Experimental report

31/08/2019

Proposal: 5-31-2604 **Council:** 4/2018

Title: Magnetic structures of layered oxide chalcogenides

Research area: Chemistry

This proposal is a new proposal

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Samples: Sr2CrO3CuSe
Sr2MnO3Cu0.95S
Sr2MnO3CuSe
Sr2CrO3CuS
Sr2MnO3CuS

Instrument	Requested days	Allocated days	From	To
D2B	3	3	08/10/2018	11/10/2018

Abstract:

This is a proposal to determine the magnetic structures of a series of first row transition metal oxide chalcogenides in order to correlate their behaviour with related compounds, and to probe the effect of oxidation. The magnetic structures of the oxide sulfides Sr2MnO3CuS and Sr2CrO3CuS and the new oxide selenides Sr2MnO3CuSe and Sr2CrO3CuSe will be determined. In the case of Sr2MnO3CuS, the magnetic structure of the stoichiometric compound will be determined and the effect of slight oxidation by the deintercalation of some of the Cu from the sulfide layers to produce Sr2MnO3Cu0.95S will be investigated. This forms part of an EPSRC-sponsored project to probe the soft chemistry of layered oxide chalcogenides and the effect on the magnetic and electronic properties.

EXPERIMENTAL REPORT

EXPERIMENT N°5-31-2604 INSTRUMENT D2B

DATES OF EXPERIMENT 08/10/2018 to 11/10/2018

TITLE Magnetic structures of layered oxide chalcogenides

EXPERIMENTAL TEAM (names and affiliation)

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Date of report 31/08/19

Layered oxide chalcogenides offer many similarities and differences compared with oxides. In particular unusual oxidation states and coordination environments for transition metals can be stablised. In the class of compounds containing transition metal oxide layers separated by coinage metal chalcogenide layers, there is sometimes the prospect of control over the metal oxidation state and hence the magnetism using chemistry. In this experiment we probed the magnetic ordering of the compound Sr_2MnO_3CuSe and the isostructural sulfide derivatives Sr_2MnO_3CuS and $Sr_2MnO_3Cu_{0.94}S$ where there is a phase width obtained

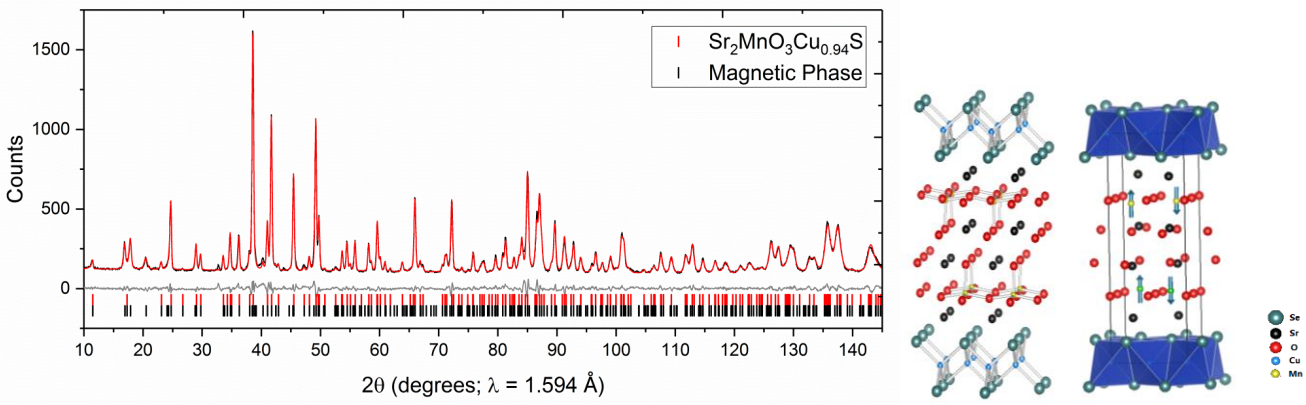

Figure 1. Refinement against D2B data for $Sr_2MnO_3Cu_{0.94}S$ at 4K. Crystal structure in *P*4/*nmm* and the magnetic ordering for $Sr_2MnO_3Cu_{0.94}S$ and Sr_2MnO_3CuSe is shown at right. Sr_2MnO_3CuS has a related magnetic structure with the cell doubled along the long axis.

