Establishing magneto-structural relationships in the solid solutions of the skyrmion hosting family of materials: GaV$_4$S$_8$–ySe$_y$

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ABSTRACT

The GaV$_4$S$_8$–ySe$_y$ ($y = 0$ to 8) family of materials have been synthesized in both polycrystalline and single crystal form, and their structural and magnetic properties thoroughly investigated. Each of these materials crystallizes in the $F43m$ space group at ambient temperature. However, in contrast to the end members GaV$_4$S$_8$ and GaV$_4$Se$_8$, that undergo a structural transition to the $R3m$ space group at 42 and 41 K respectively, the solid solutions ($y = 1$ to 7) retain cubic symmetry down to 1.5 K. In zero applied field the end members of the family order ferromagnetically at 13 K (GaV$_4$S$_8$) and 18 K (GaV$_4$Se$_8$), while the intermediate compounds exhibit a spin-glass-like ground state. We demonstrate that the magnetic structure of GaV$_4$S$_8$ shows localization of spins on the V cations, indicating that a charge ordering mechanism drives the structural phase transition. We conclude that the observation of both structural and ferromagnetic transitions in the end members of the series in zero field is a prerequisite for the stabilization of a skyrmion phase, and discuss how the absence of these transitions in the $y = 1$ to 7 materials can be explained by their structural properties.

Introduction

The $AB_2X_8$ ($A = $ Ga, Al, Ge, Ti, Fe, Co, Ni, Zn; $B = $ V, Cr, Mo, Re, Nb, Ta; $X = $ S, Se, Te) family of materials adopts a lacunar spinel structure and crystallizes in a non-centrosymmetric, $F43m$, cubic structure at ambient temperature. These materials exhibit a range of physical properties such as structural phase transitions, ferromagnetism, antiferromagnetism, superconductivity, electric-field-induced resistive switching, as well as hosting skyrmions. In fact, the discovery of skyrmions, nano-sized topologically protected magnetic particle-like spin textures, in GaV$_4$S$_8$ and GaV$_4$Se$_8$ has led to intense recent research on lacunar spinels.

Skyrmions attract widespread attention partly as promising candidates for energy-efficient high-density data storage and as spintronic devices. Skyrmions are magnetic vortices that have been observed in magnetic materials in two forms: Bloch skyrmions and Néel skyrmions, so-named because a cut across the diameter of the skyrmion reveals either a Bloch or Néel wall of spins. Magnetic skyrmions have been observed chiefly in chiral B20 and $\beta$-Mn ferromagnets, in the form of a lattice of Bloch-type skyrmions. In contrast, lattices of Néel-type skyrmions have been found in GaV$_4$S$_8$ and GaV$_4$Se$_8$. In fact, the Néel-type skyrmion lattice in the bulk has, thus far, only been observed in three materials: GaV$_4$S$_8$, GaV$_4$Se$_8$, and VOSe$_2$O$_5$. There is therefore a justifiable interest in enlarging the family of materials hosting the Néel-type skyrmion, in order to acquire a better understanding of these spin textures. Alteration of the chemical composition, e.g. substitution of a transition metal in Cu$_2$OSeO$_4$, has proven to be an effective way to expand families of skyrmion-hosting materials and obtain valuable insights into the physics of these systems. Given the many similarities in the two end members of the series: GaV$_4$S$_8$ and GaV$_4$Se$_8$ (i.e. similar structural phase transitions as well as exhibiting ferromagnetic-like ground states and hosting skyrmion phases), it is interesting to explore the properties of this family further by investigating the intermediate compositions lying between the GaV$_4$S$_8$ and GaV$_4$Se$_8$ end members.

Both GaV$_4$S$_8$ and GaV$_4$Se$_8$ can be described as cation-deficient $A_{0.5}\Box_{0.5}B_2X_4$ spinels, where the symmetry is reduced from $Fd\bar{3}m$ to $F43m$ due to the ordering of the tetrahedral sites. This results in the shifting of the $B$ atoms from the octahedral voids, forming tetrahedral $B_4$ clusters. These materials can therefore be represented with the formula $[R_4X_4]AX_4$, where
heterocubane-like \([B_{4}X_{4}]^{n+}\) and \([AX_{4}]^{n-}\) constituents resemble the arrangement of ions in NaCl\(^7\)\(^8\). Moreover, both GaV\(_4\)S\(_8\) and GaV\(_4\)Se\(_8\) undergo structural phase transitions from high-temperature cubic (\(F\bar{4}3m\)) to low-temperature rhombohedral (\(R\bar{3}m\)) symmetry at 42 K (GaV\(_4\)S\(_8\)) and 41 K (GaV\(_4\)Se\(_8\)). The structural phase transition is followed by a magnetic phase transition from paramagnetic to ferromagnetic-like at 13 and 18 K in GaV\(_4\)S\(_8\) and GaV\(_4\)Se\(_8\) respectively\(^8\)\(^{14}\).

According to previous studies\(^{8,44}\), GaV\(_4\)S\(_8\) consists of Ga\(^{3+}\) \((V^{3.25+}_{\text{T}})_{4} (S^{2-})_{8}\), where seven electrons in 3d orbitals are involved in V-V metal bonding. These electrons are, consistent with the cubic \(T_{d}\) symmetry, located at the \(a_{1}\) (two electrons), \(e\) (four electrons) and \(t_{2}\) (one electron) energy levels. A Jahn-Teller structural distortion at 42 K drives the material from a cubic to a rhombohedral crystal structure. This distortion causes a reduction of symmetry to \(C_{3v}\), removing the triply-degenerate orbitals at the \(t_{2}\) level, resulting in doubly-degenerate orbitals at the \(e\) level (higher in energy) and an orbital at the \(a_{1}\) level (lower in energy) containing one unpaired electron. In zero magnetic field both GaV\(_4\)S\(_8\) and GaV\(_4\)Se\(_8\) undergo a paramagnetic to cycloidal phase transition at 13 K and 18 K respectively\(^8\)\(^{14}\). Further reduction in temperature for GaV\(_4\)S\(_8\) yields a transition from cycloidal to a ferromagnetic-like state as opposed to GaV\(_4\)Se\(_8\) in which a cycloidal state persists down to the lowest measured temperature. Based on recent muon-spin rotation spectroscopy (\(\mu\)SR) measurements\(^{45}\), differences in the low-temperature magnetic behaviour of GaV\(_4\)S\(_8\) and GaV\(_4\)Se\(_8\) are evident. In contrast to GaV\(_4\)S\(_8\), GaV\(_4\)Se\(_8\) shows an unusual increase of the local magnetic field with increasing temperature indicating that the magnetic ground states of GaV\(_4\)S\(_8\) and GaV\(_4\)Se\(_8\) are significantly different\(^{22,24}\). Application of a 30 mT magnetic field to the cycloidal phase in GaV\(_4\)S\(_8\) and 150 mT in GaV\(_4\)Se\(_8\) has been found to stabilise Néel-type skyrmions. Moreover, the presence or absence of the skyrmion phase strongly depends on the orientation of applied field with respect to the crystallographic direction, with the most extensive skyrmion phase detected with the field oriented along the [111] crystallographic direction\(^{24}\).

We have undertaken a detailed investigation of the series of compounds obtained by systematically substituting Se at the S site, going from GaV\(_4\)S\(_8\) to GaV\(_4\)Se\(_8\), aimed at understanding the links between the structural and magnetic properties. This will help us to explore the possibility of these materials as possible skyrmion hosts. The synthesized family of polycrystalline GaV\(_4\)S\(_8−y\)Se\(_y\) materials were used to grow high-quality single crystals utilizing the chemical vapour transport technique (CVT). Single crystals and polycrystalline materials were characterized with powder and single crystal X-ray and neutron diffraction, and their magnetic properties were investigated using ac/dc magnetometry measurements. Based on our results we were able to establish magneto-structural relationships that suggest how the substitution of S with Se affects the magnetic properties and hence the presence or absence of the skyrmion phase in the GaV\(_4\)S\(_8−y\)Se\(_y\) materials. Specifically, we suggest that charge ordering that likely accompanies a structural distortion in the \(y = 0\) and \(y = 1\) materials best explains their ordered magnetic ground states. This structural distortion is not observed in the intermediate \(y\) materials, explaining why they form a magnetic spin-glass-like state at low temperature.

