Experimental report

21/05/2024

Proposal: **DIR-267** **Council:** 10/2022

Title: Searching for helimagnetism in chiral transition metal formates

Research area: Physics

This proposal is a new proposal

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Samples:
{K[Ni(HCOO)3]n}
{Na[Co(HCOO)3]n}
[Na3Mn3(HCOO)9]n

Instrument	Requested days	Allocated days	From	To
D19	7	7	04/04/2023	11/04/2023
D9	7	7	30/03/2023	06/04/2023
D10	7	0		
D2B	2	2	15/05/2023	17/05/2023
D20	2	2	26/06/2023	28/06/2023
D1B	2	0		

Abstract:

Our group opened a new research line to treat to design extended magnetic compounds with enhanced DMI. As a first approach we considered the formate-based coordination polymers (FBCP), because in the anionic form, this achiral ligand can induce non-centrosymmetric or chiral nuclear structures, reached by the arrangement around the metal cation. We synthesized single crystals and powder samples based on the formate anion and transition metal cations of formula [AM(HCOO)3]n, with A = Na, K, and M = Mn, Co, Ni, crystallising in chiral space groups P6322 or P213. Preliminary results show the presence of Long-Range magnetic Order (LRO), with Neel temperatures between 10 and 32 K.

The goal of this proposal is the refinement and elucidation of the nuclear and magnetic structures of the series of compounds [AM(HCOO)3]n, with A = Na, K, and M = Mn, Co, Ni, by using single crystal and powder neutron diffraction

In the next days a manuscript will be submitted summarizing the results of the experiments done at the ILL under the proposal DIR-267

Here we show only the abstract an some of the neutron diffraction analysis.

ABSTRACT

We present five novel three-dimensional (3D) coordination polymers (CPs), introducing two novel nuclear structures $[NaM(HCOO)_3(H_2O)]_n$ (with M = Co^{2+} or Ni^{2+}) with $P2_1$ space group, along two centric C2/c isomorphs $[KM(HCOO)_3]_n$ (with M = Mn^{2+} or Co^{2+}) and the $[KNi(HCOO)_3]_n$ $P6_322$ chiral nuclear structure. Magnetic measurements indicate that antiferromagnetic interactions predominate in the five CPs, with an antiferromagnetic J/k_B mean values calculated from Weiss temperature (ϴ) from -0.20 to -15 K. Moreover, magnetic long-range ordering (LRO) is evidenced from magnetic susceptibility and heat capacity measurements. Furthermore, single crystal and powder neutron diffraction experiments were performed and elucidate the magnetic structure of the materials, confirming the antiferromagnetic ordering and understanding the magnetic topology of these systems.

MATERIALS AND CHARACTERIZATION.

All reagents and solvents were used without any further purification.

Synthesis of *$[NaM(HCOO)_3(H_2O)]_n$* (M = Co^{2+} or Ni^{2+}, compounds **1** and **2**, respectively).

Synthesis of *$[KM(HCOO)_3]_n$* (M = Mn^{2+}, Co^{2+} or Ni^{2+}, compounds **3, 4** and **5**, respectively).

Single-crystal neutron diffraction was performed for a 2 x 1 x 1 mm^3 crystal of compound **1** mounted on a vanadium pin on the four-circle D19 diffractometer at the Institute Laue Langevin (ILL), Grenoble (France). The experiment was carried out using a constant wavelength of 1.45 Å and a displex to cool down the sample below the Neél temperature.

Powder Neutron diffraction experiments were performed on different instruments at several neutron sources: (i) the cold-neutron diffractometer DMC with a CWL of 2.45 Å and the thermal high-resolution diffractometer HRPT working with 1.7 Å both at the SINQ at the Paul Scherrer Institute (PSI). Here we will show the data for compounds **2** and **5**, measured at DMC; (ii) for compound **3** was used the time-of-flight instrument POWGEN at the Spallation Neutron Source (SNS) from Oak Ridge National Laboratory (ORNL); (iii) the high-intensity two-axis diffractometer D20 the ILL at Grenoble, France, using a CWL = 1.88 Å. Here we will show data for compound **4**.

Neutron diffraction analysis.

Compound **1** was measured at the single-crystal D19 diffractometer at the ILL using a wavelength of 1.45 Å at the paramagnetic phase (20 K) and at the ordered phase (4 K). At lowest temperature, the increase of intensity detected in three (0 *k* 0) reflections with odd *k* is indicative of some magnetic LRO with a k = (0,0,0) propagation vector.

