

## Reentrant spin-flop transition in nanomagnets

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Antiferromagnetic chains with an odd number of spins are known to undergo a transition from an antiparallel to a spin-flop configuration when subjected to an increasing magnetic field. We show that in the presence of an anisotropy favoring alignment perpendicular to the field, the spin-flop state appears for *both* weak and strong fields, the antiparallel state appearing for intermediate fields. Both transitions are second order, the configuration varying continuously with the field intensity. Such reentrant transition is robust with respect to quantum fluctuations and it might be observed in different types of nanomagnets.

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**Introduction.** The ability to manipulate atoms adsorbed on a substrate [1–3], the possibility to choose a suitable combination of substrate and adatoms, and the recent capacity to tailor microscopic interactions [4,5] permit one to obtain nanosystems with specific magnetic properties. Adatoms may interact either ferromagnetically or antiferromagnetically; the coupling with a ferromagnetic substrate may mimic an external field and it also induces spin anisotropies via spin-orbit interaction. These couplings are the building blocks of a variety of magnetic configurations, so it is not surprising that in atomic chains one can recognize phenomena and transitions originally discovered in bulk samples, then also studied in stratified systems.

The spin-flop transition is a well suited and important example of magnetic phenomenon whose study has accompanied the race to miniaturization. This transition is due to the competition between antiferromagnetic coupling and magnetic field, and it connects an antiferromagnetic configuration with spins aligned along the field to a configuration where they are almost perpendicular to the field, with a small tilting angle  $\varepsilon$  producing a nonvanishing magnetization. In the simplest case—an isotropic infinite system—the critical field for such transition is zero, because the Zeeman energy gain ( $-H\varepsilon$ ) in tilting the angle dominates upon the exchange energy loss ( $J\varepsilon^2$ ) due to spin misalignment. On the other hand, in the presence of a small easy-axis anisotropy  $\kappa < 0$ , a field applied along such axis must overcome a finite critical threshold  $H_c \approx J\sqrt{|\kappa|}$  in order to produce the spin-flop reorientation. This transition is first order, the system passing with discontinuity from the antiparallel (AP) to the spin-flop (SF) phase. The metastability region has size  $\delta H$ , with  $\delta H/H_c \approx |\kappa|$ .

When interfaces or finiteness are introduced, the magnetic phase diagram becomes richer and new effects arise. An especially relevant example is the parity effect [3,6–8]: Systems of different parity have different behaviors because an antiferromagnetic (AFM) chain of  $N$  spins has (odd  $N$ ) or has not (even  $N$ ) a finite magnetization which couples to the external field. In particular, for odd  $N$  such residual magnetization may stabilize the AP configuration with respect to the SF phase for fields which can be much larger than

$H_c$  [8–12]. Here we show that the presence of an anisotropy favoring alignment *perpendicular* to the field alters the above scenario, determining two critical fields  $H_{\pm}(N)$ , with the AP phase appearing for  $H_-(N) < H < H_+(N)$  and the SF phase outside such interval. For  $N = N^*$ ,  $H_-(N^*) = H_+(N^*)$  so that only the SF phase appears for  $N > N^*$ . Furthermore, both transitions at  $H_{\pm}(N)$  are continuous.

**Models and main results.** We consider a chain with an *odd* number  $N \equiv 2M+1$  of spins, described by the Heisenberg Hamiltonian

$$\hat{\mathcal{H}} = J \sum_{i=1}^{N-1} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_{i+1} - H \sum_{i=1}^N \hat{S}_i^z + J\kappa \sum_{i=1}^N (\hat{S}_i^z)^2. \quad (1)$$

Special attention will be given to the easy-plane case ( $\kappa > 0$ ), but we will also refer to  $\kappa \leq 0$ . Its classical counterpart (in units of  $JS^2$ ) is given by

$$E = \sum_{i=1}^{N-1} \cos(\theta_i - \theta_{i+1}) - h \sum_{i=1}^N \cos \theta_i + \kappa \sum_{i=1}^N \cos^2 \theta_i, \quad (2)$$

where the azimuthal angles  $\varphi_i$  have been taken equal, our purpose being that of characterizing the minimum-energy state (ground state); note that the physically relevant values of the anisotropy are small,  $|\kappa| \ll 1$ .

