Ph.D. thesis

Néel-type skyrmions in multiferroic lacunar spinels

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Motivation

The ever-advancing field of electronics and information technology sets newer and newer scientific and engineering challenges in sustaining the increase in the storage capacity and computing power of electronic devices. For decades, there has been an exponential growth rate in the density of the transistors on a chip as well as in the information density stored in magnetic domains in a magnetic hard drive, often referred to as Moore’s law [1]. As the characteristic sizes of the elementary electronic and magnetic building blocks, the CMOS transistors and the magnetic grains, approach the atomic scale, Moore’s law is being challenged [2] by the dramatic increase in heat dissipation [3], the quantum behavior of the electrons [4] and the thermal instability of the magnetically stored information [5]. The demand for further downscaling evoked the field of spintronics [6], i.e. the science of storing and transporting information encoded in spin degrees of freedom, reducing the energy cost of the computation and data transmission [7]. Skyrmionics [8, 9], a very recently emerging branch of spintronics, proposes the application of magnetic skyrmions – topologically protected nanometric magnetic vortices – as magnetic bits [10–12]. Owing to their particle-like behavior, nanometric size, long lifetime and high mobility, they may become the building blocks of a future nonvolatile magnetic memory [8]. Moreover, their ability to be displaced by ultra-low electric currents [13] potentially offers the storage and manipulation of information within a single, stationary electronic component [14]. Accordingly, various designs of skyrmion-based memory registers, racetrack memories [11, 15, 16] as well as logic gates [14] have been proposed. Furthermore, the condensed lattice phase of skyrmions, observed recently in several non-centrosymmetric magnets [17], could be utilized as magnonic crystals for microwave-frequency spin-wave applications [18–20]. Spin waves offer the transmission of the information encoded in the electron spins without any charge transport, allowing for the on-chip data transfer with an ultra-low power consumption. Besides the technological point of view, skyrmions provide an intriguing playground for topological phenomena, such as the topological spin-Hall effect and emergent magnetic monopoles [21–25]. These
goals have motivated intensive research for the discovery of novel materials
hosting magnetic skyrmions and for the understanding of the physics of their
manipulation with magnetic fields, electric currents and electric fields.

In my thesis, I study the properties of a new family of bulk skyrmion host
crystals, the so-called lacunar spinel compounds. GaV$_4$S$_8$, a member of this
family was the first material with a non-chiral but polar crystal structure
that was demonstrated to host magnetic skyrmions [26]. The unique sym-
metry properties of this crystal family give rise to a new class of skyrmions
exhibiting a Néel-type structure, also dressed with a magnetoelectric polar-
ization [27]. The insulating nature of the host material may also facilitate
the manipulation of skyrmions by electric fields without the need of dissi-
pative electric currents. Moreover, the polar rhombohedral symmetry char-
acterizing these compounds has a fundamental impact on the stability of
the modulated skyrmion phase, making it in general more robust than in
the Bloch-type skyrmions previously observed in cubic chiral crystals. The
aim of my work is to provide a comprehensive study of three lacunar spinel
compounds GaV$_4$S$_8$, GaV$_4$Se$_8$ and GaMo$_4$S$_8$, starting with the experimental
characterization of their structural and pyroelectric domain structure, fol-
lowed by description of their magnetic phase diagrams and the identification
of their modulated magnetic phases.
Chapter 1

