Effects of frustration on magnetic molecules: a survey from Olivier Kahn till today

Jürgen Schnack*

December 2, 2009

Abstract

In magnetism, of which molecular magnetism is a part, the term frustration is used rather sloppily. Sometimes one gains the impression that if the reason for some phenomenon is not quite clear then it is attributed to frustration. In this paper I discuss the effects of frustration that I feel are relevant for the field of molecular magnetism. As will become clear later they indeed lead to a variety of unusual magnetic properties.

1 Introduction

In an article specifically devoted to the effect of frustration on magnetic molecules Olivier Kahn demands a more thorough discussion of frustration effects. He summarizes the intellectual deficiencies when discussing for instance a triangle of spins $s = 1$ as follows:[1] "What might be frustrating for some researchers is not to be able to represent the $^1A_1$ ground state with up and down arrows." Being a physicist I silently identify "researcher" as "physicist" which provides good motivation for a survey of this phenomenon on which both chemistry and physics had their different focus.

Following the bibliographic path backwards in history the term frustration was introduced by P. W. Anderson in a private communication and employed by G. Toulouse

*Universität Bielefeld, Fakultät für Physik, Postfach 100131, D-33501 Bielefeld, Germany

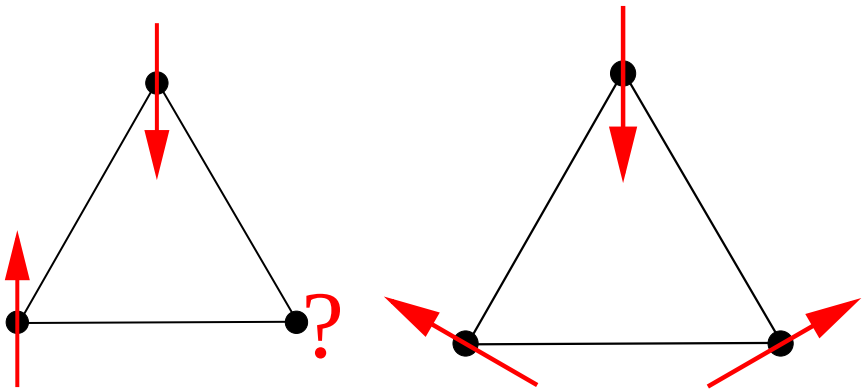

Figure 1: L.h.s.: Typical sketch of a frustrated triangular classical spin system, where the third spin “does not know where to point". R.h.s.: Classical ground state.

and S. Kirkpatrick in connection with spin glasses.[2,3] In condensed matter physics it was later transfered to the discussion of special spin lattices as for instance the kagomé or the pyrochlore lattice antiferromagnets.[4,5,6,7] There are two approaches to frustration. The first one starts by considering the graph of interactions between the participating spins.[2] This approach defines a system with “competing interactions" as frustrated. The second approach focuses on the phenomena ascribed to frustration. It is in this context that Olivier Kahn criticizes the use of the term frustration for systems that have competing interactions but no resulting specific properties. To call a spin triangle of integer spins frustrated is thus meaningless to him since it does not show the specific property of ground state degeneracy.[1]

In this article I undertake the attempt to reconcile the various viewpoints. I will therefore concentrate on geometric frustration and argue that one could consider frustration as the opposite of bipartiteness. This approach has two clear advantages: one has a strict definition of bipartiteness and one can discuss the frustration related properties in contrast to the properties of bipartite systems. The article is thus organized as follows. In section 2 I will repeat the concept of bipartiteness and discuss the resulting properties. Then the observable signatures of frustration will be introduced in section 3 as there are for instance ground-state degeneracy, low-lying singlets, non-collinear ground states, magnetization plateaus, magnetization jumps, as well as special magnetocaloric properties.

2 Bipartiteness

Before discussing the concept of bipartiteness and the resulting properties I define the Heisenberg model as the physical background model for interacting spins. In the Hamiltonian

$$\underset{\sim}{H} \quad = \quad -\sum_{i,j} J_{ij}\,\vec{\underset{\sim}{s}}_i \cdot \vec{\underset{\sim}{s}}_j + g\,\mu_B B \sum_i \underset{\sim}{s}_i^z \,, \tag{1}$$

the first term (Heisenberg Hamiltonian) models the isotropic exchange interaction between spins centered at sites i and j. J_{ij} is the exchange parameter; a negative J_{ij} corresponds to an antiferromagnetic coupling of the spins. The second term (Zeeman term) represents the interaction with the external magnetic field. For the sake of simplicity it is assumed that all spins have the same spin quantum number $s_1 = s_2 = \cdots = s_N = s$ as well as the same g-factor. With these simplifications the model is SU(2) invariant, i.e. the total spin commutes with the Hamiltonian in the following way

$$\left[\underset{\sim}{H}, \vec{\underset{\sim}{S}}^2\right] = 0 \qquad \& \qquad \left[\underset{\sim}{H}, \underset{\sim}{S}^z\right] = 0 \,. \tag{2}$$

This means that a basis exists where the basis states $|\,\nu\,\rangle$ are simultaneous eigenstates of $\underset{\sim}{H}, \vec{\underset{\sim}{S}}^2$, and $\underset{\sim}{S}^z$, i.e. $\underset{\sim}{H}\,|\,\nu\,\rangle = E_\nu\,|\,\nu\,\rangle, \vec{\underset{\sim}{S}}^2\,|\,\nu\,\rangle = S_\nu(S_\nu+1)\,|\,\nu\,\rangle$, and $\underset{\sim}{S}_z\,|\,\nu\,\rangle = M_\nu\,|\,\nu\,\rangle$.

The concept of bipartiteness has the clear advantage that it can be rigorously defined and that a number of consequences can be proven. In addition, it also provides a classical meaning. In the classical ground state of a bipartite system spins that interact ferromagnetically are mutually aligned parallel and spins that interact antiferromagnetically are mutually aligned anti-parallel. Following the pioneering work of Lieb, Schultz, and Mattis[8,9] this can now be defined without recourse to classical spin systems.

If the spin system can be decomposed into subsystems (sublattices) A and B such that all exchange parameters (also those that are zero) fulfill $J(x_A,y_B) \leq g^2$, $J(x_A,y_A) \geq g^2$, $J(x_B,y_B) \geq g^2$, the system is called bipartite. Here x_A and y_A denote the sites of spins belonging to sublattice A and x_B and y_B the sites of spins belonging to sublattice

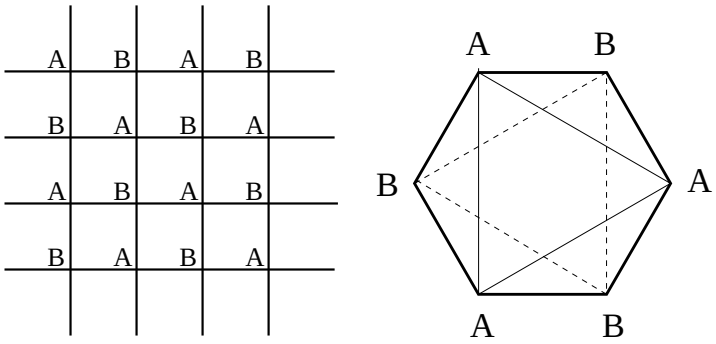

Figure 2: Schematic picture of fictitious spin systems: the square lattice on the l.h.s. is bipartite, the hexagon on the r.h.s. only if the intra-A and intra-B sublattice interactions fulfill the conditions put up by Lieb, Schultz, and Mattis.

