An approach to the magnetic ground state of the molecular magnet \{\text{Mo}_{72}\text{Fe}_{30}\}

Z-D Fu\textsuperscript{1,5}, P Kögerler\textsuperscript{1,2}, U Rücker\textsuperscript{1}, Y Su\textsuperscript{3}, R Mittal\textsuperscript{3,4} and T Brückel\textsuperscript{1,5}

\textsuperscript{1} Institut für Festkörperforschung, Forschungszentrum Jülich GmbH, Jülich 52425, Germany
\textsuperscript{2} Institut für Anorganische Chemie, RWTH Aachen, Aachen 52074, Germany
\textsuperscript{3} Jülich Centre for Neutron Science, Institut für Festkörperforschung, Forschungszentrum Jülich, Outstation at FRM II, Garching 85747, Germany
\textsuperscript{4} Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400085, India
E-mail: z.fu@fz-juelich.de and t.brueckel@fz-juelich.de

\textit{New Journal of Physics} \textbf{12} (2010) 083044 (15pp)
Received 19 May 2010
Published 24 August 2010
Online at http://www.njp.org/
doi:10.1088/1367-2630/12/8/083044

\textbf{Abstract.} The nature of the magnetic ground state of the spin-frustrated molecular magnet \{\text{Mo}_{72}\text{Fe}_{30}\} is studied using polarized neutron scattering and specific heat methods. The magnetic scattering cross section up to 2.30 Å\textsuperscript{-1} has been determined by means of diffuse neutron scattering with \textit{xyz} polarization analysis at temperatures from 1.5 to 100 K. The spin correlations observed at 1.5 K agree well with the simulation based on the three-sublattice spin configuration model for \{\text{Mo}_{72}\text{Fe}_{30}\}. The specific heat of \{\text{Mo}_{72}\text{Fe}_{30}\} has been measured from 60 mK to 15 K under zero external magnetic field. The energy gaps, 0.09(1) and 0.64(1) meV, identified by the Schottky-type anomalies in the specific heat data are in reasonable agreement with the low-lying magnetic excitations predicted by the quantum rotational band model for the three-sublattice spin configuration model. Therefore, our experimental study provides strong support that the three-sublattice spin configuration model is a good approach to the magnetic ground state of \{\text{Mo}_{72}\text{Fe}_{30}\}.

\textsuperscript{5} Authors to whom any correspondence should be addressed.
1. Introduction

Molecular magnets have attracted intense interest as the smallest well-defined quantum magnets because of the remarkable progress in synthesizing bulk samples of identical isolated magnetic molecules. In molecular magnets, each molecule contains a relatively small number of paramagnetic ions, i.e. spins, interacting via Heisenberg-type exchange. Some molecular magnets are ideal systems for studying quantum phenomena in magnetic nano-systems, such as quantum tunneling, quantum coherence and spin frustration, because intermolecular magnetic interactions in such materials are negligible compared with intramolecular interactions [1]–[3]. The collective phenomena of interacting magnetic moments may strongly depend on the topology of the magnetic structure. The spin-frustrated magnets are of great interest as they allow novel magnetic ground states and unexpected dynamics [4, 5]. These materials commonly have magnetic lattices prone to geometrical or topological frustration, such as triangular or tetrahedral based structures. If antiferromagnetically coupled spins are embedded in such structures, the system cannot, because of local geometrical constraints, minimize all the antiferromagnetic pair interactions simultaneously and settle into a long-range ordered ground state, even at sufficiently low temperatures. One famous and extensively studied two-dimensional structure with geometrical frustration is the planar Kagome lattice [6]–[8].

As one of the largest molecular magnets synthesized to date, the polyoxomolybdate [Mo$_{72}$Fe$_{30}$O$_{252}$(CH$_3$COO)$_{12}$]$_2$[Mo$_2$O$_7$(H$_2$O)$_2$](H$_2$O)$_9$150H$_2$O, {Mo$_{72}$Fe$_{30}$} for short, represents a highly frustrated spin system and provides us with a molecular analogue of the planar Kagome lattice [6]–[8]. In the {Mo$_{72}$Fe$_{30}$} molecule (see figure 1), the 30 Fe$^{3+}$ ($S = 5/2$, $L = 0$) ions serve as magnetic centers and occupy the vertices of an icosidodecahedron. –O–Mo–O– fragments act as effective superexchange pathways between Fe$^{3+}$ ions [9, 10]. The 30 spins form 20 corner-sharing triangles and are antiferromagnetically coupled among the nearest neighbors [10]. The magnetic properties of {Mo$_{72}$Fe$_{30}$} can be well described by the isotropic Heisenberg model with a single exchange constant $J$,

$$H = J \sum_{(i,j)} \vec{S}_i \cdot \vec{S}_j + g \mu_B B \cdot \sum_i \vec{S}_i,$$

