Short-range Spin Correlations in Molecular Magnet $\{Mo_{72}Fe_{30}\}$

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The spin-frustrated molecular magnets have attracted intense interest. As a molecular analogue of the kagome lattice, $\{Mo_{72}Fe_{30}\}$ is one of the largest molecular magnets synthesized to date and represents a highly frustrated spin structure. We investigated the magnetic ground state of $\{Mo_{72}Fe_{30}\}$ by means of diffuse neutron scattering with polarization analysis. We explain the obtained magnetic diffuse scattering successfully within a three-sublattice spin model, which therefore proves to be a good approach to the magnetic ground state of $\{Mo_{72}Fe_{30}\}$.

As the smallest well-defined quantum magnets, molecular magnetic materials have attracted intense interest owing to their fascinating magnetic properties and potential applications in future quantum computing and massive data storage. In molecular magnets, each molecule contains a relatively small number of paramagnetic ions, i.e. spins, interacting via superexchange interactions. The magnetic molecules are well isolated by ligands, so that intermolecular magnetic interactions can be neglected as compared to the dominating intramolecular interactions. Some of the molecular magnets are ideal systems to observe quantum magnetic phenomena, such as quantum tunneling and quantum coherence. Though most efforts in the field of molecular magnetism have been dedicated to synthesize magnets with high-spin ground states, molecular magnetism is branching out into new areas to explore new types of low-dimensional molecular-based magnets possessing attractive physical properties. In this context, the spin-frustrated molecular magnets allow exotic magnetic ground states and provide valuable test beds for the understanding to geometrical spin frustration from both experimental and theoretical points of view.

As one of the largest molecular magnets ever synthesized, the polyoxomolybdate $\{Mo_{72}Fe_{30}\}$ represents a highly frustrated spin structure with negligible intermolecular interactions. The $\{Mo_{72}Fe_{30}\}$ molecule is shown as the inset of FIG. 3. 30 Fe^{3+} (S = 5/2, L = 0) ions serve as magnetic centers and occupy the vertices of an icosidodecahedron, forming twenty corner-sharing triangles. The 30 spins are antiferromagnetically coupled with the nearest neighbors [1]. Despite the difficulty in solving the complete Hamiltonian of this system, an approximate, diagonalizable effective Hamiltonian was adopted to explain the major low-temperature properties of $\{Mo_{72}Fe_{30}\}$ [2]. 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 coplanar sublattices with angular spacing of 120° (see the inset of FIG. 3). In order to understand the magnetic ground state of $\{Mo_{72}Fe_{30}\}$, the spin correlations of $\{Mo_{72}Fe_{30}\}$ are investigated quantitatively by means of diffuse neutron scattering with polarization analysis.

The polarized neutron scattering measurements were carried out on deuterated $\{Mo_{72}Fe_{30}\}$ polycrystals at diffuse neutron spectrometer DNS, FRM II. The incident wavelength is 4.74 Å. Within the quasistatic approximation, the nuclear coherent, spin-incoherent and magnetic scattering cross sections are separated simultaneously with the full *xyz*-polarization method. The absolute scattering intensity from the sample is obtained by the calibration against the spin incoherent scattering from a Vanadium standard.

FIG. 1 shows the nuclear coherent, spin-incoherent and paramagnetic components separated from the total scattering by means of *xyz*-polarization method. The spin-incoherent scattering intensity is nearly constant, suggesting a successful separation of different scattering contributions. The nuclear coherent scattering shows a broad hump at high Q around 1.80 $Å^{-1}$, which can be attributed to the scattering from amorphous crystal water. 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 line at the bottom of FIG. 1) of $\{Mo_{72}Fe_{30}\}$. The magnetic scattering obtained is almost 40 times smaller than the total scattering intensity, leading to long counting time to acquire reasonable statistics.

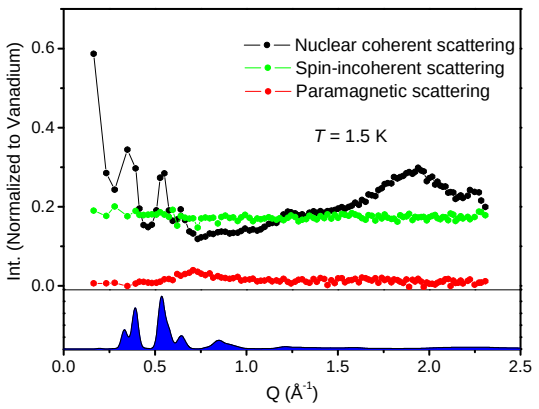

FIG. 1: Nuclear coherent (black circles), spin-incoherent (green circles) and paramagnetic (red circles) contributions to the total scattering of $\{Mo_{72}Fe_{30}\}$ at 1.5 K from xyz-polarization analysis on DNS. The blue area is the powder diffraction simulation convoluted with experimental resolution.

