The 3d-Electron Heisenberg Pyrochlore Mn$_2$Sb$_2$O$_7$

Darren C. Peets,$^{1,2}$ Hasung Sim,$^{1,2}$ Maxim Avdeev,$^3$ and Je-Geun Park$^{1,2}$

$^1$Center for Correlated Electron Systems, Institute for Basic Science (IBS), Seoul 08826, Korea
$^2$Department of Physics and Astronomy, Seoul National University, Seoul 08826, Korea
$^3$Australian Nuclear Science and Technology Organisation, Lucas Heights, NSW 2234, Australia

In frustrated magnetic systems, geometric constraints or the competition amongst interactions introduce extremely high degeneracy and prevent the system from readily selecting a low-temperature ground state. The most frustrated known spin arrangement is on the pyrochlore lattice, but nearly all magnetic pyrochlores have unquenched orbital angular momentum, constraining the spin directions through spin-orbit coupling. Pyrochlore Mn$_2$Sb$_2$O$_7$ is an extremely rare Heisenberg pyrochlore system, with directionally-unconstrained spins and low chemical disorder. We show that it undergoes a spin-glass transition at 5.5 K, which is suppressed by disorder arising from Mn vacancies, indicating this ground state to be a direct consequence of the spins' interactions. The striking similarities to 3d transition metal pyrochlores with unquenched angular momentum suggests that the low spin-orbit coupling in the 3d block makes Heisenberg pyrochlores far more accessible than previously imagined.

Strong frustration, in which interactions compete, impedes spin systems from selecting a unique global ground state at low temperature, leading to a wide variety of physics in which fluctuations, quantum mechanical effects, and fine details of the spin-spin interactions can be crucial. Due to their extremely strong magnetic frustration, pyrochlore oxides and halides host a plethora of exotic phases, such as quantum spin liquids, or emergent magnetic monopoles for classical spins. However, the spins in nearly every known magnetic pyrochlore are either Ising- or XY-like, constrained through spin-orbit coupling to point directly into or out of the tetrahedra on whose corners they reside, or in a plane perpendicular, and in no other direction. Pyrochlore lattices with directionally-unconstrained Heisenberg spins are scarce and not as well studied. With far more degrees of freedom leading to far greater degeneracy, but also a greater ability to adapt to interactions, Heisenberg pyrochlore systems may offer immense potential for unveiling new physics.

Spin-orbit coupling, the interaction responsible for coupling spins to the crystal lattice thereby constraining their directions, strengthens as the atomic number increases. Heavy magnetic ions, such as the lanthanides most commonly encountered in the pyrochlore structure, are thus best considered in terms of spin-orbit-coupled $j$-states linked to the lattice. A comparative lack of pyrochlores containing magnetic ions from earlier in the periodic table, particularly the 3$d$ block, makes pure Heisenberg physics scarce in this lattice. The best-studied 3$d$-electron pyrochlores, spinel oxides in which the B-site forms a pyrochlore lattice, typically contain Cr$^{3+}$ ($s = 3/2$), whose orbital moments should not be fully quenched and may not behave as pure Heisenberg spins. To the authors’ knowledge, only three known materials host pure Heisenberg spins in a pyrochlore lattice: FeF$_3$, the pyrochlore variant of Mn$_2$Sb$_2$O$_7$ (pyr-Mn$_2$Sb$_2$O$_7$), and recently reported NaSrMn$_2$F$_7$. All have a high-spin 3$d^5$ electron configuration with fully quenched orbital moments, and both FeF$_3$ and pyr-Mn$_2$Sb$_2$O$_7$ are challenging to prepare by conventional solid-state synthesis. Pyrochlore FeF$_3$ orders magnetically at 22 K, a more than 10-fold suppression relative to its less-symmetric and less-frustrated rhombohedral polymorph, while the 2.7 K transition in NaSrMn$_2$F$_7$ also indicates very strong frustration. Curiously, pyr-Mn$_2$Sb$_2$O$_7$ has been reported to form a spin glass around 41 K, several times higher than the magnetic transition in its less-frustrated P3$_1$ polymorph. With pyr-Mn$_2$Sb$_2$O$_7$ having a Curie-Weiss temperature just under 50 K, its putative 41 K transition would correspond to remarkably low frustration in the most-frustrated known three-dimensional magnetic lattice.

