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Magnetic excitations in molecular magnets with complex bridges: the tetrahedral molecule Ni$_4$Mo$_{12}$

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Abstract. We investigate the spectroscopic magnetic excitations in molecular magnets with complex intermediate structure among the magnetic ions. Our approach consists in introducing a modified spin Hamiltonian that allows for discrete coupling parameters accounting for all energetically favorable spatial distributions of the valence electrons along the exchange bridges connecting the constituent magnetic ions. We discuss the physical relevance of the constructed Hamiltonian and derive its eigenvalues. The model is applied to explore the magnetic excitations of the tetrameric molecular magnet Ni$_4$Mo$_{12}$. Our results are in a very good agreement with the available experimental data. We show that the experimental magnetic excitations in the named tetramer can be traced back to the specific geometry and complex chemical structure of the exchange bridges leading to the splitting and broadness of the peaks centered about 0.5 meV and 1.7 meV.

1 Introduction

The physical properties, such as energy spectra, susceptibility, etc., of magnetic clusters at the nanoscale depend on their size, shape and the presence of different bondings among the constituent chemical elements and thus the distribution of ligands between the magnetic ions (for more details see [1–4] and references therein). Some prominent examples are Mn based magnetic compounds [5–11] and spin clusters with Ni magnetic ions [12–15].

Magnetic molecules possess unique properties that can be characterized with great accuracy both experimentally and theoretically. Thus they are ideal tools to gain useful insights into the underlying coupling mechanisms. The study of basic units like tetramers [16,17] prove the importance of analytical methods in revealing the role of electrons correlations underpinning molecular magnetism. On the experimental side, Inelastic Neutron Scattering (INS) [18–21] plays a central role in determining the relevant magnetic spectra. In complement to different magnetic measurement methods, INS technique appears to be essential, and in the past decades it has been widely applied to explore the properties of spin clusters. Experiments on the spin dimer [Ni$_2$(ND$_2$)$_2$H$_4$ND$_2$]$_2$Br$_3$Br$_2$ have demonstrated the important contribution of neutron spectroscopy [22]. INS measurements were obtained for different magnetic clusters, such as: The trimer La$_4$Cu$_3$MoO$_{12}$, with strong intratrimer antiferromagnetic interactions, where the copper ions form an isolated triangle [23], the Fe based molecular wheel with eighteen spin-$\frac{5}{2}$ ions [24], the dimer SrCu$_2$(BO$_3$)$_2$ with observed multiplet excitations [25,26], the polyoxomolybdate Mn$_{72}$Fe$_{32}$ [27], and the magnetic molecule Fe$_9$ in the presence of an external magnetic field [28].

In the present work, we propose an approach based on the assumption that in a molecular magnet with multiple exchange bridges between any two magnetic centers (ions) the distribution of unpaired valence electrons is not unique. Thus, the electron’s density distribution might vary among the existing exchange bridges affecting the transition energy, and consequently leading to either a broadened excitation width or splitting in the energy spectrum. Accordingly the number of all energy levels form a set that can utterly identify the most relevant spin bonds, despite being indistinguishable. To this end, we introduce a modified microscopic spin Hamiltonian with discrete couplings that incorporates distinct spin coupling mechanisms among equivalent spins allowing one to identify the different exchange paths. The proposed Hamiltonian leads to an unperturbed energy structure that distinguishes the relevant magnetic features from those arising due the magnetic anisotropy. It is worth mentioning that the present approach was successfully applied to the study of the magnetic excitations in the trimers A$_3$Cu$_3$(PO$_4$)$_4$ with (A = Ca, Sr, Pb) [29].

Here, the present method will be validated by reproducing the experimentally obtained INS spectrum of a molecular magnet that has generated a great deal of
interest among researchers both on the theoretical, as well as the experimental sides. This is the magnetic molecule $[\text{Mo}_{12}\text{O}_{30}\text{OH}]_{10}\text{H}_{2}(\text{Ni(H}_{2}\text{O})_{3}4\text{]}$, denoted by Ni$_4$Mo$_{12}$, where four spin-1 Ni$^{2+}$ ions are sitting on the vertices of a distorted tetrahedron [30]. We would like to point out that previous studies [31,32] did not succeed to obtain the main peaks and the broadening in the INS spectrum, see Figure 1, despite including single-ion anisotropy or higher-order terms in the Heisenberg model with nearest-neighbor interaction or even using the Hubbard model.

