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Magnetic spectra in the tridiminished-icosahedron {Fe_9} nanocluster by inelastic neutron scattering

David Vaknin[1,*] and Franz Demmel[2]

[1]*Ames Laboratory and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA*

[2]*Rutherford Appleton Laboratory, ISIS Pulsed Neutron Facility, Chilton, Didcot, Oxon OX110QX, United Kingdom*

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Inelastic neutron scattering (INS) experiments under applied magnetic field at low temperatures show detailed low-lying magnetic excitations in the so-called tridiminshed iron icosahedron magnetic molecule. The magnetic molecule consists of nine iron Fe^{3+} ($s = 5/2$) and three phosphorous atoms that are situated on the 12 vertices of a nearly perfect icosahedron. The three phosphorous atoms form a plane that separates the iron cluster into two weakly coupled three- and six-ion fragments, {Fe_3} and {Fe_6}, respectively. The magnetic field INS results exhibit an $S = 1/2$ ground state expected from a perfect equilateral triangle of the {Fe_3} triad with a powder averaged g value = 2.00. Two sets of triplet excitations whose temperature and magnetic field dependence indicate an $S = 0$ ground state with two nondegenerate $S = 1$ states are attributed to the {Fe_6} fragment. The splitting may result from a finite coupling between the two fragments, single-ion anisotropy, antisymmetric exchange couplings, or from magnetic frustration of its triangular building blocks.

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Single-molecule magnets have been emerging as the necessary ingredient to transform molecular electronics into molecular spintronics, albeit not without challenges in synthesis, characterization, and theoretical modeling [1]. Progress in synthesizing, by design, bulk magnetic molecules has brought about new insights into magnetic phenomena in the nanoscale regime [2–4]. A current challenge in this research area is the synthesis of magnetic clusters that can operate as nanoswitches. One such hypothetical system is an iron based icosahedron magnetic cluster {Fe_{12}}, which theoretical calculations show undergoes a first order metamagnetic transition with an associated hysteretic behavior that renders it magnetic nanoswitchlike properties [5–7]. Although the perfect icosahedron has not yet materialized, a closely related molecule of tridiminished icosahedron {Fe_9}, with the chemical formula $[(Fe_9\text{-}\mu_3\text{-}O)_4(O_3PPh)_3(O_2CCMe_3)_{13}]$, has been synthesized and characterized [8]. In each {Fe_9} cluster, Fe^{3+} ions (spins $s = 5/2$) occupy 9 of the 12 sites of an icosahedron (see Fig. 1), whereas the remaining three vertices are occupied by P atoms of triphenylphosphonate. Analysis of exchange paths and susceptibility data indicate that the icosahedron can be divided into two nearly decoupled clusters: an {Fe_6} cluster, with an $S = 0$ ground state, and an {Fe_3} triangle with $S = 1/2$ ground state.

Here, we report on the low-lying magnetic excitations of a partially deuterated polycrystalline sample of the {Fe_9} molecule and their dependence on temperature and applied magnetic field obtained from inelastic neutron scattering (INS) measurements. INS has become a pivotal tool in determining the magnetic spectra of magnetic molecules [4] in particular, since the seminal study by Caciuffo and co-workers of the {Fe_8} molecule with frustrated antiferromagnetic (AFM) couplings that render the molecule $S = 10$ ground state [9]. Recently, INS has been employed in the Cr_8 AFM ring to detect propagation of quantum fluctuations along the ring [10], and in the related {Cr_7Ni} ring to demonstrate that under external magnetic field an avoided crossing between energy levels of different total-spin quantum numbers can be identified [11]. In a systematic study of various magnetic molecules, frustration effects have been classified by use of INS experiments [12]. Employing INS, we monitor the response of the {Fe_9} nanocluster to magnetic field and temperature to obtain a comprehensive picture of the low-lying excitations.

