Exchange couplings in the magnetic molecular cluster Mn$_{12}$Ac

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Abstract

The magnetic properties of the molecular cluster Mn$_{12}$Ac are due to the four Mn$^{3+}$ ions which have spins $S=3/2$ and the eight Mn$^{4+}$ ions with spins $S=2$. These spins are coupled by an exchange mechanism. We determine the four exchange couplings assuming a Heisenberg-type interaction between the ions. We use exact diagonalization of the spin Hamiltonian by a Lánczos algorithm and we adjust the couplings to reproduce the magnetization curve of Mn$_{12}$Ac. We also impose the constraint of reproducing a gap of 35 K between a $S=10$ ground state and a first excited state with $S=9$. We predict that there is an excited level with $S=8$ at 37 K above the ground state, only slightly above the $S=9$ excited state which lies at 35 K and the next excited state is a $S=9$ multiplet at 67 K above the $S=10$ ground state.

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I. INTRODUCTION

Molecular nanomagnets consist of a few paramagnetic ions coupled by exchange interactions and their properties are lying at the borderline between quantum and classical behavior. The best studied cluster so far is certainly Mn$_{12}$Ac. At low fields and low temperature its ground state can be described as a single spin $S=10$. The reversal of this spin occurs via a macroscopic relaxation time at $T=2$ K. This discovery has prompted a detailed examination of its magnetic behavior because of the potential use for ultimate information storage. If we concentrate only on magnetic ions, then Mn$_{12}$Ac is made of an external ring of eight Mn$^{3+}$ ions with spin $S=2$ and ring encloses a tetrahedron of four Mn$^{4+}$ ions with spin $S=3/2$. These spins are coupled by exchange so as to lead to a $S=10$ ground state. This means that there is a ferrimagnetic arrangement of the spins. It is also known that the $S=10$ manifold is split by anisotropy into sublevels with $-10 \leq S_z \leq +10$. The properties of this subset of levels have been studied in detail by various experimental techniques because of the possibility of macroscopic quantum tunneling of the spin. The anisotropy responsible for the zero-field splitting of the $S=10$ manifold is smaller than the exchange interactions that determine first of all the ferrimagnetic ground state structure. For example the degenerate $S_z = \pm 10$ states are separated from the states with $S_z = \pm 9$ (belonging to the same $S=10$ manifold) by a gap determined by inelastic neutron scattering $\approx 14$ K. So a reasonable strategy to study magnetic properties of this cluster is to ignore first any anisotropy terms in a model spin Hamiltonian by use of the simplest Heisenberg exchange and then, once these parameters are known, refine the treatment by including higher-order anisotropy terms.

Recently the full magnetization curve $M(H)$ of the cluster Mn$_{12}$Ac has been obtained by an experimental technique using explosive compression of the magnetic flux to access to very high fields in the megagauss range. Many if not all transitions between levels with different total spin have been measured. This kind of measurement is a direct probe of the inner magnetic structure of the cluster i.e. of the higher-energy scale couplings.

In this paper we determine the values of the exchange couplings between the Mn ions by using a Heisenberg spin Hamiltonian to reproduce the high-field magnetization data. We also add as a constraint the value of the gap between $S=10$ and $S=9$. With these values we are able to predict the energies and multiplicities of some of the low-lying states above the $S=10$ ground state. This explains some features of the existing inelastic neutron scattering
data that were not understood previously. In section II, we expose the details of the model Hamiltonian and the numerical technique we have used. In section III, the details of the fit are given. Finally section IV contains our conclusions.