2 The model and the method

In order to identify the experimentally observed magnetic peaks, see Figure 1, one has to calculate the scattering intensities $I_{n,n'(q)}$, of the existing transitions and analyse their dependence on the temperature and the magnitude of the neutron scattering vector. For identical magnetic ions, we have [18–21]

$$I_{n,n'(q)} \propto F^2(q) \sum_{\alpha,\beta}^{\Theta S^{\alpha\beta}}(q,\omega_{n,n'}).$$

Here $\omega_{n,n'}$ is the transition frequency, $F(q)$ is the spin magnetic form factor [33], $S^{\alpha\beta}$ are the elements of polarization factor, $S^{\alpha\beta}(q,\omega_{n,n'})$ are the magnetic scattering functions and $\alpha,\beta,\gamma \in \{x,y,z\}$.

To determine the energy level structure and the transitions corresponding to the experimentally observed magnetic spectra one needs a minimal number of parameters to account for all couplings in the system. The principal assumption is that the magnetic excitations of spin clusters obtained via INS are mainly governed by the exchange of electrons between effective spin magnetic centers. Then, the experimental data are interpreted in terms of a well defined microscopic spin model. In the absence of anisotropy, i.e. negligible spin-orbit coupling, the exchange interaction in molecular magnets can be described by the Heisenberg model

$$\hat{H} = \sum_{i \neq j} J_{ij} \hat{s}_i \cdot \hat{s}_j, \quad (2)$$

where $J_{ij} = J_{ji}$ is the exchange coupling that effectively accounts for the exchange interaction between the $i$th and $j$th ions. However, to distinguish all magnetic excitations one has to use an appropriate spin model leading to an energy sequence such that the scattering functions in (1) identifies the relevant spin bonds. Therefore, even with a selected a priori spin coupling scheme for a cluster with complex intermediate structure Hamiltonian (2) may not be fully adequate to obtain the correct energy structure.

2.1 The effective spin Hamiltonian

In order to characterize uniquely each pair of magnetic centers in a magnetic cluster, bonded via more than one intermediate bridge, we propose the following Hamiltonian

$$\hat{H} = \sum_{i \neq j} J_{ij} \hat{s}_i \cdot \hat{s}_j, \quad (3)$$

where the couplings $J_{ij} = J_{ji}$ are effective exchange constants and the operator $\hat{s}_i = (\hat{\sigma}_i^x, \hat{\sigma}_i^y, \hat{\sigma}_i^z)$ accounts for the variation in valence electron’s distribution with respect to the $i$th magnetic center.

