Metamagnetic Phase Transition of the Antiferromagnetic Heisenberg Icosahedron

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The observation of hysteresis effects in single molecule magnets like Mn_{12}-acetate has initiated ideas of future applications in storage technology. The appearance of a hysteresis loop in such compounds is an outcome of their magnetic anisotropy. In this Letter we report that magnetic hysteresis occurs in a spin system without any anisotropy, specifically where spins mounted on the vertices of an icosahedron are coupled by antiferromagnetic isotropic nearest-neighbor Heisenberg interaction giving rise to geometric frustration. At $T = 0$ this system undergoes a first-order metamagnetic phase transition at a critical field B_c between two distinct families of ground state configurations. The metastable phase of the system is characterized by a temperature and field dependent survival probability distribution.

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Introduction.—Low-dimensional magnetic systems show a variety of fascinating phenomena that are associated with geometrical frustration [1,2]. Among them are magnetization plateaus and jumps as well as unusual susceptibility minima, as observed, for example, for the kagome lattice antiferromagnet [3,4]. Some of these effects can also occur in certain strongly frustrated magnetic molecules such as the Keplerate $\{Mo_{72}Fe_{30}\}$ [5]. In this Letter we report that a first-order metamagnetic phase transition (with associated hysteresis and metastability effects) occurs for a system of spins that are mounted on the vertices of an icosahedron when an external magnetic field, B, equals a critical value B_c. These spins interact with one another only via nearest-neighbor, antiferromagnetic isotropic Heisenberg exchange, but due to geometrical frustration of the icosahedron originating from a coupling of edge sharing triangles, they undergo the metamagnetic transition despite the absence of any anisotropic energy terms. As the field proceeds through a closed cycle, the magnetization M traces the hysteresis loop shown in Fig. 1.

Our exact classical treatment shows that the abrupt transition at $T = 0$ originates in the intersection of two energy curves belonging to different families of spin configurations that are ground states below and above the critical field. The minimum of the two energy functions constitutes a nonconvex minimal energy function of the spin system and this gives rise to a metamagnetic phase transition [6]. At $T = 0$ the partition function is a nonanalytic function of B, and since the magnetization features a finite jump at B_c the transition is of first order [7]. We also show that the corresponding quantum spin system for sufficiently large spin quantum number s possesses a nonconvex set of lowest energy levels when plotted versus total spin. This is the discrete analog of the nonconvex classical minimal energy function. Therefore, the quantum spin system also features an unusual magnetization jump.

Although hysteresis is also observed, for instance, in spin glasses [1,9] it should be noted that the spin icosahedron is perfectly symmetric without any disorder or macroscopic degeneracy of the ground state. In addition, no remanent magnetization occurs; the spin icosahedron returns to its ground state when the field sweeps back to zero. It is also noteworthy that this phase transition cannot occur in frustrated spin systems of corner-sharing triangles, since there the classical spin configuration deforms continuously with the magnetic field [10].

For a classical spin system the Hamiltonian is given by

$$H(\vec{s}, B) = H_0(\vec{s}) - B\sum_{\mu} s_z(\mu) = \sum_{\mu,\nu} J_{\mu\nu}\vec{s}(\mu)\cdot\vec{s}(\nu) - B\sum_{\mu} s_z(\mu). \quad (1)$$

The coupling $J_{\mu\nu}$ between spins μ, ν is chosen as $J = 1$ between nearest neighbors and zero otherwise. Accordingly, the magnetic field is given in appropriate units. For $B = 0$ it is known that the spins adopt a non-

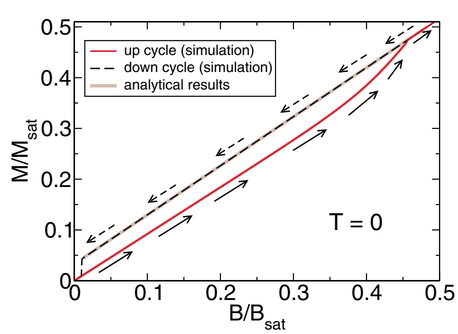

FIG. 1 (color online). Hysteresis behavior of the classical icosahedron in an applied magnetic field obtained by classical spin dynamics simulations (thick lines) as well as by analytical stability analysis (gray lines). The curves match perfectly.

coplanar ground state configuration, where each of the 12 spin vectors makes an angle of $\arccos(-1/\sqrt{5}) \approx 116.6°$ with respect to its five nearest neighbors [10]. To explore the regime $B > 0$ for $T = 0$ we use both classical simulational methods and analytical methods.

