Experimental report

21/05/2024

Proposal: 5-41-1188 **Council:** 10/2022

Title: Exploring the magnetic phase diagram of the chiral antiferromagnet [NH4][Mn(HCOO)3] at low fields

Research area: Physics

This proposal is a resubmission of 5-41-1147

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Samples: [NH4][Mn(HCOO)3]

Instrument	Requested days	Allocated days	From	To
ORIENTEXPRESS	1	2	29/05/2023	30/05/2023
			28/09/2023	29/09/2023
D9	7	3	22/05/2023	25/05/2023
D3	4	4	26/05/2023	30/05/2023
D10	7	3	20/06/2023	21/06/2023
			29/09/2023	01/10/2023

Abstract:

The existence of the Chiral Soliton Lattice (CSL) in magnets has also been confirmed in Ba2CuGeO7, CuB2O4, NdFe3(11BO3)4, and Yb(Ni1-xCux)3Al9. Among these inorganic examples, Ba2CuGeO7 and NdFe3(11BO3)4 accommodate the antiferromagnetic CSL (ACSL), where the staggered moments (instead of local moment) rotate with a period along the helical axis.
However Inoue et al. reported the synthesis of of a molecule-based chiral magnetic compound, [NH4][Mn(HCOO)3] (space group P6322), optically transparent, that apparently could host a ACSL.
However, the phase diagram of [NH4][Mn(HCOO)3] could also be described in base of a simpler model consisting of an AF magnetic state at low fields and a spin flop transition to a conical region.
In order to discern between these two hypotheses, we propose to use single crystal neutron diffraction to determine the magnetic structure in each region of the phase diagram for the 2 different orientations of the magnetic field (parallel and perpendicular) respect to the c-axis in [NH4][Mn(HCOO)3].

Report of experiments 5-41-1188:

Title: Exploring the magnetic phase diagram of $AMn(HCOO)_3$ (A = NH_4, Cs)

$[NH_4][Mn(HCOO)_3]$:

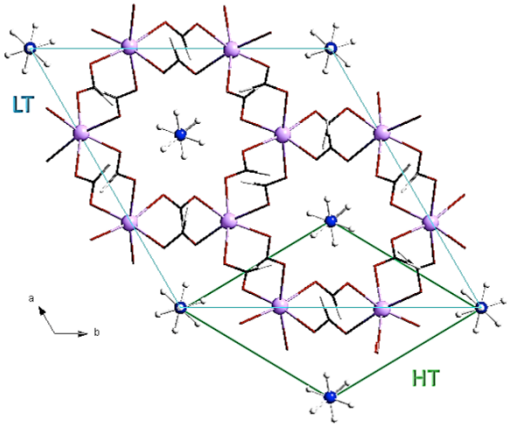
Single crystal neutron diffraction:

This experiment was performed in ILL (Grenoble, France) at D9 from 22/05/23 to 26/05/23. Two different crystals were previously oriented using Orient-Express so that the magnetic field was parallel or perpendicular to the c-axis. Then the crystals were glued to an Al pin with X60 glue and placed inside a 6T-CNRS (S20) cryomagnet. Several measurements with a neutron wavelength λ = 0.84 Å were performed until $\sin\theta/\lambda = 0.3$ Å^{-1}:

- 1st crystal: $\vec{B} \parallel c$. 93 reflections at 10 K, 0 T and 2 K, 0, 0.05, 0.1, 1, 3, 6 T.
- 2nd crystal: $\vec{B} \perp c$. 121 reflections at 10 K, 0 T and 2 K, 0, 0.05, 0.1, 1, 3 T. Q-scans at 2 K in $(00l)$, l: 3.75-6.25 at 0, 0.05, 0.1, 0.5, 1, 1.5, 2, 2.5, 3, 3.5 T.

