Low-energy spin excitations in the molecular magnetic 
cluster \( V_{15} \)

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Abstract. – We report an Inelastic Neutron Scattering (INS) study of the fully deuterated 
molecular compound \( K_6[V_{15}^{14+}As_6O_{42}]\cdot9D_2O \) \((V_{15})\). Due to geometrical frustration, the essential 
physics at low temperatures of the \( V_{15} \) cluster containing 15 coupled \( V^{4+} \) (\( S=1/2 \)) is determined 
by three weakly coupled spin-1/2 on a triangle. The INS spectra at low-energy allow us to 
directly determine the effective exchange coupling \( J_0 = 0.211(2) \) meV within the triangle and 
the gap \( 2\Delta = 0.035(2) \) meV between the two spin-1/2 doublets of the ground state. Results 
are discussed in terms of deviations from trigonal symmetry and Dzyaloshinskii-Moriya (DM) 
interactions.

Introduction. – The recent discovery of quantum tunnelling of the magnetisation vector 
in magnetic cluster complexes with high-spin ground state (GS), for example Mn\(_{12}\)-acetate 
with \( S = 10 \) \([1,2,3]\), has triggered a renewed interest in molecular magnets containing a 
small group of metallic ions embedded in organic or inorganic ligands. In such structures, 
each metallic cluster is magnetically isolated from its neighbours, and this allows the study of 
the collective behaviour and inherent quantum size effects within a finite number of magnetic 
atoms. Such molecular Magnets with high-spin GS prove to be extremely valuable candidates 
to study phenomena, critical at the nanoscopic scale, such as slow relaxation and quantum 
tunnelling of the magnetisation \([1]\), quantum coherence \([2]\) and Berry phases \([3]\). Amongst the 
existing materials, systems with low-spin GS like the polyoxovanadate K\(_6[V_{15}As_6O_{42}]\cdot9H_2O\), 
shortnaming \( V_{15} \) hereafter, are of the greatest interest as they are shown to display quantum 
coherence and slow relaxation of the magnetisation despite their low-spin GS and the absence 
of any magneto-crystalline energy barrier \([4,5]\).

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In this context, INS is an extremely valuable technique to determine the key microscopic parameters controlling the tunnelling mechanism in high-spin clusters such as Mn$^{12}$-acetate $\text{Fe}_8$ $[10]$. In this Letter we report the first Inelastic Neutron Scattering (INS) study of a fully deuterated $V_{15}$ polycrystalline powder. Frustration of the exchange interactions plays a major role in its low-energy properties which can be accurately described by three weakly coupled spin-1/2. INS allows us to determine directly the effective exchange interaction $J_0 = 0.211(2)$ meV between the spins in the triangle and the GS splitting $2\Delta = 0.035(2)$ meV.

**Magnetic properties.** – $V_{15}$ is a polyoxovanadate molecular magnet made of 15 spins s=1/2 (all $V^{4+}$ ions) $[11]$. The symmetry is trigonal (space group $R\overline{3}c$, $a = 14.029$ Å $\alpha = 79.26^\circ$). The cluster has a local $C_3$ symmetry with the $V-V$ distances varying between 2.87 Å and 3.05 Å; the intermolecular dipolar couplings are very small (few mK) and will be ignored in most situations. As first discussed in Refs. $[12, 13]$, the $V^{4+}$ ($S=1/2$) ions are arranged in three layers as shown in fig. 1a, and are antiferromagnetically (AFM) coupled to their neighbours via oxo-bridges. Each of the two hexagons in fig. 1b contains three pairs of strongly coupled spins through oxo-bridge pathways between the $(VO_5)$ square pyramids.

Three types of couplings, shown in fig. 1b, are of importance for the magnetic properties: Nearest neighbour couplings $J \approx 70$ meV and $J' \approx 13$ meV and next-nearest neighbour couplings $J'' \approx 26$ meV. In addition, each spin of the central triangle is coupled to the hexagons via $J_1 \approx J'$ and $J_2 \approx J''$. Crucially, the three spins $S=1/2$ in the triangle are not directly coupled to each other by oxygen bridges like in the hexagons. Two exchange pathways between the triangle spins should be considered: One exchange pathway occurs via the upper and lower hexagons with $d(V-O-V_{\text{hex}}-O-V) \approx 10$ Å while the other is mediated by diarsenite bridges with $d(V-O-As-O-As-O-V) \approx 10$ Å. The latter coupling can be compared to an analogous complex, $V_{12}$ $[14]$, where the coupling through arsenite bridges is $J \approx 0.7$–$0.8$ meV with $d(V-O-As-O-V) \approx 5.3$ Å. The $V-V$ distance being much larger in the title compound, one expects the couplings through the diarsenite bridges to be much smaller than 0.7 meV in $V_{15}$.