Introduction

Magnetic skyrmions are topologically non-trivial, vortex-like spin textures emerging due to the interplay between competing magnetic interactions [22, 28]. They have been experimentally observed in bulk crystals [26, 29, 30] as well as two-dimensional interfaces [31, 32], thin films [33–35] or single atomic layers [36]. Skyrmions in general are topologically quantized objects with localized, particle-like properties, arising as the solutions of various continuous-field theories [28, 37–39]. They were termed after the original model proposed by Tony Skyrme in 1962 to describe the localized nucleons as topological solitons in the pion field [37, 40]. The existence of topological magnetic structures, i.e. magnetic skyrmions in bulk magnetic crystals was first predicted by Bogdanov and Yablonskii in 1989 [28]. Bogdanov and coworkers specified the crystallographic classes allowing for magnetic interactions that stabilize a two-dimensional lattice state of magnetic skyrmions in external magnetic fields [28, 41]. Such magnetic skyrmion lattice states were first found experimentally less than a decade ago in MnSi [29], a metallic magnet with a cubic chiral crystal structure, characterized by the $P2_13$ space group symmetry [42]. The specific atomic arrangement in the MnSi crystal is termed as the B20 structure. Thereafter, the skyrmion phase has been identified in a number of new compounds, including other binary B20 crystals such as FeGe [43], MnGe [44] as well as different alloys of the B20 family, e.g. Fe$_{1-x}$Co$_x$Si [34, 45, 46], Mn$_{1-x}$Fe$_x$Si and Mn$_{1-x}$Co$_x$Si [47]. Moreover, new skymionic compounds with different crystal structures were discovered. The most important ones are the insulating Cu$_2$OSeO$_3$ (space group: $P2_13$), exhibiting multiferroic skyrmions [30, 48], and the $\beta$-Mn-type Co-Zn-Mn alloys (space group: $P4_132$), which host skyrmions at room temperature and above [49, 50]. The first compounds with a non-chiral but polar symmetry featuring a magnetic skyrmion phase was GaV$_4$S$_8$ [26], whose crystal structure belongs to the lacunar spinel family with the space group symmetry
The significance of magnetic skyrmions lies within their topological nature. Not only do they represent a novel type of magnetic ordering, but owing to their particle-like characteristics, they have several attributes that make them extremely intriguing from the perspective of applications. In itinerant magnets, magnetic skyrmions interact with conductance electrons via their emergent electromagnetic field (EEMF) originating from the non-trivial topology of their spin texture [51, 52]. The corresponding topological Hall-effect was observed in various metallic chiral magnets [53-56]. The fact that skyrmions can be easily displaced by ultra-low electric current densities offers potential applications as magnetic bits in high-capacity and low-consumption memory devices and logic gates [12-14, 57]. This goal has motivated intensive research to explore the physics of magnetic skyrmions and a quest for the discovery and engineering of skyrmion-host materials, the potential building blocks of next-generation magnetic memories. The discovery of insulating and semiconductor skyrmion-host magnets, such as Cu$_2$OSeO$_3$ [48, 58] and GaV$_4$S$_8$ [27], promises the manipulation of the skyrmions with an electric field instead of electric currents, which may further reduce the energy cost of the skyrmion-based memory elements. The manipulation of the magnetooptic skyrmion phase with electric fields has become the subject of several studies recently [59-63].

This thesis is organized as follows. In chapter 2, I briefly review the theory of magnetic skyrmions. First, a phenomenological description and classification of the skyrmionic spin textures will be presented. Then I introduce the microscopic background of the skyrmion formation, focusing mainly on bulk non-centrosymmetric magnets. The one- and two-dimensionally modulated magnetic textures will be described within the framework of a continuous-field micromagnetic description of the magnetic interactions. In particular, the specific properties of the Néel-type magnetic modulations in lacunar spinels with a polar crystal structure will be discussed, highlighting the similarities and differences between those and the Bloch-type magnetic modulations present in cubic helimagnets. Finally, I will present an overview of the most important skyrmion host materials and their special properties.

Chapter 3 focuses on the structural and magnetic properties of lacunar spinel compounds. The magnetic phase diagram of GaV$_4$S$_8$ will be presented, based on previous studies by Kézsmárki et al. [26].

Chapter 4 covers the measurement methodology used in the course of my work for the analysis of the pyroelectric and magnetic structure of the lacunar spinel compounds. Specifically, surface scanning-probe techniques, magnetization, magnetoelectric polarization measurements as well as the basics of small-angle neutron scattering (SANS) experiments will be introduced.
In chapter 5, I present my scanning-probe measurements on single crystalline samples of GaV₄S₈, analyzing the pyroelectric and ferroelastic domain structure arising upon the Jahn-Teller transition [P1].

In chapter 6, I provide further insights into the properties of the modulated magnetic phases in GaV₄S₈ via our experimental studies using SANS [P5]. In particular, I demonstrate the three-dimensional distribution of the zero-field magnetic propagation wavevectors based on SANS performed upon the wide-angle rotation of the sample, which I will refer to as reciprocal-space tomography. Then I present my ac-magnetic susceptibility measurements, revealing slow magnetization dynamics near the magnetic phase transitions in GaV₄S₈ [P2].

