

# Experimental report

16/04/2024

**Proposal:** 5-31-2917

**Council:** 10/2022

**Title:** Evolution of magnetic ordering in the layered oxide chalcogenides  $\text{Ca}_2\text{Fe}_{2.7}\text{S}_{2-x}\text{Se}_x\text{O}_3$   $x = 0.5, 1, 1.5$

**Research area:** Chemistry

**This proposal is a continuation of 5-31-2834**

**Main proposer:** Simon James CLARKE

**Experimental team:** Bradley SHEATH  
Alexis GILLETTE  
Simon James CLARKE  
Rob SMYTH

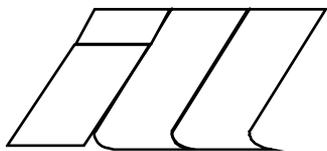
**Local contacts:** Stanislav SAVVIN  
Ines PUENTE ORENCH

**Samples:**  $\text{Ca}_2\text{Fe}_{2.7}\text{SSeO}_3$   
 $\text{Ca}_2\text{Fe}_{2.7}\text{S}_{1.5}\text{Se}_{0.5}\text{O}_3$   
 $\text{Ca}_2\text{Fe}_{2.7}\text{S}_{0.5}\text{Se}_{1.5}\text{O}_3$

Instrument	Requested days	Allocated days	From	To
D1B	3	2	22/05/2023	24/05/2023
D20	3	0		

## Abstract:

This proposal follows a measurement of the magnetic ordering in  $\text{Ca}_2\text{Fe}_{2.6}\text{S}_2\text{O}_3$  and preliminary measurements on the slightly more Fe-rich title compounds ( $\text{Ca}_2\text{Fe}_{2.7}\text{S}_{2-x}\text{Se}_x\text{O}_3$   $x = 0.5, 1, 1.5$ ) which reveal complex and different evolution of the magnetic structures on the two mixed-valent iron sublattices through a series transitions below the onset of long-range magnetic order. The aim here is to make use of the high resolution of D1B in the long d-spacing region to determine the changing magnetic models and related these to the mixed-valence and the Fe deficiency in these compounds, and to compare the behaviour across the series.



# EXPERIMENTAL REPORT

EXPERIMENT N° 5-31-2917

INSTRUMENT D1B

DATES OF EXPERIMENT 22/05/2023 to 24/05/2023

TITLE Evolution of magnetic ordering in the layered oxide chalcogenides  $\text{Ca}_2\text{Fe}_{2.7}\text{S}_{2-x}\text{Se}_x\text{O}_3$   $x = 0.5, 1, 1.5$

EXPERIMENTAL TEAM (names and affiliation)

