Many-Spin Interactions and Spin Excitations in Mn$_{12}$

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In this work, the many-spin interactions taking place in Mn$_{12}$ large-spin clusters are extensively studied using the 8-spin model Hamiltonian, for which we determine the possible parameters based on experimental data. Account of the many-spin excitations satisfactorily explains positions of the neutron scattering peaks, results of EPR measurements and the temperature dependence of magnetic susceptibility. In particular, strong Dzyaloshinsky-Morya interactions are found to be important for description of neutron scattering data. The role of these interactions for the relaxation of the magnetization is qualitatively discussed.

75.40.Mg, 75.10.Dg, 75.50.-y, 75.25.+z

INTRODUCTION

In the last years, a new kind of magnetic compounds, the magnetic molecules, has been drawing the attention of physicists as well as chemists. Such molecules each contain a large number (typically, 10 to 20) of paramagnetic ions (such as Mn, Fe or Cu) coupled by exchange interactions. Each molecule, therefore, presents a mesoscopic system that is neither totally microscopic, nor totally macroscopic, but where micro- and macroscopic behavior coexist. These materials are promising for various practical applications. On the other hand, the coexistence of quantum and classical behavior in the clusters makes them very suitable objects for study of macroscopic quantum effects in spin systems. These studies, clarifying many problems of quantum theory of measurement, are also important for development of a physical basis for practical implementation of powerful algorithms of quantum computations, quantum cryptography and quantum searching.

Particularly, the Mn$_{12}$O$_{12}$(CH$_3$COO)$_{16}$(H$_2$O)$_4$ molecules (below referred to as Mn$_{12}$) recently became a subject of great interest. Each molecule contains a cluster of twelve manganese ions surrounded by acetate radicals and water molecules. The ground state of the clusters corresponds to a large total spin $S = 10$. The clusters possess a strong easy-axis anisotropy: the zero-field splitting between the states with $S_z = \pm 10$ and $S_z = \pm 9$ (where $S_z$ is the value of $z$-projection of the total cluster spin) is 14.4 K. Being stacked into a crystal, the molecules form a tetragonal lattice; in so doing the magnetic interactions between different clusters are very small (of order of $10^{-2}$ T). Thus, the crystal consisting of these molecules can be considered as an assembly of ideal noninteracting superparamagnetic entities, each being identical to the others.

These clusters have been successfully used for the study of mesoscopic quantum effects. In particular, resonant magnetization tunneling has been unambiguously registered in experiments on Mn$_{12}$. Moreover, there are experimental results supporting the hypothesis of "ground state-to-ground state" tunneling in Mn$_{12}$ below 2 K (for more detailed discussion, see Sec. III).

However, the progress in understanding the physical properties of Mn$_{12}$ is greatly hampered by the lack of an adequate description of these clusters. Indeed, the description of Mn$_{12}$ as a single spin $S = 10$ entity has been the starting point in most works devoted to this subject. We know of only a few theoretical attempts to account for the internal spin structure of the clusters, but even in these the relativistic anisotropic interactions have not been taken into account. In view of recent experiments showing that the single-spin model is seriously deficient, it is worthwhile reconsidering the many-spin aspects of Mn$_{12}$.

In this paper we focus on the many-spin interactions in Mn$_{12}$ clusters. We account for not only isotropic exchange interactions between ions in the cluster, but also various anisotropic interactions possibly present in Mn$_{12}$. Based on the results, we propose a spin Hamiltonian for these clusters. We show that this Hamiltonian can reproduce satisfactorily most recent experimental results, such as positions of neutron scattering peaks, high-frequency EPR data and the experimental dependence of the magnetic susceptibility on temperature. We note that the account of anisotropic interactions, especially the Dzyaloshinsky-Morya interaction (which has been missing up to now), is crucial for a detailed description of the experimental data.

The paper is organized as follows. In Sec. II we describe the basic model of Mn$_{12}$ used in this work and establish roughly its domain of validity. In Sec. III we derive and discuss the spin Hamiltonian for this model. Sec. III is devoted to discussion of relevant experimental data. In Sec. IV the numerical procedure used for calculations is discussed and the possible parameters of the spin Hamiltonian are presented. Comparison with experimental data is made. The results obtained are analyzed qualitatively and discussed in Sec. V, where the interpretation
of the neutron scattering data is presented. In Sec. VI we qualitatively discuss the relation between Dzyaloshinsky-Morya interactions and magnetic relaxation in Mn\textsubscript{12}. A summary is provided in Sec. VII.

