Magnetic cluster excitations in the antiferromagnetic phase of α-$MnMoO_4$

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The tetramer-based compound α-$MnMoO_4$ exhibits four prominent peaks in the inelastic neutron scattering (INS) spectrum between 0.5 and 2.0 meV below 10 K. They are assigned to magnetic excitations of the $(Mn^{2+})_4$ rhombus shaped cluster, with resulting values of the exchange parameters $J=+0.051$ meV and $J'=-0.019$ meV along the edges and the short diagonal, respectively. The interactions within the tetramer are treated exactly in an isotropic quantum mechanical model leading to an $S=10$ cluster ground state. The weaker antiferromagnetic (AFM) intercluster interactions, $J_{int}=-4.5\times10^{-3}$ meV, are treated in a molecular-field model below the AFM transition temperature $T_N=10.7$ K. INS and susceptibility are in quantitative agreement with this approach.

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Small clusters of magnetic ions have long served as models for a detailed study and understanding of magnetic systems. Several scientific developments in the past 10 years have emphasized the importance and relevance of such studies. These include the remarkable experimental observations of quantum ($T=0$) phase transitions[1] and field-induced three-dimensional (3D) ordering in low-dimensional magnetic systems such as weakly interacting antiferromagnetic (AFM) dimers like $KCuCl_3$, $TlCuCl_3$,[2,3] $Cu_2(C_5H_{12}N_2)_2Cl_4$,[4–6] and $SrCu_2(BO_3)_2$ (Refs. 7,8) or Haldane chain systems like $Ni(C_5H_{14}N_2)_2N_3(PF_6)$.[9,10] The key ingredients are found in the complex interplay between intradimer and interdimer magnetic interactions that generates highly unusual ground states and may lead to entirely new effects like magnetization plateaus.[11]

Another emerging field, in which chemists and physicists are engaged in a transdisciplinary effort, is the area of molecular magnetism. In particular, spin clusters with large spin ground states and negative axial anisotropy were found to exhibit some outstanding properties. These so-called single-molecule magnets show magnetization hysteresis and slow magnetization relaxation at low temperatures.[12] Since single-molecule magnets occur as assemblies embedded in a crystalline environment, there exist intermolecular interactions which, in most cases, can be assumed to be negligibly small. Recently, two tetrameric Mn units in $[Mn_4O_3(OSiMe_3)(OAc)_3(dbm)_3]$ were found to be AFM coupled, each acting as a bias on its neighbor, resulting in a quantum behavior different from that of individual single-molecule magnets.[13,14]

Inelastic neutron scattering (INS) has proved to be a highly potent tool in all these studies. It is unique in allowing the direct spectroscopic determination of intramolecular and intermolecular exchange[2–4] and anisotropy splittings in zero field.[15] This is demonstrated here for the tetramer-based Mn^{2+} compound α-$MnMoO_4$.

α-$MnMoO_4$ crystallizes in the monoclinic space group C2/m and contains the tetranuclear Mn_4 clusters with 2/m (C_{2h}) symmetry shown in Fig. 1.[16] The clusters are composed of edge-sharing MnO_6 octahedra. These bridges provide pathways for superexchange interactions between the spin-only $S=\frac{5}{2}$ Mn^{2+} ions. A transition to 3D AFM order occurs at $T_N=10.7$ K.[17] The magnetic structure revealed by powder neutron diffraction is characterized by a ferromagnetic (FM) alignment of the four spins within the cluster and AFM order of the cluster spins on the two sublattices. Neighboring Mn_4 clusters are connected by MoO_4 tetrahedra, and there are eight near-neighbor clusters within shortest Mn-Mn separations of 5.18 Å and 5.93 Å, all belonging to the opposing spin sublattice.