B; g is a real number that has to be found in order to establish the partition. It is essential for this definition that antiferromagnetic interactions are represented by negative exchange parameters.

Figure 2 shows two examples. The square lattice on the l.h.s. is bipartite for antiferromagnetic nearest neighbor interactions. The hexagon on the r.h.s. shows three types of interactions. Let's assume that the interaction along the hexagon edges is antiferromagnetic as in many spin rings. Then the system would be bipartite if the other two interactions that act inside the A and the B sublattice, respectively, are ferromagnetic. In this case $g = 0$ would allow the given partition. If on the contrary any of the shown interactions inside the hexagon would also be antiferromagnetic then a valid partition cannot be found.

The proven consequences of bipartiteness are:

- Let $\mathscr{S} = |S_A - S_B|$, where S_A and S_B are the maximum possible spins on the sublattices A and B. Then the ground state of the Heisenberg Hamiltonian belongs at most to total spin $\mathscr{S}$. This immediately implies that for $S_A = S_B$ the ground state spin is zero,[9] but also explains ferrimagnetic cases.

- For all total spins S with $S \geq \mathscr{S}$ the minimal energies $E(S)$ in the sectors of total spin fulfill $E(S+1) > E(S)$. Again, for $S_A = S_B$ this holds for all total spin quantum numbers.[9] The levels of minimal energy are non-degenerate except for the trivial degeneracy related to the magnetic quantum number M.

- Bipartiteness also enables one to determine phase relations of ground state wave functions. The most prominent example is the sign rule of Marshall and Peierls, that can be connected to the momentum quantum number of periodic systems such as spin rings.[10]

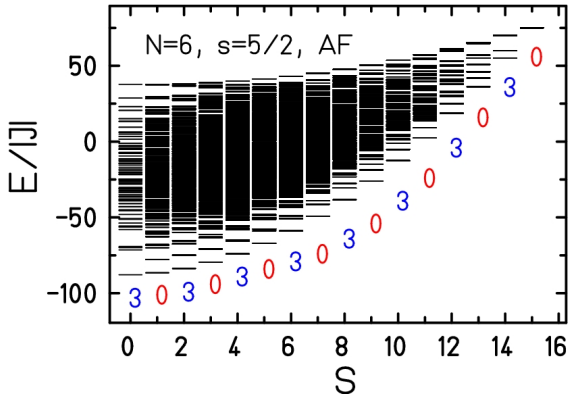

Figure 3: Energy eigenvalues of a spin ring ($N = 6, s = 5/2$) with antiferromagnetic nearest neighbor coupling as function of total spin S.

I would like to discuss these properties with the help of an example. Figure 3 shows the energy spectrum of a spin ring ($N = 6, s = 5/2$) with antiferromagnetic nearest neighbor coupling as function of total spin S. This system is bipartite. One easily recognizes that the ground state belongs to $S = 0$ which it must since both sublattices possess the same maximum possible spin of $3 \times 5/2$. One also sees that $E(S+1) > E(S)$ strictly holds for all S. The system is C_6 symmetric, or in the language of condensed matter physics translational invariant with periodic boundary conditions after six sites. This gives rise to 6 irreducible representations with complex characters, that can be expressed as

$$\exp\left\{-i\frac{2\pi k}{N}\right\} \quad , \quad k = 0, 1, \ldots, N \, . \tag{3}$$

$k = 0, 1, 2, 3, 4, 5$ labels the characters or momentum quantum numbers, respectively. The sign rule of Marshall and Peierls allows us to determine the momentum quantum numbers k (wave numbers) for the relative ground state in each subspace of total spin S. These numbers are given in the figure close to the lowest levels.

Besides the proven properties there are softer ones that seem to hold for bipartite systems.

- The lowest levels of regular, i.e. highly symmetric, bipartite antiferromagnets as a function of S are arranged in an approximate parabola (Lande interval rule, rotational bands),[11,12,13,14,15] compare Fig. 3.

- The lowest band can be understood as originating from an effective Hamiltonian where the two sublattice spins $S_A = Ns/2$ and $S_B = Ns/2$ interact antiferromagnetically.[11] This picture also motivates the existence of a second band in which an $S = 0$ level does not exist, since $S_A = Ns/2$ and $S_B = Ns/2 - 1$ cannot be coupled to $S = 0$. This effect is clearly visible in the spectrum shown in Fig. 3.

- Since the curvature of the minimal energy function $E(S)$ determines the magnetization curve at $T = 0$ or equivalently the order of successive level crossings, an approximate quadratic dependence yields with increasing field B successive crossings of levels belonging to adjacent total spin quantum numbers with practically equidistant field spacings. This means that $(S = 1, M = -1)$ crosses $(S = 0, M = 0)$ at B_1, then $(S = 2, M = -2)$ crosses $(S = 1, M = -1)$ at $B_2 \approx 2B_1$ and so on. The resulting low-temperature magnetization curve will thus be a rather regular staircase.

We will see that these properties are entirely different for frustrated spin systems.

3 Effects of frustration

In this section I discuss the various effects frustration can have on the energy spectrum and on magnetic observables. The investigation of plain triangles or tetrahedra is not really enlightening since both have a very simple energy spectrum consisting of one band of energy levels. The reason is that for both systems the Heisenberg Hamiltonian can be simplified by completing the square, i.e. the Heisenberg term is simply proportional to $\vec{\underset{\sim}{S}}^2$. Nevertheless, the degeneracy of energy eigenvalues remains an issue.[1,16]

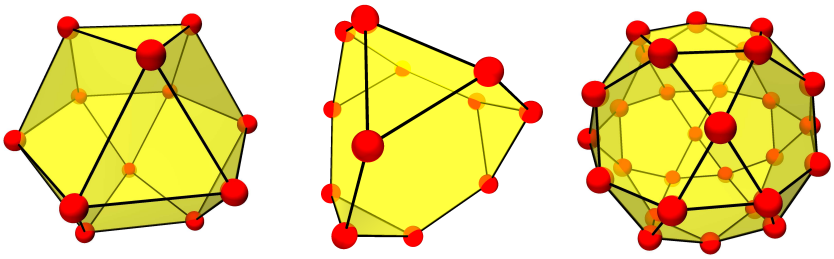

Figure 4: Structure of the cuboctahedron (left), the truncated tetrahedron (middle), and the icosidodecahedron (right).

