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Effects of antisymmetric interactions in molecular iron rings

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Abstract. The level crossing mechanism between the ground and the first excited state of Na:Fe_6 antiferromagnetically coupled iron rings is studied by torque magnetometry down to 40 mK and in magnetic fields up to 28 T. The step width at the crossing field B_c assumes a finite value at the lowest temperatures. This fact is ascribed to the presence of level anticrossing, not expected for a ring with axial, *i.e.* S_6 point group, symmetry. Assuming a reduced symmetry, we revised the model Hamiltonian of such a spin system by introducing a *Dzyaloshinsky-Moriya* (DM) term and we show, by exact diagonalization, that DM term can account for the mixing of states with different parity. In particular, analytical as well numerical analysis show that the introduction of the DM term may contribute to the broadening of the torque step as well as for the finite energy gap at B_c observed by heat capacity in a similar ring Li:Fe_6 as previously reported [9].

PACS. 75.50.Xx Molecular magnets – 75.30.Gw Magnetic anisotropy – 75.10.Jm Quantized spin models

1 Introduction

Antiferromagnetically coupled iron rings attract increasing interest as prototypes of mesoscopic magnetic systems in which quantum phenomena can be observed at a macroscopic scale. Supramolecular synthesis has in fact made considerable progresses in the recent years and among this family of antiferromagnetic wheels [1] different species, such as the Fe_6 [2,3], Fe_{10} [4], Fe_{12} [5], Fe_{18} [6], Cr_8 [7], can be grown in bulk quantity. Due to the dominant antiferromagnetic character of the nearest neighbor (n.n.) interaction, at low temperature and in zero magnetic field the ground state of rings, comprising an even number metal centers, is non-magnetic. The application of magnetic field with increasing strength gives rise to regularly spaced steps in the magnetization reflecting the spin flip process to states with progressively higher magnetic moments. In previous works we have shown how torque magnetometry can be successfully applied to study the magnetic anisotropy of these molecular rings [8,3]. Different experimental techniques, such as heat capacity and proton NMR relaxation-rate measurements [9], have been used to study in a great detail the level crossing mechanism occurring at crossing fields B_{cn}, where n is the order of the transition. Results of these combined experiments clearly show the presence of a finite energy gap at B_{cn}, that is an anticrossing mechanism, whose origin is not expected for rings with axial, *i.e.* S_6 point group symmetry [9]. In this work we report new experimental results obtained on Na:Fe_6 molecular rings by torque magnetometry at very low temperature (down to 40 mK) providing further evidence for level anticrossing at B_{c1}.

The basic Hamiltonian used to describe cyclic spin system can be written as:

$$\mathcal{H} = J\sum_{i=1}^{N}\mathbf{S}_i\cdot\mathbf{S}_{i+1} + \sum_{i=1}^{N}U_i(\mathbf{S}_i) + g\mu_B\mathbf{B}\cdot\sum_{i=1}^{N}\mathbf{S}_i \qquad (1)$$

where the first term is the Heisenberg exchange with $J > 0$ accounting for the antiferromagnetic interaction between the n.n. spins and $\mathbf{S}_{N+1} = \mathbf{S}_1$, the second term accounts for the magnetic anisotropy and the third term is the Zeeman energy of spins in an external magnetic field $\mathbf{B}$. In the case of infinite chains the *eigenvalues* and *eigenvectors* of the well known Heisenberg isotropic Hamiltonian are known only for $s = 1/2$ in one dimension [10], while reference [11] fixes the mathematical structure for antiferromagnetic/ferromagnetic interactions for closed spin chains. A semi-classical theory, the *non linear σ model*, has been also applied to molecular ferric wheels [12]. The semi-classical model reproduces the main features of these quantum systems and can be easily extended to rings with higher nuclearity. Moreover by using the *non linear σ model*, Loss and coworkers pointed out that these compounds are good candidates for the observation of macroscopic quantum coherence through coherent tunneling of the Néel vector [13], a very interesting issue currently under investigation. For small N, exact diagonalization of the spin Hamiltonian (1) have been performed [8,14] and the

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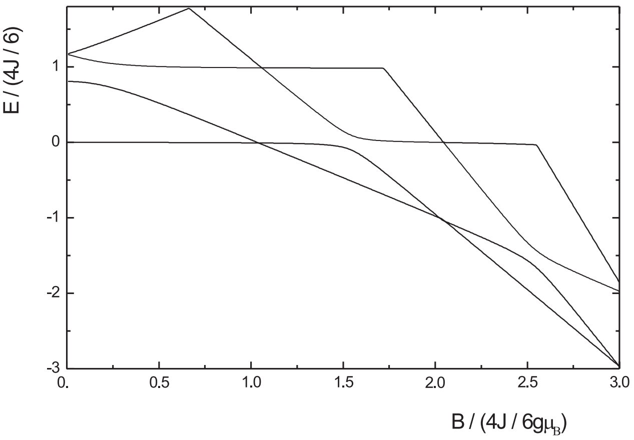

Fig. 1. Low-lying energy levels obtained by exact diagonalization of the Hamiltonian (1) with J and the anisotropy term of Na:Fe$_6$ [8].

