Structure and magnetism of the skyrmion hosting family GaV$_4$S$_{8-y}$Se$_y$ with low levels of substitutions between $0 \leq y \leq 0.5$ and $7.5 \leq y \leq 8$

S. J. R. Holt, $^1$ A. Štefančič, $^1$ C. Ritter, $^2$ A. E. Hall, $^1$ M. R. Lees, $^1$ and G. Balakrishnan$^{1,3}$

$^1$University of Warwick, Department of Physics, Coventry, CV4 7AL, United Kingdom
$^2$Institut Laue-Langevin, 71 Avenue des Martyrs, CS20156, 38042 Grenoble Cédex 9, France

Polycrystalline members of the GaV$_4$S$_{8-y}$Se$_y$ family of materials with small levels of substitution between $0 \leq y \leq 0.5$ and $7.5 \leq y \leq 8$ have been synthesized in order to investigate their magnetic and structural properties. Substitutions to the skyrmion hosting parent compounds GaV$_4$S$_8$ and GaV$_4$Se$_8$ are found to suppress the temperature of the cubic to rhombohedral structural phase transition that occurs in both end compounds and to create a temperature region around the transition where there is a coexistence of these two phases. Similarly, the magnitude of the magnetization and temperature of the magnetic transition are both suppressed in all substituted compounds until a glassy-like magnetic state is realized. There is evidence from the ac susceptibility data that skyrmion lattices with similar dynamics to those in GaV$_4$S$_8$ and GaV$_4$Se$_8$ are present in compounds with very low levels of substitution, $0 < y < 0.2$ and $7.8 < y < 8$, however, these states vanish at higher levels of substitution. The magnetic properties of these substituted materials are affected by the substitution altering exchange pathways and resulting in the creation of increasingly disordered magnetic states.

I. INTRODUCTION

In recent years there has been significant interest in the field of magnetic skyrmions and in the search for new materials which exhibit skyrmions [1]. While an increasing number of materials that host bulk Bloch skyrmions have been discovered, to date there are only a limited number of known bulk systems in which Néel skyrmions are stabilized, hence further investigation into the discovery of these systems is of great interest [2–6]. One way to increase the number of skyrmion hosting materials is to extend the families of known skyrmion materials by chemical manipulation. For example, in materials such as Cu$_2$OSeO$_3$ the substitution at the Cu site has enabled the tuning of physical parameters in the system, and hence their magnetic properties [7–9]. In the search for new skyrmion hosts it is also necessary to gain a detailed understanding of the fundamental links between the crystal structures adopted by skyrmionic materials and the magnetic states that they exhibit, to understand what makes these materials suitable hosts.

One family of materials in which a few members have been shown to stabilize Néel type skyrmions (for example GaV$_4$S$_8$ and GaV$_4$Se$_8$) are the lacunar spinels AB$_4$X$_8$ (A = Ga, Al, Ge, Ti, Fe, Co, Ni, Zn; B = V, Cr, Mo, Re, Nb, Ta; X = S, Se, Te), which have been studied due to their intriguing electronic and magnetic properties [10–23]. Lacunar spinels undergo structural phase transitions at low temperatures giving rise to a variety of magnetic phases exhibiting a plethora of interesting properties, such as skyrmions. Of these, GaV$_4$S$_8$ and GaV$_4$Se$_8$ have been extensively studied as skyrmion hosts [2,3,6,24]. Both GaV$_4$S$_8$ and GaV$_4$Se$_8$ are isostructural with a structural phase transition from a high temperature cubic F43m phase to a low temperature rhombohedral R3m structure at 42 and 43 K, respectively with a further magnetic transition at 13 and 18 K, respectively [17,22]. The high temperature cubic structure consists of V$_4$X$_4$ and GaX$_4$ tetrahedra arranged in a NaCl structure. In this structure, there are two distinct sites on which the chalcogenides can sit: either the S1/Se1 site within the V$_4$X$_4$ cluster or the S2/Se2 site within the GaX$_4$ tetrahedra. It has been suggested that the cubic to rhombohedral phase transition is driven by such mechanisms as a cooperative Jahn-Teller distortion [25] and charge order of the V$_4$ cluster formed of three V$^{3+}$ and one V$^{4+}$ ion [24]. In the low temperature rhombohedral phase a single V ion distorts along the one of the four possible cubic (111) directions in the the V$_4$X$_4$ cluster. This distortion causes a reduction in symmetry and removes the triple degeneracy of the t$_2$ orbitals splitting them into two higher energy e levels and one lower energy a$_1$ level. One other related member of the lacunar spinels, GaMo$_4$Se$_8$, has recently been reported to exhibit [5] large changes in the magnetic phase diagram brought about as a result of subtle structural distortions. GaMo$_4$Se$_8$, which adopts a cubic F43m structure at room temperature is reported to undergo a transition at low temperatures to a ground state where there is a coexistence of two distinct structural space groups, a R3m phase and a metastable Imm2 phase, exhibiting distinctly different magnetic properties strongly related to their magneto-crystalline anisotropy. In this material, the R3m phase is known to exhibit Néel type skyrmions [5] and is a clear demonstration of the tunability of these structures to effect dramatic changes in the magnetic properties.

