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Internal magnetic structure of Mn_{12} acetate by polarized neutron diffraction

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Abstract. The internal magnetic structure of $[\text{Mn}_{12}\text{O}_{12}(\text{CD}_3\text{COO})_{16}(\text{H}_2\text{O})_4] \cdot 2\text{CD}_3\text{COOH} \cdot 4\text{H}_2\text{O}$ as determined by polarized-beam single-crystal neutron diffraction is reported. The standard picture, in which the inner tetrahedron of ($S = 3/2$) Mn^{4+} ions is polarized antiparallel to an outer ring of eight ($S = 2$) Mn^{3+} ions, is confirmed directly. While the total magnetization for the molecule is in good agreement with bulk measurements, the individual moment components on each of the three symmetry-independent Mn sites are less than predicted by the standard picture. There is no evidence for net moments on the oxygen atoms, but overlap of positive and negative magnetization on the oxygen sites cannot be ruled out.

The dodecanuclear mixed-valence manganese carboxylate complex, commonly known as Mn_{12} , $\text{Mn}_{12}\text{-Ac}$ or $\text{Mn}_{12}\text{-acetate}$ was first prepared and characterized, using x-ray diffraction, by Lis [1] in 1980. This molecule has subsequently attracted substantial attention in both the physics and chemistry communities, because of its unusual low-temperature magnetic properties [2]. It exhibits anomalous hysteresis loops with steps at certain critical fields at integer multiples of 0.46 T. These field steps provide clear evidence of a quantum process, and Mn_{12} is a model system for the study of tunnelling of the magnetization (from up to down and vice versa). This is of interest for two reasons: (1) because this is a direct manifestation of quantum physics in a macroscopic observable, just as in the Josephson effect or the quantum Hall effect; and (2) because of technological interest in possible quantum demagnetization of magnetic memories. At a minimum, high-spin magnetic molecules like Mn_{12} are ideal magnetic nanoparticles, in which a direct connection can be made between microscopic intramolecular magnetic interactions and the mesoscopic physics. Some headway has been made towards understanding the magnetic energy level scheme and intramolecular interactions, both by means of inelastic neutron scattering [3–5] and EPR [6, 7].

The crystal structure determinations [1, 8] of the molecular structure of Mn_{12} give three symmetry inequivalent Mn sites, the first of which Mn(1) forms a tetrahedral (or cubane, if one includes its related O(1) oxygen atoms) core to the molecule, with an outer ring of eight Mn(2) and Mn(3) atoms. Chemical titration indicated an average oxidation state of 3.34 per

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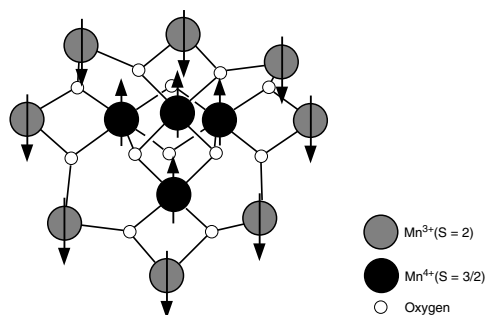


Figure 1. Schematic diagram showing the standard picture for the Mn_{12} molecule. Only the inner $\text{Mn}_{12}\text{O}_{12}$ core of the molecule is shown.

Mn atom, and consideration of the Mn–O bond lengths led Lis to propose a model in which the inner four Mn(1) ions are in the $S = 3/2$ Mn^{4+} state while the Mn(2) and Mn(3) ions are in the $S = 2$ Mn^{3+} state [1]. Subsequent magnetization measurements [9] gave the molecule a net spin $S = 10$ and this implies a model in which the inner Mn(1) tetrahedron is polarized antiparallel to the Mn(2) and Mn(3) ions, as shown schematically in figure 1. The definitive way in which to confirm this ‘standard picture’, and assign specific magnetization values to each of the Mn sites, is by magnetic neutron diffraction. One attempt using a polycrystalline sample, unpolarized neutrons and applied magnetic field has been published by Reynolds *et al* [10], and this study was consistent with the standard picture. Nevertheless, a much better way is to measure flipping ratios of polarized neutrons using a single crystal, as has been performed on the related $S = 12$ Mn_{10} cluster [11]. In this paper, we report a similar polarized-neutron study of Mn_{12} .