I. THE DIMERIZED 8-SPIN MODEL OF Mn\textsubscript{12}

The cluster Mn\textsubscript{12}, schematically shown in Fig. 1, consists of eight Mn\textsuperscript{3+} ions having the spin 2 and four Mn\textsuperscript{4+} ions having the spin 3/2. The ions are coupled by exchange interactions, indicated in Fig. 1 by different lines connecting the ions. The values of the exchange integrals are not known, but estimates are given in Ref. 8: $J_1 = -150$ cm\textsuperscript{-1} (AFM exchange), $J_2 = J_3 = -60$ cm\textsuperscript{-1}, and $|J_4| < 30$ cm\textsuperscript{-1}. These values are rough, but describe correctly the scale of exchange interactions in Mn\textsubscript{12}. Recent experiments \cite{8} show that the excitations with spin values $S < 10$ are rather close to the ground state: the distance is 40–60 K (values differ in different reports). This is less than the energy of some states with the spin $S = 10$ (namely, the states $S_z = 0, \pm 1, \pm 2, \pm 3$), i.e. the lower states of the manifold $S < 9$ are lower than the higher states of the manifold $S = 10$. Thus, an adequate description of Mn\textsubscript{12} should account for the excitations with $S < 10$; i.e. the cluster should be considered as a many-spin system.

The total number of spin states in Mn\textsubscript{12} is large even for modern computers. But we can employ the fact that the exchange antiferromagnetic interactions $J_1$ (see Fig. 1) are much larger than all the others, so corresponding pairs of ions Mn\textsuperscript{3+} and Mn\textsuperscript{4+} form dimers with the total spin $s = 1/2$ (one of this pairs is designated in Fig. 1, it includes ions C and D). This model has already been successfully used for description of spin states of the cluster. Its validity is proven by megagauss-field experiments \cite{9}, the states of dimers with the spin $s$ higher than 1/2 (excitations of dimers) come into play when the external magnetic field is about 400 T, i.e. the excitations of dimers have energy about 370 cm\textsuperscript{-1}. Analogously, the dependence of the magnetic susceptibility of the cluster versus temperature \cite{10} shows that the dimer excitations contribute when temperature becomes as high as 150–200 K.

Based on these data, we can analyze the domain of validity of the "dimerized" model. To do this, we note that the exchange interactions $J_2, J_3$ and $J_4$ mix the ground state of a dimer with the dimer excitations, and the approximation of spin-1/2 dimers corresponds to the zeroth order perturbation theory with $1/J_1$ as an expansion parameter (similar approach has been used in Ref. 13).

To clarify this point, let us consider the level $a$ having, to the zeroth order, the energy $E_a$ with respect to the ground state. Let us denote the distance between the ground state and the excitation of dimer as $E_{ex} \sim 370$ cm\textsuperscript{-1}. The first-order correction to the energy of the level $a$ is of the order of $J^2/(E_{ex} - E_a)$, where $J'$ is the magnitude of exchange interactions between dimers and nondimerized spins (see below). Thus, accounting for the first-order corrections, the distance between the ground state and the level $a$ becomes

$$E'_a = E_a + C_a J'^2 [1/(E_{ex} - E_a) - 1/E_{ex}],$$

where $C_a$ is a factor of order of unity, depending on the specific level $a$. As will be shown below, $J'$ is of order of 70 cm\textsuperscript{-1}; so the first-order correction for the levels with energies about 70 cm\textsuperscript{-1} is already considerable, of order of 4 cm\textsuperscript{-1}. This estimate, though being rough, gives the correct order of magnitude of the error introduced by the dimerized 8-spin model.

Moreover, this error restricts the region of temperatures where the dimerized model can be successfully applied. E.g., as our calculations show, to obtain the correct value of the magnetic susceptibility $\chi$ at the temperature $T$, we need to account for the levels with energies about $4–5\, kT$. Obviously, the error in positions of these levels will introduce corresponding error in the dependence $\chi(T)$. Its analytical evaluation is difficult, and the comparison of the results of calculations with the experimental data, performed in Sec. IV is the better way to understand the temperature domain of validity of the dimerized model. As our results show, the dimerized model gives reasonable results for temperatures lower than about 50 K.

Recalling that the temperatures below 30 K are of most interest, we conclude that the dimerized model is satisfactory for present needs of experimentalists.

II. THE SPIN HAMILTONIAN OF Mn\textsubscript{12}

Thus, we consider the Mn\textsubscript{12} cluster as consisting of four "small" dimer spins $s = 1/2$ and four "large" spins $S = 2$ (corresponding to the four non-dimerized ions Mn\textsuperscript{3+}), coupled by exchange interactions (see Fig. 1). Moreover, we have to account for the anisotropc relativistic interactions in the cluster, so the Hamiltonian of the system can be written as:

$$\mathcal{H} = -J \sum_i s_i^2 - J' \sum_{<i,j>} s_i s_j + H_{rel},$$

(1)

where $s_i$ are the spin operators of small dimer spins $s = 1/2$, $s_i$ are spin operators of large spins $S = 2$, and $H_{rel}$ denotes the part of the Hamiltonian describing relativistic interactions in the cluster. Summation in (1) is over pairs of spins coupled by exchange interactions. In the first term of the Hamiltonian we took into account that each small dimer spin is coupled with all the other small spins, so $2 \sum s_i s_j = (\sum s_i)^2$ up to an insufficient additive constant.

