Competing Spin Phases in Geometrically Frustrated Magnetic Molecules

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We have found a class of zero-dimensional geometrically frustrated Heisenberg spin systems exhibiting anomalous behavior in an external magnetic field B similar to that occuring in geometrically frustrated planar antiferromagnetic lattices. Our calculations for both the classical and quantum isotropic Heisenberg models show the emergence of a pronounced minimum in the differential susceptibility dM/dB at $B_{\rm sat}/3$ as the temperature T is raised from 0 K for structures based on corner-sharing triangles, specifically the octahedron, cuboctahedron, and icosidodecahedron. Low temperature measurements of magnetization M versus B for the giant Keplerate magnetic molecule $\{Mo_{72}Fe_{30}\}$ (Fe^{3+} ions with spin $s = 5/2$ on the 30 vertices of an icosidodecahedron) are consistent with our calculational results. The minimum in dM/dB is due to the fact that for low temperatures when $B \approx B_{\rm sat}/3$ there exist two competing families of spin configurations of which one behaves magnetically "stiff" leading to a reduction of the susceptibility.

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The magnetism of frustrated one-, two-, and three-dimensional lattice spin systems is a fascinating subject due to the richness of phenomena that are observed [1, 2, 3]. In this Letter we report that effects of geometrical frustration already appear for a class of *zero-dimensional* materials, namely certain magnetic molecules of high symmetry. These molecular units [4] contain a set of paramagnetic ions whose mutual interactions are described by isotropic Heisenberg exchange and where the *inter*molecular magnetic interactions (dipole-dipole for the most part) are negligible as compared to *intra*molecular Heisenberg exchange. Magnetic molecules as zero-dimensional spin systems provide a new avenue for detailed exploration of the basic issues of geometric frustration. They are particularly appealing since they offer the prospect of being modeled unencumbered by some of the complications of bulk magnetic materials.

We here report experimental and theoretical results for the occurrence of a striking anomaly in the differential susceptibility dM/dB versus magnetic field B that is exhibited by the giant Keplerate magnetic molecule $\{Mo_{72}Fe_{30}\}$ [5, 6]. This molecule features 30 Fe^{3+} ions on the vertices of an icosidodecahedron that interact via nearest-neighbor (nn) isotropic antiferromagnetic (AF) exchange ($J/k_B = 1.57$ K). Due to their near-perfect O_h-symmetric coordination environment, the Fe^{3+} ions represent ideal $s = 5/2$ spin centers with virually no anisotropy. We also present theoretical results for the classical and quantum Heisenberg model showing that the same anomaly in dM/dB occurs for a class of geometrically frustrated zero-dimensional systems, where spins mounted on the vertices of a triangle, octahedron, cuboctahedron, or an icosidodecahedron interact via nn isotropic AF exchange. As the temperature T is raised from 0 K a deep narrow minimum in dM/dB emerges in the vicinity of one-third the saturation field $B_{\rm sat}$, which upon increasing T extends over a larger field interval and its sharp features progressively deteriorate. We attribute this phenomenon to a common topological property of these polytopes, namely that each is assembled from corner-sharing triangles. In the classical case the drop in dM/dB can be understood as a result of the interplay of two effects: In the immediate vicinity of $B_{\rm sat}/3$ a family of "up-up-down" (*uud*) spin configurations are energetically competitive with the continuous family of spin configurations of lowest energy [7]. However, the *uud* spin configurations are magnetically "stiff", i.e. $dM/dB \approx 0$ for low temperatures, and thus reduce the susceptibility of the system.

We write the AF Heisenberg Hamiltonian as

$$H = J \sum_{(m,n)} \tilde{\boldsymbol{S}}_m \cdot \tilde{\boldsymbol{S}}_n + g\mu_B \boldsymbol{B} \cdot \sum_n \tilde{\boldsymbol{S}}_n, \qquad (1)$$

where J is a positive energy, the spin operators $\tilde{\boldsymbol{S}}_n$ are in units of $\hbar$, $\boldsymbol{B}$ is the external field, g is the spectroscopic splitting factor, μ_B is the Bohr magneton, and (m,n) directs that the sum is over distinct nearest-neighbor pairs. The classical counterpart of Eq.(1) is obtained by replacing each spin operator $\tilde{\boldsymbol{S}}_n$ by $\sqrt{s(s+1)}\boldsymbol{S}_n$, where $\boldsymbol{S}_n$ is a c-number unit vector [8, 9].