GaV$_4$S$_8$ hosts a variety of magnetic phases. In zero-
field there is a transition from a paramagnetic to cycloidal magnetic state [2]. Further reduction in temperature results in a commensurate magnetic state with the moments on the distorted V ion aligning ferromagnetically and the moments on the other three V ions canted in a R3m/ Shubnikov group pointing out of the cluster [24]. Application of a small magnetic field to the cycloidal phase stabilizes magnetic skyrmions, and further application of a magnetic field results in the formation of a field polarized state [2]. In comparison, GaV$_4$Se$_8$ shows a transition from a paramagnetic to a cycloidal state with decreasing temperature and remains cycloidal down to 1.5 K. Application of a small magnetic field to the cycloidal phase is found to stabilize magnetic skyrmions followed by a field polarized state at higher fields [6]. In both GaV$_4$S$_8$ and GaV$_4$Se$_8$ the skyrmions form along the [111] pseudo-cubic crystallographic direction while having strong easy axis and easy plane anisotropy respectively. The extent of the skyrmion phase strongly depends on the orientation of applied magnetic field with respect to the crystallographic direction [6]. Muon-spin rotation (µSR) measurements have shown that there are large differences in the magnetic ground states of GaV$_4$S$_8$ and GaV$_4$Se$_8$, with GaV$_4$Se$_8$ showing a peculiar increase in local magnetic fields with an increase of temperature [20, 27].

Given that both GaV$_4$S$_8$ and GaV$_4$Se$_8$ host skyrmions, we have investigated in a previous study the entire solid solution formed between these two parent materials, by substituting S with Se, in an attempt to see if any of the intermediate phases exhibit the pre-requisite magnetic and structural properties to host skyrmions [24]. This study revealed that the solid solutions formed for $1 \leq y \leq 7$ (in integer intervals) remain cubic down to 1.5 K, thus preventing the formation of Néel type skyrmions. In addition, it was found that these intermediate compositions do not exhibit magnetic ordering, and instead have glassy-like magnetic ground states indicative of magnetic disorder within the system. This study highlights the important structure-magnetism correlations in these materials. The substitution of S/Se, for example, in the two parent materials was not expected to produce a large disruption to the local structural units but this was not the case, as was evidenced.

