Experimental report

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Proposal: **5-31-2608** **Council:** 4/2018

Title: Investigation of the nuclear and magnetic structures of GaV4S8-ySey materials

Research area: Physics

This proposal is a new proposal

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Samples: GaV4S6Se2
GaV4S7Se
GaV4S4Se4

Instrument	Requested days	Allocated days	From	To
D20	1	2	17/09/2018	19/09/2018
D2B	2	2	19/09/2018	21/09/2018

Abstract:

Skyrmions, nano-sized topological objects, have recently been found in GaV4S8 and GaV4Se8 materials. In the search of new Skyrmion hosting materials, we have synthesised the GaV4S8-ySey (y = 0 to 8) family of materials. In contrasts to the long range ferromagnetic ordering exhibited by GaV4S8 and GaV4Se8, a canted antiferromagnetic state is found in materials with y between 2 and 6. Here we propose to investigate the nuclear and magnetic structures of GaV4S7Se, GaV4S6Se2 and GaV4S4Se4 samples with neutron diffraction in order to explore the drastic change in the observed magnetism in this family. We will be using polycrystalline samples (D2B and D20)for our investigations.

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Investigation of the nuclear and magnetic structures of $GaV_4S_{8-y}Se_y$ materials

1. Introduction

Recently, there has been vast interest in magnetic skyrmions due to their potential applications, such as high-density magnetic storage devices [1]. Only a few materials are currently known to host skyrmions *e.g.* MnSi [2], Cu_2OSeO_3 [3], GaV_4S_8 [4] and GaV_4Se_8 [5]. In the search for new skyrmionic materials manipulation of known compounds is a relatively fruitful route. To this end, we have chosen to examine $GaV_4S_{8-y}Se_y$ compounds, with y = 0 to 8.

GaV_4S_8 and GaV_4Se_8 both belong to a family of Mott insulators and have been found to host Skyrmions [3, 4]. Both GaV_4S_8 and GaV_4Se_8 undergo structural phase transitions from high-temperature cubic ($F\bar{4}3m$) to low-temperature rhombohedral ($R3m$) at 42 K and 41 K respectively. A magnetic transition occurs at 13 K in GaV_4S_8 and 18 K and GaV_4Se_8 leading to the onset of Néel skyrmions in applied magnetic field. In GaV_4S_8 the skyrmion spocket forms in small applied magnetic fields (10-100 mT) and in the temperature range 8-13 K, compared to GaV_4Se_8 where the skyrmion pocket extends to larger applied magnetic fields (70-370 mT) and temperature range (2-18 K).

Polycrystalline materials of the $GaV_4S_{8-y}Se_y$ (y = 0 to 8) family were used for the neutron diffraction experiments. These had been previously characterised using powder X-ray diffraction and *dc* magnetometry experiments to investigate whether the intermediate members of this family of materials are potential skyrmion hosting materials.

2. Experiment details

Powder neutron diffraction experiments were performed on the D20 diffractometer with a neutron wavelength of 2.417 Å for magnetic structure determination using ~3-4g of each sample. Initially, GaV_4S_8 was measured at three temperatures for 3 hours at each temperature, first temperature in the cycloidal phase (9 K), second in the low temperature magnetic phase (1.5 K), and third in the paramagnetic phase (15 K) to obtain magnetic difference patterns. Data was collected in an analogous way for $GaV_4S_{7.9}Se_{0.1}$ measured at 1.5 K, 9 K, and 15 K. Each temperature measurement was 6.5 hours long due to the smaller magnetic moment. $GaV_4S_6Se_2$ was measured at 1.5 K and 15 K for 1 hour each, but no magnetic scattering was be observed.

