Experimental report

05/04/2022

Proposal: **EASY-867**

Council: 10/2020

Title: Magnetic and Crystal Structure of Ca2Fe2.75O3S0.5Se1.5

Research area: Chemistry

This proposal is a new proposal

Main proposer: **Simon James CLARKE**

Experimental team:

Local contacts: Stanislav SAVVIN

Samples: Ca2Fe2.75O3S0.5Se1.5

Instrument	Requested days	Allocated days	From	To
D2B	12	12	15/05/2021	16/05/2021

Abstract:

A new phase of stoichiometry Ca2Fe2.75O3S0.5Se1.5 has been synthesised as a high purity, 3g batch. The Ca2Fe2.6O3S2 sulfide end member, along with two other solid solution phases Ca2Fe2.65O3S1.5Se0.5 and Ca2Fe2.7O3SSe, all show long range antiferromagnetic order (as confirmed by neutron scattering data previously collected on D2B, experiment 5-31-2732). Ca2Fe2.6O3S2 exhibits one magnetic ordering transition at around 80K and a second between 300K and 373K. Magnetometry data for Ca2Fe2.75O3S0.5Se1.5 between 2K and 300K show evidence for two magnetic transitions- one around 80K and another around 160K. This is in contrast to the other three phases, which only have the 80K transition present in this temperature range. We propose measuring this sample at 5K, 120K and 300K so as to explore the magnetic order below both transitions, between the first and second transition and above both transitions. This is a follow up of the previous D2B experiment 5-31-2732 and will complete the study of the solid solution phases for publication in a high impact journal.

EXPERIMENTAL REPORT

EXPERIMENT N° EASY-867 INSTRUMENT D2B
DATES OF EXPERIMENT 15/05/2021 to 16/05/2021

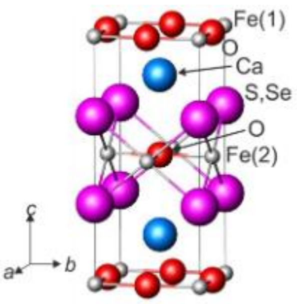
TITLE Magnetic and Crystal Structure of $Ca_2Fe_{2.75}O_3S_{0.5}Se_{1.5}$

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 05/04/22



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.

We previously investigated the magnetic and crystal structures of $Ca_2Fe_{2.6}O_3S_2$, $Ca_2Fe_{2.65}O_3S_{1.5}Se_{0.5}$ and $Ca_2Fe_{2.7}O_3SSe$ (experiment 5-31-2732). This experiment was a study of the more selenide rich $Ca_2Fe_{2.75}O_3S_{0.5}Se_{1.5}$ phase. The data collected on D2B in this experiment (Figure 1) reveal that both Fe(1) and Fe(2) layers are long-range magnetically ordered, with transition temperatures of just below 100K for the Fe(2) layer and between 300K and 343K for the Fe(1) layer. Through the assignment of various magnetic modes to each set of magnetic peaks (Figure 1), models of the magnetic ordering over the temperature range have been proposed (Figure 2). Canted antiferromagnetism is likely to be exhibited by both layers, with a spin-reorientation predicted in the Fe(1) layer upon warming from 100K to 162K, at which temperature the moments lie in the ab-plane. At 5K, the refined moments of 3.30(6) μ_B and 2.52(11) μ_B indicate the presence of Fe^{3+} d^5 and Fe^{2+} d^6 in the Fe(1) and Fe(2) layers respectively.