It is possible to qualitatively illustrate in simple terms the main results that are more rigorously studied in the following sections. Assuming the SF configuration to be uniform, as in the infinite system,  $\theta_i = (-1)^i \theta$ , from (2) its classical energy per site is about  $e_{\text{SF}}(\theta) \simeq \cos 2\theta - h \cos \theta + \kappa \cos^2 \theta$ , which is minimal for  $2 \cos \theta = h/(2+\kappa)$ , giving  $e_{\text{SF}} \simeq -1 - h^2/8$ . As for the AP configuration,  $\theta_i = i\pi$ , one easily finds  $e_{\text{AP}} = -1 + \kappa - h/N$ , the last term being due to the balance between  $M+1$  up and  $M$  down spins, respectively. The condition  $e_{\text{AP}} < e_{\text{SF}}$  reads

$$\frac{h^2}{8} - \frac{h}{N} + \kappa < 0, \quad (3)$$

implying that the AP phase is energetically favored for

$$N < N_c(h, \kappa) = \frac{h}{\kappa + h^2/8}, \quad (4)$$

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i.e., for  $h$  between two “critical” field values

$$h \in [h_-, h_+], \quad h_{\pm}(N, \kappa) = \frac{4}{N} \left( 1 \pm \sqrt{1 - \frac{\kappa N^2}{2}} \right). \quad (5)$$

Hence, when raising the field from zero: first, the system enters in the SF phase; at  $h_-$  such phase is left and the AP one shows up; finally, beyond  $h_+$  the system reenters the SF phase. Evidently, this happens for small enough  $N \lesssim \sqrt{2/\kappa}$ , a value beyond which the intermediate AP configuration disappears. It is worth stressing that for a vanishing or easy-axis anisotropy ( $\kappa \leq 0$ ), the lower critical field  $h_- \leq 0$ , meaning that at small field the system is in the AP state for any  $N$ , and the only transition at  $h_+$  is left.

The above SF-AP-SF reentrant transition should be accessible to experiment (see the Discussion). However, as real systems at a few Kelvin are quantum mechanical, one has to account for the effect of quantum fluctuations (QFs). Any classically ordered state, such as the AP one, is usually weakened by QFs. For instance, the quantum three- and two-dimensional isotropic antiferromagnets are subject to *spin reduction* [13], namely, QFs make the ground-state sublattice magnetization smaller than  $S$ , while in the one-dimensional case the ground state does not even show order, the Néel AFM state being unstable under soft spin-wave excitations. Therefore, it makes sense to ask whether QFs destroy the reentrant transition in the finite chain or not, a question that can be answered by studying the stability of the AP state under QFs. A naïve approach is to apply the renormalization scheme [14] known as self-consistent harmonic approximation (SCHA) as done in Refs. [15–18] for a translation invariant two-dimensional AFM. In this approach, zero- $T$  QFs can be substantially accounted for by the classical system, but taking spins reduced by a factor  $\alpha(S) = 1 - D$  (i.e., each quantum spin  $\hat{S}_i$  has a classical counterpart  $\alpha S_i$ ). In the one-dimensional case

$$D = \frac{1}{(2S+1)N} \sum_k \sqrt{1 - \cos^2 k} = \frac{2}{\pi(2S+1)}. \quad (6)$$

It is then straightforward to see from Eq. (1) that  $J$  gains a factor  $\alpha^2$ , and  $H$  a plain factor  $\alpha$ , so  $h$  is replaced by  $h/\alpha$  in Eqs. (2) and (3), and eventually the quantum transition fields are expected at  $h_{\pm}^{(q)} = \alpha h_{\pm}(N, \kappa)$ . According to this argument the AP region should be maintained, but with smaller critical fields,  $h_{\pm}^{(q)} < h_{\pm}$ . However, as we will see in more detail later on, this argument fails because it assumes homogeneous QFs. Instead, the breaking of translation symmetry causes, in the vicinity of the chain ends, smaller fluctuations of the odd spins (parallel to the field) and larger ones for the even ones (antiparallel to the field). The picture of “equal spin reduction” breaks down and the boundary spins, which are less affected by QFs, remain more “resistant” towards the incipient SF configuration. As a consequence, the stability of the AP state is unexpectedly reinforced, and  $h_{\pm}^{(q)}$  becomes even larger than  $h_{\pm}(N, \kappa)$ .