To zeroth order in $J_1$, the exchange integrals of the dimerized models are connected with the initial exchange parameters $J_2, J_3$ and $J_4$ as follows:
\[ J = -J_2/2, \quad J' = -J_3 + 2J_4. \] (2)

Since the values of \( J_2, J_3 \) and \( J_4 \) are not known, the parameters \( J \) and \( J' \) are to be determined from experimental data (see Sec. [IV]).

Furthermore, different types of relativistic anisotropic magnetic interactions possibly present in Mn\(_{12}\) clusters should be included in the Hamiltonian. A large easy-axis anisotropy in the cluster is one of most important features to be taken into account. Generally, this anisotropy arises due to the single-site anisotropy of large spins (spins of Mn\(^{3+}\) ions) and various kinds of anisotropic exchange. We performed calculations for three basic types of easy-axis anisotropy in the cluster:

\[
H_{\text{rel}}^1 = -K_z \sum_{i=1}^{4} (S_i^z)^2, \quad (3a)
\]

\[
H_{\text{rel}}^2 = -J_{zz} \sum_{\langle i,j \rangle} s_i^z s_j^z, \quad (3b)
\]

\[
H_{\text{rel}}^3 = -J_{zz} \sum_{\langle i,j \rangle} s_i^z S_j^z, \quad (3c)
\]

where summations in (3a) and (3c) are over exchange-coupled pairs of spins. Anisotropy parameters \( \{K_z, J_{zz}\} \) have been chosen to give a correct value of the zero-field splitting between the states \( S_z = \pm 10 \) and \( S_z = \pm 9 \) (14.4 K). All three types of anisotropy give rather close energies of low-lying excitations (of energy less than 40 K), but higher excitations are reproduced best if the anisotropy is assumed to be of single-site type (3a), so we can conclude that the easy-axis anisotropy is primarily of single-site type. This result agrees with the conclusion drawn in Ref. [2]. We will consider only this kind of anisotropy.

Another potentially important sort of relativistic interaction is an in-plane anisotropy of large spins, i.e. \( H_{\text{rel}} \) can include a contribution of the form:

\[
H_{\text{rel}}^* = K_1 \left[ (S_1^x)^2 + (S_2^x)^2 + (S_3^x)^2 + (S_4^x)^2 \right], \quad (4)
\]

where the presence of fourth-order symmetry axis in the cluster is directly taken into account. The small spins \( s = 1/2 \) are excluded since \( (\sigma_x)^2 = (\sigma_y)^2 = (\sigma_z)^2 = 1 \) for Pauli matrices \( \sigma_x, \sigma_y \) and \( \sigma_z \); and only spins of non-dimerized Mn\(^{3+}\) ions give a nontrivial contribution. These ions are surrounded by eight oxygen ions forming a distorted octahedron. The axes of oxygen octahedra are significantly tilted from the \( c \)-axis of the cluster, therefore, this term can be relatively large, even comparable to the easy-axis anisotropy. But, surprisingly, our results show that this kind of interaction gives negligible effect, except for trivial renormalization of the easy-axis anisotropy constant \( K_z \) in (3a). If we account for this renormalization, the positions and the wave functions of excited levels remain almost unaffected even for \( K_1 = 3K_z \) (i.e., for the in-plane anisotropy three times larger than the easy-axis one). Thus, this kind of interaction can be excluded from further considerations.

Another important interaction is Dzyaloshinskii-Morya (DM) antisymmetric (DM) antisymmetric exchange. To our knowledge, the possible presence of DM-interactions in Mn\(_{12}\) was first suggested in Ref. [5] but little attention has been paid until now. Our results show that these interactions are, indeed, very important and have rather large magnitude.

A pair of ions coupled by DM-interaction is described by the Hamiltonian

\[
H_{DM} = D \cdot [S_1 \times S_2], \quad (5)
\]

and the magnitude of the DM-vector \( D \) can be estimated as \( D \sim \lambda A \), where \( A \) is the isotropic (nonrelativistic) exchange coupling between ions and \( \lambda \) is the spin-orbit coupling constant (which is rather small for transition ions). For comparison, the magnitude of easy-axis anisotropy is estimated as \( K_z \sim \lambda^2 A \), i.e. is of next order of smallness in comparison with \( D \). Thus, the DM-interactions in Mn\(_{12}\) can be expected to be important.

In the 8-spin model of the cluster there are DM-interactions of two kinds:

\[
H_{DM}^{1,2} = \sum_{\langle i,j \rangle} D_i^{ij} \cdot [s_i \times s_j], \quad (6a)
\]

\[
H_{DM}^{1,2} = \sum_{i} \sum_{j} D_i^{ij} \cdot [s_i \times s_j], \quad (6b)
\]

Summation in (6a) is over exchange-coupled pairs of spins; summation in (6b) is over all pairs of dimer spins, since all dimer spins interact with each other. We studied both kinds of DM-interaction and found that the second kind, i.e. \( H_{DM}^{1,2} \) involving small spins can be neglected. Therefore, we can neglect the interactions of the type (6b).

