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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

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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.

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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 magnetic skyrmions and in the search for new materials of great interest [2–6]. One way to increase the number of further investigation into the discovery of these systems is covered, to date there are only a limited number of known bulk systems in which Néel skyrmions are stabilized; hence 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 Fd$ar{3}$m 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 [17,23]. 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/Sel 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$^{4+}$ and one V$^{5+}$ 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 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 Fd$ar{3}$m 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, an R3m phase and a metastable Im$ar{3}$m2 phase, exhibiting distinctly different magnetic properties strongly related to their magnetocrystalline 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

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commensurate magnetic state with the moments on the distorted V ion aligning ferromagnetically and the moments on the other three V ions canted in an $R3m$ 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] pseudocubic 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 ($\mu^+\text{SR}$) 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 [26,27].

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 prerequisite 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 or 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 intrinsically 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- and Se-substituted compositions at which the transition from a skyrmion hosting to a non-skyrmion hosting material occurs and to 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 and 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 $F4\bar{3}m$ and rhombohedral $R3m$ structural phases in the region surrounding the temperature of the structural phase transition. This phenomenon 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 $K\alpha_1$ 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 [24,28].

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 while 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 $0 \leq y < 0.5$ and $7.5 \leq y \leq 8$ could all be indexed in $F4\bar{3}m$ cubic symmetry. A representative pattern is shown in Fig. 1 for one of the materials investigated, GaV$_4$S$_{0.4}$Se$_{7.6}$. The patterns show that the materials form predominantly as single phase with low levels of
impurity peaks belonging to VSe$_2$.

Rietveld refinement (red solid line), and difference (olive green solid line). $R_p = 15.4$, $R_{wp} = 21.3$, and $R_{e_xpt} = 11.1$. * indicates small impurity peaks belonging to VSe$_2$.

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 F$\bar{4}$3m phase to a lower-temperature rhombohedral R$m$3m structure, as previously reported [17,19]. The Rietveld refinements performed on the parent and substituted GaV$_4$S$_{8-y}$Se$_y$ compounds with $0 \leq y \leq 0.1$, $0.4 \leq y \leq 0.5$, and $7.5 \leq y \leq 8$ 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. 3. Here, the results of the refinements reveal that there is a coexistence of two phases having F$\bar{4}$3m and R$m$3m symmetry. This is seen as a splitting of the cubic (880) peak depicted in the inset of Fig. 3 for the refinement at 1.5 K where the coexistence of both cubic and rhombohedral peaks is evident. The lower-temperature rhombohedral R$m$3m structure is pseudocubic, which results in the nuclear diffraction peaks being close to those of the high-temperature cubic F$\bar{4}$3m phase. Hence, the structural phase transition is best revealed as a splitting of high-order cubic Bragg peaks. This is illustrated in Fig. 4 for GaV$_4$S$_{8-y}$Se$_y$ and is similar to what is observed in all of the compounds that undergo a structural phase transition ($0 \leq y \leq 0.4$ and $7.5 \leq y \leq 8$). Figure 4 also shows the shift of the angle at which the R$m$3m 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% F$\bar{4}$3m phase to 100% R$m$3m 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 while...
Simultaneously broadening it. This broadening of the transition creates a wide temperature region in which refinements show the presence of both the cubic (880) peak located between the (4 0 16) and (8 4 0) Bragg peaks in the temperature range 1.5–41.4 K.

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

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 R$\bar{3}$m 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$$_4$ tetrahedra and S in the V$_X$$_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$$_4$ tetrahedra. The improved statistics obtained with powder neutron diffraction over that obtained in the laboratory x-ray diffraction data allows the more accurate refinement and determination of the preferential site occupancy, even for low levels of substitutions. For GaV$_4$S$_{8-y}$Se$_y$ with 0 < $y$ ≤ 0.5, all the substituted Se was observed to occupy Ga$_X$$_4$ tetrahedra, and all substituted S in 7.5 ≤ $y$ < 8 was observed to occupy V$_X$$_4$ clusters. When undergoing the structural phase transition from the cubic to rhombohedral phase, the V$_X$$_4$ clusters can distort along any of four possible cubic ⟨111⟩ 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 ZFCW 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 < $y$ < 8) produces a more pronounced decrease in the magnitude of magnetization than the addition of Se to the GaV$_4$S$_8$ (0 < $y$ < 0.5). As the magnetic phases that are stabilized change with substitution, it is difficult to pinpoint exactly where the paramagnetic-to-magnetic transition occurs. The difference in the dc susceptibility, shown in Fig. 7, between the $y = 0$ and 0.1 compositions is apparent as the smaller peak centered at 12.5 K in the $y = 0$ compound has merged with the lower-temperature transition. Compositions with 0.2 ≤ $y$ ≤ 0.4 then follow a trend of decreasing transition temperature and reduction of the bulk magnetization at lowest temperature. Neutron diffraction measurements for $y = 0.4$ indicate that the material contains only ~30% of the rhombohedral phase at 1.5 K. In the Se-rich materials, a dramatic change in the magnetization is observed between $y = 7.9$ and 7.8 indicating the changing nature of the magnetic state. For 7.6 ≤ $y$ ≤ 7.8 the magnetization decreases in magnitude with a broad transition beginning at 12 K with $y = 7.8$ peaking at ~5.7 K due to the freezing of the spins at lower temperatures. One of the likely
reasons for the decrease in magnetic susceptibility is due to the substituent disrupting the magnetic exchange pathways. The observation of the strong preferred substitution sites in these materials suggests that substitution of S in the V4X4 clusters has a greater effect on the exchange pathways than that of Se in the GaX4 tetrahedra. Density functional theory results on substituted GaV4S8−xSex from Ref. [26] support the evidence for the alteration of exchange pathways based on substitution at different sites. These results are complementary to our previous studies [24] and highlight the progression of the ordered magnetism of the parent compounds towards the spin-glass-like state for compounds with 1 ≤ y ≤ 7.