Results

The phase purity of polycrystalline materials used for the crystal growth was determined by powder X-ray diffraction. The diffraction profiles of the GaV\(_4\)S\(_8−y\)Se\(_y\) samples with \(y\) ranging between 0 and 8 could be indexed in a cubic \(F\bar{4}3m\) symmetry, as shown in Fig. 1a and Supplementary Figs. S2 and S3. The lattice parameter \(a\) increases monotonically with the increasing Se substitution levels, as expected when substituting \(S^{2-}\) (ionic radius of 1.70 Å) with larger \(Se^{2-}\) (1.98 Å) anions (Supplementary Table S1)\(^{36}\). Materials with \(y\) between 0 and 5 are phase pure, while small amounts (up to 3.3%) of VSe\(_2\) impurity were observed in the GaVSSe\(_2\) and GaV\(_4\)Se\(_8\) samples. In contrast to the rest of the materials investigated, the presence of two cubic phases with slightly different lattice parameters was detected in the GaV\(_4\)S\(_2\)Se\(_6\) sample. The refinement of S and Se occupancies revealed higher concentrations of sulphur in GaV\(_4\)S\(_8−y\)Se\(_y\) materials than the nominal concentrations used during the synthesis, except in GaV\(_4\)S\(_4\)Se\(_4\). Furthermore, the Se\(^{2-}\) is found to preferentially occupy the site near the Ga cations (Ga\(_4\)X\(_4\) tetrahedron), while S\(^{2-}\) is found to prefer the site near V cations (V\(_4\)X\(_4\) heterocubane).

The compositions of single crystals with \(y\) between 0 and 8 were determined by refining single crystal X-ray diffraction data, and were further checked using energy dispersive x-ray measurements as shown in Table 1. The obtained lattice parameters can be seen to follow Vegard’s law (Fig. 1b). Single crystal X-ray diffraction shows that GaV\(_4\)S\(_8−y\)Se\(_y\) \((y = 0\) to 8) adopts the same crystal structure down to 50 K, where Ga\(_4\)X\(_4\) and V\(_4\)X\(_4\) units exhibit the NaCl-like arrangement as shown in Fig. 1c. In contrast to the two end compounds, GaV\(_4\)S\(_8\) and GaV\(_4\)Se\(_8\), substitutional disorder is observed in all the intermediate solid solutions examined. To model the substitutional disorder properly, different refinement approaches were used: either allowing the atomic positions of S and Se to refine separately or constraining them. The most reliable structural models were obtained when S2 and Se2 in the Ga\(_4\)X\(_4\) tetrahedra were fixed to occupy the same atomic position, and the atomic positions of S1 and Se1 in the V\(_4\)X\(_4\) unit were allowed to refine separately, but were constrained by the crystal symmetry. The occupancies of sulphur and selenium were allowed to be freely refined, with the total occupancy constrained to 1, and there is clear evidence that S prefers to occupy the atomic position in the V\(_4\)X\(_4\) cluster, while the Se prefers to be situated in the Ga\(_4\)X\(_4\) tetrahedron (Supplementary Table S2 and S3). These findings are slightly at odds with the hard-soft acids-bases\(^{17}\) concept, where Ga\(^{3+}\) is classified as a harder acid than V\(^{3+}\), and S\(^{2-}\) is classified as a stronger base than Se\(^{2-}\), and therefore it would be expected that Se\(^{2-}\) would prefer to bind

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Figure 1. a) Powder X-ray diffraction profile of GaV₄S₄Se₄. The experimentally-obtained diffraction profile at ambient temperature (blue open circles), refinement based on the model obtained from single crystal X-ray diffraction at room temperature (red solid line), difference (olive green solid line) and predicted peak positions (black tick marks). b) Lattice parameters of GaV₄S₈₋ₓSeₓ obtained from EDX, shown as open black circles, and single crystal X-ray diffraction shown as red circles. The grey dashed line represents Vegard’s law between GaV₄S₈ and GaV₄Se₄. The error bars are too small to be seen. c) Structural model of material GaV₄S₄Se₄ (refined composition GaV₄S₄.₃₆Se₃.₆₄) obtained from single crystal X-ray diffraction at 120 K. The V₄S₂.₈₅/Se₁.₁₅ heterocubane (top right) and GaS₁.₅₁Se₂.₄₉ tetrahedra (bottom right), and their NaCl-like arrangement in the crystal structure (left side).

Table 1. Composition of the single crystals obtained from EDX analysis and from the refinement of single crystal X-ray diffraction (SCXRD) data.

| Nominal          | EDX               | SCXRD   |
|------------------|------------------|---------|
| GaV₄S₈           | GaV₄S₇.₉₉₉(₆)    | GaV₄S₈ |
| GaV₄S₂Se        | GaV₄S₇.₅₉₁(₆),Se₀.₄₀₄(₆) | GaV₄S₆.₇₄₈(₁₇),Se₁.₂₅₂(₁₇) |
| GaV₄S₂Se₂       | GaV₄S₆.₆₇₅(₁₅),Se₁.₃₂₅(₁₅) | GaV₄S₅.₆₈₂(₂),Se₂.₃₂(₂) |
| GaV₄S₂Se₃       | GaV₄S₅.₄₃₅(₅),Se₂.₅₇₅(₅) | GaV₄S₄.₂₀₃(₃),Se₃.₈₈₃(₃) |
| GaV₄S₂Se₄       | GaV₄S₄.₃₀₆(₈),Se₃.₆₉₄(₈) | GaV₄S₃.₁₂₄(₄),Se₄.₈₈₄(₄) |
| GaV₄S₂Se₅       | GaV₄S₳.₁₁₈(₁₄),Se₴.₈₈₂(₁₄) | GaV₄S₂.₂₀₅(₅),Se₵.₈₈₅(₅) |
| GaV₄S₂Se₆       | GaV₄S₂.₁₃₅(₁₅)     | GaV₄S₁.₀₉₅(₅),Se₶.₉₁₅(₅) |
| GaV₄S₂Se₇       | GaV₄S₀.₉₈₂(₂),Se₷.₀₁₂(₂) | GaV₄S₀.₉₉₅(₃) |
| GaV₄Se₆         | GaV₄Se₀.₉₉₅(₃)     | GaV₄Se₈ |
|                  |                   |         |
Figure 2. a) Structural model of material GaV₄S₈ obtained from the data collected on single crystal X-ray diffraction at 30 K. b) The distorted and c) not distorted V₄S₄ heterocubane like entity based on the data collected at 30 and 120 K respectively. d) Correlation between V-V (red triangles), V-S₁/Se₁ (green triangles) bond distances and Se₂ (red circles), Se₁ (green circles) site occupancies and the lattice parameters a (blue circles) obtained from single crystal X-ray diffraction on a laboratory diffractometer. The grey dotted line represents the idealized Vegard’s law.

