Experimental report

07/09/2022

Proposal: 5-31-2880 **Council:** 4/2021

Title: Magnetic ordering in layered manganese oxide sulfides prepared by soft chemistry

Research area: Chemistry

This proposal is a new proposal

Main proposer: Simon James CLARKE

Experimental team:

Local contacts: Stanislav SAVVIN
Emmanuelle SUARD
Ines PUENTE ORENCH
Vivian NASSIF
Claire COLIN

Samples: S2MnO2LiS2
Sr2MnO2Li1.5S2
Sr2MnO2Li2S2
SrCaMnO2Cu3.5S3
Sr2MnO2Li2Se2
Sr2MnO2Na2Se2
Sr2MnO2Li2Te2
SrCaMnO2Cu3.2S3

Instrument	Requested days	Allocated days	From	To
D2B	2	1	03/10/2021	04/10/2021
D1B	0	1	18/09/2021	19/09/2021

Abstract:

This proposal is to explore the changes in the magnetic ordering in layered oxide chalcogenides as a function of Mn oxidation state in MnO2 sheets using a series of compounds prepared with variable Mn oxidation states by soft chemistry. The samples Sr2MnO2Li2-xS2 (x = 0, 0.5 1.0) are obtainable by soft chemical methods and offer a chance to probe the changes in magnetic structure with oxidation state of Mn ranging from +2 (for x = 0) to +3 (x = 1) for Mn ions in MnO2 sheets, via the mixed-valent intermediate. This will enable comparison with related materials and layered manganite oxides.

EXPERIMENTAL REPORT

EXPERIMENT N° 5-31-2880 INSTRUMENT D2B/D1B

DATES OF EXPERIMENT 18/09/2021 to 19/09/2021 (D1B) 3/10/2021 to 04/10/2021 (D2B)

TITLE Magnetic Ordering in layered manganese oxide sulfides prepared by soft chemistry

EXPERIMENTAL TEAM (names and affiliation)

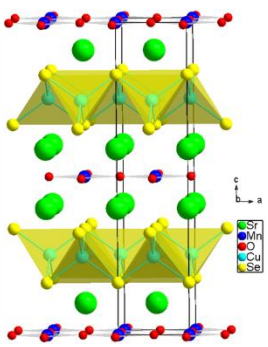
Souvik GIRI INORGANIC CHEMISTRY LAB, OXFORD UNIV GB

Viktoria FALKOWSKI INORGANIC CHEMISTRY LAB, OXFORD UNIV GB

Simon CLARKE INORGANIC CHEMISTRY LAB, OXFORD UNIV GB.

LOCAL CONTACT SAVVIN, Stanislav

Date of report 05/09/22



Oxychalcogenides are one class of mixed anion compounds derived from very well studied oxide material. $Ae_2MnO_2Cu_{2-\delta}Ch_2$ (Ae = Sr, Ba; Ch = S, Se, Te) is an interesting class of compounds in oxychalcogenide family showing diverse magnetic and electronic properties[1]. Here Mn is in a distorted octahedral environment with two long Mn-*Ch* equatorial bonds. Our aim of this experiment was to probe the ordering of Mn moments in compounds with different Mn-*Ch* bond lengths and Mn oxidation states.

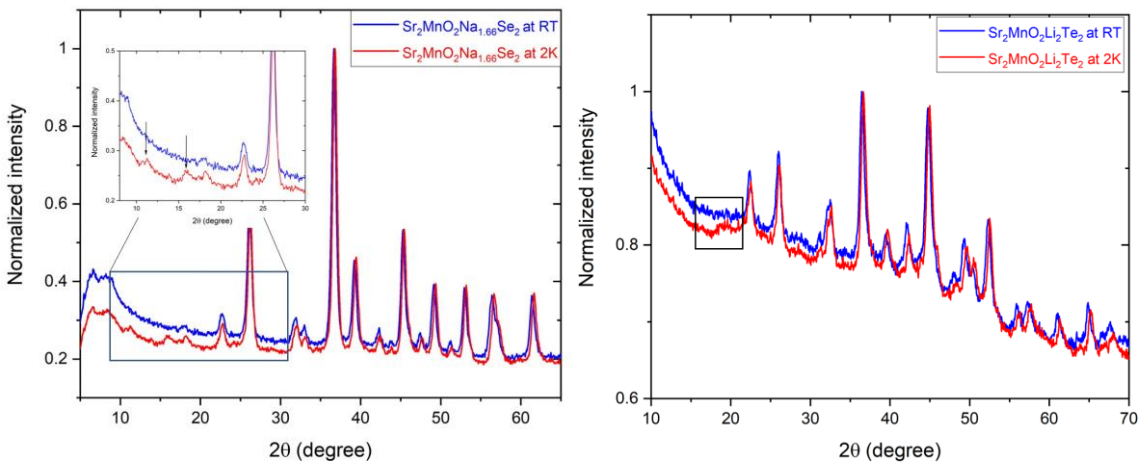


Figure 1. left: Raw D2B data for $Sr_2MnO_2Na_{1.66}Se_2$ above and below the ordering temperature. The data shows that there are extra intensities at high d spacing at 2K which are magnetic in origin. **Right:** In contrast to left the compound $Sr_2MnO_2Li_2Te_2$ does not any clear extra Bragg reflection below its ordering temperature. Only a broad extra intensity is observed which shows lack of 3D long range magnetic ordering in this compound.

