

Enhanced magnetocaloric effect in frustrated magnetic molecules with icosahedral symmetry

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We investigate the magnetocaloric properties of certain antiferromagnetic spin systems that have already been or very likely can be synthesized as magnetic molecules. It turns out that the special geometric frustration which is present in antiferromagnets that consist of corner-sharing triangles leads to an enhanced magnetocaloric effect with high cooling rates in the vicinity of the saturation field. These findings are compared with the behavior of a simple unfrustrated spin ring as well as with the properties of the icosahedron. To our surprise, also for the icosahedron large cooling rates can be achieved but due to a different kind of geometric frustration.

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I. INTRODUCTION

Antiferromagnetic finite-size spin systems with icosahedral symmetry constitute very interesting frustrated materials with rather unusual magnetic properties. Among such properties are jumps to the saturation magnetization in the cuboctahedron and the icosidodecahedron^{1,2} as well as metamagnetic phase transitions at zero temperature for instance in the icosahedron and dodecahedron.^{3,4,5,6} Some of these properties, for instance the large magnetization jump to saturation, are as well present in the Kagome or other lattice antiferromagnets.⁷ The finite-size systems, nevertheless, have the advantage that due to their smallness many properties can be investigated (numerically) exactly with possible benefits for our knowledge about infinitely extended frustrated spin systems. In this article we investigate the magnetocaloric properties of certain spin clusters with icosahedral symmetry that turn out to be interesting as well.

Magnetocalorics has a long tradition especially in connection with cooling by adiabatic demagnetization. The first successful attempts to reach the sub-Kelvin region date back more than 70 years.⁸ It is equally well possible to extend such an adiabatic process to a full Carnot-cycle and thus use the magnetization work for magnetic refrigeration.⁹ In the past paramagnetic salts have been the working medium in both cases which limits the cooling rate to be not more than 2 K/T. Nowadays gadolinium compounds such as $\text{Gd}_5\text{Ga}_5\text{O}_{12}$ or $\text{Gd}_5\text{Si}_2\text{Ge}_2$ are known to be very efficient refrigerant materials.^{10,11}

A unified explanation of a magnetocaloric effect that is enhanced compared to a paramagnet is provided by the observation that the cooling rate assumes extreme values close to configurations with a large excess entropy. This can happen at certain phase transitions such as the first order [ferromagnetic(I) \leftrightarrow ferromagnetic(II)] phase transition observed in $\text{Gd}_5\text{Si}_2\text{Ge}_2$ compounds,¹⁰ at mag-

netic field driven transitions across a quantum critical point,^{12,13} or at special values of the magnetic field where many ground state Zeeman levels are degenerate.^{13,14,15}

In this article we demonstrate that an enhanced magnetocaloric effect should be observable in certain highly frustrated magnetic molecules of icosahedral symmetry. We discuss the cuboctahedron¹⁶ and the icosidodecahedron¹⁷ which are already synthesized Archimedean solids as well as the icosahedron which in its full symmetry could not yet be achieved chemically.^{16,18,19} Some of the aspects of our investigation have been previously discussed in connection with the classical¹¹ as well as in the quantum version¹⁵ of the Kagome lattice antiferromagnet and some one-dimensional antiferromagnets.^{13,20} We also like to mention that magnetocaloric studies have been carried out in the field of molecular magnetism recently, but were mainly focused on low-field behavior.^{21,22,23,24,25,26,27,28}

The article is organized as follows. In Sec. II we discuss the basics of magnetocalometry, whereas in Sec. III we present the magnetocaloric properties of icosahedral bodies and compare them with those of a non-frustrated spin ring of the same size. The paper closes with a summary.

II. BASIC THERMODYNAMICS

A. Heisenberg Model

The spin systems discussed in this article are modeled by an isotropic Heisenberg Hamiltonian augmented with a Zeeman term, i.e.,

$$\tilde{H} = - \sum_{u,v} J_{uv} \vec{s}(u) \cdot \vec{s}(v) + g\mu_B B \tilde{S}_z . \quad (1)$$

$\vec{s}(u)$ are the individual spin operators at sites u , $\vec{S} = \sum_u \vec{s}(u)$ is the total spin operator, and S_z its z -component along the homogeneous magnetic field. J_{uv} are the matrix elements of the symmetric coupling matrix. A negative value of J_{uv} corresponds to antiferromagnetic coupling. For the symmetric polytopes discussed in the following an antiferromagnetic nearest-neighbor exchange of constant size J is assumed.