Classical simulations at $T = 0$.—The behavior of classical spin systems subject to an applied magnetic field both at $T \approx 0$ and finite temperatures can be very effectively studied with the help of a stochastic spin dynamics approach [11]. Here, the spin system is coupled to a heat bath in a Langevin-type approach by using a Landau-Lifshitz-damping term as well as a fluctuating force with white noise characteristics, which are related to temperature by a fluctuation-dissipation theorem. Starting from an arbitrary initial configuration, the spin system can be investigated either at zero temperature by observing the relaxation to its ground state or at finite temperature by following its time evolution.

We consider first $T = 0$. The spins are subjected to an external magnetic field that increases from zero linearly with time but at a very slow rate. The dynamical evolution of the spins is monitored as a function of time and the results are stored within an animation file [12] enabling direct visualization of the spin vectors. In the first stage the configuration of the spin vectors evolves continuously with B until suddenly there is an abrupt change in their orientations at $B/B_{\mathrm{sat}} \approx 0.47$ followed by further continuous evolution until at saturation, all spin vectors are parallel to $\vec{B}$. If now B is slowly reduced, the magnetization M follows the dashed curve shown in Fig. 1, rather than the solid curve traced in the up cycle.

Analytical results for $T = 0$.—For a classical spin system, the ground states are defined as states $\vec{s} = [\vec{s}(1), \ldots, \vec{s}(N)]$ which minimize the energy (1). Therefore, the (degenerate) ground states must fulfill the following necessary condition, compare Eq. (21) in [10],

$$\sum_{\nu} J_{\mu\nu}\vec{s}(\nu) = \kappa_{\mu}\vec{s}(\mu) + \frac{1}{2}\vec{B}(\mu = 1, \ldots, N), \qquad (2)$$

where κ_{μ} denote suitable Lagrange parameters. Although this system of equations can only be solved numerically in most cases, we are confident that the following statements about ground states of the icosahedron subject to magnetic fields are correct [13].

For $B = 0$ the orientation of the individual spins is such that they form four groups of three spins where each group i is characterized by a common polar angle θ_i and uniformly spaced azimuthal angles [10].

For $B > 0$ we numerically solve (2) with the assumption that the azimuthal angles remain fixed and only the four polar angles vary [13]. Thus we obtain a 1-parameter family (the "4-θ family") of possible ground states. Interestingly, it provides a local minimum of the energy only for $0 \leq M \leq 5.61441$. One might assume that the 4-θ family also provides a global minimum of energy, i.e., a ground state, for the same interval $0 \leq M \leq 5.61441$, but this is wrong: there exists a different 1-parameter family of solutions of (2) which has a lower energy than the 4-θ family for $M > M_0 \simeq 4.92949$. This family can be characterized by two spin vectors which are aligned parallel to $\vec{B}$ and 10 spin vectors with a common polar angle θ and uniformly spaced relative azimuthal angles. The end points of the latter 10 spin vectors form a regular decagon, and we will call this set of states the "decagon family." As discussed below, the decagon family provides a local minimum of the energy for $0.54102 \leq M \leq 12$. These families give rise to two convex curves in the E versus M diagram, $E_1(M)$ for the 4-θ family and $E_2(M)$ for the decagon family, which intersect at the point with coordinates (M_0, E_0), where $M_0 \simeq 4.92949$ and $E_0 \simeq -11.150$.

We have strong numerical evidence that the minimum of the two curves provides the absolute minimum $E_{\mathrm{min}}(M)$ of $H_0(\vec{s})$ for given M [13]. The latter function $E_{\mathrm{min}}(M)$ is therefore not convex and this translates to a jump in the magnetization, $\Delta M = M_2 - M_1$, at a critical field B_{c}; compare [6]. One can identify B_{c} as the slope of the common tangent of the curves $E_1(M)$ and $E_2(M)$ illustrated in Fig. 2. This construction is equivalent to the statement that the total energies of the two phases, $E_1(M_1) - BM_1$ and $E_2(M_2) - BM_2$, are equal for $B = B_{\mathrm{c}}$. According to the Ehrenfest classification the phase transition is of first order. Equivalently, B_{c} can be obtained by a Maxwell construction in the M versus B diagram. The pertinent quantities for the phase transition are given in Table I.