The crystal field in Mn\(_{12}\), governing the DM-interactions, possesses certain symmetry elements, thus imposing restrictions on the values of \( D^{ij} \). It is reasonable (and rather standard) to assume that the crystal field is determined mainly by the oxygen octahedra surrounding manganese ions in the cluster; so the symmetry of the crystal field is governed by the mutual arrangement of the oxygen octahedra. The following two symmetry elements are of interest for us. The first one is the fourth-order rotary-reflection axis parallel to the \( c \)-axis of the cluster. This symmetry is obviously preserved in the 8-spin model of the cluster, so the two DM-vectors \( D^{ij} \) and \( D^{1,8} \) (see Fig. [a]) define all the other \( D^{ij} \). The other element of symmetry is the mirror plane \( \rho \) parallel to the \( z \)-axis passing through the ions \( C \) and \( D \) (see Fig. [b]). The oxygen octahedra surrounding the ions \( A \) and \( B \) (see Fig. [a]) are invariant with a good degree of accuracy with respect to reflection in the plane \( \rho \) (inspection of the structure data supplied in Refs. [3,4] shows this); this symmetry is also preserved in the 8-spin model. Thus, the vector \( D^{1,8} \) (Fig. [a]) defines all the other DM-vectors in the Hamiltonian (5):
$D_{1,8}^{1} = -D_{1,5}^{1} = D_{2,5}^{1} = -D_{2,6}^{2} = -D_{3,6}^{3} = D_{3,7}^{4} \quad (7a)$

$\quad = -D_{4,7}^{4} = D_{4,8}^{4},$

$D_{1,8}^{1} = D_{1,5}^{1} = D_{2,5}^{1} = -D_{2,6}^{2} = -D_{3,6}^{3} = -D_{3,7}^{4} \quad (7b)$

$\quad = D_{4,7}^{4} = D_{4,8}^{4},$

$D_{1,8}^{1} = -D_{1,5}^{1} = D_{2,5}^{1} = -D_{2,6}^{2} = D_{3,6}^{3} = -D_{3,7}^{4} \quad (7c)$

$\quad = D_{4,7}^{4} = -D_{4,8}^{4}.$

Obviously, any other vector $D_{i,j}^{k}$ can be taken as a basis instead of $D_{1,8}^{1}$. No other symmetry elements allow for further reduction, so DM-interactions in Mn$_{12}$ are described using three parameters: $D_{x,y}^{1,8}$, $D_{y}^{1,8}$ and $D_{z}^{1,8}$. Below, these parameters are denoted simply as $D_{x}$, $D_{y}$ and $D_{z}$.

As our results show, in the DM-Hamiltonian the terms proportional to $D_{y}$ produces negligible matrix elements (a few percent in comparison with other terms). It occurs due to symmetry reasons: the inspection of the relations shows that the components $D_{x}$ and $D_{z}$ transform antisymmetrically with respect to reflection in the plane $\rho$, but the component $D_{y}$ transforms symmetrically. The matrix elements of the terms proportional to $D_{y}$ nearly cancel each other, leading to negligible matrix elements. Therefore, these terms are excluded from consideration and we set $D_{y} = 0$ with negligible error.

Finally, having studied all the interactions described above, we can write down the Hamiltonian of the cluster in the following form:

$$\mathcal{H} = -J \left( \sum_{i} s_{i} \right)^{2} - J' \sum_{(k,l)} s_{k} s_{l} - K_{z} \sum_{i=1}^{4} \left( S_{i}^{z} \right)^{2} \quad (8)$$

$$\quad + \sum_{(i,j)} D_{i,j}^{k} \cdot \left[ s_{i} \times s_{j} \right],$$

where the DM-vectors $D_{i,j}^{k}$ obey the relations with the parameter $D_{y}^{1,8} \equiv D_{y} = 0.$

### III. REVIEW OF RELEVANT EXPERIMENTAL RESULTS

At present, data of various experiments on magnetic molecules Mn$_{12}$Ac are available, including the temperature dependence of the effective magnetic moment of the cluster $\mu_{eff}(T)$. The results of EPR experiments [11] [12] and dynamic susceptibility measurements [15] [14] [13] [12] [11] [10] [9] are in excellent agreement with the neutron scattering data [14] and specific heat data [12]. Unfortunately, only few of these data can be used for determining the parameters of the 8-spin Hamiltonian for Mn$_{12}$ clusters.

Recent high-frequency EPR experiments [3] refined the description of the easy-axis anisotropy of the cluster and showed that the anisotropy Hamiltonian in the single-spin model can be approximated as follows:

$$H = \alpha S_{z}^{2} + \beta S_{y}^{2} + \gamma (S_{x}^{2} + S_{y}^{2}), \quad (9)$$

$$\alpha = -0.56 \text{ K}, \quad \beta = -11.08 \cdot 10^{-4} \text{ K},$$

$$\gamma = 2.88 \cdot 10^{-5} \text{ K},$$

where $S_{x}, S_{y}$ and $S_{z}$ denote the operators of the total spin of the cluster. It means, in terms of a many-spin approach, that the energies of the low-lying levels with spin $S = 10$ obey Eq. (9). It is worth noting that the derived values of quartic corrections $\beta$ and $\gamma$ are rather large and, as our calculations show (see below), seem to be poorly explained using the single-spin description of Mn$_{12}$, i.e. when accounting only for the states belonging to the $S = 10$ manifold. Our results show that the excited levels with $S < 10$ are necessary to give reasonable values for the quartic corrections.

