Experimental report

15/07/2022

Proposal:	**EASY-893**	**Council:**	10/2020

Title: Elucidating the origin of the magnetic behaviour of cathode material K1.33Mn8O16

Research area: Materials

This proposal is a new proposal

Main proposer: **Liam NAGLE-COCCO**

Experimental team:

Local contacts: Emmanuelle SUARD

Samples: K1.33Mn8O16

Instrument	Requested days	Allocated days	From	To
D20	6	6	25/08/2021	26/08/2021

Abstract:

Cryptomelane is an abundant Mn-based mineral which we recently demonstrated is a promising material for Zn-ion batteries, exhibiting a highly reversible transition with charge/discharge cycling and a high capacity of more than ~300 mA h g-1 in the potential window of 1.0 to 1.8 V. Further, magnetic characterization of the material using DC/AC susceptibility indicates a material rich with competing phenomena at low temperatures, with two clear transitions observed. Curie-Weiss fitting indicating antiferromagnetic correlations. Heat capacity shows additional transitions, at 24 K, 42 K, 49 K, and 54 K, and low temperature XRD indicates these are not due to structural changes.

This EASY proposal requests two magnetic neutron measurements, one at 60 K (above any magnetic transitions) and one at 5 K, to search for magnetic Bragg peaks which could provide indication of the magnetic ground state of this material. We further ask that a measurement could be conducted at 30 K if time allows, though we accept this may not be possible and the 5 K and 60 K measurements are the priority.

EASY-893: Elucidating the origin of the magnetic behaviour of cathode material $K_{1.440(4)}Mn_8O_{16}$

Experimental report, submitted by L. A. V. Nagle-Cocco

Key points

- We have obtained the first structural solution for a magnetic neutron diffraction study of a sample of cryptomelane with stoichiometry $K_{1.440(4)}Mn_8O_{16}$.
- In the temperature regime 25 < *T*(K) < 55, we find that the neutron diffraction data is best solved by a superposition of two magnetic propagation vectors: k=[0,0,0] commensurate and k=[0,0,~0.37] incommensurate.
- For the temperature regime *T* < 25 K, we find the persistence of magnetic Bragg peaks albeit at different positions to 25 < *T*(K) < 55, casting doubt on previous reports of spin-glass behaviour in the material.
- We have written a manuscript which we hope to submit shortly.[i]

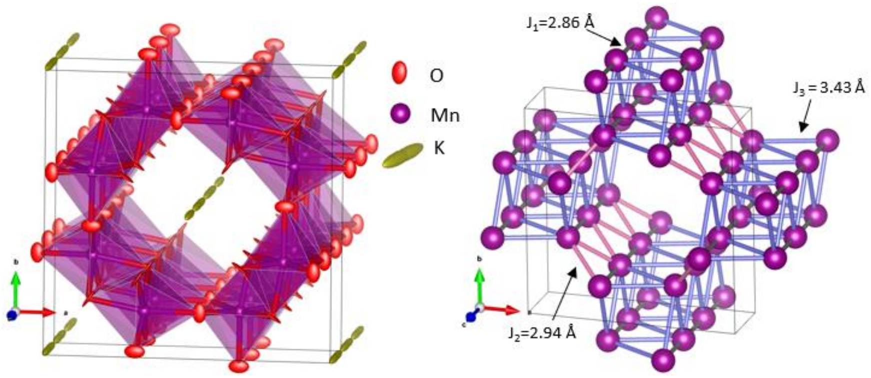

Figure 1: crystallographic structure of K1.440(4)Mn8O16 as determined by Rietveld refinement. Left: nuclear structure, with MnO6 polyhedra shown in purple, and K and O ions reflected as ellipses of 95% probability. Right: magnetic Mn lattice, with the three competing neighbouring interactions highlighted in different colours.

Introduction

Cryptomelane consists of MnO_2 channels doped with K^+ cations. We investigated it using diffraction, DC and AC magnetic susceptibility, and heat capacity. It was found to exhibit two magnetic transitions. At 30 K and 50 K it exhibited hysteresis in isothermal magnetization measurements, which vanished at 1.8 K. This is shown in Figure 2.

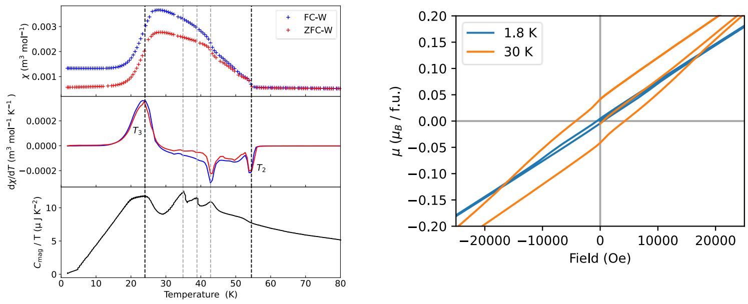

Figure 2: left: DC susceptibility and magnetic heat capacity. Black dashed lines indicate magnetic transitions due to cryptomelane. Grey dashed lines indicate magnetic transitions due to Mn_3O_4 impurity. Right: isothermal magnetization, showing hysteresis at 30 K but no hysteresis at 1.8 K.