Since $M(B)$ has a jump at $B = B_{\mathrm{c}}$ the susceptibility $\chi = \frac{dM}{dB}$ diverges at $B = B_{\mathrm{c}}$ and $T = 0$. Recall that the susceptibility is given by the variance of the magnetization multiplied with β. Since in the case of a metamagnetic phase transition of the kind described above the ground state is degenerate for $T \to 0$ and $B \to B_{\mathrm{c}}$, the variance remains finite in this limit and $\chi(B_{\mathrm{c}}, \beta)$ diverges linearly with β; i.e., the critical exponent is one.

Stability and hysteresis.—In order to investigate the stability of the two families of ground states, we performed a standard stability analysis by constructing the stability matrix, which contains second derivatives of the energy

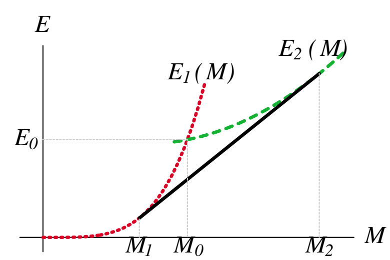

FIG. 2 (color online). Schematic representation of two minimal energy curves $E_1(M)$ and $E_2(M)$, whose minimum $E_{\mathrm{min}}(M)$ is not convex. Their common tangent (solid line) has a slope of B_{c}.

TABLE I. Characteristic values of the first-order phase transition of the spin icosahedron; compare Fig. 2. $B_{sat} = 2(5 + \sqrt{5})$ denotes the saturation field. $\chi_i = \frac{dM_i}{dB}|_{B=B_c}$, $i = 1, 2$ denote the limit values of the susceptibility.

$B_c \simeq 5.87614$,	$B_c \simeq 0.40603 B_{sat}$,
$M_1 \simeq 4.71461$,	$M_2 \simeq 5.10784$,
$E_1(M_1) \simeq -12.4324$,	$E_2(M_2) \simeq -10.1218$,
$E_0 \simeq -11.150$,	$M_0 \simeq 4.92949$,
$\chi_1 \simeq 1.13294$,	$\chi_2 = \frac{5}{4+\sqrt{5}} \simeq 0.8018$.

with respect to the coordinates and thus is a measure of the local curvature of the energy landscape. Since the energy is invariant under rotations about the z axis, one eigenvalue of the stability matrix must be zero. We call a state satisfying (2) "stable" if the stability matrix has only positive eigenvalues apart from one zero eigenvalue. This is related to the fact that the given state provides a local minimum of the energy.

By applying this procedure to the two families of possible ground states of the icosahedron, we determine numerically the above-mentioned stability ranges of the families: the 4-θ family is stable for $0 \leq M \leq 5.61441$ and the decagon family is stable for $0.54102 \leq M \leq 12$. This implies that the system at $T \simeq 0$ will not immediately jump from the 4-θ family into the decagon family if B increases beyond B_c but remains in its family until $M > 5.61441$. Conversely, the decagon family will remain the *de facto* spin configuration of the icosahedron if B is lowered beyond B_c until $M < 0.54102$. In fact, these hysteresis effects are observed in our simulational studies; see Fig. 1.

The metamagnetic transition is quite robust to variations in the values of the individual couplings $J_{\mu\nu}$ up to deviations of 10% [13]. In particular, the hysteresis loop persists though its area shrinks, primarily via an increase of the lower critical field of the metastable phase.

Quantum calculations.—We now discuss how the metamagnetic phase transition is manifested in the quantum Heisenberg icosahedron. Classically, the phase transition consists of a discontinuity of the magnetization as a function of the magnetic field. Quantum mechanically, the magnetization curve for $T = 0$ is already a staircase of successive steps of unit height $\Delta M = 1$, which result from crossings of levels with adjacent total magnetic quantum numbers M and $M + 1$. In the context of this phase transition, we are looking for a magnetization jump of unusual height, i.e., $\Delta M > 1$. It is clear that such a jump must occur because it occurs in the classical limit $s \rightarrow \infty$. The remaining questions, therefore, are: for which intrinsic spin quantum number s does such a jump occur, and are there other signs of the phase transition at smaller s?