Experience collected in condensed matter physics demonstrates that prominent frustration effects can be observed in certain spin lattices with antiferromagnetic nearest neighbor coupling with the kagomé and the pyrochlore lattices being the most prominent ones. Molecular realizations that come close to the structure of the kagomé lattice do exist in the form of cuboctahedra and icosidodecahedra.[17,18,19,20,21,22] These systems, as can be seen in Fig. 4, consist of corner sharing triangles. There are of course many other frustrated molecules, among them the truncated tetrahedra,[23] and (unfortunately chemically incomplete) icosahedra.[24] Not every one of them shows all of the below discussed properties.

3.1 Ground state degeneracy

An important effect of frustration can be given by a degenerate ground state. Olivier Kahn discusses this degeneracy for antiferromagnetic triangles with half-integer spins. Besides the trivial M-degeneracy of the $S = 1/2$ ground state one observes a twofold degeneracy, which in the language of cyclic groups is due to the symmetry $k \Leftrightarrow (N-k)$, compare eq. (3). The ground state of the respective systems with integer spins is non-degenerate, and thus does not show this frustration effect.[1] Nevertheless, even in the absence of ground state degeneracy there can be other frustration effects as we will see later.

More generally one can state that all symmetric systems of half-integer spins which can be described by trigonal point groups are characterized by doublet ground states[25] which belong to the irreproducible representation ${}^2E$. A physical consequence of a

degenerate ground state is that these spin systems are very likely to be perturbed by small interactions not present in the Hamiltonian (1). Such interactions are given by structural, e.g. spontaneous Jahn-Teller distortions, antisymmetric exchange[26,27] or spin-Peierls transitions.[28]

3.2 Spin rings

A natural extension of triangles is given by odd-membered spin rings. In contrast to a large number of synthesized even-membered spin rings such as ferric or chromium wheels,[14,29,30,31,32] odd-membered rings are difficult to synthesize due to steric hindrance of the ligands. Nevertheless, thanks to synthetic cleverness several odd-membered antiferromagnetic rings exist, although not quite as symmetric as their even-membered counterparts.[33,34,35,36,37,38] In the classical ground state of a perfect odd-membered ring adjacent spins are no longer aligned antiparallel, their orientation can for instance be described as non-collinear, i.e. a Möbius strip.[34,35]

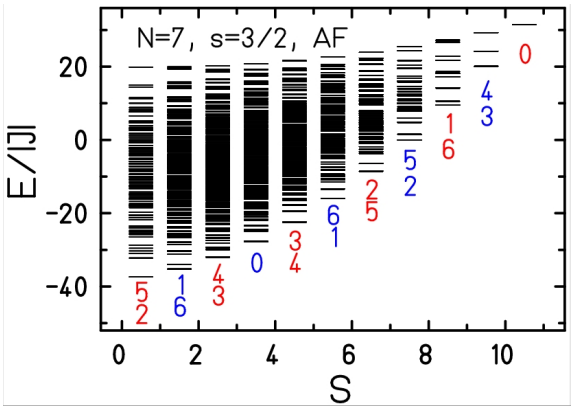

Figure 5: Energy eigenvalues of a spin ring ($N = 7, s = 3/2$) with antiferromagnetic nearest neighbor coupling as function of total spin S.

Figure 5 shows the energy spectrum of a spin ring ($N = 7, s = 3/2$) with antiferromagnetic nearest neighbor coupling as function of total spin S. The numbers close to the lowest levels for each S denote again the momentum quantum numbers of this relative ground state. In contrast to bipartite rings one sees that many of them are twofold degenerate (in addition to their M-degeneracy). This is a consequence of the symme-

try $k \Leftrightarrow (N-k)$ which only for $k=0$ allows a non-degenerate relative ground state. $k = N/2$ is impossible for odd-membered rings.

There is striking numerical evidence that the momentum quantum numbers k for odd-membered rings are not random, but follow certain rules as they do for even-membered rings.[39] It seems that one can even formulate a generalized rule that holds both for even-membered (bipartite) as well as for odd-membered (frustrated) rings,

$$k \equiv \pm a \left\lceil \frac{N}{2} \right\rceil \mod N \ , \quad a = Ns - M \ . \tag{4}$$

Here $\lceil N/2 \rceil$ denotes the smallest integer greater than or equal to $N/2$. It is interesting to see, that k is independent of s for a given N and a. This means that the sequence of k values starting at the largest S value, i.e. for $a = 0$, is the same for rings of the same size N but with different single spins s. Table 1 provides an example. In addition it was found that for all N except three, the degeneracy is minimal, i.e. completely given by the M-degeneracy and the k-degeneracy.[40]

		a						
N	s	0	1	2	3	4	5	...
9	1/2	0	$5 \equiv 4$	$10 \equiv 1$	$15 \equiv 3$	$20 \equiv 2$	-	-
9	1	0	$5 \equiv 4$	$10 \equiv 1$	$15 \equiv 3$	$20 \equiv 2$	$25 \equiv 2$	...

Table 1: Example of k quantum numbers for an odd-membered ring with $N = 9$ and $s = 1/2$ as well as $s = 1$. $20 \equiv 2$ means that $a\lceil N/2 \rceil$ is 20, which is equivalent to 2 when taking the modulus with respect to N. If $k \neq 0$, then $N-k$ is also ground state k quantum number. One see that the k numbers are the same for the two cases. The first sequence is only shown down to $a = 4$, which constitutes already the $S = 1/2$ ground state in this case.

Summarizing, the clear frustration effect for odd-membered rings is the non-trivial degeneracy of relative ground state levels that does not appear for even-membered rings.

I would like to remark that frustration of antiferromagnetic even membered spin rings can also be introduced by an antiferromagnetic next nearest neighbor interaction. Again, depending on the ratio of the two interactions the ground state can be non-collinear.[41,42] However, it could be demonstrated that the level ordering $E(S+1) >$

$E(S)$ is rather robust for small next nearest neighbor interactions.[43,44]

3.3 Low-lying singlets

The idea of a non-trivial ground state degeneracy is also used in discussions of frustrated classical spin systems such as the triangle shown in Fig. 1. The classical ground state on the r.h.s. is two-fold non-trivially (i.e. orbitally) degenerate because the two lower spins could be exchanged to yield another ground state. The two ground states differ in their chirality which expresses itself in different signs of the z-component of the orbital (pseudo spin) moment.[25] The trivial degeneracy is given by collective rotations of the full ground state. In several classical systems, e.g. the kagomé lattice antiferromagnet, the non-trivial degeneracy is actually infinity, i.e. macroscopic, and this means it scales with the size of the system. Nevertheless, for such systems one may find (or believe or have numerical evidence) that the ground state of the corresponding quantum system is non-degenerate. In the language of higher-order spin wave theory one would express this observation as that the classical degeneracy is lifted “by quantum fluctuations", a concept that sometimes is also denoted as “order from disorder".[45] However, the classically degenerate ground states do not move far, they appear as low-lying singlets (below the first triplet) in the quantum spectrum.[46,47]