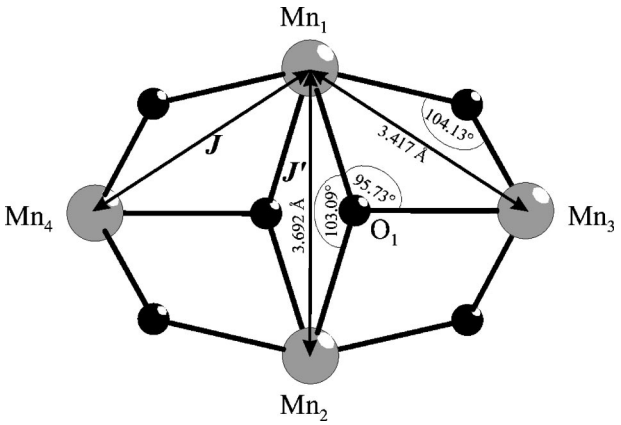

FIG. 1. Structure of the Mn_4 cluster with the intermediate oxygen atoms and the relevant distances and angles indicated. J and J' are the exchange parameters along the edges and the short diagonal of the rhombus, respectively.

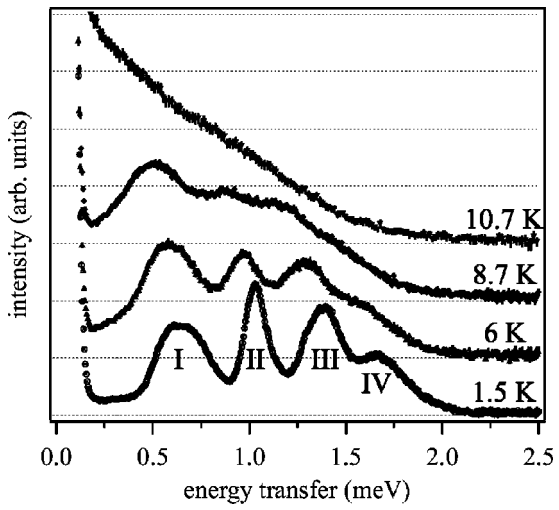

FIG. 2. INS spectra of polycrystalline α-$MnMoO_4$ measured on the time-of-flight instrument FOCUS at SINQ at four temperatures. $\lambda = 4.75$ Å, sum of all scattering angles. The inelastic features I to IV are discussed in the text.

With respect to the magnetic interactions and excitations we thus expect an interesting situation. A very high cluster spin $S_{cluster} = 10$ resulting from the dominant FM interactions within the tetramer and weaker AFM interactions between the cluster spins. The combination of bulk magnetic measurements and spectroscopic INS results allows the determination of the relevant interaction parameters. Figure 2 shows the INS spectra of polycrystalline α-$MnMoO_4$ for $\lambda = 4.75$ Å between 1.5 K and 10.7 K obtained on the time-of-flight spectrometer FOCUS at the spallation neutron source SINQ, PSI Villigen, Switzerland. At 1.5 K well-defined inelastic peaks or bands with varying widths and labeled I to IV are observed. With increasing temperature the bands become broader, shift to lower energy, and finally merge into a broad shoulder on the elastic line above ~ 10 K. The intensities of the four bands at 1.5 K exhibit very distinct dependencies on the modulus of the scattering vector $\vec{Q}$. These data are shown in Fig. 3 for the bands I to IV. The band positions are independent of Q within experimental error.

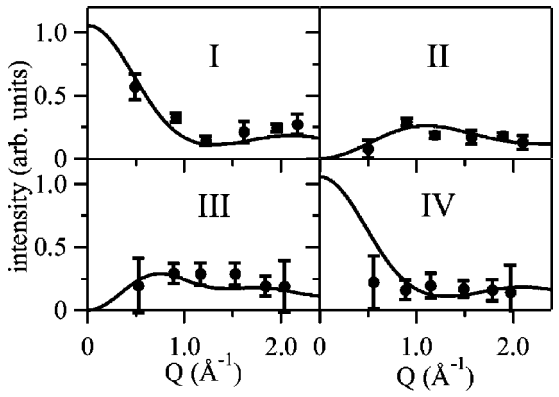

FIG. 3. Experimental and calculated [using Eqs. (4)] Q dependencies of the INS intensities.