Using a Lanczos procedure which yields numerically exact lowest energy eigenvalues in subspaces with constant total magnetic quantum number M, we are able to evaluate magnetization curves at $T = 0$ for various intrinsic spin quantum numbers. Figure 3 shows the relevant parts of the magnetization curves at $T = 0$ for $s = 1/2, \ldots, 4$. For integer values of s the magnetization plateau of smallest width is highlighted; for half-integer values of s we highlight two such plateaus. With increasing s these widths shrink and already at $s = 4$ a magnetization jump of $\Delta M = 2$ occurs. This corresponds to a nonconvex part of the discrete energy levels versus M.

In Fig. 3 we also provide a curve which bisects the magnetization plateaus of smallest width. Assuming that the bisector value of B/B_{sat} is described by a polynomial in $1/s$, we obtain as an estimate for the classical transition field $B/B_c \approx 0.40 \pm 0.01$, which is in very good agreement with the classical result (see Table I). The uncertainty originates from the limited number of data points (eight) as well as from fluctuations between integer and half-integer values of s.

Classical finite-temperature simulations.—We have restricted our investigation to the determination of the lifetime of the high-field phase (decagon family) in its metastable regime ($B/B_c < 1$). The lifetime has been determined by the following procedure: first, the system is

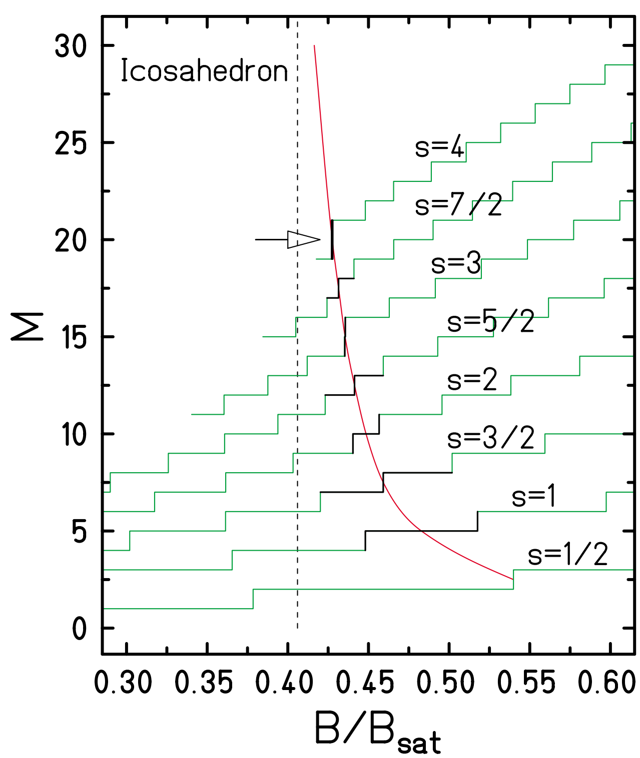

FIG. 3 (color online). Magnetization curves for $T = 0$ and various values of the intrinsic spin quantum number s: the magnetization plateaus of smallest width are highlighted on each curve. At $s = 4$ a magnetization jump of $\Delta M = 2$ occurs, marked by the arrow. At $s = 3$ a tiny plateau persists. The solid curve shows that the field values that bisect the smallest plateaus converge to the classical transition field (dashed line).

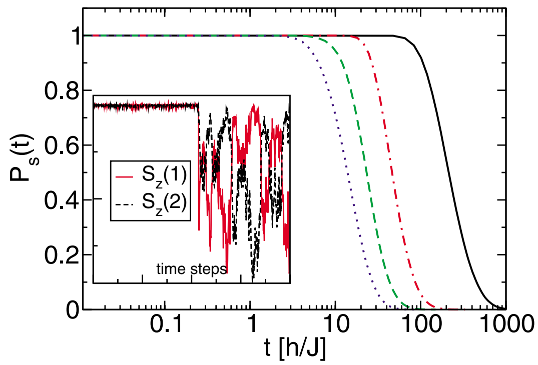

FIG. 4 (color online). Survival probability $P_s(t)$ for the metastable decagon phase subject to an external field $B/B_{sat} = 0.27$ for temperatures $k_B T/J = 0.025, 0.015, 0.005, 0.0005$ (left to right). Time is given in units of Planck's constant divided by the coupling. Inset: example trajectory of the system's time evolution at finite temperature.

prepared in the decagon phase at $T = 0$. Then the field is lowered to a value below the critical field value B_c. Starting from these initial conditions the temperature is set to a value $T > 0$ and the trajectory of the system is calculated numerically by solving the stochastic Landau-Lifshitz equation.