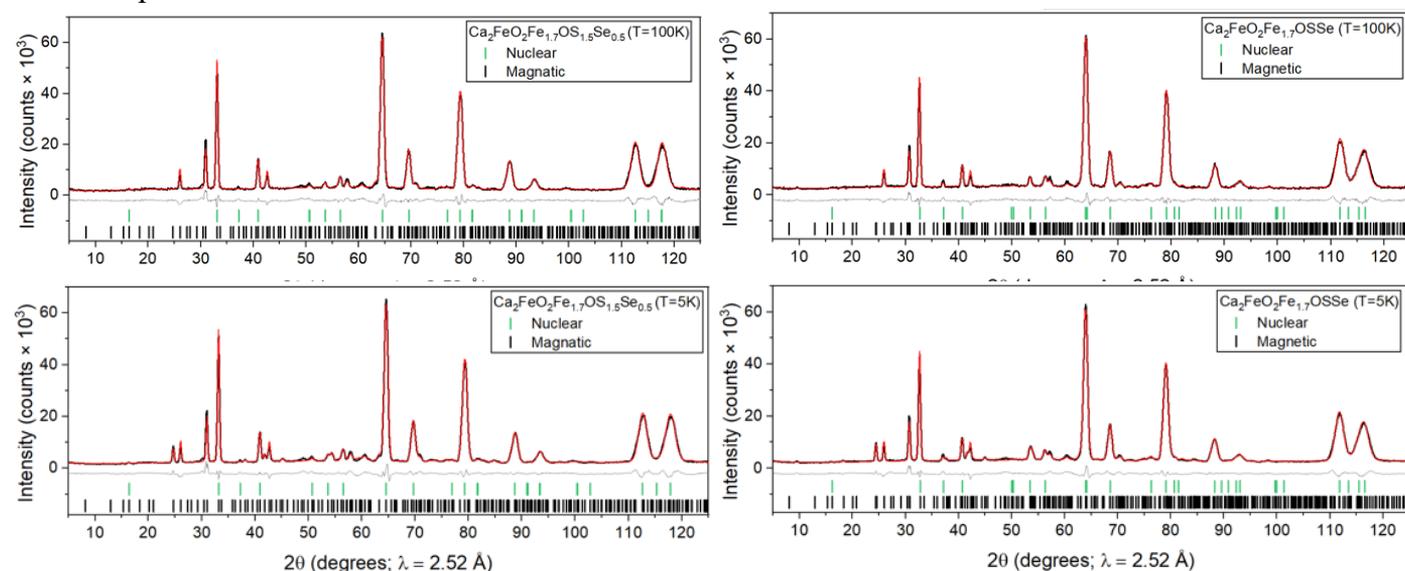
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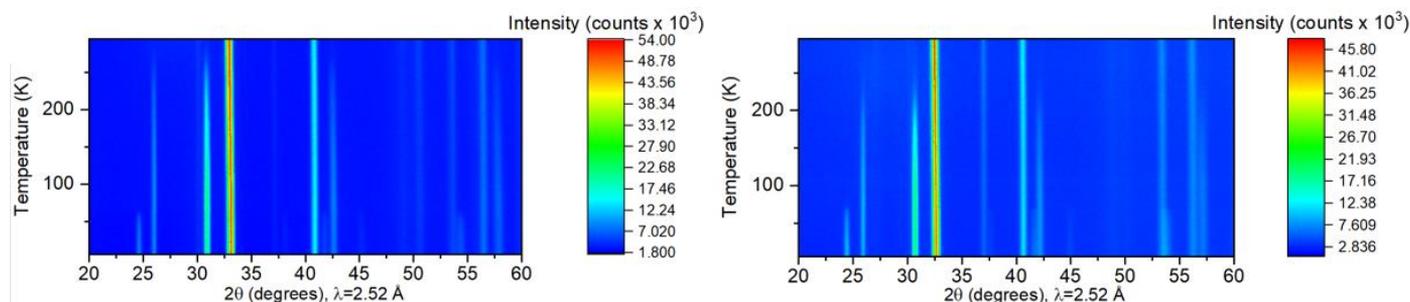
Simon CLARKE INORGANIC CHEMISTRY LAB, OXFORD UNIV GB