One very attractive feature of the polytopes under consideration is that their exact classical ground state energy is known [10]. For $B \leq B_{sat}$ it is given by

$$E_0(B) = -\frac{3}{2} N_\Delta J_c [1 + 3 \left(\frac{B}{B_{sat}} \right)^2], \qquad (2)$$

where $J_c = s(s+1)J$ is called the classical Heisenberg exchange constant, $B_{\rm sat} = 6J_c/\mu_c$, $\mu_c = g\mu_B\sqrt{s(s+1)}$, and N_Δ is the number of corner-sharing triangles ($= 4, 8, 20$ for the octahedron, cuboctahedron, and icosidodecahedron, respectively). A plot of this quantity versus $B/B_{\rm sat}$ is shown in Fig. 1 (solid curve). The ground state magnetic moment and differential susceptibilty are given by $M_0(B) = -dE_0/dB$ and $dM_0(B)/dB$, respectively. For $B = 0$ each spin system is decomposable into 3 sublattices of $N/3$ spins each; all spins of a given sublattice are mutually parallel; the sublattices are characterized by three coplanar unit vectors with angular spacings of 120°. The magnetization of the system is linear in B until $B_{\rm sat}$ and constant (fully saturated configuration) for larger fields. The linear rise with B can be pictured in terms of the folding of an "umbrella" [7] defined by the three sublattice unit vectors as they close towards the field vector $\boldsymbol{B}$.

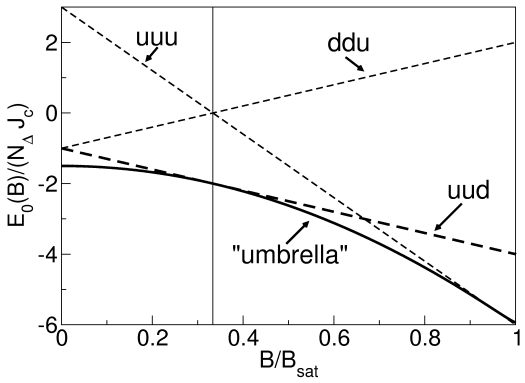

FIG. 1: Total energy vs. magnetic field for $T = 0$ K for the classical AF triangle, octahedron, cuboctahedron, and icosidodecahedron. The solid curve is given by Eq. 2. The dashed curves correspond to collinear structures discussed in the text.

Also shown in Fig. 1 are the energy curves for three other specific configurations of interest. These are configurations where the three (unit) spin vectors associated with each triangle are constrained to be collinear and the resultant vector is either parallel or anti-parallel to $\boldsymbol{B}$. These configurations are labeled as *uuu* (up-up-up), *uud*, and *ddu*. For each of these collinear configurations the magnetic moment of the polytope is independent of B and thus dM/dB vanishes and one can describe these configurations as being magnetically "stiff". The fully saturated *uuu* configuration is of minimal energy for $B > B_{\rm sat}$. The *uud* configuration is of special interest since its energy coincides with the minimal energy of the spin system for $B = B_{\rm sat}/3$ and exceeds the minimal energy for any other choice of field. For $T = 0$ K and for any choice of B other than $B_{\rm sat}$ the *uud* configuration will not play a role. However, for $T > 0$ K and for B in the vicinity of $B_{\rm sat}/3$ a significant contribution to the partition function will arise from the set of configurations derived by infinitesimal modifications of the *uud* configuration. These slightly modified *uud* configurations lead to a reduction of the differential susceptibility of the system because of their magnetic stiffness. Our qualitative considerations for $T > 0$ K are confirmed by the results of our classical Monte Carlo simulations for the three polytopes as shown in Fig. 2. Fig. 3 displays the results for a classical model of $\{Mo_{72}Fe_{30}\}$, namely 30 classical spins on the vertices of an icosidodecahedron, as substitutes for quantum spins with $s = 5/2$. As T is increased from 0 K a sharp narrow drop emerges that is situated at $B_{\rm sat}/3$ (vertical dashed line). As T continues to increase the drop extends over a larger interval and its sharp features progressively wash away. One also observes a temperature dependence of the field associated with the minimum in dM/dB, i.e., it decreases with increasing T.

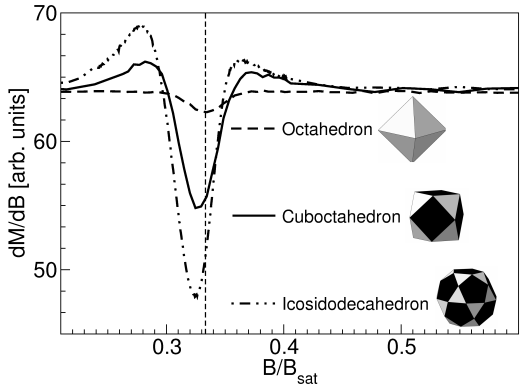

FIG. 2: Low-temperature ($k_BT/J_c = 10^{-2}$) simulational results for dM/dB vs. B for classical spins on the octahedron, cuboctahedron, and icosidodecahedron.