As mentioned above, a linear increase of the lattice parameter a was observed and the obtained values are seen to follow Vegard’s law, depicted as the grey dotted line in Fig. 2d. The inter-constituent (GaX₄ and V₄X₄) distances and the Ga-S₂/Se₂ distances increase linearly, following the same trend as the lattice parameters. However, the intra V₄X₄ bond distances, angles and tetrahedron (V₄, S₁ and Se₁) volumes in the intermediate compounds (y between 1 and 7) do not show this trend (Supplementary Table S3). A close examination of the structural models reveals that V-V distances within the cluster increase much more slowly than expected as a function of y, while V-S₂/Se₂ distances increase slightly faster. Moreover, a higher deviation from the linearity in V-V distance can be observed in the material y = 4. This can be partially explained by the S₁ and Se₁ site occupancies. However, the trend of the Se₁ site occupancy does not exactly follow the trend of the V-V bond distances, as shown in Fig. 2d. In contrast, the changes of the V-S₂/Se₂ bond distances are in very good agreement with changes of Se₂ site occupancy. These findings indicate that the tendency of S²⁻ and Se²⁻ to occupy the atomic positions in the V₄X₄ cluster and in the GaX₄ tetrahedron respectively is the driving force for the structural motifs observed in the GaV₄S₈−ySe₉ series. Additionally, the volumes of the GaX₄ and V₄ tetrahedra increase with increasing Se substitution levels (as expected, the volume of V₄ tetrahedra follow the same trend as V-V bond distances), however, the volume of (S₁)₄ and (Se₁)₄ tetrahedra stays nearly constant throughout the series (Fig. S4).

The end compounds, GaV₄S₈ and GaV₄Se₈, undergo a structural phase transition at 42 K and 41 K respectively. At this transition, one of the vanadium and one of the sulphur/selenium atoms move along the [111] crystallographic direction, as shown in Fig. 2a, reducing the F43m to R3m symmetry, where the cubic diagonal becomes the c crystallographic lattice. Lattice parameters of a = b = 6.8098(3) Å and c = 16.7100(17) Å were obtained for GaV₄S₈ at 30 K, below the structural transition, and are in good agreement with the reported values. Three of the V₁-V₂ bond distances (2.8927(13) Å) and the rhombohedral angle of 59.62(3)° deviates from 60° observed in cubic symmetry; see Fig. 2. Also, three V₁-S₂ (2.9290(12) Å) and three V₂-S₁ (2.9293(16) Å) bond distances are longer than the remaining six V₂-S₂ (2.8882(13) Å) bond distances as shown in Fig. 2. Additionally, the GaS₄ tetrahedron distorts along the crystallographic c direction with one Ga-S₄ (2.271(2) Å) bond distance elongated compared to the remaining three
Figure 3. a) Powder neutron diffraction profiles of GaV$_4$S$_8$ measured on the D2B diffractometer at the ILL, showing the splitting of the cubic (448) peak below the structural phase transition of 42 K indicating a structural phase transition from a $F\bar{4}3m$ to $R3m$ structure. The black solids circles correspond to data taken at 1.5 K, red at 9 K, olive at 15 K, blue at 30 K, orange at 41 K and magenta at 50 K. b) Magnetic difference pattern of GaV$_4$S$_8$ at 1.5−15 K. The experimentally-obtained diffraction profile on a powder sample, using the D20 diffractometer at the ILL (blue open circles), refinement based on the commensurate $R3m'$ model (red solid line), difference (olive green solid line) and predicted peak positions (black tick marks). c) Magnetic model obtained from refinement of the magnetic difference pattern in the $R3m'$ Shubnikov group, where the magnetic moments on V1 atoms are shown as blue arrows and those on V2 atoms are shown as green arrows.

Ga-S3 (2.2664(10) Å) bond distances (Fig. 2). The observed structural distortion is in very good agreement with that reported previously. However, the changes in bond distances obtained in single crystals are less pronounced than those seen in polycrystalline samples.

Neutron Diffraction
To complement the X-ray diffraction data, powder neutron diffraction was performed on the end compound (GaV$_4$S$_8$) and one intermediate solid solution (GaV$_4$S$_6$Se$_2$) with representative properties of the solid solutions, to obtain the nuclear structures at a range of temperatures. Powder neutron diffraction data obtained on GaV$_4$S$_8$ measured at 50 K, above the structural transition, refine in the high temperature $F\bar{4}3m$ space group (Supplementary Table S4). Due to the small coherent scattering cross section of V, the positions of the V atoms were constrained to those obtained in single crystal X-ray diffraction. The evidence of a structural phase transition from cubic to a pseudo-cubic rhombohedral structure can be clearly seen through the splitting of some of the cubic Bragg peaks such as the cubic (448) peak as shown in Fig. 3a. Below the structural phase transition at 41 K, the crystal structure remains the same until 1.5 K and refines in the $R3m$ space group, as shown in Supplementary Table S4. These results are in good agreement with those reported in the literature. Powder neutron diffraction data for GaV$_4$S$_6$Se$_2$ show the absence of a structural phase transition, with data refining in a $F\bar{4}3m$ space group down to 1.5 K, as shown in Supplementary Fig. S5. The site location and occupancy of S$^{2−}$ and Se$^{2−}$ within the V$_4$X$_4$ units are in good agreement with X-ray diffraction results. Similar to the X-ray diffraction data, S1 and Se1 are found to occupy different sites within the V$_4$X$_4$ cluster with a higher fraction of S$^{2−}$ located within the V$_4$X$_4$ cluster and Se$^{2−}$ preferentially occupying sites in the GaX$_4$ tetrahedron.

Similar to powder neutron diffraction, one single crystal of the end composition (GaV$_4$S$_8$) and one single crystal of a member of the intermediate materials (GaV$_4$S$_6$Se$_2$) with indicative properties of the set of intermediate solid solutions were chosen for investigation. The data obtained for GaV$_4$Se$_8$ refines in a $F\bar{4}3m$ space group at 55 K whereas the data between 30 to 1.5 K refine in a $R3m$ space group, in very good agreement with both our X-ray data and the literature (see Supplementary Table. S6). As in the analysis of the powder neutron diffraction, the positions of the vanadium atoms were constrained to those obtained from single crystal X-ray diffraction. The low temperature measurements show that GaV$_4$S$_6$Se$_2$ does not undergo a structural phase transition, and remains cubic down to 1.5 K, similar to all the other intermediate compositions examined. The
Magnetic Neutron Scattering

Magnetic structures for the end compound GaV$_4$S$_8$ and two representative members of the intermediate solid solutions (GaV$_4$S$_8$Se$_2$ and GaV$_4$S$_4$Se$_4$) were probed using both powder and single crystal diffraction. The magnetic scattering was isolated by taking the difference pattern between 1.5 and 15 K, above and below the magnetic transition. For GaV$_4$S$_8$, the magnetic peaks are located at the same positions as the nuclear Bragg peak positions and have a symmetrical peak shape indicating a $k = 0$ propagation vector as seen in Fig. 3c. Magnetic symmetry analysis with help of the program BASIREPS was used to determine the allowed irreducible representations (IR) and their basis vectors (BV) for the two vanadium sites. Testing the different allowed IRs showed that the magnetic difference pattern for GaV$_4$S$_8$ refines best in a R3m' magnetic structure, shown in Fig. 3b. The V1 atoms refine to have a magnetic moment of 0.30(6) $\mu_B$, pointing along the hexagonal $c$ axis whereas the V2 magnetic moments have a smaller moment of 0.18(7) $\mu_B$ and are canted outward from the cluster. The localization of a higher moment on the distorted V1 site is consistent with density functional theory (DFT) calculations showing a higher spin density residing on the distorted V1 atom as opposed to the V2 atom.

It is worth noting that, due to the nature of powder neutron diffraction, it cannot be established if the orientations of the moments are in the configuration shown in Fig. 3b or pointing in the opposite direction with the same magnitude, i.e. moments on the V2 atoms pointing in towards the cluster with the moment on the V1 atom pointing in the negative crystallographic c axis. Attempts were made to refine the structure with only one magnetic moment per V$_4$ cluster to be localized either on the V1 site or in the centre of the cluster. However, a single magnetic moment per V$_4$ cluster does not produce the correct ratios of peak intensities, supporting the fact that both V1 and V2 carry a magnetic moment.