The INS measurements were performed on approximately 4 g of polycrystalline sample that was sealed under helium atmosphere in a copper can and placed in a dilution refrigerator with the capability to cool the sample to a base temperature of 0.1 K, and to apply a magnetic field up to 5 T. The inelastic neutron spectra were collected on the OSIRIS time-of-flight spectrometer at ISIS, which was set up at a fixed final neutron energy of $E_f = 1.845$ meV that was selected by a pyrolytic graphite PG(002) analyzer [13]. The energy resolution that OSIRIS provides is approximately 23–27 μeV over the energy-transfer range from zero to 2 meV [13]. The obtained energy *versus* momentum-transfer ($E - Q$) slices of the spectra exhibit distinct excitations that are dispersionless as expected from noninteracting (i.e., zero-dimensional) magnetic molecules. We also note that the variation of the magnetic form factor of Fe^{3+} is less than 5% over the measured Q range. We therefore integrate intensities over the measured Q range to improve signal statistics, without loss of information. The theory of INS for magnetic molecules has been extensively detailed in the literature [4,14].

Figure 2 shows intensities integrated over the $Q = 0.7$–1.8 Å^{-1} range versus neutron energy loss (designated positive) at the lowest temperature achievable with the cryomagnet, nominally $T = 0.1$ K at 0 and 2 T. To obtain the genuine magnetic spectra from the sample we reduce the data by using a procedure we employed in similar INS studies of the {$Mo_{72}Fe_{30}$} and {Cr_8} magnetic molecules [15,16]. The quasielastic term representing the instrumental resolution function, the incoherent and static disorder due to the sample, is modeled by a sum of two cocentered peaks: a dominant Gaussian and a minor Lorentzian. To obtain reliable parameters of the Gaussian/Lorentzian, the spectra at various

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[*] vaknin@ameslab.gov

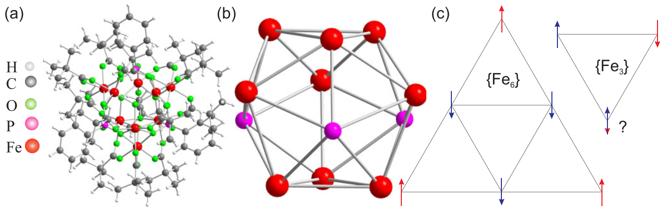

FIG. 1. (Color online) (a) {Fe$_9$} molecule used in this study. (b) The core icosahedron is occupied by nine iron and three phosphorus ions. The three phosphorus atoms separate the iron atoms into two {Fe$_6$} and {Fe$_3$} fragments. (c) The topology (and exchange pathways) in the {Fe$_6$} and {Fe$_3$} clusters. Arrows, representing spins, illustrate geometrical frustration but do not correspond to actual spin orientations in each fragment.

temperatures are refined simultaneously, with extra peaks due to magnetic excitations from the sample, while maintaining the same values of these parameters for the refinements of the various data sets at all measured temperatures and fields. By subtracting the cocentered Gaussian/Lorentzian function from data, such as those shown in the inset of Fig. 2(a) we obtain the intrinsic magnetic excitations from the sample as shown in Fig. 2(a) at 0.1 K at 0 and at 2 T [17]. Using this procedure we obtain the spectra as a function of temperature at zero magnetic field (Fig. 3) and as a function of applied magnetic field at base temperature Fig. 2(b). The spectra at base temperature consist of two types of excitations: one that appears at zero magnetic field and the other emerges only with the application of external magnetic field. We note that the spectra in Fig. 2 show a weak peak at ∼0.2 meV that did