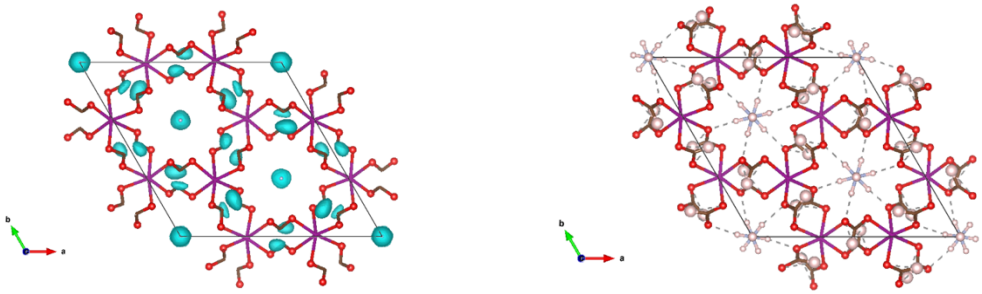
The cell parameters were obtained from the refinement of the UB matrix at high and low temperature, as a phase transition corresponding to the ordering of the NH_4 at T = 254 K was already reported in [9].

- RT (SG $P6_322$):
  $a = b = 7.36$ Å; $c = 8.47$ Å;
  $\alpha = \beta = 90º$; $\gamma = 120º$
- Low-T (SG $P6_3$):
  $a = b = 12.60$ Å; $c = 8.48$ Å;
  $\alpha = \beta = 90º$; $\gamma = 120º$



10 K, 0 T:

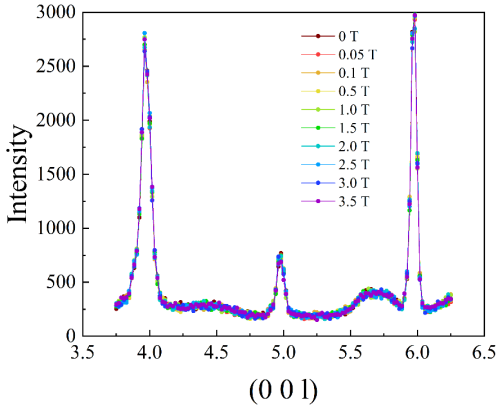
The reflections of both crystals were combined into 128 independent ones, and a fit was performed using isotropic DW factors and assuming the starting positions of the H atoms from the Fourier map.



Left: Crystal structure of $[NH_4][Mn(HCOO)_3]$ w/o H atoms. The blue volumes represent the missing density from the Fourier maps, from which the position of the H atoms is deduced. Right: Crystal structure of $[NH_4][Mn(HCOO)_3]$ obtained from the refinement at 10 K, 0 T.

Nuclear structure parameters of $[NH_4][Mn(HCOO)_3]$:

Temperature (K)	**10**
Space group	$P6_3$
$a = b$ (Å)	12.60
c (Å)	8.48
$\alpha = \beta$ (º)	90
γ (º)	120
R_{Bragg}	2.22
Mn1 6c (x,y,z)	0.345(7), 0.329(7), 0.61(1)
O1 6c (x,y,z)	0.427(3), 0.262(3), 0.46(2)
O2 6c (x,y,z)	0.437(3), 0.158(3), 0.23(2)
O3 6c (x,y,z)	0.408(3), 0.491(3), 0.44(2)
O4 6c (x,y,z)	0.499(3), 0.605(3), 0.23(2)
O5 6c (x,y,z)	0.167(3), 0.228(3), 0.45(2)
O6 6c (x,y,z)	0.062(4), 0.242(3), 0.25(2)
C1 6c (x,y,z)	0.378(3), 0.193(3), 0.33(2)
H1 6c (x,y,z)	0.304(6), 0.174(6), 0.31(2)
C2 6c (x,y,z)	0.477(3), 0.514(3), 0.33(2)
H2 6c (x,y,z)	0.498(7), 0.460(6), 0.32(2)
C3 6c (x,y,z)	0.133(3), 0.284(3), 0.37(1)
H3 6c (x,y,z)	0.157(4), 0.382(5), 0.38(1)
N1 2b (1/3,2/3,z)	2/3, 1/3, 0.56(2)
H11 6c (x,y,z)	0.571(4), 0.296(3), 0.51(2)
H12 2b (1/3,2/3,z)	2/3, 1/3, 0.69(2)
N2 2b (1/3,2/3,z)	1/3, 2/3, 0.55(2)
H21 6c (x,y,z)	0.360(4), 0.607(4), 0.52(2)
H22 2b (1/3,2/3,z)	1/3, 2/3, 0.64(2)
N3 2a (0,0,z)	0, 0, 0.16(2)
H31 6c (x,y,z)	0.019(6), 0.088(6), 0.20(1)
H32 2a (0,0,z)	0, 0, 0.04(2)
$U_{iso,\ Mn}$ (Å^2)	0(1)
$U_{iso,\ O}$ (Å^2)	2.0(4)
$U_{iso,\ C}$ (Å^2)	0.3(5)
$U_{iso,\ H}$ (Å^2)	2(1)
$U_{iso,\ N}$ (Å^2)	1.4(8)
$U_{iso,\ HX1}$ (Å^2)	1.9(8)
$U_{iso,\ HX2}$ (Å^2)	3(1)