Powder neutron diffraction patterns of GaV$_4$S$_8$Se$_2$ show no difference between the diffractograms measured at 1.5 and 15 K, as shown in Supplementary Fig. S5, confirming the absence of any magnetic intensity. Additionally, single crystal neutron diffraction of GaV$_4$S$_4$Se$_4$ revealed no magnetic scattering intensity at 1.5 K. There is a strong indication that no long-range magnetic ordering is present in solid solutions based on our results obtained on the two representative materials.

Magnetic Measurements

Bulk magnetization measurements on single crystals were carried out to identify the nature of magnetic ordering occurring within the GaV$_4$S$_{8-x}$Se$_x$ family of materials. Obvious differences in the magnetic susceptibilities across the GaV$_4$S$_{8-x}$Se$_x$ family are observed, as shown in Fig. 4a. The end compounds, GaV$_4$S$_8$ and GaV$_4$Se$_8$, undergo long-range ferromagnetic-like ordering at 13 and 18 K, respectively, with GaV$_4$S$_8$ having a susceptibility over twice as large as its selenium counterpart GaV$_4$Se$_8$. The structural phase transitions can be observed as large discontinuities in the inverse magnetic susceptibilities, as shown in Supplementary Fig. S6, as was previously reported in the powder materials. This highlights the magnetostructural link between the cubic and rhombohedral phase, with the discontinuities likely related to the lifting of the degeneracy of V orbitals from the structural phase transition leading to a change in the location of spin density and hence magnetic interactions. The effective moment calculated from the susceptibility by using the Curie law $\mu_{\text{eff}} = 797.8/\chi$ is given in Fig. 4c. A discontinuity in the effective moment $\mu_{\text{eff}}$ can be seen at the temperature of the structural phase transition in GaV$_4$S$_8$ (42 K) and GaV$_4$Se$_8$ (41 K), and a large increase in $\mu_{\text{eff}}$ is seen with decreasing temperature. The peak in effective moment is in good agreement with the onset of long-range magnetic order. Above the structural phase transition in GaV$_4$S$_8$ and GaV$_4$Se$_8$, $\mu_{\text{eff}}$ continuously increases in the temperature region between ~50 and 300 K, as previously reported. This means that the Weiss temperature cannot be accurately extracted from $\chi$ vs $T$ measurements, although it can be seen that the interactions change from antiferromagnetic to ferromagnetic at the structural phase transition. Based on the $M$ vs $\mu H$ measurements shown in Fig. 4d, the saturation magnetization at applied fields of 5 T and 1.8 K was found to be 0.87(2) $\mu_B$/f.u. and 0.85(2) $\mu_B$/f.u. for GaV$_4$S$_8$ and GaV$_4$Se$_8$, respectively. These values are in good agreement with those reported previously. Additionally, the value of 0.87(2) $\mu_B$/f.u. for GaV$_4$S$_8$ is also in good agreement with the value of 0.84(7) $\mu_B$/f.u., the total magnetic moment per V$_4$ cluster, obtained from our neutron diffraction refinements.

A large suppression in both the magnetic transition temperature and the magnitude of the magnetization is evident in all of the intermediate compounds measured, as seen in Fig. 4a, suggesting that the absence of a structural phase transition has a dramatic effect on the magnetism. Examination of the magnetization at low temperatures shows a bifurcation of the zero-field-cooled-warming (ZFCW) and field-cooled-warming (FCW) susceptibility curves, shown in Fig. 4b, indicative of either a canted antiferromagnetic ordering or a glassy transition. It is notable that similar behaviour has been seen in related compounds. Our recent $\mu^+$SR measurements show no evidence for long-range magnetic ordering in the intermediate compounds and instead indicate the presence of a glass-like state. In Fig. 4c, it can be seen that even though GaV$_4$S$_8$Se$_4$ does not undergo a structural phase transition, the effective moment starts to decrease rapidly at a similar temperature to where
Figure 4. a) Magnetic susceptibility vs temperature for the GaV\(_4\)S\(_8\)–ySe\(_y\) family measured in the applied magnetic field of 10 mT. b) Bifurcation of zero-field cooled warming, shown as open black circles, and field cooled warming, shown as closed red circles for GaV\(_4\)S\(_4\)Se\(_4\). c) Evolution of the effective moment \(\mu_{\text{eff}}\) with temperature for GaV\(_4\)S\(_8\), GaV\(_4\)S\(_4\)Se\(_4\), and GaV\(_4\)Se\(_8\) single crystals calculated from magnetization measurements. d) Magnetic isotherms to investigate the saturation magnetization at 1.8 K of the GaV\(_4\)S\(_8\)–ySe\(_y\) in an applied magnetic field \(\mu_0H\).

Figure 5. a) Real \(\chi'\) and imaginary \(\chi''\) component of the ac susceptibility on GaV\(_4\)S\(_4\)Se\(_4\) single crystals spanning the freezing transition \(T_f\) for a range of frequencies. b) Temperature dependence of the specific heat in zero field for GaV\(_4\)S\(_4\)Se\(_4\) plotted on a semi-logarithmic scale for clarity. The phonon contribution is shown as a solid red line. The inset shows the magnetic entropy recovered after subtracting the phononic contribution from the specific heat. The 1\(\sigma\) error band is shown in blue. The grey dashed lines in the inset show the values for \(R\ln2\) and \(R\ln3\) corresponding to the theoretical entropy of a spin 1/2 and spin 1 system respectively.
the structural phase transitions occur in GaV₄S₈ and GaV₄Se₄, suggesting the onset of magnetic correlations. The effective moment behaves qualitatively very differently with temperature in the intermediate compounds, consistent with a lack of ordered magnetic response and the likely formation of a low-temperature glassy state.

In order to investigate the magnetic behaviour of one of the intermediate compositions in depth, ac susceptibility measurements on GaV₄S₄Se₄ single crystals were performed. Fig. 5a shows behaviour again indicative of a spin glass, with the peak of the in-phase and out-of-phase components of susceptibility shifting in temperature and amplitude, depending on the applied ac frequency. The peaks observed in the ac susceptibility data are caused by a freezing of the spins in the material, and hence correspond to a freezing temperature $T_f$. The freezing temperature for GaV₄S₄Se₄ can be seen to be $\sim 2.4$ K. The frequency dependence of the peaks in $\chi'_ac$ can be characterized by a shift of the freezing temperature per decade of frequency given by

$$
\delta T_f = \frac{\Delta T_f}{T_f \Delta (\log_{10} \nu)},
$$

where $\nu$ is the frequency of the applied ac magnetic field. For GaV₄S₄Se₄, $\delta T_f$ is found to be $\sim 0.015$. This shift is in good agreement with those observed for canonical spin-glasses.

**Heat Capacity**

Heat capacity measurements on polycrystalline GaV₄S₄Se₄ were performed to confirm the absence of a structural phase transition and investigate the onset of magnetic order in the intermediate compositions. Unlike the GaV₄S₈ and GaV₄Se₈, no sharp lambda anomaly, indicative of the structural phase transition, can be seen for GaV₄S₄Se₄, as shown in Fig. 5b. Moreover, at low temperatures a broad peak can be seen centered at $\sim 3.1$ K. The position of this peak is located at $\sim 20\%$ above $T_f$, inline with known spin glass materials, and indicates the slowing down and freezing of magnetic moments above $T_f$.

The phonon contributions were estimated using one Debye and three Einstein modes. Fitting was performed in the temperature region between 45 to 300 K with a Debye temperature of 201(4) K, and three Einstein frequencies corresponding to temperatures of 263(8), 465(8), and 508(13) K. By subtracting the phonon contribution, the associated magnetic entropy can be calculated as shown in the inset of Fig. 5b. The magnetic entropy can be seen to be recovered up to approximately 42 K where the entropy is in good agreement with the value of $R \ln 2$, the entropy corresponding to a spin 1/2 system. These heat capacity results are consistent with those of magnetometry, indicating that there are short-range magnetic correlations occurring at temperatures far above the spin glass transition. The phonon subtracted heat capacity below $T_f$ shows $T^{3\%}$ like dependence deviating from the linear expected behaviour of a canonical spin glass.