Thus we have measured $Sr_2MnO_2Li_2Se_2$, $Sr_2MnO_2Na_{1.66}Se_2$, and $Sr_2MnO_2Li_2Te_2$, which have different Mn coordination environments due to different metal-chalcogenide layer composition

From the initial analysis, we have extracted the structural information from Rietveld refinement which confirms $Sr_2MnO_2Li_2Se_2$, $Sr_2MnO_2Na_{1.66}Se_2$, $Sr_2MnO_2Li_2Te_2$ crystallizes in tetragonal *I4/mmm* space group with varying cell parameters because of different metal chalcogenide layer. Between these 3 compounds, $Sr_2MnO_2Li_2Te_2$ does not show any extra Bragg reflection on cooling; the other two compounds show the emergence of new small Bragg peaks at higher d spacing. These reflections can be indexed in a $\sqrt{2}a * \sqrt{2}a * c$

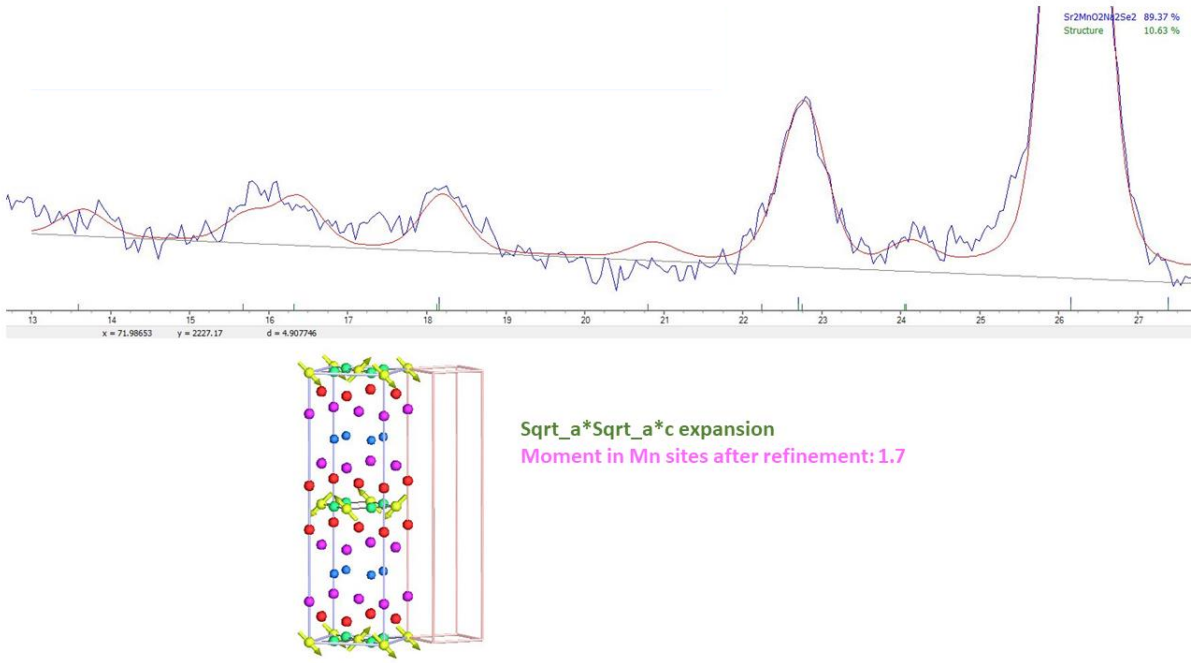


Figure 2. Preliminary magnetic structure of $Sr_2MnO_2Na_{1.66}Se_2$ from D2B

expansion of the nuclear unit cell, and a preliminary structure for $Sr_2MnO_2Na_{1.66}Se_2$ is shown in Figure 2. We are further analysising the magnetic structure with Reitveld refinement. $Sr_2MnO_2Na_{1.66}Se_2$ also shows metamagnetism and will be the subject of a further neutron proposal to measure it in applied magnetic field.

We also measured the related compounds $SrCaMnO_2Cu_{4-x}S_3$ through the magnetic ordering transition on D1B and these data are under analysis.

Overall the experiment was a full success and we are grateful for the efforts of the local contact in running the experiment in full during the Covid-19 restrictions. Analysis is in progress. This compound will also be explored using PXRD and XANES/EXAFS. The work carried out in this experiment will be published in an international journal and will form a significant part of the D.Phil thesis of Souvik Giri.

[1] Clarke, S. J. *et al. Inorg. Chem.* **2008**, *47,* 8473-8486.