Modification of the spin structure of high-molecular-weight magnetic clusters in strong magnetic fields

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The alteration of the spin structure of the high-spin organic cluster $Mn_{12}Ac$ in a strong magnetic field is theoretically investigated. The magnetization of the material is calculated as a function of the external magnetic field and the temperature. It is shown that the magnetic field induces a transformation of the spin structure of $Mn_{12}Ac$ from quasi-ferrimagnetic with average magnetic moment of order 20 μ_B per molecule to quasi-ferromagnetic with moment $\approx 44\ \mu_B$. In contrast to the analogous transformation of a Néel ferrimagnet, which is continuous and takes place via an intermediate angular phase, in $Mn_{12}Ac$ this process is manifested at low temperatures as a cascade of discrete quantum jumps, each of which is a transition accompanied by an increase in the spin number of the complex. At high temperatures the behavior of the magnetic cluster approaches that described by the classical theory. The nature of the quantum jumps is discussed from the point of view of magnetic-field-induced crossover of the energy levels of the ground state of the magnetic cluster. © *1996 American Institute of Physics.* [S1063-7761(96)01406-0]

1. INTRODUCTION

Interest in molecular magnetism has grown considerably in recent years. Of especial interest in this area of study are high-spin organic clusters containing ions of the transition metals Fe, Mn, etc.[1–8] New materials, based on such complexes exhibit extremely interesting and useful properties, such as, for example, giant magnetostriction, magnetic resistivity, the magnetocaloric effect, the presence of bistability on scales of one molecule, and macroscopic quantum tunneling of magnetization.[2] At the same time, problems arise in the study of these materials that are of fundamental interest for condensed matter physics and magnetism.

Magnetic clusters are mesoscopic objects, i.e., they are characterized by behavior of an intermediate type, encompassing, in addition to classical features that are characteristic of "solid-state" magnetic materials, specific quantum properties that are characteristic of individual atoms and molecules.

The traditional model of paramagnetism is not always a suitable basis for interpreting the magnetic properties of cluster systems; the same is true of existing models of superparamagnetism. Quantum fluctuations play an important role in our understanding of the low-temperature properties of these systems.[9,10]

In the present paper we investigate one of the more typical and interesting clusters, $Mn_{12}Ac$, synthesized and actively investigated in recent years.[6–8] The structure of this cluster is schematically depicted in Fig. 1. Its general formula is $(Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4)\ 2CH_3COOH4H_2O$. The outer part of the cluster is formed by eight Mn^{3+} ions, and the inner tetrahedron is formed by four Mn^{4+} ions. The Mn ions interact with each other through the oxygen ions. In addition, on the periphery of the molecule there are acid radicals and four molecules of water.

The spins of the ground state of the Mn^{3+} and Mn^{4+} ions are $S=2$ and $S=3/2$, respectively, and the spin of the ground state of the cluster is $S=10$ (Ref. 6). Such a ground state agrees with the magnetization[6,7,11] and EPR data.[6] To a good approximation the cluster may be considered as a system possessing axial symmetry. Crystals based on $Mn_{12}Ac$ having a tetragonal structure with S_4 axis are known. Two very interesting properties of the $Mn_{12}Ac$ cluster are the presence of bistability at the molecular level,[2] and of macroscopic quantum tunneling of the magnetization.[12,13] It is fair to say that the latter property has still not received an adequate explanation, since according to the existing theory[14,15] macroscopic tunneling of the magnetization is forbidden in axially symmetric clusters.

The ground state $S=10$ is interpreted as the result of an antiferromagnetic interaction between the Mn^{3+} and Mn^{4+} ions, so that such a cluster can be considered as a ferrimagnet at the molecular level.[1)] It is well known that in ferrimagnets two phase transitions take place as the magnetic field increases (see, e.g., Refs. 18 and 19): a) from the ferrimagnetic phase to a noncollinear–angular phase, and b) from the angular phase to the ferromagnetic phase. These phase transitions are continuous, i.e., second-order (in an isotropic system). In the angular phase the magnetic susceptibility is constant and equal to $1/\lambda$, where λ is the constant of the exchange interaction acting between the sublattices. Weak anisotropy (the energy of which is much less than the intersublattice exchange energy) does not greatly alter this picture.