*Classical model.* Because of the broken translation invariance, minimum energy configurations must be sought in the  $N$ -dimensional space  $\theta_1, \dots, \theta_N$ , minimizing the energy (2). Defining  $s_i = \sin(\theta_i - \theta_{i-1})$ , the equations  $\partial E / \partial \theta_i = 0$  can be

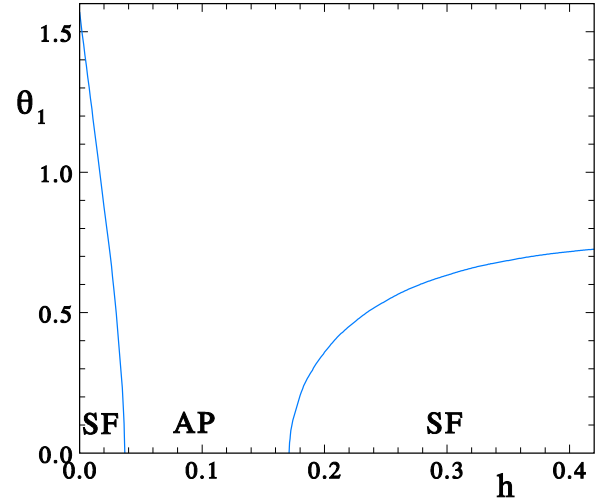


FIG. 1. (Color online) The angle  $\theta_1$  corresponding to the classical ground-state configuration as a function of  $h$ , for  $N = 15$  and  $\kappa = 0.001$ . It varies with continuity in the whole range of  $h$ . For large  $h$  (not shown)  $\theta_1$  attains a maximum, then it decreases because the SF phase gets ferromagnetic for  $h \simeq 2(2 + \kappa)$ .

cast in the form of a two-dimensional mapping [7],

$$\begin{aligned} s_{i+1} &= s_i - h \sin \theta_i + \kappa \sin 2\theta_i, \\ \theta_{i+1} &= \theta_i + \sin^{-1} s_{i+1}. \end{aligned} \quad (7)$$

The function  $\sin^{-1}$  in (7) has two solutions; since the AFM exchange coupling is strong, we must choose the solution such that  $(\theta_{i+1} - \theta_i) \in [\frac{\pi}{2}, \frac{3\pi}{2}]$ . The absence of spins at  $i = 0$  and  $i = N+1$  can be accounted for by the boundary conditions  $s_1 = s_{N+1} = 0$ . The angle  $\theta_1$  is determined imposing that after  $N$  iterations we can satisfy the condition  $s_{N+1} = 0$ . It is worth remarking that the AP configuration  $\theta_i = i\pi$  is always a solution of Eqs. (7). Its energy must be compared with possible nonuniform solutions (SF) in order to identify the ground state.

In Fig. 1 we plot the angle between the first (or last) spin and the field for  $N < N^*$ , so that two transitions are crossed when increasing  $h$ . The continuous character of both transitions will be discussed in the final section. Generally speaking, it is possible to numerically determine the phase diagram in the  $(h, N)$  plane for different values of  $\kappa$  using the map method, but this would be very lengthy. In Ref. [9] the limit of the AP phase has been determined *analytically* when  $\kappa = 0$ , the transition corresponding to the vanishing of  $s'_{N+1}(\theta_1)$  in  $\theta_1 = 0$ . In fact, it is possible to extend the same procedure [19] to the anisotropic case, obtaining the curves shown in Fig. 2. We have also derived the analytical phase boundaries by studying the stability of the AP phase, which is also needed for the quantum treatment explained below. In the classical limit this approach yields the very same results obtained by the map analysis [9,19]. In view of the quantum treatment it is useful to extend the model to include an exchange anisotropy, described by adding to Eq. (1) the term

$$-J\lambda \sum_{i=1}^{N-1} \hat{S}_i^z \hat{S}_{i+1}^z. \quad (8)$$

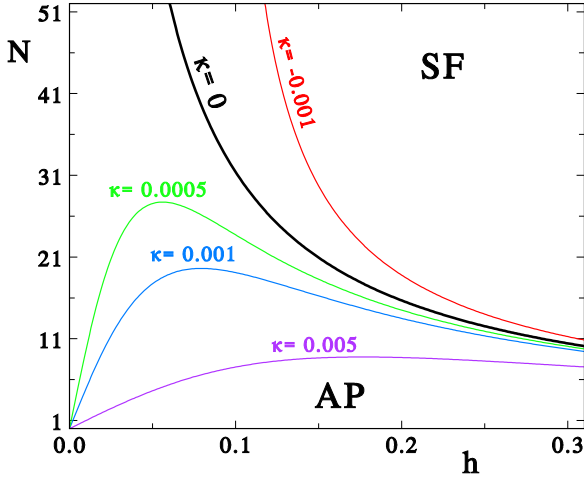


FIG. 2. (Color online) Phase diagram for a classical spin chain of length  $N$  (odd), for easy-plane, easy-axis, and no anisotropy.