The aim of this experiment was to determine the magnetic structure in each of these temperature regimes, by magnetic neutron diffraction.

Experiment

We posted our sample to the ILL. It was measured at room-temperature on D2B by Emmanuelle Suard and at low-temperature on D20 by Clemens Ritter. Nuclear crystallographic Rietveld refinements were performed using Topas. For magnetic crystallographic analysis, difference patterns were obtained by subtracting the data at 60 K from the low-temperature data. These difference patterns were analysed using FullProf.

Room-temperature refinement

We performed a combined Rietveld refinement at room-temperature of cryptomelane, using the data from D2B in conjunction with synchrotron data from Diamond. Our crystal structure is consistent with previous reports[ii] (refined in the *I4/m* space group), but is not phase pure, with a small Mn_3O_4 magnetic impurity which must be included in magnetic analysis.

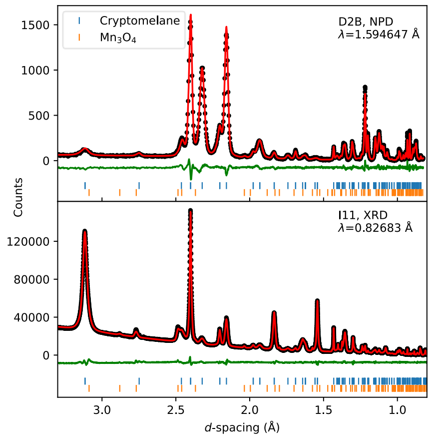

Figure 3: Combined Rietveld refinement of neutron diffraction (D2B, Institut Laue Langevin) and x-ray diffraction (I11, Diamond)

Low-temperature data

The low-temperature magnetic data from D2B is shown in Figure 4 for the difference patterns at 2.5 K and 47 K.

Figure 5 shows a Rietveld refinement for the data at 47 K, using a helical model, with an incommensurate (K_{IC}=[0,0,~0.37]) and commensurate (K_C=[0,0,0]) component.

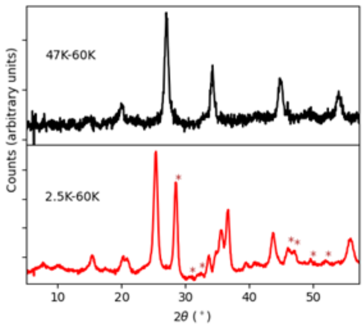

Figure 4: Peak structure for the two temperature regimes. Mn_3O_4 peaks marked by red asterisk.

Discussion

Our findings are of interest to the wider literature. Our observation of Bragg peaks at 2.5 K are important to the wider literature because prior reports indicated that the magnetic structure in this temperature regime is spin-glass-like[iii]; however, this is not consistent with Bragg peaks, and so we have shown that the spin-glass-like properties must be extrinsic, i.e. a surface effect or the consequence of local variations of K^+ content within the bulk material.

Additionally, our work is important within the literature because it vindicates previous theoretical[iv] and experimental works which proposed a helical magnetic ordering in cryptomelane. In particular, our findings appear consistent with the helical ferrimagnetism proposed by Sato *et al.*[v]

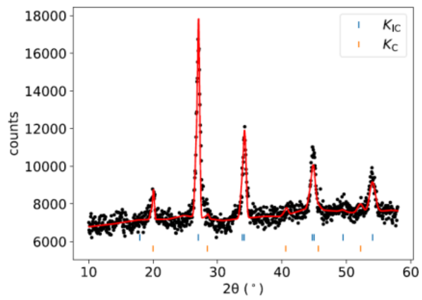

Figure 5: Rietveld refinement of K_{IC} and K_C to the difference pattern 47 K-60 K

Next steps

- The study has been written up as a manuscript and will soon be submitted to a peer-reviewed journal for publication.
- The study may also be used in the PhD thesis of Liam Nagle-Cocco.

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[i] Nagle-Cocco, L. A. V., *et al. In preparation.*
[ii] Vicat, Jean, *et al.* Acta Crystallographica Section B: Structural Science 42.2 (1986): 162-167.
[iii] Barudžija, Tanja, *et al*. Journal of alloys and compounds 665 (2016): 261-270.
[iv] Mandal, S., *et al*. Physical Review B 90.10 (2014): 104420.
[v] Sato, Hirohiko, *et al*. Physical Review B 59.20 (1999): 12836.