Another set of results, very useful for elucidating the many-spin interactions in Mn$_{12}$Ac, is the neutron scattering results supplied in Ref. [10]. The experiments have been performed at very low temperatures (mostly, 1.5 K to 2.5 K), where only the lowest levels $S_{z} = \pm 10$ are populated. Since the selection rule for neutron scattering is $\delta S_{z} = 0, \pm 1$, only the levels with $S_{z} = \pm 9$ can give rise to scattering peaks (the levels with $S_{z} = \pm 11$ have too large energies and can be excluded).

Results of these experiments can be summarized as follows. A prominent peak of spin origin at about 0.3 THz has been detected and attributed to the transitions to the levels with $S = 10, S_{z} = \pm 9$, in excellent agreement with all previous data (0.3 THz corresponds to about 14.4 K). At higher energies, two sets of peaks have been detected around 1.2 THz and 2.0 THz. The fitting proposed in Ref. [10] gives two peaks in the first set (at energies about 57 K and 66 K) and three peaks in the second set (at energies 90 K, 96 K and 105 K); but authors indicate clearly that possibly more peaks are present (most likely, three peaks in the first set and four or five in the second).

Another interesting detail of the neutron scattering spectra is a very broad mode situated at about 0.2 THz; this mode disappears when the temperature is less than about 2 K.

The authors have not managed to interpret these features, except for the peak at 0.3 THz. They pointed out that there is particular difficulty in interpretation of the peaks at 1.2–1.3 THz: the model they used for susceptibility fitting gives two degenerate levels $S = 9$ at about 33 K, an obvious contradiction with the neutron scattering spectrum. We show below that the 8-spin model developed here can overcome these difficulties and gives correct positions for neutrons peaks at 1.2 THz along with a correct description of the susceptibility data.

Thus, we found the following experimental results to be relevant for the purpose of a quantitative description of the Mn$_{12}$ clusters. The distance between the ground state and the first excited level(s) is 14.4 K. The energies (the anisotropy splittings) of the low-lying levels, belonging to the $S = 10$ manifold, obey formula (9). There are two or three neutron peaks around 60–70 K, two of them are situated at 57 K and 66 K. Also, there are up to five peaks around 100 K, three of them are at 90 K, 96 K and...
105 K. The temperature dependence of the susceptibility
(or, equivalently, the dependence $\mu_{eff}(T)$) has the form
displayed in Refs. 3, 5 and Fig. 1.

The other experimental results, though providing important
information about Mn$_{112}$, are much less suitable for
our purposes (to a large extent, because different, a priori equally probable, interpretations are possible).

**IV. NUMERICAL CALCULATIONS AND PARAMETERs OF THE 8-SPIN MODEL.
COMPARISON WITH EXPERIMENT**

Having derived the spin Hamiltonian for the 8-spin model of Mn$_{112}$, we attempted to extract its parameters
from the relevant experimental data.

We used the following two-step numerical scheme. At
the first step, the relativistic term $H_{rel}$ has been ne-
glected resulting in an isotropic exchange Hamiltonian.

The eigenstates of this Hamiltonian are degenerate with
respect to $S_z$. Thus, it is sufficient to take into account
only the states with $S_z = 0$, so the exchange Hamiltonian
(represented by a matrix $1286 \times 1286$) has been diagonal-
ized within the subspace spanned by these states. Then,
as the second step, the relativistic anisotropic interactions
have been taken into account. Among the states obtained
at the first step (having $S_z = 0$), we retain only those
with the energy less than $E_{cut}$ (a sufficiently large value
for this parameter has been chosen) and generate
the corresponding states with different $S_z$ (basis states).

Then the complete Hamiltonian (9) has been diagonal-
ized within the subspace spanned by the generated basis
states. Calculations with different values of $E_{cut}$ have
been performed to assure that the positions of lower levels
are obtained with desired accuracy. Typical values of $E_{cut}$
were about 250 K: the levels with higher energies are not
worth including due to the limited accuracy of the
8-model itself (see Sec. 3).

Based on the procedure described above, the fitting
of relevant experimental data (Sec. 11) has been made
and the possible parameters of the 8-spin Hamiltonian
determined.