B. Magnetocaloric effect

The magnetocaloric effect consists in cooling or heating of a magnetic system in a varying magnetic field. Some basic thermodynamics yields the adiabatic (i.e. isentropic, $S = \text{const.}$) temperature change as function of temperature and applied magnetic field,

$$\left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C(T, B)} \left(\frac{\partial S}{\partial B}\right)_T. \quad (2)$$

This rate is also called cooling rate. $C(T, B)$ is the temperature- and field-dependent heat capacity of the system. For a paramagnet this rate is simply¹¹

$$\left(\frac{\partial T}{\partial B}\right)_S^{\text{para}} = \frac{T}{B}. \quad (3)$$

This situation changes completely for an interacting spin system. Depending on the interactions the adiabatic cooling rate $\frac{\partial T}{\partial B}$ can be smaller or bigger than the paramagnetic one and even change sign, i.e. one would observe heating during demagnetization and cooling during magnetization.^{13,28} For the purpose of clarity this will be shortly illuminated with the help of an antiferromagnetically coupled dimer of two spins with $s = 1/2$, where a singlet constitutes the ground state and a triplet the excited state. Following (2) one notices that in the vicinity of the magnetic field B_c , where the lowest triplet level crosses the singlet, the entropy changes drastically at low temperatures due to the fact that at the crossing field the ground state is degenerate whereas elsewhere it is not. This behavior is displayed in Fig. 1, where below and above the crossing field the cooling rate, i.e. the slope of the isentropes, assumes large values.

III. MAGNETOCALORIC EFFECT IN MAGNETIC MOLECULES

Regarding the use as a magnetic refrigerant material magnetic molecules possess several advantageous properties. They can be synthesized in a great variety of structures and they can host various paramagnetic ions. Very often they also do not interact magnetically with each other in a bulk sample due to large distances between the magnetic centers of different molecules that are provided by extended ligands, which means that the magnetic properties of a single molecule can be assigned to

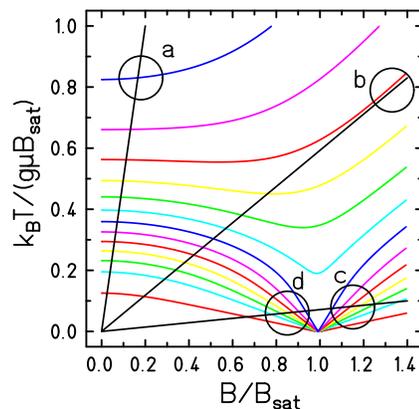


FIG. 1: (Color online) The curves show isentropes of the antiferromagnetically coupled dimer of two spins with $s = 1/2$. The straight lines represent isentropes of a paramagnet. Compared to a paramagnet the cooling rate of the antiferromagnetic dimer can be smaller (a), about the same (b), much bigger (c), or even negative (d).

the macroscopic sample. If it would be possible to obtain structures with exhibit extraordinarily large ground-state degeneracies at certain magnetic fields one could exploit these materials for very efficient magnetization cooling.

Every antiferromagnetically coupled spin system exhibits ground state level crossings such as the aforementioned spin dimer. The cooling rate at such a crossing can assume large values, but it turns out that it is possible to even increase the rate in a special class of highly frustrated magnetic molecules of icosahedral symmetry. This will be discussed for the cuboctahedron, which is chemically realized as a $\{\text{Cu}_{12}\text{La}_8\}$ molecule,¹⁶ and for the icosidodecahedron, which is chemically realized as a $\{\text{Mo}_{72}\text{Fe}_{30}\}$ molecule¹⁷ and a $\{\text{Mo}_{72}\text{V}_{30}\}$ molecule²⁹ as well as for the not yet synthesized icosahedron. The behavior of these frustrated spin systems is compared with the behavior of an antiferromagnetic, but not frustrated spin ring with $N = 12$ sites. All results are obtained by means of numerical diagonalization.

The geometric structures of the discussed bodies can be visualized for instance at the following Refs. 1,2,30.