A detailed derivation of the effective Hamiltonian (3) is very lengthy and falls beyond the scope of this study (the case of magnetic dimers is published in Ref. [34]). In the following we will give a brief account of the main steps leading to construct the ensuing Hamiltonian (3). Let us point out that our computations are based on the Molecular Orbital Theory [35] in terms of the complete active space self consistent field method [36,37]. We assume that each exchange bridge connecting two magnetic centers possess a number of paired valence electrons, nuclei and thus favor a particular spatial distributions of electrons. The canonical Hamiltonian leading to (3) accounts for the kinetic energy, electron-electron and electron-nuclei interactions of all valence electrons within the adiabatic approximation. The electrons are considered as delocalized, occupying molecular orbitals $\phi_{k,m_{\mu}}(r_i), k \in \mathbb{N}$, given by linear combinations of atomic orbitals $\psi_{\mu_{\eta,m_{\mu}}}(r_i)$, where $r_i$ are the coordinates of the $i$th electron, $\mu_{\eta}$ label the electronic shell and subshell with respect to the $i$th electron and $\eta$ nucleus, $m_{\mu}$ is the spin magnetic quantum number of the $i$th electron. The state function of each electron configuration is given by a linear combination of Slater determinants (of the orbitals $\phi_{k,m_{\mu}}(r_i)$), where the symmetrization is performed with respect to the spin quantum numbers $s_{ij}$ of all electron pairs. The corresponding basis set gives the number of all probable electrons distributions along all exchange bridges. In the simplest case of $N$ valence electrons with $N$ − 2 pairs, one
of the basis states is written as
\[
\Psi_{S,M}^{k,k'}(r_1, \ldots, r_N) \equiv \sum_{P_{1,N}} c_{P_{1,N}} \frac{\Phi_i^{(2i-1,2i)}(r_{2i-1}, r_{2i})}{\sqrt{2^N N!}} \times \Psi_{S,M}^{k,k'}(r_{N-1}, r_N),
\]
where the sum runs over all permutations on the set of coordinates \(r_1 \ldots r_N\). Both unpaired electrons occupy \(k\)th and \(k'\)th molecular orbitals with
\[
\Psi_{S,N-1,M}^{k,k'}(r_{N-1}, r_N) = \frac{1}{4^{N-1} N!} \left[ \phi_k(r_{N-1}) \phi_{k'}(r_N) + (-1)^{s_{N-1,M}} \phi_{k'}(r_{N-1}) \phi_k(r_N) \right].
\]
The remaining, paired electrons, are described by the states
\[
\Phi_{s_{2i-1,2i}}^{(r_{2i-1}, r_{2i})} = \frac{1}{2} \left[ \phi_i(r_{2i-1}) \phi_i(r_{2i}) + (-1)^{s_{2i-1,2i}} \phi_i(r_{2i-1}) \phi_i(r_{2i}) \right].
\]
Moreover, for \(i, j = 1, \ldots, N\) the permutation coefficients
\[
c_{r_i,r_j} = (-1)^{i+j+1}, \quad c_{r_j,r_i} = (-1)^{s_{N-1,M}}(-1)^{i+j+1},
\]
account for the antisymmetry of (4) and the spin part is given by
\[
|S,M\rangle = \otimes_{i=1}^{N} |s_{2i-1,2i}, m_{2i-1,2i}\rangle.
\]
The effective Hamiltonian accounting for all possible configurations of interactions is built according to the expectation values of the initial Hamiltonian representing all electron-electron and electron-nuclei interactions. The effective state associated with (4) is represented by \(|\Psi_{S,M}^\tau\rangle\), where \(\tau = (k,k')\). The generic function describing the multiple bridged structure includes all probabilities related with the spatial distribution of unpaired electrons. Thus, we may compute the eigenstates of the ensuing spin Hamiltonian in terms of an appropriate linear combination of the effective states. In the case of (4), this is given by the superposition
\[
|s,m\rangle = \sum_{\tau} c_S^{\tau} |\Psi_{S,M}^\tau\rangle, \quad \text{(5)}
\]
where \(\tau\) runs over the number of all existing electrons’ configurations that depend on all intermediate bridges and \(s = 0, 1\), \(m = 0, \pm 1\) are the corresponding effective spin and magnetic quantum numbers, that obey the conservation of angular momentum \(S \equiv s, M \equiv m\). Further, \(c_S^{\tau}\) is the associated probability coefficient that depends on \(S\). The expectation values of the canonical Hamiltonian are a part of the eigenstates relevant to (5). Within the framework of the given example they are represented by the sum
\[
E_{s,m} = \sum_{\tau} \left| c_S^{\tau} \right|^2 E_{S,M}^{\tau}. \quad \text{(6)}
\]
The elements in the last sum are functions of the Coulomb \(U, V\), hopping \(t\), and direct exchange integrals \(D_r\) relevant to each intermediate bridge. For example,
\[
E_{1,M}^r = V_r - D_r, \quad M = 0, \pm 1,
\]
\[
E_{0,0}^r = D_r + \frac{U_r + V_r}{2} - \frac{(U_r - V_r)^2}{4}. \quad \text{(9a)}
\]
Within the effective spin space, determined by \(s\) and \(m\), one can account for only one transition with energy \(|\Delta E| = |E_{1,m} - E_{0,0}|\) due to the 3-fold degeneracy of the triplet level. However, for different spatial distributions of the considered electrons the values of (6) alter and accordingly the energy of the transition changes. Such effect is not related neither to the magnetic anisotropy nor higher order multiple interactions. Therefore, conventional bilinear spin Hamiltonians with only one exchange coupling and additional interacting terms is not able to account for the variation in \(\Delta E\).

In order to address these features we introduce Hamiltonian (3) that depends upon the parameters described hereafter.

2.2 Properties of the \(\hat{\sigma}\)–operators
For a single spin the square and the \(z\) component of each operator \(\hat{\sigma}\) are completely determined in the basis of the total spin component \(s^2\), such that for all \(i\) and \(\alpha \in \{x, y, z\}\)
\[
\hat{\sigma}_i^\alpha |\ldots, s_i, m_i, \ldots\rangle = a_i^{s_i,m_i}\hat{\sigma}_i^\alpha |\ldots, s_i, m_i, \ldots\rangle, \quad \text{(7)}
\]
where \(a_i^{s_i,m_i} \in \mathbb{R}\). Furthermore, the \(\sigma\) rising and lowering operators obey the equations
\[
\hat{\sigma}_i^\pm |\ldots, s_i, m_i, \ldots\rangle = a_i^{s_i,m_i}\hat{\sigma}_i^\pm |\ldots, s_i, m_i, \ldots\rangle, \quad \text{(8)}
\]
For all \(i\), the square of \(\sigma_i\) commutes only with its \(z\) component. Its eigenvalues depend on \(m_i\) and according to (7) and (8) one can distinguish two cases: (1) \(m_i = \pm s_i\); (2) \(-s_i < m_i < s_i\), where \(s_i \neq 0\), with the respective eigenvalues
\[
\left( a_i^{s_i,\pm s_i} \right)^2 s_i^2 + a_i^{s_i,\pm s_i} a_i^{s_i,\pm (s_i-1)} s_i, \quad \text{(9a)}
\]
\[
\frac{1}{2} a_i^{s_i,m_i} \left[ a_i^{s_i,m_i+1} + a_i^{s_i,m_i-1} \right] s_i(s_i + 1) + a_i^{s_i,m_i+1} a_i^{s_i,m_i-1} m_i^2

