Spin dynamics of heterometallic Cr\textsubscript{7}M wheels (M = Mn, Zn, Ni) probed by inelastic neutron scattering

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Inelastic neutron scattering has been applied to the study of the spin dynamics of Cr-based antiferromagnetic octanuclear rings where a finite total spin of the ground state is obtained by substituting one Cr\textsuperscript{3+} ion (s = 3/2) with Zn (s = 0), Mn (s = 5/2) or Ni (s = 1) di-cations. Energy and intensity measurements for several intra-multiplet and inter-multiplet magnetic excitations allow us to determine the spin wavefunctions of the investigated clusters. Effects due to the mixing of different spin multiplets have been considered. Such effects proved to be important to correctly reproduce the energy and intensity of magnetic excitations in the neutron spectra. On the contrary to what is observed for the parent homonuclear Cr\textsubscript{8} ring, the symmetry of the first excited spin states is such that anticrossing conditions with the ground state can be realized in the presence of an external magnetic field. Heterometallic Cr\textsubscript{7}M wheels are therefore good candidates for macroscopic observations of quantum effects.

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I. INTRODUCTION

Magnetic wheels are polynuclear molecular clusters with a ring-shaped cyclic structure and a dominant antiferromagnetic (AF) coupling between nearest-neighbor ions. For an even number of spin centers, the ground state is a singlet and the excitation spectrum is characterized by rotational and spin-wave like bands. Heterometallic rings with S\textsubscript{\neq} 0 can be obtained from an S = 0 homonuclear ring by chemical substitution of one or two magnetic centers. Theoretical calculations suggest that such systems could exhibit interesting quantum-coherence phenomena and are therefore of considerable interest. Indeed, the replacement of a magnetic ion in a cyclic structure allows one to modify the topology of the exchange interactions, that in turn plays a key role in determining the macroscopic behavior of the system.

Here we report the results of inelastic neutron scattering (INS) experiments on heterometallic AF rings, and we show that the spin level sequence and dynamics are substantially modified with respect to those of the parent compound. The investigated wheels are derived from the spin-compensated neutral [Cr\textsubscript{8}F\textsubscript{8}(O\textsubscript{2}CCMe\textsubscript{3})\textsubscript{16}] ring by substitution of one divalent cation (M = Mn, Zn and Zn respectively). Recent investigations have shown that, within this Cr\textsubscript{7}M family, S = 3/2 rings exhibit magnetocaloric effects that could be exploited below T \textless~2 K, whilst Cr\textsubscript{7}Ni could be a suitable candidate for the physical implementation of qubits. The suggested opportunities are linked to properties that are very sensitive to the spin energy spectrum and to the composition of the spin wavefunctions. A reliable determination of these quantities is therefore relevant, and INS is known to be the most appropriate technique to address this problem.

Our INS experiments on Cr\textsubscript{7}M provide energy and intensity for several transitions between the anisotropy-split lowest spin multiplets. The analysis of the data leads to an accurate determination of the main features of the microscopic intra-cluster interactions, including nearest-neighbor isotropic exchange, zero-field splitting and dipole-dipole interaction parameters (inter-cluster interactions are very weak, of the order of 10 neV). The results obtained indicate that anticrossing conditions between the ground state and excited low-lying energy levels with the same symmetry can be met in Cr\textsubscript{7}M, by applying a suitable magnetic field. This is at variance with the situation in the parent Cr\textsubscript{8} ring, where ground state crossings involve states with different symmetry.

ground state of the so-obtained Cr\textsubscript{7}M wheels has a non-zero total spin (S = 1/2, 1 and 3/2 for M = Ni, Mn and Zn respectively). Recent investigations have shown that, within this Cr\textsubscript{7}M family, S = 3/2 rings exhibit magnetocaloric effects that could be exploited below T \textless~2 K, whilst Cr\textsubscript{7}Ni could be a suitable candidate for the physical implementation of qubits. The suggested opportunities are linked to properties that are very sensitive to the spin energy spectrum and to the composition of the spin wavefunctions. A reliable determination of these quantities is therefore relevant, and INS is known to be the most appropriate technique to address this problem.