The cuboctahedron is one of the smallest antiferromagnetic spin systems that can host independent localized magnons.^{1,2,7} These localized states are intimately connected with an enhanced degeneracy of energy levels and – in extended spin systems such as the Kagome lattice antiferromagnet – with the appearance of flat bands. In addition, the possibility to arrange several independent magnons on the (finite) spin lattice results in a linear dependence of the minimal energy $E_{\text{min}}(M)$ on the total magnetic quantum number M . Therefore, at the saturation field B_{sat} a massive degeneracy of ground state levels can be achieved.

Figure 2 shows that even in a system as small as the cuboctahedron the ground state multiplicity at the saturation field can reach a rather large value, in this case of

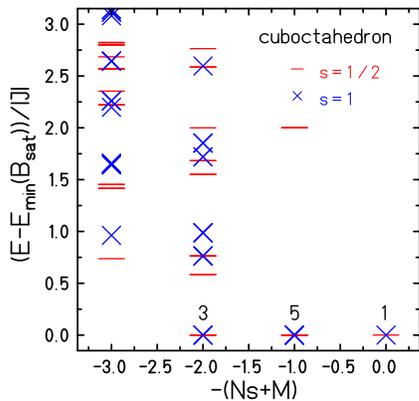


FIG. 2: (Color online) Low-lying energy levels of the cuboctahedron with $s = 1/2$ (dashes) and $s = 1$ (x-symbols) at the saturation field B_{sat} . The attached numbers give the multiplicity d_M of each M -level.

nine independent of spin quantum number.^{1,2} Thus, the entropy assumes a non-zero value at zero temperature of $S_0 = S(T = 0, B = B_{\text{sat}}) = k_B \ln(9)$. All isentropes with $S \leq S_0$ therefore arrive at the phase space point $(T = 0, B = B_{\text{sat}})$.

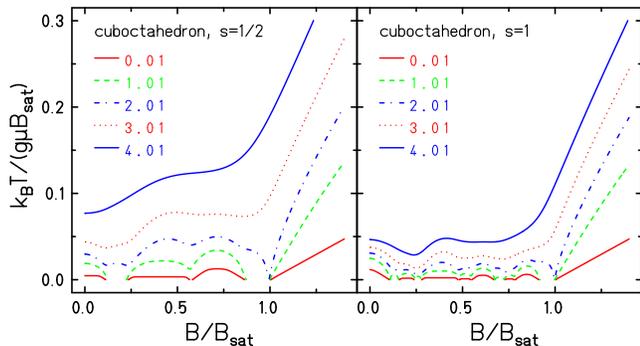


FIG. 3: (Color online) Isentropes of the cuboctahedron with $s = 1/2$ and $s = 1$. The entropies here and in the following are given in units of Boltzmann's constant k_B ; from the upper left to the lower right the values of S/k_B are 0.01, 1.01, 2.01, 3.01, and 4.01, respectively. $B_{\text{sat}} = (12s|J|)/(g\mu_B)$.

Figure 3 displays various isentropes of the cuboctahedron both for $s = 1/2$ (l.h.s.) as well as for $s = 1$ (r.h.s.). Both temperature and magnetic field are normalized to the saturation field here and in the following. One clearly sees that the low-entropy curves, $S \leq S_0$, approach the B -axes in a rather universal way independent of the magnitude of the spin s . Close to the saturation field the slope of the isentropes, i.e. the cooling rate, can assume large values. Below the saturation field the isentropes remain rather flat, i.e. the temperature does not increase again when going to $B = 0$. This is of course an important property because otherwise the system would heat up again when switching off the field.

The non-frustrated ring system, Fig. 4, does not possess the later property nor does it exhibit large cooling

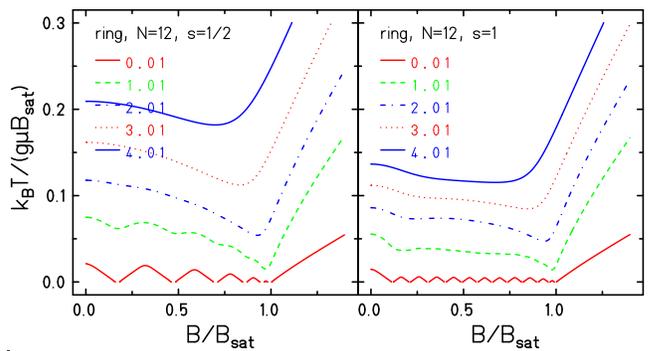


FIG. 4: (Color online) Isentropes of the a bipartite, i.e. non-frustrated spin ring with $N = 12$ spins $s = 1/2$ and $s = 1$. $B_{\text{sat}} = (8s|J|)/(g\mu_B)$.

