Experimental report

20/05/2022

Proposal: **5-31-2834**

Council: 10/2020

Title: Evolution of the magnetic orderingin the layered oxide chalcogenide Ca2Fe2.6S2O3

Research area: Chemistry

This proposal is a new proposal

Main proposer: **Simon James CLARKE**

Experimental team: Stanislav SAVVIN

Local contacts: Ines PUENTE ORENCH
Vivian NASSIF
Claire COLIN

Samples: Ca2Fe2.6S2O3

Instrument	Requested days	Allocated days	From	To
D1B	1	1	27/06/2021	28/06/2021
D20	1	0		

Abstract:

This proposal follows a measurement of the magnetic ordering in Ca2Fe2.6S2O3 and will enable a detailed description of the evolution of the magnetic scattering of the two magnetic sublattices through a transition at around 80 K and a second transition between 300 and 375 K. It will establish the relationship between the magnetic ordering on the two Fe sublattices, both of which have Fe in unusual ligand fields, and will enable the magnetic ordering to be correlated with the details of the crystal structure.

EXPERIMENTAL REPORT

EXPERIMENT N° 5-31-2834 INSTRUMENT D1B

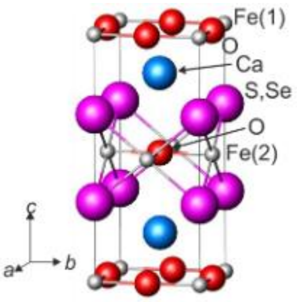
DATES OF EXPERIMENT 27/06/2021 to 28/06/2021

TITLE Evolution of the magnetic ordering in the layered oxide chalcogenide $Ca_2Fe_{2.6}S_2O_3$

EXPERIMENTAL TEAM (names and affiliation)
Bradley SHEATH INORGANIC CHEMISTRY LAB, OXFORD UNIV GB
Simon CLARKE INORGANIC CHEMISTRY LAB, OXFORD UNIV GB.

LOCAL CONTACT SAVVIN, Stanislav

Date of report 20/05/22



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 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

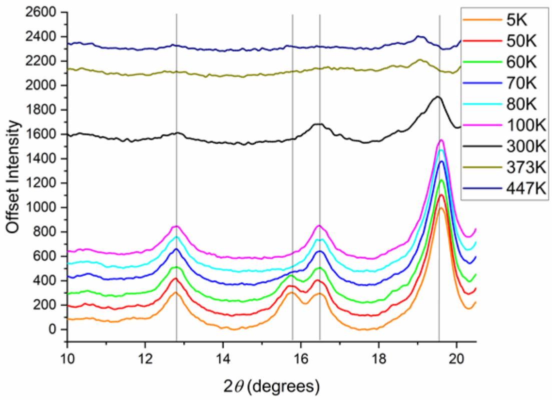


Figure 1. Raw D2B data for $Ca_2Fe_{2.6}O_3S_2$ at variable temperatures. The data show clearly for the first time that there are two magnetic ordering transitions with two sets of magnetic peaks appearing below 400 K, one of which is associated with the magnetic ordering transtion evident in the susceptiblity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

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.

This experiment was performed in addition to the corresponding D2B experiment (exp. 5-31-2732). The D2B diffractograms will best support the nuclear structure determination and Fe-vacancy ordering analysis of this phase whereas the D1B diffractograms- with higher resolution at higher d-spacing values- will help most in the determination of the magnetic ordering on the two Fe sub-lattices. The data previously collected on D2B (Figure 1) revealed 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. These are likely to be antiferromagnetic ordering transitions. Solution of the magnetic structure as temperature is varied is in progress, making full use of the vast number of measurements performed between 5 K and 373 K (Figure 2).

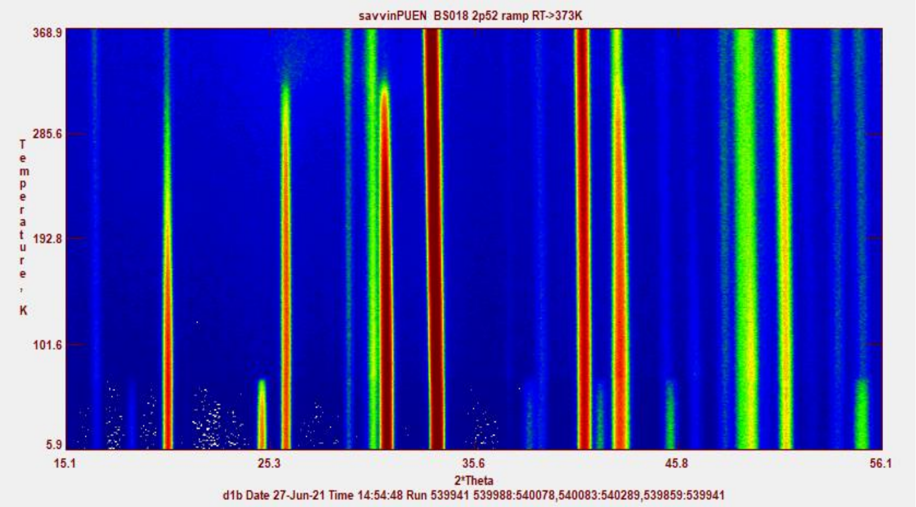


Figure 2. Variable temperature D1B data for $Ca_2Fe_{2.6}O_3S_2$. The data show clearly again that there are two magnetic ordering transitions with two sets of magnetic peaks appearing below 400 K, one of which is associated with the magnetic ordering transtion evident in the susceptiblity at ~70K [1].

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 Mössbauer spectroscopy 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 Bradley Sheath.

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