In order to further examine how the evolution of the magnetic states is intricately linked to structural transformations and instabilities, we have now synthesized and investigated selected compositions very close to the two end compounds in the GaV$_4$S$_{8-y}$Se$_y$ family of materials ($y = 0$ to 0.5 and $y = 7.5$ to 8). By effecting extremely subtle distortions by these low level substitutions, we have been able to examine the stability of these local structural units, which are crucial to these materials acting as skyrmion hosts. We have also been able to evaluate the critical S/Se substituted compositions at which the transition from a skyrmion hosting to a non-skyrmion hosting material occurs and determine the mechanisms leading to this. Detailed structural analysis has been carried out using both X-ray and neutron diffraction. The magnetic properties have been investigated using ac/dc magnetometry to understand the strong correlations between the structure and magnetic behaviors existing in these systems and to probe the critical phenomena in this narrow composition range. Our results indicate that small levels of substitution create a coexistence of both cubic $F\bar{4}3m$ and rhombohedral $R3m$ structural phases in the region surrounding the temperature of the structural phase transition. This phenomena is coupled with a reduction of the structural transition temperature with increasing substitution levels, until the structural transition is no longer present for $y = 0.5$ and nearly eradicated for $y = 7.5$. The magnetic susceptibility is dramatically suppressed and the nature of the magnetic phase diagram is significantly altered with increasing levels of substituents. We show that both the structural and magnetic properties of the substituted materials exhibit marked changes for substitution levels as low as 2.5% (i.e. $0 \leq y < 0.2$ and $7.8 < y \leq 8$) in both parent compounds, thus demonstrating the fragility of the systems to substitutional or similar disorder and its effect on the ability of these systems to host skyrmions.

II. EXPERIMENTAL DETAILS

Polycrystalline GaV$_4$S$_{8-y}$Se$_y$, samples with $y = 0$, 0.1, 0.2, 0.3, 0.4, 0.5, 7.5, 7.6, 7.7, 7.8, 7.9, and 8 were synthesized by the standard solid-state reaction method similar to that used for the synthesis of polycrystalline GaV$_4$S$_8$ and GaV$_4$Se$_8$ [24]. Powder X-ray diffraction was performed on a Panalytical X-Pert Pro diffractometer operating in Bragg-Brentano geometry equipped with a monochromatic Cu K$_{\alpha1}$ source and a solid-state PIXcel one-dimensional detector, to determine the phase purity and crystallographic structure of the polycrystalline materials at room temperature. Rietveld refinements were carried out using the TOPAS academic v6.0 software refinement based on the structural model obtained by single crystal X-ray diffraction in our previous study [23, 28].

Powder neutron diffraction was performed on the D2B diffractometer at Institut Laue Langevin (ILL) to establish the nuclear structures between 1.5 and 50 K. Powder samples were sealed in thin-walled cylindrical vanadium containers of 8 to 12 mm diameter and placed in a standard orange cryostat. A neutron wavelength of 1.594 Å was used to obtain high-resolution diffractograms for nuclear structure refinements. Structural Rietveld refinements have been used to simultaneously fit the diffractograms of a single composition whilst imposing physical behavior using TOPAS academic v6.0 [28].

The magnetic properties of the polycrystalline materials were measured using a Quantum Design Magnetic Property Measurement System, superconducting quantum interference device (SQuID) magnetometer. dc temperature-dependent magnetic susceptibility ($\chi$) measurements were carried out at temperatures between 1.8
and 300 K in an applied field of 10 mT using a zero-field-cooled-warming (ZFCW) protocol. ac susceptibility measurements were performed with a 113 Hz ac field of 0.3 mT after zero-field-cooling to each measuring temperature and then applying a dc magnetic field.

### III. RESULTS AND DISCUSSION

#### A. Powder X-ray diffraction

Room temperature powder X-ray diffraction data of the polycrystalline GaV$_4$S$_{8-y}$Se$_y$ with 0 ≤ y ≤ 0.5 and 7.5 ≤ y ≤ 8 could all be indexed in $Fm\bar{3}m$ cubic symmetry. A representative pattern is shown in Fig. 1 for one of the materials investigated, GaV$_4$S$_{8.4}$Se$_{7.6}$. The patterns show that the materials form predominantly as single phase with low levels of impurities such as VSe$_2$ for 7.5 ≤ y ≤ 8 and V$_2$S$_3$ for 0 ≤ y ≤ 0.5. Figure 1 indicates a monotonically increasing lattice parameter with increasing Se content which was also observed in our earlier study covering a much wider substitution range $^{21}$.

#### B. Powder Neutron Diffraction

The structural properties of the family have been examined using high resolution powder neutron diffraction on the D2B diffractometer at the ILL.