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as confirmed by the vanishingly small level repulsion observed by heat capacity measurements. The occurrence of anticrossing conditions suggests that Cr$_7$M wheels are good candidates for the macroscopic observation of quantum phenomena arising from $S$-mixing, such as the quantum fluctuation of the magnitude of the total spin.

A correct interpretation of the experimental spectra requires a generalization of the orientation-averaged INS cross-sections for polycrystals, as proposed by Waldmann.

II. EXPERIMENTAL DETAILS

Deuterated micro-crystalline samples of (C$_2$D$_5$)$_2$NH$_2$[Cr$_7$MF$_8$(O$_2$(C$_2$D$_5$))$_{16}$] (M$^{2+}$ = Ni, Mn, Zn) have been prepared according to a slightly modified literature procedure, by dissolving chromium fluoride tetrahydrate (Aldrich) in a mixture of trimethyl-$d_5$-acetic acid and diethyl-$d_9$-amine (98% deuterated, Aldrich) before adding an excess of the second metal salt (nickel carbonate hydroxide tetrahydrate, manganese chloride tetrahydrate or basic zinc carbonate). The preparation of trimethyl-$d_5$-acetic acid starting from acetone-$d_5$ was adapted from standard methods.

All compounds were purified additionally on a silica gel column using toluene as the eluent and finally crystallized from a mixture of pentane/acetone by evaporation of the mixture of solvents at 313-318 K. X-ray diffraction analyses for all three compounds showed that crystals don’t have any solvent molecules in the crystal lattice. The observed Bragg peaks could be indexed in the tetragonal $P4$ space group, with lattice parameters at 100 K of $a = b = 19.9598(2)$ Å, $c = 16.0609(2)$ Å for Cr$_7$Ni; $a = b = 19.9375(2)$ Å, $c = 16.1079(2)$ Å for Cr$_7$Mn and $a = b = 19.8973(2)$ Å, $c = 16.0227(2)$ Å for Cr$_7$Zn. The magnetic rings have a diameter of about 10 Å and the metal atoms have an shape of almost regular planar octagon (Figure 1).

INS measurements have been performed at the Institute Laue-Langevin in Grenoble (France), with the direct-geometry time-of-flight spectrometer IN5, using about 2 grams of each compound. A flat disk geometry has been chosen for the aluminum sample holder (1.1 mm thickness, 5 cm diameter), in order to reduce multiple-scattering background. Neutron spectra have been recorded with the sample kept at different temperatures, between $T = 2$ K and $T = 12$ K, inside a standard liquid-$^4$He cryostat. Solid angle and detector efficiency calibrations have been performed using the spectrum of a vanadium metal sample. Neutron incident wavelengths $\lambda = 4$ Å, 5 Å and 9 Å were used, corresponding to instrumental resolutions at the elastic peak of 0.147 meV, 0.091 meV, and 0.019 meV respectively. The three sets of measurements allowed us to cover an energy-transfer range from $h\omega \sim 0.04$ meV to about 4 meV. The angular interval spanned by the detector banks corresponds to scattering vector amplitudes varying between $Q \sim 0.55$ Å$^{-1}$ and 2.6 Å$^{-1}$ at $h\omega \sim 1$ meV, and between $Q \sim 0.85$ Å$^{-1}$ and 2.2 Å$^{-1}$ at $h\omega \sim 3.7$ meV (for $\lambda = 4$ Å).