The polarized-neutron diffraction method extracts real-space magnetization densities by Fourier transforming the magnetic structure factors, which are in turn determined from the polarization dependence of the neutron cross-section. In the experiment, for each Bragg reflection with Miller indices (hkl) , the flipping ratio $R(hkl)$ between the intensity measured with the neutron polarization first parallel and then antiparallel to the applied magnetic field is measured. These flipping ratios are related to the nuclear and magnetic structure factors F_N and F_M by the relation

$$R(hkl) = \frac{F_N F_N^* + P_1 (F_N F_M^* + F_N^* F_M) + F_M F_M^*}{F_N F_N^* + P_2 (F_N F_M^* + F_N^* F_M) + F_M F_M^*}. \quad (1)$$

P_1 and P_2 are the polarizations of the incident neutron beam when polarized parallel and antiparallel to the field direction. For non-centrosymmetric structures, like that of Mn_{12} , F_N and F_M are in general both complex. However, the projection of the structure onto the tetragonal (001) basal plane possesses a centre of symmetry, and therefore the structure factors of the $(hk0)$ reflections are all real. For this set of reflections, equation (1) can be solved for F_M , so long as F_N is known:

$$F_M = F_N (X \pm \sqrt{X^2 - 1}) \quad (2)$$

where

$$X = \frac{P_1 - R P_2}{R - 1}. \quad (3)$$

In the course of this work, we discovered that Lis’s room-temperature x-ray structure [1] gave nuclear structure factors F_N that were inconsistent with our neutron data, and we therefore

performed a new low-temperature neutron structure determination [8] on a similar deuterated single crystal from the same batch as that used in this study. The essential conclusions from this study were that (1) while our sample was nominally fully deuterated, all labile deuterium atoms were in fact protonated, (2) the orientations of the methyl groups were determined, (3) both water (of crystallization) molecules were located including their hydrogen positions and (4) the two half-occupied solvent acetic acid molecules were located accurately, including all their deuterium/hydrogen atoms. In the latter case, this made sense as the acetic acid molecules sit in a hydrophobic pocket that can accommodate the molecule in one of two symmetry-related orientations. In addition, there is some distortion of the central $Mn_{12}O_{12}$ cage, compared to Lis's room-temperature result, as has been pointed out qualitatively by Mirebeau *et al* [5]. Finally, the mosaic spread of the crystal was determined to be $\sim 0.4^\circ$, and this gives support to the recent analysis by Bellessa *et al* [12] of their low-temperature tunnelling data. None of this matters greatly for the purposes of the present paper, other than that the structure is now known to $\sim 5\%$, and that we now have reliable values of F_N to employ in equations (2) and (3).

In this paper, we report a single-crystal neutron-diffraction study of a nominally fully deuterated single crystal, of mass ~ 50 mg at 20 K. Our experiment was performed on the D3 polarized-beam diffractometer at the Institut Laue Langevin using a neutron wavelength of 0.843 Å. In this configuration $P_1 = 0.9367 \pm 0.0003$ and $P_2 = -0.9487 \pm 0.0001$. As mentioned above, the mosaic spread of our crystal is approximately 0.4° FWHM. The crystal was aligned with its *c*-axis vertical and parallel to the applied magnetic field of 4.6 T. The experiment was performed at 1.7 K, a temperature much less than the energy of the first excited state, from $m = \pm 10$ to $m = \pm 9$, which lies at ~ 14 K.

