Experimental report

18/01/2021

Proposal: **5-31-2684**

Council: 4/2019

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

Research area: Physics

This proposal is a continuation of 5-31-2608

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Samples: GaV4S8
GaV4Se8
GaV4S7.7Se0.3
GaV4S0.3Se7.7
GaV4S0.1Se7.9
GaV4S7.8Se0.2
GaV4S7.6Se0.4
GaV4S7.9Se0.1
GaV4S0.2Se7.8

Instrument	Requested days	Allocated days	From	To
D2B	4	4	06/02/2020	10/02/2020
D20	4	3	07/02/2020	10/02/2020

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. Large changes in the magnetic phase diagrams have been observed via magnetometry in samples with small amounts of substitution to GaV4S8 and GaV4Se8 making these ideal to be studied with neutron diffraction. We have shown samples with small amounts of substitution exhibit a mixed structural phase and propose to study this over the range y=0-0.4 and 7.6-8 using neutron diffraction. 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. After our previous investigation of the $GaV_4S_{8-y}Se_y$ family of compounds, with y = 0 to 8 we have narrowed our search to $0 \leq y \leq 0.5$ and $7.5 \leq y \leq 8$.

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, *dc* and *ac* 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 $\sim$10 g of each sample. GaV_4S_8 was measured at three temperatures, 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.

For structure determination the data was collected on D2B using the high-resolution option with a neutron wavelength of 1.594 Å using $\sim$10 g of each sample. Data was collected on samples with $7.5 \leq y \leq 8$ at multiple temperatures between 1.5 and 50 K.

3. Results

Structural analysis was performed on data taken on the D2B diffractometer using TOPAS and FullProf software [6, 7]. GaV_4Se_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 for $GaV_4S_{0.3}Se_{7.7}$. The phase transition in the substituted samples was found to extended over a larger temperature region than the pristine counterparts (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 higher levels of substituent the co-existence of both phases can be observed while temperature of the phase transition is suppressed.