Figure. 2 shows the DC susceptibility represented as $\chi_T$ versus $T$ for the fully deuterated version of $V_{15}$. No difference in the $\chi_T$ could be observed with the undeuterated compound $[12]$. The essential information from the susceptibility can be summarized as follows: At $T = 300$ K the $\chi_T$ product does not saturate as expected for a truly paramagnetic regime thereby indicating that the spins are still strongly correlated. Below 100 K, the $\chi_T$ curve exhibits a plateau at around 1.1 emu K mol$^{-1}$, a value consistent with three uncoupled s=1/2 spins. At lower temperature, a further drop of $\chi_T$ suggests a S=1/2 GS. In this regime, the dimers in the hexagons are firmly in a singlet state ($T < 0.1J$) and the cluster magnetic properties can be accounted for by three spin-1/2 coupled by weak effective antiferromagnetic exchange interactions within the central triangle. An obvious starting point is then the $S = 1/2$ AFM Heisenberg model on a triangle:

$$\mathcal{H}_0 = J_{12}S_1S_2 + J_{23}S_2S_3 + J_{13}S_1S_3,$$

where $S_1$, $S_2$, $S_3$ denote the spin operators on sites 1, 2, and 3, respectively (see fig. 1b) and $J_{ij}$ is the Heisenberg exchange parameter between spin $i$ and $j$. We first assume the equilateral triangle case: $J_{ij} = J_0$ for all $(ij)$ pairs. For an antiferromagnetic coupling ($J_0 > 0$), the GS consists of two degenerate $S=1/2$ Kramers doublets separated from the $S = 3/2$ excited state by an energy $3J_0/2$. The wave functions of the two degenerate $S=1/2$ Kramers doublets are given by $\Psi^0_{ij} = |0, \frac{1}{2}, \frac{1}{2}, \pm \frac{1}{2}>$ and $\Psi^+_{ij} = |1, \frac{1}{2}, \frac{1}{2}, \pm \frac{1}{2}>$ in the basis $|S_{12}, S_3, S, M_S>$ or any linear combination of them.

As a function of magnetic field the $M_S = -3/2$ component of the $S = 3/2$ spin state
crosses the $M_S = -1/2$ level of the ground state at a critical field $H_0 = 3J_0/2g\mu_B$. Recently, Chiorescu et al. observed a jump in the low-temperature magnetisation at $H_0 \approx 2.8$ T [8], which gave the first evaluation of the effective coupling: $J_0 = 0.211$ meV. The calculated susceptibility using the Heisenberg model of eq. [1] and $J_0 = 0.211$ meV matches very well our experimental $\chi T$ versus $T$ behaviour between 2 K and 40 K as shown in fig. 2. However this simple model must be refined according to several experimental results. Firstly, the magnetisation curve at low temperature exhibits an anomalous broadening of the jump at $H_0$ [8] which could not be explained by the equilateral triangular Heisenberg model and, more importantly, magnetisation relaxation experiments [7] suggest the presence of a tunnel splitting $2\Delta$ of the order of 9 meV within the $S = 1/2$ GS. This was ascribed to antisymmetric Dzyaloshinskii-Moriya (DM) terms [15]. In order to gain more insight, we have undertaken an INS study to directly probe the low-energy levels of this material.