II. THE SPIN HAMILTONIAN

The core of the magnetic cluster of formula \( \text{Mn}_{12}\text{O}_{12}(\text{CH}_3\text{COO})_{16}(\text{H}_2\text{O})_4 \) is depicted in Fig. 1. There is an outer ring of eight ions \( \text{Mn}^{3+} \) with spin \( S=2 \), \( S_5, \ldots S_{12} \) that encircles four ions \( \text{Mn}^{4+} \) with \( S=3/2, S_1, \ldots S_4 \). In Fig. 2 we draw a simplified representation of the cluster taking into account only the connectivity of exchange interactions \([2, 5]\). There are four most important exchange paths (bonds in the following). They are \( J_1 \) which relate each spin 3/2 to a spin \( S=2 \), there is also a \( J_2 \) coupling between the outer ring and the inner tetrahedron involving four triangles i.e. eight bonds, then \( J_3 \) between the four spins \( S=3/2 \) with a tetrahedral structure so there are six such bonds, and \( J_4 \) between the \( S=2 \) ions which means eight bonds. The simplest guess for the exchange is thus a Heisenberg spin Hamiltonian:

\[
\mathcal{H} = J_1 \{ S_1 \cdot S_7 + S_2 \cdot S_9 + S_3 \cdot S_{11} + S_4 \cdot S_5 \} \\
+ J_2 \{ S_6 \cdot (S_1 + S_4) + S_8 \cdot (S_1 + S_2) + S_{10} \cdot (S_2 + S_3) + S_{12} \cdot (S_3 + S_4) \} \\
+ J_3 \{ S_1 \cdot S_2 + S_2 \cdot S_3 + S_3 \cdot S_4 + S_4 \cdot S_1 + S_1 \cdot S_3 + S_2 \cdot S_4 \} \\
+ J_4 \{ S_5 \cdot S_6 + S_6 \cdot S_7 + S_7 \cdot S_8 + S_8 \cdot S_9 + S_9 \cdot S_{10} + S_{10} \cdot S_{11} + S_{11} \cdot S_{12} + S_{12} \cdot S_5 \}
\]

where we use the labeling of the spins given in Fig. 2. In this work we ignore the effect of anisotropy and use the Hamiltonian Eq.(1). As a consequence the total spin is a good quantum number. The total dimension of the Hilbert space of the magnetic degrees of freedom is \( 10^8 \) which is too huge for brute force diagonalization. Previous works \([2, 6, 7]\) have used various approximate schemes usually based on some assumptions about the relative order of magnitude of the \( J \)'s. In the Florentine coupling scheme \([2]\) one starts from a large antiferromagnetic value for \( J_1 \). Hence the cluster is described as a first approximation by four dimers \( \text{Mn}^{3+}\text{-Mn}^{4+} \) with spin \( S=1/2 \) and four remaining \( \text{Mn}^{3+} \) ions with spin \( S=2 \). It is then feasible to treat the system of four spins \( S=1/2 \) and four spins \( S=2 \). However it is not clear that this hypothesis is able to explain the experimental results at hand. There are many results from neutron scattering \([3]\), magnetization \([8]\) and heat capacity \([9]\) that point
to the presence of excited states not too far from the S=10 ground state. It is thus desirable to obtain values of the exchange parameters without recourse to any \textit{a priori} assumption of their relative strength. A recent study by exact diagonalization \cite{13} using the point symmetry group of the magnetic cluster concluded that $J_1 = 215$ K, $J_2 = 85$ K, $J_3 = 85$ K, $J_4 = -64.5$ K. Since these data refer to transitions involving the lowest energy levels for a given spin value, the Lánczos algorithm appears to be particularly well suited.

The recent megagauss magnetization data \cite{4} provide further information on the strength of the exchange interactions. We have used the Lánczos algorithm \cite{10} applied to the Hamiltonian Eq.(1). If we use conservation of spin projection on a given axis, say it $z$, then the Hilbert space dimensions are much reduced. The largest subspace corresponds to $S_z = 0$ with dimension 8581300, while the subspace in which we have to find the ground state has dimension 817176 for $S_z = 10$. The corresponding dimensions are given in table I. Although the use of total spin would reduce further the dimensionality, it is much more complicated to program in an efficient way.