by partial deintercalation of Cu from the sulfide layer. Related isostructural compounds were also investigated as in the proposal. Data were collected on D2B at low temperatures. The results on these nominally Mn^{3+} compounds revealed checkerboard-type antiferromagnetic

ordering of the nearest neighbours Mn moments with a large ordered moment for Sr_2MnO_3CuSe consistent with Mn^{3+}, but the ordered moment in the stoichiometric sulfide analogue Sr_2MnO_3CuS was unexpectedly much lower (Table 1) and there was a subtle change in the magnetic periodicity along the *c* axis. On oxidation to $Sr_2MnO_3Cu_{0.94}S$ the larger moment was restored and the magnetic structure was similar to that of Sr_2MnO_3CuSe. This suggests that in Sr_2MnO_3CuS there is some partial charge transfer from the sulfide states to the Mn ions so that they are slightly reduced and the ordered moment is reduced slightly by disorder, but the oxidative removal of some Cu oxidises all the Mn to the +3 oxdation state and so results in a large ordered moment. This observation requires further investigations of the physical properties using masurements on single crystals.

Table 1. Comparative moments for $Sr_2MnO_3Cu_{1-x}Ch$

Compound	Sr_2MnO_3CuSe	Sr_2MnO_3CuS	$Sr_2MnO_3Cu_{0.94}S$
Diffractometer	D2B (ILL)	D2B (ILL)	D2B (ILL)
μB per Mn ion at base temperature	3.76(6)	2.83(6)	3.60(4)

Measurements on the isostructural Sr_2CrO_3CuSe system revealed relatively weak magnetic reflections consistent with antiferromagnetic ordering (Figure 2). Analysis of the data are ongoing. The work of this experiment has been reported in the the thesis of X. Xu [1].

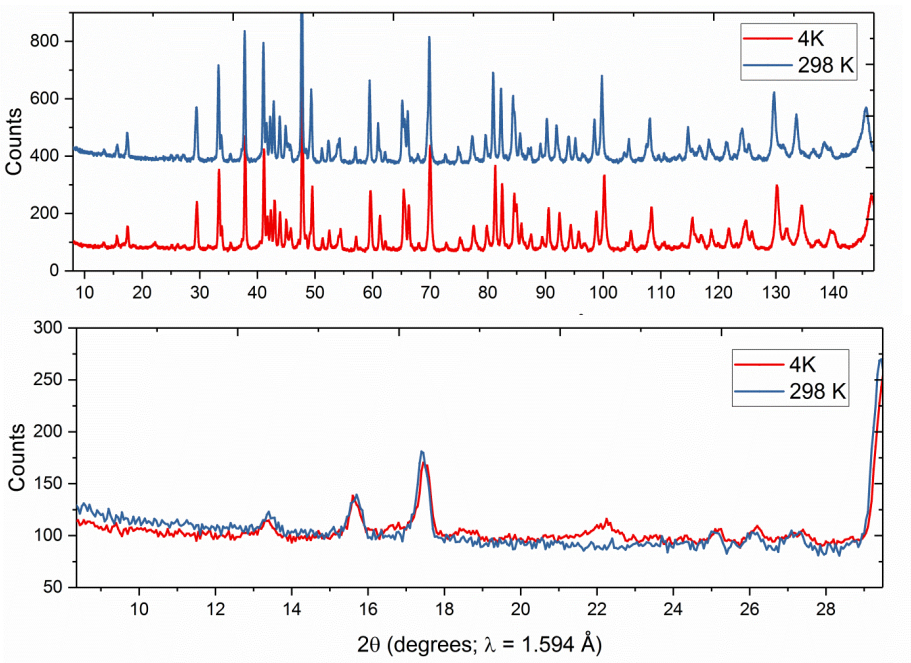

Figure 2. Dffraction patterns for Sr_2CrO_3CuSe showing weak magnetic reflections at 4K.

[1] Xiaoyu Xu, *D.Phil. thesis*, *University of Oxford* 2019.