In terms of the two dominant exchange interactions J and J', along the edges and across the short diagonal of the Mn_4 rhombus, respectively, the exchange Hamiltonian for the clusters can be written as (see Fig. 1)

$$\hat{H}_{intra} = -2J(\vec{S}_1\cdot\vec{S}_3 + \vec{S}_1\cdot\vec{S}_4 + \vec{S}_2\cdot\vec{S}_3 + \vec{S}_2\cdot\vec{S}_4) - 2J'\vec{S}_1\cdot\vec{S}_2. \tag{1}$$

We couple the spins within the cluster as follows: $\vec{S}_{12} = \vec{S}_1 + \vec{S}_2$, $\vec{S}_{34} = \vec{S}_3 + \vec{S}_4$, $\vec{S} = \vec{S}_{12} + \vec{S}_{34}$. The use of a Heisenberg Hamiltonian is justified by the $S_i = \frac{5}{2}$ spin-only character of Mn^{2+}. In the 3D AFM ordered phase, each cluster experiences an internal mean field H_{int} generated by exchange interactions between neighboring clusters via O-Mo-O bridges. As a result we get the following energy eigenvalues:

$$\begin{aligned} E(S_{12},S_{34},S,M_S) = &-J[S(S+1) - S_{12}(S_{12}+1) \\ &- S_{34}(S_{34}+1)] - J'[S_{12}(S_{12}+1) \\ &- S_i(S_i+1)] - g\mu_B H_{int} M_S. \end{aligned} \tag{2}$$

From the parallel alignment of the cluster spins in the ordered phase, determined by neutron diffraction,[17] we conclude that J in Eq. (2) is dominant and positive, i.e., FM. The interaction J' across the short diagonal can be either FM or AFM. For a negative J' value the lowest energy cluster states, with increasing energy, are given by:

$$\begin{aligned} |0\rangle &: E(5,5,10,10) = -50J - 12.5J' - 10g\mu_B H_{int}, \\ |1\rangle &: E(5,5,10,9) = -50J - 12.5J' - 9g\mu_B H_{int}, \\ |2\rangle &: E(4,5,9,9) = -40J - 2.5J' - 9g\mu_B H_{int}, \\ |3\rangle &: E(5,4,9,9) = -40J - 12.5J' - 9g\mu_B H_{int}, \\ |4\rangle &: E(5,5,9,9) = -30J - 12.5J' - 9g\mu_B H_{int}. \end{aligned} \tag{3}$$

A positive J' value would interchange states $|2\rangle$ and $|3\rangle$ and give equally good agreement with the experimental results. With a Mn_1-O_1-Mn_2 bridging angle of 103° a negative, i.e., AFM J' value appears more reasonable, and we tentatively assign the four bands I, II, III, and IV in Fig. 2 to transitions from the ground state $|0\rangle$ in Eqs. (3) to the four excited states $|1\rangle$, $|2\rangle$, $|3\rangle$ and $|4\rangle$, respectively. This assignment is supported by considering the intensities and their Q dependencies.

Neutron cross sections for magnetic excitations in numerous spin clusters have been derived.[18,19] Well-defined selection rules are obtained, and for the Mn_4 clusters in $MnMoO_4$ the following three cross sections for $|S_{12}S_{34}SM_S\rangle$ to $|S'_{12}S'_{34}S'M'_S\rangle$ transitions are relevant and nonzero:[19] for transition II we have

$$\Delta S = -1,\ \Delta M_S = -1,\ \Delta S_{34} = 0,\ \Delta S_{12} = -1:$$

$$\sigma \propto F^2(Q)\left[1 + (-1)^{-\Delta S_{12}}\frac{\sin(QR_{12})}{QR_{12}}\right]|A_1^q|^2, \tag{4a}$$

for transition III

TABLE I. Experimental and calculated INS excitation energies [Eqs. (3)] and relative intensities. For the calculation of intensities Eqs. (4) were integrated over the same Q range as the experimental data and scaled to 1 for band I. The cluster ground state is $|5,5,10,10\rangle$. Parameter values: $J=0.051$ meV, $J'=-0.019$ meV, $g\mu_B H_{int}=0.72$ meV.