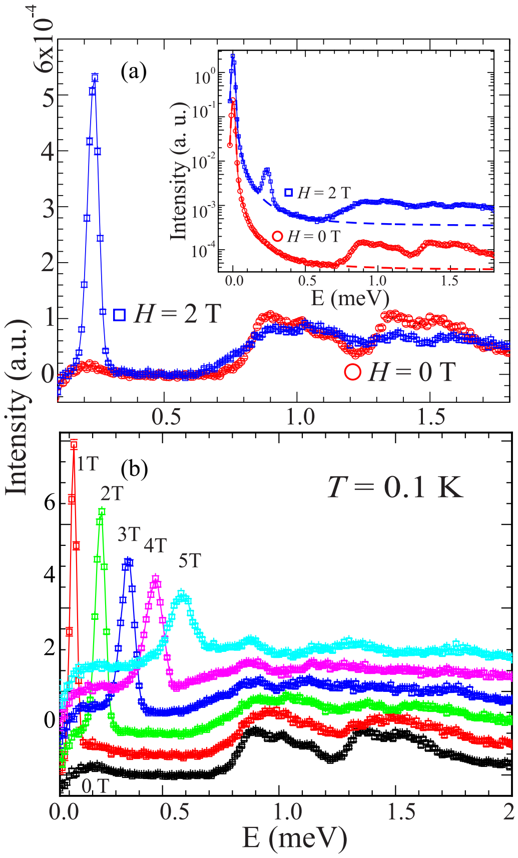

FIG. 2. (Color online) (a) Inset: Intensity *versus* neutron energy loss integrated over the $Q = 0.7–1.8$ Å^{-1} for {Fe$_9$} at $T = 0.1$ K at 0 and at 2 T. Dashed line is the instrumental resolution function (including incoherent scattering from our sample). The subtraction of the resolution function from the raw data (inset) yields the intrinsic magnetic spectra. (b) Same as (a) at $T = 0.1$ K and at various applied magnetic fields showing the emergence of an $S = 1/2$ state from the {Fe$_3$} cluster, and its effect on the two excited $S = 1$ states of the {Fe$_6$} cluster. Spectra at each field are shifted vertically for clarity.

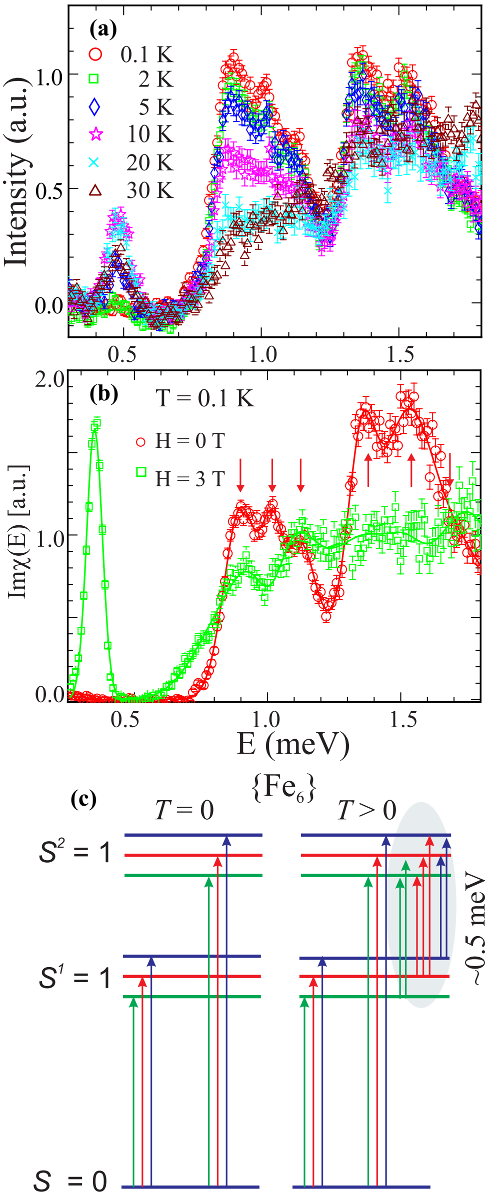

FIG. 3. (Color online) (a) Intensity *versus* neutron energy loss at various temperatures after extracting the signals from the raw data. (b) The imaginary part of the dynamical susceptibility (see text) at base temperature at $H = 0$ and 3 T. The solid line is a fit to the data at $H = 0$ using the sum of six Gaussians, the positions of which are indicated by arrows. (c) Illustration of the energy levels of the {Fe$_6$} cluster at $T = 0$ K and at higher temperatures, showing the emergence of the peak at 0.5 meV from the partially populated $S^1 = 1$ to the next $S^2 = 1$ level.

not show any magnetic field or temperature dependence. We therefore attribute this excitation to a low energy vibrational and or rotational excitation of the molecule and therefore is irrelevant to the present study.

Figure 3(a) shows intrinsic spectra of two excitations centered at $E_1 \approx 1.0$ and at $E_2 \approx 1.5$ meV at various temperatures that we attribute to $S^1 = 1$ and $S^2 = 1$ spin states, as justified below. Each of the two excitations is adequately described by three Gaussians with peak positions that are evenly displaced at E_i and at $E_i \pm \Delta E_i$ where $\Delta E_1 \approx 0.1$ and $\Delta E_2 \approx 0.12$ meV. This is demonstrated by a fit to the data with a sum of six Gaussians (solid line) to the imaginary part of the dynamical susceptibility Im $\chi(E)$ in Fig. 3(b) at 0.1 K at zero field. In our case, the dynamic susceptibility is practically q independent given by [4]

