

Quantum Magneto-Oscillations in a Supramolecular Mn(II)-[3 × 3] Grid

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The magnetic grid molecule Mn(II)-[3 × 3] has been studied by high-field torque magnetometry at ³He temperatures. At fields above 5 T, the torque versus field curves exhibit an unprecedented oscillatory behavior. A model is proposed which describes these magneto-oscillations well.

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Among the known magneto-oscillatory effects, the de Haas–van Alphen (dHvA) effect in metals (and the group of effects related to it) is the most prominent example, having had a formative influence on our modern picture of solid state physics [1]. The dHvA effect originates from a quantization of closed electron orbits into Landau levels in a magnetic field, so that the density of states at the Fermi energy exhibits a markedly oscillatory evolution as a function of magnetic field. Currently, it finds application in a wide range of materials, e.g., heavy fermion compounds [2], low-dimensional organic metals [3], high-temperature superconductors [4], two-dimensional electron gases [5], or in the recently discovered superconductor MgB₂ [6].

In this work, we report on a new magneto-oscillatory effect, discovered in the molecular nanomagnet [Mn₉(2POAP-2H)₆](ClO₄)₆ · 3.57 MeCN · H₂O, the so-called Mn-[3 × 3] grid. Molecular nanomagnets are compounds with many magnetic metal ions linked by organic ligands to form well-defined magnetic nanoclusters. They have attracted much interest since they can exhibit fascinating quantum effects at the mesoscopic scale. For instance, quantum tunneling of the magnetization has been observed in the clusters Mn₁₂ or Fe₈ [7]. We have performed high-field torque magnetometry on the Mn-[3 × 3] grids at ³He temperatures and observed striking magneto-oscillations in the torque signal. We show that they arise from the interplay between antiferromagnetic interactions within a molecule and Zeeman splitting on the one hand and the magnetic anisotropy on the other hand.

In the Mn-[3 × 3] grid molecules, nine spin-5/2 Mn(II) ions occupy the positions of a regular 3 × 3 matrix, held in place by a lattice of organic ligands [inset of Fig. 1]. These grids were characterized recently by magnetization and torque measurements and found to exhibit unusual magnetic properties [8]. The Mn ions within a molecule experience an antiferromagnetic interaction leading to

a total spin $S = 5/2$ ground state at zero field. At a field of about 7 T, the ground state changes abruptly to a new state, a $S = 7/2$ level, accompanied by a change of the sign of the magnetic anisotropy. Notably, intermolecular magnetic interactions are at best on the order of a few 10 mK. This is evident from the crystal structure (the smallest separation between two molecules in the crystal is $> 8 \text{ \AA}$), but has been checked also experimentally [9]. Accordingly, even at ³He temperatures the magnetism of a macroscopic crystal sample reflects that of a single molecule.

Single crystals of Mn-[3 × 3] were prepared as reported [10]. They crystallize in the space group C_2/c . The cation [Mn₉(2POAP-2H)₆]⁶⁺ exhibits a slightly distorted S_4 molecular symmetry; the C_2 axis is perpendicular to the grid plane. The average distance between

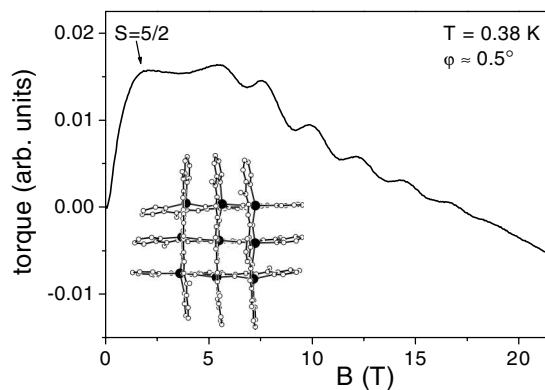


FIG. 1. Torque versus magnetic field of a Mn-[3 × 3] single crystal at low temperature. As the magnetic field lies almost in the plane of the grid molecule, the signal is very small and might be affected by a significant, but smooth background (e.g., due to Faraday forces). The peak at ≈ 2 T stems from the zero-field splitting of the $S = 5/2$ ground state. The inset shows the structure of the cation [Mn₉(2POAP-2H)₆]⁶⁺ (with Mn in black and H atoms omitted).