- \frac{1}{2} a_i^{s_i,m_i} m_i \left[ a_i^{s_i,m_i+1}(m_i + 1) + a_i^{s_i,m_i-1}(m_i - 1) \right]. \quad \text{(9b)}
\]
On the other hand when the spins of \(i\)th and \(j\)th magnetic ions are coupled, with total spin operator \(\hat{S}_i j = \hat{\sigma}_i + \hat{\sigma}_j\), the relation (7) enters a more general and complex expression. To explore the properties of the coupled spins one has to work with the total \(\sigma\)-operator \(\hat{\sigma}_i j\). Its \(z\) component and square are completely determined in the basis of the spin operator \(\hat{S}_{ij}^z\). Similar to equation (7) for all \(i \neq j\) and \(\alpha \in \{x, y, z\}\), we have
\[
\hat{\sigma}_{ij}^\alpha |\ldots, s_{ij}, m_{ij}, \ldots\rangle = a_{ij}^{s_{ij},m_{ij}}\hat{\sigma}_{ij}^\alpha |\ldots, s_{ij}, m_{ij}, \ldots\rangle, \quad \text{(10)}
\]
where \( a_{ij}^{s_{ij},m_{ij}} \in \mathbb{R} \). The corresponding rising and lowering operators obey

\[
\hat{\sigma}_{ij}^{\pm} \cdots, s_{ij}, m_{ij}, \ldots \rangle = a_{ij}^{s_{ij},m_{ij}} \hat{\sigma}_{ij}^{\pm} \cdots, s_{ij}, m_{ij}, \ldots \rangle.
\]

The eigenvalues of \( \hat{\sigma}_{ij}^2 \) depend on \( m_{ij} \). Therefore having in mind the following two cases \( m_{ij} = \pm s_{ij} \), and \(-s_{ij} < m_{ij} < s_{ij}\), where \( s_{ij} \neq 0 \), the eigenvalues read

\[
\begin{align*}
\left( a_{ij}^{s_{ij},\pm s_{ij}} \right)^2 s_{ij}^2 + a_{ij}^{s_{ij},\pm s_{ij}} a_{ij}^{s_{ij},\pm (s_{ij}-1)} s_{ij}, & \quad (12a) \\
\frac{1}{2} a_{ij}^{s_{ij},m_{ij}} \left[ a_{ij}^{s_{ij},m_{ij}+1} + a_{ij}^{s_{ij},m_{ij}-1} \right] s_{ij} (s_{ij}+1) + a_{ij}^{s_{ij},m_{ij}} m_{ij} & \quad (12b)
\end{align*}
\]

The corresponding \( \sigma \)-operators share a single coefficient and for \( i \neq j \) and \( \alpha \in \{x, y, z\} \), we have

\[
\hat{\sigma}_{ij}^{\alpha} \cdots, s_{ij}, m_{ij}, \ldots \rangle = a_{ij}^{s_{ij},m_{ij}} \hat{\sigma}_{ij}^{\alpha} \cdots, s_{ij}, m_{ij}, \ldots \rangle.
\]

We further assume that the \( \sigma \)-operators preserve the corresponding spin magnetic moment and for a non coupled spin obey the following constraints

\[
\hat{\sigma}_{i}^{\pm} \cdots, s_{i}, m_{i}, \ldots \rangle = m_{i} \cdots, s_{i}, m_{i}, \ldots \rangle,
\]

\[
\hat{\sigma}_{ij}^{\pm} \cdots, s_{ij}, m_{ij}, \ldots \rangle = s_{i} (s_{i}+1) \cdots, s_{i}, m_{i}, \ldots \rangle.
\]

Similarly, when the \( i \)th and \( j \)th spins are coupled, for all \( i \neq j \) we have

\[
\hat{\sigma}_{ij}^{\pm} \cdots, s_{ij}, m_{ij}, \ldots \rangle = m_{ij} \cdots, s_{ij}, m_{ij}, \ldots \rangle,
\]

\[
\hat{\sigma}_{ij}^{\pm} \cdots, s_{ij}, m_{ij}, \ldots \rangle = s_{ij} (s_{ij}+1) \cdots, s_{ij}, m_{ij}, \ldots \rangle.
\]

Taking into account (14) together with expressions (9b) for all \( m_{i} \) we have \( a_{i}^{s_{i},m_{i}} = 1 \). Further, according to constraints (15) and equations (12) we distinguish three cases:

- \( s_{ij} = 0 \): The associated parameter remains unconstrained and there exist a set of coefficients \( c_{ij}^{n} \in \mathbb{R} \) for all \( n \in \mathbb{N} \), such that

\[
\begin{align*}
\sum_{n=0}^{\infty} c_{ij}^{n} \left( \begin{array}{c}
1, \cdots, 1
\end{array} \right) = \left( \begin{array}{c}
s_{ij}
\end{array} \right).
\end{align*}
\]

The values of \( c_{ij}^{n} \) depend on the number of unpaired valence electrons and intermediate nonmagnetic ions of the respective exchange bridges. Depending on the type of exchange these effective coefficients are functions of the Coulomb, hopping and exchange integrals. Thereby, for a linear cluster with only one bonding anion between magnetic cations and a unique electron’s spatial distribution, one would obtain the limit \( |c_{ij}^{n} - c_{ij}^{k}| \to 0 \), \( \forall n \neq k \), where \( c_{ij}^{n} \to 1 \). Accordingly, the changes in electron’s distribution could be considered as negligible pointing to sharpened peaks in the magnetic spectrum. On the other hand, the inequality \( |c_{ij}^{n} - c_{ij}^{k}| > 0 \) for all \( n \neq k \), would have to be considered as a sign for the presence of exchange paths of different energy, i.e. more than one favorable spatial distribution of unpaired electrons, and therefore of increased excitation width in energy. As an example, if \( i \)th and \( j \)th magnetic centers are linked via more than one exchange bridge of complex chemical structure, then one may expect that the exchange path is not unique. In such case according to (5) and (6) the transition energy reads

\[
|\Delta E_{n}| = \sum_{\tau} |c_{n,\tau}^{r}|^2 E_{\tau,M}^{r} - |c_{n,0}^{r}|^2 E_{0,0}^{r},
\]

where \( n \) assigns a unique transition energy to a certain number of favorable spatial distributions. Hence, with Hamiltonian (3) and taking into account (17) we can express all existing transitions by

\[
\Delta E_{n} = \frac{1}{2} J_{ij} (3c_{ij}^{n} \pm 1), \quad a_{ij}^{1,0} = \pm 1.
\]

The set of values \( \Delta E_{n} \) will correspond to a broadened peak in the magnetic spectrum. Applying the relation \( \Delta E_{n} = 2J_{ij}^{n} \), where \( J_{ij}^{n} \) is the \( n \)th value of the Heisenberg type exchange coupling from (18) we thus obtain

\[
\begin{align*}
c_{ij}^{n} = \frac{4}{3} J_{ij}^{n} + \frac{1}{3}, & \quad a_{ij}^{1,0} = \pm 1.
\end{align*}
\]

As we will see later this approach allows one to explain in details the experimentally observed splitting and broadening of magnetic spectra in the molecular magnet Ni\textsubscript{4}Mo\textsubscript{12}, see e.g. Figure 1.

### 3 The tetramer Ni\textsubscript{4}Mo\textsubscript{12}

The indistinguishable spin-one Ni\textsuperscript{2+} ions of the spin cluster compound Ni\textsubscript{4}Mo\textsubscript{12}, are arranged on the vertices of a distorted tetrahedron, see Figure 2. For this molecule the bonds Ni1-Ni2 and Ni3-Ni4 are slightly shorter about 0.03 Å than the other four [32]. Notice that the intermediate bridges contain ions of molybdenum, oxygen and hydrogen.
3.1 Energy levels

According to the selected coupling scheme we denote the eigenvalues of (20) by $E^m_{a_{12}^{s_{12},s_{34}},s}$. The ground state is the singlet $|1,1,0,0\rangle$. Therefore, using (15) we get $a_{12}^{s_{12},s_{34}} = a_{34}^{s_{12}} = 1$ and taking into account (20) we obtain

$$E_{1,1,0}^0 = -8J.$$

With the triplet eigenstates $|0,1,1,m\rangle$, $m_{34} = m = 0, \pm 1$, the spins of Ni1 and Ni2 ions are coupled in singlet, the parameter $a_{12}^{s_{12},s_{34}}$ remains unconstrained and can be determined using INS experimental data. For the corresponding energies we get

$$E_{0,1,1}^m = -2Ja_{12}^{0,1,m} - 4Ja_{12}^{0,0}, \quad m = 0, \pm 1,$$

where according to (16) we have $a_{34}^{s_{12}} = \pm 1$. Analyzing the Ni4Mo12 spectrum we further obtain $a_{12}^{s_{12}} \in \{c_{12}, c_{12}^2\}$. When the singlet bond is Ni3-Ni4 the eigenstates are $|0,1,1,m\rangle$, $m_{12} = m = 0, \pm 1$, the value of $a_{34}^{s_{12}}$ remains unconstrained and according to (20) we have