$$\mathrm{Im}\,\chi(E) \propto I(E)\left[1 - e^{-E/k_B T}\right]^{-1}, \tag{1}$$

where k_B is the Boltzmann constant. As the temperature increases, an excitation emerges at exactly the difference between the centers of the two excited states at $E_1 - E_2 \approx 0.5$ meV, characteristic of discrete thermally induced excitation from the lower, now populated level S^1, to the upper nearby S^2 state. This new excitation ($E_1 - E_2 \approx 0.5$) is narrower than the combined triplet as expected by selection rules between these two $S = 1$ states as schematically shown in Fig. 3(c), namely, $\Delta S = 0$ and for the magnetic quantum numbers, $\Delta M = M^1 - M^2 = 0, \pm 1$. Further evidence that these excitations are magnetic in origin is demonstrated by the strong effect the magnetic field has on the spectra; in particular, in shifting the spectra to lower and higher energies (albeit smeared and impossible to resolve) from the E_i's as expected from Zeeman effect on the magnetic quantum states M. These observations are consistent with the low-lying magnetic states of the {Fe_6} cluster as shown schematically in Fig. 3(c). While two degenerate excited $S = 1$ states at approximately 1 meV (with six degenerate magnetic quantum numbers) have been predicted in a previous study for this molecule [8], the INS presented here shows a more detailed magnetic structure with two $S = 1$ states that are split into their quantum numbers. Similar splitting in the spin excitations of the singlet ground state of $SrCu_2(BO_3)_2$ has been attributed to the Dzyaloshinski-Moriya-type interaction [18]. Such splitting can also be due to finite coupling between the two {Fe_6}-{Fe_3} fragments or due to single-ion anisotropy albeit very weak at that as the $3d^5$ configuration of Fe^{3+} has orbital angular momentum approaching $L = 0$, and hence the second order spin-orbit coupling, which commonly induces a single-ion-anisotropy term, is practically negligible, but cannot be excluded *a priori*. Alternatively, magnetic frustration that originates from the triangular building blocks of the {Fe_6} fragment (see Fig. 1), although as conjectured settle into a total spin $S = 0$ for this cluster [19], may yet possess more nuanced excited states as those reported here.

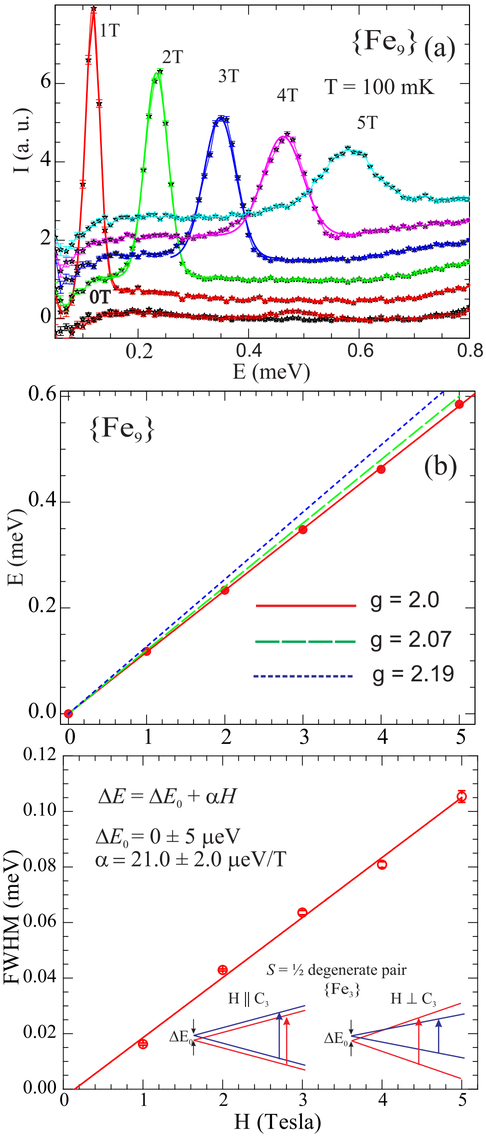

FIG. 4. (Color online) (a) Intensity versus energy loss at various magnetic fields showing a single excitation that shifts linearly and broadens with the increase in magnetic field. (b) Peak position of the excitations as a function of magnetic field with a linear fit that corresponds to a powder-averaged $g = 2.00$. (c) Linewidth of the excitations shown in (a) as a function of magnetic field. The solid line is a linear fit with parameters included in the figure.