(1)

where $\vec{S}_i$, $\vec{S}_j$ are spin operators in units of $\hbar$, $B$ is the external field, $g$ is the spectroscopic splitting factor, $\mu_B$ is the Bohr magneton, and $J$ is the exchange constant and found to be about 0.134 meV, indicating antiferromagnetic exchange interactions [10]. The complete matrix diagonalization of this Hamiltonian is not feasible because the total dimension of
Figure 1. Ball-and-stick representation of the \( \{ \text{Mo}_{72}\text{Fe}_{30} \} \) molecule (Fe: red; green: blue spheres; Mo: purple spheres; O: black spheres; C, H: not shown). The arrows (red, green, blue) denote the classical spin vectors within the frustrated three-sublattice spin model. Twenty Fe\(^{3+} \) triangles are highlighted in yellow.

Hilbert space for this large spin system is \( 6^{30} \). Despite this unsolvable difficulty at present, an approximate, diagonalizable effective Hamiltonian was adopted to explain the major low-temperature properties of \( \{ \text{Mo}_{72}\text{Fe}_{30} \} \) \[11\]. The classical version of this effective Hamiltonian represents a frustrated ground state spin configuration called the ‘three-sublattice’ model, where the 30 spins can be divided into three sublattices and the sublattices are characterized by three coplanar unit vectors with an angular spacing of 120° \[12\]. This model successfully predicts the magnetic field dependence of the magnetic moment and the susceptibility of \( \{ \text{Mo}_{72}\text{Fe}_{30} \} \) \[10, 12\]. The resultant quantum rotational band (QRB) theory is used to approximate the low-lying section of the magnetic excitation spectrum and is supported by some experimental observations by means of inelastic neutron scattering (INS), nuclear magnetic resonance and muon spin relaxation \[11, 13, 14\]. However, experimental support of the three-sublattice spin model remains very indirect, as long as there are no direct observations of the magnetic ground state of the \( \{ \text{Mo}_{72}\text{Fe}_{30} \} \) molecule.

To understand the magnetic properties of \( \{ \text{Mo}_{72}\text{Fe}_{30} \} \), it is very important to have a good knowledge of the magnetic ground state and the low-temperature spin dynamics, as well as a practicable theoretical model to represent the experimental observations for \( \{ \text{Mo}_{72}\text{Fe}_{30} \} \). A key insight into this physics can be achieved from two aspects: the spin correlation functions and the low-lying magnetic excitations.

The spin correlation functions of frustrated magnetic systems containing hydrogen are difficult to measure at low temperatures because magnetic diffuse neutron scattering is often weak compared with nuclear diffuse scattering and thermal diffuse scattering. However, diffuse neutron scattering with polarization analysis allows one to separate nuclear coherent, magnetic and nuclear spin-incoherent scattering simultaneously and unambiguously \[15\]. In the present work, the quantitative short-range spin correlations in the large spin-frustrated molecular magnet \( \{ \text{Mo}_{72}\text{Fe}_{30} \} \) are being investigated for the first time, by means of diffuse neutron scattering.
with polarization analysis at various temperatures. The obtained spin correlations are consistent with the simulation using the three-sublattice spin configuration model. We demonstrate that \{Mo\textsubscript{72}Fe\textsubscript{30}\} represents a highly frustrated spin structure, characterized by the short-range spin correlations.

The low-lying magnetic excitations can be predicted directly by QRB theory. In this context, the low-temperature specific heat is extremely valuable, since no external magnetic field is required, and therefore the Zeeman effect that disturbs the order of the energy levels can be avoided. In our zero-field specific heat data, Schottky anomalies with their unique shape for two-level systems are observed and serve as a clear signature to identify the energy gaps. Using this complementary method for INS, our work gives additional strong support to the existing theoretical descriptions of low-lying magnetic excitations in \{Mo\textsubscript{72}Fe\textsubscript{30}\}.