In a given subspace we use the iterative Lánczos algorithm that brings the Hamiltonian into tridiagonal form. This is done typically in at most one hundred iterations which is enough to obtain the ground state energy with a precision of $\approx 10^{-10}$. The advantage of the Lánczos algorithm is that it requires only to perform the product of the Hamiltonian on a vector. Since spin Hamiltonians are very sparse matrices, one needs only to store in fact two vectors to use the Lánczos algorithm. Even with the huge dimensions that appear in table I, this is feasible on present day computers.

If we now consider the effect of a magnetic field \cite{11}, then due to the rotational symmetry of the Hamiltonian, the magnetic field couples to a conserved quantity and we just have to shift energies:

$$E_{S_z}(B) = E_{S_z}(B = 0) - g\mu_B BS_z,$$

where $E_{S_z}(B = 0)$ is an eigenenergy of (1) in the sector with spin projection $S_z$. As a function of the applied field there will be crossings of levels with different values of $S_z$. The magnetization curve of the cluster Mn$_{12}$Ac is a series of discrete jumps and plateaus due to the finite size of this spin system. It is only for the thermodynamic limit that one gets smooth magnetization curves for spin systems. The critical field corresponding to the
transition $S^z$ to $S^z + 1$ is given by:

$$B_{\text{crit}}(S^z \rightarrow S^z + 1) = \frac{1}{g\mu_B}(E_{0,S^z+1}(B = 0) - E_{0,S^z}(B = 0)),$$

where $E_{0,S^z}(B = 0)$ is the ground state energy in the sector with given $S^z$. We have used $g=2$ in this paper.

### III. REPRODUCING MAGNETIZATION DATA

To determine the exchange parameters, we have used the data coming from various experimental sources. First it is well established that the ground state has total spin $S=10$. These states are exactly degenerate in our case since we make the simplifying assumption of exact rotational symmetry. Then the gap between this $S=10$ manifold and the first excited state with $S=9$ is known from magnetic susceptibility measurements \cite{12} to be 35 K. The remaining piece of high-energy information comes from the megagauss experiment of ref. \cite{4}. In this experiment one measures the differential susceptibility $dM/dH$ vs. $H$. For a system with a series of discrete jumps as Mn$_{12}$Ac, a spike in the differential susceptibility corresponds to a change of the spin of the ground state. The lowest-lying spike lies at $B_1 = 382$ T and is interpreted \cite{7} as the transition from the ground state with $S=10$ to an $S=11$ state and then there are three spikes at $B_2 = 416$ T, $B_3 = 448$ T, and $B_4 = 475$ T corresponding to the crossing of $S=12, 13, \text{and } 14$ states respectively. At higher fields there is a huge spike centered at 530 T which presumably corresponds to several unresolved crossings, maybe $S=15$ and $S=16$. Above this field value it is difficult to locate the other remaining transitions so no other values were determined in Ref. \cite{4}. We have used the four values that are determined with good accuracy $B_1, \ldots, B_4$. We compute the corresponding theoretical values $B_{i\text{theo}}$ and measure the quality of the fit by the following quantity:

$$\epsilon = \sum_{i=1}^{4} \left( \frac{B_i - B_{i\text{theo}}}{B_i} \right)^2.$$

We have performed calculations of the levels with $S^z=9$ up to $S^z=22$ on a grid of values of the ratios of the exchange couplings $J_2/J_1$, $J_3/J_1$ and $J_4/J_1$ between +2 and -2 by steps of 0.1. In this range of parameters, we first reject values for which $S^z=10$ is not the ground state. Then we look for regions with small $\epsilon$ parameter defined in Eq.(4). In these regions, we fix the absolute scale of energy via $J_1$ by requiring that the critical fields should be equal
to the experimental value $B_1 = 382$ T. This leads to approximate values for the other critical fields $B_2, \ldots, B_4$. We next refine the search by including only the regions in which the gap $S=10-S=9$ is close to its experimental value of 35 K. This is now done by adjusting the four dimensionful couplings $J_1, \ldots, J_4$. We observe that the biggest effect on the overall spectrum structure is due to $J_1$ and $J_2$. The best values are close to $J_1 \approx 119$ K, $J_2 \approx 118$ K. This corresponds to $\epsilon \approx 10^{-4}$. In Fig. 3 we plot the variation of the fitting parameter $\epsilon$ in the $J_1$-$J_2$ plane close to the best values of these parameters. If we search for a region of small $\epsilon$ by tuning these two parameters only then we find that this region is quite insensitive to the choice of $J_3$ and $J_4$. This is illustrated in Fig. 4 where $\epsilon$ is given in the $J_3$-$J_4$ plane.