Table 2 shows the magnetic irreps $m\Gamma_1$ and $m\Gamma_2$, the Fourier coefficients (Sk) and basis vectors for the $P2_1$ space group and propagation vector (000). In the magnetic structure labeled with $m\Gamma_1$ the magnetic moment at $\{1|000\}$ transforms to $\{2_{0y0}|0\frac{1}{2}0\}$ by keeping invariant his y-component whereas changes its sign for x and z components. The contrary happens for a magnetic structure labelled with $m\Gamma_2$

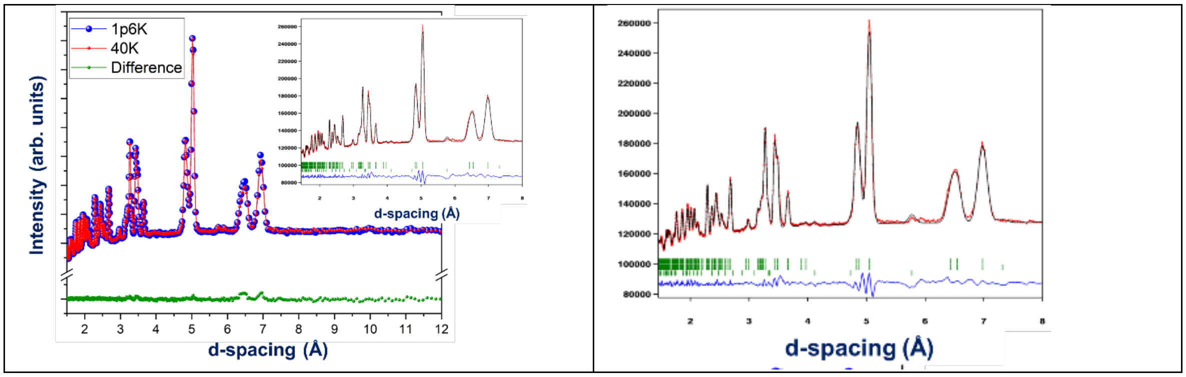
A simple calculation of the magnetic structure factor (M_q) and the magnetic interaction vector ($M_{\perp q}$) for the (0k0) lines with k-odd for the space group $P2_1$ shows that for $m\Gamma_2$ the magnetic interaction vector is null $M_{\perp(0k0)}=0$ and therefore any magnetic structure described with $m\Gamma_2$ will never explain the magnetic contribution observed in (0, -1, 0); (0, -3, 0) and (0, -5, 0), in the ordered phase. As consequence the only possibility points to a magnetic structure labeled with $m\Gamma_1$ with allows an antiferromagnetic component perpendicular to the b-axis and a ferromagnetic component parallel to b-axis.

Compound **2** was measured in the DMC instrument at the SINQ facility of the Paul Scherrer Institute, using a constant wavelength of 2.45 Å for the measurements at the paramagnetic phase (40 K) and the ordered phase (1.6 K). A slight increase in the diffraction peaks around 20 and 40 2θ degrees in the low temperature pattern is indicative of long-range magnetic ordering and as no additional peaks appears, we are allowed to elucidate a propagation vector k = (0,0,0).

Compound **3** was measured at paramagnetic phase (4 K) and ordered phase (2 K) in the time-of-flight instrument POWGEN, and the patterns refined using the X-ray model at room temperature. The appearance of new peaks and the increment of intensity observed on Bragg's positions in the 2 K pattern is indicative of magnetic ordering and in agreement with the susceptibility and heat capacity measurements, affording to index this magnetic contribution with a propagation vector k = (0,0,0).

Compound **4** has been measured at the constant-wavelength (λ = 1.88 Å) D20 instrument at the ILL at the paramagnetic phase (50 K) and the ordered phase (1.6 K), according to the susceptibility and heat capacity measurements. In the low temperature pattern, the appearance of a new peak and the increase of intensity in other Bragg's reflections is indicative of magnetic contribution, which agrees with the allowed reflections for the system and therefore, able to be indexed with a k = (0,0,0), expectable for a compound **3** isomorph.

Compound **5** was measured in the DMC instrument using a constant wavelength of 2.45 Å for the measurements at the paramagnetic phase (30 K) and the ordered phase (1.6 K). In this case, no new peaks can be observed but just a small increment of intensity of the low angle Bragg's reflections are evidenced, affording us to assume a propagation vector k = (0,0,0).