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 the 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 diagrams compared to the pristine materials. In Fig. 8(a) the phase diagram of GaV4S8−xSex can be compared to that observed for GaV4S8, however, there has been a loss of some features. The clear pocket, centered at 12 K and 50 mT, associated with the existence of a skyrmion lattice for GaV4S8 can no longer be seen in y = 0.2 material. Figure 8(b) shows that for GaV4S7.8Se0.2 there is a complete suppression of all of the features that are observed for GaV4S8 with a peak seen at ∼11 K in zero field, indicating the onset of magnetism ordering. This onset can be seen at ∼11.5 K in the dc susceptibility shown in Fig. 7.

To further investigate the glassy-like transition observed for y = 7.8 (shown in Fig. 7) we have examined the frequency dependence of the ac susceptibility around the freezing transition. The measured ac susceptibility for two different frequencies is shown in Fig. 9(a) and a clear decrease in temperature of the peak can be seen as the frequency of the applied ac magnetic field is decreased. This indicates the presence of a glassy-like magnetic state in this material and is consistent with our observations of a similar state in members of this family with higher levels of substitution [24]. In GaV4S7.8Se0.2, the observed peak corresponds to a freezing temperature Tf of ∼5.4 K from the dc susceptibility curve shown in Fig. 7. Figure 9(b) shows the frequency dependence of Tf. The shift of the freezing temperature per decade of frequency

\[
\frac{\Delta T_f}{T_f(\log_{10} \nu)}
\]

where \(\nu\) is the frequency of the applied ac magnetic field, is ∼0.016, in good agreement with what is observed for GaV4S4S4 and canonical spin glasses [24,32].

The powder ac susceptibility phase diagrams shown in Ref. [26] for y = 0, 0.1, 7.9, and 8 contain features that can be associated with the skyrmin, cycloidal, and ferromagnet-iclike magnetic phases in these materials. The attribution of these features to magnetic phases in the substituted materials are supported by \(\mu^+\)SR measurements [26]. A comparison of the phase diagrams determined from ac susceptibility data for the two parent compounds would appear to suggest that for compositions of GaV4S8−xSex, with 0 ≤ y < 0.2 and 7.8 ≤ y ≤ 8 skyrmions lattices could be stabilized. However, for 0.2 ≤ y ≤ 7.8 the lack of these features suggests that skyrmion 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 GaX4 tetrahedra affects the intercluster exchange, whereas S into the V4X4 cluster affects the intracluster 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

FIG. 8. Phase diagrams of the normalized real component \(\chi'\), of the ac susceptibility in an ac field of 0.3 mT with a frequency of 113 Hz as a function of temperature and dc applied magnetic field for GaV4S8−xSex. \(\chi_{\text{max}}\) is consistent for all plots but \(\chi_{\text{max}}'\) is unique to each composition due to the varying orders of magnitude present. (a) y = 0.2 (\(\chi_{\text{max}}' = 1.4 \times 10^{-5}\)) with y = 0 inset (\(\chi_{\text{max}}' = 7.7 \times 10^{-5}\)) and (b) y = 7.8 (\(\chi_{\text{max}}' = 2.57 \times 10^{-4}\)) with y = 8 inset (\(\chi_{\text{max}}' = 4.47 \times 10^{-4}\)). Dashed lines in the insets show the temperature-field region plotted in the main panels.

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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$_8$ 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 $V_4X_4$ clusters and Ga$X_4$ 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 ranges $0 \leqslant y \leqslant 0.5$ and $7.5 \leqslant y \leqslant 8$, 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 ($R\bar{3}m$) 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 the preferential sites the S and Se occupy in the lattice. Studies of the evolution 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 skyrmion hosting materials. This indicates that skyrmion 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 skyrmion 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$_8$ [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 ofskyrmion materials.

Data are available from the ILL [33].

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