In the present paper we examine a similar process, the transition from the ferrimagnetic state to the ferromagnetic state for the magnetic cluster $Mn_{12}Ac$, and establish that such a process differs qualitatively from the classical. Specifically, the transition from the ferrimagnetic state to the ferromagnetic state consists of a sequence of quantum jumps of the magnetization, each of which is accompanied by an increase in the spin number of the complex. At high temperatures the jumps smooth out and the magnetization curve approaches its classical analog.

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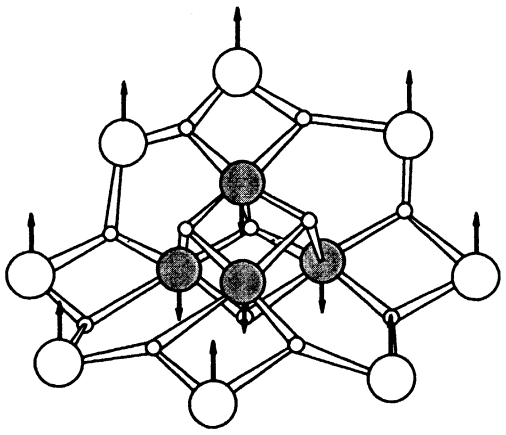

FIG. 1. Schematic depiction of the nucleus of the organic cluster $Mn_{12}Ac$. The large white circles represent the Mn^{3+} ions, the hatched circles represent the Mn^{4+} ions ($S=3/2$), and the small white circles represent oxygen atoms. The acid ligands and the four water molecules are not shown.[2]

2. THE HAMILTONIAN

The exchange interactions between the Mn ions are schematically depicted in Fig. 2. It is assumed that the exchange interactions are described by the Heisenberg Hamiltonian, which for the cluster under consideration has the form[6]

$$H=-2J_1(\mathbf{S}_1\mathbf{S}_2+\mathbf{S}_3\mathbf{S}_4+\mathbf{S}_5\mathbf{S}_6+\mathbf{S}_7\mathbf{S}_8)-2J_2(\mathbf{S}_2\mathbf{S}_9+\mathbf{S}_4\mathbf{S}_9+\mathbf{S}_4\mathbf{S}_{10}+\mathbf{S}_6\mathbf{S}_{10}+\mathbf{S}_6\mathbf{S}_{11}+\mathbf{S}_8\mathbf{S}_{11}+\mathbf{S}_8\mathbf{S}_{12}+\mathbf{S}_2\mathbf{S}_{12})-2J_3(\mathbf{S}_2\mathbf{S}_4+\mathbf{S}_2\mathbf{S}_6+\mathbf{S}_2\mathbf{S}_8+\mathbf{S}_4\mathbf{S}_6+\mathbf{S}_4\mathbf{S}_8+\mathbf{S}_6\mathbf{S}_8)-2J_4(\mathbf{S}_1\mathbf{S}_9+\mathbf{S}_1\mathbf{S}_{12}+\mathbf{S}_3\mathbf{S}_9+\mathbf{S}_3\mathbf{S}_{10}+\mathbf{S}_5\mathbf{S}_{10}+\mathbf{S}_5\mathbf{S}_{11}+\mathbf{S}_7\mathbf{S}_{11}+\mathbf{S}_7\mathbf{S}_{12})+\mu H\sum_{i=1}^{12}\hat{S}_{iz}, \tag{1}$$

where $\mu=g\mu_B$ ($g\approx 2$).

This Hamiltonian is a $10^8\times 10^8$ matrix in the space of spin states, which renders direct numerical analysis of this system impossible. Therefore, to study the energy spectrum of the system, we will use a hierarchy of interactions and a perturbation theory based on them. According to Ref. 6 the exchange integrals in Eq. (1) have the following order-of-magnitude values: $J_1\approx -150\ \mathrm{cm}^{-1}$, $J_2\sim J_3\approx -60\ \mathrm{cm}^{-1}$, $|J_4|\leqslant 30\ \mathrm{cm}^{-1}$. Note also that the energy of the single-axis magnetic anisotropy can be represented in the form[6]

$$E_A=-\sum D_i S_{iz}^2, \tag{2}$$

where the z axis is assumed to coincide with the axial symmetry axis of the molecule, $D\approx 0.5\ \mathrm{cm}^{-1}$. Thus, the energy of the single-axis anisotropy is significantly less than the exchange energy and to first order can be neglected in a study of magnetic restructuring processes in the cluster taking place in strong magnetic fields.