**Neutron scattering experiment.** – We used a $m \sim 4$ g polycrystalline sample of fully deuterated V$_{15}$ placed under Helium in a rectangular flat Al slab (3 × 5 cm) of 3 mm thickness. The INS experiments were performed on the Time-of-Flight (TOF) spectrometer NEAT [11] at the BENS (Hahn-Meitner Institute, Germany) using cold neutrons with an incident wavelength of $\lambda_i = 8.0$ Å and at the ISIS Facility (Rutherford Appleton Laboratory, United Kingdom) using the backscattering TOF spectrometer IRIS with a final neutron wavelength of $\lambda_f = 6.66$ Å and the pyrolytic graphite (PG002) analyzer. On NEAT, the angle between the incoming beam and the plane of the sample holder was 135° and the experimental energy resolution $\Delta E_0$, measured from a vanadium sample and averaged over all scattering angles, was 43 $\mu$eV for zero energy transfer. The energy resolution $\Delta E$ depends on the energy transfer $\hbar \omega$ [17, 18] as shown in fig. 3b. Data reduction was carried out using the program INX, and the fitting procedure included the energy dependence of the instrumental resolution. On IRIS, the experimental resolution varies from 17 $\mu$eV at the elastic position to $\approx 28 \pm 2$ $\mu$eV at $\hbar \omega \approx \pm 0.3$ meV. The program ICON was used for data reduction.

The low-energy part of the scans obtained on NEAT is depicted in fig. 3a at several temperatures with an average momentum transfer $Q_{av} \approx 0.6$ Å$^{-1}$ [14]. At $T = 2$ K, the energy loss side (left-hand side) shows a single broad peak centered at $\hbar \omega \approx -0.315$ meV. As the temperature increases, a peak at the same energy appears on the energy gain side. The instrumental resolution at the inelastic peak positions is 32 $\mu$eV and 55 $\mu$eV in loss and gain, respectively, as shown in fig. 3b. The observed peaks have weakly temperature-dependent widths with FWHM values between 57 and 76 $\mu$eV on the loss side and between 82 and 100 $\mu$eV on the gain side. This is about twice the instrumental resolution, and we conclude that the peak contains more than one transition. In fact, the peaks have a flat-top shape in energy-loss suggesting that the observed broad peak is made of two unresolved INS transitions. Figure 3 shows the low-energy part of the spectrum obtained on IRIS at 1.5 K and 10 K with an average momentum transfer $Q_{av} \approx 1.1$ Å$^{-1}$ [14]. The peaks at $\hbar \omega = \pm 0.315$ meV correspond to those observed on NEAT but are superimposed on the thermal diffuse scattering of the PG002 analyzer. Again, the peaks on either side of the elastic line are broader than the instrumental resolution.

The mean energy of the peak corresponds to the energy expected for the $S = 1/2 \leftrightarrow S = 3/2$ INS transition in the equilateral Heisenberg model ($\hbar \omega_0 = 3J_0/2 = 0.315$ meV) with $J_0 = 0.211$ meV inferred from the magnetisation jump at $H \approx 2.8$ T. To account for the broader-than-resolution peak, we analysed the data as follows: The broad peak centered at 0.315 meV was fitted using two Gaussians at positions $\hbar \omega_1^0 = 3J_0/2 \pm \Delta$. The widths are kept fixed at the instrumental resolution values. Only $J_0$, $\Delta$ and an overall temperature-dependent intensity scaling factor, $I_T$, are allowed to float. In a first approximation, $I_T$ is
set equal for both transitions as no significant differences can be observed in their intensities within the experimental accuracy. The best fit is obtained for $J_0 = 0.211 \pm 0.002$ meV and $2\Delta = 0.035 \pm 0.002$ meV. The results are shown as solid lines in fig. 3a.

From these transitions alone, it is not possible to assess whether the splitting originates from the $S=1/2$ GS doublets or from the $S=3/2$ excited state. In both cases, the thermal energy, even at the lowest temperature (2 K), is much larger than $2\Delta \approx 0.4$ K, and the change in the population factor between 2 K and higher temperatures is too small to be measured in the relative intensities of the two transitions $\hbar\omega_0^\pm$. However, by subtracting the 10 K data from the 1.5 K data shown in fig. 2, it is apparent that two weak positive peaks occur at $\hbar\omega_1^\pm = \pm 0.035$ meV. Figure 4 shows the difference $\delta I = I_{1.5K} - I_{10K}$ in the low-energy region [$\hbar\omega$] $\leq 70$ \(\mu\)eV. These two peaks are symmetric around the elastic line and their energies coincide exactly with the value of the splitting inferred from the higher energy peaks. Even though the accuracy of the subtracting procedure is not good enough to analyze them quantitatively, the fact that the transitions at $\hbar\omega_1^\pm$ have a larger intensity at 1.5 K than at 10 K strongly suggests that the splitting is within the two $S=1/2$ doublets and not within the $S=3/2$ excited state [20].