thermodynamic properties of the spin system can be computed. In Figure 1 we report the low-lying energy levels for the antiferromagnetically coupled spin system described by (1). In the limit of dominant Heisenberg interaction the total spin S of the cluster can be used to describe the ground state, and both numerical and semiclassical approaches show that, at low temperatures and in zero field, the ground state is a *singlet* ($S = 0$) while the excited states $S = 1, 2, \ldots$, which are spin waves characteristic of cyclic systems [15], are separated by finite energy values E_n that approximately follow the Lande's interval rule $E_n = (2J/N)S(S + 1)$. The magnetic anisotropy gives rise to zero field splitting of multiplets while the application of the external magnetic field lowers the energy of excited states provoking a progressive spin flip as observed in magnetization or torque measurements. Since the crossing states have different parity, the puzzling question is to find mixing terms that account for the level repulsion observed at B_c [9]. In fact exact diagonalization as well as general symmetry consideration [8,14,16], show that terms in (1) do not mix states with different parity and therefore we need to consider non-Heisenberg spin-spin interactions. Nakano and Miyashita proposed to introduce antisymmetric interactions in order to explain dynamical effects in ferric wheels [17]. However these interactions must respect the symmetry of the system, a condition that was not taken into account by Nakano and Miyashita. It is very likely that antisymmetric interactions are present in molecular clusters and it is interesting to see to which extent they can account for level anticrossing. There are quite a lot of studies, both theoretical and experimental, that demonstrate the importance of this type of exchange in spin glasses [18] and frustrated magnetic systems [19]. Such interactions can influence the ground state energy and the dimerization of spin-Peierls systems like CuGeO$_3$ [20], moreover they describe weak ferromagnetism in predominantly antiferromagnetic systems such as La$_2$CuO$_4$ [21]; antisymmetric coupling also give rise to a contribution to the magnetic Raman process in the quasi-one-dimensional transition-metal oxide as NaV$_2$O$_5$ [22]. One aim of this work is to clarify which interaction is allowed by the symmetry of the ferric wheels. We will consider the antisymmetric interaction:

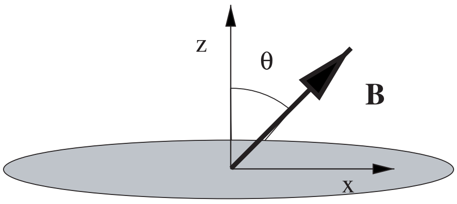

Fig. 2. Angle $0 \leq \theta \leq \frac{\pi}{2}$ between the magnetic field and the z-axis perpendicular to the xy-plane of the iron ring.

$$\mathbf{d} \cdot (\mathbf{S}_2 \times \mathbf{S}_1) \tag{2}$$

where $\mathbf{d}$ is the vector predicted by Dzyaloshinsky [23] and then theoretically developed by Moriya [24]. Equation (2) accounts for antisymmetric spin-spin interaction and Moriya showed that such a term can be derived by the tensor describing anisotropic super-exchange between two neighboring spins. We shall first discuss the $\mathbf{d}$ vector allowed by the ring symmetry, then we shall estimate its effects.

The article is organized as follows: in Section 2 we report new experimental results obtained by torque magnetometry on Na:Fe$_6$ crystals at very low temperature; in Section 3 we discuss the theoretical model starting from a general interaction between n.n. spins and introducing the DM term in (1); in Section 4 we describe the computational method; in Section 5 we report results of exact diagonalization of the Hamiltonian, finally Section 6 is dedicated to a general discussion of results.

2 Experimental results

[NaFe$_6$(OCH$_3$)$_{12}$(C$_{17}$H$_{15}$O$_4$)$_6$]ClO$_4$ (Na:Fe$_6$ in short) single crystals having approximate dimensions 100 × 100 × 200 μm were grown as described in reference [2]. A small CuBe cantilever combined with a capacitance bridge was used as torque magnetometer [8,3]. The θ angle between the magnetic field $\mathbf{B}$ and the z axis perpendicular to the xy-plane of the iron rings is defined in Figure 2 and in this work we report results obtained at $\theta = 45°$ for which the torque signal is maximum.

We report here new results of experiments performed on two different single crystals (hereafter named #A and #B) by means of a dilution refrigerator down to 40 mK and we compare them with data previously obtained on a third crystal (sample #C) by using a ^{3}He cryostat down to 0.45 K from reference [8].

Figure 3 shows a typical torque signal measured as a function of magnetic field $\mathbf{B}$ at 220 mK on sample #A. Different sweep rates, ranging from 0.01 T/s to 0.06 T/s, were used in order to check whether time dependent phenomena, such as blocking of magnetization, occur. In practice, a complete sweep from 15 T to 20 T and back took

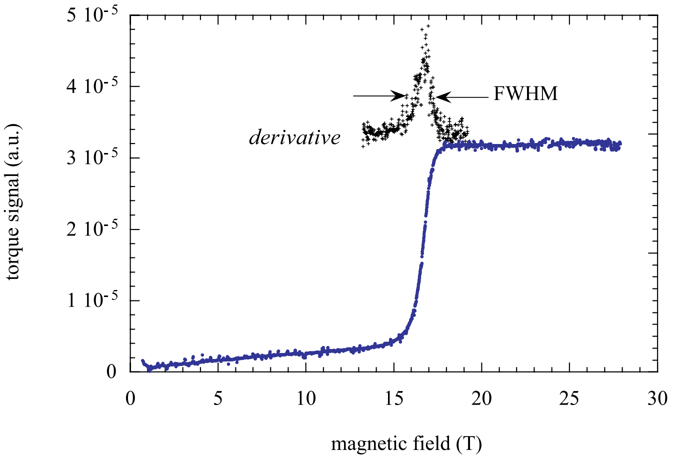

Fig. 3. Torque signal measured as a function of magnetic field up to 28 T at 220 mK and $\theta = 45°$ on Na:Fe$_6$ crystal (sample #A).