the Mn(II) ions is 3.93 Å; the smallest distance between clusters is larger than 8 Å. Consistent with the planar structure, the Mn-[3 × 3] grid exhibits a practically uniaxial magnetic behavior, and uniaxial and molecular C_2 symmetry axes coincide [8]. Magnetic torque was measured with a homemade silicon cantilever device [8,11] inserted into the M10 magnet at the Grenoble High Magnetic Field Laboratory using a ^3He evaporation cryostat. Resolution of the sensor was about 10^{-11} Nm, the weight of the crystals investigated was about 20 μg , nonlinearity was less than 2%, and the accuracy of the *in situ* alignment of the C_2 crystal axis with respect to the magnetic field was 0.3° . Only raw torque data are shown here. Background signals were, if not noted otherwise, negligible. Temperature was measured with a RuO_2 thick film resistor.

Figure 1 presents the field dependence of the torque of a Mn-[3 × 3] single crystal at 0.38 K. The magnetic field was applied almost perpendicular to the C_2 axis of the molecule; the angle φ between the magnetic field and the plane of the grid was about 0.5° . At low fields, the torque rises quickly to reach a maximum at about 2 T. This part of the signal stems from the $S = 5/2$ ground state and shows the expected behavior [12]. At higher fields, however, above about 5 T, the overall torque signal decreases with the superimposition of pronounced oscillations, which fade out with increasing field strength. Such magneto-oscillations have not been observed in molecular nanomagnets so far [13], and their observation is a main result of this work.

An overview of the dependence of the torque curves on the magnetic field orientation is given in Fig. 2(a). The oscillations are clearly visible for angles smaller than about 10° . For larger angles, the torque decreases strongly at higher fields and actually crosses the zero line, consistent with the observations in Ref. [8] (the torque measurements reported there did not show the oscillations because they were performed at too high a temperature).

The magnetic properties of molecular metal complexes are generally described by a spin Hamiltonian, which, assuming an idealized structure, for Mn-[3 × 3] becomes

$$H = -J_R \left(\sum_{i=1}^7 \mathbf{S}_i \cdot \mathbf{S}_{i+1} + \mathbf{S}_8 \cdot \mathbf{S}_1 \right) - J_C (\mathbf{S}_2 + \mathbf{S}_4 + \mathbf{S}_6 + \mathbf{S}_8) \cdot \mathbf{S}_9 + D_R \sum_{i=1}^8 S_{i,z}^2 + D_C S_{9,z}^2 + g\mu_B \mathbf{S} \cdot \mathbf{B}, \quad (1)$$

with $\mathbf{S} = \sum_i \mathbf{S}_i$. It consists of the isotropic nearest-neighbor exchange terms, the second order ligand-field terms, and the Zeeman terms [17]. J_R characterizes the couplings of the eight peripheral Mn ions, J_C those involving the central Mn ion (spins at “corners” are numbered 1, 3, 5, 7; those at “edges” 2, 4, 6, 8; and the central spin 9).