Analysis. – To rationalise the observed splitting $2\Delta$, the equilateral triangular Heisenberg model must be refined. Two types of processes can be put forward: (a) Antisymmetric Dzyaloshinski-Moriya (DM) interactions [21], which occur as a result of spin-orbit coupling in non-centrosymmetric binuclear units (this is true for the edge sharing VO$_5$ units in V$_{15}$) and (b) deviations from purely trigonal symmetry: Removing the restriction $J_{12} = J_{13} = J_{23}$ in eq. 1 will release part of the exchange frustration and lift the degeneracy of the $S=1/2$ ground state.

Chiorescu et al. [7] first invoked DM terms as being responsible for the splitting in the ground state of V$_{15}$. The DM Hamiltonian may be written as

$$
\mathcal{H}_{\text{DM}} = \sum_{ij} D_{ij} \cdot (S_i \times S_j),
$$

where $D_{ij}$ is the DM vector for the pair $(ij)$ between $S_i$ and $S_j$ along the triangle. In pure trigonally symmetric trimuclear systems, $D_{ij}$ is identical for each bond pair and points parallel to the unique trigonal axis ($D_{ij} = Dz$) possibly leading to a non-collinear 120°-type spin arrangement in the XY plane. Including DM interactions in the total Hamiltonian, $\mathcal{H}_1 = \mathcal{H}_0 + \mathcal{H}_{\text{DM}}$, generates a splitting $2\Delta_1 = \sqrt{3}D$ between the two $S = 1/2$ Kramers doublets of energy $E^\pm = \pm \Delta_1$, and the eigenfunctions are now given by specific mixture of $\Psi_0^\pm$ and $\Psi_1^\pm$ [22, 23]. The observed splitting, $2\Delta = 0.035$ meV would then lead to $D \approx 0.02$ meV. The order of magnitude of $D$ can be theoretically estimated from the Moriya expression [21]: $D \approx (\Delta g / g_0)J_0$ where $\Delta g$ is the deviation of the average g-factor value, $g = 1.96$, from the free-ion value $g_0 = 2.00$. In our case, this would lead to a theoretical $D$ of $\approx 4.2 \mu$eV, a value 4.7 times smaller than the value deduced from the experimentally determined $2\Delta$. This discrepancy is indicative that the GS splitting is most probably not solely due to DM interactions. Next, we consider deviations from trigonal symmetry. Elements of non purely trigonal symmetry are present in the structure [1]: Despite the $C_3$ point symmetry of the complex in the average structure, disordered water molecules in the lattice can lead to local non-trigonal components, thereby inducing isosceles ($J_{12} = J$ and $J_{13} = J_{23} = J'$) or scalene triangles ($J_{12} > J_{13} > J_{23}$ in eq. 3) owing to the slight bond distance and angle differences. The GS degeneracy is then lifted with a gap $2\Delta_2$ between the two Kramers doublets given by $2\Delta_2 = (u^2 + v^2 - uv)^{1/2}$ with $u = J_{12} - J_{23}$ and $v = J_{13} - J_{23}$. No splitting of the $S = 3/2$
state is induced by this symmetry reduction. The lifting of the ground states degeneracy corresponds to a partial removal of the frustration in the equilateral triangular model.

In the isosceles case with $J > J'$ [24], the energy gap between the two Kramers doublets becomes $2\Delta_2 = J - J'$ where $\Psi_0^\pm$ is the ground state separated by $2\Delta_2$ from the $\Psi_1^\pm$ state. Using this model to analyze the INS data, we obtain $J = 0.223$ meV and $J' = 0.188$ meV, and the corresponding calculated $\chi T$ curve between 100 K and 1.8 K is shown in fig. 2 (dashed curve). The result is not distinguishable to that of the equilateral model in this temperature range since $T \geq |J - J'|$ down to $T = 1.8$ K. It shows, in passing, that the powder susceptibility alone, above $T = 1.8$ K (i.e. $T \gg 2\Delta$), does not provide conclusive information on the important splitting within the $S = 1/2$ ground states [25]. Both the DM interaction and a symmetry reduction of the equilateral triangle can induce a splitting in the ground state, and the observed 35 $\mu$eV gap in $V_{15}$ may be a combination of both processes.