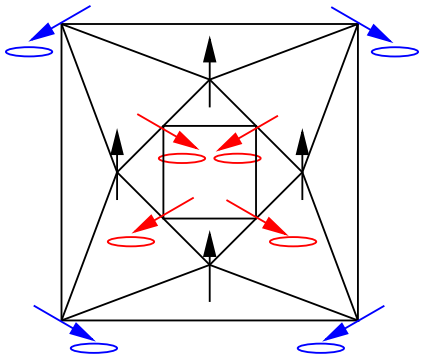

Figure 6: Planar graph of the cuboctahedron: the classical spins reside at the vertices, the solid edges denote the antiferromagnetic exchange interactions. Two groups of classical spins (outer and inner square) can independendly be rotated without changing the ground state energy.

Figure 6 provides an interesting example of non-trivial classical ground-state de-

generacy that is related to the kagomé. It shows the graph of antiferromagnetic interactions in a cuboctahedron with spins at the vertices. The classical ground state is given by states with relative angles of 120° between neighboring spins. There exist an infinite number of non-trivially degenerate ground states that can be produced by independent collective rotations of groups of four spins (outer and inner square). The same holds for the kagomé where the squares are just replaced by hexagons. A quantum treatment lifts this degeneracy, and the quantum ground state of the cuboctahedron is non-degenerate.

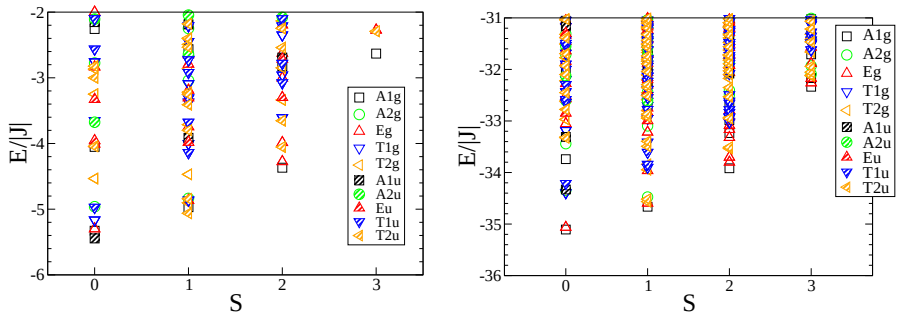

Figure 7: Low-lying energy spectrum of the antiferromagnetic cuboctahedron for $s = 1/2$ (l.h.s.) and for $s = 3/2$ (r.h.s.). The levels are characterized by the irreducible representations of O_h.

Figure 7 shows the low-lying energy spectrum of the antiferromagnetic cuboctahedron for $s = 1/2$ (l.h.s.) and for $s = 3/2$ (r.h.s.). The ground states of both systems are non-degenerate. One notices that several levels (in the case of $s = 1/2$) and one additional level (in the case of $s = 3/2$) exist below the first triplet.[48,49,50,51] Such a behavior is also expected for molecules of icosidodecahedral structure and numerically evaluated for the case of $s = 1/2$ which would correspond to the vanadium Keplerate.[48,52]

Although the low-lying singlets are magnetically silent they have a great impact on the specific heat which at low temperatures may thus exhibit extra features. For the cuboctahedron for $s = 1/2$ for instance one observes a sharp additional peak at low temperatures.[48] The magnetic susceptibility is only mildly influenced through the partition function. Numerical studies suggest that the number of low-lying singlets decreases with increasing number of the individual spin quantum number of the system.[48,50]

3.4 Magnetization plateaus

Regular, i.e. highly symmetric, bipartite finite antiferromagnets possess a low-temperature magnetization curve that has the form of a regular staircase. Frustrated systems may exhibit unusual deviations thereof. Such deviations appear more pronounced in infinitely extended quantum antiferromagnets as again the kagomé and pyrochlore lattice since there even the $(T = 0)$ magnetization curve is a continuous (even differentiable) curve except for plateaus and jumps.

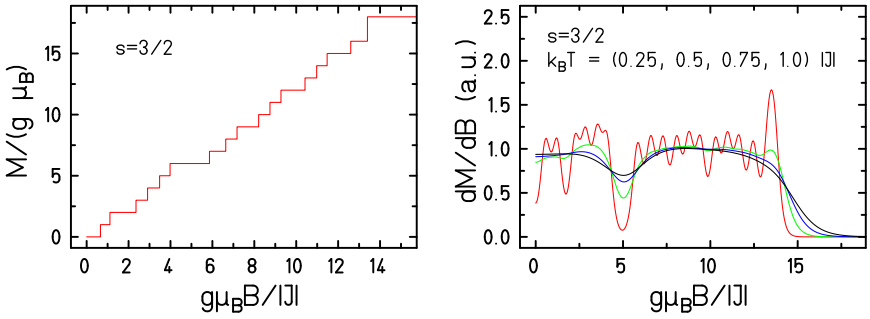

Figure 8: L.h.s.: Magnetization curve at $T = 0$ for the antiferromagnetic cuboctahedron with $s = 3/2$. R.h.s.: Differential susceptibility for the same system for several small temperatures. The higher the temperature the smoother the corresponding curve. At temperatures $k_B T \geq 0.75|J|$ only one feature persists, the dip at $g\mu_B B/|J| \approx 5$ which is approximately one third of the saturation field.

In finite antiferromagnets the magnetization curve at $T = 0$ is a (non-differentiable) staircase anyhow due to successive level crossings. Nevertheless, unusual plateaus can be identified. Figure 8 shows the magnetization curve at $T = 0$ for the antiferromagnetic cuboctahedron with $s = 3/2$. One can clearly see that the plateau at $1/3$ of the saturation magnetization is wider than the others. The differential susceptibility on the r.h.s. demonstrates that it is thermally also much more stable since it leads to a magnetization dip even at those temperatures where the features stemming from the other steps of the staircase have already disappeared.[50]

The plateau at $1/3$ of the saturation magnetization appears in systems built of corner sharing triangles such as the kagomé lattice antiferromagnet[53,54,55,56,57] or molecular realizations such as the cuboctahedron and the icosidodecahedron.[48,52,58] Its stability is classically related to the dominating contribution of so-called "up-up-down" (*uud*)

spin configurations to the partition function.[57,59] Recently it could be shown for the cuboctahedron and the icosidodecahedron that the corresponding quantum states indeed also dominate the quantum partition function.[52] It is worth mentioning that the differential susceptibility of a simple quantum mechanical triangle (both for integer and half-integer spins) also shows the dip at $1/3$ for non-zero temperatures although it does not exhibit the plateau at $T = 0$. The reason is given by the special degeneracy of energy levels for larger S. This is the point where a spin triangle of integer spins with a boring ${}^1A_1$ ground state shows its frustration effects.

