An alternate model for magnetization plateaus in the molecular magnet $V_{15}$

Indranil Rudra$^1$, S. Ramasesha$^1$ and Diptiman Sen$^2$

$^1$ Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India
$^2$ Centre for Theoretical Studies, Indian Institute of Science, Bangalore 560012, India

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Starting from an antiferromagnetic Heisenberg Hamiltonian for the fifteen spin-1/2 ions in $V_{15}$, we construct an effective spin Hamiltonian involving eight low-lying states (spin-1/2 and spin-3/2) coupled to a phonon bath. We numerically solve the time-dependent Schrödinger equation of this system, and obtain the magnetization as a function of temperature in a time-dependent magnetic field. The magnetization exhibits unusual patterns of hysteresis and plateaus as the field sweep rate and temperature are varied. The observed plateaus are not due to quantum tunneling but are a result of thermal averaging. Our results are in good agreement with recent experimental observations.

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The synthesis of high-nuclearity transition metal clusters such as Mn$_{12}$, Fe$_8$ and $V_{15}$ has provided an impetus to the study of magnetism on the nanoscale. These transition metal clusters are basically isolated transition metal complexes involving multi-dentate ligands; the chemical pathway between the metal ions in the transition metal complex dictates the nature of exchange interactions. The complex interplay of the topology of exchange interactions, magnetic dipolar interactions and spin-lattice coupling has yielded a rich physics on the nanoscale which includes quantum tunneling, quantum coherence [2,3] and quantum spin-lattice coupling has yielded a rich physics on the nanoscale which includes quantum tunneling, quantum coherence [2,3]. Quantum coherence-decoherence studies are important from the standpoint of application of these systems in quantum coherence-decoherence studies are important from the standpoint of application of these systems in quantum computations [4].

There have been several models proposed to understand these phenomena [5]. Quantum hysteresis and interference have largely been studied by using an effective spin Hamiltonian with dipolar interactions and spin-lattice coupling has yielded a rich physics on the nanoscale which includes quantum tunneling, quantum phase interference and quantum coherence [2,3]. Quantum resonance tunneling is characterized by the observation of discrete steps or plateaus in the magnetic hysteresis loops at low temperatures. The signature of quantum interference is seen in the variation of the tunnel splitting as a function of the azimuthal angle of the transverse field for tunneling between $M_a = -10$ and $10 - n$ states in molecular magnets with ground state spin-10 [6]. Quantum coherence-decoherence studies are important from the standpoint of application of these systems in quantum computations [5].

The schematic structure of $V_{15}$ is shown in Fig. 1. Structural and related studies on the cluster indicate that within each hexagon, there are three alternating exchange pathways and their strengths [9] are also shown in Fig. 1. What is significant in the cluster is the fact that the spins in the triangle do not experience direct exchange interactions of any significance. The exchange Hamiltonian of the cluster is solved using a valence bond basis in each of the total spin subspaces, for all the eigenstates. It is found that two spin-1/2 states and a spin-3/2 state are split-off from the rest of the spectrum by a gap of 0.6$J$ [7]. These eight states almost exclusively correspond to the triangle spins and they are the only states which will make significant contributions to sub-kelvin properties. We therefore set up an effective Hamiltonian in the Fock space of the three spins. We find that the form

$$H_{sp_{-sp}} = \epsilon I + \alpha (S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_1)$$
\[ H_{\text{dip}} = \gamma \left[ (S_z^3 + S_z^3) + i (S_z^4 - S_z^4) \right]. \]  (2)

We have also introduced a coupling between the spin states of the cluster and the phonons. The spin-phonon interaction Hamiltonian which preserves the \( C_3 \) symmetry is phenomenologically given by [11]
\[ H_{\text{sp-ph}} = q (b + b^\dagger) \left[ (S_z^4 + S_z^4) + i(S_z^4 - S_z^4) \right. \]
\[ \left. + (S_z^2 - \frac{1}{3} S_z^2) \right]. \]  (3)

where \( q \) is the spin-phonon coupling constant, \( b (b^\dagger) \) is the phonon annihilation (creation) operator, and \( \hbar \omega \) is the phonon frequency. For simplicity, we have assumed a single phonon mode although the molecule has various possible vibrational modes. The form of the interaction in Eq. (3) means that the phonons couple only to states with spin-3/2. We have restricted the dimensionality of the Fock space of the phonons to 15 considering the low temperatures of interest.