1. **Structural phase transition**

Both GaV$_4$S$_8$ and GaV$_4$Se$_8$ were found to undergo a structural phase transition from a high temperature cubic $Fm\bar{3}m$ phase to a lower temperature rhombohedral $R3m$ structure, as previously reported $^{17, 19}$. The Rietveld refinements performed on the parent and substituted GaV$_4$S$_{8-y}$Se$_y$ compounds with 0 ≤ y ≤ 0.1, 0.4 ≤ y ≤ 0.5, and 7.5 ≤ y ≤ 8 reveal some interesting structural properties of the family including a region of structural phase coexistence. As an example, a typical Rietveld refinement of the high resolution neutron diffraction data collected on the y = 7.5 sample is shown in Fig. 2. Here, the results of the refinements reveal that there is a coexistence of two phases having $Fm\bar{3}m$ and $R3m$ symmetry. This is seen as a splitting of the cubic (8 8 0) peak depicted in the inset of Fig. 3 for the refinement at 1.5 K where the coexistence of both cubic and rhombohedral peaks is evident. The lower temperature rhombohedral $R3m$ structure is pseudo-cubic, which results in the nuclear diffraction peaks being close to those of the high temperature cubic $Fm\bar{3}m$ phase. Hence, the structural phase transition is best revealed as a splitting of high order cubic Bragg peaks. This is illustrated in Fig. 4 for GaV$_4$S$_{0.3}$Se$_{7.7}$ and is similar to what is observed in all of the compounds that undergo a structural phase transition (0 ≤ y ≤ 0.4 and 7.5 ≤ y ≤ 8). Figure 4 also shows the shift of the angle at which the $R3m$ Bragg peaks occur, illustrating the thermal expansion of the c axis and contraction of the a axis, reflecting the increasing rhombohedral distortion.

Figure 5 depicts the observed structural phase transitions quantified as the percentage remainder of the cubic phase as a function of temperature and composition. It can be seen that the two end phases, GaV$_4$S$_8$ and GaV$_4$Se$_8$, undergo, as expected, a sharp structural phase transition, from 100% $Fm\bar{3}m$ phase to 100% $R3m$ phase at 42 and 43 K, respectively. The sharp transitions for these two parent compounds indicate the first-order nature of their transitions, in agreement with literature $^{3, 17}$. Figure 5 shows that at both the S and Se ends of
the series, the addition of substituents suppresses the onset temperature of the structural phase transition whilst simultaneously broadening it. This broadening of the transition creates a wide temperature region in which refinements show the presence of both the $F\bar{4}3m$ and $R3m$ structural phases. Indication of the phase coexistence comes from features such as the appearance of a shoulder on the right side of the cubic $(8\ 8\ 0)$ peak in Fig. 4 at 30.5 and 28.5 K. Additionally, at lower temperatures there is still some intensity from the cubic $(8\ 8\ 0)$ peak located between the $(4\ 0\ 16)$ and $(8\ \bar{4}\ 0)$ rhombohedral peaks. Broadening of the structural phase transition is indicative of a disorder-broadened first-order phase transition [29, 30]. A certain amount of broadening is likely to be inherent to a particular substitution level as small levels of substitution preclude the possibility of homogeneity across all unit cells in the material. The extra broadening of the phase coexistence region observed for $y = 7.8$ in Fig. 4 compared to the other compositions investigated is most likely related to an increase of the variance of the local substitution level within the sample of this composition.

For GaV$_4$S$_{8.5}$Se$_{7.5}$ with $7.5 \leq y \leq 8$, Fig. 5 shows a clear decrease of the transition temperature with the addition of substituents. The region of cubic and rhombohedral coexistence for GaV$_4$S$_{0.5}$Se$_{7.5}$ extends to low temperatures and the structural phase transition is incomplete with a coexistence of the two structural phases observed down to 1.5 K. For the S rich materials, $y = 0.5$ remains cubic down to 1.5 K and $y = 0.4$ exhibits a coexistence of the $F\bar{4}3m$ and $R3m$ phase at 1.5 K. A similar trend of the decrease of the transition temperature with the addition of substituents is seen for compositions in the range $0 \leq y \leq 0.5$, conforming to what is expected for higher substitution levels ($1 \leq y \leq 7$), all of which remain cubic [24].