III. SPIN HAMILTONIAN AND INS MAGNETIC CROSS SECTION

The investigated systems are ensembles of independent identical magnetic units, each one described by the Hamiltonian operator:

$$H = \sum_{i=1}^{6} J_{Cr-Cr} s_i \cdot s_{i+1} + J_{Cr-M} (s_7 \cdot s_8 + s_8 \cdot s_1) + \sum_{i=1}^{8} s_i \cdot D_i \cdot s_i + \sum_{i<j=1}^{8} s_i \cdot D_{ij} \cdot s_j. \quad (1)$$

In the above equation we assume that sites $i = 1 - 7$ of the octanuclear ring are occupied by Cr$^{3+}$ ions, and site $i = 8$ is filled by the M dication. The first term is the isotropic, nearest-neighbor Heisenberg-Dirac-Van Vleck exchange interaction, with $J_{Cr-Cr}$ and $J_{Cr-M}$ being the exchange integrals for Cr-Cr and Cr-M pairs, respectively. The second term in Eq. 1 describes the local crystal-field interaction, whereas the third term gives the dipole-dipole intra-cluster interaction, evaluated within the point-dipole approximation. Assuming the $\hat{z}$-axis along the perpendicular to the ring plane, the second-order local anisotropy is expected to be dominated by the axial terms $d_i$, with smaller rhombic terms $e_i$.
ticular, it may fail to describe correctly the scattering molecular nanomagnets is not of general validity. In particular, described in [19] for polycrystalline samples of considered.

The parameters of the spin Hamiltonian (Eqs. 1-2) have been determined from a best fit of the neutron spectra of basis vectors

\[ I_{nm}(Q) = \sum_{ij} F_i^*(Q) F_j(Q) \times \left\{ \frac{2}{3}[j_0(QR_{ij}) + C_0^2 j_2(QR_{ij})]s_z, s_z + \frac{2}{3}[j_0(QR_{ij}) - \frac{1}{2}C_0^2 j_2(QR_{ij})](s_x, s_x + s_y, s_y) + \frac{1}{2}j_2(QR_{ij}) \left[ C_1^2 (s_z, s_x) + s_z, s_z + C_{-1}^2 (s_z, s_y) + s_y, s_y \right] \right\}, \]

where \( F(Q) \) is the magnetic form factor, \( R_{ij} \) gives the relative position of ions \( i \) and \( j \),

\[
\begin{align*}
C_0^2 &= \frac{1}{2} [3(R_{ijz}^2)^2 - 1] \\
C_2^2 &= \frac{R_{ijz}^2 - R_{ijy}^2}{R_{ijy}} \\
C_{-2}^2 &= \frac{2R_{ijx}R_{ijy}}{R_{ijy}} \\
C_{-1}^2 &= \frac{R_{ijx}R_{ijz}}{R_{ijy}} \\
C_{2}^2 &= \frac{R_{ijy}R_{ijz}}{R_{ijy}} ,
\end{align*}
\]

and

\[
\tilde{s}_\alpha, \tilde{s}_{ij} = \langle n | s_\alpha | m \rangle \langle m | s_{ij} | n \rangle \quad (\alpha, \gamma = x, y, z) .
\]  

Eq. 4 is the explicit form of the formula given by Waldmann in [20]. Besides being valid whatever the symmetry and amplitude of the magnetic anisotropy, Eq. 4 can be easily implemented in a numeric code.

The parameters of the spin Hamiltonian (Eqs. 1-2) have been determined from a best fit of the neutron spectra based on calculations of Eq. 4. We recall that from the INS selection rules only transitions with \( \Delta S = 0, \pm 1 \) and \( \Delta M = 0, \pm 1 \) have non-zero intensity. In the fitting procedure, a Gaussian lineshape is associated with each allowed transition, with a Full Width at Half Maximum (FWHM) equal to the instrumental resolution and an area proportional to the calculated transition strength. For high-energy transitions, a broadening of the final state reflecting lifetimes effects has been assumed. The parameters defining the Hamiltonian have then been varied until the best agreement between calculated and experimental spectra was obtained.

The anisotropic part of the spin Hamiltonian can be written in terms of irreducible tensor operators (ITO) of rank \( k = 2 \), and therefore mixes states with different \( S \) and \( M \), or at least states with different \( S \) if the anisotropy is purely axial. Therefore the total spin \( S \) is not a good quantum number and the total Hamiltonian cannot be diagonalized within each \( (2S + 1) \)-dimensional block. This difficulty can be overcome by the procedure proposed in [23] and used to evaluate the mixing between the lowest lying \( S \) multiplets in the \( \text{Cr}_8 \) ring [15].