Neutron scattering data are of primary interest for us.
We focus our attention on the positions of the neutron
peaks, since the amplitudes depend strongly on details
of the experiments. We first assume an ideal experi-
ment, where the resolution of the setup is infinite and
the neutrons with all possible scattering vectors are de-
tected (i.e., the detector has infinite aperture). In this
case, at zero temperature, the cross-section of neutron
scattering at the energy $E$ is

$$\sigma(E) = \int_{\mathbb{R}^3} d^3 q \ F(q) \sum_{a,b} (\delta_{a,b} - q_a q_b / q^2) \times \sum_{m,n} \exp[iq(r_m - r_n)]$$

where $\delta$ is a constant, $F(q)$ is the form-factor of manganese ions, $q$ is a scattering vector, $n, m$ enumerate
different ions, and $a, b$ refer to the Cartesian coordinates
($x, y, z$). The integration is performed over all vectors
$q$. $E(\psi)$ denotes the energy of the state $\psi$, $|0\rangle$ denotes
the ground state, which is the only one populated at zero
temperature. The transitions with $\Delta S_z = 0, +1$ can be
neglected since there is only one state $S_z = 10$ and no
states $S_z = 11$. In this case, the total cross-section (10)
is proportional to the quantity

$$V = \sum_i |\langle \phi_i^{(9)} | \psi \rangle|^2,$$

where the state $\psi$ has the energy $E(\psi) = E$ with re-
spect to the groundstate; i.e., the state $\psi$ is the final
state of the neutron scattering process and gives rise to
a neutron peak at the energy $E(\psi)$ of the amplitude pro-
portional to $V$. The summation in (11) is performed
over all basis levels having $S_z = 9$; these levels are den-
oted as $\phi_i^{(9)}$. Equation (11) expresses the simple fact
that only the transitions with $\Delta S_z = -1$ are allowed
in the neutron scattering process, since the transitions with
$\Delta S_z = 0, +1$ are absent. Below, the quantity $V$ is re-
ferred to as a normalized cross-section for the level $\psi$.
Our results show that $V$ discriminates easily the eigen-
states which can give rise to noticeable neutron scattering
peaks.

Furthermore, the values of parameters $\alpha$ and $\beta$ de-
scribing the easy-axis anisotropy in Eq. 10, have been
taken into account in determination of the cluster pa-
rameters. The energies of the five lowest levels, having
spin $S = 10$, have been approximated by a fourth-order
polynomial, following Eq. (4), and the coefficients $\alpha$ and
$\beta$ have been extracted and compared to the experimental
data.

As a result of calculations, the following three sets of
the cluster parameters have been found to provide the
best fitting of experimental data:

Set A: $J = 0, J' = 105 K, K_z = 5.69 K, D_z = -1.2 K,$ $D_x = 25 K$;

Set B: $J = 23.8 K, J' = 79.2 K, K_z = 5.72 K, D_z = 10 K, D_x = 22 K$;

Set C: $J = 41.4 K, J' = 69 K, K_z = 5.75 K, D_z = 10 K,$ $D_x = 20 K$.

The positions of neutron peaks calculated for these sets
of parameters are presented in Fig. 1. The graphs show
the dependence of normalized cross-section vs. the level
energy. It is seen from these figures, that the normal-
ized cross-section is extremely small (less than $10^{-2}$)
for most of levels, and only few states can give rise to no-
ticeable neutron scattering peaks. Moreover, to facilitate
the analysis of the data for reader, the positions of neutron peaks are listed in the Table I. The values of the easy-axis anisotropy parameters $\alpha$ and $\beta$ are listed in the Table I.

As the results show, each of the parameter sets reproduces reasonably well its own portion of the experimental results. All the sets give reasonably good positions of the low-energy neutron peaks at 0.3 THz (14.4 K), 1.19 THz (57 K) and 1.38 THz (66 K). The parameter set A also gives the values of anisotropy parameters $\alpha$ and $\beta$, rather close to the experimental ones, but the neutron peaks corresponding to higher energies (around 2 THz) are reproduced poorly. The parameter sets B and C give correctly only the order of magnitude of $\alpha$ and $\beta$, but reproduce better the positions of the high-energy neutron peaks.

Finally, the temperature dependence of the effective magnetic moment $\mu_{\text{eff}}$ of the cluster has been calculated for all three sets of parameters using the formula

$$\mu_{\text{eff}}(T) \equiv \sqrt{3\chi(T) \cdot kT},$$

where $\chi$ is the susceptibility of the cluster, $k$ is Boltzmann’s constant and $T$ is the temperature. The susceptibility $\chi(T)$ has been calculated in a way reproducing the experimental procedure. The Zeeman term, describing the effect of an external field has been introduced into the Hamiltonian (8). The field magnitude $H = 1 \text{ mT}$ has been chosen following Ref. 16. The resulting Hamiltonian has been diagonalized, and the component of the cluster spin $S_H$ along the field has been calculated by means of quantum-statistical averaging over the Gibbs canonical ensemble. This routine has been repeated several times for different orientations of the field, and the obtained values of $S_H$ have been averaged. It corresponds to a powder sample measurements, when the crystallites are randomly oriented with respect to the field. The susceptibility $\chi$, following a standard experimental procedure, has been calculated as a ratio of the resulting average cluster spin to the field magnitude $H$. Finally, the value $\mu_{\text{eff}}$ has been obtained applying Eq. (12).