In our previous study [24] we suggested a couple of possible mechanisms that could be responsible for the suppression of the structural phase transition in this family of materials. These are the uneven local distribution of S/Se compared to neighboring unit cells creating a large elastic energy cost for the structural distortion, and the S/Se disorder within the sample changing electron diffusion pathways and preventing the structural phase transition.

A similar observation has been made by Powell et al. [20] in their investigations of the related GaV$_{4-x}$Mo$_x$S$_8$ family of materials, where there is a suppression of the structural phase transition in the intermediate materials, with these samples remaining in the cubic phase down to low temperatures. They suggest that this is due to the lifting of the electron degeneracy on a local level within the substituted V$_4$S$_4$ clusters, a mechanism which is equally applicable to the GaV$_4$S$_{8-y}$Se$_y$ series. The structural phase transition usually lifts the electron degeneracy upon cooling in the end compositions, but if the addition of substituents removes the electron degeneracy instead, then it could suppress the phase transition. The consequences of the substitution related to the magnetic behavior are addressed in Sec. III C. Our observations of the coexistence of two structural phases in GaV$_4$S$_{8-y}$Se$_y$ are very similar to the observations of Powell et al. in some of the intermediate GaV$_{4-x}$Mo$_x$S$_8$ materials [20], where they also report the coexistence of $F\bar{4}3m$ and $R3m$ structural phases in some of the intermediate compositions investigated.

FIG. 3. Experimentally obtained neutron diffraction profile at 1.5 K (blue open circles) for GaV$_4$S$_{0.5}$Se$_{7.5}$, Rietveld refinements (red solid line), difference (olive green solid line), predicted peak positions of the $F\bar{4}3m$ (black tick marks), and predicted peak positions of the $R3m$ (orange tick marks). $R_p = 6.5$, $R_{wp} = 8.5$, and $R_{exp} = 4.8$. The inset shows the coexistence of the $(8\ 8\ 0)$ $F\bar{4}3m$ diffraction peak with the hexagonal $R3m$ $(4\ 0\ 16)$ and $(8\ \bar{4}\ 0)$ peaks at 1.5 K.

FIG. 4. High-resolution neutron diffractograms taken using the D2B diffractometer at the ILL show splitting of the cubic $(8\ 8\ 0)$ $F\bar{4}3m$ Bragg peak for GaV$_4$S$_{0.5}$Se$_{7.5}$ into the hexagonal $R3m$ $(4\ 0\ 16)$ and $(8\ \bar{4}\ 0)$ Bragg peaks in the temperature range 1.5 to 41.4 K.
FIG. 5. Structural phase transition from cubic \( F\overline{4}3m \) phase to a rhombohedral \( R3m \) by quantitative phase analysis of high-resolution neutron diffractograms collected on the D2B diffractometer at the ILL using Rietveld refinements of GaV\(_4\)S\(_{8-y}\)Se\(_y\) powders. Top: \( y = 0, 0.1, 0.4, \) and 0.5. Bottom: \( y = 8, 7.9, 7.8, 7.7, 7.6, \) and 7.5.

2. Structural Distortion

The distortion of the lattice when transforming from the cubic to the rhombohedral phase can be quantified by examining the \( c/a \) lattice parameter ratio of the \( R3m \) phase in the hexagonal setting. This ratio takes a constant value of \( \sqrt{6} \) as the rhombohedral distortion goes to zero. The magnitude of the distortion as a function of temperature observed in the GaV\(_4\)S\(_{8-y}\)Se\(_y\) powders examined is plotted in Fig. 6. The addition of substituents in both the S and Se ends of the family of materials is found to reduce the distortion of the \( R3m \) phase. As the temperature is increased, all the compositions examined show a similar gradual decrease in the amount of distortion followed by a sharp discontinuity at the rhombohedral to cubic phase transition temperature. This discontinuity in the distortion is further evidence for the first-order nature of the structural transition.