First, the minimum ensemble of spin manifolds required to reproduce the INS cross-section at high-energy transfer is determined assuming isotropic exchange only. Then the complete Hamiltonian is diagonalized in the corresponding subspace. In this way one obtains the energy spectrum and the spin states \( |n\rangle \) as linear combinations of basis vectors \( |(\hat{S})SM\rangle \) labelled by the set of intermediate spin states \( \langle \hat{S} \rangle \), with coefficients \( \langle \hat{S} \rangle SM |n\rangle \).

A stringent test for the spectroscopic assignment of
the observed transitions is provided by the $Q$ dependence of their intensity, which is essentially determined by the geometry of the cluster and the composition of the spin wavefunctions. This dependence can be easily measured with properly calibrated detectors at different scattering angles, and the results can be compared with calculations using Eq. 4.

### IV. EXPERIMENTAL RESULTS

#### A. Cr–Ni

Figure 2 shows the angle-integrated INS intensity recorded at $T = 2$ K for the Cr–Ni sample, with IN5 operated at $\lambda = 5$ Å. The two peaks emerging at 1.19 meV and 1.34 meV correspond to transitions between the $|S = 1/2, M = \pm 1/2\rangle$ ground state and the anisotropy split sublevels of the $|S = 3/2\rangle$ first excited spin state, $|S = 3/2, M = \pm 1/2\rangle$ and $|S = 3/2, M = \pm 3/2\rangle$. The solid line represents the intensity corresponding to the Hamiltonian given by Eqs. (1-2), with parameters $J_{Cr-Cr} = 1.46$ meV, $J_{Cr-Ni} = 1.69$ meV, $d_{Cr} = -0.03$ meV, and $d_{Ni} = -0.6$ meV. The $d_{Cr}$ value is the one determined for the CrK ring [15] and was kept fixed in the fitting procedure. As the INS response appears to be quite insensitive to the in-plane anisotropy, the non-axial part of the Hamiltonian has been neglected. With the parameters determined in this work, the ground state composition is dominated by the $|S = 1/2\rangle$ component, with a small $|S = 3/2\rangle$ contamination (about 1%); the first excited state is an almost pure $|S = 3/2\rangle$ multi-

![FIG. 2: Low energy transfer INS response for Cr–Ni at 2 K at $\lambda = 5$ Å. The displayed intensity is the sum for the whole detector bank. Background from the sample holder has been subtracted. The solid line is the intensity calculated with the approximate formula for the cross-section, taking into account S-mixing; broken line: calculated response with S-mixing set to zero. Inset: intensity calculated with S-mixing neglected is shown in Figure 2 by the dashed line.](image2)

The dependence can be easily measured with a small $|S = 3/2\rangle$ contamination (about 1%).

In the inset of Figure 2 the experimental data are compared with the curve calculated by the approximate INS cross-section reported in ref. 19, and the Hamiltonian parameters quoted above. Due to the large anisotropy at the Ni site, the Borras-Almenar et al. approximation is not adequate in the present case, and its use instead of Eq. 4 would lead to a completely wrong estimate of the Hamiltonian parameters. This difference is more evident.

![FIG. 3: Cr–Ni INS intensity of the peaks at 1.19 meV (circles) and 1.34 meV (triangles) as a function of the scattering vector amplitude, Q. Data have been obtained with incident wavelength $\lambda = 5$ Å and sample temperature $T = 2$ K. Calculated curves are represented by solid lines (to be compared with filled circles) and dashed lines (to be compared with triangles). Panel a) shows the result obtained with the INS cross-section as reported in IR; panel b) shows the output of Eq. 4. In both cases $J_{Cr-Cr} = 1.46$ meV, $J_{Cr-Ni} = 1.69$ meV, $d_{Cr} = -0.03$ meV, and $d_{Ni} = -0.6$ meV. The inset in panel b) shows the INS response integrated from 1.1 and 1.4 meV as a function of Q, compared with the calculated curve.](image3)
when comparing the $Q$ dependence of the transition intensities with theoretical estimates provided by the two formulae. As shown in Figure 3, the intensity of the transition involving the $|S = 3/2, M = \pm 1/2\rangle$ excited level at 1.19 meV is underestimated over a large $Q$ interval by the expression given in [18], whilst the intensity of the transition towards the $|S = 3/2, M = \pm 3/2\rangle$ state at 1.34 meV is overestimated by more than a factor two. In comparison, an excellent agreement between calculated curves and observed data is obtained when using Eq. [19] (Figure 3).