In a Heisenberg pyrochlore, the most likely magnetic ground state would be a counterpart of the all-in-all-out state found in Ising pyrochlore antiferromagnets, but the considerable degeneracy could make a variety of other states possible, or may prevent long-range order. The lack of purely-Heisenberg systems and the anomalously low frustration in pyr-Mn$_2$Sb$_2$O$_7$ have hampered the search for novel physics. We show that the spin glass transition in pyr-Mn$_2$Sb$_2$O$_7$ is actually 5.5 K, corresponding to much higher frustration, and this transition is suppressed by Mn vacancies. The Mn$^{2+}$ magnetic ion adopts a 3$d^5$ high-spin electronic configuration, with no orbital degree of freedom, leaving the spin directions fully unconstrained. The magnetic behavior is strikingly similar to that in several closely-related 3d pyrochlores having unquenched orbital moments, indicating that the low spin-orbit coupling in the 3d transition metals may render a much broader family of materials as effective Heisenberg pyrochlore systems.

When prepared by conventional solid-state synthesis, Mn$_2$Sb$_2$O$_7$ forms in a distorted, chiral variant of the trigonal Weberite structure, but the desired py-
rochlore polymorph (Fig. 1a inset) can be stabilized at lower temperatures[19, 19]. We prepared powder samples of pyr-Mn$_2$Sb$_2$O$_7$ following Brisse[13], with precursor ‘antimonic acid’ prepared from SrCl$_2$ (Alfa Aesar, 99.997%) and deionized water as in Ref. 25. The precursor was ground with Mn(Ac)$_2$-4H$_2$O (Aldrich, 99.99%) then reacted for 12h at a temperature from 50 to 550°C in Al$_2$O$_3$ crucibles in air. Powder diffraction and magnetic measurements were used to verify phase purity and Mn site occupancy.

X-ray powder diffraction patterns were collected using a Bruker D8 Discover diffractometer with a CuKα source, while a Rigaku MiniFlex II was used to collect patterns on precursor ‘antimonic acid’ and monitor reaction completeness. Magnetization measurements were performed in a Quantum Design MPMS-XL magnetometer in RSO measurement mode: a ~10 mg powder sample was gently compressed inside a gelatin capsule, which was closed with Kapton tape and inserted into a plastic straw. The sample holder contribution was below the noise level. AC susceptibility was measured in the same magnetometer using the DC sample transport, at zero applied field. Specific heat was measured on a thin plate of pressed powder by the relaxation time method in zero applied field. Specific heat was measured at ANSTO, Australia, from 6.5 to 164°C (room temperature) and 2.4395 Å (low temperature). Diffraction data were Rietveld-refined in FullProf by the least-squares method[20]. Throughout this paper, molar quantities refer to formula units.

The temperature-dependent DC magnetization of pyr-Mn$_2$Sb$_2$O$_7$, shown in Fig. 1 indicates a magnetic transition at $T_f = 5.5$ K, below which the zero-field-cooled and field-cooled magnetization data (Fig. 1) diverge, implying that the spins order or freeze. This transition broadens and moves to higher temperature in field (Fig. 1), becoming indistinct above ~0.5 T. This is more clearly visible in the derivative (Fig. 1), which also shows that there is no evidence for any other transition. In particular, the transition reported around 41 K[14, 15] is absent. As shown in Fig. 1b, above ~80 K the magnetization obeys the Curie-Weiss law with a Curie-Weiss temperature $T_{CW} = -4.9$ K indicating predominantly antiferromagnetic interactions. Deviations from Curie-Weiss behaviour below ~80 K indicate the onset of short-range correlations more than an order of magnitude above $T_f$, while the approximately order-of-magnitude difference between $T_{CW}$ and $T_f$ indicates strong frustration. The paramagnetic moment of 5.59 μB is consistent with the spin-only expectation of 5.92 μB for high-spin 3d$^5$, confirming the absence of an orbital contribution and demonstrating that pyr-Mn$_2$Sb$_2$O$_7$ is indeed a Heisenberg spin system.