We represent the Hamiltonian (1) in the form

$$H=H_0+V, \tag{3}$$

where

$$H_0=H_{01}+H_z=-2J_1(\mathbf{S}_1\mathbf{S}_2+\mathbf{S}_3\mathbf{S}_4+\mathbf{S}_5\mathbf{S}_6+\mathbf{S}_7\mathbf{S}_8)+\mu H\sum_{i=1}^{8}\hat{S}_{iz}. \tag{4}$$

The perturbation V includes the exchange interactions J_2, J_3, and J_4 and the rest of the Zeeman interaction.

Let us first consider the eigenfunctions and energy levels of the Hamiltonian H_{01}.

Let S_{12}, S_{34}, S_{56}, and S_{78} be the spins of the corresponding pairs, coupled by the strong exchange interaction J_1.

Obviously, S_{ij} take the values 1/2, 3/2,..., 7/2. The energy spectrum of the Hamiltonian H_{01} can be represented in the form

$$\frac{E(1)}{(-J_1)}=S_{12}(S_{12}+1)+S_{34}(S_{34}+1)+S_{56}(S_{56}+1)+S_{78}(S_{78}+1). \tag{5}$$

The set of quantum numbers S_{12}, S_{34}, S_{56}, S_{78} corresponds to the following eigenfunction of the operator H_{01}:

$$\psi\left(S_{12}m_{12};S_{34}m_{34};S_{56}m_{56};S_{78}m_{78}\right)=\left(\sum_{m_1,m_2}C^{S_{12},m_{12}}_{S_1,m_1,S_2,m_2}|S_1m_1\rangle|S_2m_2\rangle\right)\times\left(\sum_{m_3m_4}C^{S_{34},m_{34}}_{S_3,m_3,S_4,m_4}|S_3m_3\rangle|S_4m_4\rangle\right)\times\left(\sum_{m_5,m_6}C^{S_{56},m_{56}}_{S_5,m_5,S_6,m_6}|S_5m_5\rangle|S_6m_6\rangle\right)\times\left(\sum_{m_7,m_8}C^{S_{78},m_{78}}_{S_7,m_7,S_8,m_8}|S_7m_7\rangle|S_8m_8\rangle\right), \tag{6}$$

where $C^{S_{12},m_{12}}_{S_1m_1S_2m_2}$, etc. are the corresponding Clebsch–Gordan coefficients.

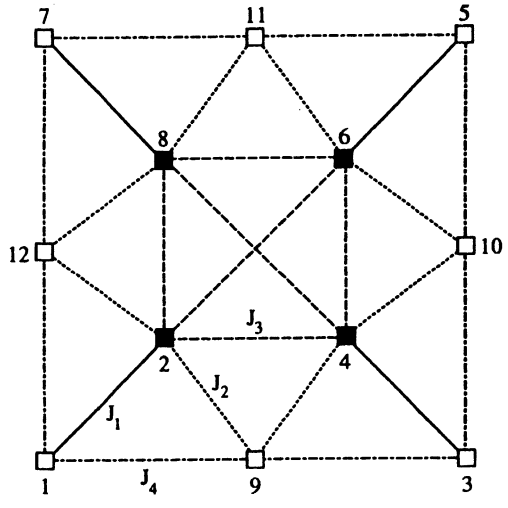

FIG. 2. Schematic depiction of the exchange bonds in the $Mn_{12}Ac$ cluster.[6]

TABLE I. Energy levels and wave functions of the Hamiltonian H_{01}.