a few minutes and in this lapse of time curves taken with increasing and decreasing field overlap each other within our experimental accuracy. This check was repeated at the lowest temperature and hysteresis was never observed, indicating that possible time dependent phenomena could only occur in a time scale much shorter than what we used in our experiments. Further details of the curve reported in Figure 3 are worth to be observed. Below B_c, the torque signal is positive and it slightly increases – almost linearly– for increasing field. Conversely above B_c the torque signal τ is essentially flat, *i.e.* field independent. The quasi-linear increase of the torque signal below B_c reveals a non vanishing magnetic character of the ground state, in contrast to what expected for a purely singlet state. In Figure 3 is also plotted the derivative of the torque signal τ with respect to the external field intensity B. The bell shape of $\mathrm{d}\tau/\mathrm{d}B$ *vs.* B curves allows one to determine the crossing field B_c as well as the width of the step. The crossing field B_c can be defined as the field at which the derivative $\mathrm{d}\tau/\mathrm{d}B$ is maximum while the broadening of the torque step is evaluated by directly measuring the full width at half maximum $FWHM$ of the $\mathrm{d}\tau/\mathrm{d}B$ *vs.* B curves. Note that this definition of $FWHM$ does not depend on the shape of $\mathrm{d}\tau/\mathrm{d}B$ *vs.* B curve that may change with temperature.

In Figure 4 we plot the $FWHM$ of the $\mathrm{d}\tau/\mathrm{d}B$ *vs.* B measured on the three samples as a function of temperature. At the lowest temperatures the step width measured on sample #B is slightly smaller than that measured on sample #A, $FWHM = 0.4 \pm 0.1$ T instead of $FWHM = 0.5 \pm 0.1$ T respectively for #B and #A, suggesting a better quality of sample #B. At the highest temperatures, data of the three samples lie on the same curve and this demonstrates the good reproducibility of results. Above 300 mK, the experimental $FWHM$ data fit well the linear temperature dependence $FWHM$=$3.53k_BT/\mu_BgS$ as expected from the Zeeman term [8]. Below $\sim$ 200 mK, there is a clear deviation from this linear temperature dependence: The step width approaches a finite value for vanishing temperature. Both intrinsic (level anticrossing) and extrinsic factors may contribute to a T-independent broadening of the step width. We expect, for instance, that an inevitable loss of solvent during the sample mounting may provoke different magnetic exchange strengths with a consequent spread of crossing fields B_c within the crystal. This can account for the slightly different $FWHM$ observed on sample #A and #B, but the large $FWHM = 0.4 \pm 0.1$ T observed is not compatible with the good crystallographic quality of the small samples used in our experiments. Based on these considerations and on heat capacity and NMR relaxation-rate results that clearly evidence the presence of a finite energy gap at B_c [9] we are lead to consider in the next section the origin of the anticrossing mechanism.

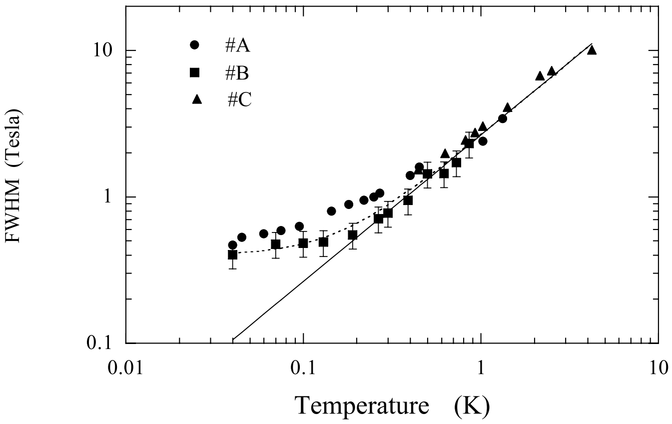

Fig. 4. Temperature dependence of the step width measured on three different Na:Fe$_6$ crystals. The continuous line represents the linear temperature dependence $FWHM = 3.53k_BT/\mu_BgS$ as expected from Zeeman term (see Ref. [8]) while the dashed line is an empirical curve $FWHM = \{\Delta B_c^2 + (3.53k_BT/\mu_BgS)^2\}^{1/2}$ with $\Delta B_c = 0.4$ T. Data of sample #C are taken from reference [8].

3 Model description

Let consider first the general Hamiltonian for N interacting Fe^{3+} ($s = 5/2$) in an external magnetic field $\mathbf{B}$:

$$\mathcal{H} = \sum_{i,j=1}^{N} \mathbf{S}_i \cdot \mathcal{J}_{ij} \cdot \mathbf{S}_j \; + \; g\mu_B \mathbf{B} \cdot \sum_{i=1}^{N} \mathbf{S}_i, \qquad (3)$$

where N is the number of sites in a ring, $\mathbf{S}_{N+1} = \mathbf{S}_1$, and $\mathbf{S}_i$ is the 5/2-spin operator in the i-site. The first term of the Hamiltonian (3) is a spin bilinear operator containing the tensor $\mathcal{J}_{ij}$ that describes the most general interaction between two spins. Any second-rank tensor, like $\mathcal{J}_{ij}$, can be decomposed into the sum of symmetric and antisymmetric tensors [27] and the symmetric part can be easily taken traceless. We consider only next neighbor exchange interaction (symmetric and antisymmetric)

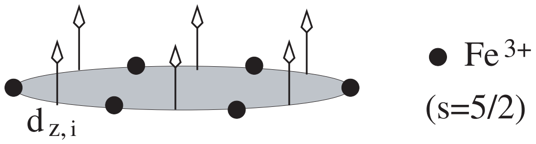

Fig. 5. The z component of DM vectors $d_{z,i}$ in the case of S_6 symmetry of an iron ring of six spins $s_i = \frac{5}{2}$.