2. Experimental details

The \{Mo\textsubscript{72}Fe\textsubscript{30}\} samples were synthesized at Rheinisch-Westfälische Technische Hochschule (RWTH) Aachen University according to the method described in [9]. \{Mo\textsubscript{72}Fe\textsubscript{30}\} polycrystals were deuterated to minimize incoherent scattering from hydrogen atoms for use in diffuse neutron scattering measurements. The sample was sealed in a copper holder in a helium atmosphere. Polarized neutron scattering measurements were carried out on the diffuse neutron scattering instrument DNS [16] at the FRM II research reactor (Garching, Germany), equipped with a \(^4\)He closed cycle cryostat and an orange-type liquid helium cryostat. The energy of the incident neutron beam was 3.6 meV (corresponding to a wavelength of 4.74 Å), allowing the structure factor to be determined up to the scattering vector \(Q\) of 2.30 Å\(^{-1}\). Within the quasistatic approximation, the nuclear coherent, spin-incoherent and magnetic scattering cross sections were separated simultaneously with the \(xyz\)-polarization method in the spin-flip (SF) and non-spin-flip (NSF) channels [15]. In the \(xyz\)-polarization analysis, the multidetectors of DNS define the \(x-y\) plane, which makes the scattering vector \(Q\) always perpendicular to the \(z\) direction. The SF and NSF differential cross sections were then measured for the \(xyz\)-polarized incident beam, giving, in total, six partial cross sections, labeled \(\frac{d\sigma_{\text{SF}}}{d\Omega}^{x,y,z}\) and \(\frac{d\sigma_{\text{NSF}}}{d\Omega}^{x,y,z}\). The quantitative value of the differential magnetic cross section, \(\frac{d\sigma_{\text{Mag}}}{d\Omega}\), in units of barn (sr)\(^{-1}\) (f.u.)\(^{-1}\), can be extracted from either

\[
\frac{d\sigma_{\text{Mag}}}{d\Omega} = 2 \left( \frac{d\sigma_{\text{SF}}^{x}}{d\Omega} + \frac{d\sigma_{\text{SF}}^{y}}{d\Omega} - 2 \frac{d\sigma_{\text{SF}}^{z}}{d\Omega} \right) \tag{2}
\]

or

\[
\frac{d\sigma_{\text{Mag}}}{d\Omega} = 2 \left( 2\frac{d\sigma_{\text{NSF}}^{x}}{d\Omega} - \frac{d\sigma_{\text{NSF}}^{y}}{d\Omega} - \frac{d\sigma_{\text{NSF}}^{z}}{d\Omega} \right) \tag{3}
\]

The two expressions correspond to independent measurements, and the magnetic differential cross section is taken as their average after verifying their equivalence to check for systematic errors. In order to obtain the absolute scattering cross section from the sample, a vanadium standard was measured separately under the same experimental settings. Data were then normalized to the incoherent scattering of the vanadium standard. The flipping ratio correction was made using the reference measurements from an ideal isotropic incoherent scatterer, a NiCr alloy.

A rhombohedral single crystal of non-deuterated \{Mo\textsubscript{72}Fe\textsubscript{30}\}, with dimensions of about \(2 \times 2 \times 1 \text{ mm}^3\) and about 5 mg mass, was used in the heat capacity measurements. The zero-field heat capacity was measured down to 60 mK using a commercial Quantum Design Physical
Figure 2. Nuclear coherent (black circles), spin-incoherent (green circles) and paramagnetic (red circles) contributions to the total scattering for \( \{\text{Mo}_{72}\text{Fe}_{30}\} \) at 1.5 K from \( xyz \)-polarization analysis at DNS. The blue area indicates a simulation of the powder diffraction pattern for \( \{\text{Mo}_{72}\text{Fe}_{30}\} \), including the convolution with the experimental resolution.

Property Measurement System equipped with a dilution insert. The heat capacity values were extracted using the relaxation method [17, 18]. The background heat capacity of the microcalorimeter and Apiezon \( N \) grease was measured carefully in a separate run and subtracted from the raw data to obtain the absolute heat capacity of the sample.

3. Results and discussion

3.1. Diffuse neutron scattering with polarization analysis

Figure 2 shows the nuclear coherent, spin-incoherent and paramagnetic components of the total scattering from \( \{\text{Mo}_{72}\text{Fe}_{30}\} \) at 1.5 K using \( xyz \)-polarization analysis at DNS. Data are plotted as a function of \( Q \). The spin-incoherent scattering intensity is nearly constant, suggesting a successful separation of the different scattering contributions. The nuclear coherent scattering shows a broad hump at high \( Q \) values around 1.80 Å\(^{-1}\), which we attribute to the scattering from amorphous crystal water [19]. The high intensity of nuclear coherent scattering below 0.25 Å\(^{-1}\) originates from the background of the incident neutron beam. Several nuclear Bragg peaks are located within the \( Q \) range 0.25–1.00 Å\(^{-1}\), which are consistent with the simulation of the powder diffraction pattern (marked as the blue area at the bottom of figure 2) of \( \{\text{Mo}_{72}\text{Fe}_{30}\} \). The magnetic contribution (red circles in figure 2) is weak, leading to long counting times to obtain reasonable statistics. Without time-of-flight analysis, the magnetic scattering data are actually integrated over the energy-transfer window of DNS.