ψ	i	M	$E_1/\lvert J_1\rvert$
(1/2 1/2 1/2 1/2)	1	2	3
(3/2 1/2 1/2 1/2)	2	3	6
(3/2 3/2 1/2 1/2)	3	4	9
(5/2 1/2 1/2 1/2)	-	4	11
(3/2 3/2 3/2 1/2)	4	5	12
(5/2 3/2 1/2 1/2)	-	5	14
(3/2 3/2 3/2 3/2)	5	6	15
(5/2 3/2 3/2 1/2)	-	6	17
(7/2 1/2 1/2 1/2)	-	5	18
(5/2 5/2 1/2 1/2)	-	6	19
(5/2 3/2 3/2 3/2)	6	7	20
(7/2 3/2 1/2 1/2)	-	6	21
(5/2 5/2 3/2 1/2)	-	7	22
(7/2 3/2 3/2 1/2)	-	7	24
(5/2 5/2 3/2 3/2)	7	8	25
(7/2 5/2 1/2 1/2)	-	7	26
(5/2 5/2 5/2 1/2)	-	8	27
(7/2 3/2 3/2 3/2)	-	8	27
(7/2 5/2 3/2 1/2)	-	8	29
(5/2 5/2 5/2 1/2)	8	9	30
(7/2 5/2 3/2 3/2)	-	9	32
(7/2 7/2 1/2 1/2)	-	8	33
(7/2 5/2 5/2 1/2)	-	9	34
(5/2 5/2 5/2 5/2)	9	10	35
(7/2 7/2 3/2 1/2)	-	9	36
(7/2 5/2 5/2 3/2)	-	10	37
(7/2 7/2 3/2 3/2)	-	10	39
(7/2 7/2 5/2 1/2)	-	10	41
(7/2 5/2 5/2 5/2)	10	11	42
(7/2 7/2 5/2 3/2)	-	11	44
(7/2 7/2 7/2 1/2)	-	11	48
(7/2 7/2 5/2 5/2)	11	11	49
(7/2 7/2 7/2 3/2)	-	12	51
(7/2 7/2 7/2 5/2)	12	13	56
(7/2 7/2 7/2 7/2)	13	14	63

The states (3) are degenerate in m_{ij}. The energy level with the given set of spins S_{12}, S_{34}, S_{56}, S_{78} correspond to the wave functions

$$|S_{12}S_{34}S_{56}S_{78}\rangle=\frac{1}{\sqrt{N}}\sum_P (S_{12}m_{12}S_{34}m_{34}S_{56}m_{56}S_{78}m_{78}), \tag{7}$$

where P are nontrivial permutations of the spins S_{ij} (together with m_{ij}), N is the number of these permutations, $m=m_{12}+m_{34}+m_{56}+m_{78}$ is the magnetic quantum number of the subcluster in the given state, $-M\leqslant m\leqslant M$, and $M=S_{12}+S_{34}+S_{56}+S_{78}$.

The energy levels $E_{(1)}/|J_1|$, wave functions ψ, and their corresponding M values are listed in Table I.

Before going on to the magnetic field dependence of the spectrum of energy levels, let us consider the matrix elements of the operator $\Sigma\tilde{S}_{iz}$. It is obvious that the matrix of this operator is diagonal in the space of eigenfunctions of the operator H_{01} since $\Sigma\tilde{S}_{iz}$ and H_{01} commute. The diagonal elements of this operator are equal to m.

The eigenfunctions of the Hamiltonian

$$H_0=H_{01}+\mu H\sum_i S_{iz}$$

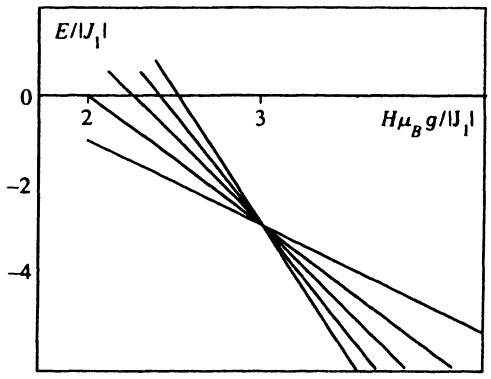

FIG. 3. Schematic representation of the behavior of the energy spectrum near the critical field.

are obviously the functions (7), and the eigenvalues are equal to

$$E(1,m)=E(1)+2m\mu_B H. \tag{8}$$

To determine the physical properties of the cluster in strong magnetic fields for $T\leqslant 300$ K, it is sufficient to trace out the behavior of the lower energy levels in a field. It follows from Table I and Eq. (8) that as the field grows, the lower energy levels corresponding to the m-values $m=-M$ (i.e., corresponding to the minimum possible values of m) interact in successions. Here, from the states listed in Table I the actual states are only those for which the value of M increases with growth of the energy $E(1)$ (there are 13 of them in all, and they are marked in Table I by an i). The behavior of these lower levels in a field is described by the formula