**Discussion**

Our structural analysis of single crystals confirms that the end compounds, GaV₄S₈ and GaV₄Se₈, undergo a structural phase transition from cubic ($F43m$) to rhombohedral ($R3m$) symmetry at 42 and 41 K respectively, as previously reported. The vanadium and $X$ atoms in the $V_4X_4 (X = S$ or Se) heterocubane-like entity face along all four [111] crystallographic directions in the cubic structure. At the structural phase transition one of the vanadium and the $X$ pairs of atoms distorts, elongating along the cubic diagonal, reducing the symmetry from cubic to rhombohedral, as shown in Fig. 2. This distortion has an equal probability to occur along any of the four [111] crystallographic directions. (In addition, our powder neutron diffraction measurements indicate the presence of noticeable negative thermal expansion in GaV₄S₈ in the rhombohedral phase (Table S4). In the temperature region between 30 and 9 K, the lattice parameter $c$ increases by 0.04%, while the lattice parameter $a$ contracts by 0.01%, resulting in a negative thermal expansion. The origin of this subtle negative thermal expansion is a subject of further investigation.)

The structural phase transition is followed by long-range ferromagnetic-like ordering at 13 K and 18 K for GaV₄S₈ and GaV₄Se₈ respectively. Our powder neutron diffraction measurements allowed the determination of the magnetic structure of GaV₄S₈ revealing that, on the neutron time scale, spins are localized on the individual vanadium cations. A magnetic moment of 0.30(6) $\mu_B$ on V1 points along the $c$ axis, while a V2 cation moment of magnitude 0.18(7) $\mu_B$ is canted outward from the $V_4$ cluster (Fig. 3b), yielding a magnetic moment of 0.84(7) $\mu_B$ in the spin-polarized state. This value is in very good agreement with the magnetic moment of 0.87 $\mu_B$ obtained from our magnetization measurements ($M$ vs $\mu_B H$ at 1.8 K) and with previously-reported values. The spin arrangement on V cations in the $V_4S_4$ cluster observed in our magnetic model is similar to the arrangement of spin density on V cations in GaV₄S₈ obtained from DFT calculations.

To date, the electronic state and the origin of long-range ferromagnetic-like ordering in GaV₄S₈ and GaV₄Se₈ have been explained via a recombination of $d$ orbitals on the V cations, leading to the formation of a molecular system with $S = 1/2$ per $V_4$ cluster. In this picture the structural phase transition is driven by the Jahn-Teller effect, distorting one of the V and S atoms from an ideal cubic symmetry. This model has been used to successfully explain a range of physical properties in this series,
We note that the experimentally-obtained magnetic moment \( \mu \) is considerably lower than the 1 \( \mu_B \) anticipated for a \( S = 1/2 \) system. Additionally, the ionic radius of the V\(^{3+}\) cation is 0.64 Å, and so the bond distances between V cations within the cluster (∼ 2.9 Å) are exceptionally long to permit a significant overlap of \( d \) orbitals, required for this model. Similarly, direct exchange interactions over the inter-cluster distance of ∼ 3.9 Å are unlikely.

Here we present an alternative interpretation. It is notable that both intra- and inter-cluster V cations are bonded to bridging S anions with an angle of ∼ 102°. This configuration permits ferromagnetic superexchange interactions between spins located on the V cations via \( S^2^- \) or \( Se^2^- \). We propose, therefore, that the low-temperature electronic state (and consequently the origin of long-range ferromagnetic ordering in Ga\(_4\)V\(_8\)S\(_8\)) follows from the structural phase transition at 42 K, where there is a freezing out of a delocalized electron onto one of the vanadium atoms, forming three V\(^{3+}\) and one V\(^{4+}\) cations (i.e. a charge-ordered state). Evidence for the presence of V\(^{3+}\) and V\(^{4+}\) in the ratio of 0.75:0.25 in both cubic and rhombohedral structures comes from bond-valence analysis performed using the SoftB software. Charge ordering is also consistent with a sharp increase of the resistivity at the structural phase transition observed previously.

Compared to the end compounds (Ga\(_4\)V\(_8\)S\(_8\) and Ga\(_4\)V\(_8\)Se\(_8\)), the solid solutions (with \( y \) between 1 and 7) show quite distinct behaviour. Substitutional disorder is found to be present in all intermediate compounds (shown in Fig. 1 c), where Se prefers to occupy the positions in the Ga\(_4\) tetrahedron, while S prefers to occupy the positions in the V\(_4\) heterocubane-like cluster. The solid solutions do not undergo a structural phase transition and do not exhibit long-range ferromagnetic ordering. However an irreversible bifurcation between ZFCW and FCW traces in the \( \chi \) vs \( T \) measurements is observed in these materials, that probably reflects the presence of a spin glass-like state. From the point of view of our interpretation, this implies that substitution of cations on either the B or A site has a profound effect on the ability of the material to undergo a structural phase transition. However, there is still an appreciable electronic response in this temperature region, demonstrated by the drastic decrease of \( \mu_{\text{eff}} \), observed in the \( \mu_{\text{eff}} \) vs \( T \) curves depicted in Fig. 4c.

The mechanism preventing a structural phase transition in intermediate compositions (\( y = 1 \) to 7) requires further investigation. However, in general terms we can comment that the orbital degeneracy of V\(^{3+}\)-based compounds would often be expected to be lifted by a Jahn-Teller (JT) distortion which, if it happens at each site via a coherent lattice distortion, implies orbital ordering. Generally, three energy scales decide whether this occurs. These are the on-site Coulomb repulsion \( U \), the electronic bandwidth \( W \) and intra-atomic Hund rule coupling \( J_h \). In an insulator, \( U \gg W \) and we expect a JT distortion; in a metal (where \( W \gg U \)), the JT distortion is suppressed. Where \( U \) and \( W \) are similar, it is also possible that the Hund’s rule coupling overcomes on-site repulsion and leads to a charge ordering, involving double electron occupancy on some sites (V\(^{3+}\)) and single occupancy on others (V\(^{4+}\)). This charge ordering occurs via a mechanism involving a delocalization effect, where some of the electronic energy levels become band-like and consequently reduce the energy penalty for the double electron occupancy required for charge ordering. In the compounds Ga\(_4\)V\(_8\)S\(_8\) and Ga\(_4\)V\(_8\)Se\(_8\), we might expect that their insulating nature puts them in the JT regime. However, the possible delocalization of charges over V\(_4\) clusters that occurs in these systems, could push the systems into the regime where \( U \) and \( W \) are similar and explain how the charge ordering mechanism leads to the distortion in these materials.

At a JT transition the distortion of the structure costs elastic energy as \( \alpha q^2 \) (where \( q \) is a displacement coordinate and \( \alpha \) a constant) while the resulting splitting of the electronic states (through local crystal field levels and Hund’s rule coupling) saves energy as \( -\beta q \) (where \( \beta \) is a constant). An equilibrium distortion (with \( q_0 = \beta / 2\alpha \)) leads to a net saving in energy and a JT distortion results. To avoid a JT distortion in the intermediate materials, we could imagine either (i) the distortion costs too much energy or (ii) the electronic energy saving is not large enough, or both. In the charge-ordering scenario, (i) still applies in cases where there is a distortion, but here the electronic energy saving occurs because delocalization leads to a reduction in the Coulomb energy cost of having two electrons on a site. In this case, any reduction in the ability of electrons to diffuse between sites can reduce delocalization and hence also suppress the transition.