Excitations involving spin manifolds with higher energy can be observed by reducing the incident wavelength. Results obtained with $\lambda = 4$ Å at $T = 2$ K and $T = 12$ K are shown in Figure 4. At $T = 2$ K, weak excitations are observed between 3 and 4 meV. In addition, the weighted average axial anisotropy parameter $d = -0.045$ meV [24] is about 1.7 times larger than previously reported, because of the very large anisotropy of the Ni ion that was not estimated in previous works.

### B. Cr$_7$Zn

Substitution of a diamagnetic Zn$^{2+}$ ion for one Cr$^{3+}$ in the AF Cr$_8$ ring results in a $|S = 3/2\rangle$ spin ground state, whose anisotropy splitting can be observed by high-resolution INS experiments. Figure 5 shows the spectra recorded on IN5 with incident wavelength 9 Å (energy resolution at the elastic peak of 19 μeV), with the sample kept at 2 and 10 K.

Assuming crystal-field parameters similar to those determined in the Cr$_8$ parent compound, we expect an easy-axis anisotropy for the $S = 3/2$ spin manifold and an easy-plane splitting for the lowest $S = 5/2$ multiplet. In this hypothesis, the peak observed at about 0.01 meV is an intra-multiplet transition involving the system $|S = 3/2\rangle$ states (3/2, 0, 0, 0, 3/2), whose anisotropy split components of the $|S = 3/2\rangle$ ground state, whose anisotropy splitting can be observed by high-resolution INS experiments. Figure 5 shows the spectra recorded on IN5 with incident wavelength 9 Å (energy resolution at the elastic peak of 19 μeV), with the sample kept at 2 and 10 K.

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As shown in Figure 4, intermultiplet transitions at higher energy are observed with incident wavelengths of 4 and 5 Å. The peaks appearing in the $T = 2$ K spectrum are due to transitions from the split $|S = 3/2\rangle$ ground state towards $|S = 1/2\rangle >$ (0.83 meV), $|S = 5/2\rangle >$ (1.91 meV), $|S = 1/2\rangle >$ and $|S = 3/2\rangle >$ (2.25 meV), $|S = 1/2\rangle >$ (3.0 meV), and unresolved $|S = 5/2\rangle >$ and $|S = 3/2\rangle >$ states (3.6 meV).
angles), measured with incident wavelength of (a) $5 \, \text{Å}$ and (b) $4 \, \text{Å}$. The 0.4 meV peak in panel b is spurious. Smooth lines are best fits of the experimental data to a superposition of Gaussian line-shapes associated to allowed transitions. Each Gaussian contribution has an area proportional to the transition strength calculated with Eq. 4 assuming isotropic anisotropy splitting of the excited levels, so that the energy proportional to the axial crystal field parameter. As shown in Figure 6 the $\lambda = 9 \, \text{Å}$ high-resolution spectrum recorded at $T = 2 \, \text{K}$ shows a broad excitation that can be fitted by the superposition of two Gaussians, each with a FWHM equal to the instrumental resolution (19 meV) and centered at 0.095 and 0.11 meV, respectively. This is a clear indication of a sizeable rhombic term in the zero-field splitting Hamiltonian. By fixing the $d_{Cr}$ parameters to the values determined by INS for the parent Cr$_8$ compound ($d_{Cr} = -0.03 \, \text{meV}$), the best fit of the data is obtained for $d_{Mn} = -3 \, \mu\text{eV}$ (a factor two hundred smaller than the Ni case) and $e_{Cr} = e_{Mn} = 0$. If the S mixing is neglected, the ZFS parameters describing the anisotropic splitting of the $S = 1$ ground multiplet can be obtained by projecting the complete Hamiltonian onto the corresponding subspace. We obtain $H_{S=1} = D(S^2 - S(S + 1)/3) + E(S_x^2 - S_y^2)$ with a rhombicity $E/D = 0.13$. The latter is reduced by S