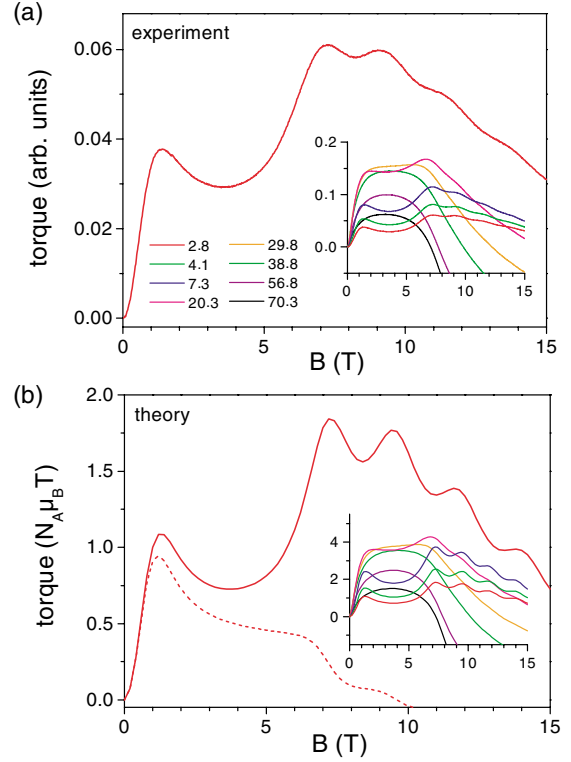


FIG. 2 (color online). (a) Experimental and (b) calculated torque curves as functions of the magnetic field of a Mn-[3 × 3] single crystal at 0.4 K for various orientations of the magnetic field (the legend gives the angle φ between the field and the grid plane). The main panel shows the curves for $\varphi = 2.8^\circ$. The dashed line in (b) represents the calculated torque curve for 0.4 K and 2.8° , but with effects of level mixing artificially forced to zero.

The dimension of the Hilbert space is huge for Mn-[3 × 3]. However, recently it has been shown that the field dependent low-temperature properties can be very well described by an effective spin Hamiltonian, in which the spin operators for the corner and edge spins are combined to sublattice spin operators \mathbf{S}_A and \mathbf{S}_B , respectively, with $S_A = S_B = 4 \times 5/2$ [18]. Physically, this approach works well because the internal spin structure due to the dominant Heisenberg interaction is essentially classical [19]. In this approach, Mn-[3 × 3] is described by

$$H_{\text{eff}}^{3 \times 3} = -\tilde{J}_R \mathbf{S}_A \cdot \mathbf{S}_B + \tilde{D}_R (S_{A,z}^2 + S_{B,z}^2) - J_C \mathbf{S}_B \cdot \mathbf{S}_9 + D_C S_{9,z}^2 + g\mu_B \mathbf{S} \cdot \mathbf{B}, \quad (2)$$

with $\tilde{J}_R = 0.526J_R$, $\tilde{D}_R = 0.197D_R$ [18]. In Ref. [8], $|J_C| \ll |J_R|$ was suggested. With this parameter regime, however, the experimental results could not be reproduced satisfactorily. We thus tried $J_C = J_R \equiv J$, and also set $D_C = D_R \equiv D$, as suggested by recent inelastic neutron scattering (INS) measurements [20]. As long as J_C and J_R are not too different, the calculated properties were found to be only weakly affected. A similar situation holds for D_C and D_R . J and D were determined such that the

position of the first ground state level crossing and the zero-field splitting of the $S = 5/2$ ground state in the calculated energy spectrum match the experimental values of ≈ 7 T and ≈ 3 K, respectively [8]. The results are $J = -5.0$ K and $D = -0.14$ K, in agreement with INS experiments [20].

The torque curves calculated with $H_{\text{eff}}^{3 \times 3}$ using the given parameters are presented in Fig. 2(b). Apparently, the model Hamiltonian reproduces the data, and, in particular, the oscillations, very well [21]. Their origin shall be discussed in the following in more detail.

For illustration, Fig. 3 shows the calculated energy spectrum as a function of magnetic field for an angle of $\varphi = 2.8^\circ$. As magnetic anisotropy is weak, $|D| \ll |J|$, the total spin \mathbf{S} is almost conserved. It is convenient to rotate the spin operators such that S_z^i is parallel to the magnetic field \mathbf{B} . Levels may then be classified by the eigenvalues of \mathbf{S}^2 and S_z^i , S and M , and be written as $|S, M\rangle$.