The field dependence of the magnetization (Fig. 2a) is S-shaped and exhibits hysteresis at low temperatures, which persists to at least 1.5 T with no clear onset field. The derivative (Fig. 2b) shows clearer evidence of the hysteresis and a lack of any sharp phase transition. Abrupt changes in the hysteresis loops where the field sweep rate was changed indicate strong relaxation effects on the timescale of minutes. To verify this, Fig. 2 shows the results of field-training the sample by cooling to 1.8 K in a 0.1 T field, then monitoring the ensuing magnetization decay after reducing the field to zero. The magnetization is well described by a stretched exponential $M(t) = M_0 + M_R \exp(-t/t_p)^{1-P}$, with a non-relaxing offset $M_0 = 21.6(2)$ cm$^3$ Oe mol$^{-1}$, a substantial relaxing component $M_R = 31.7(14)$ cm$^3$ Oe mol$^{-1}$, time scale $t_p$ of 835(112) s, and exponent of 0.7843(97). An S-shaped hysteresis loop with rate- or time-dependent hysteresis is one key hallmark of a spin glass[27].

The zero-field AC susceptibility $\chi$ measured with an excitation amplitude of 1 Oe, shown in Figs. 2c,d, also shows fingerprints of strong relaxation. A broad peak at low frequencies in the real component $\chi'$ agrees well with the magnetization transition, then shifts to significantly higher temperatures as the frequency increases. The imaginary component, $\chi''$, becomes weakly positive on cooling through the transition, indicating dissipation as the low-frequency measurement field aids the system in finding a ground state. By tracking the frequency dependence of the intrinsic low-temperature transition, the Mydosh parameter $\varphi = \Delta T_N/T_N \Delta \log f = 0.044$
FIG. 2. Magnetic response of pyr-Mn$_2$Sb$_2$O$_7$. (a) $M(H)$ loops; slight hysteresis at 1.8 and 4 K is more evident in (b) the derivative $dM/dH$. This smooth field and temperature evolution shows no evidence for an abrupt phase transition. Jumps in the derivative correspond to changes in sweep rate. (c) A broad peak in the real part of the zero-field AC susceptibility at $T_1 = 5.5$ K, the same temperature identified in $M(T)$, shifts substantially as the drive frequency increases. (d) The loss, $\chi''$, is weakly positive below the transition. (e) Strong relaxation is visible at 1.8 K. The sample was cooled in a field of 0.1 T, then the field was removed and the zero-field relaxation monitored. (f) Evolution of the intrinsic transitions and frustration in $M_2$Sb$_2$O$_7$ for $M$=Ni, Co, Mn, based on Ref. [15].

Low-temperature data are highlighted in the inset, and data on Weberte Sr$_2$Sb$_2$O$_7$ serve as a baseline. (b) The broad peak in $c_p(T)/T$ is modified only slightly in field. Magnetic entropy is apparent to at least 40 K. (c) The approximate magnetic entropy calculated by subtracting the Sr$_2$Sb$_2$O$_7$ data. The entropy expected for $s = 5/2$ cannot all be found below $\sim$20 K in the $c_p/T$ peak.