Our next observation is that once $J_1$ and $J_2$ are determined, the remaining couplings $J_3$ and $J_4$ may be varied to obtain more precisely the $S=10-S=9$ gap of 35 K. The agreement with the gap is given in Fig. 5 where we have plotted the gap value in the plane $J_3$-$J_4$. We find that $J_4$ is significatively antiferromagnetic $J_4 \approx 23$ K while it is difficult to give a precise estimate for $J_3$: it barely differs significatively from zero. A tentative value is $J_3 \approx -8$ K. Taking into account the experimental uncertainties on the critical fields, we estimate that $J_3$ and $J_4$ are determined with an error bar of $\approx 6$ K. The determination of $J_3$ and $J_4$ does not affect much the values of $J_1$ and $J_2$, as can be seen in Fig. 6.

As proposed in previous works, we find that $J_1$ is larger than $J_3$ and $J_4$. However, we clearly need a second coupling $J_2$ which should be close to $J_1$ (taking into account the uncertainties on all the experimental results). The part of the spectrum relevant to magnetization data corresponding to this preferred set of parameters is given in Table II.

It is interesting to compare our results with those already available in the literature. In the first works [2], the assumption of large $J_1$ combined with a perturbative treatment lead to $J_1=225$ K, $J_2=90$ K, $J_3=90$ K, $J_4=0$ K. In fact this set of parameters does not lead to a $S=10$ ground state, as first pointed out by Raghu et al. [13]. There is another set of parameters $J_1=215$ K, $J_2=85$ K, $J_3=-85$ K, $J_4=-45$ K suggested by Chudnovsky [14]. However this set which has a correct $S=10-S=9$ ordering leads to a gap of 223 K, much too large. A recent study by exact diagonalization [13] concluded that $J_1=215$ K, $J_2=85$ K, $J_3=85$ K, $J_4=-64.5$ K. This set has a correct ordering of 9-10 levels with a gap which is adjusted to the experimental value of 35 K but we find that it does not lead to a satisfactory magnetization curve. This set gives critical fields equal to $B_1 = 192$ T, $B_2 = 239$ T, $B_3 = 356$ T and $B_4 = 406$ T (the $\epsilon$ parameter is 0.4 instead of our value of $\approx 10^{-4}$).
With our preferred set of exchange parameters we can then compute some of the excited levels that are above the first excited manifold with $S=9$. We find that there is a $S=8$ manifold sitting at 37 K above the $S=10$ ground state so very close to the $S=9$ states that have been used to constrain our fit. Then there is a $S=9$ multiplet which is found at 67 K above the ground state. This picture is close to what is found from susceptibility measurements [12] where two close $S=9$ levels are necessary to reproduce the low-temperature behavior. However the scheme is not exactly the same: the multiplicities do not coincide.

Our new picture has some interesting consequences for the interpretation of neutron data. There is some evidence from inelastic neutron scattering [13] for a mode at 1.2 THz i.e. 70 K, this may correspond to the second $S=9$ multiplet that we find at 67 K. This is allowed by neutron scattering selection rule starting from the $S=10$ ground state. It is then normal that neutrons do not see the $S=8$ states at 37 K = 0.73 THz because of the selection rules however it not yet clear why neutrons do not see the first excited state with $S=9$ at 35 K = 0.72 THz.

