Exchange constants and spin dynamics in Mn$_{12}$-acetate
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Abstract
We have obtained new inelastic neutron scattering (INS) data for the molecular magnet Mn$_{12}$-acetate which exhibit at least six magnetic peaks in the energy range 5–35 meV. These are compared with a microscopic Heisenberg model for the 12 quantum spins localised on the Mn ions, coupled by four inequivalent magnetic exchange constants. A fit to the magnetic susceptibility under the constraint that the spin of the ground state be $S = 10$ yields two dominant exchange constants of very similar value, $J_1 \approx J_2 \approx 65$ K ($\approx 5.5$ meV), and two smaller exchange constants $J_3$ and $J_4$. We compute the low-lying excitations by exact numerical diagonalisation and demonstrate that the parameters determined from the ground state and susceptibility fit provide qualitative agreement with the excitations observed by INS.

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PACS: 75.30.Et; 75.50.Xx; 78.70.Nx
Keywords: Magnetic molecular materials; Heisenberg model; Susceptibility – magnetic; Neutron scattering – inelastic

Magnetic molecules present a fascinating new class of materials with a wide variety of applications (for a recent review see [1]). Coherent quantum phenomena in these mesoscopic systems are one focus of recent research [2]. Despite being among the first generation of molecular magnets to be synthesised, Mn$_{12}$-acetate [3] remains that with the largest barrier to thermally activated tunnelling. Although much work has been devoted to Mn$_{12}$-acetate over the past decade, the microscopic mechanisms for the observed low-energy phenomena have remained controversial.

Here we discuss a microscopic exchange model for Mn$_{12}$-acetate. Twelve quantum spins $S_i$ are coupled by Heisenberg exchange interactions

$$H = \sum_{i,j} J_{ij} S_i \cdot S_j \quad (1)$$

with four different exchange constants $J_1$, $J_2$, $J_3$ and $J_4$, as represented in Fig. 1.

Fig. 1. Magnetic exchange model for Mn$_{12}$-acetate. Arrows denote the twelve Mn ions: eight Mn$^{3+}$ ions on the crown have local spin $S = 2$ while four Mn$^{4+}$ ions in the core have $S = 3/2$. Lines show exchange paths with interaction parameters $J_1$, $J_2$, $J_3$ and $J_4$. Many experimental studies, including inelastic neutron scattering (INS) [4], show that the ground state (GS) of Mn$_{12}$-acetate has total spin $S = 10$. This may
be rationalised by considering an arrangement of 8 parallel spins $S = 2$ on the crown Mn$^{3+}$ ions oriented antiparallel to 4 aligned $S = 3/2$ spins on the core Mn$^{4+}$ ions (Fig. 1). The $S = 10$ GS imposes a strong constraint on the allowed exchange constants in (1), excluding [5,6] a number of parameter sets proposed in the literature, such as that obtained by the \textit{ab initio} local density approximation [7].

The magnetic susceptibility $\chi$ is a valuable quantity in the determination of magnetic exchange constants. Fig. 2 shows two results for $\chi$, measured with an ordinary sample under an applied field of 1 T [8], and with a deuterated sample at 0.1 T [6]. Both data sets agree well for temperatures between 40 and 300 K despite the different conditions, demonstrating the reliability of the susceptibility measurement at high temperatures.

Exchange constants can then be determined by comparison with a symbolic high-temperature series expansion. In combination with a numerical test of the ground-state requirement, this restricts the possible parameters to a narrow region around $J_1 \approx J_2 \approx 60 \, K$, $J_3 \approx J_4 = 5-10 \, K$ [6].

Columns A, B and C of Table 1 list three choices of parameters in this region (parameter set A was used in [6]). Columns D and E contain the parameter sets proposed in [9] and [10] respectively. The lines in Fig. 2 show the susceptibility $\chi$ obtained from an average of four different Padé approximants to the 8th-order high-temperature series [6] evaluated with the corresponding parameters. The last row of Table 1 lists the effective $g$-factor entering the absolute value of $\chi$ (electron paramagnetic resonance [11] yields $g_{\text{eff}} = 1.968$). Parameter sets A, B and C yield good agreement with the experimental results, whereas the results for sets D and E are in clear disagreement. We conclude that the exchange constants proposed in Refs. [9,10] are incompatible with $\chi$.

A number of magnetic excitations in the range of 5 to 35 meV has been observed by INS experiments performed on different spectrometers [12,6]. The points in Fig. 3 show the spectrum obtained on the MARI spectrometer at ISIS with an incident energy $E_i = 17 \, \text{meV}$. Five magnetic excitations can be identified unambiguously in this data, and are shown by the lines in Fig. 3, which are fits with Gaussian curves on a linear background. Analysis of their $Q$- and $T$-dependence identifies these five excitations as magnetic and at least the lowest two of spin $S = 9$ [6]. A further magnetic excitation at 27 meV is the first candidate for an $S = 11$ excitation [6], in accord with high-field magnetisation measurements; this energy sets a lower bound for the numerical calculations.

Fig. 2. Static magnetic susceptibility. Filled and open circles are measured respectively on a deuterated sample under a field of 0.1 T [6] and on a non-deuterated sample at 1 T [8]. Lines are obtained from an 8th-order high-temperature series expansion for the parameter sets in Table 1.