The pronounced magnetic-field-dependent excitation shown in Fig. 4(a) indicates effectively a second ground state for the system that naturally is attributed to the {Fe_3} fragment of the molecule, suggesting the absence or a very weak coupling between the two fragments. The excitation shifts to higher energies and broadens with the increase in magnetic field, with a peak position that is perfectly linear in magnetic field with a slope that yields a Zeeman splitting of an $S = 1/2$ ground state with a $g = 2.00(2)$ [see Fig. 4(b)]. This is consistent with the theoretical ground state of the trinuclear {Fe_3} fragment with a single exchange coupling among nearest neighbors, namely, a doubly degenerate $S = 1/2$ ground state [20] with small variations from the values obtained by EPR measurements [8]. The close to perfect $g = 2.0$ value is a remarkable result as it is an angular average over any crystalline anisotropy for polycrystalline sample with random crystallographic orientation with respect to the applied magnetic field. A possible explanation as to the field-dependent linewidth shown in Fig. 4(c) may be explained by assuming a special g-value anisotropy reported in Ref. [8]. This study reported an effective g value that depends on the angle between the external magnetic field and the noncrystallographic C_3 axis of the three-spin triangle such that $g_\perp = 2.003$ for H perpendicular, and a pair of values $g_\parallel = 1.79$ and 2.25 for H parallel to the C_3 axis. For a crystalline with angle θ between the C_3 axis and a field direction we write an effective g value $g_{\rm eff} = 2.00 \pm \Delta g\ \cos(\theta)$, where $\Delta g \approx 0.21$ so that the Zeeman splitting for a single crystal is

$$E_{S=1/2} = [2.00 \pm \Delta g\ \cos(\theta)]\mu_B H. \qquad (2)$$

Averaging over θ yields a single value at $\langle E_{S=1/2}\rangle = 2.0\mu_B H$ as observed, with a second moment average, i.e., linewidth $\langle \Delta E\rangle \propto \Delta g \mu_B H$, linear in H as shown in Fig. 4(b). The linear dependence of the FWHM as a function of H shown in Fig. 4(c) indicates no (or unresolved) energy gap close to the ground state that for the perfect {Fe$_3$} triangle consists of a degenerate pair of $S = 1/2$ doublets [20]. This behavior suggests that the $S = 1/2$ ground state is doubly degenerate as expected from a magnetically frustrated triangle [19,20] diminishing the possibility of a mutual coupling between the two fragments. Based on the linewidth behavior of the excitations at low magnetic fields, we estimate that any splitting due to the removal of this degeneracy is on the order or less than 5 μeV. The first excited state for the perfect $s = 5/2$ {Fe$_3$} with a single AFM exchange coupling J in a Heisenberg Hamiltonian ($\mathcal{H} = -J\Sigma \mathbf{S}_i \cdot \mathbf{S}_j$) is a total spin $S = 3/2$ at $E = 3/2J$ from the ground state, and based on the value reported for $J \approx 22$ meV [8] is beyond the energy range available with OSIRIS.

To summarize, high resolution inelastic neutron scattering experiments on the {Fe$_9$} tridiminished iron icosahedra magnetic molecule yield comprehensive magnetic spectra that provide the necessary benchmark for theoretical development of a complete Hamiltonian for this system. The INS unequivocally shows two sets of ground states, $S = 0$ and $S = 1/2$, that are attributed to the two {Fe$_6$} and {Fe$_3$} fragments of the molecule that may be very weakly coupled. We find that the degeneracy predicted for the first $S = 1$ excited states of the {Fe$_6$} fragment is removed presumably by finite coupling between the fragments or by inherent frustration in the triangular building blocks of the fragment. Our magnetic-field-dependent results at base temperature reveal a remarkable single $S = 1/2$ ground state with $g = 2.0$ as expected from a perfect equilateral triangle {Fe$_3$} fragment. The absence of a clear nearby excited state for the {Fe$_3$} fragment suggests the $S = 1/2$ is doubly degenerate as expected from a frustrated triangular arrangement of half-integer spins [10,19]. More generally, the two fragments {Fe$_3$} and {Fe$_6$} with triangular building blocks may shed light on the effect of topological magnetic frustration in magnetic molecules.

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