$$E_{1,0,1}^m = -2Ja_{12}^{1,0,m} - 4Ja_{34}^{0,0}, \quad m = 0, \pm 1,$$

where $a_{12}^{1,0} = \pm 1$. Without loss of generality we set $a_{34}^{0,0} = c_{34}$. For all remaining triplets, i.e. $|1,1,1,m\rangle$, $|2,1,1,m\rangle$, and $|1,2,1,m\rangle$, where $m = 0, \pm 1$, the corresponding coefficient are constrained, $a_{12}^{s_{12},m_{12}} = 1$ and $a_{34}^{s_{34},m_{23}} = 1$. Thus, we obtain

$$E_{1,2,1}^m = E_{2,1,1}^m = E_{2,2,1}^m = E_{1,1,1}^m = -6J.$$

The tetramer Ni3Mo12 exhibits also a singlet bond at the quintet level. The energies associated with the Ni1-Ni2 singlet bond and eigenstates $|0,2,2,m\rangle$, where $m_{34} = m$ are

$$E_{0,2,2}^m = 2Ja_{34}^{2,m} - 4Ja_{12}^{0,0}, \quad m = 0, \pm 1, \pm 2,$$

where, the coefficients are determined by $a_{34}^{0,0} = \pm 1$ and $a_{12}^{2,0} \in \{c_{12}, c_{12}^2\}$.

Similarly, if the spins of third and fourth ions are in a singlet state, where the corresponding eigenstates are $|2,0,2,m\rangle$, then the Hamiltonian in (20) yield the following energy values

$$E_{2,0,2}^m = 2Ja_{12}^{2,m} - 4Ja_{34}^{0,0}, \quad m = 0, \pm 1, \pm 2,$$

where $a_{12}^{2,0} = \pm 1$.

With respect to the other twelve quintet eigenstates the coefficients $a_{12}^{s_{12},m_{12}} = a_{34}^{s_{34},m_{34}} = 1$ and therefore

$$E_{2,2,2}^m = E_{1,1,2}^m = E_{2,1,2}^m = E_{1,2,2}^m = -2J.$$

For the remaining two levels we obtain $a_{12}^{s_{12},m_{12}} = 1$ and $a_{34}^{s_{34},m_{34}} = 1$. The energy sequence follows the Landé interval rule $E_{n+1} - E_n = 2J$, see e.g. Figure 3. The septet level is twenty one fold degenerate and it is defined by
the eigenstates $|2, 1, 3, m\rangle$, $|1, 2, 3, m\rangle$, $|2, 2, 3, m\rangle$ with $m = 0, \pm 1, \pm 2, \pm 3$. All corresponding energies have equal value

$E_{2,1,3}^m = E_{1,2,3}^m = E_{2,2,3}^m = 4J$.

Applying the nonet state $|2, 2, 4, m\rangle$, where $m = 0, \ldots, \pm 4$ we end up with $E_{2,2,4}^m = 12J$.

The described energy level structure is illustrated in Figure 3. In what follows we find the following notations more convenient

$E_0 = -8J$, $E_1 = -2J - 4Jc_{12}$, $E_2 = -6J$, $E_3 = -2J - 4Jc_{34}$, $E_4 = 2J - 4Jc_{12}$, $E_5 = 4J$, $E_6 = 2J - 4Jc_{34}$, $E_7 = 2J + 4Jc_{12}$, $E_8 = -2J$, $E_{10} = 12J$.

### 3.2 Scattering intensities

The INS selection rules are $\Delta s = 0, \pm 1$, $\Delta m = 0, \pm 1$ and $\Delta s_{12} = 0, \pm 1$, $\Delta s_{34} = 0, \pm 1$. Here the transitions $\Delta s_{12} \neq 0$ and $\Delta s_{34} \neq 0$ are not allowed simultaneously. Within the applied coupling scheme we obtain $S^{\alpha\beta}(q, \omega_{n'n'}) + S^{\beta\alpha}(q, \omega_{n'n'}) = 0$, $\forall n, n'$, $\alpha \neq \beta$ and $\sum_\alpha S^{\alpha\alpha} = 2$. The energy of the first experimental magnetic excitation is approximately 0.4 meV. The corresponding peak is depicted in Figure 1, see also [32]. This excitation is related with the transition between the ground state and the local singlet state $|0, 1, 1, \pm 1\rangle$. The associated scattering functions are

$$S^{\alpha\alpha}(q, \omega_{10}) = \frac{4}{9}[1 - \cos(q \cdot r_{12})]p_0, \quad S^{zz}(q, \omega_{10}) = 0, \quad (21)$$

where $p_0$ is the population factor and $\alpha = x, y$. The magnetic excitation at 0.6 meV shown in Figure 1 is associated with the eigenstate $|1, 0, 1, \pm 1\rangle$ and the scattering functions