We have performed exact diagonalisation for the model Hamiltonian (1), both to verify the $S = 10$ GS and to determine the low-lying excitations. The lowest excited states in the sectors with spin $S \leq 8$ are listed in Table 1 in ascending order of energy (for sets A, D and E these extend results presented in [6,9,10]). Spatial symmetry is described by a momentum $k$ such that the wavefunction acquires a phase factor $e^{i k}$ under a 90° rotation of the model in Fig. 1. The letters in Fig. 3 show the energies of the lowest $S = 9$ excitations for the corresponding data sets in Table 1. A constant energy 1.29 meV has been added to all calculated energies to account for magnetic anisotropy effects [6].

Fig. 3. Magnetic excitations. Points show the INS spectrum obtained on MARI with $T = 8 \, K$, $E_i = 17 \, \text{meV}$ and $1 \leq Q \leq 2 \, \text{Å}^{-1}$. Lines are Gaussian fits on a linear background. Letters represent numerical results for the $S = 9$ excitations listed in Table 1 for the corresponding parameter choices. A constant energy 1.29 meV has been added to all calculated energies to account for magnetic anisotropy effects [6].
Table 1

Energy $E$ and symmetry $k$ of low-lying excitations for a Mn$_{12}$-acetate exchange model with different parameter sets. Exchange constants are given in Kelvin [K]. The GS has spin $S = 10$ in all five cases. No energetic correction is applied for uniaxial anisotropy of the cluster.

|          | (A) [6] | (B) | (C) | (D) [9] | (E) [10] |
|----------|---------|-----|-----|---------|----------|
| $J_1$    | $67.2$  | $J_1$ | $64.5$ | $J_1 = 64$, $J_2 = 65$, | $J_1 = 119$, $J_2 = 118$, |
| $J_2$    | $61.8$  | $J_2$ | $60.3$ | $J_3 = 11$, $J_4 = 4$, | $J_1 = 115$, $J_2 = 84$, |
| $J_3$    | $7.8$   | $J_3 = 4.2$, $J_4 = 6.3$ | $J_3 = -8$, $J_4 = 23$, | |
| $J_4$    | $5.6$   | $J_4$ | $6.3$ | $J_3 = -4$, $J_4 = 17$ | |

| $E$ [K] | $k$ | $E$ [K] | $k$ | $E$ [K] | $k$ | $E$ [K] | $k$ |
|---------|-----|---------|-----|---------|-----|---------|-----|
| $S = 8$ |      | $5.52$  | $5.07$ | $5.13$  | $6.82$ | $7.35$  | $8.49$ |
|         | $\pi$ | $\pi$ | $\pi$ | $\pi$ | $\pi$ | $\pi$ | $\pi$ |
| $S = 9$ | $28.48$ | $\pm \pi/2$ | $29.15$ | $\pm \pi/2$ | $29.92$ | $\pm \pi/2$ | $33.99$ | $\pm \pi/2$ |
|         | $\pi$ | $40.71$ | $\pi$ | $48.22$ | $\pi$ | $35.76$ | $\pi$ | $\pi$ |
|         | $0$ | $81.82$ | $0$ | $102.96$ | $0$ | $65.11$ | $0$ | $77.12$ |
|         | $\pm \pi/2$ | $113.42$ | $\pm \pi/2$ | $132.51$ | $\pm \pi/2$ | $174.55$ | $\pm \pi/2$ | $124.63$ | $\pm \pi/2$ |
| $S = 10$ | $154.43$ | $\pi$ | $175.62$ | $\pi$ | $267.13$ | $\pi$ | $179.93$ | $\pi$ |
|         | $0$ | $297.02$ | $0$ | $308.05$ | $\pi$ | $501.03$ | $0$ | $436.52$ |
| $S = 11$ | $285.58$ | $\pm \pi/2$ | $285.63$ | $\pm \pi/2$ | $295.02$ | $\pm \pi/2$ | $507.87$ | $\pi$ | $435.95$ | $\pi$ |
|         | $0$ | $289.27$ | $\pi$ | $297.79$ | $\pi$ | $509.01$ | $\pm \pi/2$ | $436.83$ | $\pm \pi/2$ |
| $g_{eff}$ | $1.935$ | $1.935$ | $1.92$ | $2.12$ | $2.1$ |

Transitions from the $S = 10$ GS to states with $S \leq 8$ are not observable by INS due to selection rules. However, our results predict further low-lying excitations with $S < 9$. In particular, the $S = 8$ excitations in Table 1 may be interpreted as scattering states of a pair of the lowest $S = 9$ states ($k = \pm \pi/2$).

In summary, we have determined the microscopic exchange parameters of Mn$_{12}$-acetate as $J_1 \approx J_2 \approx 65$ K, and $J_3, J_4 \approx 5–10$ K. Earlier proposals [5,9,10] are inconsistent with the magnetic susceptibility, and do not match our new INS results. Further improvements to the optimal parameter set would require a treatment of the uniaxial anisotropies at the single-ion level, which would be expected to reduce the spread of the $S = 9$ levels, thereby improving agreement with the INS data.

Acknowledgments: This work was supported by the Swiss National Science Foundation, the TMR programme Molnanomag of the European Union (No: HPRN-CT-1999-00012), and by the Deutsche Forschungsgemeinschaft through grant SU 229/6-1.

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