$$E_i^0=\epsilon_i(0)|J_1|-\mu(i+1)H. \tag{9}$$

Here

$$\epsilon_i(0)=3i\sum_{k=1}^{5}\delta_{ki}+5(i-2)\sum_{k=6}^{9}\delta_{ki}+7(i-4)\sum_{k=10}^{13}\delta_{ki}, \tag{10}$$

where $i=1,\ldots,13$. The critical fields for which the ground state changes are given by the formulas

$$H_{c1}=3|J_1|/g\mu_B,\quad H_{c2}=5|J_1|/g\mu_B,\quad H_{c3}=7|J_1|/g\mu_B,$$

and for $H=H_{c1}$ the levels E_i^0 with $i=1,\ldots,5$ simultaneously intersect (see Fig. 3); similarly, for $H=H_{c2}$ the levels E_i^0 with $i=5,\ldots,9$ intersect; and for $H=H_{c3}$ the levels E_i^0 with $i=9,\ldots,13$ intersect. For these fields at $T=0$ K the magnetization of the subcluster changes discontinuously to 8 μ_B. In fact, in the formation of the ground state of the Hamiltonian H_0 only the states $|1/2,1/2,1/2,1/2\rangle$, $|3/2,3/2,3/2,3/2\rangle$, $|5/2,5/2,5/2,5/2\rangle$, and $|7/2,7/2,7/2,7/2\rangle$ participate.

In this situation it is very important to take account of the corrections due to the influence of the perturbation V, which are capable of altering this ever so distinct picture of the shift of the ground state in a field. Before we start into an analysis of the influence of V on the behavior of the lower

TABLE II. Energy levels $\epsilon_i(h)$ (see formula (11)).

State	$\delta\epsilon$, ($\delta_k=\tau_k/\lvert\tau_1\rvert$, $k=2,3,4$)	S_{1z}	S_{2z}
1	$-3\delta_3+16\delta_2-32\delta_4$	-1	1/2
2	$-9.6\delta_3+9.6\delta_2-33.6\delta_4$	$-21/20$	3/10
3	$-11.48\delta_3+3.2\delta_2-35.2\delta_4$	$-11/10$	1/10
4	$-8.64\delta_3-3.2\delta_2-36.8\delta_4$	$-23/20$	$-1/10$
5	$-1.08\delta_3-9.6\delta_2-38.4\delta_4$	$-6/5$	$-3/10$
6	$-3.92\delta_3-14.63\delta_2-41.37\delta_4$	$-181/140$	$-16/35$
7	$-6.89\delta_3-19.66\delta_2-44.34\delta_4$	$-97/70$	$-43/70$
8	$-8.91\delta_3-24.69\delta_2-47.31\delta_4$	$-207/140$	$-27/35$
9	$-10.35\delta_3-29.71\delta_2-50.29\delta_4$	$-11/7$	$-13/14$
10	$-18.67\delta_3-34.29\delta_2-53.71\delta_4$	$-47/28$	$-15/14$
11	$-24.22\delta_3-38.86\delta_2-57.14\delta_4$	$-25/14$	$-17/14$
12	$-27\delta_3-43.43\delta_2-60.57\delta_4$	$-53/28$	$-19/14$
13	$-27\delta_3-48\delta_2-64\delta_4$	-2	$-3/2$

levels of the cluster, note that the ground state of the cluster in weak fields $S=10$ can be realized only under the condition that the ground states of ions 9–12 (not entering into the subcluster) are the states $|S_n m_{S_n}\rangle$, $n=9,\ldots,12$, where $S_n=2$, $m_{S_n}=-2$. Moreover, this situation also apologies to the case of strong fields. Thus, the actual states of the entire cluster in the first approximation are

$$\Psi_i=\psi_i\prod_{n=9}^{12}|S_n m_{sn}=-2\rangle.$$

Let us now average the perturbation V together with the rest of the Zeeman interaction over the states Ψ_i. Omitting lengthy expressions and formulas, we simply present the final results for the actual lower energy levels of the cluster with the necessary corrections taken into account.

In dimensionless units $\epsilon_i=E_i(h)/|J_1|$, $h=2\mu_B H/|J_1|$ we obtain

$$\epsilon_i(h)=\epsilon_i(0)+\delta\epsilon_i-h(i+9), \tag{11}$$

where the quantities $\epsilon_i(0)$ are given by Eq. (10) and the quantities $\delta\epsilon_i$ are given in Table II.