Figure 3 presents the differential magnetic cross section, \( d\sigma/d\Omega \), extracted from the total scattering cross section at 1.5, 2.5, 10, 20, 50 and 100 K from DNS measurements. The absolute magnetic cross sections are determined by calibration against the scattering of a known mass...
Figure 3. Temperature evaluation of the differential magnetic scattering cross section $d\sigma/d\Omega$ obtained from DNS measurements for a deuterated $\{\text{Mo}_{72}\text{Fe}_{30}\}$ polycrystalline sample. The data at different temperatures are to scale and are displaced vertically by $1.5 \text{ b sr}^{-1}$ per Fe atom for clarity. The solid and dashed lines indicate the pure and 91% scaled paramagnetic form factor of Fe$^{3+}$, respectively.

of vanadium standard. The scale of $d\sigma/d\Omega$ in figure 3 corresponds to the experimental curve at 100 K. The data at other temperatures are displaced vertically by $1.5 \text{ b sr}^{-1}$ per Fe atom for clarity. In the pure paramagnetic phase of $\{\text{Mo}_{72}\text{Fe}_{30}\}$, the Fe$^{3+}$ moments should have no significant spin pair-correlations and the $Q$ dependence of the differential magnetic cross section should follow the paramagnetic form factor. As shown in figure 3, the magnetic scattering above 50 K monotonically decreases with scattering vector $Q$, and agrees with the pure paramagnetic form factor of Fe$^{3+}$ ions [20]. This result is also consistent with the temperature dependence of the magnetic susceptibility of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ [10]. Below 20 K, a diffuse peak at $Q \approx 0.70 \text{ Å}^{-1}$ is seen to evolve and sharpen upon cooling, indicating the presence of short-range antiferromagnetic spin correlations. No long-range magnetic ordering can be detected, even down to 1.5 K, owing to the strong geometrical spin frustration of the single molecules and the lack of magnetic interaction between different molecules.

The total differential magnetic cross section within the experimental energy window of DNS is determined by integration over the scattering vector $Q$ at each temperature, shown as
Figure 4. Temperature dependence of the total magnetic cross section (black squares) integrated over the $Q$ range $0.39 < Q < 2.27 \text{ Å}^{-1}$ for $\{\text{Mo}_{72}\text{Fe}_{30}\}$. The dashed line is a guide to the eye.

black squares in figure 4. The integration is done over the $Q$ range $0.39 < Q < 2.27 \text{ Å}^{-1}$. The exchange interaction energy between the nearest Fe$^{3+}$ neighbors is estimated to be $\sim 1 \text{ meV}$ [10]. The energy of the incident neutrons in these measurements is $3.6 \text{ meV}$. Therefore, the data can be interpreted within a quasi-static approximation for the magnetic cross section. The total differential magnetic cross section of a pure paramagnet is given, ignoring the Debye–Waller term, by

$$\frac{d\sigma}{d\Omega} = \sum_{Q} \frac{2}{3} \left( \frac{\gamma e^2}{mc^2} \right)^2 \left\{ \frac{1}{2} g f(Q) \right\}^2 S(S+1) \text{ b sr}^{-1},$$

where $(\gamma e^2/mc^2) = -0.54 \times 10^{-12} \text{ cm}$ is the magnetic scattering length, $S$ is the spin quantum number of the scattering ion, $f(Q)$ is the magnetic scattering form factor, and the Landé splitting factor $g = 2$ is taken [10]. Within the $Q$ range $0.39 < Q < 2.27 \text{ Å}^{-1}$, $\sum_{Q} (f(Q))^2 = 1.533$ [20]. Accordingly, the total magnetic cross section within this $Q$ range for the pure paramagnetic Fe$^{3+}$ ion can be determined as $2.608 \text{ b sr}^{-1}$ per Fe atom. As shown in figure 4, the values obtained from measurements are nearly constant and close to the paramagnetic limit. Thus, it can be estimated that $\sim 91\%$ of the total magnetic cross section expected from the pure paramagnetic phase of $\{\text{Mo}_{72}\text{Fe}_{30}\}$ has been observed at the investigated temperatures within the energy and $Q$ window of DNS. The dashed line in figure 3 shows $91\%$ of the paramagnetic form factor of Fe$^{3+}$, which agrees well with the data at $100 \text{ K}$.

In order to determine the nature of the short-range magnetic ordering for the magnetic ground state of $\{\text{Mo}_{72}\text{Fe}_{30}\}$, we compare our experimental data with a simulation based on the three-sublattice spin configuration model introduced above. In agreement with our specific heat measurements presented in section 3.2, the QRB model [11] predicts low-lying $S = 1$ and 2 ground states at energies of $0.021$ and $0.081 \text{ meV}$, respectively. At $1.5 \text{ K}$, these levels are appreciably populated. However, within the three-sublattice model, the $S = 2$ ground state corresponds to a rather small canting of $2^\circ$ away from the coplanar $S = 0$ ground state. Within the statistical accuracy of our neutron scattering data, the resulting, minor change in spin correlations will not be detectable and thus we can safely assume that the spin correlations at...
Figure 5. Spin vectors $S_1$, $S_2$, $S_3$ and their projections. The Fe$^{3+}$ ions at Sites 1 and 2 belong to different sublattices. $S_3$ is generated by a rotation of $S_2$ by 180° around the direction of $S_1$.