Low-temperature neutron diffraction patterns collected through $T_1$ are shown in Figs. [4] and [5]. The transition introduces no new peaks nor significant changes to the intensities of existing peaks, as further demonstrated by taking the difference across the transition. It is worth noting that there is no low-temperature structural transition that could reduce the frustration. Fig. [3] highlights the presence of a diffuse magnetic component near the (111) nuclear Bragg peak at a $d$-spacing of $\sim$5.8 Å, which becomes indistinct above 20 K, in line with the magnetization and specific heat results. The temperature dependence is shown in Fig. [4], based on fitting each difference pattern to a Gaussian with a sloping background. pyr-Mn$_2$Sb$_2$O$_7$ now meets all the canonical criteria and has all the earmarks of a spin glass: the ZFC and FC magnetization differ, strong relaxation is observed, the AC susceptibility is strongly frequency dependent, there is only a broad hump below the transition in the specific heat, and long-range order is absent.
Mn ions in pyr-Mn$_2$Sb$_2$O$_7$ populate an extremely high-symmetry lattice which should be essentially free from chemical disorder, so there should be nothing extrinsic to the spin system that could locally lock the spins and force a glass transition. Since pyr-Mn$_2$Sb$_2$O$_7$ most likely forms through substituting Mn atoms into the pre-existing pyrochlore matrix of Sb$_2$O$_7 \cdot nH_2$O \cite{13}, a manganese deficiency is possible and manganese vacancies may be the dominant defect. X-ray diffraction indicated Mn deficiencies in incompletely-reacted material and those prepared from Mn-poor mixtures, but the Mn site refined to full occupancy in all samples reported above. Mn-deficient samples show a significant suppression of $T_c$, often with no evidence for even the onset of a transition above 1.8 K, but with much stronger field-enhancement in the specific heat — an incompletely-reacted example is shown in Fig. 5. This suppression by disorder strongly suggests that the magnetic freezing is intrinsic. As thermal fluctuations diminish on cooling, it presumably becomes more difficult to rotate any one spin because of the increasing number of spins coupled to it: effectively a diverging mass term. Intriguingly, this behavior is not observed in FeF$_3$, which enters an all-in-all-out magnetic ground state \cite{18,32}. The latter has been explained through density functional theory \cite{33}, but similar calculations for pyr-Mn$_2$Sb$_2$O$_7$ have not been performed. In FeF$_3$ nearest-neighbor antiferromagnetic Heisenberg, bi-quadratic, and Dzyaloshinskii-Moriya interactions were all required to adequately model the spin system. In pyr-Mn$_2$Sb$_2$O$_7$, which has a smaller unit cell and rather different ligand coordination, these may be expected to have completely different strengths. In particular, the Mn tetrahedron in pyr-Mn$_2$Sb$_2$O$_7$ contains a central O2 atom, offering a much more direct exchange pathway. Modelling the interactions in this material and the resulting magnetic ground state will be an important avenue for future theoretical exploration.

One important question is why we observe a bulk ordering transition at 5.5 K while previous reports placed it around 41 K \cite{14,15}. We attribute the previous results to trace quantities of unreacted Mn$_3$O$_4$, which has a ferrimagnetic transition around this temperature \cite{34,35}. Samples which were Mn-rich or incompletely reacted often exhibited a strong transition around 41 K in the magnetization even when phase-pure by x-ray diffraction; however, there was no trace of the transition in the specific heat. Because the Mn$_3$O$_4$ ferrimagnetic moments are large and readily field-trained, even trace quantities can dominate the low-field magnetization. This makes it crucial to completely eliminate this impurity if the intrinsic physics of pyr-Mn$_2$Sb$_2$O$_7$ are to be investigated. Previous measurements on pyr-Mn$_2$Sb$_2$O$_7$ display hints of intrinsic behaviour at low temperatures in the inverse magnetization \cite{14}, but the data otherwise concentrate, understandably, on the obvious 41 K transition.