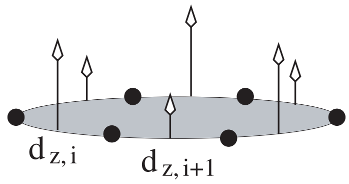

Fig. 6. Alternating DM vectors along the z-direction in a dimerized ring.

and magnetic anisotropy due to single-ion and dipolar interactions. In this way the Hamiltonian (3) can be written as:

$$\begin{aligned}\mathcal{H} = \; & J\sum_{i=1}^{N}\mathbf{S}_i\cdot\mathbf{S}_{i+1}+\sum_{i=1}^{N}\mathbf{d}_i\cdot(\mathbf{S}_i\times\mathbf{S}_{i+1})\\ & +\sum_{i=1}^{N}\mathbf{S}_i\cdot\mathcal{D}_{ii}^{an}\cdot\mathbf{S}_i+\; g\mu_B\mathbf{B}\cdot\sum_{i=1}^{N}\mathbf{S}_i \qquad (4)\end{aligned}$$

or more compactly:

$$\mathcal{H}=\mathcal{H}_{Hei}+\mathcal{H}_{DM}+\mathcal{H}_{an}+\mathcal{H}_{\text{Zeeman}}. \qquad (5)$$

In the first term $\mathcal{H}_{Hei}$, J describes the usual Heisenberg antiferromagnetic interactions in the case of equivalent Fe^{3+} sites (more complex situation will be discussed below), the second term $\mathcal{H}_{DM}$ is the antisymmetric spin Hamiltonian describing the *Dzyaloshinsky−Moriya* (DM) interaction, in $\mathcal{H}_{an}$, $\mathcal{D}_{ii}^{an}$ is a symmetric traceless tensor that describes the single ion anisotropy and $\mathcal{H}_{\text{Zeeman}}$ is the Zeeman term. Note that the (5) reduces to (1) just taking $\mathcal{H}_{DM} = 0$.

Here we discuss in detail the $\mathcal{H}_{DM}$ term. The vector $\mathbf{d}_i$ contains the three antisymmetric independent elements of the decomposition of general tensor $\mathcal{J}_{ij}$. This term can be obtained considering the spin-orbit coupling on two magnetic ions and the exchange interaction as a perturbation of the unperturbed states [28,27,25]. According to the original Dzyaloshinsky work [23], the DM vectors are strictly connected to the symmetry of the spin system. The crystal structure of Na:Fe$_6$, as determined by X-ray diffraction at room temperature [2], has S_6 point group symmetry. We can simply see by geometrical arguments (see Fig. 5) that total effects of DM vectors must vanish, and a true level crossing at B_c is expected (as shown in Fig. 1). Yet, the new experimental results reported in this work as well as heat capacity and NMR relaxation-rate measurements of finite energy gap at B_c [9] show an anticrossing mechanism and in this framework the presence of an antisymmetric term is required. Here we simply assume that the S_6 axial symmetry is reduced to C_3 symmetry with the inversion point in the center of the ring. New experimental work is certainly required in order to clarify when and how this lowering of symmetry occurs. With C_3 symmetry, it turns out that the DM interactions $\mathcal{H}_{DM}$ can actually be finite because the single interaction between n.n. spins is not subject to axial symmetry and we can figure out the orientation of the $\mathbf{d}_i$ vectors, representing the coupling between next neighbor spins. It turns out (see Fig. 6) that the geometrical construction of each $\mathbf{d}_i\cdot(\mathbf{S}_i\times\mathbf{S}_{i+1})$ coupling allows a difference between $d_{z,i}$ and $d_{z,i+1}$, *i.e.*:

$$|d_{z,\;i}-d_{z,\;i+1}|\neq 0, \qquad (6)$$

while we can neglect $d_{x,i}$ and $d_{y,i}$ components in the plane of the ring because they do not contribute to level anticrossing (see Appendix A).

4 Diagonalization technique

The level crossing mechanism for antiferromagnetic rings is well characterized by the energy gap at $B_{c,n}$ and by the steps in the magnetization as well as in the magnetic anisotropy (measured by torque) at given crossing field $B_{c,n}$, where n is the order of the transition.

The numerical technique used for exact diagonalization of (5) is based on the Lanczos method. The dimension of the Hamiltonian matrix (5) is $[(2s+1)^N\times(2s+1)^N]$ and in the case of $N = 6$ and $s = 5/2$, a 46 656 basis is required. The intrinsic symmetry of the spin and of the ring allows, however, to work with $\approx 1\%$ of the total matrix elements.