$$S^{\alpha\alpha}(q, \omega_{30}) = \frac{4}{9}[1 - \cos(q \cdot r_{34})]p_0, \quad S^{zz}(q, \omega_{30}) = 0, \quad (22)$$

where $\alpha = x, y$. The functions (21) differ from (22) due to the spatial orientations of the spin bonds with $r_{12} \cdot r_{34} = 0$. For the same reason, we deduce that the third cold peak at 1.7 meV, see Figure 1, is related with the transition between the ground state and non magnetic triplet $|0, 1, 1, 0\rangle$. For $\alpha = x, y$ the corresponding scattering functions read

$$S^{\alpha\alpha}(q, \omega_{64}) = \frac{4}{3}[1 - \cos(q \cdot r_{12})]p_4, \quad S^{zz}(q, \omega_{64}) = 0, \quad (23)$$

The excited magnetic transition at around 1.2 meV shown by green and red items in Figure 1 is nicely reproduced by the scattering functions

$$S^{\alpha\alpha}(q, \omega_{64}) = \frac{4}{3}[1 - \cos(q \cdot r_{12})]p_4, \quad S^{zz}(q, \omega_{64}) = 0, \quad (23)$$

where $\alpha = x, y$. The initial state is given by the triplet state $|1, 1, 1, \pm 1\rangle$ with two triplet bonds and the final one appears to be $|0, 1, 1, 0\rangle$. Hence if the neutron scatters from the Ni3-Ni4 dimers, then we have $q \cdot r_{12} = 0$ and $q \cdot r_{34} > 0$. Nevertheless, with the coefficients $a_{12}^{3,4,12}$ and $a_{34}^{3,4,34}$ one can uniquely identify the two spin bonds and distinguish $I_{10}$ from $I_{30}$. Moreover, one can distinguish the eigenvalues of tetramer Hamiltonian corresponding to $m = 0$ and $m \neq 0$, with

$S^{zz}(q, \omega_{n'n'}) = 0$ and $S^{xx}(q, \omega_{n'n'}) = 0$, $S^{yy}(q, \omega_{n'n'}) = 0$, respectively. This affects directly the integrated intensities, such that choosing $r_{12} = (0, 0, r^z)$ and $r_{34} = (r^x, 0, 0)$ from (1) yields

$I_{10} \propto \gamma_{10} \left[ 1 - \frac{\sin(qr)}{qr} \right] F^2(q)$,

$I_{30} \propto \gamma_{30} \left[ 1 - \frac{6\sin(qr)}{5(qr)^3} - 3\frac{\sin(qr)}{5qr} + 6\frac{\cos(qr)}{5(qr)^2} \right] F^2(q)$,

$I_{50} \propto \gamma_{50} \left[ 1 - 3\frac{\sin(qr)}{(qr)^3} + 3\frac{\cos(qr)}{(qr)^2} \right] F^2(q)$,

$I_{64} \propto \gamma_{64} \left[ 1 - \frac{\sin(qr)}{qr} \right] F^2(q)$,

where

$$\gamma_{10} = \frac{8}{9}p_0, \quad \gamma_{30} = \frac{20}{27}p_0, \quad \gamma_{50} = \frac{8}{27}p_0, \quad \gamma_{64} = \frac{4}{3}p_4,$$

and $r = |r_{12}| = |r_{34}|$. The integrated intensities as a function of temperature are shown in Figure 4. According to reference [32] the average distance between Ni–Ni ions is $r = 6.68$ Å. The magnitude of the scattering vector
is fixed at \( q = 1 \, \text{Å}^{-1} \) and the calculated form factor for Ni\(^{2+} \) di-cations is \( F(q) = 256(16 + q^2 r_o^2)^{-2} \), where \( r_o = 0.529 \, \text{Å} \) is the Bohr radius. The dependence of normalized intensities, \( I_{n'n'} \rightarrow I_{n'n'}/\gamma_{n'n'} \), on the scattering vector is shown in Figure 5.

3.3 Energy of the magnetic transitions

The energy transition \( E_{ij} \) between \( i \)th and \( j \)th levels, corresponding to the calculated scattering intensities are

\[
E_{10} = 6J - 4Jc_{12}^1, \quad E_{30} = 6J - 4Jc_{34}^1, \\
E_{50} = 10J - 4Jc_{12}^1, \quad E_{64} = 8J - 4Jc_{12}^2. \tag{23}
\]

From the last equations we can take advantage of one more constraint to determine \( J, E_{50} - E_{10} = 4J \). According to the experimental data [31,32] the ground state magnetic excitations are grouped in two relatively broadened peaks. The first peak is centered at about 0.5 meV and the second one at 1.7 meV. Furthermore, the first peak is composed of two subbands with energies \( E_{10} = 0.4 \) meV and \( E_{30} = 0.6 \) meV. The width of the second peak can be explained by the presence of an energy band, where the transition energies are restricted in the region 1.6 meV to 1.8 meV. Therefore, setting \( E_{50} = 1.7 \) meV we obtain \( E_{50} - E_{10} = 1.3 \) meV and \( J = 0.325 \) meV. The computed energy transitions are depicted in Figure 3. The centers of both energy bands referring to the value \( c_{12}^1 = 1.153 \) are shown by dashed lines. The energies of all transitions and the corresponding parameters are given in Table 2.