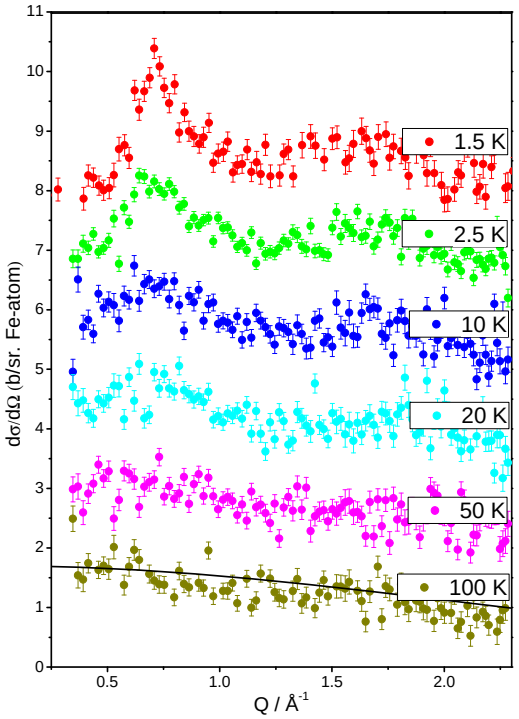

FIG. 2: Temperature evaluation of the differential magnetic scattering cross section $d\sigma_{mag}/d\Omega$ obtained from DNS measurements on deuterated $\{Mo_{72}Fe_{30}\}$ polycrystals. The data at different temperatures are displaced vertically by 1.5 b sr^{-1} per Fe atom each for clarity. The solid line is the pure paramagnetic form factor of Fe^{3+} (S = 5/2).

FIG. 2 presents the differential magnetic cross section, $d\sigma_{mag}/d\Omega$, extracted from the total scattering cross section at 1.5, 2.5, 10, 20, 50, and 100 K from DNS measurements. The magnetic scattering above 50 K agrees with the pure paramagnetic form factor of Fe^{3+} ions (black line in FIG. 2). Below 20 K, a diffuse peak at $Q \approx 0.70$ 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 owning to the strong geometrical spin frustration of the individual molecules and the lack of intermolecular magnetic interactions.

In order to determine the nature of the short-range magnetic order for the magnetic ground state of $\{Mo_{72}Fe_{30}\}$, we compare our experimental data with a simulation based on a rigid three-sublattice spin model consisting of classical S = 5/2 Fe^{3+} spins. The analysis of the data starts with the equation given by I. A. Blech and B. L. Averbach in Ref. [3] for the differential magnetic scattering cross section of spin pairs, which, already in powder average, can be written as,

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

where $(\gamma e^2/mc^2)$ = -0.54×10^{-12} cm is the magnetic scattering length, S is the spin quantum number of the scattering ion, $f(Q)$ is the magnetic scattering form factor, r_n is the distance from an atom at an arbitrary origin to the nth atom in the same molecule, and a_n and b_n are related to the probability of finding spin pairs with parallel components.

Only the spin correlations within individual molecules are considered in the simulation because the inter-molecular magnetic correlations are negligible. It should be noticed that actually every molecule in the sample could possess a specific ground state within the three-sublattice spin model, because the three spin sublattices can rotate as long as the 120° angle among their unit vectors is fulfilled. Therefore the final simulation should take a numerical average over all versions of the three-sublattice spin model, as shown by the blue line in FIG. 3. The simulation agrees well with the measured profile of the magnetic diffuse scattering.

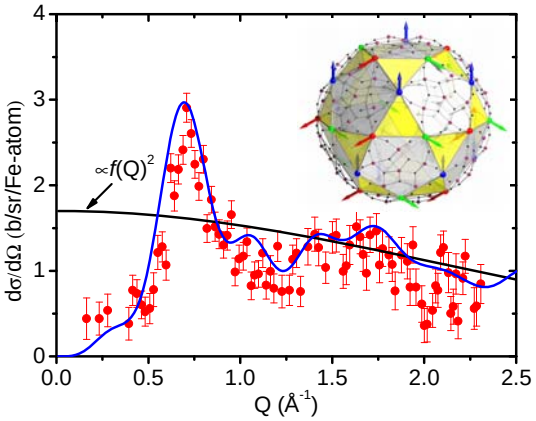

FIG. 3: Magnetic diffuse scattering at 1.5 K (red circles) and the simulation (blue line); Inset: one $\{Mo_{72}Fe_{30}\}$ molecule showing the three-sublattice spin model.

In conclusion, we have measured the short-range spin correlations from the spin-frustrated molecular magnet $\{Mo_{72}Fe_{30}\}$ by means of polarized neutron scattering method [4]. 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 model. We therefore demonstrate that the three-sublattice spin model could be a good approach to the magnetic ground state of $\{Mo_{72}Fe_{30}\}$.

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