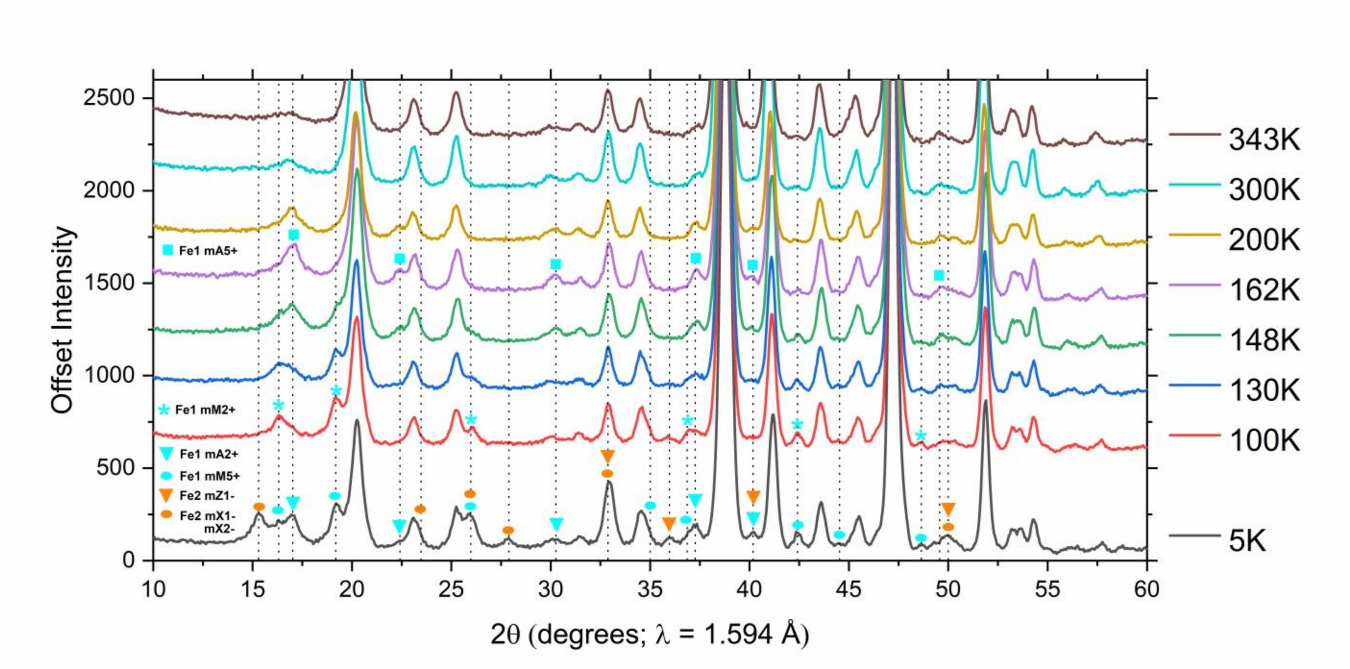


Figure 1. Raw D2B data for $Ca_2Fe_{2.75}O_3S_{0.5}Se_{1.5}$ at variable temperatures. The magnetic reflections are labelled with their corresponding magnetic mode.

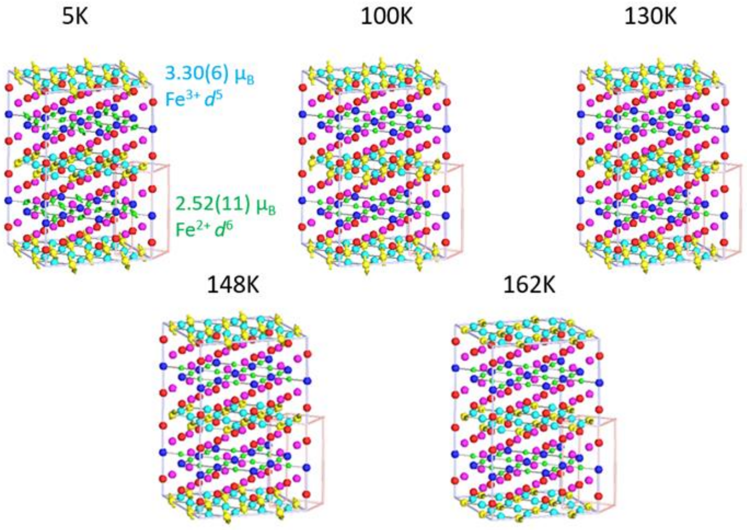


Figure 2. Magnetic models for $Ca_2Fe_{2.75}O_3S_{0.5}Se_{1.5}$ at variable temperatures. The Fe(1) layer orders between 343K and 300K whereas the Fe(2) layer orders just below 100K. Upon warming, the moments in the Fe(1) layer reorientate between 100K and 162K, at which temperature the moments lie in the ab-plane.

Overall this experiment was incredibly useful as it provided an interesting addition to the data collected on other members of this series of compounds and we are grateful for the efforts of the local contact in running the experiment in full during the Covid-19 restrictions. Analysis is almost complete. This compound 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.