IV. CONCLUSIONS

We have studied the energy levels of a Heisenberg spin model Hamiltonian appropriate to describe the magnetic cluster Mn$_{12}$Ac. We obtain a determination of four exchange couplings: $J_1=119$ K, $J_2=118$ K, $J_3=-8$ K, $J_4=23$ K. Such a set of parameters reproduces the magnetization curve observed in megagauss experiments, leads to a $S=10$ ground state and a gap of 35 K to a first excited level with $S=9$ as measured experimentally. The numerical method we have used does not rely upon any approximations, so the main source of uncertainty in the values we quote comes from the measurement of the critical fields in the magnetization process. We predict that there is an excited level with $S=8$ at 37 K only slightly above the $S=9$ excited state which lies at 35 K and the next excited state is a $S=9$ multiplet at 67 K above the $S=10$ ground state. These findings explain part of the existing neutron scattering data.
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TABLE I: Hilbert space dimension of subspaces of given $S^z$ for the system of eight spin-2 and four spin-3/2.

| $S^z$ | Dimension |
|-------|-----------|
| 22    | 1         |
| 21    | 12        |
| 20    | 78        |
| 19    | 364       |
| 18    | 1361      |
| 17    | 4312      |
| 16    | 11968     |
| 15    | 29744     |
| 14    | 67216     |
| 13    | 139672    |
| 12    | 269148    |
| 11    | 484144    |
| 10    | 817176    |
| 9     | 1299632   |
| 8     | 1954108   |
| 7     | 2785384   |
| 6     | 3772176   |
| 5     | 4862352   |
| 4     | 5974048   |
| 3     | 7003944   |
| 2     | 7842070   |
| 1     | 8390440   |
| 0     | 8581300   |
TABLE II: Ground state energies in each fixed $S^z$ sector with corresponding critical magnetic fields for coupling constant set $J_1=88.9$ T ($\approx 119$ K), $J_2=88.0$ T ($\approx 118$ K), $J_3=-6.0$ T ($\approx -8$ K) and $J_4=17.0$ T ($\approx 23$ K) for which the gap is 26 T ($\approx 35$ K).

| $S^z$ | Energy (T) | Critical fields (T) |
|-------|------------|---------------------|
| 10    | -3196.2    | 381.0               |
| 11    | -2815.2    | 411.7               |
| 12    | -2403.5    | 444.1               |
| 13    | -1959.4    | 477.6               |
| 14    | -1481.8    | 512.5               |
| 15    | -969.3     | 548.4               |
| 16    | -420.9     | 584.9               |
| 17    | 164.0      | 622.1               |
| 18    | 786.1      | 659.7               |
| 19    | 1445.8     | 697.2               |
| 20    | 2143.0     | 733.9               |
| 21    | 2876.9     | 764.9               |
| 22    | 3641.8     |                     |
FIG. 1: The core of the magnetic cluster Mn$_{12}$Ac.

FIG. 2: The spins in Mn$_{12}$Ac
FIG. 3: Variation of the fitting parameter $\epsilon$ as a function of $J_1$ and $J_2$. The remaining couplings are taken to be $J_3=-6.0$ T (-8 K), $J_4=17.0$ T (23 K). The grey levels are proportional to $-\log(\epsilon \times 10^4)$. 
FIG. 4: Variation of the fitting parameter $\epsilon$ as a function of $J_3$ and $J_4$. The remaining couplings are taken to be $J_1=88.9$ T (119 K), $J_2=88.0$ T (118 K). The grey levels are now proportional to $2/(1 + \epsilon \times 10^4)$. 
FIG. 5: Variation of the gap as a function of $J_3$ and $J_4$. The remaining couplings are taken to be $J_1=88.9$ T, $J_2=88.0$ T. Grey levels are plotted via $1/1 + |(\Delta - 26)/26|$.

FIG. 6: Variation of the gap as a function of $J_1$ and $J_2$. The remaining couplings are taken to be $J_3=-6.0$ T, $J_4=17.0$ T. Grey levels are given by the relative variation $|(\Delta - 26)/26|$.