rates at low temperatures close to the saturation field. The second property is easily understood because the massive degeneracy at the saturation field does not occur in an antiferromagnetic ring. Therefore, only isentropes with $S < k_B \ln(2)$ approach the field axis. The first property, however, is related to the overall structure of the low-lying levels. In finite bipartite systems the levels are arranged in rotational bands^{31,32} which means that in each sector of total magnetic quantum number M the excited states are separated from the ground state in the respective sector by a non-vanishing gap. Thus at lower magnetic fields a certain entropy can only be realized by populating higher-lying levels, i.e. by acquiring a higher temperature.

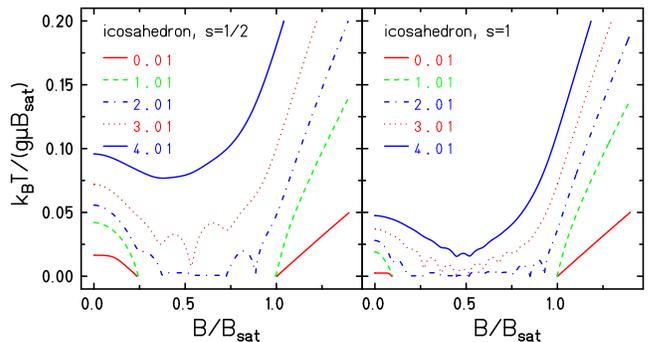


FIG. 5: (Color online) Isentropes of the icosahedron with $s = 1/2$ and $s = 1$. $B_{\text{sat}} = (14.472s|J|)/(g\mu_B)$.

The behavior of the icosahedron is intermediate. The antiferromagnetic icosahedron is also a geometrically frustrated spin system but differs from the cuboctahedron in some aspects. Each spin has five nearest neighbors (cuboctahedron – four), and the structure consists of edge-sharing triangles instead of corner-sharing triangles as for the cuboctahedron. Therefore, the icosahedron does not possess independent one-magnon states and consequently a similar degeneracy at the saturation field cannot be expected, compare Fig. 5.

Nevertheless, it turns out that the special frustration

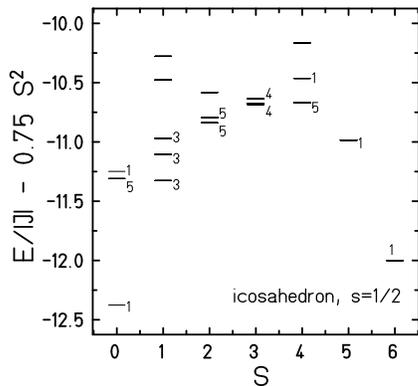


FIG. 6: Low-lying energy levels of the icosahedron with $s = 1/2$. The attached numbers give the multiplicity d_M of each M -level. Note that the energies are rescaled in each sector of total spin S .

of the icosahedron leads to different (quasi) degeneracies in several Hilbert subspaces with total spin S . This can be seen in Fig. 6 where the low-lying levels of the icosahedron with $s = 1/2$ are displayed. Note that for better visibility the energies are rescaled in each sector of total spin S . The numbers display the multiplicities d_M of the M -levels. These are the relevant degeneracies in an applied field. The total degeneracy at $B = 0$ is $d = d_M \cdot (2S + 1)$. Thus, we find also for the icosahedron, that at certain magnetic field values, not necessarily at the saturation field, highly degenerate levels will cross and give rise to notable ($T = 0$)–entropy. This can for instance be observed for the isentropes with $S = 2.01k_B$, which is displayed by the dashed-dotted line in Fig. 5. It approaches the field axis very closely at about $0.9B_{\text{sat}}$.

The unusually large degeneracy in many sectors of total spin is also the reason for the interesting property that the isentropes remain at rather small temperatures for decreasing magnetic fields. This is in strong contrast to spin rings and reflects the fact that populating the degenerate levels produces sufficient entropy without increasing the temperature. The upturn at small fields close to $B = 0$ is mainly due to the non-degenerate ground state in the sector with $S = 0$ which is separated by large gaps from excited states.