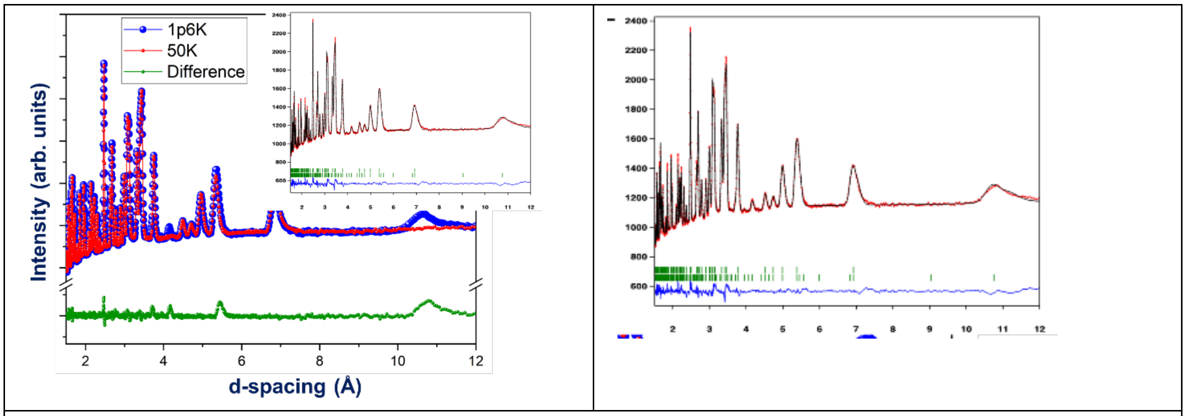


Figure 8. Ordered and disordered neutron pattern difference (main) and Rietveld refinement (inset) for compounds 2 (left) and 4 (right).

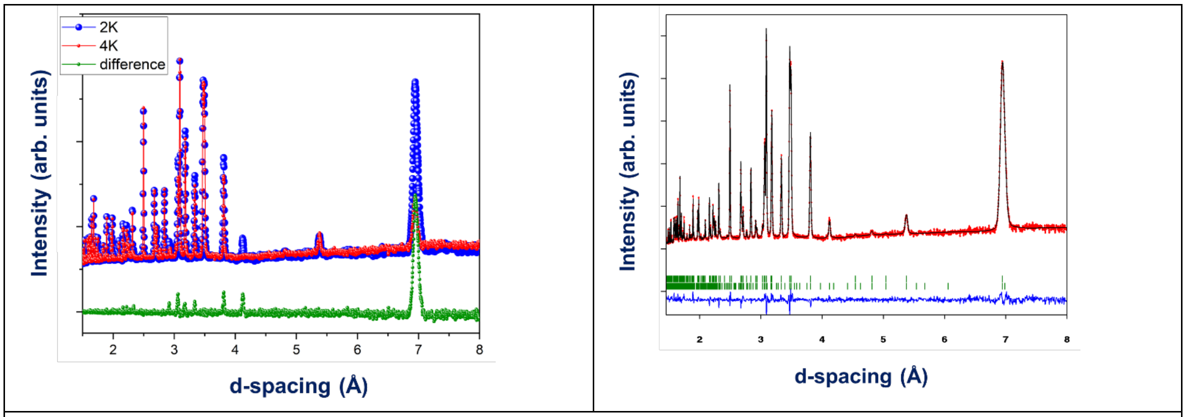


Figure 10. Ordered and disordered neutron pattern difference (left) and Rietveld refinement (right) for compound 3.

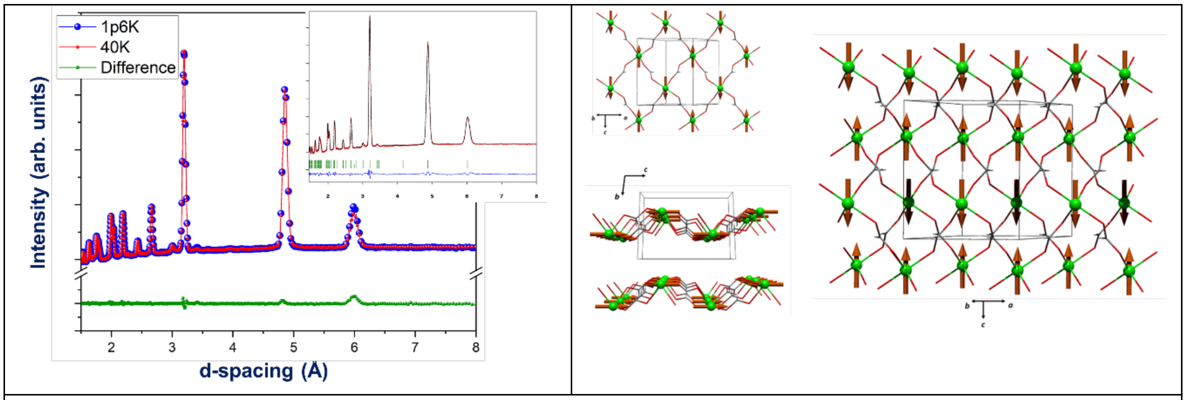


Figure 12. Left: Ordered and disordered neutron pattern difference (main) and Rietveld refinement (inset) and right: Solved magnetic structure for compound 5.