1.5 K predicted by the three-sublattice model should be very close to those of the $S = 0$ ground state. Experimentally, the true $S = 0$ ground state of {Mo72Fe30} is very difficult to reach in diffuse neutron scattering, because the thermal conductivity of {Mo72Fe30} is poor and a large amount of sample is required in such measurements. Therefore, the model used to reproduce the neutron scattering data is based on the $S = 0$ ground state of {Mo72Fe30}. The spin correlations are calculated for a rigid configuration of classical $S = 5/2$ Fe spins corresponding to the three-sublattice model. The analysis of the data starts with the equation given by Blech and Averbach in [22] for the differential magnetic scattering cross section of spin pairs, which, in the powder average, can be written as

$$
d\sigma_{\text{mag}} / d\Omega = \frac{2}{3} S(S+1) \left( \frac{\gamma e^2}{mc^2} \right)^2 f^2(Q) + \left( \frac{\gamma e^2}{mc^2} \right)^2 f^2(Q) \times \sum_n \left[ a_n \sin Qr_n + b_n \left( \frac{\sin Qr_n}{Q^3 r_n^2} - \frac{\cos Qr_n}{Q^2 r_n^2} \right) \right],
$$

(5)

where ($\gamma e^2/mc^2$) and $f(Q)$ have been introduced in equation (4), $r_n$ is the distance from an atom at an arbitrary origin to the $n$th atom in the same molecule, and $a_n$ and $b_n$ are related to the probability of finding spin pairs with parallel components and expressed as

$$a_n = \langle S_y \cdot S_y' \rangle_n,$$

$$b_n = 2\langle S_x \cdot S_x' \rangle_n - \langle S_y \cdot S_y' \rangle_n,$$

(6)

where $S_x$, $S_y$, $S_y'$ and $S_y$ are defined in figure 5. Before using equation (5) to simulate the spin correlations of {Mo72Fe30}, it should be noticed that actually there exist an infinite number of specific ground state configurations when employing the three-sublattice model to this icosidodecahedral spin structure, because the three spin sublattices can rotate as long as the 120° angular spacing among their unit vectors is fulfilled. In any case, we may start with the correlation between two spins, $S_1$ and $S_2$, from two different sublattices in this model, as shown in figure 5. $S_2$ can take all relative orientations, keeping the 120° angular spacing with respect...
Figure 6. Magnetic diffuse scattering at 1.5 K in absolute units or \{Mo_{72}Fe_{30}\} (red circles); simulation of the spin pair-correlations for one \{Mo_{72}Fe_{30}\} molecule under the three-sublattice spin configuration model (blue line). Green dashed line: 91% scaled simulation curve.

to the direction of \(S_1\). As such, we can always obtain the spin \(S_3\) (see figure 5) by a rotation of \(S_2\) by 180° about the direction of \(S_1\). After averaging the total spin correlations of the two spin pairs, \(S_1S_2\) and \(S_1S_3\), the mean \(a_n\) and \(b_n\) are obtained as

\[
\overline{a_n} = -\frac{1}{2} S(S+1) \sin^2 \psi, \\
\overline{b_n} = -\frac{1}{2} S(S+1)(2 \cos^2 \psi - \sin^2 \psi).
\] (7)

For spin pairs in the same sublattice, the coefficients \(a_n\) and \(b_n\) are

\[
a_n = S(S+1) \sin^2 \psi, \\
b_n = S(S+1)(2 \cos^2 \psi - \sin^2 \psi).
\] (8)

Obviously, the spin pair-correlations in the three-sublattice spin model of \{Mo_{72}Fe_{30}\} depend only on \(\psi\), namely the vector of the spin at the origin. Expressions (7) and (8) have already been given by Blech and Averbach [22] in their original publication.

Based on the above discussion, we simulated the spin correlations of \{Mo_{72}Fe_{30}\} within one molecule because all the molecules are identical and the intermolecular magnetic correlations are negligible. The Fe^{3+} ion at the origin is chosen arbitrarily. The numerical simulation is performed for 250,000 different spin vectors randomly laid at the origin, i.e. 250,000 versions of the spin ground states of the \{Mo_{72}Fe_{30}\} molecule. A satisfactory degree of convergence was achieved in our simulation. The averaged spin correlations are plotted in figure 6 as a blue line, which is quite close to the measured profile of the magnetic diffuse scattering. Both the pronounced peak at \(\sim 0.70 \text{ Å}^{-1}\) and the broad feature at \(\sim 1.60 \text{ Å}^{-1}\) are well reproduced in the simulation. The dashed green line in figure 6 represents the 91% scaled simulation curve, which agrees better with the experimental data since 91% of the magnetic scattering was observed in our measurements at DNS.