Such a different anisotropy makes our results more general and allows us to show that they do not depend on the details of the anisotropy, but only on its sign. The exact result for the phase boundary is

$$N_c(h, \kappa, \lambda) = \frac{\tan^{-1} \left[ \frac{1}{2} \frac{h+2\lambda\mu}{\kappa+\lambda\mu} a(h, \kappa+\lambda) \right]}{\tan^{-1} a(h, \kappa+\lambda)}, \quad (9)$$

where  $\tan^{-1}$  is defined with the codomain  $[0, \pi]$ ,  $\mu = (1-\lambda/2)(1-\kappa-\lambda-h/2)$ , and

$$a(h, x) = \sqrt{[(1-x)^2 - h^2/4]^{-1} - 1}. \quad (10)$$

When  $\kappa$  and  $\lambda$  are small,  $\mu \simeq 1$ , so that  $N_c$  only depends on the sum  $\kappa+\lambda$ , i.e., exchange- and single-site anisotropies are almost equivalent in the classical system.

In Fig. 2 we report the results of the above analysis for three cases: easy-axis anisotropy ( $\kappa < 0$ ), no anisotropy ( $\kappa = 0$ ), and easy-plane anisotropy ( $\kappa > 0$ ). All the curves are qualitatively reproduced by Eq. (5): for  $\kappa > 0$  the AP state exists for  $h_- < h < h_+$  up to a value  $N^*$  of the chain length; for  $\kappa \leq 0$  such state exists for  $0 < h < h_+$ , with  $h_+(N)$  vanishing at large  $N$  for  $\kappa = 0$  and going to the limit  $h_+(\infty) \approx \sqrt{|\kappa|}$  for  $\kappa < 0$ .

*Quantum model.* In order to estimate the effects on the finite quantum chain one has to account for the lack of translation symmetry and for the different behavior of the two sublattices by means of a more accurate quantum SCHA. The strategy is to study the linear excitations in the AP ordered phase, which is assumed to be stable if the corresponding frequencies are positive: At the phase boundary at least one frequency vanishes, so that calculating the quantum-renormalized mode frequencies allows us to draw conclusions for the quantum phase diagram.

We restrict the quantum approach to the case of exchange anisotropy, which can be treated unambiguously with respect to single-site anisotropy: For instance, the latter is completely ineffective for  $S = 1/2$ , as  $(\hat{S}^z)^2 = 1/4$ . Therefore, we consider the Hamiltonian (1) with  $\kappa = 0$  and with the additional term (8). Performing the canonical transformation  $(\hat{S}^x, \hat{S}^y, \hat{S}^z) \rightarrow (-\hat{S}^x, \hat{S}^y, -\hat{S}^z)$  on the even indexed sites we

get the following Hamiltonian:

$$\hat{\mathcal{H}} = -J \sum_{i=1}^{N-1} (\hat{S}_i^x \hat{S}_{i+1}^x - \hat{S}_i^y \hat{S}_{i+1}^y + \lambda \hat{S}_i^z \hat{S}_{i+1}^z) + H \sum_{i=1}^N (-)^i \hat{S}_i^z.$$

The AP state corresponds to the fully aligned (Néel) state: Evidently, it is not an eigenstate of  $\hat{\mathcal{H}}$ . However, the exact ground state is expected to be “close” to it, as happens with the ground state of bulk antiferromagnets; in the latter case, the ground state and its linear excitations are found by means of a Bogoliubov transformation for the Fourier-transformed operators. But in our problem there is no translation symmetry, so the procedure is necessarily more involute.