Chapter 7 includes the investigation of the magnetic structures and the phase diagram in a new skyrmion host material, GaV₄Se₈. I present my analysis of SANS experiments [P4] in which I assign the magnetic phase transitions to each structural domain. I also present my pyrocurrent [P3] and magnetocurrent measurements, demonstrating the magnetoelectric nature of the magnetic structures in GaV₄Se₈ and exploring the magnetic phase diagram based on the measurement of the magnetically induced polarization.

Finally, the structural [P6] and magnetic characterization [P7] of the newest lacunar spinel compound, GaMo₄S₈, will be presented in chapter 8. The reciprocal-space tomographic image of the magnetic structures in zero-field will be analyzed and compared to that obtained in GaV₄S₈. I also present the results of my static magnetization measurements in comparison with field-dependent SANS experiments in order to establish the magnetic phase diagram of this material.
Chapter 2

Theory and classification of magnetic skyrmions

This chapter provides a brief theoretical description of magnetic skyrmions summarizing the phenomenological and topological classification of skyrmionic textures, and the microscopic grounds of the formation of modulated spin structures in non-centrosymmetric magnets.

2.1 Structural and topological properties of magnetic skyrmions

Magnetic skyrmions are whirling spin structures with topological, particle-like properties. The topological nature of the skyrmions follows from a classical, continuum spin model with fixed spin lengths, where the spin configuration on a 2-dimensional plane is described by a mapping of the $\mathbb{R}^2$ Euclidean space to the spin space of the $S^2$ unit sphere. The skyrmion number, which is a topological invariant, is defined by the integral of the solid angle enclosed by the spins over the whole plane [22]:

$$N_{sk} = \frac{1}{4\pi} \int \int d^2r S \left( \partial_x S \times \partial_y S \right).$$ (2.1)

Generally, the Euclidean plane is considered as the stereographic projection of an $S^2$ unit sphere, where the base point of the sphere corresponds to the origin of the plane and the north pole is projected to a circular boundary in the infinity. In a visual sense, the skyrmion number represents how many times the spin space is fully covered, or 'wrapped around' by the physical (Euclidean) space through the mapping, $r \rightarrow S(r)$. Broadly speaking, a skyrmion
is a spin texture with a non-zero integer topological number, which is topologically different from the uniform ferromagnetic state, which is described by $N_{sk} = 0$. Being a topological invariant, the integer skyrmion number cannot be changed through the continuous deformation of the spin arrangement, which provides a 'topological protection' to the skyrmions, i.e. an energy barrier separating the states with different topological numbers. Switching between states with different topological numbers would require the modulus of the local magnetization – fixed by the assumptions of the continuous model – to cross zero, therefore topological defects on a ferromagnetic background, i.e. skyrmions, are expected to have a long lifetime and particle-like properties. On the atomic scale, the switching barrier is associated to the energy needed to align three spins in a coplanar arrangement, i.e. $S_1(S_2 \times S_3) = 0$ [64]. The continuous-field description of the magnetization and the topological features emerging from this approach provide an adequate description only if the skyrmion size is much larger than the crystallographic unit cell. For slowly varying spins with respect to the atomic length scales, the continuous model is a good approximation, and the skyrmionic spin textures indeed exhibit topological properties, such as the emergent electromagnetic field and the topological- or the skyrmion Hall-effect [22].

For the structural characterization of the skyrmion textures, let us parametrize both the spatial and the spin coordinates in a polar coordinate system, as $\mathbf{r} = (r \cos \phi, r \sin \phi)$ and $\mathbf{S}(\mathbf{r}) = \left[ \cos \Phi(\phi) \sin \Theta(r), \sin \Phi(\phi) \sin \Theta(r), \cos \Theta(r) \right]$, assuming an axial symmetry around the origin. The skyrmion number then becomes [22]:

$$N_{sk} = \frac{1}{4\pi} \int_0^\infty dr \int_0^{2\pi} d\phi \frac{d\Theta(r)}{dr} \frac{d\Phi(\phi)}{d\phi} \sin \Theta(r) = -\frac{1}{4\pi} \left[ \cos \Theta(r) \right]_{r=0}^{r=\infty} \left[ \Phi(\phi) \right]_{\phi=0}^{\phi=2\pi}.$$