Since the end members of the series have similar electronic behaviour, it seems unlikely that S/Se disorder radically alters the electronic structure, such that these materials lie in a different energetic regime. Indeed, the behavior of \( \mu_{\text{eff}} \) suggests that all of the compounds are susceptible to a change in the electronic structure around 40 K. (However, we note that the \( \mu^+ \) SR results suggested that the ground states of the two end systems are quite different to each other, so a change in the electronic states with substitution cannot be ruled out.) To explain the lack of structural transition in the intermediate materials, it is more probable that either the S/Se disorder creates a large elastic energy cost for a structural distortion or, if the distortion is driven by charge ordering, that electron delocalization is suppressed by the S/Se disorder. In the first hypothesis, the uneven local distribution of S and Se in the V\(_4\)X\(_4\) units, where neighbouring units contain slightly different concentrations of S and Se, could prevent a structural distortion and therefore retain the material in the cubic symmetry. The second hypothesis involves the disorder shutting down electron diffusion pathways via S and Se anions, reducing electron delocalization and consequently preventing the mechanism for charge ordering of V cations, which seems to be the driving force for the structural phase transition. Finally
we note that while our proposed charge-ordering scenario provides a plausible explanation for the magnetic properties discussed in this paper, whether it also provides a straightforward and complete description of other (non-magnetic) behaviour of this system remains an open question, deserving of future investigation.

All of the results of our investigation on this series, when taken together, provide a direct link between the structural phase transitions and the observation of magnetic transitions in the materials. This is the case in the two end members, GaV₄S₈ and GaV₄Se₈, which exhibit both these features whilst the intermediate compositions investigated exhibit neither of these transitions. The two parent compounds still remain the only members which host a skyrmion phase, making them unique, and the observation of both of the transitions appear to be prerequisites for the stabilization of the skyrmion phases.

Polycrystalline and single crystal samples of the entire series of compounds GaV₄S₈−ₓSe₈ (y = 0 to 8) have been synthesized and single crystals of the materials obtained by the CVT technique. Both the polycrystalline and single crystal samples have been thoroughly investigated for the structural properties through the use of powder and single crystal x-ray as well as neutron diffraction. Additionally, the magnetic properties of the whole series of materials have been studied using dc and ac magnetic susceptibility, magnetization and heat capacity measurements. Our results show that while both GaV₄S₈ and GaV₄Se₈ both undergo structural phase transitions, followed by magnetic ordering at 13 and 18 K respectively, all the intermediate compositions retain their cubic symmetry down to the lowest temperature investigated (1.5 K). These intermediate compositions do not exhibit long-range magnetic order but are, however, found to exhibit a spin glass-like behaviour with freezing temperatures of about 2.5 K, as ascertained from ac susceptibility and heat capacity measurements. Examining the magnetic structure of GaV₄S₈ in detail, there is a clear indication of the localization of spins on the V atoms within the V₄X₄ cluster which appears to favour a charge ordering mechanism. The results presented form a thorough investigation of both the structural and magnetic properties of this entire family of interesting materials. In the search for additional members of this family beyond the two end compositions to host skyrmions, this study throws light on the crucial links that exist between the structure and magnetism in these materials. Given the subtle nature of the local structural distortions in the intermediate compositions as a function of temperature, one strategy that emerges from our study is the possibility that investigating materials with much smaller substitutional levels close to the two end members (y between 0.1 and 0.5, and 7.5 and 7.9) maybe promising. The study of these materials forms part of our ongoing investigations to provide additional insight into structure-property correlations in this interesting family.

**Methods**

**Synthesis and crystal growth**

Polycrystalline GaV₄S₈−ₓSe₈, materials with y between 0 and 8 were synthesized by thoroughly grinding stoichiometric amounts of V (99.5%, metals basis, Sigma-Aldrich), S (99.999%, Acros Organics), and Se (99.999%, Alfa Aesar) powders inside an argon-filled glove box. The mixtures of powders were transferred into silica tubes along with stoichiometric amounts of Ga (99.999%, metals basis, Alfa Aesar) granules and 50 mg of I₂ (99.99%, Alfa Aesar; added to prevent the formation of V₂S₈). The tubes were then evacuated and sealed. The mixtures were heated at a rate of 10 °C/h to 600 °C and at a rate of 5 °C/h to 820 °C, kept at this temperature for 200 h, followed by water quench cooling. This yielded black polycrystalline air-stable powders with metallic lustre.

Single crystals of GaV₄S₈−ₓSe₈ were grown using the chemical vapour phase transport (CVT) technique. Polycrystalline materials (1.5 g), described above, and 3.3 mg/cc of the transporting agent I₂ or PtCl₂, were sealed in evacuated silica tubes. The growth of single crystals was achieved by heating the source part of the tube to 900 °C and the sink part to 850 °C for four weeks. Black octahedral single crystals with well-defined facets of various sizes ranging from several microns up to 2 × 2 × 2 mm³ (Supplementary Fig. S1) were obtained.

**Energy Dispersive X-ray Measurements**

Energy dispersive X-ray (EDX) analysis was performed on single crystals attached to conductive carbon tabs with a facet parallel to the sample stub, using a scanning electron microscope (Zeiss Gemini500) equipped with an XMAX150 Detector (Oxford Instruments Analytical system). The 25 keV energy beam and K lines were used to determine the atomic percentage of Ga, V, S, and Se atoms in the crystals.

**Powder and Single Crystal X-ray Diffraction**

The phase purity determination and structural investigations of the polycrystalline materials were carried out using a Panalytical X-Pert Pro diffractometer operating in Bragg-Brentano geometry, equipped with monochromatic Cu Kα₁ (λ = 1.5406 Å) source and solid-state PIXcel one-dimensional detector in the 2Θ range between 10 and 90° (2 h scan) at ambient temperature. Rietveld refinements were carried out using the TOPAS academic v6.0 software.

Single crystal X-ray diffraction data were collected on ∼ 50 – 100 µm sized crystals at 120 and 30 K using a Rigaku Oxford diffraction SuperNova diffractometer, equipped with dual wavelength (Cu/Mo) microfocus X-ray source (Mo Kα₁.
\( \lambda = 0.71073 \ \text{Å} \), Atlas S2 CCD area detector and Oxford Cryosystems N-Helix cryo cooling system. The structures were solved by the direct method and refined by full-matrix least squares on \( F^2 \) for all data using SHELXTL\textsuperscript{60} and SHELXL\textsuperscript{61} embedded in the Olex2\textsuperscript{62} software.

**Powder and Single Crystal Neutron Diffraction**

Two complementary sets of powder neutron diffraction experiments were performed at the Institute Laue Langevin (ILL) on the D2B and D20 diffractometers, to determine the nuclear and magnetic structures of two of the materials in the series, namely GaV\(_4\)S\(_8\) and GaV\(_4\)S\(_8\)Se\(_2\). The D2B diffractometer was used to obtain high-resolution diffractograms for nuclear structure characterization using a neutron wavelength of 1.594 Å over the temperature range 1.5 – 50 K. High-intensity powder neutron diffraction was performed on the D20 diffractometer using a wavelength of 2.417 Å to determine the magnetic scattering over the temperature range 1.5 – 50 K. The GaV\(_3\)S\(_8\) and GaV\(_4\)S\(_8\)Se\(_2\) powder samples ranging from 3-4 g were sealed in thin-walled cylindrical vanadium containers of 8 mm diameter and placed in a standard orange cryostat. Structural and magnetic Rietveld refinements were carried out using the TOPAS academic v6.0 and FullProf software\textsuperscript{63}.

Single crystal neutron diffraction experiments were performed using the SXD diffractometer at the ISIS Neutron and Muon spallation source\textsuperscript{64}. Data was collected on \( \sim 2 \times 2 \times 2 \ \text{mm}^3 \) crystals of GaV\(_4\)S\(_8\)Se\(_4\) and GaV\(_4\)Se\(_8\). The samples were mounted in an aluminum loop on top of an Al pin and were placed in a vanadium cryostat which was evacuated to \( \sim 10^{-5} \ \text{mbar} \). Data were processed using the SXD2001 software and intensities extracted using a least squares procedure\textsuperscript{64} with 3D Gauss-ellipsoids, line fittings, and box fittings with time-of-flight asymmetry as the profile function. The nuclear structures were refined using the JANA software\textsuperscript{65}.