Thus, we conclude that the three-sublattice spin configuration can explain the magnetic diffuse neutron scattering from \{Mo_{72}Fe_{30}\} successfully. The spin correlations measured from
Figure 7. Low-temperature specific heat data (black circles) and the best fit (red line) in terms of the combination of the lattice contribution (green line) and the Schottky contributions (see figure 8). The lattice contribution is the sum of the Einstein mode (dash-dot line) and the Debye mode (dashed line). Inset: low-temperature specific heat data with the total fit on a log–log scale.

this large, spin-frustrated magnetic system arise mainly from the individual molecules, due to the intrinsic properties of \(\{\text{Mo}_{72}\text{Fe}_{30}\}\) as a molecular magnet. It should be noted that the division of the three sublattices from 30 \(\text{Fe}^{3+}\) ions is not unique and our simulations cannot distinguish the different versions because they possess the same spin correlation functions [23].

3.2. Specific heat

Figure 7 shows the temperature dependence of the specific heat measured with zero external magnetic field within the temperature range 0.06–15 K from non-deuterated \(\{\text{Mo}_{72}\text{Fe}_{30}\}\) crystal. Since one \(\{\text{Mo}_{72}\text{Fe}_{30}\}\) molecule is composed of more than 1000 atoms, the lattice contribution to the total specific heat is significant, as compared with the magnetic contribution, even at low temperatures. Lacking a non-magnetic reference of \(\{\text{Mo}_{72}\text{Fe}_{30}\}\), the determination of the lattice contribution is difficult. Here we adopt a model with a combination of Debye and Einstein modes to the lattice specific heat. In figure 7, there is an obvious anomaly at \(\sim 3\) K and a small hump at \(\sim 0.3\) K, which can be seen clearly in the inset of figure 7 with a log–log scale. These two Schottky-like anomalies are fitted with conventional two-level Schottky models, accounting for the magnetic specific heat. Together, a satisfying total fit to the experimental specific heat is obtained, as shown by the red line in figure 7. In the inset of figure 7, it can be seen that the sample still possesses significant heat capacity even at 60 mK. After analyzing the raw data, we think this is because of the large crystal water content in our sample, which makes it very difficult for the sample to lose internal energy and settle at such a low temperature during the limited experimental time. This may explain the small divergence of the fitting curve and the specific heat data below 0.2 K.
Table 1. Fitting parameters for different methods (see text) to fit the total specific heat of \{Mo_{72}Fe_{30}\}. Evidence of the energy gap between the ground state and the first excited state from the INS study in [13] is also given for comparison.

| Methods          | Debye temperature $\Theta_D$ (K) | Energy gap $\Delta T_1$ (meV) | Energy gap $\Delta T_2$ (meV) |
|------------------|----------------------------------|--------------------------------|--------------------------------|
| Linear term used | 420.3 ± 25.1                     | 0.11 ± 0.01                     | 0.63 ± 0.01                     |
| Einstein term used | 349.7 ± 12.1                     | 0.09 ± 0.01                     | 0.64 ± 0.01                     |
| INS [13]         |                                  | ~ 0.6                           |                                |

The green line in figure 7 represents the lattice contribution to the total specific heat, described by the combination of Debye and Einstein terms [24, 25],

$$C_{\text{Latt}} = C_{\text{Ein}} + C_{\text{Debye}},$$

with the Einstein term

$$C_{\text{Ein}} = 3R_n \left( \frac{T_E}{T} \right)^2 \exp \left( \frac{T_E}{T} \right) \left[ \exp \left( \frac{T_E}{T} \right) - 1 \right]^{-2}$$

and the Debye term

$$C_{\text{Debye}} = R \frac{234r_D T^3}{\Theta_D^3}.$$
Figure 8. Magnetic specific heat contribution (black circles) obtained by subtracting the lattice contribution from the total specific heat data. The best fit using the Schottky terms is represented by the red line and the blue line, respectively.

kinds of excitations could also lead to a linear contribution to the specific heat. Nevertheless, we choose the method using the Einstein term, which seems to be more reasonable in our case. As seen in table 1, although the Debye temperature changes a lot in different methods, we are not very sensitive to this parameter due to the limited temperature range investigated and the energy gaps of the Schottky terms nearly remain the same. Therefore, it is not necessary to determine exactly the nature of the lattice specific heat of \{Mo_{72}Fe_{30}\} because the energy gaps relevant to magnetism are virtually unaffected by the specific model used.