The relevance of these results to magnetic materials is demonstrated by our experimental data for the

differential susceptibilty of the giant Keplerate magnetic molecule $\{Mo_{72}Fe_{30}\}$. Fig. 4 presents our experimental results (in arbitrary units) for 0.42 K which clearly show the existence of a drop in dM/dB at about $B_{\rm sat}/3$. The high-field magnetization has been measured in pulsed magnetic fields (sweep rate 150000 Tesla/s) at the Okayama High Magnetic Field Laboratory by using a standard inductive method. The sample is immersed in liquid ^{3}He to maintain good contact with the thermal bath. However, the drop in dM/dB in the experimental curve is much broader than that of the simulational curve at 0.42 K. This suggests that as a result of the high sweep rate the effective spin temperature is much higher in the experiment because of an excess population in the excited states. The very slow relaxation time, which may be due to both the lack of phonons as well as an effect of the frustration, appears to be responsible for a non-isothermal magnetization process. Similar behavior has been found previously for earlier measurements on $\{Mo_{72}Fe_{30}\}$ of M versus B also obtained using a pulsed-field technique [11].

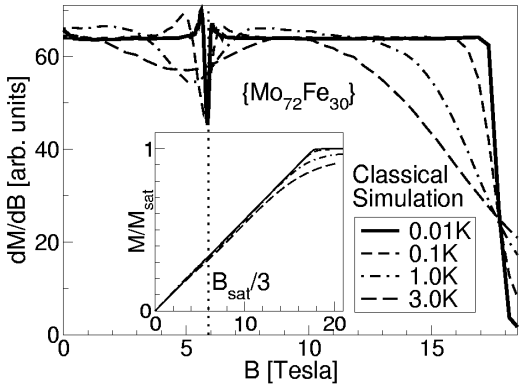

FIG. 3: Differential susceptibility dM/dB versus B for the classical Heisenberg model of $\{Mo_{72}Fe_{30}\}$ obtained by Monte Carlo simulations for temperatures given in the legend.

To explore the role of quantum effects we have calculated dM/dB for the triangle and the octahedron of spins with arbitrary s as well as for a cuboctahedron ($N = 12$) with $s = 1/2$ and $s = 1$. For the latter system this involves numerical diagonalization of matrices defined on a Hilbert space of dimension 3^{12} (= 531441). Even by fully exploiting the symmetries of the Hamiltonian this is at the limit of present day computing capabilities. The results for the cuboctahedron with $s = 1$ are shown in Fig. 5 for different temperatures. As in the previous figures one again encounters a strong reduction of dM/dB. The minimum is located exactly at $M_{\rm sat}/3$, but since B and M are not strictly proportional for a quantum system the drop occurs for fields slightly larger than $B_{\rm sat}/3$. For $T = 0$ K M vs. B can be described as a "staircase" of 12 steps originating from ground state Zeeman

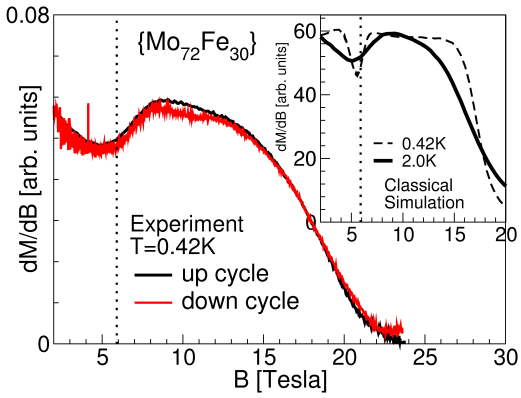

FIG. 4: Experimental results (in arbitrary units) for a sample of $\{Mo_{72}Fe_{30}\}$ performed at 0.42 K using a pulsed-field technique.In the inset Monte Carlo results for 0.42 K and 2.0 K are given.

level crossings and dM/dB consists of a set of Dirac delta functions at the crossing fields. For $T > 0$ K the abrupt magnetization steps are smoothed out and dM/dB exhibits finite peaks. Our results for the triangle and the octahedron for general spins s exhibit the same overall behavior seen in Fig. 5.

