Experimental report

24/08/2022

Proposal: **5-31-2861**

Council: 4/2021

Title: Magnetic ordering in the quaternary chalcogenides Ba_2FeMCh_5 (M = Sb, Bi) (Ch = S, Se)

Research area: Chemistry

This proposal is a new proposal

Main proposer: **Simon James CLARKE**

Experimental team: Emmanuelle SUARD

Local contacts: Stanislav SAVVIN
Emmanuelle SUARD
Ines PUENTE ORENCH
Vivian NASSIF
Claire COLIN

Samples: Ba_2FeSbS_5
Ba_2FeBiS_5
$Ba_2FeSbSe_5$
$Ba_2FeBiSe_5$
$SrCaMnO_2Li_4S_3$ + Cu

Instrument	Requested days	Allocated days	From	To
D2B	2	2	01/10/2021	03/10/2021
D1B	0	1	15/09/2021	16/09/2021

Abstract:

This proposal is to explore the magnetic ordering present in a family of semiconducting quaternary chalcogenides containing Fe^{3+} ions. The compounds exhibit long range order with T_N ranging from 13K in Ba_2FeSbS_5 to 79 K in $Ba_2FeBiSe_5$, increasing by ~45 K as Se replaces S and by ~22 K as Bi replaces Sb. The spins are likely to order via unusually long Fe-Ch-M-Ch-Fe superexchange pathways, and neutrons are the key to establishing and comparing the long range magnetic structures and testing the computational explanation for the variation in T_N values.

EXPERIMENTAL REPORT

EXPERIMENT N° 5-31-2861 INSTRUMENT D1B and D2B

DATES OF EXPERIMENT 15/09/2021 to 16/09/2021

TITLE Magnetic ordering in the quaternary chalcogenides Ba_2FeMCh_5 (M = Sb, Bi) (Ch = S, Se)

EXPERIMENTAL TEAM (names and affiliation)

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LOCAL CONTACT SAVVIN, Stanislav

Date of report 24/08/22

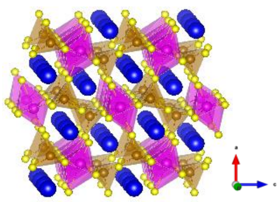

Fig. 1. Structure of Ba_2FeMS_5. Atoms are Fe: brown; M: pink; S: yellow; Ba: blue.

Sulfides can exhibit different crystal structures and properties compared to the well-studied oxides. Recently Geng et al. [1] reported the quaternary sulfides Ba_2FeSbS_5 and Ba_2FeBiS_5, which are semiconductors with the structure given in Fig. 1. They contain Fe^{3+} in edge-sharing FeS_4 tetrahedra and M^{3+} (M = Sb, Bi) in edge-sharing MS_6 distorted octahedra. Magnetometry data showed clear antiferromagnetic transitions at 13 K Ba_2FeSbS_5 for and 35 K for Ba_2FeBiS_5 [1].

The two samples were run on both the D1B and D2B diffractometer. Magnetic Bragg reflections, positioned on a k-vector of (1/2, 0, 1/2), were seen for both materials. These are highlighted by the black triangles in Fig. 2. The magnetic models which give the best fit for these data shown in Fig. 2 are depicted in Fig. 3. It should be noted that two small Bragg peaks of magnetic origin are also seen in the data for Ba_2FeSbS_5 (highlighted by the black squares in Fig. 2) and seem to represent an incommensurate modulation in the long-range magnetic ordering. We are investigating this with the help of our local contact Stanistav Savvin.

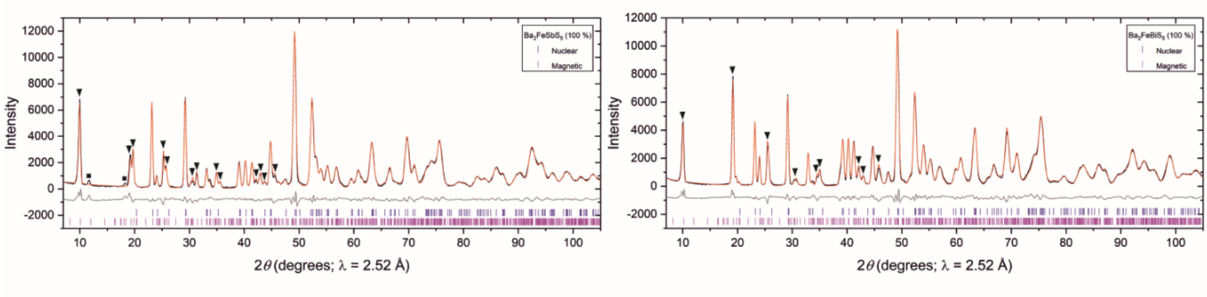

Fig. 2. NPD pattern of Ba_2FeSbS_5 (left) and Ba_2FeBiS_5 (right) measured at 2 K on the D1B instrument at the ILL showing the observed (black), calculated (red) and difference (grey) curves. The black triangles denote magnetic reflections with $k = (^1/_2\ 0\ ^1/_2)$ and the black squares indicate two low intensity magnetic reflections which cannot be accounted for using a commensurate magnetic ordering model.