In summary, the 3$d$-electron Heisenberg pyrochlore pyr-Mn$_2$Sb$_2$O$_7$ undergoes a transition around 5.5 K into a spin glass state with dominantly antiferromagnetic interactions. Short-range magnetic correlations survive to much higher temperatures, and strong frustration is evident. The manganese content can be tuned continuously from zero to full occupancy, offering a very interesting control knob for future disorder studies. Measurements to lower temperatures will be required to establish whether the specific heat resembles that in kagome order-by-disorder systems \cite{36,38}. The physical properties of...
pyr-Mn$_2$Sb$_2$O$_7$ bear a striking similarity to those of the magnetic pyrochlores Ni$_2$Sb$_2$O$_7$ and Co$_2$Sb$_2$O$_7$,[10,11] and more recently NaSrCo$_2$F$_7$, NaCaNi$_2$F$_7$, NaCaFe$_2$F$_7$, and NaSrFe$_2$F$_7$,[16,39,40] which should all have unquenched orbital moments. This suggests that spin-orbit coupling may be so weak in 3d transition metal pyrochlores as to be effectively irrelevant to the frustrated spins, greatly broadening the suite of materials available for investigating effective Heisenberg physics on the most frustrated known three-dimensional lattice. The very recently reported NaSrMn$_2$F$_7$,[16] with quenched orbital moments but A-site cation disorder, also behaves in a similar manner.

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* Current address: State Key Laboratory of Surface Physics, Department of Physics, and Advanced Materials Laboratory, Fudan University, Shanghai 200438, China.

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Supplementary Information: Structure Refinement

![Graph](image)

Fig. 6. Refined room temperature powder diffractograms for pyr-Mn$_2$Sb$_2$O$_7$: (a) x-ray and (b) neutron diffraction. Data are in red, the fit is in black, the residual is in blue, and vertical bars mark the calculated Bragg positions. The residual has been shifted for clarity.

Table I. Refined atomic positions for pyr-Mn$_2$Sb$_2$O$_7$ in space group $Fd3m$ (# 227) at room temperature.

| Site | Mult. | $x$  | $y$  | $z$  | $B_{iso}$ (Å$^2$) |
|------|-------|------|------|------|------------------|
| Mn   | 16d   | 0.5  | 0.5  | 0.5  | 2.85(16)         |
| Sb   | 16c   | 0.0  | 0.0  | 0.0  | 2.11(10)         |
| O1   | 48f   | 0.32744(16) | 0.125 | 0.125 | 0.604(22) |
| O2   | 86    | 0.375 | 0.375 | 0.604(22) |

The high background in the neutron data is attributed to the presence of hydrogen — the material is prepared at relatively low temperatures from a hydrate and an organic Mn source, both of which are rich in H atoms, and takes the form of an extremely fine powder with a high surface-to-volume ratio and considerable potential to host adsorbed water. In analyzing this sample, the Mn site was allowed to deviate from full occupancy as a test for Mn vacancies. The x-ray refinement was not improved — the refined Mn content was 1.99(5), indicating full occupancy. However, the joint refinement suggested vacancies on the Mn and Sb sites when the occupancy of each was allowed to vary, and excess scattering on the O1 site in particular. This may indicate the presence of remnant hydrogen atoms, but without a model for what species would be present (e.g., H$_2$O, H$_3$O$^+$), we were not able to reach firm conclusions. The refined structure of pyr-Mn$_2$Sb$_2$O$_7$ is summarized in Tab. I and selected bond lengths and bond angles that may be of particular interest for the magnetic interactions are presented in Tab. II.

Table II. Selected bond lengths and bond angles for pyr-Mn$_2$Sb$_2$O$_7$ at room temperature, based on the refinement presented in Fig. 6 and Tab. I.

| Sites       | Bond length   | Bond angle   |
|-------------|---------------|--------------|
| Mn–O1       | 2.5001(8) Å   |              |
| Mn–O2       | 2.19115(14) Å |              |
| Sb–O1       | 1.9532(7) Å   |              |
| Mn–O1–Mn    | 91.38(4)°     |              |
| Mn–Mn       | 3.5781(3) Å   |              |