Shown in the inset of Fig. 4 is a single trajectory of a sample system. We exploit the unique property of the decagon family that two spins persist in pointing in the direction of $\vec{B}$, i.e., $s_z(1) \approx s_z(2) \approx 1$, until abruptly breaking away. This allows one to obtain an accurate determination of the decay time for this system. By performing 10^5 such runs for each choice of T and analyzing the histograms of the resulting decay times, one can determine the lifetime distribution. A common measure is the so-called survival probability $P_s(t)$ which is the probability of the metastable state not having decayed by the time t. In Fig. 4 we have plotted $P_s(t)$ for the metastable state for various temperatures and an external field in the metastable regime. An appropriate choice for the lifetime, t_s, is the root of $P_s(t_s) = 0.5$. We find that t_s increases with decreasing temperature and appears to diverge for $T \to 0$ as $1/T$. Although one obtains similar probability distributions for systems showing thermally activated magnetization switching [14], we emphasize that our model Hamiltonian does not contain any additional energy term providing an energy barrier. In fact, it is the special geometry of the icosahedron that causes the system to show metastability.

Summary and outlook.—In this Letter, we have shown that the antiferromagnetic Heisenberg spin icosahedron undergoes a metamagnetic phase transition and displays rich hysteresis and metastability phenomena when subject to a varying external field. Given this, the metamagnetic transition of the Heisenberg icosahedron may be of interest for potential applications in the area of nanomagnetic switches. It is also relevant in connection with magnetocalorics, since the magnetization jump is accompanied by an enhanced magnetocaloric effect [15,16]. It is therefore very encouraging that recent progress in the synthesis of magnetic molecules offers the prospect of realizing the Heisenberg icosahedron [17,18].

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[1] J. Greedan, J. Mater. Chem. **11**, 37 (2001).
[2] *Quantum Magnetism*, edited by U. Schollwöck, J. Richter, D. Farnell, and R. Bishop, Lecture Notes in Physics Vol. 645 (Springer, New York, 2004).
[3] Y. Narumi, K. Katsumata, Z. Honda, J.-C. Domenge, P. Sindzingre, C. Lhuillier, Y. Shimaoka, T. C. Kobayashi, and K. Kindo, Europhys. Lett. **65**, 705 (2004).
[4] J. Schulenburg, A. Honecker, J. Schnack, J. Richter, and H.-J. Schmidt, Phys. Rev. Lett. **88**, 167207 (2002).
[5] C. Schröder, H. Nojiri, J. Schnack, P. Hage, M. Luban, and P. Kögerler, Phys. Rev. Lett. **94**, 017205 (2005).
[6] C. Lhuillier and G. Misguich, *High Magnetic Fields* (Springer, New York, 2002), pp. 161–190.
[7] According to Ehrenfest's classification scheme, a first-order transition is characterized by a discontinuous first derivative of the free energy. At $T = 0$ such transitions can happen in a finite system, i.e., without thermodynamic limit. For quantum systems, such transitions are known as quantum phase transitions [8].
[8] S. L. Sondhi, S. M. Girvin, J. P. Carini, and D. Shahar, Rev. Mod. Phys. **69**, 315 (1997).
[9] K. Binder and A. P. Young, Rev. Mod. Phys. **58**, 801 (1986).
[10] H.-J. Schmidt and M. Luban, J. Phys. A **36**, 6351 (2003).
[11] V. P. Antropov, S. V. Tretyakov, and B. N. Harmon, J. Appl. Phys. **81**, 3961 (1997).
[12] We invite the reader to examine movies of our simulations at http://www.fh-bielefeld.de/fb2/schroeder.
[13] H.-J. Schmidt, J. Schnack, C. Schröder, and M. Luban (unpublished).
[14] G. Brown, M. A. Novotny, and P. A. Rikvold, J. Appl. Phys. **87**, 4792 (2000).
[15] O. Derzhko and J. Richter, Phys. Rev. B **70**, 104415 (2004).
[16] M. E. Zhitomirsky and A. Honecker, J. Stat. Mech.: Theor. Exp. **2004**, P07012 (2004).
[17] A. J. Blake, R. O. Gould, C. M. Grant, P. E. Y. Milne, S. Parsons, and R. E. P. Winpenny, J. Chem. Soc. Dalton Trans. **1997**, 485 (1997).
[18] E. K. Brechin, A. Graham, S. G. Harris, S. Parsons, and R. E. P. Winpenny, J. Chem. Soc. Dalton Trans. **1997**, 3405 (1997).