The magnetic contribution is then obtained by subtracting the lattice contribution from the total specific heat, shown as circles in figure 8. Two Schottky-type anomalies are evident in figure 8, which can be well fitted with the two-level Schottky model \[29\],

\[ C_{\text{Sch}} \propto R \left( \frac{\Delta T}{T} \right)^2 \frac{\exp(\Delta T / T)}{[1 + \exp(\Delta T / T)]^2}, \]

(12)

where \( R \) is the gas constant and \( \Delta T \) is the energy gap (in K) between Schottky levels. The fitting results of the two anomalies are plotted as the red and the blue line in figure 8 and labeled as \( C_{\text{Sch1}} \) and \( C_{\text{Sch2}} \), respectively. The corresponding energy gaps \( \Delta T \) of \( C_{\text{Sch1}} \) and \( C_{\text{Sch2}} \) are then determined as 0.09 ± 0.01 and 0.64 ± 0.01 meV, respectively.

Now we study these low-lying magnetic excitations revealed from the specific heat data, in the light of the QRB theory for \{Mo_{72}Fe_{30}\}. Based on the three-sublattice spin configuration, an effective Heisenberg-type Hamiltonian is adopted with the absence of an external magnetic field and the spin anisotropy term \[11, 12\],

\[ \hat{H}_{\text{eff}} = \frac{J}{5} (\hat{S}_A \cdot \hat{S}_B + \hat{S}_B \cdot \hat{S}_C + \hat{S}_C \cdot \hat{S}_A). \]

(13)

Accordingly, the energy eigenvalues of Hamiltonian (13) are given by

\[ E(S) = \frac{J}{10} [S(S+1) - S_A(S_A+1) - S_B(S_B+1) - S_C(S_C+1)], \]

(14)
where $S_A$, $S_B$, $S_C$ are the spin quantum numbers of the three sublattices ($0 \leq S_{A,B,C} \leq 25$). $S$ is the total spin quantum number ($0 \leq S \leq 75$) and $J \approx 0.134 \text{meV}$ is the exchange constant [10, 11]. The degeneracies of the ground state ($S_A = S_B = S_C = 25$) and the first excited state ($S_A = 24, S_B = S_C = 25$ and the permutations) are $(2S + 1)^2$ and $27 \cdot (2S + 1)^2$, respectively [13].

The resultant low-lying energy spectrum is shown in figure 9. The black lines and red short lines stand for the ground state and the first excited state rotational bands, respectively.

At very low temperatures, the low-lying energy levels are most populated, among which the transitions are expected. The arrows in figure 9 indicate some possible intra- and interband transitions. As shown in figure 9, the energy of the intraband transitions between ground state levels is close to the energy gap $\Delta T_1 = 0.09(1) \text{meV}$ revealed by the Schottky term $C_{\text{Sch1}}$. There are some possible transitions between the ground state and the first excited state. A typical one is shown as the blue arrow with an energy gap of 0.70 meV, close to $\Delta T_2 = 0.64(1) \text{meV}$ obtained by $C_{\text{Sch2}}$. Because the intra- and interband energy gaps are not uniform and a small energy difference cannot be identified by specific heat, the two Schottky terms should actually account for a number of transitions with two sets of similar energies. In our case, we are unable to perform a many-level Schottky fitting to the magnetic contribution of the specific heat data, since we do not know exactly the transitions involved in the Schottky effect. However, the fit using a simple two-level Schottky model yields a satisfactory match with the experimental data. In an INS measurement on deuterated \{Mo$_{72}$Fe$_{30}$\} [13], the energy gap between the ground state and the first excited state is determined as $\sim 0.6 \text{meV}$, which is close to what we found in the specific heat data (see table 1). However, the intraband transitions within ground states could not be measured due to the high background of the INS at small energy transfer. Thus the anomaly at 0.3 K in the specific heat data of \{Mo$_{72}$Fe$_{30}$\} is considered to be due to the Schottky effect arising from the thermal population of discrete ground state energy levels, while the one at 3 K originates from the Schottky effect between the ground states and the first excited states.
The energy gaps that we found in the specific heat data basically reflect the low-lying magnetic excitations in \( \{\text{Mo}_{72}\text{Fe}_{30}\} \).

Hence, the Schottky anomalies observed in low-temperature specific heat measurements originate from the intraband transitions within the ground state levels, as well as the interband transitions between the ground state and the first excited state levels. Their energy gaps are in reasonable agreement with the theoretical prediction of the QRB model and the result of inelastic neutron scattering. These results give additional strong experimental support to the QRB theory and the three-sublattice spin configuration model of \( \{\text{Mo}_{72}\text{Fe}_{30}\} \) at very low temperatures. It is suggested that the QRB theory is still practicable in explaining the low-lying magnetic excitations of \( \{\text{Mo}_{72}\text{Fe}_{30}\} \) up to about 10 K with no external field.