It is important to note that the perturbation V for the quantities J_1, J_2, J_3, and J_4 from Ref. 6 does not split the intersection points of the lower levels, which were calculated above on the basis of an analysis of the Hamiltonian H_0, but shifts them somewhat.

For $h<h_{c1}$ the ground state is the state ψ_1 with energy ε_1 (see Eq. (9)), for $h_{c1}<h<h_{c2}$ it is the state ψ_5 with energy $\epsilon_5(h)$, for $h_{c2}<h<h_{c3}$ it is the state ψ_9 with energy $\epsilon_9(h)$, and for $h>h_{c3}$ it is the state ψ_{13} with energy $\epsilon_{13}(h)$.

The critical fields h_{c1}, h_{c2}, and h_{c3} have the form

$$h_{c1}=3+0.48\delta_3-6.4\delta_2-1.6\delta_1,$$

$$h_{c2}=5-2.32\delta_3-5.03\delta_2-2.9\delta_1,$$

$$h_{c3}=7-4.16\delta_3-4.5\delta_2-3.43\delta_1,$$

where $\delta_k=J_k/|J_1|$. Note that the complete sequence of transitions ($\psi_1\to\psi_2\to\ldots\to\psi_{12}\to\psi_{13}$) is realized for $J_3>0$.

Before going on to the magnetization, let us dwell briefly on the question of quantum reduction of the magnetic moments of the ions of the subcluster consisting of two sublattices, one of which is formed by the magnetic moments of the ions 1, 3, 5, and 7, and the second—by the moments of the ions 2, 4, 6, and 8 (see Fig. 2).

Table II lists calculated values of the mean values of the spins of ions 1 and 2: S_{1z} and S_{2z} for each ground state ψ_i, which reflects the detailed picture of the transition from a ferrimagnetic structure to a ferromagnetic structure of the magnetic moments of the subcluster. Particularly noteworthy is the strong quantum reduction of the spins in the low-field (ferrimagnetic) collinear phase (ψ_1): thus, $S_{2z}=1/2$, $S_{1z}=-1$ in place of the classical values $S_{2z}=3/2$, $S_{1z}=-2$.

3. MAGNETIZATION OF THE CLUSTER $Mn_{12}Ac$

The dependence of the magnetization of the cluster on the field strength and temperature (for not too high T, $T\leqslant 300$ K) is given by the expression

$$\mu(H)=2\mu_B\frac{\sum_{i=1}^{13} i\exp(-\epsilon_i(h)/\tau)}{\sum_{i=1}^{13}\exp(-\epsilon_i(h)/\tau)}+18\mu_B, \tag{12}$$

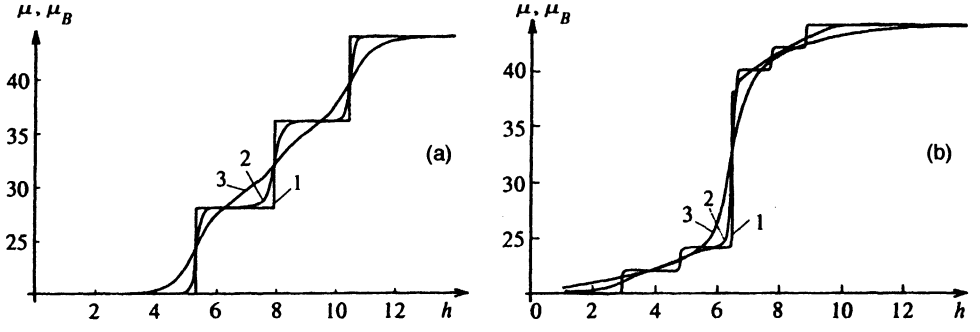

FIG. 4. Dependence of the magnetization of the $Mn_{12}Ac$ cluster on the magnetic field at different temperatures: $T=4.2$ K (*1*), 77 K (*2*), 300 K (*3*). The magnetization is measured in units of Bohr magnetons per molecule of $Mn_{12}Ac$, the magnetic field is measured in units of $H_{sc}=|J_1|/2\mu_B$, and the temperature is measured in units of $T_{sc}=|J_1|/k_B$, for $J_1=150\,\mathrm{cm}^{-1}$, $H_{sc}\approx 1.48$ MOe, and $T_{sc}\approx 216$ K. a) $J_1=-150\,\mathrm{cm}^{-1}$, $J_2=-60\,\mathrm{cm}^{-1}$, $J_3=-60\,\mathrm{cm}^{-1}$, $J_4=0$; b) $J_1=-150\,\mathrm{cm}^{-1}$, $J_2=-60\,\mathrm{cm}^{-1}$, $J_3=60\,\mathrm{cm}^{-1}$, $J_4=0$.