**Magnetic Measurements**

Quantum Design Magnetic Property Measurement System, MPMS-5S and MPMS-7XL, superconducting quantum interference device (SQuID) magnetometers were used for the investigation of the magnetic properties of the polycrystalline samples and single crystals as a function of temperature and field. dc temperature-dependent magnetic susceptibility (\( \chi \)) measurements were carried out in an applied field of 10 mT and 2 T in the temperature region between 1.8 and 300 K under both zero-field-cooled-warming (ZFCW) and field-cooled-warming (FCW) protocols. The magnetic moments were obtained from \( M \) vs \( B \) measurements in applied fields between 0 and 5 T at 1.8 K. ac frequency-dependent susceptibility (\( \chi'' \)) measurements were performed on non-oriented single crystals at zero applied magnetic field between 1.8 and 3.5 K.

Heat capacity measurements were performed in a Quantum Design Physical Property Measurement System from 1.8 \( \leq T \leq 300 \ \text{K} \). A He\textsuperscript{3} insert was used to obtain temperatures down to 0.5 K.

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Table S1. Refined parameters of GaV$_4$S$_{8-y}$Se$_y$ (y = 0 to 8) in the $F\overline{4}3m$ space group at room temperature from powder X-ray diffraction data taken on a laboratory diffractometer.

| y  | 0   | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   |
|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| a Å | 9.66294(7) | 9.71632(6) | 9.78401(4) | 9.8542(9) | 9.92004(6) | 9.98498(5) | 9.9800(2) | 10.03670(16) | 10.0920(7) | 10.1410(23) |
| V ($\text{Å}^3$) | 902.25(2) | 917.288(16) | 936.593(12) | 957.25(2) | 976.203(17) | 995.500(16) | 994.02(7) | 1011.05(5) | 1027.87(2) | 1042.905(8) |
| sof S1 | 1 | 0.910(10) | 0.719(11) | 0.574(8) | 0.413(9) | 0.176(10) | 0.06(4) | 0.096(18) | 0.05 | N/A |
| sof S2 | 1 | 0.938(11) | 0.882(10) | 0.798(9) | 0.692(8) | 0.497(10) | 0.355(5) | 0.42(2) | 0.544(4) | 0.940(18) | N/A |
| sof Se1 | N/A | 0.090(10) | 0.281(11) | 0.426(8) | 0.587(9) | 0.824(10) | 0.45(5) | 0.58(2) | 0.95 | 1 |
| sof Se2 | N/A | 0.062(11) | 0.118(10) | 0.202(9) | 0.308(8) | 0.503(10) | 0.455(5) | 0.58(2) | 0.770(14) | 1 |

Formula based on sof GaV$_4$S$_8$GaV$_4$S$_7$.$_39$Se$_0$.$_61$GaV$_4$S$_6$.$_40$Se$_1$.$_60$GaV$_4$S$_5$.$_49$Se$_2$.$_51$GaV$_4$S$_4$.$_42$Se$_3$.$_58$GaV$_4$S$_2$.$_69$Se$_5$.$_31$GaV$_4$S$_2$.$_44$Se$_5$.$_56$23.3(9)%GaV$_4$S$_2$.$_06$Se$_5$.$_94$76.7(9)%GaV$_4$S$_1$.$_12$Se$_8$.$_88$GaV$_4$S$_9$. N/A

| Phase purity | Phase pure | Phase pure | Phase pure | Phase pure | Phase pure | Phase pure | Two phases | VSe$_2$ impurity 3.3% | VSe$_2$ impurity 2.0% |
|-------------|------------|------------|------------|------------|------------|------------|------------|------------------------|------------------------|
| $R_{wp}$    | 17.07      | 16.95      | 16.99      | 18.08      | 17.65      | 17.77      | 26.81      | 31.10                  | 23.21                  |
| $R_{exp}$   | 14.90      | 13.90      | 13.32      | 14.12      | 13.47      | 12.48      | 19.40      | 9.47                   | 12.50                  |
| $\chi^2$   | 1.31       | 1.49       | 1.63       | 1.64       | 1.72       | 2.03       | 1.91       | 10.79                  | 3.45                   |

Atomic positions

| Ga on 4a | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
|----------|---|---|---|---|---|---|---|---|---|
| V on 16e (x, x, x) | 0.60508(14) | 0.60516(14) | 0.60487(14) | 0.60442(16) | 0.60338(16) | 0.60327(18) | 0.6042(8) | 0.6034(3) | 0.6025(3) |
| S1 on 16e (x, x, x) | 0.3709(2) | 0.3730(7) | 0.3722(7) | 0.3694(4) | 0.3686(4) | 0.3790(15) | 0.376(3) | 0.374(6) | 0.398(2) | N/A |
| S2 on 16e (x, x, x) | 0.8631(2) | 0.8634(2) | 0.8640(19) | 0.86454(19) | 0.86399(18) | 0.86237(16) | 0.8649(3) | 0.8656(6) | 0.8657(3) | N/A |
| Se1 on 16e (x, x, x) | N/A | 0.359(4) | 0.360(2) | 0.367(7) | 0.369(6) | 0.367(15) | 0.366(16) | 0.5071(18) | 0.3689(18) |
| Se2 on 16e (x, x, x) | N/A | 0.8634(2) | 0.8640(19) | 0.86454(19) | 0.86399(18) | 0.86237(16) | 0.8649(3) | 0.8637(3) | 0.8594(18) |

* Higher $R_{wp}$ and $\chi^2$ values are due to the presence of the preferred orientation in VSe$_2$ (trigonal, $P\overline{3}m1$).
Table S2. Crystallographic data of GaV on a laboratory diffractometer.

| x(A) | y(A) | z(A) | F(000) | D(λ=1.5418) | D(λ=1.5418) |
|------|------|------|--------|--------------|--------------|
| 0    | 0    | 0    | 4482   | 1.251        | 1.090        |
| 0    | 1    | 1    | 4625   | 1.158        | 1.059        |
| 0    | 2    | 2    | 4817   | 1.064        | 0.987        |
| 0    | 3    | 3    | 5005   | 0.972        | 0.894        |
| 1    | 0    | 0    | 5005   | 0.881        | 0.803        |
| 1    | 1    | 1    | 5193   | 0.790        | 0.712        |
| 1    | 2    | 2    | 5381   | 0.700        | 0.623        |
| 1    | 3    | 3    | 5569   | 0.611        | 0.533        |
| 2    | 0    | 0    | 5569   | 0.520        | 0.441        |
| 2    | 1    | 1    | 5757   | 0.431        | 0.352        |
| 2    | 2    | 2    | 5945   | 0.341        | 0.262        |
| 2    | 3    | 3    | 6133   | 0.250        | 0.172        |
| 3    | 0    | 0    | 6133   | 0.160        | 0.081        |
| 3    | 1    | 1    | 6321   | 0.070        | 0.001        |
| 3    | 2    | 2    | 6509   | -0.040       | 0.079        |
| 3    | 3    | 3    | 6697   | -0.150       | 0.189        |

Table S3. Crystallographic data for GaV on a laboratory diffractometer.

| y | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| Atomic positions |
| Ga on 4a | 0.3904(7); 0.60576(2) | 0.605(29)2; | 0.604(82)2; | 0.603(93)3; | 0.603(89)3; | 0.603(97)4; | 0.603(97)4; | 0.604(73)4; | 0.603(73)4; |
| V on 16e | 0.37072(18) | 0.37166(7) | 0.62793(3); | 0.373(3); | 0.374(7); | 0.375(1); | 0.375(1); | 0.376(1); | 0.376(1); |
| S1 on 16e | 0.3641(3); | 0.364(2); | 0.635(4); | 0.364(2); | 0.364(2); | 0.364(2); | 0.364(2); | 0.364(2); | 0.364(2); |
| S2 on 16e | 0.8641(8); | 0.8642(6); | 0.8642(6); | 0.8642(6); | 0.8642(6); | 0.8642(6); | 0.8642(6); | 0.8642(6); | 0.8642(6); |
| Se on 16e | 0.8641(8); | 0.8642(6); | 0.8642(6); | 0.8642(6); | 0.8642(6); | 0.8642(6); | 0.8642(6); | 0.8642(6); | 0.8642(6); |