4 Conclusion

We propose a formalism for exploring the physical properties of molecular magnets with non trivial bridging structure. The underlying concept lies on the hypothesis that due the cluster symmetry, as well as its shape, size and the chemical structure that surrounds the magnetic ions, the spatial distribution of valence electrons is not unique leading to a variation of the relevant Coulomb, hopping and direct exchange energies.

Studying the INS spectra of the compound Ni\(_4\)Mo\(_{12}\) with the Hamiltonian (3) we were able to derive a detailed picture for the neutron scattering intensities

| Table 1. Calculated values of integrated intensities \( I_{n'n'} \) [arb. units] at temperatures 2.4, 9.3 and 23 K, shown in Figure 4 as blue squares, green circles and red triangles, respectively. |
| --- | --- | --- | --- | --- |
| Transitions | I | II | III | IV |
| \( E_{n'n'} \) [meV] | \( I_{10} \) | \( I_{30} \) | \( I_{50} \) | \( I_{64} \) |
| 2.4 [K] | 0.137(6) | 0.120(3) | 0.051(5) | 0.008(9) |
| 9.3 [K] | 0.039(8) | 0.034(8) | 0.014(9) | 0.026(5) |
| 23 [K] | 0.019(5) | 0.017(1) | 0.007(3) | 0.021(1) |

| Table 2. Values of the coupling constants and the quantities \( c_{12}, c_{34} \) for all magnetic excitations with energies given in equation (23). The results are obtained by taking into account the experimental data of references [31,32]. |
| --- | --- | --- | --- |
| Transitions | I | II | III |
| \( J_{c12} \) [meV] | 0.325 | 0.325 | 0.325 |
| \( J_{c34} \) [meV] | 0.372 | – | – |
| \( c_{12}^1 \) | 1.1923 | 1.1923 | 1.1153 |
| \( c_{12}^1 \) | – | 1.0384 |
| \( c_{34} \) | – | – | – |

Fig. 4. Intensities as a function of the absolute temperature. \( I_{10}, I_{30} \) and \( I_{50} \) correspond to the ground state transitions with energies 0.4 meV, 0.6 meV and 1.7 meV, respectively. The intensity \( I_{64} \) in the inset stands for the excited transition with energy 1.15 meV. The blue squares, the green circles and red triangles point to the values of intensities in Table 1.

Fig. 5. Normalized by \( \gamma_{n'n'} \) intensities as a function of the scattering vector along with the experimental data of reference [32]. \( I_{10}, I_{30} \) and \( I_{50} \) correspond to ground state transitions with energies 0.4 meV, 0.6 meV and 1.7 meV, respectively. The intensity \( I_{64} \) stands for the excited transition with energy 1.15 meV. The inset shows the intensity \( I_{64} \) that coincides with the function \( I_{10} \).
(Figs. 4 and 5). Hamiltonian (20) leads to energy spectrum with two energy bands, shown in Figure 3. These bands are related to the fact that the tetramer cluster exhibits two distinguishable with respect to the coefficients $a_{12}^{34, m_{12}}$ and $a_{34}^{34, m_{34}}$ bands. We ascribe this feature to the difference in the chemical environment around Ni1-Ni2 and Ni3-Ni4 couples that give rise to distinct spatial distributions of the valence electrons. This allowed a unique identification of the magnetic excitations. Thereby, the obtained energy bands explain the width of second ground state peaks centered at 1.7 meV and the splitting of the first one centered at 0.5 meV. In particular, for $s_{12} = 0$, $s_{34} = 0$ and $i = 1, 2$ we get $|c_{12}| > 1$ and $|c_{34}| > 1$, respectively. Besides, according to (19) we have $J < J_{c12}$ and $J < J_{c34}$, see Table 2. These inequalities signal that the strength of the exchange is amplified. Furthermore, the inequality $J_{c34} < J_{c12}$ indicates that most probably the density of electrons along Ni3-Ni4 bond is lower than that along the Ni1-Ni2.

To conclude we would like to anticipate that the results for the magnetization and low-field magnetic field susceptibility of the tetramer Ni$_4$Mo$_{12}$ are in concert with the experimental measurements. These results will be the subject of a separate paper.

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