For the pyrochlore the argumentation is analogous with the difference that in this case a half-magnetization plateau is stabilized by "up-up-up-down" (*uuud*) configurations.[60]

3.5 Magnetization jumps

Many observable effects of frustration had their first (theoretical) discovery in condensed matter physics of infinite lattices. But a certain class of unusual magnetization jumps was discovered in connection with the antiferromagnetic Keplerate molecules of icosidodecahedral structure.[61] Figure 9 displays on the l.h.s. the minimal energies of an antiferromagnetic icosidodecahedron with $s = 1/2$. The highest four levels follow a strict linear dependence (highlighted by the straight line), which results in a magnetization jump to saturation of $\Delta\mathscr{M}/(g\mu_B) = 3$, compare r.h.s. of Fig. 9. Jumps of non-trivial height, i.e. with $\Delta\mathscr{M}/(g\mu_B) > 1$, will always occur if the curve of minimal energy levels as function of total spin is not convex, i.e. linear or concave.[62] Antiferromagnetic clusters with a rotational-band of minimal energies, that is thus automatically convex, will therefore never exhibit such jumps.

In the case of the special jumps observed in the icosidodecahedron it turned out that an analytical model could be devised that describes the many-body states of minimal energy close to the highest energy, i.e. those connected by a straight line on the l.h.s. of Fig. 9 in terms of new quasi-particles, independent localized magnons.[63,64] Such states govern the low-temperature high-field behavior of many frustrated antiferromagnets such as the kagomé and the pyrochlore lattice again, but also several other spin struc-

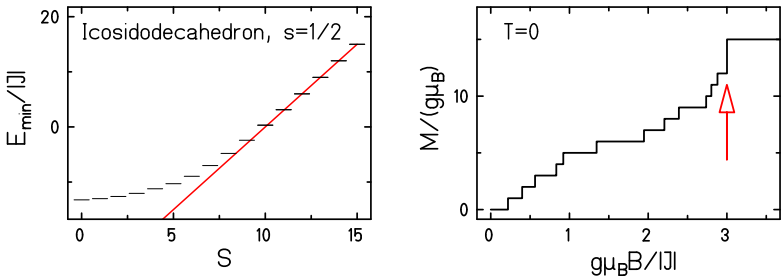

Figure 9: Minimal energies of an antiferromagnetic icosidodecahedron with $s = 1/2$ (l.h.s.) and resulting magnetization curve at $T = 0$ (r.h.s.).

tures as for instance special saw-tooth chains like azurite.[65,66,67] The number of these special many-body states does not depend on the individual spin quantum number but on the topological structure of interactions. It may easily grow exponentially with the size of the system, as for lattices.[68,69,70] Due to the dependence on the graph of interactions similar states do exist for the Hubbard model,[71] where they lead to flat-band ferromagnetism, a phenomenon which was discovered already 15 years ago.[72,73,74,75]

The magnetization jump at the saturation field is a real quantum phenomenon; it is connected to the simultaneous crossing of many Zeeman levels. This means that even at $T = 0$ such systems possess non-zero entropy.[76,77,78] Therefore, in the vicinity of the saturation field one can observe strong magnetocaloric effects. Isentropes (curves of constant entropy) exhibit steep and opposite slopes on either sides of the saturation field, i.e. it would be possible to heat or cool the system by just varying the external magnetic field. This was also predicted for the classical counterparts.[79] Complementary to this high-field magnetocaloric effect there is of course the possibility to try to achieve a huge ground state spin which would lead to a pronounced zero-field magnetocaloric effect.[80,81,82,83,84]

Frustrated antiferromagnetic lattices of corner-sharing triangles or tetrahedra are well investigated, systems of edge-sharing polygons or bodies – except for the triangular lattice antiferromagnet – not so much. In the case of molecules this would refer for instance to the dodecahedron or the icosahedron, the latter being a rather natural structure for instance in cluster physics, but difficult to realize in supramolecular chemistry.[24] It was theoretically found that these special systems show another frustration

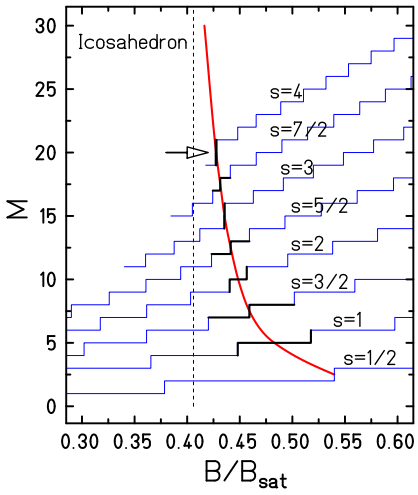

Figure 10: Parts of the $T = 0$ magnetization curves for antiferromagnetic icosahedra with $s = 1/2, 1, 3/2, 2, 5/2, 3, 7/2, 4$ (from bottom to top).

effect, again a jump, but not at saturation. Such a transition is sometimes called metamagnetic phase transition[85,86,87] since it constitutes a so-called $(T = 0)$-phase transition where one can switch with the help of the external magnetic field between the phases left and right of the jump. In classical investigations the switching is accompanied by metastability and a hysteresis.[86] Figure 10 displays parts of $(T = 0)$-magnetization curves for various single spin quantum numbers s. Since the unusual magnetization jump is most pronounced for classical spin icosahedra it is expected to show up for larger s. As can be see in the figure a jump of twice the normal height occurs for $s = 4$, but for the smaller spins shrinking magnetization steps act as precursors.

3.6 Reduction of local moments

As a last example I would like to discuss the influence of a frustrating interaction on local spin moments. Such moments can nowadays be measured in order to better understand the internal magnetization distribution and thus the low-energy wave functions. Experimental probes are for instance Nuclear Magnetic Resonance[88] or – and then even element-selective – X-ray magnetic circular dichroism.[89] I would like to use a fictitious star-like molecule for this discussion, compare l.h.s. of Fig. 11, that is similar to recently synthesized and investigated examples.[90,91,92,93]

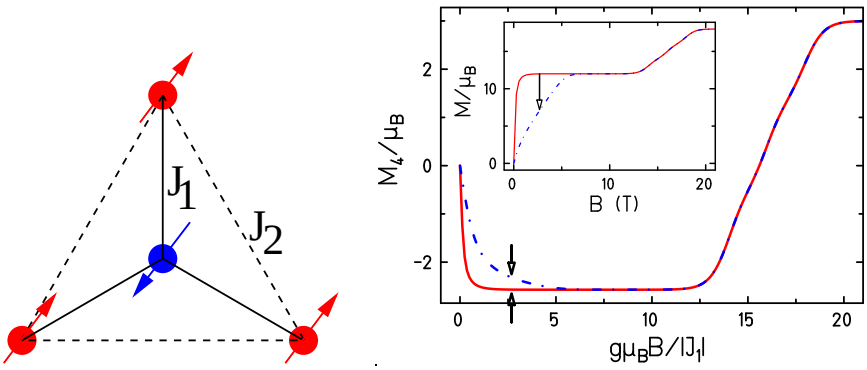

Figure 11: L.h.s.: Sketch of a fictitious magnetic molecule with two exchange pathways. R.h.s.: Local magnetization for the central spin at $T = 0.5|J_1|$ for $J_2 = 0$ (solid curve) and $J_2 = 0.5J_1$ (dashed dotted curve). The inset shows the total magnetization and the main figure the contribution of the central spin.