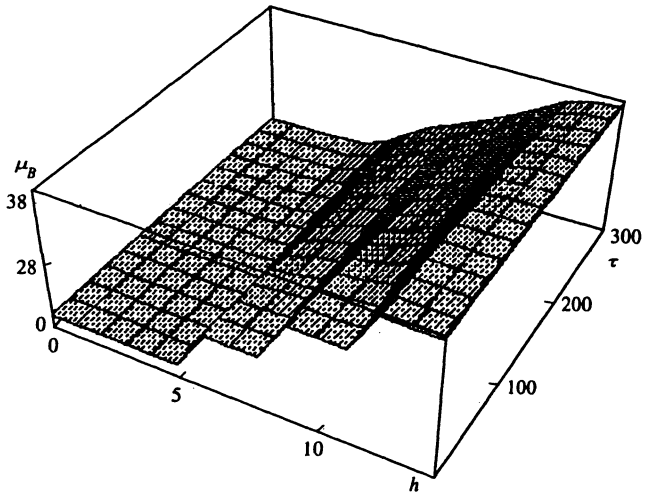

FIG. 5. The dependence $\mu=\mu(H,T)$ of the $Mn_{12}Ac$ cluster (see formula (12)).

where $\tau=T/|J_1|$ is the reduced temperature and $\varepsilon_i(h)$ is given by formula (11).

Figure 4a presents a typical dependence of the magnetic moment at low temperatures of the cluster $Mn_{12}Ac$ on the external magnetic field. The magnetization was calculated for the following values of the exchange parameters: $J_1=-150\,\mathrm{cm}^{-1}$, $J_2=J_3=-60\,\mathrm{cm}^{-1}$, $|J_4|=0$. Figure 4b shows the dependence $\mu(H)$ for another choice of the exchange parameters ($J_1=-150\,\mathrm{cm}^{-1}$, $J_2=-60\ \mathrm{cm}^{-1}$, $J_3=60\,\mathrm{cm}^{-1}$, $|J_4|=0$) and demonstrates the high sensitivity of the magnetization curves to the choice of the exchange parameters.

Figure 5 plots the surface $\mu=\mu(h,\tau)$ for $J_1=-150\ \mathrm{cm}^{-1}$, $J_2=J_3=-60\,\mathrm{cm}^{-1}$, $|J_4|=0$.

It is necessary to point out that the values of the above exchange integrals of the Hamiltonian (1) derived are approximate in character. They were estimated on the basis of magnetization data obtained in relatively weak fields in which the ferrimagnetic properties of the cluster are not manifested.

According to our calculations, the quantum jumps of the magnetization of the cluster $Mn_{12}Ac$ fall in the region of ultrastrong magnetic fields 10^6-10^7Oe. Methods for creating such fields with the help of magneto-cumulative generators and single-turn solenoids have been developed, as have measuring techniques in this range of fields.[20–23] The graphs presented above show that measurements of the magnetization in superstrong fields can give useful information about the exchange parameters.

4. CONCLUSION

In conclusion, we may summarize by noting that we have investigated a new mesoscopic quantum phenomenon in the ferrimagnetic cluster $Mn_{12}Ac$, consisting in the result that under the action of an external field there takes place a reorientation of spins in the cluster from ferrimagnetic ordering to ferromagnetic. This induced reorientation, in contrast to the classical effect of a continuous turning of the sublattices in macroscopic ferrimagnets, takes place by way of quantum jumps. Measurement of the magnetization curves of magnetic clusters such as $Mn_{12}Ac$ in ultrastrong fields should make it possible not only to detect a new mesoscopic quantum phenomenon, but also to determine the exchange constants of the cluster by a direct method.

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