by the cryostat walls. The instrumental resolution in this configurations is not high enough to resolve the small anisotropy splitting of the excited levels, so that the energy separation of the doublets around 0.83 and 1.91 meV reflects the splitting of the ground state. Hot peaks associated to excitations from the first excited $|S = 1/2 >$ level appear at $T = 12 \, \text{K}$ around 1.39 and 2.6 meV. The solid and broken lines in Figure 6 are intensities calculated at the two temperatures assuming an exchange parameter very similar to the one reported for the Cr$_8$ ring in ref. [13]. $J_{Cr-Cr} = 1.43 \, \text{meV}$ for every nearest-neighbor Cr-Cr pairs, $J_{Cr-Zn} = 0$ (as Zn is diamagnetic) and $d_{Cr} = -0.028 \, \text{meV}$. The agreement with experimental data is very good and justifies the use of just one value for the $J_{Cr-Cr}$ exchange integrals, although the use of a less symmetric magnetic model would improve the fitting at high energy transfer. The spectroscopic assignments are confirmed by the $Q$ dependence of the transition intensities, as shown in Figure 7 where experimental data for some of the excitations observed are compared with curves calculated with Eq. 4. It is interesting to notice that the general behavior predicted for cyclic spin clusters by Waldmann [20] is followed also in the present case where the ring symmetry is broken by the dication.

C. Cr$_7$Mn

Substitution of one high-spin, $s = 5/2$, Mn$^{2+}$ ion for a Cr$^{3+}$ in the Cr$_8$ ring results in an uncompensated $|S = 1 >$ ground state. In the presence of purely axial anisotropy, the zero-field splitting would lead to a quasitriplet structure, with an $|S = 1, M = \pm 1 >$ doublet and an $|S = 1, M = 0 >$ singlet separated by an energy proportional to the axial crystal field parameter. As shown in Figure 7 the $\lambda = 9 \, \text{Å}$ high-resolution spectrum recorded at $T = 2 \, \text{K}$ shows a broad excitation that can be fitted by the superposition of two Gaussians, each with a FWHM equal to the instrumental resolution (19 μeV) and centered at 0.095 and 0.11 meV, respectively. This is a clear indication of a sizeable rhombic term in the zero-field splitting Hamiltonian. By fixing the $d_{Cr}$ parameters to the values determined by INS for the parent Cr$_8$ compound ($d_{Cr} = -0.03 \, \text{meV}$), the best fit of the data is obtained for $d_{Mn} = -3 \, \mu\text{eV}$ (a factor two hundred smaller than the Ni case) and $e_{Cr} = e_{Mn} = 0$. If the S mixing is neglected, the ZFS parameters describing the anisotropic splitting of the $S = 1$ ground multiplet can be obtained by projecting the complete Hamiltonian onto the corresponding subspace. We obtain $H_{S=1} = D(S^2 - S(S + 1)/3) + E(S_x^2 - S_y^2)$ with a rhombicity $E/D = 0.13$. The latter is reduced by S