To proceed, we use the magnon creation and annihilation operators defined by the Holstein-Primakoff [20] transformation:  $\hat{S}_i^x + i\hat{S}_i^y = \sqrt{2S} - \hat{a}^\dagger \hat{a}$ ,  $\hat{S}_i^z = S - \hat{a}^\dagger \hat{a}$ . Then, we introduce coordinates and momenta defined by  $\hat{q}_i = (\hat{a}_i^\dagger + \hat{a}_i)/\sqrt{2S+1}$  and  $\hat{p}_i = i(\hat{a}_i^\dagger - \hat{a}_i)/\sqrt{2S+1}$ , in such a way that  $[\hat{q}_i, \hat{p}_j] = i\delta_{ij}(S + \frac{1}{2})^{-1}$  (the classical limit occurring for  $S \rightarrow \infty$ ). It is easier to work with their Weyl symbols [21]  $q_i$  and  $p_i$ , so complex quantities do not appear, and expanding up to quartic terms [18] one is left with a quadratic Hamiltonian and a quartic interaction,

$$\mathcal{H}_2 = \sum_{i=1}^{N-1} [p_i p_{i+1} - q_i q_{i+1} + \lambda(z_i + z_{i+1})] - h \sum_{i=1}^N (-)^i z_i,$$

$$\mathcal{H}_4 = \sum_{i=1}^{N-1} \left[ \frac{1}{4} (z_i + z_{i+1})(q_i q_{i+1} - p_i p_{i+1}) - \lambda z_i z_{i+1} \right],$$

where  $z_i \equiv (p_i^2 + q_i^2)/2$ . Note that  $\mathcal{H}_2 = \frac{1}{2}(\mathbf{p}^t \mathbf{A}^2 \mathbf{p} + \mathbf{q}^t \mathbf{B}^2 \mathbf{q})$  is a quadratic form with  $[\mathbf{A}^2, \mathbf{B}^2] \neq 0$ , so its reduction to independent normal modes [22–24] is nontrivial. First, one has to assume the  $N \times N$  matrices  $\mathbf{A}^2$  and  $\mathbf{B}^2$  to be positive definite: Thanks to their structure, this can be assessed analytically, and gives the classical AP phase boundary mentioned above. Then, one performs the canonical transformation  $(\mathbf{q}, \mathbf{p}) \rightarrow (\mathbf{A}\mathbf{q}, \mathbf{A}^{-1}\mathbf{p})$ , so that  $\mathcal{H}_2 \rightarrow \frac{1}{2}(\mathbf{p}^t \mathbf{p} + \mathbf{q}^t \mathbf{A} \mathbf{B}^2 \mathbf{A} \mathbf{q})$  and eventually the eigenfrequencies  $\omega_k^2$  arise as eigenvalues of  $\mathbf{A} \mathbf{B}^2 \mathbf{A}$ , while the decoupled modes have the ground-state QFs  $\langle p_k^2 \rangle = \omega_k/(2S+1)$  and  $\langle q_k^2 \rangle = 1/[\omega_k(2S+1)]$ . Renormalizations come into play through  $\mathcal{H}_4$ , which is treated within the SCHA [14], yielding for  $\mathbf{A}^2$  and  $\mathbf{B}^2$  corrections which self-consistently depend on the correlators generated by  $\mathcal{H}_2$ . Such a perturbative approximation is the more reliable the smaller the corrections it gives. For systems in three and two dimensions the high coordination degree yields small fluctuations, which only slightly modify the ground state and the low temperature phase, while in the present quasi-one-dimensional system the matrix elements of  $\mathbf{A}^2$  and  $\mathbf{B}^2$  are corrected by terms of order  $1/S$  which become rapidly large when considering small spin values; however, if one “switches on quanticity” starting from large spin values, the trend towards an extension of the AP region is evident. The above procedure can be easily implemented numerically and the final quantum results are reported in Fig. 3, which confirms the overall classical scenario of Fig. 2.