One can understand that the pronounced minimum in the susceptibility occurs for classical as well quantum spins by examining the partition function for the particularly simple example of the triangle where the results can be obtained by exact analytical methods. For integer spins s the quantum partition function may be written as

$$Z(t,b) = (\sinh(b\sigma_0))^{-1} \sum_{n=0}^{3s} G_n \, e^{-\frac{\sigma_n^2}{2t}} \sinh(b\sigma_n), \qquad (3)$$

where $b = \mu_c B/(k_B T)$, $t = k_B T/J_c$, $\sigma_n = (n + \frac{1}{2})/\sqrt{s(s+1)}$, $G_n = \Gamma_n/\sqrt{s(s+1)}$, and Γ_n is the multiplicity factor, namely the number of distinct ways of achieving total spin n upon adding three distinct (integer) quantum spins s. In particular $\Gamma_n = 2(n + \frac{1}{2})$ for $0 \le n \le s$ and $\Gamma_n = 3(s+\frac{1}{2}) - (n+\frac{1}{2})$ for $s+1 \le n \le 3s$. The analogous formulas are easily derived for half-integer spins s. Formula (3) for Z is very similar to that for the classical Heisenberg triangle which may be written as [9]

$$Z(t,b) = b^{-1} \int_0^3 {\rm d}S \, G(S) \, e^{-\frac{S^2}{2t}} \sinh(bS). \qquad (4)$$

Here $G(S) = 2S$ for $0 \le S \le 1$ and $G(S) = 3 - S$ for $1 \le S \le 3$, arising from considering the geometrical volume available to three unit vectors such that the magnitude of their vector sum lies within a shell of radius S and unit thickness. Indeed it is straightforward to verify that in the limit $s \to \infty$ the quantum result (Eq. (3)) agrees

with the classical formula (Eq. (4)). In the quantum formula the multiplicity factor corresponds to the classical geometrical function $G(S)$. Each of these quantities has two distinct branches, depending on whether n is in the interval $[0, s]$ or $[s+1, 3s]$ or whether S is in the interval $[0, 1]$ or $[1, 3]$. In fact, the existence of two distinct branches becomes manifest in various higher derivatives of $Z(t, b)$ at nonzero temperatures for fields in the vicinity of $B = B_{\rm sat}/3$. For $0 < t \ll 1$ there exists a narrow field range at about $B_{\rm sat}/3$ such that each of the functions $\exp(-\sigma_n^2/(2t))\sinh(b\sigma_n)$ and $\exp(-S^2/(2t))\sinh(bS)$ has a very narrow maximum for $\sigma_n \approx 1$ and $S \approx 1$ but nevertheless samples the two branches. This is the mathematical orgin of the pronounced minimum in dM/dB at $B = B_{\rm sat}/3$.

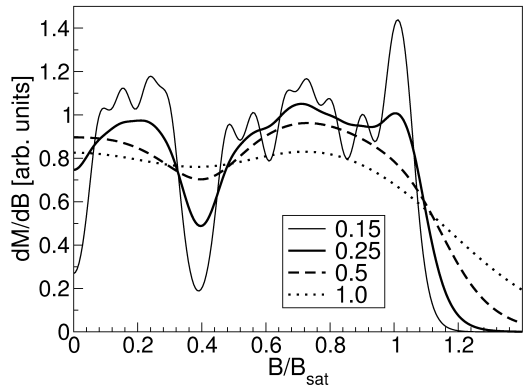

FIG. 5: Differential susceptibility dM/dB versus $B/B_{\rm sat}$ of the quantum Heisenberg cuboctahedron ($s = 1$) for values of k_BT/J shown in the legend.

Plateau like structures in the magnetization versus B in various two- and three-dimensional lattices built of corner-sharing triangles lattices at one-third of the saturated moment have been under investigation for the past two decades as an expression of geometric frustration [1, 2, 3, 12, 13]. Moreover, theoretical studies of the classical Heisenberg antiferromagnet on the Kagomé lattice show that dM/dB has a pronounced minimum at one-third of $B_{\rm sat}$ [14]. However, the study of selective magnetic molecules such as $\{Mo_{72}Fe_{30}\}$ can give new insights for this subject since such molecules are much better accessible both experimentally and theoretically.

In summary, we have shown that for a class of geometrically frustrated magnetic polytopes, namely the octahedron, the cuboctahedron and the icosidodecahedron, field-induced competitive spin configurations exist which manifest themselves in an pronounced minimum in the differential susceptibility dM/dB in the vicinity of $B_{\rm sat}/3$. We have also presented experimental results for the giant Keplerate magnetic molecule $\{Mo_{72}Fe_{30}\}$ that are consistent with our classical Monte Carlo results for the icosidodecahedron. Furthermore, we have shown that this feature reflects a general intrinsic property of the very building block of these specific polytopes, namely the simple AF equilateral Heisenberg spin triangle, and emerges for both classical and quantum spins. Moreover, we have found for each of these polytopes that the specific heat versus B also exhibits anomalous behavior in the vicinity of $B_{\rm sat}/3$ [15]. A measurement of this quantity for $\{Mo_{72}Fe_{30}\}$ at very low temperatures would be of great interest.

Acknowledgments

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