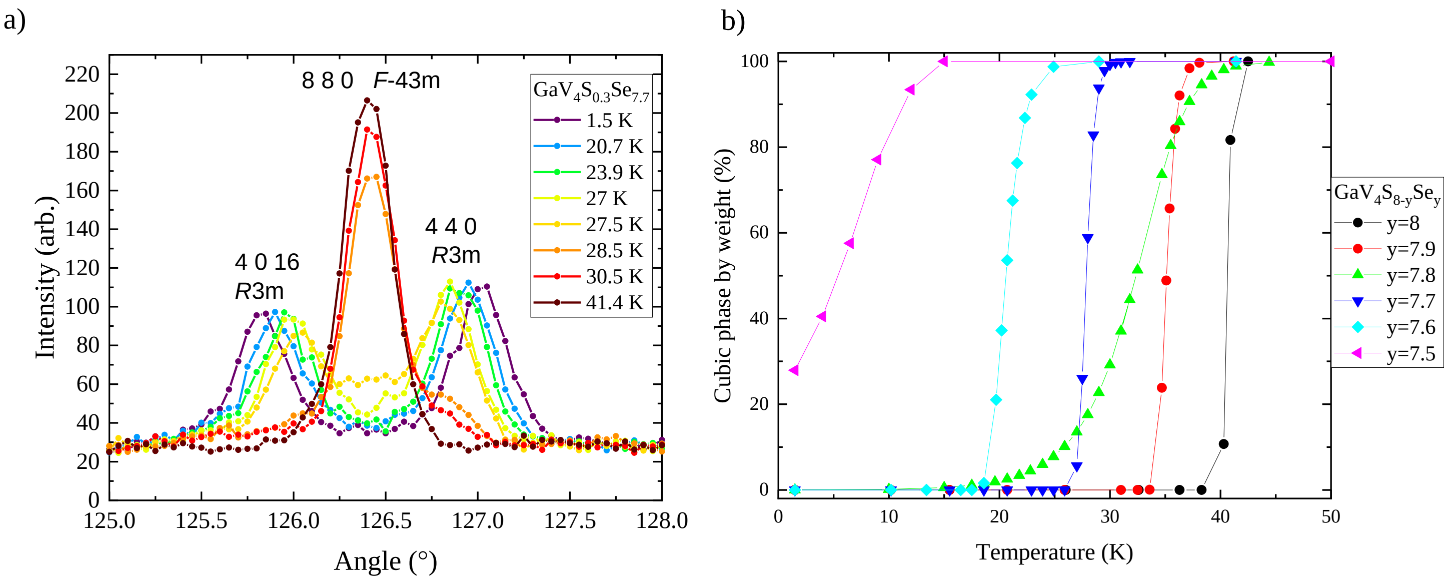

Figure 1 – Structural phase transition as shown by the cubic 448 peak for a) $GaV_4S_{0.3}Se_{7.7}$ c) Quantitative phase analysis of $GaV_4S_{8\text{-}y}Se_y$

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 0.23(2) μ_B on the V1 atoms and 0.217(14) μ_B on the V2 atoms. Data was also taken at 9 K where the magnetic structure could be deemed to be incommensurate and the propagation vector to be in the *a-b* plane.

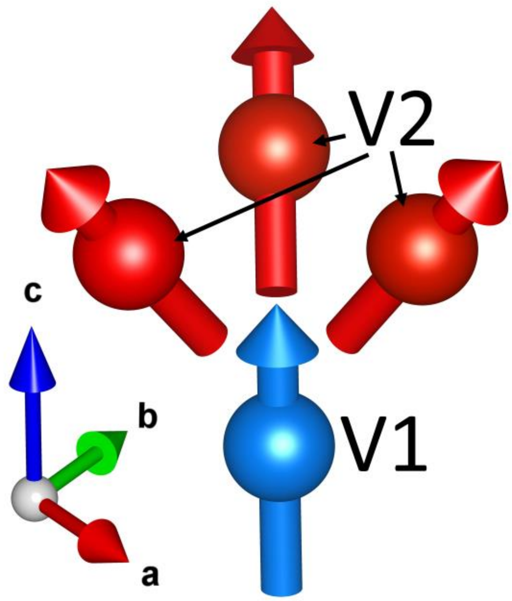

Figure 3 - GaV_4S_8 magnetic structure at 1.5 K.

4. Conclusions and future work

The structural phase transition in $GaV_4S_{8-y}Se_y$ 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.

5. References

[1] W. Wang, *et al.*, *Adv. Mater*. 28, 6887 (2016).
[2] S. Mühlbauer, *et al.*, *Science* 323, 915 (2009).
[3] S. Seki, X. Z. Yu, S. Ishiwata and Y. Tokura, *Science* 336, 198 (2012).
[4] I. Kézsmárki, *et al.*, *Nat. Mater*. 14, 4402 (2015).
[5] Y. Fujima, N. Abe, Y. Tokunaga, and T. Arima, *Phys. Rev. B* 95, 180410(R) (2017).
[6] A. A. Coelho, TOPAS ACADEMIC, version 4, Brisbane, Australia (2005)
[7] J. Rodriguez-Carvajal, *Physica B*. 192, 55 (1993)

6. Publications resulting from this work

Stefancic, Ales, *et al*. "Establishing magneto-structural relationships in the solid solutions of the skyrmion hosting family of materials: GaV4S8-ySey." SCIENTIFIC REPORTS 10.1 (2020).

Holt, S. J. R., *et al*. "Structure and magnetism of the skyrmion hosting family GaV 4 S 8− y Se y with low levels of substitutions between 0≤ y≤ 0.5 and 7.5≤ y≤ 8." Physical Review Materials 4.11 (2020): 114413.

Another publication is currently being prepared supported by laboratory-based characterisation measurements.