For structure determination the data was collected on D2B using the high-resolution option with a neutron wavelength of 1.594 Å and the same amounts of sample were used. In the case of GaV_4S_8 measurements were taken at 1.5, 9, 15, 30, and 50 K for 3 hours at each temperature. Shorter scans of 30 mins were taken at 40, 41, and 43 K to more precisely determine the temperature of the structural phase transition. Data on $GaV_4S_{7.9}Se_{0.1}$ was collected at 1.5, 9, 15, 30, and 50 K for 1 hour at each temperature to get statistically significant structural data. Shorter, 30 min, measurements were also performed at 33, 34, 35, 35.5, 36, 36.8, 38, 39, 40, 41, and 42 K to calculate the proportions of the cubic and rhombohedral phases in the sample. To investigate the phase transition in $GaV_4S_{7.6}Se_{0.4}$ measurements for 3.5 hours at 1.5 K and 50 K were carried out to precisely determine the quantity of the mixed structural phases (cubic and rhombohedral) present at 1.5 K. $GaV_4S_{7.5}Se_{0.5}$ was measured at 1.5, 30, and 50 K for 3 hours at each temperature to obtain high quality structural data.

3. Results

Structural analysis was performed on data taken on the D2B diffractometer using TOPAS and FullProf software [6, 7]. GaV_4S_8 was found to undergo a structural phase transition from a high temperature $F\bar{4}3m$ cubic space group to a low temperature pseudo-cubic (Rhombohedral) $R3m$ space group at 42 K. This phase transition can be monitored by observing the spitting of the cubic (448) peak, as shown in Figure 1a. The phase transition in $GaV_4S_{7.9}Se_{0.1}$ was found to extended over a larger temperature region than its pristine counterpart (Figure 1b). This revealed that during the phase transition the $F\bar{4}3m$ sand $R3m$ phases co-exist. Quantitative phase analysis using Reitveld refinements in TOPAS was used to obtain the weight percentage of each of the phases at a range of temperatures in each composition. Figure 1c shows the relative amount of $F\bar{4}3m$ and $R3m$ phases. For y=0.4 composition the co-existence of both phases can be observed whist for y=0.5 no structural phase transition is observed, and the sample stays fully cubic down to base temperature.

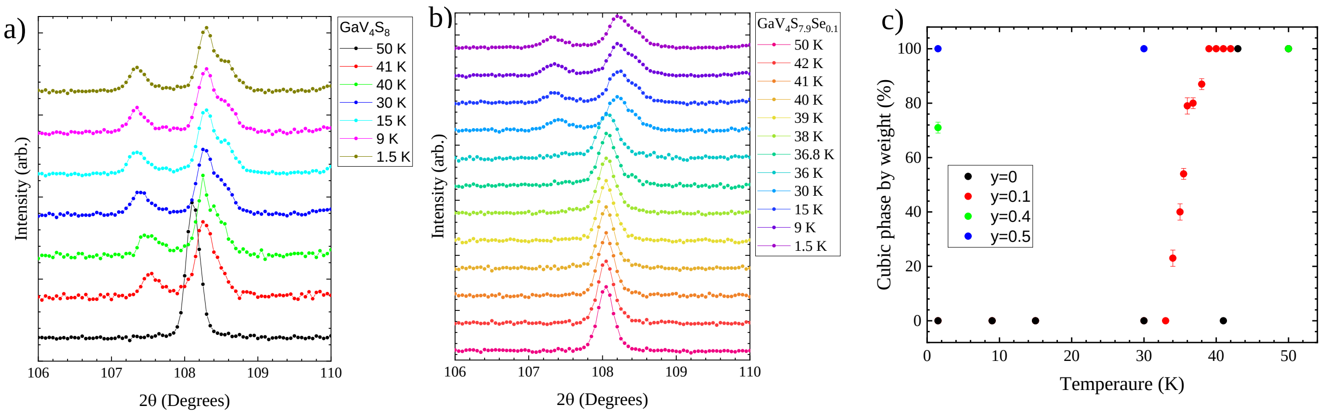

Figure 1 – Structural phase transition as shown by the cubic 448 peak for a) GaV_4S_8 and b) $GaV_4S_{7.9}Se_{0.1}$. c) Quantitative phase analysis of $GaV_4S_{8-y}Se_y$

Magnetic neutron diffraction data was collected on the D20 diffractometer and refined using the FullProf software [7]. The magnetic scattering pattern in GaV_4S_8 collected at 1.5 K was refined using commensurate R3m' magnetic structure as can be seen in Figure 3. The magnetic moments were found to be 0.185(18) μ_B on the V1 atoms and 0.266(3) μ_B on the V2 atoms. Data was also taken at 9 K where the magnetic structure could be deemed to be incommensurate, however, the data was not statistically good enough to unambiguously identify the k-vector.

