle| \simeq \frac{1}{2} |\langle\uparrow|\sin\phi|\uparrow\rangle - \langle\downarrow|\sin\phi|\downarrow\rangle| \simeq 1 - \frac{\tilde{J}}{N\hbar\tilde{\omega}_0}. \quad (\text{B2})$$

The terms  $\langle\downarrow|\sin\phi|\uparrow\rangle$  are of order  $\exp[-\tilde{S}/\hbar]$  and hence negligible in the weak tunneling regime. Similarly, we also find

$$|\langle e|\sin^3\phi|g\rangle| \simeq 1 - 3\frac{\tilde{J}}{N\hbar\tilde{\omega}_0}. \quad (\text{B3})$$

### APPENDIX C: EFFECTIVE LAGRANGIAN FOR AN OPEN AF SPIN CHAIN

In this appendix we show that an open spin chain with an odd number  $N-1$  of spins  $\mathbf{s}_i$ ,  $i=2,3,\dots,N$ , can be mapped onto the Lagrangian of a modified FW. For simplicity we restrict ourselves to the chain

$$H = J \sum_{i=2}^{N-1} \hat{\mathbf{s}}_i \cdot \hat{\mathbf{s}}_{i+1} + \hbar \mathbf{h} \cdot \sum_{i=2}^N \hat{\mathbf{s}}_i - k_z \sum_{i=2}^N \hat{s}_{i,z}^2. \quad (\text{C1})$$

Again, we assume that the system exhibits AF order and use the staggering  $\mathbf{s}_i = (-1)^i \mathbf{s} \mathbf{n} + \mathbf{l}$  for the spin fields, with  $\mathbf{l} \cdot \mathbf{n} = 0$ . Spatial variations of the fields  $\mathbf{n}$  and  $\mathbf{l}$  are strongly suppressed in the small system under consideration. We hence can proceed as in Sec. IV and carry out the Gaussian integral over  $\mathbf{l}$ . We obtain

$$\begin{aligned} L_{\text{chain}}[\mathbf{n}] &= \frac{(N-1)^2 \hbar^2}{8J(N-2)} \left\{ -(\mathbf{h} + h_A n_z \mathbf{e}_z - i\mathbf{n} \times \dot{\mathbf{n}})^2 \right. \\ &\quad \left. + [(\mathbf{h} + h_A n_z \mathbf{e}_z) \cdot \mathbf{n}]^2 \right\} - (N-1) k_z s^2 n_z^2 \\ &\quad - s\hbar [\mathbf{h} \cdot \mathbf{n} - i\dot{\phi}(1 + \cos\theta)], \end{aligned} \quad (\text{C2})$$

where  $h_A = -2sk_z/(N-1)\hbar$ . Evidently, by appropriate definition of  $\tilde{J}$  and  $\tilde{\omega}_0$ , the Lagrangian of the open spin chain can be mapped onto that of the modified FW [Eq. (31)] with excess spin  $\delta s = s$ .

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- <sup>44</sup>However, we do *not* claim that this is an indication that our ansatz, Eq. (26), provides a full *microscopic* description of the local spin directions.
- <sup>45</sup>Note that also the anisotropy energy favors a spin configuration as sketched in Fig. 3(c) such that the condition  $h_x \gg |\delta S|8J/N$  can be relaxed. Consequently, also for Ga dopants a tunneling scenario is feasible.
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