*Discussion.* We have proven that an AFM chain composed by an odd number of spins undergoes an unusual reentrant spin-flop transition, if the magnetic field is applied along a

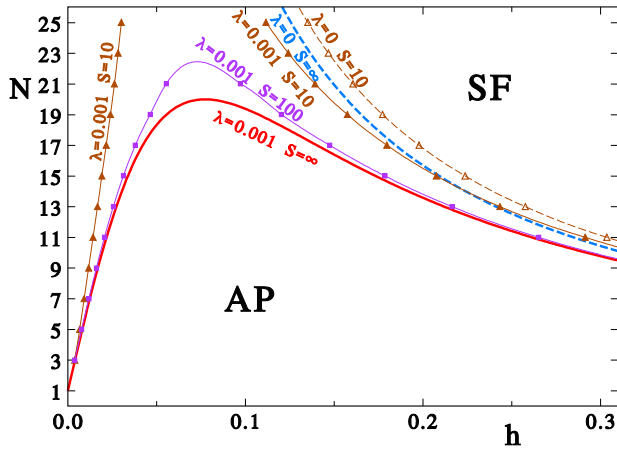


FIG. 3. (Color online) Phase diagram for a quantum spin chain of length  $N$  (odd), for easy-plane exchange anisotropy  $\lambda = 0.001$  and no anisotropy  $\lambda = 0$  and for selected spin values.

hard axis. This result appears to be rather robust: The details of the anisotropy and the classical or quantum character of the model are irrelevant. In fact, the qualitative explanation of the double transition we have given in Eqs. (3)–(5) is fairly simple and the subsequent sections confirm such a result. It is worth stressing that, at least classically, the ground state of the chain in the presence of an easy-plane anisotropy favoring the  $\hat{x}\hat{y}$  plane ( $\kappa > 0$ ) does not change if the anisotropy is easy axis and favors any direction in such plane [25].

Figure 1 shows that  $\theta_1$  varies with continuity with  $h$ , making second order the SF-AP (at  $h = h_-$ ) and the AP-SF (at  $h = h_+$ ) transitions. Such character is in contrast with the standard spin-flop transition appearing when the field is applied along an easy axis ( $\kappa < 0$ ). In this case, the infinite system undergoes a first order transition at  $h_c = 2\sqrt{|\kappa|(2 - |\kappa|)}$ , with a metastability region of size  $\delta h \approx |\kappa|^{3/2}$ . This behavior is maintained for finite systems if (odd)  $N$  is large enough. When  $\kappa = 0$ ,  $h_c = 0$  and the transition gets continuous, which is not surprising, since the metastability region is negligibly small with respect to  $h_c$ , when  $\kappa \rightarrow 0^-$ . The continuous character at  $\kappa = 0$  is preserved when  $\kappa > 0$ , as we have verified for  $N = 15$  (Fig. 1) and for large  $N$  (not shown).

Our models, either classical [Eq. (2)] or quantum [Eq. (1)], have several possible experimental counterparts. We cite here the most relevant two, namely, layered systems and chains of magnetic adatoms on a magnetic substrate. A superlattice  $A/B$ , if one of the two materials ( $A$ ) is ferromagnetic and the indirect coupling between  $A$  layers, mediated by the spacer  $B$  is antiferromagnetic, can be studied by our model Eq. (2), where each spin represents the effective magnetization of a single  $A$  layer (quantum effects are therefore negligible, since  $S$  is macroscopic and the temperature is high). In fact, Fe/Cr(211) superlattices have been used [6] to study surface effects on the spin-flop transition, but the field was applied in an easy direction ( $\kappa < 0$ ). So, parity effects were visible, but the distinctive spin-flop transitions appearing for odd  $N$  when the field is along a hard axis were overlooked.

In the last few years, much experimental effort has been devoted to completely different magnetic systems undergoing a spin-flop transition: magnetic atoms deposited on a substrate and forming a linear chain. An existing experimental setup which is appropriate for our study is a recent one [3], where Mn adatoms were deposited and manipulated on top of a Ni(110) surface. In that paper authors successfully compare experiment and theory for the ground states of a dimer ( $N = 2$ ) and a trimer ( $N = 3$ ). For  $N = 3$  they actually find an AP state, which is in agreement with our phase diagram if we use their experimental values  $h \simeq 0.5$  and  $\kappa \approx 0.001$ . The limit of using adatom chains for studying SF transitions is that the field is fixed, because it is not a true magnetic, external field. On the contrary, changing  $N$  is much easier than for layered systems. However, recent experimental results suggest that tuning the parameters of Eqs. (1) and (2) is indeed possible [4,5].

Our results might also be relevant for a third class of nanosystems, namely, molecular nanomagnets [26–28]. In this case, the coupling between spins is weaker and an external magnetic field can be applied to tune the configuration. In conclusion, the SF-AP-SF reentrant transition we have discussed in this Rapid Communication might be really accessible to experiments.

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