Band	Excited state	E_{obs} (meV)	E_{calc} (meV)	I_{obs}	I_{calc}
I	5 5 10 9	0.65±0.04	0.72	1.00±0.02	1.00
II	4 5 9 9	1.04±0.03	1.04	0.63±0.02	0.62
III	5 4 9 9	1.36±0.05	1.23	0.81±0.08	0.65
IV	5 5 9 9	1.68±0.10	1.74	0.61±0.10	0.69

$$\Delta S=-1,\ \Delta M_S=-1,\ \Delta S_{34}=-1,\ \Delta S_{12}=0:$$

$$\sigma\propto F^2(Q)\left[1+(-1)^{-\Delta S_{34}}\frac{\sin(QR_{34})}{QR_{34}}\right]|A_3^q|^2, \qquad (4b)$$

and for transitions I and IV ($\Delta S=0,-1$, respectively)

$$\Delta S=0(-1),\ \Delta M_S=-1,\ \Delta S_{34}=0,\ \Delta S_{12}=0:$$

$$\sigma\propto F^2(Q)\left\{\left[1+(-1)^{-\Delta S_{12}}\frac{\sin(QR_{12})}{QR_{12}}\right]|A_1^q|^2+\left[1+(-1)^{-\Delta S_{34}}\frac{\sin(QR_{34})}{QR_{34}}\right]|A_3^q|^2+\left[4\frac{\sin\left(\frac{Q}{2}\sqrt{R_{12}^2+R_{34}^2}\right)}{\frac{Q}{2}\sqrt{R_{12}^2+R_{34}^2}}\right]A_1^qA_3^q\right\}. \qquad (4c)$$

In Eqs. (4), R_{ij} is the separation of the Mn^{2+} ions i and j, $F(Q)$ is the magnetic form factor and A_j^q are matrix elements of the form $\langle S'_{12}S'_{34}S'M'_S|\hat{T}_j^q|S_{12}S_{34}SM_S\rangle$ where $\hat{T}_j^q$ is a tensor operator of rank 1 with $q=1$. The expressions in square brackets are so-called structure factors, which are responsible for the very distinct character of the various transitions.[20] The agreement between the experimental and calculated INS excitation energies and intensities is shown in Table I. Calculated and observed Q dependencies of the four transitions are shown in Fig. 3. The experimental energies and intensities have been obtained by fitting Gaussian functions to the peaks. The best agreement is obtained with the following parameter values: $J=0.051\pm0.004$ meV, $J'=-0.019\pm0.003$ meV and $g\mu_B H_{int}=0.72\pm0.04$ meV. The overall agreement of energies, relative intensities and their Q dependencies is good, considering the simplicity of our theoretical approach. The deviations are due to the dispersive character of the transitions resulting from intercluster interactions, which are not explicitly considered in our model. The different shapes and widths of bands I, III, and IV in Fig. 2, which are up to three times larger than the instrumental resolution, reflect this energy dispersion.

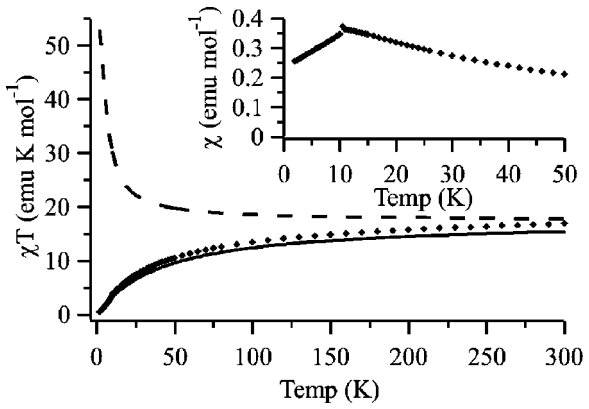

FIG. 4. Magnetic susceptibility represented as χT vs T. Dots: experimental points. Dashed line: calculated for isolated Mn_4 clusters with $J=0.051$ meV, $J'=-0.019$ meV, and $g=2.0$. Full line: including intercluster interactions with $J_{int}=-4.5\times10^{-3}$ meV. The inset shows χ vs T data below 50 K.