FIG. 6: INS spectra for Cr$_7$Zn at 2 K (circles) and 12 K (triangles), measured with incident wavelength of (a) $5 \, \text{Å}$ and (b) $4 \, \text{Å}$. The 0.4 meV peak in panel b is spurious. Smooth lines are best fits of the experimental data to a superposition of Gaussian line-shapes associated to allowed transitions. Each Gaussian contribution has an area proportional to the transition strength calculated with Eq. 4 assuming isotropic anisotropy splitting of the excited levels, so that the energy proportional to the axial crystal field parameter. As shown in Figure 6 the $\lambda = 9 \, \text{Å}$ high-resolution spectrum recorded at $T = 2 \, \text{K}$ shows a broad excitation that can be fitted by the superposition of two Gaussians, each with a FWHM equal to the instrumental resolution (19 μeV) and centered at 0.095 and 0.11 meV, respectively. This is a clear indication of a sizeable rhombic term in the zero-field splitting Hamiltonian. By fixing the $d_{Cr}$ parameters to the values determined by INS for the parent Cr$_8$ compound ($d_{Cr} = -0.03 \, \text{meV}$), the best fit of the data is obtained for $d_{Mn} = -3 \, \mu\text{eV}$ (a factor two hundred smaller than the Ni case) and $e_{Cr} = e_{Mn} = 0$. If the S mixing is neglected, the ZFS parameters describing the anisotropic splitting of the $S = 1$ ground multiplet can be obtained by projecting the complete Hamiltonian onto the corresponding subspace. We obtain $H_{S=1} = D(S^2 - S(S + 1)/3) + E(S_x^2 - S_y^2)$ with a rhombicity $E/D = 0.13$. The latter is reduced by S

FIG. 7: Q dependence of the peaks appearing in the Cr$_7$Zn inelastic spectra shown in Figure 6 compared with theoretical estimates (solid lines). Triangles $|S = 3/2 >$ $|S = 1/2 >$ at 0.83 meV; circles $|S = 1/2 >$ $|S = 3/2 >$ at 1.38 meV; squares $|S = 3/2 >$ $|S = 5/2 >$ at 1.91 meV; open circles $|S = 3/2 >$ $|S = 5/2 >$ at 3.6 meV.
the anisotropy split components of the |S = 1 > ground state are observed. The solid line is the intensity calculated assuming both axial and in-plane anisotropy. The dash-dot lines represent the individual contributions to the broad, unresolved excitation from the transitions between the split |S = 1, M = ±1 > quasi-doublet and the |S = 1, M = 0 > singlet. The dot line gives the intensity calculated with S-mixing set to zero. The elastic peak and a quasielastic contribution have been included.

Both peaks therefore correspond to excitations within the lowest rotational-like band and their energy follows the Landé rule very closely. In these conditions, only an average exchange parameter can be estimated. Assuming $J_{Cr-Cr} = J_{Cr-Mn} = 1.43$ meV, calculations provide the spectra shown in Figure 9 by smooth lines. The agreement is satisfactory and a model with more parameters would not be justified by the data. Alternatively, by fixing $J_{Cr-Cr} = 1.46$ meV as in Cr$_7$Ni, the same results are obtained with $J_{Cr-Mn} = 1.37$ meV. The assignment of the two transitions to the Landé-band is corroborated by the Q-dependence of their intensity, shown in Figure 10. For both peaks a pronounced oscillatory behavior is observed, whilst an almost flat Q dependence is expected for transitions to states not belonging to the rotational band.

FIG. 8: Cr$_7$Mn high-resolution INS spectra collected with $\lambda = 9$ Å at $T = 2$ K. Two intra-multiplet transitions within the anisotropy split components of the |S = 1 > ground state are observed. The solid line is the intensity calculated assuming both axial and in-plane anisotropy. The dash-dot lines represent the individual contributions to the broad, unresolved excitation from the transitions between the split |S = 1, M = ±1 > quasi-doublet and the |S = 1, M = 0 > singlet. The dot line gives the intensity calculated with S-mixing set to zero. The elastic peak and a quasielastic contribution have been included.

The energy spectra of the heterometallic Cr$_7$Mn magnetic wheels resulting from our INS investigation are shown in Figure 11 as functions of the total spin, S. A parabolic band, formed by states with minimal energy for each S value, is easily identified. The levels belonging to this parabolic band have energies that closely follow the Landé interval rule, $E_S = \Delta_{10}[S(S + 1) - S_0(S_0 + 1)]/[S_1(S_1 + 1) - S_0(S_0 + 1)]$, where $S_0$ is the spin of the ground state and $\Delta_{10}$ is the energy of the first excited level, with spin $S_1$. Excitations involving adjacent

FIG. 9: Inelastic spectra at $T = 2$ K (circles) and $T = 12$ K (triangles) obtained for Cr$_7$Mn with an incident wavelength $\lambda = 4$ Å. The peak at 0.4 meV is due to spurious effects. Smooth lines are intensities calculated at 2 K (solid) and 12 K (dashed). The elastic peak and a quasielastic contribution have been included.