At zero field, the dominant isotropic exchange results in a $S = 5/2$ ground state followed by excited states with $S = 7/2, 9/2, 11/2, \dots$. Upon application of a magnetic field, the levels are shifted by the Zeeman energy, $g\mu_B MB$, leading to a series of ground state level crossings (LCs) at characteristic fields at which the ground state switches abruptly from $5/2 \rightarrow 7/2, 7/2 \rightarrow 9/2, 9/2 \rightarrow 11/2$, and so on (we abbreviated $|S, -S\rangle$ by the value of S). This is shown for the first two LCs in the inset of Fig. 3. The change of the slope of the ground state from $-5/2g\mu_B$ to $-7/2g\mu_B$ and $-9/2g\mu_B$ is apparent.

The effect of the ligand-field terms is to mix spin levels with $|\Delta S| = 0, 1, 2$ [22,23]. The $\Delta S = 0$ mixing leads to a zero-field splitting of each spin multiplet, which, e.g., is clearly visible in Fig. 3 for the six levels of the $S = 5/2$ ground state. Importantly, because of $|\Delta S| = 1$, the ligand-field terms also mix the levels which

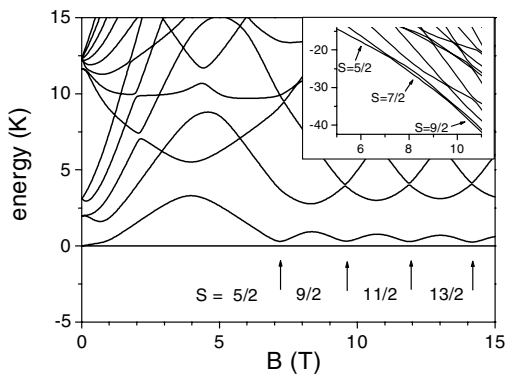


FIG. 3. Energy spectrum versus magnetic field for Mn-[3×3] at $\varphi = 2.8^\circ$ (energy of the lowest state was set to zero at each field). The arrows indicate the ground state level crossings, and the numbers the (approximate) total spin quantum number S of the respective ground states. The inset details the energy spectrum near the first two level crossing, where the ground state changes as $S = 5/2 \rightarrow 7/2$ and $S = 7/2 \rightarrow 9/2$. In contrast to the main panel, energies are given here with respect to the ground state energy at zero field.

are involved in a LC. This results in a repulsion of the two states whenever they come close, and the LCs split, as seen by the energy gaps at the LC fields in Fig. 3 (which are about 0.3 K at the angle of 2.8°).

The abrupt changes of the magnetic character of the ground state at the LCs lead to a steplike field dependence of the magnetization and torque. These magnetization and torque steps are frequently observed [24], e.g., in molecular ferric wheels [13–16]. However, as we show now, the level mixing at the LCs leads also to peaklike contributions in the torque (but not the magnetization). For the sake of completeness, we mention that the mixing of levels with $|\Delta S| = 2$ is pronounced only for excited states [23], and is of little relevance here.

Near each LC only two states, $|S, -S\rangle$ and $|S+1, -S-1\rangle$, are relevant at low temperatures, and the energy spectrum can be described by a two-level Hamiltonian

$$H_{S,S+1} = \begin{pmatrix} \epsilon_S & \Delta/2 \\ \Delta/2 & \epsilon_{S+1} \end{pmatrix}.$$

Here, $\epsilon_S(B, \varphi)$ and $\epsilon_{S+1}(B, \varphi)$ describe the field and angle dependence of the two levels *excluding* level mixing at the LC, but *including* the effects of the zero-field splitting. The level mixing itself is parametrized by a possibly field and angle dependent Δ . Up to first order, the energies ϵ_S can be written as $\epsilon_S(B, \varphi) = -bS + \Delta_S(\varphi)$ with the reduced field $b = g\mu_B B$ [15,16]. $\Delta_S(\varphi)$ accounts for the magnetic interaction and the zero-field splitting and thus does not depend on the magnetic field. The LC field is given by $b_c(\varphi) = \Delta_{S+1} - \Delta_S$. Importantly, in first order the level mixing is also independent of the field: It is determined by the matrix element between the two states and the ligand-field terms in Eq. (1), $\Delta = \langle S, -S | H'_{LF} | S+1, -S-1 \rangle$. Thus $\Delta = \Delta(\varphi)$.