4. Summary

We have measured the short-range spin–spin correlations from the spin-frustrated molecular magnet \( \{\text{Mo}_{72}\text{Fe}_{30}\} \) by means of diffuse neutron scattering with polarization analysis. The spin correlations collected at 1.5 K agree well with the simulation of the Fourier transform of the spin pair-correlation function using the three-sublattice spin configuration model. The spin correlations are found to localize within individual molecules, which is reasonable for \( \{\text{Mo}_{72}\text{Fe}_{30}\} \) as a molecular magnet. The low-temperature specific heat data with zero external magnetic field are analyzed and identify the low-lying magnetic excitations with energies of \( \sim 0.09(1) \) and 0.64(1) meV, which are in reasonable agreement with the prediction of QRB theory. As far as we know, this is the first time that experimental evidence of the energy gap between the lowest rotational bands in \( \{\text{Mo}_{72}\text{Fe}_{30}\} \) has been found. The validity of the QRB theory is supported. In conclusion, we find that the three-sublattice spin configuration can explain our experimental results well, in terms of both the spin correlations and the magnetic excitations. The three-sublattice spin configuration model is therefore a good approach to the magnetic ground state of \( \{\text{Mo}_{72}\text{Fe}_{30}\} \).

Acknowledgments

The authors thank W Schweika and R Hermann for helpful discussions. The authors also thank B Schmitz and H Schneider for help with the heat capacity and diffuse neutron scattering measurements.

References

[1] Sessoli R, Gatteschi D and Caneschi A 1993 Nature 365 141
[2] Thomas L, Lioni F, Ballou R, Gatteschi D, Sessoli R and Barbara B 1996 Nature 383 145
[3] Wernsdorfer W and Sessoli R 1999 Science 284 133
[4] Barmwell S T and Gingras M J P 2001 Science 294 1495
[5] Grohol D, Matan K, Cho J H, Lee S H, Lynn J W, Nocera D G and Lee Y S 2005 Nature Mater. 4 323
[6] Syozi I 1951 Prog. Theor. Phys. 6 306
[7] Broholm C, Appli G, Espinosa G P and Cooper A S 1990 Phys. Rev. Lett. 65 3173
[8] Schweika W, Valldor M and Lemmens P 2007 Phys. Rev. Lett. 98 067201
[9] Müller A, Sarkar S, Shah S Q N, Böge H, Schmidtmann M, Sarkar Sh, Kögerler P, Hauptfleisch B, Trautwein A X and Schünemann V 1999 Angew. Chem. Int., Ed. Engl. 38 3238

New Journal of Physics 12 (2010) 083044 (http://www.njp.org/)
[10] Müller A, Luban M, Schröder C, Modler R, Kögerler P, Axenovich M, Schnack J, Canfield P, Bud’ko S and Harrison N 2001 ChemPhysChem 2 517
[11] Schnack J, Luban M and Modler R 2001 Europhys. Lett. 56 863
[12] Axenovich M and Luban M 2001 Phys. Rev. B 63 100407
[13] Garlea V O et al 2006 Phys. Rev. B 73 024414
[14] Lago J et al 2007 Phys. Rev. B 76 064432
[15] Schärpf O and Capellmann H 1993 Phys. Status Solidi a 135 359
[16] Schweika W and Böni P 2001 Physica B 297 155
[17] Kraftmakher Y 2002 Phys. Rep. 356 1
[18] Hwang J S, Lin K J and Tien C 1997 Rev. Sci. Instrum. 68 94
[19] Bellissent-Funel M-C, Teixeira J and Bosio L 1987 J. Chem. Phys. 87 2231
[20] Brown P J 1995 Magnetic form factors International Tables for Crystallography vol C ed A J C Wilson (Dordrecht: Kluwer Academic) p 391
[21] Squires G L 1978 Introduction to the Theory of Thermal Neutron Scattering (Cambridge: Cambridge University Press)
[22] Blech I A and Averbach B L 1964 Physics 1 31
[23] Hasegawa M and Shiba H 2004 J. Phys. Soc. Japan 73 2543
[24] Barron T H K and Morrison J A 1957 Can. J. Phys. 35 799
[25] Affronte M, Lasjaunias J C and Cornia A 2000 Eur. Phys. J. B 15 633
[26] Zhou Z, Uher C, Xu D, Johnson W L, Gannon W and Aronson M C 2006 Appl. Phys. Lett. 89 031924
[27] Burgess S and Shepherd I W 1977 Chem. Phys. Lett. 50 112
[28] Foret M, Courtens E, Vacher R and Suck J 1996 Phys. Rev. Lett. 77 3831
[29] Tari A 2003 The Specific Heat of Matter at Low Temperatures (London: Imperial College Press)