The two panels of Fig. 7 summarize the above discussion for the three systems with $N = 12$ by comparing the isentropes with $S = 2k_B$. One sees that at low temperatures close to the saturation field the cuboctahedron indeed achieves the largest cooling rate. In the extreme quantum case, i.e. for $s = 1/2$ it also outperforms the two other systems when looking at the achievable temperatures for $B \rightarrow 0$. Nevertheless, for the icosahedron similarly large cooling rates can be achieved due to a different kind of geometric frustration. For larger spin quantum numbers, i.e. for becoming more classical, the differences between the cuboctahedron and the icosahedron tend to disappear. The unfrustrated ring systems always shows poorer cooling.

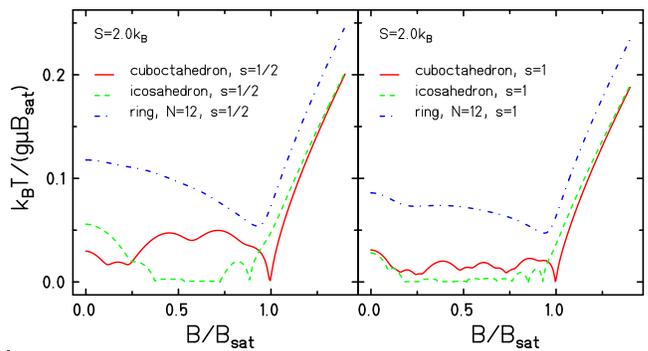


FIG. 7: (Color online) Isentropes with $S = 2k_B$ of the cuboctahedron, the icosahedron, and the ring with $N = 12$ with spins $s = 1/2$ (l.h.s.) and $s = 1$ (r.h.s.).

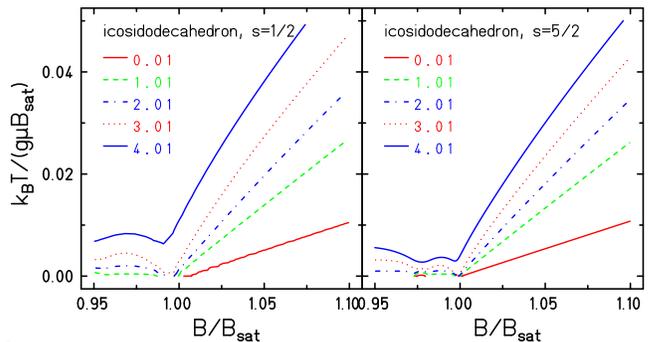


FIG. 8: (Color online) Isentropes of the icosidodecahedron with $s = 1/2$ and $s = 5/2$. $B_{\text{sat}} = (12s|J|)/(g\mu_B)$.

Finally we like to discuss the behavior of the antiferromagnetic icosidodecahedron which also possess icosahedral symmetry. This Archimedean solid is closely related to the cuboctahedron. It also consists of corner-sharing triangles, and each spin has four nearest neighbors.^{2,30} But compared to the cuboctahedron it has a much bigger ground-state degeneracy of 38 at the saturation field, again independent of spin quantum number. Figure 8 shows some isentropes of the icosidodecahedron for the two experimentally relevant cases of $s = 1/2$ and $s = 5/2$. Due to the much larger Hilbert space these isentropes can be evaluated exactly only close to the saturation field since there only some small subspaces contribute. The magnetothermal behavior is very similar to the cuboctahedron with the noticeable difference that now isentropes with entropies up to $S_0 = S(T = 0, B = B_{\text{sat}}) = k_B \ln(38) \approx 3.63k_B$ head towards $T = 0$ at the saturation field.

IV. SUMMARY

In summary we can say that the investigated frustrated antiferromagnetic bodies show an enhanced cooling rate in comparison to non-frustrated (bipartite) spin rings. This rate is especially large for those systems that show

a large degeneracy of levels, either at the saturation field (cuboctahedron) or elsewhere (icosahedron).

A few words seem to be in order regarding the question how realistic the outlined scenario is. In realistic systems the perfect degeneracy of levels at the saturation field will certainly be lifted, thus keeping the entropy $S(T = 0, B = B_{\text{sat}})$ at a small value. Nevertheless, the low-energy density of states will remain large in the vicinity of the saturation field, since the originally degenerate levels move not too far, thus the magnetothermal properties will be left qualitatively unchanged, see also the studies in Refs. 14.

Finally we like to mention that similar effects can be observed in interacting electron systems described by the Hubbard model. This is related to the appearance of flat bands in these systems.^{33,34,35,36}

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