(2.2)

Choosing the boundary conditions such that $\Theta(r = 0) = \pi$ and $\Theta(r = \infty) = 0$, corresponding to a $180^\circ$ rotation of the magnetization when approaching the periphery of the skyrmion from its center, fixes the value of the radial integral to be 2, i.e. $N_{sk} = -\frac{1}{2\pi} \left[ \Phi(\phi) \right]_{\phi=0}^{\phi=2\pi}$. The term on the right-hand side is connected to the quantity called vorticity, defined as $m := \frac{1}{2\pi} \left[ \Phi(\phi) \right]_{\phi=0}^{\phi=2\pi}$. This quantity is related to the winding number, the one-dimensional analogue of the skyrmion number, characterizing the mapping from a closed loop $S^1$ over the $\mathbb{R}^2$ Euclidean space to the in-plane component of the spins, defined over $S^1$. With the chosen boundary conditions, the skyrmion number is equal with the vorticity up to a negative sign $N_{sk} = -m$ [22, 23, 65]. The internal structure of the skyrmion is further characterized
by the helicity, $\gamma$, defined as:

$$\Phi(\phi) = m\phi + \gamma. \quad (2.3)$$

Figure 2.1 presents the internal structures of the topologically non-trivial skyrmions ($m = +1$, $N_{sk} = -1$) and antiskyrmions ($m = -1$, $N_{sk} = 1$) [65] for the different values of $\gamma = 0, \pm\pi/2, \pi$. Of particular interest are the states with $m = +1$ and $\gamma = \pm\pi/2$, called Bloch-type skyrmions, because in each radial cross section the spins rotate in a plane perpendicular to the radial direction, establishing a spin helix present in Bloch-type domain walls. Similarly, the $m = +1$ and $\gamma = 0, \pi$ states are termed as Néel-type skyrmions, because in each radial section the spins rotate in a plane spanned by the z axis and the radial direction, i.e. cycloidal or Néel-type magnetic modulations are formed. In antiskyrmions the rotation plane of the spins varies with the polar angle, $\phi$. Specifically, for the helicity value $\gamma = 0$, Bloch- and Néel-type spin modulations arise along the two pairs of orthogonal axes characterized by $\phi = 0^\circ, 90^\circ$ and $\phi = \pm 45^\circ$, respectively.

The structures characterized with different helicities, but exhibiting the same vorticity, are topologically equivalent, i.e. they can be transformed to each other through the continuous rotation of the spins. Note that in antiskyrmions, the structures with different $\gamma$ helicity numbers can also be transformed into each other by rigid $\gamma/2$ rotations around the center. Nevertheless, topological equivalence does not imply an energetic degeneracy of
the various spin patterns. It is the interaction responsible for the modulation of the spins (most importantly the Dzyaloshinsky-Moriya interaction) which determines both the specific vorticity and helicity numbers featuring the lowest energy. For instance, the $\gamma = \pm \pi/2$ solutions represent chiral counterparts, therefore one of them might be selected as the ground state in the presence of a chiral interaction, depending on the handedness of the host crystal. As a result, chiral skyrmions with opposite helicities are favored in the two enantiomers of a chiral crystal. Similarly, in a non-chiral but polar skyrmion host material, either the $\gamma = 0$ or $\gamma = \pi$ states are selected, distinguished by the inversion symmetry operation, which is not a symmetry of the polar point groups.

### 2.2 Theoretical background of skyrmion formation in non-centrosymmetric magnets

The emergence of non-collinear topological spin structures in magnetic materials is governed by the competition of multiple magnetic interactions favoring different relative orientations of the interacting spins. As a result, a modulation in the spin direction develops with a wavelength determined by the relative strength of these interactions. Such a competition may arise under various circumstances:

- In materials lacking the inversion symmetry, the competition between the Dzyaloshinsky-Moriya interaction (DMI) and the Heisenberg-exchange interaction is responsible for the formation of the modulated spin textures. The inversion symmetry may be broken by an interface in thin films or heterostructures [8, 66], as well as in a bulk crystal without any inversion centers [17]. In this thesis, I will focus on non-centrosymmetric bulk magnetic crystals, being relevant for the subject of my studies, the lacunar spinel compounds.