Rietveld refinements of the neutron data confirm the preferential site occupation of Se in the Ga\(X\)\(_4\) tetrahedra and S in the V\(_4\)X\(_4\) clusters as expected for this system \[24\]. This occupational preference is attributed to the larger Se\(^{2-}\) preferring the tetrahedral coordination of the Ga\(X\)\(_4\) tetrahedra. The improved statistics obtained with powder neutron diffraction over that obtained in the laboratory X-ray diffraction data, allows the more accurate refinement/determination of the preferential site occupancy, even for low levels of substitutions. For GaV\(_4\)S\(_{8-y}\)Se\(_y\) with \( 0 < y \leq 0.5 \), all the substituted Se was observed to occupy Ga\(X\)\(_4\) tetrahedra, and all substituted S in 7.5 \( \leq y < 8 \) was observed to occupy V\(_4\)X\(_4\) clusters. When undergoing the structural phase transition from the cubic to rhombohedral phase, the V\(_4\)X\(_4\) clusters can distort along any of four possible cubic \( \langle 111 \rangle \) directions.

C. \( dc \) and \( ac \) magnetization

The nature of magnetic ordering was examined using bulk magnetization measurements on the synthesized powders in the GaV\(_4\)S\(_{8-y}\)Se\(_y\) series. Figure 7 shows the \( dc \) magnetic susceptibility of the powders investigated. The magnitude of the magnetization observed is significantly larger in GaV\(_4\)S\(_8\) compared to GaV\(_4\)Se\(_8\) due to the different magnetic ground states. These parent compounds GaV\(_4\)S\(_8\) and GaV\(_4\)Se\(_8\) undergo long-range ferromagnetic-like ordering at 13 and 18 K, respectively in agreement with literature \[2, 6\]. A dramatic decrease is seen in the zero-field-cooled warming \( dc \) susceptibility for both GaV\(_4\)S\(_8\) and GaV\(_4\)Se\(_8\) with increasing levels of substituents. The addition of S to GaV\(_4\)Se\(_8\) \( (7.5 \leq y \leq 8) \) produces a more pronounced decrease in the magnitude of magnetization than the addition of Se to the GaV\(_4\)S\(_8\) \( (0 \leq y \leq 0.5) \). As the magnetic phases that are stabilized change with substitution, it is difficult to pinpoint
FIG. 7. Temperature dependence of the dc magnetic susceptibility in an applied magnetic field of 10 mT collected after zero-field cooling for powders of the GaV$_4$S$_{8-y}$Se$_y$ family. Top: $0 \leq y \leq 0.4$. Bottom: $7.6 \leq y \leq 8$.

The dynamics of the magnetism in these materials can be probed using $ac$ susceptibility. Different magnetic phases have different characteristics in $ac$ susceptibility, therefore once a magnetic phase is identified, $ac$ susceptibility can be a powerful technique to examine the magnetic phase diagram [31]. It is important to note that due to the easy axis and easy plane anisotropy in these materials the angle of applied magnetic field with respect to the crystallographic axis can affect the magnetic phases stabilized and the fields at which they occur. However, when measuring polycrystalline materials what is observed is effectively an average of all crystallographic orientations. Examining the $ac$ susceptibility phase diagrams for $y = 0.2$ and 7.8, shown in Fig. 8, reveals a dramatic change in the topography of both phase dia-
observations of a similar state in members of this family with higher levels of substitution \[24\]. In GaV$_4$S$_{0.2}$Se$_{7.8}$, the observed peak corresponds to a freezing temperature $T_f$ of $\sim 5.4$ K from the $dc$ susceptibility curve shown in Fig. 7. Figure 9(b) shows the frequency dependence of $T_f$. The shift of the freezing temperature per decade of frequency $\frac{\Delta T_f}{T_f \Delta \log f}$, where $\nu$ is the frequency of the applied $ac$ magnetic field, is $\sim 0.016$ in good agreement with what is observed for GaV$_4$S$_4$S$_4$ and canonical spin-glasses \[24\] \[22\].

