Experimental report

15/11/2020

Proposal: **5-31-2732** **Council:** 10/2019

Title: Magnetic ordering in the layered oxide chalcogenides Ca2Fe3-deltaCh2O3 (Ch = S, Se)

Research area: Chemistry

This proposal is a new proposal

Main proposer: **Simon James CLARKE**

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Local contacts: Stanislav SAVVIN

Samples: $Ca_2Fe_{2.6}S_2O_3$
$Ca_2Fe_{2.6}S_{1.5}Se_{0.5}O_3$
$Ca_2Fe_{2.6}SSeO_3$

Instrument	Requested days	Allocated days	From	To
D2B	3	2	11/09/2020	13/09/2020

Abstract:

This proposal is to explore the magnetic ordering and structural details in a new series of layered oxide chalcogenides $Ca_2Fe_{2.6}(S_{1-x}Se_x)_2O_3$ ($0 < x < 0.5$) in which two iron sites present two independent sublattices. The experiment will enable the relationship between the magnetic ordering on the two sublattices and Fe-site vacancy ordering, which depends on the chalcogenide composition, to be probed in detail. The systems will be compared with related compounds containing comparable motifs such as $SrFeO_2$. The work forms part of the EPSRC grant EPSRC (EP/P018874/1) "Soft chemical control to achieve new layered architectures and strongly correlated states."

EXPERIMENTAL REPORT

EXPERIMENT N° 5-31-2732 INSTRUMENT D2B

DATES OF EXPERIMENT 10/09/2020 to 12/09/2020

TITLE Magnetic ordering in the layered oxide chalcogenides $Ca_2Fe_{3-\delta}Ch_2O_3$ (*Ch* = S, Se)

EXPERIMENTAL TEAM (names and affiliation)
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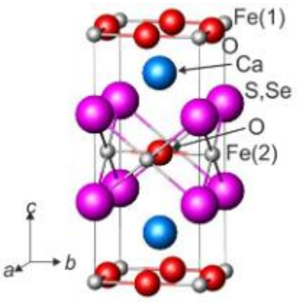
LOCAL CONTACT SAVVIN, Stanislav

Date of report 15/11/20



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. Recently Zhang et al. [1] described a new series of compounds $Ca_2Fe_{2.6}O_3(S_{1-x}Se_x)_2$ with the structure shown left. These compounds contain Fe ions in two different distorted octahedral coordination environments. Fe(1) occurs in FeO_2 sheets with the Fe(1) ions coordinated by four oxide ions in square planar coordination and weakly by two chalcogenide ions to form axially distended FeO_4Ch_2 octahedra which share oxide vertices. Fe(2), by contrast, is in a FeO_2Ch_4 octahedron compressed along the axial Fe–O bonds and

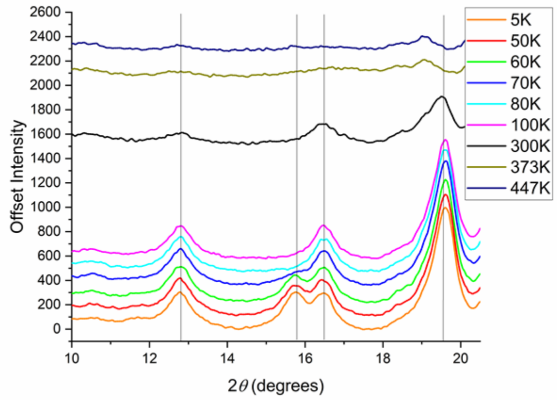


Figure 1. Raw D2B data for $Ca_2Fe_{2.6}O_3S_2$ at variable temperatures. The data show clearly for the first time that there are two magnetic ordering transitions with two sets of magnetic peaks appearing below 400 K, one of which is associated with the magnetic ordering transtion evident in the susceptiblity at ~70K [1].

where the octahedra share faces. Fe(2) sites are twice as abundant as Fe(1) sites and the idealised composition with all Fe sites fully occupied would be $Ca_2Fe_3O_3S_2$ with Fe in a formal oxidation state of +2. Refinements and the synthesis show that the Fe(2) site is only 80% occupied giving a formula of $Ca_2Fe_{2.6}O_3S_2$, consistent with partial oxidation to Fe3+ or with partial oxidation of the chalcogenide. The data collected on D2B in this experiment (Figure 1) reveals two sets of magnetic Bragg peaks associated with two magnetic transitions- one around 77 K [1] and the other between 300 K and 373 K revealed in this experiment. These are likely to be antiferromagnetic ordering transitions. Solution of the magnetic structures together with Fe(2) vacancy ordering is in progress. The observation that $Ca_2Fe_{2.6}O_3S_2$ is Mott-Hubbard insulating suggests that Fe is partially oxidised to the +3 state, although the valence distribution over the two sites and how this might change with the nature of the chalcogenide ion is not known. In order to obtain pure samples of the solid solution phases, a greater Fe stoichiometry was necessary, giving compositions of $Ca_2Fe_{2.65}O_3S_{1.5}Se_{0.5}$ and $Ca_2Fe_{2.7}O_3SSe$, and these were also measured in the experiment. 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. These compounds will also be explored using Mössbauer spectroscopy. 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 Bradley Sheath.

[1] Zhang, H. et al. J. Phys. Condens. Matter **2016**, 28, 145701.