The evolution of the magnetization as a function of the magnetic field has been studied by using the total Hamiltonian \( H_{\text{total}} \), given by
\[ H_{\text{total}} = H_{\text{sp-sp}} + H_{\text{dip}} + H_{\text{sp-ph}} + \hbar \omega (b^\dagger b + 1/2) \]
\[ + h_x(t) S_x + h_z(t) S_z, \]  (4)

where we have assumed that besides an axial field \( h_z(t) \), a small transverse field \( h_x(t) \) could also be present to account for any mismatch between the crystalline \( z \)-axis and the molecular \( z \)-axis. The numerical method involves setting up the Hamiltonian matrix in the product basis of the spin and phonon states \( |i,j\rangle \), where \( |i\rangle \) corresponds to one of the eight spin configurations of the three spins, and \( j \) varies from 0 to 14, corresponding to the fifteen phonon states retained in the problem. The values we have assigned to the different parameters are \( \gamma = 10^{-3}, q = 10^{-4} \) and \( \hbar \omega = 1.25 \times 10^{-4} \), all in units of the exchange \( J \) (see Fig. 1).

To study the magnetization phenomena, we start with the direct product eigenstates of \( H_{\text{sp-sp}} \) and \( \hbar \omega (b^\dagger b + 1/2) \), and independently evolve each of the 120 states \( \psi_{ij} \) by using the time evolution operator
\[ \psi(t + \Delta t) = e^{-iH_{\text{total}} \Delta t/\hbar} \psi(t). \]  (5)
or coercivity; all the hysteresis plots pass through the origin. The effect of varying the rate of scanning the field is also shown in Fig. 5. We find that as the scanning rate increases, the hysteresis in the plot of magnetization vs field decreases, and the plateau feature is almost identical in both the scanning directions. This could be because of the slow relaxation of the magnetization which is indeed the reason why the plateaus occur in the first place. We also find that the transverse field term does not affect any of our results significantly.

To summarize, we have derived an effective Hamiltonian from the exchange Hamiltonian of the full V$_{15}$ system. In the presence of a time varying magnetic field, the states of the effective Hamiltonian are allowed to evolve under the influence of magnetic dipolar interactions and a spin-phonon coupling. During the time evolution, the magnetization is followed as a function of the applied magnetic field. The calculated $M$ vs $H$ plots show magnetization plateaus at low temperatures. The width of the plateau at low temperature as well as the temperature at which the plateau vanishes are in excellent agreement with experimental values. It is also shown that the number of plateaus observed depends upon the scanning speed of the magnetic field. When the magnetic field is cycled, the hysteresis plots pass through the origin indicating the absence of remnance and coercion. The hysteresis is pronounced for slow scanning speeds. From our results, it appears that the magnetization plateaus in V$_{15}$ is not a consequence of quantum resonant tunneling but is a result of thermal averaging. We also find that the magnetization does not show any oscillation with time during evolution indicating the absence of quantum tunneling.

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FIG. 2. (a) Eigenstates of the effective spin Hamiltonian $H_{sp-sp}$. (b) Eigenstates in the presence of a moderate axial field. Arrows show the states connected by the dipolar terms and the transverse field. (c) is the same as (b) but in a stronger field, (d) describes the effect of spin-phonon terms (shown by arrows with broken lines) on (c).

FIG. 3. Plot of magnetization vs axial field at different temperatures. Inset shows plateau width as a function of temperature (full circles). Triangles in the inset correspond to the values from the fit to an exponential function.

FIG. 4. Magnetization as a function of axial field for a faster sweep rate at three different temperatures.

FIG. 5. Magnetization vs axial field for a full cycling of the field at different temperatures and sweep rates.