The dominant FM J value is responsible for the parallel alignment of the Mn^{2+} spins within the clusters in the ordered phase.[17] Taking the spin of each cluster as a *macrospin*, the internal field can be expressed as follows:[21]

$$g\mu_B H_{int}=2\langle\hat{S}_{cluster}\rangle zJ_{int}, \qquad (5)$$

where $\langle\hat{S}_{cluster}\rangle=10$, J_{int} is the near-neighbor intercluster parameter, and $z=8$ is the number of neighbors on the opposite sublattice. We derive a value $J_{int}=-4.5\times10^{-3}$ meV for this AFM parameter, which is about an order of magnitude smaller than the intracluster parameters, in good agreement with the structure. From the molecular-field parameters we can estimate the 3D-ordering temperature T_N using[21,22]

$$T_N=0.77\frac{S(S+1)}{3k}8J_{int}. \qquad (6)$$

We obtain a value of 11.9 K, in very good agreement with the experimental $T_N=10.7$ K, see inset of Fig. 4. This confirms the validity of considering each cluster as one magnetic unit with $S=10$ down to 1.5 K, and treating the intercluster interaction by a molecular field model. Also in agreement with this is the observed decrease of the excitation energies of the transitions I to IV between 1.5 K and 10.7 K (see Fig. 2). This is a direct result of the decrease of the internal field in this temperature range. The observed broadening of the bands with increasing temperature is due to the population of excited states, and the resulting hot transitions, which overlay with the cold ones.

In Fig. 4, we compare the experimentally observed magnetic susceptibility, represented as χT versus T, with the calculated values using the parameters derived above by INS. The dashed curve corresponds to a situation with $J_{int}=0$, i.e., no intercluster interactions. It shows the typical behavior of a ferromagnetically coupled cluster, i.e., a rise of χT with decreasing temperature. This is in sharp contrast to the experimental data, which clearly show a drop of χT with decreasing temperature. Including the intercluster J_{int} in the

calculation leads to the full line in Fig. 4. It is in excellent agreement with the experimental data, considering the simplicity of the model with no adjustable parameter. Despite the fact that the dominant intracluster parameter J is FM, the magnetic susceptibility above the ordering temperature shows the typical temperature dependence of an antiferromagnetically coupled system due to the AFM nature of both J' and J_{int} and to the large number $z=8$ of near-neighbor clusters. We conclude that extensive AFM near-neighbor correlations between clusters persist in the paramagnetic phase to temperatures well above T_N.

The FM nature of the dominant interaction parameter J along the edges of the rhombus is extraordinary. In most insulating Mn^{2+} and high spin Fe^{3+} compounds nearest-neighbor superexchange is AFM. We ascribe the FM coupling in the Mn_4 clusters of the title compound to the particular bonding situation at the oxygen atom labeled O_1 in Fig. 1. We note a particularly small angle of 95.7° at O_1 for the pathway J, and this is the dominant FM interaction within the cluster.

In conclusion we have shown, using powder INS and susceptibility measurements, that the magnetic properties of the tetramer-based cluster α-$MnMoO_4$ in the 3D AFM ordered phase are extremely well described by considering an assembly of weakly antiferromagnetically interacting Mn_4 clusters with an $S=10$ cluster ground state. Several INS transitions below $T_N=10.7$ K enable us to accurately determine both the FM interactions within the clusters and, in the mean field approximation, the weaker effective AFM interactions between the clusters. It is unprecedented for molecular magnetic behavior to be observed in a three-dimensional antiferromagnetic lattice. This demonstrates that cluster magnetic phenomena can be observed not only in molecular materials but also in continuous lattices which happen to display an ordered clustering of the magnetic ions.

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