Once the Hamiltonian (5) has been diagonalized, we can compute the magnetization of the rings:

$$\mathcal{M}=\frac{\partial}{\partial\mathbf{B}}\langle\mathcal{H}\rangle=\langle S_z\rangle\cos\theta+\langle S_x\rangle\sin\theta. \qquad (7)$$

Furthermore, we can calculate the torque $\mathbf{T} = \mathcal{M}\times\mathbf{B}$ acting on a ring. Setting the magnetic field in the $xz-$plane (see Fig. 2), we have only the T_y components, hence differentiating the Zeeman term in (5) with respect to θ it is easy to find:

$$T_y=-\left.\frac{\partial\mathcal{H}_{\text{Zeeman}}}{\partial\theta}\right|_B=-g\mu_B B(\langle S_x\rangle\cos\theta-\langle S_z\rangle\sin\theta). \qquad (8)$$

Taking into account the finite temperature used in the experiments, we introduce the Boltzmann factor as follows:

$$\langle T_y\rangle=\frac{\langle\alpha|T_y|\alpha\rangle\mathrm{e}^{-E_\alpha/(k_BT)}+\langle\beta|T_y|\beta\rangle\mathrm{e}^{-E_\beta/(k_BT)}}{\mathrm{e}^{-E_\alpha/(k_BT)}+\mathrm{e}^{-E_\beta/(k_BT)}}, \qquad (9)$$

where $|\alpha\rangle$ and $|\beta\rangle$ are the first two lowest-lying states and E_α and E_β their *eigenvalues* respectively. In the case of $B_{c1}(\theta)$ we have $|\alpha\rangle = |0\rangle$ that is magnetically isotropic so the torque reflects only the contribution due to the state $|\beta\rangle = |1,-1\rangle$.

Finally we also evaluate the energy gap at B_c by an analytical method. In the limit of dominant Heisenberg $\mathcal{H}_{Hei}$ interaction, we can find possible matrix elements that mix states with different parity of the full Hamiltonian (5). If we take two maximal negative polarized states of the total spin of the ring, that is $|S^{tot}, -S^{tot}\rangle$ and $|(S^{tot}+1), -(S^{tot}+1)\rangle$, where $S^{tot} = 0, 1, \dots$ and $S^{tot}+1$ is the total spin of the successive state, we can calculate the matrix elements that, in turn, allow us to obtain the energy gap $\Delta_{B_{c,n}}$ at $B_{c,n}$:

$$\begin{aligned}\Delta_{B_{c,n}} = \; & \frac{N}{3}\,|d_{z,i} - d_{z,i+1}| \\ & \times \left\langle S^{tot}+1, -\left(S^{tot}+1\right)|\mathcal{H}|S^{tot}, -S^{tot}\right\rangle \sin\theta. \end{aligned} \tag{10}$$

The matrix element of (10) is evaluated in Appendix A. Note that $\Delta_{B_{c,n}}$ simply depends on $\sin\theta$. As it is possible to see from the rigid-rotor model proposed in [14], the xy-plane is the most important to study the anisotropy of single-ion parameters and the consequent shift of the level crossing $B_{cn}(\theta)$.

5 Numerical results

We set $\mathcal{D}^{an}_{zz}/J = 0.0183$ for Na:Fe$_6$ [8]. Obviously the single ion-anisotropy must be traceless, so $\mathcal{D}^{an}_{xx} = \mathcal{D}^{an}_{yy} = -\mathcal{D}^{an}_{zz}/2$, the positive sign of the tensor points to hard magnetic axis. The magnetic field orientations is in xz-plane, see Figure 2, as in the experiments. A rough estimation of $\mathbf{d}_i$ can be $|\mathbf{d}_i| \approx (\Delta g/g)\,J$, where $\Delta g = |g_{Fe} - g^o|$, g_{Fe} is the effective gyromagnetic factor and g^o the gyromagnetic factor for the free-electron [25]. We analyzed different cases: 1) alternated J, *i.e.* $J_i \neq J_{i+1}$ ($(J_i - J_{i+1})/k_B = 3.0583$ K), and $\mathbf{d} = 0$; 2) $J = 31.43$ K, and $\mathbf{d}_i = \mathbf{d}_{i+1} = 0.0183J$; 3) $J = 31.43$ K, and $\mathbf{d}_i \neq \mathbf{d}_{i+1}$ ($|\mathbf{d}_i - \mathbf{d}_{i+1}| = 0.0136J$). The computed pattern of the low-lying energy levels for the antiferromagnetically coupled spin system described by (5) and with $\theta = \pi/4$ is shown in Figure 7. For sake of clarity, in this figure are reported the *eigenvalues* of the Hamiltonian (5) just for the case 1) (dotted line) and for the case 3) (solid line). In the first case the dimerization of isotropic coupling in the symmetrical Hamiltonian $\mathcal{H}_{Hei}$ does not contribute to $\Delta_{B_{c,n}}$, in fact $\mathcal{H}_{Hei}$ is not able to mix the lowest-lying states. Note that neither the case 2) (*i.e.* $\mathbf{d}_i = \mathbf{d}_{i+1} \neq 0$, not plotted in Fig. 7) gives rise to level anticrossing. On the other hand the dimerization of the antisymmetric coupling $\mathbf{d}_i \neq \mathbf{d}_{i+1}$ is able to produce a level repulsion at $\Delta_{B_{c,n}}$ (see Fig. 7). This is one important result of our numerical computation.

Note that the level repulsion, obtained by exact diagonalization, agrees with the condition (10), in which the separations between the two lowest lying levels increases with θ: the level anti-crossing is equal to zero for $\theta = 0$ (crossing) and maximum for $\theta = \pi/2$, $\mathbf{B}$ in the $xy-$plane. The energy difference Δ between the two lowest lying levels is plotted in Figure 8. At the second crossing, $\Delta_{B_{c,2}}$ is twice $\Delta_{B_{c,1}}$, the energy gap at the first crossing, in reasonable agreement with the matrix element computed in (10) (see Appendix A).