A total of 25 inequivalent ($hk0$) reflections were collected, with magnetic structure factors F_M as listed in table 1. Using these values and equations (2) and (3), the only uncertainty is in choosing the roots of the quadratic equation, and this corresponds to deciding whether F_M is greater or less than F_N . Initially, we assumed $F_N > F_M$. At first, the standard picture (model 1 in tables 1 and 2), which has $-3 \mu_B$ on Mn(1) and $+4 \mu_B$ on Mn(2) and (3) was assumed. The magnetic structure factors were calculated and while agreement with observation was very good for some reflections, it was very poor for others. In the poor cases, the absolute value of the observed F_M was much less than the calculated value, and this is to be expected if one assumes $F_N > F_M$ when in fact $F_N < F_M$. The magnetic structure factors were therefore redetermined for these badly fitting reflections using the other root of equation (2). These values are listed in table 1. To obtain a first estimate of the actual moment associated with each site, the Mn(1) magnetization was modelled by that due to the spin of a free Mn^{4+} ion, and the Mn(2) and Mn(3) magnetizations by Mn^{3+} ions. This corresponds to the 'standard picture' and is listed as model 1 in tables 1 and 2. These moment magnitudes were then allowed to vary in a least-squares fit of the calculated to observed magnetic structures, giving the results listed under model 2 in tables 1 and 2. This model gives a magnetic moment of $20.56 \pm 0.90 \mu_B$ for the whole molecule, and this is not significantly different from the value for $S = 10$, nor the bulk magnetization measurement of $19 \mu_B$ [9]. However, the Mn(1) moments are reduced by $\sim 23\%$ and the Mn(2)/Mn(3) moments by $\sim 7\%$ compared to the values corresponding to the spins on the ions. This reduction is in very good agreement with the recent first-principles calculation by Pederson and Khanna [13], who calculate similar reduced moments when they include the acetate groups. In contrast, earlier calculations of the bare $Mn_{12}O_{12}$ cluster essentially gave model 1 [14]. We also tried a model with moments allowed on all the relevant oxygen and carbon atoms, namely those bridging the Mn ions directly or in carboxylate groups: this gave very little improvement in the *R*-factor, the fitted moments were generally comparable with their errors and we therefore conclude that model 2 contains essentially all the information that can be extracted from our experiment by least-squares fitting.

Table 1. Observed and calculated magnetic structure factors F_M for Mn₁₂ acetate at 1.7 K and 4.6 T. The models are described in table 2.

hkl	No of equivalent reflections	F_M (obs)	σ_{F_M}	F_M (model 1)	F_M (model 2)
200	4	-37.56	0.30	-35.28	-30.10
400	2	0.62	0.58	5.34	5.50
600	4	-1.47	0.10	-1.66	-1.72
310 ^a	4	13.20	0.32	20.22	17.47
510	4	-28.01	0.26	-29.73	-27.82
710	4	-11.67	0.35	-10.88	-10.31
910	4	13.06	0.24	15.38	13.32
420	4	7.08	0.18	7.17	06.86
130	4	22.30	0.21	24.75	21.53
330	4	-15.63	0.10	-17.25	-16.18
530 ^a	4	22.18	0.87	29.60	28.18
930	4	10.82	0.44	13.04	10.90
240 ^a	4	20.92	0.92	24.45	22.47
440	4	7.36	0.08	10.35	8.16
640	2	-10.77	0.92	24.45	22.47
150	4	7.64	0.11	7.06	7.10
350 ^a	4	-25.52	1.65	-32.92	-28.69
550	2	-4.44	0.72	-6.36	-3.89
750 ^a	3	-27.97	2.95	-24.76	-22.14
460 ^a	2	31.55	6.77	24.44	20.36
660	4	15.53	0.27	18.85	15.71
170 ^a	1	22.03	5.08	18.28	17.84
570	4	-9.93	0.16	-13.10	-10.13
480	2	3.54	1.79	7.46	4.98
190	1	-13.16	1.43	-17.63	-16.40
Goodness of fit χ^2				157	53
R -factor (%)				22.0	17.3
Number of parameters in model				3 (fixed)	3

^a Reflections with $F_M > F_N$.**Table 2.** Parameters (magnetic moments in μ_B) for the magnetic-structure models of Mn₁₂ acetate.

Atom	Model 1	Model 2	Theory ^a
Mn(1)	-3 (fixed)	-2.34 ± 0.13	-2.6
Mn(2)	4 (fixed)	3.69 ± 0.14	3.6
Mn(3)	4 (fixed)	3.79 ± 0.12	3.6
Total	20	20.56 ± 0.90	

^a See [13].