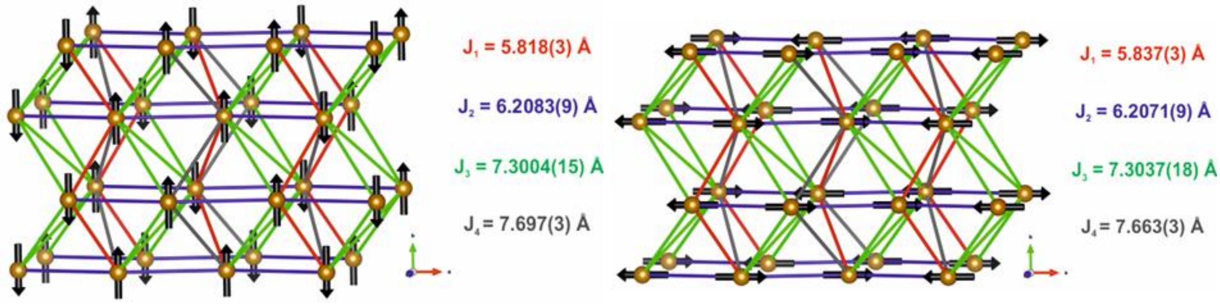

Fig. 3. Magnetic models for Ba_2FeSbS_5 (left) and Ba_2FeBiS_5 (right) where the distances given for the magnetic interactions have been refined from the NPD data collected at 2 K on the D2B instrument.

The saturated moment for Ba_2FeSbS_5 is 3.6 μ_B and for Ba_2FeBiS_5 is 3.8 μ_B, which are reduced from the expected 5 μ_B for Fe^{3+} d^5 ions due to significant covalency in the Fe-S bonds. These two materials show the same ordering pattern of the Fe moments reported for the $Ba_2FeSbSe_5$ material by Maier et al. [2]. Exploration of the critical exponents will be carried out using the variable temperature D1B data shown in Fig. 4.

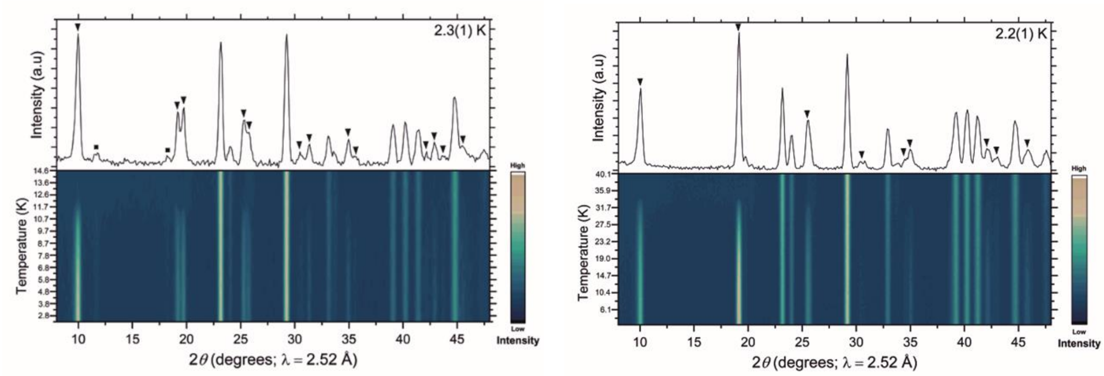

Fig. 4. Variable temperature NPD patterns of Ba_2FeSbS_5 (left) and Ba_2FeBiS_5 (right) measured on the D1B instrument at the ILL.

The data gathered on the D2B instument were useful for the detailed structural refinement, whereas that gathered on D1B was important for the analysis of the magnetic models, due to their high resolutions at the relevant d-spacings. The D1B data were especially useful in determining the most likely magnetic model for the long-range ordering of Fe and it is these data only which exhibit the presence of the two small incommensurately modulated magnetic Bragg peaks.

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. The remaining analyses are in progress. 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] Geng, L. et al. Inorg. Chem. **2011**, 50, 2378-2384.
[2] Maier, S. et al. Phys. Rev. B. **2021**, 103, 54115.