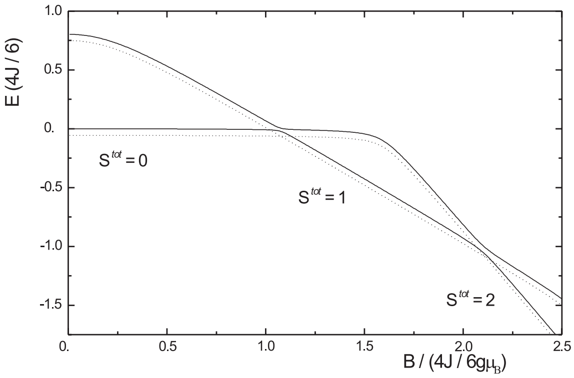

Fig. 7. Low-lying energy levels for Na:Fe$_6$ with $|\mathbf{d}_i - \mathbf{d}_{i+1}| = 0.0136J$ (solid line), and with $J_i - J_{i+1} = 3.0583$ K and $\mathbf{d} = 0$ (dotted line). In this case, levels are shifted downward for sake of clarity. The orientation of magnetic field is $\theta = \frac{\pi}{4}$.

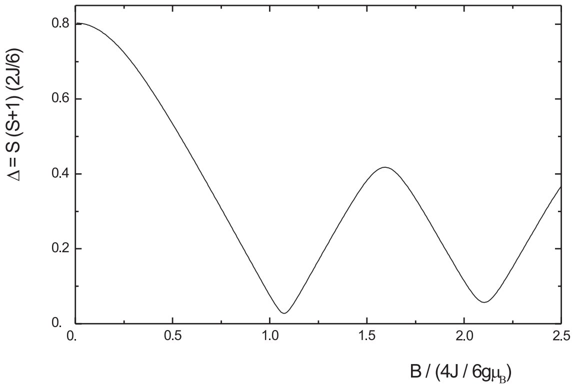

Fig. 8. Energy separation (Δ) between the ground state and the first exited state. The orientation of the magnetic field is $\theta = \pi/4$, $J = 31.43K$, and $|\mathbf{d}_i - \mathbf{d}_{i+1}| = 0.0136J$.

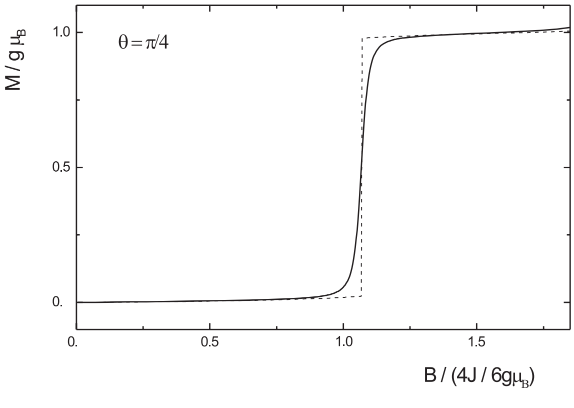

Fig. 9. The computed magnetization as a function of magnetic field at zero temperature, with $|\mathbf{d}_i - \mathbf{d}_{i+1}| = 0.0136J$ (solid line), and $\mathbf{d}_i = \mathbf{d}_{i+1} = 0$ (dotted line).

In Figure 9 we show the magnetization computed for Na:Fe$_6$ molecular rings as described in the previous section and with $T = 0$, $\theta = \pi/4$. Without the antisymmetric terms $\mathcal{H}_{DM}$ we obtain the right step-like curve at $B_{c1}(\theta)$, in agreement with reference [14], as expected for a system

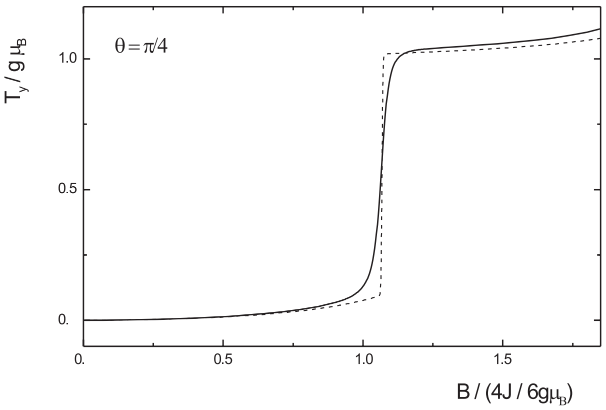

Fig. 10. The computed torque signal as a function of magnetic field ($T = 40$ mK), with $|\mathbf{d}_i - \mathbf{d}_{i+1}| = 0.0136J$ (solid line), and $\mathbf{d}_i = \mathbf{d}_{i+1} = 0$ (dotted line).

with the S_6 symmetry. Imposing the symmetry lowering and $|\mathbf{d}_i - \mathbf{d}_{i+1}| = 0.0136J$, we can observe a finite broadening of the magnetization step at $B_{c1}(\theta)$.

The computed torque at $T = 40$ mK reported in Figure 10 is equal to zero for every field value B at $\theta = 0$ and $\theta = \pi/2$ while for $B > B_{c1}$ and $\theta = \pi/4$ the torque obtains its maximum intensity as actually found in experiments [8,3]. Note that the simulation of the torque signal reported in Figure 10 shows a non vanishing signal obtained for $B < B_{c1}$. This is due to the mixing between the $|0\rangle$ and the $|2, -2\rangle$ states by the anisotropy term $\mathcal{H}_{an}$. With $\mathbf{d}_i = \mathbf{d}_{i+1}$ the torque signal presents a step-like behavior near crossing field $B_c \approx 4J/6g\mu_B$ while a finite broadening of the step is obtained by setting $|\mathbf{d}_i - \mathbf{d}_{i+1}| = 0.0136J$. So we conclude that the introduction of $\mathcal{H}_{DM}$ with $\mathbf{d}_i \neq \mathbf{d}_{i+1}$ may contribute to the broadening of the magnetization and to that of the torque step.