LOCAL CONTACT SAVVIN, Stanislav

Date of report 16/04/24

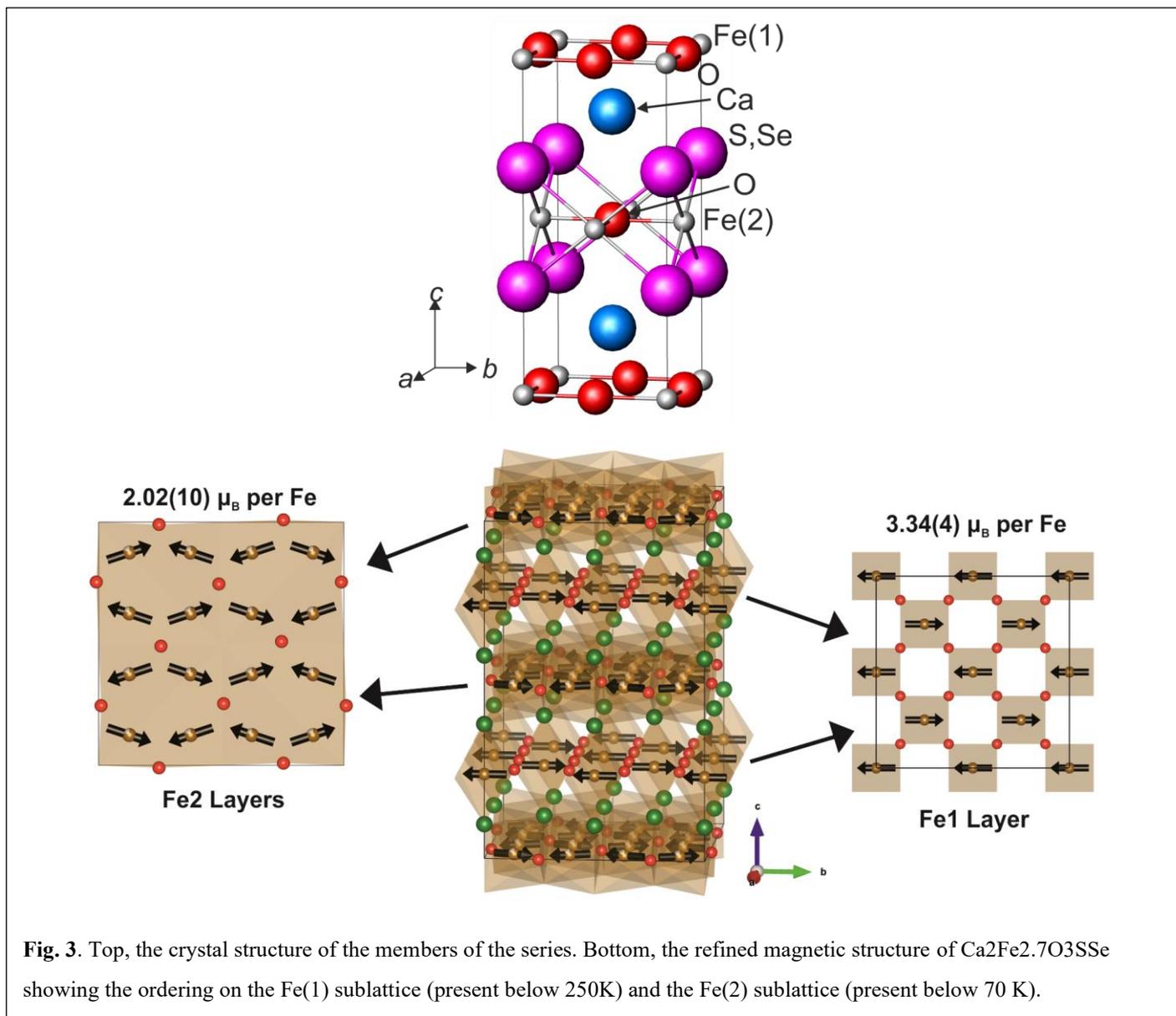


**Fig. 1.** NPD pattern of  $\text{Ca}_2\text{Fe}_{2.7}\text{O}_3\text{S}_{1.5}\text{Se}_{0.5}$  (left) and  $\text{Ca}_2\text{Fe}_{2.7}\text{O}_3\text{SSe}$  (right) measured at 100 K (top) and 5 K (bottom) on the D1B instrument at the ILL showing the observed (black), calculated (red) and difference (grey) curves.



**Fig. 2.** Variable temperature NPD patterns of  $\text{Ca}_2\text{Fe}_{2.7}\text{O}_3\text{S}_{1.5}\text{Se}_{0.5}$  (left) and  $\text{Ca}_2\text{Fe}_{2.7}\text{O}_3\text{SSe}$  (right) measured on the D1B instrument at the ILL.

The series of compounds investigated in this experiment are a series of layered oxide chalcogenides with Fe in two coordination environments and forming two sublattices. The Fe(2) sublattice is deficient in Fe, but the 25% vacancies only order in the pure sulfide. The selenide-containing materials have disordered vacancies on the Fe(2) sublattice. The D1B experiment focused on the magnetic ordering as a function of composition. Full temperature sweeps on the three title samples were performed and the data for the  $x=0.5$  and  $1.0$  samples have been fully analysed as shown in Figure 1 and Figure 2. The  $x=1.5$  sample requires further analysis.



The data gathered on the D1B instrument were useful for the structural analysis of the magnetic structure to accompany previous measurements on D2B of the structure [1].

The work carried out in this experiment is judged to be a success and will be published in an international journal and will form a significant part of the D.Phil thesis of Alexis Gillette.

[1] B. C. Sheath, D.Phil. Thesis, University of Oxford 2023