Figure 11 shows on the r.h.s. the magnetization of the fictitious molecule with three spins $s = 5/2$ in the outer triangle and a central spin with $s_4 = 3/2$. The coupling J_1 is antiferromagnetic. For $J_2 = 0$ the system is bipartite and the ground state spin according to Lieb, Schultz, and Mattis is at most $\mathscr{S} = |S_A - S_B| = 3 \times 5/2 - 3/2 = 6$. That this is indeed the case can be inferred from the solid magnetization curve in the inset, where one can see that the magnetization immediately follows a Brillouin function of a total spin $S = 6$ for small magnetic fields. In addition the main graphics shows the magnetization contribution of the central spin which at low temperatures ($T = 0.5|J_1|$ in the example) and low-fields points opposite to the three outer spins with a practically maximal amplitude of $\mathscr{M}_4 \approx 3\mu_B$.

With increasing frustration due to the antiferromagnetic interaction J_2 the properties change. Figure 11 shows as a second example the case of $J_2 = 0.5J_1$ for the same temperature. The dashed-dotted curve in the inset displays how much the total magnetization shrinks especially at low field values. The arrow depicts an example case. As can be seen in the main graphics the contribution of the central spin also changes but not too much, which leads to the conclusion that the frustration more strongly modifies the joint moment of the three outer spins. This is a special example of the more general phenomenon of reduction of correlations $\langle \vec{s}_i \cdot \vec{s}_j \rangle$ between spins due to frustration.[94]

3.7 Outlook

Although the article describes the major frustration effects for antiferromagnetic spin systems they can of course be discussed in more depth. For the interested reader I would like to recommend three specialized books.[95,96,97] Nowadays, research interests in condensed matter physics focus on e.g. quantum (i.e. $T = 0$) phase transitions driven by frustration as for instance in antiferromagnetic spin chains with antiferromagnetic next nearest neighbor coupling or on exotic behavior as spin liquid or spin ice.[7,98,99,100] The modern language is a description in terms of quasi-particles. For example, the frustration effects in spin chains with nearest and next nearest antiferromagnetic interactions are denoted as “condensation of triplets". The afore discussed magnetization jumps in the cuboctahedron, icosidodecahedron, kagomé, or pyrochlore can be well understood by introducing localized independent magnons as quasi particles. How far these concepts go and how real the quasi-particles are demonstrates the recent experimental verification of “magnetic monopoles" in spin ice.[101]

Although magnetic molecules are only of finite size (zero-dimensional) many of the exciting properties carry over as I hope I have shown.

Acknowledgment

This work was supported by the German Science Foundation (DFG) through the research group 945. I would also like to thank Roman Schnalle and Christian Karlewski for producing some of the figures for me as well as Roman Schnalle, Stephen Blundell (Oxford), Johannes Richter (Magdeburg) and Boris Tsukerblat (Be’er Sheva) for carefully reading the manuscript. Johannes Richter suggested to show Fig. 6.

References

[1] O. Kahn, *Chem. Phys. Lett.*, 1997, **265**, 109–114.

[2] G. Toulouse, *Comm. Phys.*, 1977, **2**, 115–119.

[3] S. Kirkpatrick, *Phys. Rev. B*, 1977, **16**, 4630–4641.

[4] A. P. Ramirez, *Annu. Rev. Mater. Sci.*, 1994, **24**, 453.

[5] J. Greedan, *J. Mater. Chem.*, 2001, **11**, 37.

[6] R. Moessner, *Can. J. Phys.*, 2001, **79**, 1283.

[7] S. T. Bramwell and M. J. P. Gingras, *Science*, 2001, **294**, 1495–1501.

[8] E. H. Lieb, T. Schultz and D. C. Mattis, *Ann. Phys. (N.Y.)*, 1961, **16**, 407.

[9] E. H. Lieb and D. C. Mattis, *J. Math. Phys.*, 1962, **3**, 749.

[10] W. Marshall, *Proc. Royal. Soc. A (London)*, 1955, **232**, 48.

[11] P. W. Anderson, *Phys. Rev.*, 1952, **86**, 694–701.

[12] M.-H. Julien, Z. Jang, A. Lascialfari, F. Borsa, M. Horvatić, A. Caneschi and D. Gatteschi, *Phys. Rev. Lett.*, 1999, **83**, 227.

[13] J. Schnack and M. Luban, *Phys. Rev. B*, 2000, **63**, 014418.

[14] G. L. Abbati, A. Caneschi, A. Cornia, A. C. Fabretti and D. Gatteschi, *Inorg. Chim. Acta*, 2000, **297**, 291.

[15] O. Waldmann, *Phys. Rev. B*, 2001, **65**, 024424.

[16] D. Dai and M.-H. Whangbo, *J. Chem. Phys.*, 2004, **121**, 672–680.

[17] A. Müller, S. Sarkar, S. Q. N. Shah, H. Bögge, M. Schmidtmann, S. Sarkar, P. Kögerler, B. Hauptfleisch, A. Trautwein and V. Schünemann, *Angew. Chem. Int. Ed.*, 1999, **38**, 3238.

[18] A. Müller, M. Luban, C. Schröder, R. Modler, P. Kögerler, M. Axenovich, J. Schnack, P. C. Canfield, S. Bud'ko and N. Harrison, *Chem. Phys. Chem.*, 2001, **2**, 517.

[19] M. Axenovich and M. Luban, *Phys. Rev. B*, 2001, **63**, 100407.

[20] N. Kunisada, S. Takemura and Y. Fukumoto, *J. Phys.: Conf. Ser.*, 2009, **145**, 012083 (4pp).

[21] B. Botar, P. Kögerler and C. L. Hill, *Chem. Commun.*, 2005, 3138–3140.

[22] A. M. Todea, A. Merca, H. Bögge, J. van Slageren, M. Dressel, L. Engelhardt, M. Luban, T. Glaser, M. Henry and A. Müller, *Angew. Chem. Int. Ed.*, 2007, **46**, 6106–6110.

