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 similar to that occurring 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 \( B_{sat}/3 \) 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 \( \{\text{Mo}_{72}\text{Fe}_{30}\} \) (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 \( B \approx B_{sat}/3 \) 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. 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 contain a set of paramagnetic ions whose mutual interactions are described by isotropic Heisenberg exchange and where the intermolecular magnetic interactions (dipole-dipole for the most part) are negligible as compared to intramolecular 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 \( \{\text{Mo}_{72}\text{Fe}_{30}\} \). This molecule features 30 Fe\(^{3+}\) ions on the vertices of an icosidodecahedron that interact via nearest-neighbor (nn) isotropic antiferromagnetic (AF) exchange (\( J/J_B = 1.57 \) 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 \( B_{sat} \), 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 \( B_{sat}/3 \) a family of “up-up-down” \((uud)\) spin configurations are energetically competitive with the continuous family of spin configurations of lowest energy. 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
\[ H = J \sum_{(m,n)} \tilde{S}_m \cdot \tilde{S}_n + g\mu_B B \cdot \sum_n \tilde{S}_n, \tag{1} \]
where \( J \) is a positive energy, the spin operators \( \tilde{S}_n \) are in units of \( h \), \( B \) is the external field, \( g \) is the spectroscopic splitting factor, \( \mu_B \) 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 \( \tilde{S}_n \) by \( \sqrt{s(s+1)} \tilde{S}_n \), where \( \tilde{S}_n \) 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 \( B \leq B_{\text{sat}} \) it is given by
\[ E_0(B) = -\frac{3}{2} N_\Delta J_c [1 + 3 \left( \frac{B}{B_{\text{sat}}} \right)^2], \tag{2} \]
where \( J_c = s(s+1)J \) is called the classical Heisenberg exchange constant, \( B_{\text{sat}} = 6J_c/\mu_B \), \( \mu_B = g\mu_B \sqrt{s(s+1)} \), and \( N_\Delta \) is the number of corner-sharing triangles (= 4, 8, 20 for the octahedron, cuboctahedron, and icosidodecahedron, respectively). A plot of this quantity versus \( B/B_{\text{sat}} \) is shown in Fig. 1 (solid curve). The ground state magnetic moment and differential susceptibility 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 \( B_{\text{sat}} \) and constant (fully saturated configuration) for larger fields. The linear rise with \( B \) can be pictured in terms of the folding of an “umbrella” defined by the three sublattice unit vectors as they close towards the field vector \( B \).

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 \( B \). These configurations are labeled as \( uuu \) (up-up-up), \( uud \), and \( uud \). 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 \( B > B_{\text{sat}} \). The \( uud \) configuration is of special interest since its energy coincides with the minimal energy of the spin system for \( B = B_{\text{sat}}/3 \) and exceeds the minimal energy for any other choice of field. For \( T = 0 \) K and for any choice of \( B \) other than \( B_{\text{sat}} \) the \( uud \) configuration will not play a role. However, for \( T > 0 \) K and for \( B \) in the vicinity of \( B_{\text{sat}}/3 \), 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. 2 displays the results for a classical model of \( \text{Mn}_7\text{Fe}_{20} \), 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 \( B_{\text{sat}}/3 \) (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 \((k_B T/J_c = 10^{-2})\) simulational results for \( dM/dB \) vs. \( B \) for classical spins on the octahedron, cuboctahedron, and icosidodecahedron.](image-url)

The relevance of these results to magnetic materials is demonstrated by our experimental data for the
differential susceptibility of the giant Keplerate magnetic molecule \( \{\text{Mo}_{72}\text{Fe}_{30}\} \). Fig. 3 presents our experimental results (in arbitrary units) for 0.42 K which clearly show the existence of a drop in \( dM/dB \) at about \( B_{\text{sat}}/3 \). 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 of 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 \( \{\text{Mo}_{72}\text{Fe}_{30}\} \) of \( M \) versus \( B \) also obtained using a pulsed-field technique [11].

To explore the role of quantum effects we have calculated \( dM/dB \) for the triangle and the octahedron for general spins \( s \). For \( s = 1 \) we obtain exact analytical results. Integer spins \( s \) can be obtained by exact analytical methods. For integer spins \( s \), the susceptibility occurs for classical as well quantum spins by examining the partition function for the particular simple example of the triangle where the results can be obtained by exact analytical methods. For half-integer spins \( s \), the partition function may be written as

\[
Z(t,b) = (\sinh(b\sigma_0))^{-1} \sum_{n=0}^{3s} G_n \exp\left(\frac{-t^2}{2b}\right) \sinh(b\sigma_n),
\]

where \( b = \mu_c B/(k_BT) \), \( t = k_BT/J_c \), \( \sigma_n = (n + \frac{1}{2})/\sqrt{s(s+1)} \), \( G_n = \Gamma_n/\sqrt{s(s+1)} \), and \( \Gamma_n \) 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 \( 0 \leq n \leq s \) and \( \Gamma_n = 3(s+\frac{1}{2})-(n+\frac{1}{2}) \) for \( s+1 \leq n \leq 3s \). 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

\[
Z(t,b) = b^{-1} \int_0^3 dS G(S) \exp\left(\frac{-t^2}{2b}\right) \sinh(bS).
\]

Here \( G(S) = 2S \) for \( 0 \leq S \leq 1 \) and \( G(S) = 3 - S \) for \( 1 \leq S \leq 3 \), 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 result (Eq. 4).
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 $B = B_{sat}/3$. For $0 < t < 1$ there exists a narrow field range at about $B_{sat}/3$ 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 origin of the pronounced minimum in $dM/dB$ at $B = B_{sat}/3$.

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 $B_{sat}$ [14]. However, the study of selective magnetic molecules such as $\{\text{Mo}_7\text{Fe}_{30}\}$ 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 $B_{sat}/3$. We have also presented experimental results for the giant Keplerate magnetic molecule $\{\text{Mo}_7\text{Fe}_{30}\}$ 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 $B_{sat}/3$ [13]. A measurement of this quantity for $\{\text{Mo}_7\text{Fe}_{30}\}$ at very low temperatures would be of great interest.

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\[ \begin{align*}
\text{FIG. 5: Differential susceptibility } dM/dB \text{ versus } B/B_{sat} \text{ of the quantum Heisenberg cuboctahedron (} s = 1 \text{) for values of } k_BT/J \text{ shown in the legend.}
\end{align*} \]