The curves $\mu_{\text{eff}}$ calculated for the three sets of cluster parameters, are presented in Fig. 4 along with the experimental data. All the sets give almost coinciding curves, and below 50 K the agreement with experiment is good. The region of temperatures higher than 50 K can not be reproduced satisfactorily: as our test calculations showed, to obtain the correct value of effective moment $\mu_{\text{eff}}$ at the temperature $T$, we need to account for the levels with energies about 4–5 $kT$. When calculating the curves presented, only the levels with energies less than 250 K have been taken into account, thus restricting the correctly described temperature region.

V. QUALITATIVE ANALYSIS OF THE RESULTS AND INTERPRETATION OF EXPERIMENTAL DATA

At present, having rather limited number of the relevant experimental data, it is hard to distinguish between the parameter sets A, B and C. The easy-axis anisotropy parameters $\alpha$ and $\beta$ are obtained with good precision in EPR experiments, but the magnetization measurement data suggest other values for these parameters; so, comparison of the experimental values of $\alpha$ and $\beta$ with our results can not serve as a definitive basis for judgement. Also, the quality of the description of the high-energy neutron peaks can not be decisive, since the disagreement can be attributed to the limited accuracy of the dimerized 8-spin model itself. Megagauss-field experiments along with careful measurements of the low-energy peaks (around 1.2 THz) and fitting of their amplitudes seems to be a promising strategy for future investigations.

Nevertheless, the results already obtained provide new important information about the role of many-spin interactions in Mn$_{12}$ clusters. In this section we focus our attention on the qualitative consideration of the results obtained and discuss the interpretation of the experimental data.

First, it is worthwhile to note that the consideration of states with spin $S$ less than 10 leads to rather large quartic corrections to the energy of easy-axis anisotropy. If these excited states are not taken into account, i.e. if only the states with $S = 10$ are included, the value of $\beta$ is of order of $10^{-5}$ K.

Another important fact is the large magnitude of the Dzyaloshinski-Morya (DM) interactions in the cluster Mn$_{12}$. In our opinion, this can be attributed to the low symmetry of the cluster. Indeed, the strength of the DM-interaction is governed to a large extent by asymmetry of crystal field acting on the interacting ions. An instructive example is provided in Ref. 26: the DM-interaction can emerge for ions located at the surface of a magnet, even though these interactions are prohibited for ions in the bulk of the magnet. In some sense the Mn$_{12}$ molecule possesses “surface” everywhere, and the symmetry of the crystal field is rather low.

The presence of the large Dzyaloshinsky-Morya term in the Hamiltonian provides a key to an explanation of the neutron scattering data. First, the DM-terms lead to the appearance of the two neutron peaks around 1.2 THz. If these terms are absent, there are two degenerate levels with $S_z = 9$ around 1.2 THz. Among all the interactions we considered (see Sec. I), only the DM-interaction can lift this degeneracy and provide a large splitting (about 9 K), as observed in experiments. Similarly, according to our calculations, several peaks around 2 THz appear only due to DM-interactions.

The origin of the peak at 0.3 THz has been completely explained in Ref. 12: it appears because of easy-axis anisotropy splitting the levels with different $S_z$. Our re-
The relaxation of magnetization has been extensively studied within the single-spin model of Mn$_{12}$. The Hamiltonian (1) of this model provides transitions with $\Delta S_z = \pm 4$ only, and an external transversal field $H_x$ is necessary to allow the $\Delta S_z = \pm 1$ transitions. Different sources of this field have been considered: a hyperfine field induced by nuclear spins and a dipole-dipole field induced by other clusters. There are certain difficulties facing these interpretations. E.g., as reported in Refs. [1], [2], the relaxation rate increases on dilution of Mn$_{12}$ in solution, although the dipole-dipole interactions between the clusters decreases; this seems to be difficult to explain with the relaxation mechanism based on intercluster dipole-dipole interactions. The other mechanism, based on the hyperfine fields, cannot easily explain the high value of the crossover temperature.

Strong Dzyaloshinsky-Morya interactions constitute another source of magnetic relaxation in Mn$_{12}$. It obviously allows the $\Delta S_z = \pm 1$ transitions. On solution, the dipole-dipole fluctuating fields between the clusters decrease, thus decreasing the decohering influence of the environment, so the relaxation rate increases. This agrees with experimental results. Relatively large magnitude of DM-interactions can, in principle, explain the high value (2 K) of the crossover temperature. This shows that the quantitative study of DM-based relaxation in Mn$_{12}$ is important.

Nevertheless, we emphasize that, to our knowledge, current information is not sufficient for judgement in favor of some single relaxation mechanism. At present, all of them can be considered as equally probable, and the possibility of a combination of different mechanism exists.

Independent of the problem of relaxation in Mn$_{12}$, DM-interactions present an interesting and important mechanism for magnetic relaxation. It can be significant, for example, in nanosized particles, where large DM-interactions can arise due to reduced symmetry at the surface. The relaxation based on this interaction is rather unusual: it is related not to the potential barrier created by easy-axis anisotropy, but to the barrier created by isotropic exchange. The point is that the Dzyaloshinsky-Morya term $H_{DM}$ couples the states with different values of total spin $S$, i.e.

$$\langle S, S_z \mid H_{DM} \mid S \pm 1, S_z \pm 1 \rangle \neq 0.$$  \hspace{1cm} (13)

This feature differs drastically from standard consideration of relaxation in small particles, where only the anisotropy barrier is usually taken into consideration.