Nevertheless, the relatively high values of χ^2 in these fits suggest that there are significant features in the magnetization that are not included in the model(s). In an attempt to identify these features, the projection of the magnetization density onto the (001) plane was reconstructed using the maximum-entropy method [15, 16]. The resulting map is shown in figure 2. The main features are, as expected, regions of density associated with the Mn sites,

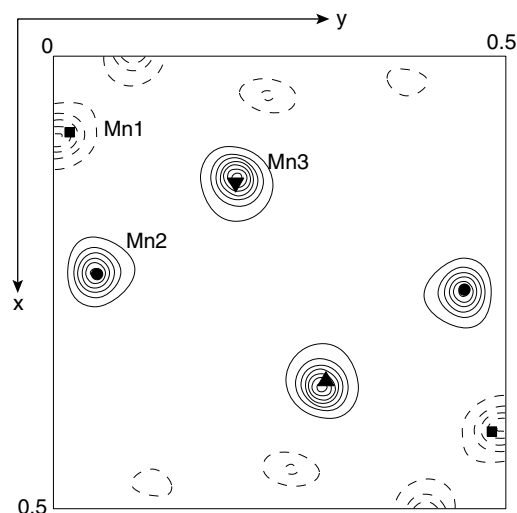


Figure 2. Maximum-entropy projection onto the (001) tetragonal basal plane of the magnetization density in Mn_{12} acetate at 1.7 K and 4.6 T. The contours are drawn at equal intervals of $1 \mu_B \text{ \AA}^{-2}$. Negative contours are shown as dashed lines. The molecule centres are at (0, 0, 0) and (0.5, 0.5, 0.5).

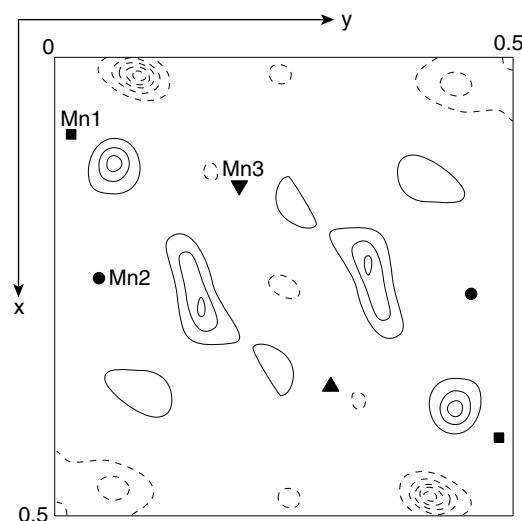


Figure 3. Maximum-entropy projection onto the (001) tetragonal basal plane of the difference between the observed magnetization density in Mn_{12} acetate and that predicted by model 2 including the fitted Mn moments listed in table 2. The contours are drawn at equal intervals of $0.25 \mu_B \text{ \AA}^{-2}$. Negative contours are shown as dashed lines. The molecule centres are at (0, 0, 0) and (0.5, 0.5, 0.5).

although there are small regions of negative density elsewhere. It is possible to obtain greater reliability in the maximum-entropy method by postulating an *a priori* density which is close to the expected one. In the present case, shown in figure 3, we postulate a flat density and use the differences between the observed structure factors and those calculated for model 2 as data. The most significant features in figure 3 are negative and positive regions that appear to be closely associated with the central part of the molecule, but which are not centred on any

particular atomic site. There is no evidence for any delocalized moment, of the type that has been inferred from deuterium NMR studies [17] of this system, although it seems probable that the deficit of moment on the Mn sites is due to overlap of areas of positive and negative spin transferred to the ligand ions. The features in the difference density map would then be due to incomplete spatial overlap of the positive and negative transferred spin.

In summary, we have confirmed the basic nature of the 'standard picture' of the Mn₁₂ magnetic structure directly and in a model-independent manner. While the total moment of the molecule is in good agreement with bulk measurements, the moments on individual sites are somewhat reduced with respect to the standard picture and there is extra magnetization elsewhere in the molecule. This extra magnetization is neither delocalized, nor can it be associated with particular O and C atom sites in the structure.

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