6 Discussion

The main experimental result reported in this work is the observation of a finite broadening of the torque step at very low temperature in antiferromagnetically coupled ferric wheels. This result, together with heat capacity and NMR relaxation-rate results [9] provide evidence for level anticrossing in these molecular clusters. Consequently we were led to introduce an antisymmetric term in the spin Hamiltonian of these systems and to performed exact diagonalization of (5) in order to see to which extent DM interaction may contribute to this level anticrossing. Here we further discuss the origin and the effects of the presence of the *Dzyaloshinsky-Moriya* (DM) term in the Hamiltonian.

As we mentioned in the previous section the appearance of the DM interaction is strictly connected to the symmetry of the system. Nakano and Miyashita [17] introduced the DM interaction considering only two n.n. spins but they did not take into account the symmetry of the ring. For iron rings with S_6 symmetry, $\mathcal{H}_{DM}$ does not contribute to the level anticrossing and the reduction the symmetry to C_3 is mandatory in order to have non vanishing effects of $\mathcal{H}_{DM}$. General symmetry arguments show that, in a centrosymmetric ring any perturbation is not able to provoke an energy separation $\Delta_{B_{cn}}$ between the lowest-lying states at B_{cn} [11]. That is why we assumed a dimerized molecule although this point needs to be confirmed by accurate X-ray investigations. The mechanism leading to the dimerization is an interesting issue. For instance it will be interesting to check whether the *Jahn-Teller* mechanism plays a role for dimerization of iron rings, or whether the dimerization is induced by the lowering of T or by the presence of magnetic field. We just note that numerical simulations that we performed for a simple spin model systems show that the total energy of a dimerized ring is lower than that of the ideal symmetric ring.

A first important result of our numerical simulations is that the introduction of the DM term can reproduce quite easily the finite energy gap directly measured by heat capacity on Li:Fe$_6$ [9]. In reference [9] we estimated $\Delta_{Bc1}/k_B = 0.86$ K and $\Delta_{Bc2}/k_B = 2.36$ K. Using the model Hamiltonian (5) we may exactly reproduce these values taking J/k_B=21.58 K, $\mathcal{D}_{zz}^{an}$=-0.02J, and $|\mathbf{d}_i - \mathbf{d}_{i+1}| = 0.043J$. It is worth to stress that the simple dimerization of the symmetric part of the exchange interaction, *i.e.* $J_i \neq J_{i+1}$, as well as the introduction of $\mathbf{d}_i = \mathbf{d}_{i+1} \neq 0$ are not sufficient to produce a level anticrossing. Only the introduction of the condition $\mathbf{d}_i \neq \mathbf{d}_{i+1}$ gives a level repulsion at B_c within the framework of our model. Note that $|\mathbf{d}_i - \mathbf{d}_{i+1}| = 0.043J$ obtained for Li:Fe$_6$ is larger than in the case of Na:Fe$_6$. This is not surprising since the guest alkaline ion (Li, Na) inside the Fe ring is actually able to change the interactions among the Fe ions by slightly distorting the wheels as we demonstrate in our previous work [3]. In both cases, however, $|\mathbf{d}_i - \mathbf{d}_{i+1}|$ are only few percent of the exchange constant J, consistently with the perturbation method we used.

We already observed by torque magnetometry a broad step width at crossing fields in Na:Fe$_6$ and Fe$_{10}$ [8,3]. In the present work we extended the torque measurements down to very low temperature 40 mK and we actually found in two different Na:Fe$_6$ crystals that the *FWHM* of the step approaches a T-independent value as T vanishes. Numerical diagonalization shows that the introduction of the DM term in the spin Hamiltonian may actually give a temperature independent contribution to the broadening of the torque signal if we take $\mathbf{d}_i \neq \mathbf{d}_{i+1}$. It is worth to observe that analytical evaluation of the energy gap at B_c (see Eq. (10)) as well numerical calculation of the torque signal at different θ angle show that the level repulsion should vanish as θ gets close to 0 (easy plane) and it should be maximum for $\theta = \pi/2$. This is a special feature due to the introduction of the DM term that should be further checked by experiments. Unfortunately, due to the difficulty of torque experiments at very low temperatures, the angular dependence of *FWHM* has not been systematically studied yet, but it is an important test to perform in the next future.

In conclusion, the finite broadening of torque step observed at very low temperature in Na:Fe$_6$ supports results of recent heat capacity and NMR relaxation-rate experiments [9] indicating strong level repulsion. We showed that DM interaction may contribute to level anticrossing if we assume a reduced symmetry of system. This hint needs to be corroborated by further experimental and theoretical work.