Conclusion. – Our neutron scattering results on a deuterated powder of $V_{15}$ show directly and unambiguously that the effective Heisenberg coupling between the 3 $S=1/2$ spins in the triangle is $J_0 \approx 0.211$ meV and the presence of a splitting in the $S=1/2$ ground states of $2\Delta \approx 35\mu$eV. This splitting is twice as large as that reported in Ref. [7] from a two-level Landau-Zener model analysis of the magnetisation relaxation. Our value is more accurate as it is based on a direct spectroscopic observation of the gap. This splitting can be attributed to deviations from the trigonal symmetry and/or Dzyaloshinskii-Moriya antisymmetric interactions.

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Within the limited $Q$-range available ($0.6 \leq Q \leq 1.5 \ \text{Å}^{-1}$), we find that the $Q$-dependence of the transition intensities agrees with the expected behaviour for a polycrystalline trinuclear cluster, $I = I_0 |F(Q)|^2 (1 - \sin(QR_0)/QR_0)$, where $|F(Q)|$ is the magnetic form factor and $R_0 = 5.96 \ \text{Å}$. 

20. The INS intensities being controlled by the population factor of the initial state, transitions within the $S=3/2$ states (if split) would have a smaller intensity at $T = 1.5K$ than at $T = 10K$. 

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23. We restrict the discussion on the isosceles case due to its isospectrality with the the scalene case (see Schmidt H.-J. and Luban M., *J. Phys. A: Math. Gen.*, 34 (2001) 2389). 

24. In contrary to the case where the regime $T \leq 2\Delta$ can be accessed experimentally (see Gatteschi D., Sessoli R., Plass. W., Müller A., Krickemeyer E., Meyer J., Sölter D. and Adler P., *Inorg. Chem.*, 35 (1996) 1926, and reference therein).
Fig. 1 – (a) Structure of the cluster anion in $[V_{15}As_6O_{42}]^{6-}$ cluster. The 15 $V^{4+}$ (dark solid spheres) form two outer distorted hexagonal layers and an inner triangular layer. (b) Schematic representation of the AFM exchange couplings between $V^{4+}$ ions according to the type of oxygen bridges involved in the exchange paths (distance and angle). The magnetic Hamiltonian is defined as $H = \sum_{\langle i,j \rangle} J_{ij} S_i S_j$ with $\langle i,j \rangle$ pairs as indicated. $S_1, S_2$ and $S_3$ in the triangle are loosely connected through the hexagons and diarsenite bridges.

Fig. 2 – DC SQUID magnetic susceptibility obtained on a 160 mg powder sample of deuterated $V_{15}$ at an applied external field $H = 0.1$ T. The powder averaged Landé g-factor is set to 1.96 from EPR data: $g_a = g_b = 1.95, g_c = 1.98$ [12, 13]. Solid and dashed lines are calculated curves from eq.1 for an equilateral triangle ($J_{12} = J_{23} = J_{13} = 0.211$ meV) and an isosceles triangle ($J_{12} = J_{23} = 0.223$ meV and $J_{12} = 0.188$ meV), respectively (see text).
Fig. 3 – (a) INS spectra of fully deuterated V$_{15}$ obtained on NEAT (HMI) at $\lambda_i = 8.0$ Å with detector angles $23^\circ \leq 2\theta \leq 71^\circ$. Data were collected at several temperatures and corrected for the background (empty sample holder) and detector efficiency (Vanadium metal reference). The solid lines are fits to the data as explained in the text. (b) Instrumental resolution $\Delta E$ as a function of the energy transfer $\hbar \omega$ calculated for NEAT. The calculation of the energy dependence of $\Delta E$ is performed according to NEAT specifications [17] and rescaled by hand to match the measured elastic energy resolution $\Delta E_0$. (c) INS spectra at 1.5 K and 10 K obtained on IRIS (ISIS) with $\lambda_f = 6.66$ Å$^{-1}$ and for detector angles $28.5^\circ \leq 2\theta \leq 128^\circ$. Data were corrected similarly as for NEAT. The $T = 1.5$ K Data after subtraction of the thermal diffuse scattering is shown a solid lines.

Fig. 4 – Difference between the 1.5 K and the 10 K IRIS data. The arrows indicate the positive peaks discussed in the text.