Magnetic diffraction data was collected for $GaV_4S_{7.9}Se_{0.1}$ 9 K and 1.5 K in which the magnetic signal was clearly visible. At both 1.5 K and 9 K, a commensurate R3m' magnetic structure was used for the refinement giving values of 0.13(2) μ_B on V1 and 0.31(5) μ_B on V2 for the magnetic moments at 1.5 K and 0.13(3) μ_B for V1 and 0.18(6) μ_B for V2 at 9 K, see Figure 4. $GaV_4S_6Se_2$ showed no magnetic scattering, this is attributed to the presences of a canted antiferromagnetic phase with a very low magnetic moment.

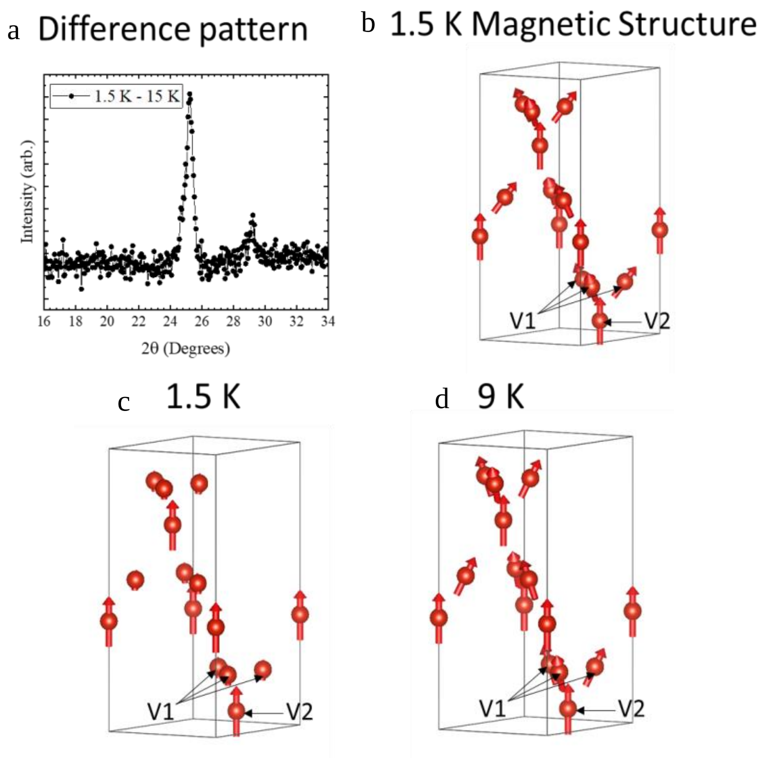

Figure 3 - GaV_4S_8 a) magnetic difference pattern and b) magnetic structure at 1.5 K. Magnetic structure of $GaV_4S_{7,9}Se_{0.1}$ at c) 1.5 K and d) 9 K

4. Conclusions and future work

The structural phase transition in GaV_4S_8 from a cubic to rhombohedral space group was followed in this diffraction experiment in the temperature range 50 - 1.5 K and a low temperature commensurate R3m' magnetic structure has been identified. Se substituted samples in the $0 < y < 0.5$ range have been shown to go through a gradual structural phase transition, whereas the $y = 0.5$ sample does not undergo a structural transition. The $y = 0.1$ sample also shows a commensurate R3m' magnetic structure at 1.5 K and 9 K. A continuation proposal will be submitted to further investigate the magnetism in the ranges $0 \leq y \leq 0.5$ and $7.5 \leq y \leq 8$ compounds with up to 10g of phase pure samples.

5. References

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6. Publications resulting from this work

A publication is currently being prepared supported by laboratory-based characterisation measurements and single crystal neutron diffraction measurements obtained on SXD at ISIS.