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Appendix A

We study a cyclic system comprising 6 antiferromagnetically coupled spins and we consider two bipartite spin systems: the sub-system A composed by the spins on even sites with total spin $S_A = \sum_{i=2,4,6} S_i$ ($N/2$ spins up), and the sub-system B composed by the spins on odd sites with total spin $S_B = \sum_{i=1,3,5} S_i$ ($N/2$ spins down). In this way the total spin is $S^{tot} = S_A - S_B$. Introducing a tensorial representation of the spin operators, we can build irreducible tensor of order k composed by $(2k+1)$ elements (in our case we have $k = 1$ order vectors) [26,27]. So we have a set of irreducible tensor operators, corresponding to the index $m = 1, 0, -1$, defined as $\mathcal{T}_{11}(S_i)$, $\mathcal{T}_{10}(S_i)$, $\mathcal{T}_{1-1}(S_i)$ respectively and where S_i are the spins on single site of two sub-systems A and B. Now we take the coupling of i-site with $(i+1)$-site expressed by tensor product, $\mathcal{T}'_{KM}(S_i, S_{i+1}) = \{\mathcal{T}_{km}(S_i) \otimes \mathcal{T}_{k'm'}(S_{i+1})\}_{KM}$, where K and M characterize the order of the coupling tensor, and we call $\mathcal{T}''_{KM}(S_i, S_i) = \{\mathcal{T}_{km}(S_i) \otimes \mathcal{T}_{k'm'}(S_i)\}_{KM}$ the product of the spin component on each site. Hence the three spin components are:

$$\begin{aligned} S_{x,i} &= -\frac{1}{\sqrt{2}}\left[\mathcal{T}_{11}(S_i) - \mathcal{T}_{1-1}(S_i)\right] \\ S_{y,i} &= -\frac{\mathrm{i}}{\sqrt{2}}\left[\mathcal{T}_{11}(S_i) + \mathcal{T}_{1-1}(S_i)\right] \\ S_{z,i} &= \mathcal{T}_{10}(S_i). \end{aligned}$$

For our approximation we need to connect the state

$$|S_A S_B; S^{tot}, -S^{tot}\rangle$$

with the state

$$\left| S_A S_B; S^{tot}+1, -\left(S^{tot}+1\right)\right\rangle.$$

For the symmetry of the anisotropy term $\mathcal{H}_{an}$ of the Hamiltonian (5), the only tensor elements that connect such states are:

$$S_{x,i}S_{z,i} + S_{z,i}S_{x,i} = -\left[\mathcal{T}''_{21}(S_i, S_i) + \mathcal{T}''_{2-1}(S_i, S_i)\right] \quad (11)$$

$$S_{y,i}S_{z,i} + S_{z,i}S_{y,i} = \mathrm{i}\left[\mathcal{T}''_{21}(S_i, S_i) + \mathcal{T}''_{2-1}(S_i, S_i)\right]. \quad (12)$$

These elements are able to connect the singlet state ($S^{tot} = 0$) with the quintet state ($S^{tot} = 2$) and also the triplet state ($S^{tot} = 1$) with the quintet state. However (11) and (12) are not able to connect the total singlet state with the triplet state (tensor $\mathcal{T}''_{2-1}$). The last possibility is permitted only by the DM term, $\mathcal{H}_{DM}$:

$$(S_i \times S_{i+1})_x = \mathrm{i}\left[\mathcal{T}'_{11}(S_i, S_{i+1}) - \mathcal{T}'_{1-1}(S_i, S_{i+1})\right] \quad (13)$$

$$(S_i \times S_{i+1})_y = \mathcal{T}'_{11}(S_i, S_{1+1}) + \mathcal{T}'_{1-1}(S_i, S_{i+1}) \quad (14)$$

that give a component $\mathcal{T}'_{1-1}$, while the component $(S_i \times S_{i+1})_z$ does not contribute. We take the total spin system and we evaluate the matrix element

$$\left\langle S_A S_B; S^{tot}+1, -\left(S^{tot}+1\right) \left| \mathcal{T}'_{1-1}(S_i, S_{+1}) \right| S_A S_B; S^{tot}, -S^{tot} \right\rangle \quad (15)$$

applying the well-known Wigner rules in the 3-$\{j\}$ and 6-$\{j\}$ symbology [26,27], we can write (15) as

$$\begin{aligned} &(-1)^{2S^{tot}} \begin{pmatrix} S^{tot}+1 & 1 & S^{tot} \\ S^{tot}+1 & -1 & -S^{tot} \end{pmatrix} \\ &\times \left\langle S_A S_B, S^{tot}+1 \,||[\mathcal{T}'_1(S_i) \otimes \mathcal{T}'_1(S_{i+1})]_1|\, S_A S_B, S^{tot} \right\rangle \\ &= \left[3\left(2S^{tot}+3\right)\right]^{1/2} \sum_{|S^{tot}-1| \le j \le S^{tot}+1} \begin{Bmatrix} 1 & 1 & 1 \\ S^{tot} & S^{tot}+1 & j \end{Bmatrix} \\ &\times \left\langle S_A S_B, S^{tot}+1 \,|\mathcal{T}'_1(S_i)|\, S_A S_B, j \right\rangle \langle S_A S_B, \\ &j|\mathcal{T}'_1(S_{i+1})|S_A S_B, S^{tot} \rangle \\ &= \frac{(-1)^{2S^{tot}}}{2\sqrt{2}N^2} \\ &\times \frac{(S^{tot}+1)\left\{(S^{tot}+1)\left[(2S_A+1)^2 - (S^{tot}+1)^2\right]\right\}^{1/2}}{(2S^{tot}+3)^{1/2}}. \end{aligned} \quad (16)$$

Thus in case of Fe$_6$ $S_a = 15/2$, $N/2 = 3$ the matrix element (16) is 0.36218… for $S^{tot} = 0$, 0.7888… for $S^{tot} = 1$, 1.2125… for $S^{tot} = 2$ and so on.

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