[23] C. P. Pradeep, D.-L. Long, P. Kögerler and L. Cronin, *Chem. Commun.*, 2007, 4254–4256.

[24] E. I. Tolis, L. P. Engelhardt, P. V. Mason, G. Rajaraman, K. Kindo, M. Luban, A. Matsuo, H. Nojiri, J. Raftery, C. Schröder, G. A. T. F. Tuna, W. Wernsdorfer and R. E. P. Winpenny, *Chem. Eur. J.*, 2006, **12**, 8961–8968.

[25] N. Zamstein, A. Tarantul and B. Tsukerblat, *Inorg. Chem.*, 2007, **46**, 8851–8858.

[26] B. Tsukerblat, A. Tarantul and A. Müller, *J. Mol. Struct.*, 2007, **838**, 124–132.

[27] P. Kögerler, B. Tsukerblat and A. Müller, *Dalton Trans.*, 2010.

[28] J. Richter, O. Derzhko and J. Schulenburg, *Phys. Rev. Lett.*, 2004, **93**, 107206.

[29] K. L. Taft, C. D. Delfs, G. C. Papaefthymiou, S. Foner, D. Gatteschi and S. J. Lippard, *J. Am. Chem. Soc.*, 1994, **116**, 823.

[30] O. Waldmann, R. Koch, S. Schromm, J. Schülein, P. Müller, I. Bernt, R. W. Saalfrank, F. Hampel and E. Balthes, *Inorg. Chem.*, 2001, **40**, 2986.

[31] J. van Slageren, R. Sessoli, D. Gatteschi, A. Smith, M. Helliwell, R. Winpenny, A. Cornia, A. Barra, A. Jansen, E. Rentschler and G. Timco, *Chem. Eur. J.*, 2002, **8**, 277–285.

[32] F. Larsen, J. Overgaard, S. Parsons, E. Rentschler, A. Smith, G. Timco and R. Winpenny, *Angew. Chem. Int. Edit.*, 2003, **42**, 5978–5981.

[33] F. Larsen, E. McInnes, H. El Mkami, G. Rajaraman, E. Rentschler, A. Smith, G. Smith, V. Boote, M. Jennings, G. Timco and R. Winpenny, *Angew. Chem. Int. Edit.*, 2003, **42**, 101–105.

[34] O. Cador, D. Gatteschi, R. Sessoli, F. K. Larsen, J. Overgaard, A. L. Barra, S. J. Teat, G. A. Timco and R. E. P. Winpenny, *Angew. Chem. Int. Edit.*, 2004, **43**, 5196–5200.

[35] O. Cador, D. Gatteschi, R. Sessoli, A.-L. Barra, G. A. Timco and R. E. P. Winpenny, *J. Magn. Magn. Mater.*, 2005, **290-291**, 55–60.

[36] H. C. Yao, J. J. Wang, Y. S. Ma, O. Waldmann, W. X. Du, Y. Song, Y. Z. Li, L. M. Zheng, S. Decurtins and X. Q. Xin, *Chem. Commun.*, 2006, 1745–1747.

[37] Y. Furukawa, K. Kiuchi, K. ichi Kumagai, Y. Ajiro, Y. Narumi, M. Iwaki, K. Kindo, A. Bianchi, S. Carretta, P. Santini, F. Borsa, G. A. Timco and R. E. P. Winpenny, *Phys. Rev. B*, 2009, **79**, 134416.

[38] N. Hoshino, M. Nakano, H. Nojiri, W. Wernsdorfer and H. Oshio, *J. Am. Chem. Soc.*, 2009, **131**, 15100–15101.

[39] K. Bärwinkel, H.-J. Schmidt and J. Schnack, *J. Magn. Magn. Mater.*, 2000, **220**, 227.

[40] K. Bärwinkel, P. Hage, H.-J. Schmidt and J. Schnack, *Phys. Rev. B*, 2003, **68**, 054422.

[41] T. Masuda, A. Zheludev, A. Bush, M. Markina and A. Vasiliev, *Phys. Rev. Lett.*, 2004, **92**, 177201.

[42] S. Drechsler, J. Malek, J. Richter, A. Moskvin, A. Gippius and H. Rosner, *Phys. Rev. Lett.*, 2005, **94**, 039705.

[43] J. Richter, N. Ivanov, K. Retzlaff and A. Voigt, *J. Magn. Magn. Mater.*, 1995, **140**, 1611–1612.

[44] J. Richter, N. Ivanov, A. Voigt and K. Retzlaff, *J. Low Temp. Phys.*, 1995, **99**, 363.

[45] C. L. Henley, *Phys. Rev. Lett.*, 1989, **62**, 2056–2059.

[46] C. Waldtmann, H. U. Everts, B. Bernu, C. Lhuillier, P. Sindzingre, P. Lecheminant and L. Pierre, *Eur. Phys. J. B*, 1998, **2**, 501–507.

[47] E. Berg, E. Altman and A. Auerbach, *Phys. Rev. Lett.*, 2003, **90**, 147204.

[48] R. Schmidt, J. Schnack and J. Richter, *J. Magn. Magn. Mater.*, 2005, **295**, 164–167.

[49] R. Schnalle and J. Schnack, *Phys. Rev. B*, 2009, **79**, 104419.

[50] J. Schnack and R. Schnalle, *Polyhedron*, 2009, **28**, 1620–1623.

[51] R. Schnalle, *Ph.D. thesis*, Osnabrück University, 2009.

[52] I. Rousochatzakis, A. M. Läuchli and F. Mila, *Phys. Rev. B*, 2008, **77**, 094420.

[53] P. Azaria, C. Hooley, P. Lecheminant, C. Lhuillier and A. M. Tsvelik, *Phys. Rev. Lett.*, 1998, **81**, 1694–1697.

[54] J. L. Atwood, *Nat. Mater.*, 2002, **1**, 91–92.

[55] M. E. Zhitomirsky, *Phys. Rev. Lett.*, 2002, **88**, 057204.

[56] A. Honecker, O. A. Petrenko and M. E. Zhitomirsky, *Physica B*, 2002, **312**, 609–611.

[57] D. C. Cabra, M. D. Grynberg, P. C. W. Holdsworth, A. Honecker, P. Pujol, J. Richter, D. Schmalfuß and J. Schulenburg, *Phys. Rev. B*, 2005, **71**, 144420.

[58] C. Schröder, H. Nojiri, J. Schnack, P. Hage, M. Luban and P. Kögerler, *Phys. Rev. Lett.*, 2005, **94**, 017205.

[59] H. Kawamura and S. Miyashita, *J. Phys. Soc. Jpn.*, 1985, **54**, 4530–4538.

[60] K. Penc, N. Shannon and H. Shiba, *Phys. Rev. Lett.*, 2004, **93**, 197203.

[61] J. Schnack, H.-J. Schmidt, J. Richter and J. Schulenburg, *Eur. Phys. J. B*, 2001, **24**, 475.