Selected bond distances in Å, angles in ° and tetrahedral volumes in Å³.
### Table S4. Powder neutron diffraction refined parameters of GaV$_4$S$_8$ on D2B diffractometer at the ILL.

| Temperature (K) | 50   | 30   | 15   | 9    | 1.5  |
|-----------------|------|------|------|------|------|
| **Space Group** | $F43m$ | $R3m$ | $R3m$ | $R3m$ | $R3m$ |
| **a Å**        | 9.64823(5) | 6.80183(6) | 6.80101(6) | 6.80098(6) | 6.80084(6) |
| **c Å**        | N/A | 16.7984(3) | 16.8034(3) | 16.8058(3) | 16.8053(3) |
| **$V$ ($\text{Å}^3$)** | 898.139(13) | 673.055(18) | 673.091(18) | 673.182(17) | 673.133(18) |
| **$R_{wp}$**   | 4.79 | 4.61 | 4.62 | 4.52 | 4.53 |
| **$R_{exp}$**  | 3.77 | 3.77 | 3.77 | 3.77 | 3.77 |
| **$\chi^2$**   | 1.62 | 1.49 | 1.50 | 1.44 | 1.44 |

**Atomic positions**

| Ga on 4a | S1 on 16e (x, x, x) | S2 on 16e (x, x, x) | S on 9b (x, 2x, z) | S3 on 9b (x, 2x, z) | S4 on 3a (0, 0, z) |
|----------|---------------------|---------------------|--------------------|--------------------|---------------------|
| 0 | 0.37023(12) | 0.86405(11) | 0.1802(3) | 0.1347(4) | 0.1353(4) |

### Table S5. Single crystal neutron diffraction refined parameters of GaV$_4$S$_4$Se$_4$ from data collected on the SXD diffractometer at ISIS. Positions of the V atoms are constrained to those from the single crystal X-ray diffraction.

| Temperature (K) | 55   | 1.5  |
|-----------------|------|------|
| **Space Group** | $F43m$ | $F43m$ |
| **Z**           | 4    | 4    |
| **a Å**        | 9.89110(10) | 9.89250(10) |
| **$V$ ($\text{Å}^3$)** | 967.684(17) | 968.095(17) |
| **$M_R$ (g/mol)** | 700.7 | 700.7 |
| **$\rho_{calc}$ (g/cm$^3$)** | 4.8094 | 4.8074 |
| **Crystal size (mm$^3$)** | $1 \times 1.5 \times 1.5$ | $1 \times 1.5 \times 1.5$ |
| **2θ range (°)** | 3.61 to 73.22 | 3.56 to 73.25 |
| **reflection collected** | 512 | 1798 |
| **indep. Reflect.** | 509 | 1784 |
| **constraints/ paramet.** | 5/12 | 5/12 |
| **$R_{int}$**   | 0.0804, 0.1610 | 0.0804, 0.1506 |
| **$R_1, wR_2$ [$I \geq 2\sigma (I)$]** | 2.03 | 2.65 |

**Atomic positions**

| Ga on 4a | V on 16e (x, x, x) | S1 on 16e (x, x, x) | Se1 on 16e (x, x, x) | S2 on 16e (x, x, x) | Se2 on 16e (x, x, x) |
|----------|-------------------|---------------------|---------------------|--------------------|---------------------|
| 0 | 0.60408 | 0.8638(2) | 0.8638(2) | 0.86332(5) | 0.3740(11) |
| 0 | 0.60408 | 0.86401(8) | 0.86401(8) | 0.3717(5) | 0.3656(5) |
Table S6. Single crystal neutron diffraction refined parameters of GaV₄Se₈ on SXD diffractometer at the ISIS.

| Temperature (K) | 55   | 30   |
|-----------------|------|------|
| Space Group     | F43m | R3m  |
| a Å             | 10.11750(10) | 7.1490(18) |
| c Å             | N/A  | 17.524(6)  |
| V (Å³)          | 1035.666(18) | 775.6(4)   |
| MR (g/mol)      | 905.2 | 905.2   |
| \( \rho_{calc} \) (g/cm³) | 5.8052 | 5.8135   |
| Crystal size (mm³) | 2 × 2 × 2 | 2 × 2 × 2 |
| \( 2\theta \) range (°) | 3.44 to 82.14 | 3.44 to 78.84 |
| Reflection collected | 4740 | 3637   |
| Indep. Reflect. | 2948 | 2638   |
| Constraints/Paramet. | 0/15 | 8/16   |
| \( R_{int} \)  |      |      |
| \( R_1, wR_2 \) \[ I \geq 2\delta (I) \] | 0.0701, 0.1426 | 0.0652, 0.1276 |
| Goodness-of-fit on \( F^2 \) | 1.40 | 1.52   |

Atomic positions

|          | Ga on 4a | Ga on 3a (z fixed) | 0 |
|----------|----------|--------------------|---|
| S1 on 16e (x, x, x) | 0.36822(5) | S1 on 3a (0, 0, z) | 0.63170(14) |
| S2 on 16e (x, x, x) | 0.86332(5) | S2 on 9b (x, 2x, z) | 0.17595(9) 0.45560(12) |
| S3 on 9b (x, 2x, z) | 0.18184(10) 0.95444(12) | S4 on 3a (0, 0, z) | 0.13636(14) |
Figure S1. Crystals of GaV₄S₈₋₂ySe₂y (a) y = 0, (b) y = 1, (c) y = 2, (d) y = 3, (e) y = 4, (f) y = 5, (g) y = 6, (h) y = 7, and (i) y = 8 photographed on millimetre paper.
Figure S2. Powder X-ray diffraction profiles of GaV$_4$S$_8$, GaV$_4$S$_7$Se$_1$, GaV$_4$S$_6$Se$_2$, and GaV$_4$S$_5$Se$_3$. The experimentally-obtained diffraction profile at ambient temperature (blue open circles), refinement based on the model obtained from single crystal X-ray diffraction at room temperature (red solid line), difference (olive green solid line) and predicted peak positions (black tick marks).
Figure S3. Powder X-ray diffraction profiles of GaV$_4$S$_3$Se$_5$, GaV$_4$S$_2$S$_6$, GaV$_4$SSe$_7$, and GaV$_4$Se$_8$. The experimentally-obtained diffraction profile at ambient temperature (blue open circles), refinement based on the model obtained from single crystal X-ray diffraction at room temperature (red solid line), difference (olive green solid line) and predicted peak positions (black tick marks).
Figure S4. Top: volume of the $V_4$ tetrahedra and the S/Se site 2 tetrahedra. Bottom: volume of the S and Se tetrahedra within the V cluster for different compositions of GaV$_4$S$_{8-y}$Se$_y$. 
**Figure S5.** GaV$_4$S$_6$Se$_2$ powder neutron diffraction profile taken on the D20 diffractometer at the ILL. The experimentally-obtained diffraction profile at 15 K (blue open circles), refinement based on the model obtained from single crystal X-ray diffraction at room temperature (red solid line), difference (olive green solid line) and predicted peak positions (black tick marks). The inset shows the (111) diffraction peak taken at 15 K (black open circles) and 1.5 K (red closed circles) and difference (grey closed circles). At 1.5 and 15 K the lattice parameter refine in an $F\bar{4}3m$ to be 9.7673(4) and 9.7669(4) respectively.
Figure S6. Inverse magnetic susceptibility vs temperature for GaV$_4$S$_8$, GaV$_4$S$_4$Se$_4$, and GaV$_4$Se$_8$ measured in an applied magnetic field of 10 mT.