The powder $ac$ susceptibility phase diagrams shown in Ref. \[20\] for $y = 0$, 0.1, 7.9, and 8 contain features that can be associated with the skyrmion, cycloidal, and ferromagnetic-like magnetic phases in these materials. The attribution of these features to magnetic phases in the substituted materials are supported by $\mu^+\text{SR}$ measurements \[20\]. A comparison of the phase diagrams determined from $ac$ susceptibility data for the two parent compounds, would appear to suggest that for compositions of GaV$_4$S$_{8-y}$Se$_y$ with $0 \leq y < 0.2$ and $7.8 < y \leq 8$ skyrmion lattices could be stabilized. However, for $0.2 \leq y \leq 7.8$ the lack of these features suggests that skyrmionic lattices with similar dynamics to the parent compounds may no longer exist.

The differences in the magnetic response of the substituted materials compared to the end compounds have two main possible sources. The first, of local origin, is the preferred substitution modifying the exchange pathways and hence the global magnetism. The preferential substitution of Se into the GaX$_4$ tetrahedron affects the inter-cluster exchange whereas S into the V$_4$X$_4$ cluster affects the intra-cluster exchange. The second source is the reduction of the structural distortion that can modify the nature of the exchange including the Dzyaloshinskii-Moriya interactions leading to the different magnetic phases present. There is a smaller change to the distortion (as quantified by the $c/a$ ratio) but a larger change in the magnetism observed at the GaV$_4$Se$_{3y}$ end of the family compared to the GaV$_4$S$_8$ end. This suggests that an alteration of the exchange pathways brought about as a result of the preferred occupancy of S and Se in the V$_4$X$_4$ clusters and GaX$_4$ tetrahedra, has a larger effect on the resulting magnetic properties than any changes caused by the structural distortion.

**IV. CONCLUSIONS**

We have undertaken a detailed investigation of the structural and magnetic properties of the GaV$_4$S$_{8-y}$Se$_y$ family of materials for substitutions in the range $0 \leq y \leq 0.5$ and $7.5 \leq y \leq 8$, to gain a greater understanding of the effects of low levels of substitutions. Powder neutron diffraction measurements show strong evidence for the first order nature of the structural phase transition in this family. The addition of substituents to the parent compounds leads to a gradual shift of the structural phase transition to lower temperatures, combined...
with a reduction in the structural distortion until a critical amount of the substituents completely suppresses the transition. In the compositions which undergo the structural transition, the disorder effects lead to the observation of a striking region of coexistence of the cubic ($F\bar{4}3m$) and rhombohedral ($R3m$) phases, in the vicinity of the structural phase transition.

Bulk magnetic property measurements show a decrease in the dc magnetization with addition of substituents. This process occurs faster at the Se end where the addition of S into the crystal lattice is seen to have a larger effect on the magnetic exchange pathways, due to the preferential sites the S and Se occupy in the lattice. Studies of the ac susceptibility to examine the magnetic phase diagrams for these materials show that the phase diagrams for substitution levels as low as $y = 0.2$ and 7.8 are significantly altered from those observed in the parent skymion hosting materials. This indicates that skymion lattices with similar dynamics to the parent compounds are present only in materials with less than 2.5% substitution levels, i.e. $0 \leq y < 0.2$ and $7.8 < y \leq 8$.

We conclude that the substitution of S and Se even at very low levels (2.5%) brings about a large enough disruption to the crystal structure, and this combined with their preferential site occupancies is sufficient to alter the magnetic phases exhibited by these materials in comparison to the end compounds. The fragility of the structure to any manipulation is strongly linked to the ability of these lacunar spinel structures to host skymion lattices. Our findings on the effect of subtle structural distortions adds to the evidence that already exists from studies on similar lacunar spinels such as GaMoSe$_2$ [5]. Studies such as this are vital to obtain a deeper understanding of the structure-magnetism correlations in the lacunar spinel family as well as in other families of skymion materials.

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