[62] C. Lhuillier and G. Misguich, in *High Magnetic Fields*, ed. C. Berthier, L. Levy and G. Martinez, Springer, Berlin, 2002, pp. 161–190.

[63] J. Schulenburg, A. Honecker, J. Schnack, J. Richter and H.-J. Schmidt, *Phys. Rev. Lett.*, 2002, **88**, 167207.

[64] J. Richter, J. Schulenburg, A. Honecker, J. Schnack and H.-J. Schmidt, *J. Phys.: Condens. Matter*, 2004, **16**, S779.

[65] M. E. Zhitomirsky and H. Tsunetsugu, *Prog. Theor. Phys. Suppl.*, 2005, **160**, 361–382.

[66] R. Szymczak, M. Baran, R. Diduszko, J. Fink-Finowicki, M. Gutowska, A. Szewcyk and H. Szymczak, *Phys. Rev. B*, 2006, **73**, 094425.

[67] K. C. Rule, A. U. B. Wolter, S. Suellow, D. A. Tennant, A. Bruehl, S. Koehler, B. Wolf, M. Lang and J. Schreuer, *Phys. Rev. Lett.*, 2008, **100**, 117202.

[68] O. Derzhko and J. Richter, *Phys. Rev. B*, 2004, **70**, 104415.

[69] H.-J. Schmidt, J. Richter and R. Moessner, *J. Phys. A: Math. Gen.*, 2006, **39**, 10673–10690.

[70] M. E. Zhitomirsky and H. Tsunetsugu, *Phys. Rev. B*, 2007, **75**, 224416.

[71] O. Derzhko, A. Honecker and J. Richter, *Phys. Rev. B*, 2007, **76**, 220402.

[72] H. Tasaki, *Phys. Rev. Lett.*, 1992, **69**, 1608–1611.

[73] A. Mielke, *J. Phys. A-Math. Gen.*, 1992, **25**, 6507–6515.

[74] A. Mielke, *J. Phys. A-Math. Gen.*, 1992, **25**, 4335–4345.

[75] A. Mielke and H. Tasaki, *Commun. Math. Phys.*, 1993, **158**, 341–371.

[76] M. E. Zhitomirsky and A. Honecker, *J. Stat. Mech.: Theor. Exp.*, 2004, P07012.

[77] J. Schnack, R. Schmidt and J. Richter, *Phys. Rev. B*, 2007, **76**, 054413.

[78] A. Honecker and M. E. Zhitomirsky, *J. Phys.: Conf. Ser.*, 2009, **145**, 012082 (4pp).

[79] M. E. Zhitomirsky, *Phys. Rev. B*, 2003, **67**, 104421.

[80] R. D. McMichael, R. D. Shull, L. J. Swartzendruber, L. H. Bennett and R. E. Watson, *J. Magn. Magn. Mater.*, 1992, **111**, 29–33.

[81] L. H. Bennett, R. D. McMichael, H. C. Tang and R. E. Watson, *J. Appl. Phys.*, 1994, **75**, 5493–5495.

[82] M. Affronte, A. Ghirri, S. Carretta, G. Amoretti, S. Piligkos, G. A. Timco and R. E. P. Winpenny, *Appl. Phys. Lett.*, 2004, **84**, 3468–3470.

[83] M. Evangelisti, A. Candini, A. Ghirri, M. Affronte, E. K. Brechin and E. J. McInnes, *Appl. Phys. Lett.*, 2005, **87**, 072504.

[84] M. Evangelisti, A. Candini, M. Affronte, E. Pasca, L. J. de Jongh, R. T. W. Scott and E. K. Brechin, *Phys. Rev. B*, 2009, **79**, 104414.

[85] D. Coffey and S. A. Trugman, *Phys. Rev. Lett.*, 1992, **69**, 176–179.

[86] C. Schröder, H.-J. Schmidt, J. Schnack and M. Luban, *Phys. Rev. Lett.*, 2005, **94**, 207203.

[87] N. P. Konstantinidis, *Phys. Rev. B*, 2007, **76**, 104434.

[88] E. Micotti, Y. Furukawa, K. Kumagai, S. Carretta, A. Lascialfari, F. Borsa, G. A. Timco and R. E. P. Winpenny, *Phys. Rev. Lett.*, 2006, **97**, 267204.

[89] V. Corradini, F. Moro, R. Biagi, U. del Pennino, V. D. Renzi, S. Carretta, P. Santini, M. Affronte, J. C. Cezar, G. Timco and R. E. P. Winpenny, *Phys. Rev. B*, 2008, **77**, 014402.

[90] R. W. Saalfrank, A. Scheurer, I. Bernt, F. W. Heinemann, A. V. Postnikov, V. Schünemann, A. X. Trautwein, M. S. Alam, H. Rupp and P. Müller, *Dalton Trans.*, 2006, 2865–2874.

[91] S. Khanra, B. Biswas, C. Golze, B. Büchner, V. Kataev, T. Weyhermuller and P. Chaudhuri, *Dalton Trans.*, 2007, 481–487.

[92] M. Prinz, K. Kuepper, C. Taubitz, M. Raekers, B. Biswas, T. Weyhermüller, M. Uhlarz, J. Wosnitza, J. Schnack, A. V. Postnikov, C. Schröder, S. J. George, M. Neumann, and P. Chaudhuri, *Inorg. Chem.*

[93] I. S. Tidmarsh, L. J. Batchelor, E. Scales, R. H. Laye, L. Sorace, A. Caneschi, J. Schnack and E. J. L. McInnes, *Dalton Trans.*, 2009, 9402–9409.

[94] J. Schnack, *Phys. Rev. B*, 2000, **62**, 14855.

[95] *Quantum Magnetism*, ed. U. Schollwöck, J. Richter, D. Farnell and R. Bishop, Springer, Berlin, Heidelberg, 2004, vol. 645.

[96] *Frustrated spin systems*, ed. H. Diep, World Scientific, Singapore, 2005.

[97] *Introduction to Frustrated Magnetism*, ed. C. Lacroix, F. Mila and P. Mendels, Springer, Berlin & Heidelberg, 2010.

[98] G. Misguich, B. Bernu, C. Lhuillier and C. Waldtmann, *Phys. Rev. Lett.*, 1998, **81**, 1098–1101.

[99] H. Manaka, Y. Hirai, Y. Hachigo, M. Mitsunaga, M. Ito and N. Terada, *J. Phys. Soc. Jpn.*, 2009, **78**, 093701.

[100] B. Fåk, F. C. Coomer, A. Harrison, D. Visser and M. E. Zhitomirsky, *Europhys. Lett.*, 2008, **81**, 17006.

[101] S. T. Bramwell, S. R. Giblin, S. Calder, R. Aldus, D. Prabhakaran and T. Fennell, *Nature*, 2009, **461**, 956–959.