Q-scans:

Q-scans were measured on the 2nd crystal ($\vec{B} \perp c$) at 2 K. The scans were performed around the $(00l)$ reflection with l: 3.75-6.25 at 0, 0.05, 0.1, 0.5, 1, 1.5, 2, 2.5, 3 and 3.5 T.

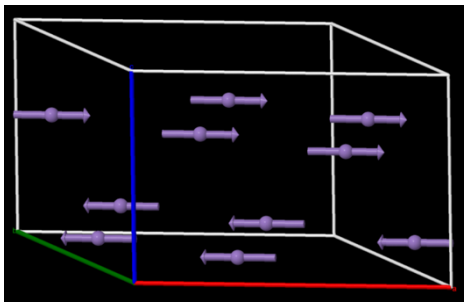
No evidence of a propagation vector different from (0,0,0) was observed, which suggests either a very large period of the soliton lattice or that the magnetic behavior corresponds just to a spin-flop.

2 K, 0 T:

The reflections of both crystals were combined into 128 independent ones, and a fit of the magnetic structure was performed, with the nuclear structure fixed by the refined model at 10 K, 0 T. The symmetry of this magnetic phase is described by the irreducible representation theory, which tells us that the magnetic representation for the Mn atom in position 6c for the space group $P6_3$ and propagation vector $\vec{k} = (0, 0, 0)$ is:

$$\Gamma_{6c} = 3m\Gamma_1(1) + 3m\Gamma_2(1) + \mathbf{3m\Gamma_3\Gamma_5(2)} + 3m\Gamma_4\Gamma_6(2)$$

After a systematic try and error, the best refinement was obtained for the irrep $3m\Gamma_3\Gamma_5$, which corresponds to the magnetic space group (MSG) $P2_1$ (# 4.7), as also reported in [9]. In this magnetic structure, the Mn magnetic moments form FM layers in the ab-plane, which are in turn coupled AFM along the c-axis. Although the magnetic moments direction is not restricted by symmetry, the results of the refinement indicate a moment of $\mu_{Mn} = 4.2(1)\ \mu_B$ along the a-axis, and a negligible contribution along the b and c-axes.



Magnetic structure of $[NH_4][Mn(HCOO)_3]$ obtained from the refinement at 2 K, 0 T.

2 K, $\vec{B} \parallel c$: 1st crystal (93 reflec., 68 indep.):

The data (68 independent reflections from the 1st crystal) were fitted using the MSG $P2_1$ (# 4.7) for each applied field. Only the magnetic structure was refined, with the nuclear structure fixed by the refined model at 10 K, 0 T. The results are shown in the following table:

2 K, $\vec{B} \perp c$: 2nd crystal (121 reflec., 83 indep.):

The data (83 independent reflections from the 2nd crystal) were fitted using the MSG $P2_1$ (# 4.7) for each applied field ($\vec{B} \parallel (3\ 0\ 0)$). Only the magnetic structure was refined, with the nuclear structure fixed by the refined model at 10 K, 0 T. The results are:

B (T)//c	μ_{Mn} (μ_B)	R_{Bragg}
0	(4.2(1), 0, 0)	7.17
0.05	(3.4(1), 0, 1.4(3))	6.72
0.1	(3.0(3), 0, 0(7))	14.8
1	(3.2(2), 0, 1.2(5))	7.21
3	(3.2(2), 0, 1.4(3))	6.90
6	(2.8(2), 0, 2.1(3))	8.34

B (T) $\perp c$	μ_{Mn} (μ_B)	R_{Bragg}
0	(4.2(1), 0, 0)	5.42
0.05	(4.9(2), 5.4(2), 0)	5.21
0.1	(5.1(2), 5.0(3), 0)	5.33
1	(4.7(3), 5.4(2), 0)	5.65
3	(5.2(2), 4.9(3), 0)	5.43