FIG. 10: Q-dependence of the peaks appearing in the Cr$_7$Mn inelastic spectrum at 12 K, compared with theoretical estimates: |S = 1 $\rightarrow$ S = 2 $\rightarrow$ at 1.6 meV (triangles and solid line); |S = 2 $\rightarrow$ |S = 3 $\rightarrow$ at 2.3 meV (circles and dashed line). The Q-dependence of the intramultiplet transition at 0.1 meV ($T = 2$ K) is compared with calculations in the inset.

V. DISCUSSION

The energy spectra of the heterometallic Cr$_7$Mn magnetic wheels resulting from our INS investigation are shown in Figure 11 as functions of the total spin, S. A parabolic band, formed by states with minimal energy for each S value, is easily identified. The levels belonging to this parabolic band have energies that closely follow the Landé interval rule, $E_S = \Delta_{10}[S(S + 1) - S_0(S_0 + 1)]/[S_1(S_1 + 1) - S_0(S_0 + 1)]$, where $S_0$ is the spin of the ground state and $\Delta_{10}$ is the energy of the first excited level, with spin $S_1$. Excitations involving adjacent
levels of the parabolic band have intensities with similar Q dependencies, with an oscillatory behavior and a pronounced maximum at a Q value related to the radius of the wheel. As discussed in [2, 3], these excitations are related to the combined quantum rotation of the oppositely oriented total spin on each Néel sublattice of the AF wheel.

Effects due to the mixing of different spin multiplets have been considered. Such effects proved to be important to correctly reproduce the energy and intensity of magnetic excitations in the neutron spectra. An interesting difference between the spin wavefunctions of the parent Cr₈ ring and those of the heterometallic derivatives concerns their symmetry. In Cr₈ the ground state and the first excited state belong to different irreducible representations of the molecule point group, whereas they have the same symmetry in the substituted wheels. This has important consequences on the system behavior in the presence of an external magnetic field. In Cr₈ the Zeeman splitting of the |S = 1, ±1 > doublet leads to a crossing with the ground state at B = 6.9 T with no level repulsion and a vanishingly small Schottky anomaly in the heat capacity. On the other hand, according to the results of the diagonalization of the Hamiltonian Eqs. 1–2, anticrossings between the lowest lying levels are expected in the Cr₇M compounds. At the anticrossing conditions, a finite Schottky anomaly will occur, with an amplitude that depends on the angle between the applied magnetic field and the easy-axis. Moreover, the enhancement of S-mixing at the level anticrossings will produce maxima in the torque signal corresponding to oscillations of the total spin amplitude, as observed for the Mn|[3 × 3] grid.

In the investigated series, Cr₇Ni is particularly interesting. The amount of S-mixing in this ring is quite small, corresponding to about 1% admixture of S ≠ 1/2 components in the ground state. Cr₇Ni can therefore be considered as an effective S = 1/2 system suitable for the implementation of the qubit.

VI. SUMMARY

Intra-multiplet and inter-multiplet excitations involving spin manifolds with energy smaller than 4 meV have been measured with Inelastic Neutron Scattering in polycrystalline samples of the heterometallic wheels Cr₇M (M = Ni, Mn, Zn). The minimum set of exchange and local crystal field parameters necessary to describe the physics of each investigated compound has been determined by comparing the experimental spectra with theoretical cross-sections. The results obtained show that chemical substitution of magnetic ions in a cyclic structure can be used to tailor the magnetic properties of the wheels, by controlling the microscopic exchange interaction. Finally, the explicit form of the general powder-averaged INS cross-section given in Ref. 20 and suitable to describe molecular nanomagnets of any symmetry has been presented.

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