Isotropic exchange interactions are usually rather strong, but it does not necessarily means that the DM-based relaxation is negligible. E.g., in spin-frustrated systems the height of the exchange barrier can be considerably reduced. Moreover, it can be significant in certain non-frustrated systems. For the relaxation based on DM-interactions, the relaxation time should be governed by the ratio $D/A$, where $D$ is the absolute value of...
Dzyaloshinsky-Morya vector and $A$ is the exchange integral. On the other hand, for "conventional" relaxation mechanism, when the anisotropy barrier is overcome, the ratio $U/K$ governs the relaxation rate, where $K$ is the anisotropy constant and $U$ is the strength of the interaction between the spins and their dissipative environment (e.g., spin-phonon coupling constant). Situations with $D/A \gg U/K$ are not impossible. Therefore, quantitative investigations of relaxation mechanisms based on DM-interactions is of great interest and importance.

VII. SUMMARY

In the present work, we have performed an extensive study of spin excitations in $\text{Mn}_{12}$, explicitly accounting for its many-spin internal structure. The dimerized 8-spin model of the $\text{Mn}_{12}$ cluster has been used. Along with isotropic exchange coupling, various kinds of anisotropic relativistic interactions have been studied: anisotropic exchange coupling between the cluster ions, single-site anisotropies of easy-axis and in-plane type, and various kinds of Dzyaloshinsky-Morya (DM) interactions. Surprisingly, most of these interactions play only a minor role.

As a result, we propose a basic many-spin Hamiltonian which includes isotropic exchange couplings, single-site anisotropies of easy-axis type and DM-interactions between the cluster spins. Three possible sets of parameters are determined from the relevant experimental data. The results of our calculations reproduce satisfactorily various experimental results, such as positions of neutron scattering peaks, high-frequency EPR data and the experimental dependence of the magnetic susceptibility on temperature.

In particular, our results suggest rather strong Dzyaloshinsky-Morya interactions are present in the $\text{Mn}_{12}$ cluster. We have discussed qualitatively the possible relation of these interactions to the unusual magnetic relaxational properties of $\text{Mn}_{12}$. We emphasized that DM-interactions present interesting relaxation mechanisms worth further investigations.

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FIG. 1. Schematic plot of the Mn_{12} cluster. Small black circles represent Mn^{4+} ions, large white circles — Mn^{3+} ions. Different types of lines connecting the ions (solid, dashed, dotted and dash-dotted) correspond to different types of exchange interactions ($J_1$, $J_2$, $J_3$ and $J_4$).

FIG. 2. A schematic plot of the 8-spin system representing the Mn_{12} cluster. White large circles represent large spins ($S = 2$), and dark small squares represent small dimer spins ($s = 1/2$).

FIG. 3. Dependence of the normalized cross-section vs. level energy (in K), calculated for the three sets of the cluster parameters (A, B and C, see text). The levels producing noticeable neutron peaks can be easily discriminated from the others.

FIG. 4. Temperature dependence of the effective magnetic moment of the cluster $\mu_{\text{eff}}$ (in Bohr’s magnetons). Results of calculations with the three sets of parameters are shown: the set A (solid line), the set B (dashed line) and the set C (dotted line). Large solid squares represent experimental data. The results of calculations with the sets A and B are very close to each other, and the corresponding curves merge on the figure.

| Low-energy peaks (1.2 THz) | 57 K   | 58.2 K | 55.2 K | 56.7 K |
|----------------------------|--------|--------|--------|--------|
| maybe, more                | 76.6 K | 75.7 K |

| High-energy peaks (2 THz)  | 90 K   | 124.4 K | 98.3 K | 88.8 K |
|----------------------------|--------|---------|--------|--------|
| maybe, more                | 127.1 K | 122.1 K |

TABLE I. The positions of neutron peaks: comparison between experimental data and calculated results. Calculations have been made for the three possible sets of the cluster parameters (A, B and C, see text). The levels with normalized cross-section more than 0.05 and energy less than 130 K are included in the table.

| Experiment | Set A | Set B | Set C |
|------------|-------|-------|-------|
| 14.4 K     | 14.4 K | 14.4 K | 14.4 K |

| Experiment | Set A | Set B | Set C |
|------------|-------|-------|-------|
| 14.4 K     | 14.4 K | 14.4 K | 14.4 K |

TABLE II. Parameters $\alpha$ and $\beta$ of the easy-axis anisotropy: comparison between experimental data and calculated results. Calculations have been performed for the three possible sets of the cluster parameters (A, B and C, see text).

|          | Experiment | Set A | Set B | Set C |
|----------|------------|-------|-------|-------|
| $\alpha$ (K) | 0.56       | 0.63  | 0.68  | 0.67  |
| $\beta$ (mK)  | 1.11       | 0.7   | 0.45  | 0.49  |
Fig. 1
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Fig. 2
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Fig. 3
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Fig. 4
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