At zero temperature, the magnetic moment is given by $m = -\partial\epsilon/\partial B$, where ϵ is the lowest energy as calculated from $H_{S,S+1}$. We decompose the magnetic moment into $m = m_S + \delta m$. Here, m_S is the magnetic moment for fields well below the LC field b_c so that δm describes the changes of m at the LC. Similarly, the torque $\tau = -\partial\epsilon/\partial\varphi$ is decomposed into $\tau = \tau_S + \delta\tau$. In our model, one obtains

$$\delta m(b, \varphi) = \frac{1}{2} [1 + (b - b_c)G(b, \varphi)], \quad (3)$$

$$\delta\tau(b, \varphi) = \delta m \frac{\partial b_c}{\partial\varphi} - \frac{1}{2} G(b, \varphi) \Delta \frac{\partial\Delta}{\partial\varphi}, \quad (4)$$

with $G(b, \varphi) = [(b_c - b)^2 + \Delta^2]^{-1/2}$. Therefore, as a function of the magnetic field the magnetic moment exhibits a step at the LC which is broadened by the level mixing (and by temperature if $T > 0$). In contrast, the torque consists of two contributions. The first term, being proportional to δm , leads to a broadened torque step. These magnetization and torque steps, as mentioned already, are well known [14–16,24]. The second term,

however, whose field dependence is controlled by $G(b, \varphi)$ only, leads to a peaklike contribution centered at the LC field b_c . This is apparent by noting that $G(b, \varphi)$ is basically the square root of the Lorentz function. Importantly, as this peak arises only for nonzero level mixing it is a direct signature of it. It is absent in the magnetic moment since the level mixing Δ is markedly angle dependent but virtually field independent.

Thus, the torque curve consists of a series of steps and peaks at each LC field. For Mn-[3 × 3], the steps are small and the peaks at each LC field superimpose to produce an oscillatory field dependence. This is clearly seen in Fig. 2(b), which also presents the 2.8° torque curve as it is calculated with the level mixing at the LCs set to zero artificially (i.e., only mixing of levels with $\Delta S = 0$ was retained). This curve exhibits only thermally broadened steps at the LC fields, demonstrating the connection of the oscillations with nonzero level mixing.

In view of the simplicity of our model Hamiltonian, the agreement between theoretical and experimental curves is really good, though it is not perfect. Most notably, the experimental peaks are significantly broader and smaller than the theoretical ones. The agreement can be improved by using a larger temperature value in the calculation, $T_{\text{eff}} = T + x$. We call x the Dingle temperature because of the analogy to the practice in the dHvA work [1], but we emphasize the different underlying physics. The experiment suggests $x \approx 80$ mK. Several intrinsic and extrinsic effects can be envisaged to be responsible for this additional broadening and more detailed investigations are needed.

In conclusion, in the molecular grid Mn-[3 × 3] we have observed a new type of quantum magneto-oscillations in the field dependence of the magnetic torque. We have shown that they are associated with level crossings which appear regularly as a function of field due to the combined effect of the magnetic interaction and the Zeeman term. These level crossings are split because of pronounced level mixing induced by the magnetic anisotropy which are accompanied by peaklike signals in the torque producing the spectacular, oscillatory field dependence. This effect should be observable in a number of other molecular magnetic clusters, like, e.g., dimers of two different magnetic centers with an antiferromagnetic coupling. The magnetic oscillations demonstrated in this study provide direct access to quantum properties, which will help our understanding of molecular nanomagnets.

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