- In magnetic thin films a uniaxial anisotropy promoting a spin alignment normal to the surface may compete with the long-ranged dipolar interaction favoring an in-plane alignment of the spins. As a result, microscopic magnetic domains emerge. Disregarding interface effects, the spatial inversion symmetry is preserved in these systems, thus the sense of the spin rotation in the domain walls is degenerate, i.e. can be both clockwise and counterclockwise. With the application of an external magnetic field perpendicular to the surface, the magnetic domain walls transform into an array of micron-sized skyrmions, originally termed as
magnetic bubbles [67], with the $\gamma = 0$ and $\gamma = \pi$ states being degenerate. Recently, several centrosymmetric crystals, such as the tetragonal manganite La$_{1-x}$Sr$_x$MnO$_3$ ($x=0.175$) [68] and the hexagonal MnNiGa alloy [69] have been shown to host skyrmionic bubbles featuring a large variety of internal structures owing to the helicity degree of freedom.

- Frustrated-exchange [70] or four-spin interactions [36] can lead to the emergence of atomically small skyrmions, as observed in a single atomic layer of Fe on an Ir(111) substrate. Under the influence of these interactions the energy of skyrmions and antiskyrmions ($m = \pm 1$) would be degenerate, supporting any value of $\gamma$ [22]. However, in these ultrathin films, the interfacial DMI also plays a role in stabilizing the skyrmionic solution with the vorticity $m = 1$, as well as selecting the unique helicity state [36]. Recently, topologically non-trivial skyrmionic structures have been found in the bulk form [71] as well as in nanostructures [72] of the centrosymmetric kagome magnet, Fe$_3$Sn$_2$, featuring a frustrated exchange interaction along with a strong uniaxial anisotropy.

### 2.2.1 Microscopic model of the formation of non-collinear spin structures

For the microscopic description of the non-collinear magnetic ordering in isotropic non-centrosymmetric crystals, the following effective spin-Hamiltonian is considered:

$$H = -\sum_{i,j} J_{ij} S_i S_j + \sum_{i,j} D_{ij} (S_i \times S_j). \quad (2.4)$$

The first term in Eq. 2.4 represents the isotropic Heisenberg exchange interaction between the spins at the $i, j$ sites. A nearest-neighbor Heisenberg interaction with a ferromagnetic character $J_{ij} > 0$ gives rise to a uniformly magnetized, ferromagnetic ground state. The second term is the antisymmetric exchange, or Dzyaloshinsky-Moriya interaction (DMI), arising due to the spin-orbit coupling in non-centrosymmetric magnets [73, 74]. This interaction favors the perpendicular alignment of the neighboring spins. In case of homogeneous Heisenberg-exchange and DMI terms, ($J_{ij} = J$ and $D_{ij} = D$) the interplay of the two interactions leads to an incommensurately modulated magnetic ground state of the spin system, constituting a long-wavelength spiral structure, where the spins rotate in the plane perpendicular to the D vector. The periodicity of the spin spiral is determined by the relative strength of two interactions, $\lambda = 2\pi a J / |D|$, where $a$ is the distance between the neighboring spins. The direction of the DMI vector $D_{ij}$
for a pair of spins depends on the symmetry of the bond [74]. If the center of the bond is an inversion center, the DMI vanishes. If the normal plane intersecting the bond is a mirror plane, $D_{ij}$ must be perpendicular to the bond, whereas if the mirror plane contains the bond, only the perpendicular component of $D_{ij}$ to the mirror plane is non-vanishing. For a two-fold rotation axis perpendicular to the bond, $D_{ij}$ is perpendicular to this axis. If the axis of the bond is an n-fold rotation axis, then only $D_{ij}$ parallel to the bond is allowed by symmetry [74].

Since the DMI with a relativistic origin is typically much weaker than the Heisenberg exchange [74], the wavelength of the spin helicoids are 1-2 orders of magnitudes larger than the chemical lattice constant, $\lambda \gg a$.

As the spin varies slowly on the atomic scales, the magnetic structures are conveniently treated within the framework of a continuous-field approximation. Such a micromagnetic treatment provides a straightforward means for the phenomenological determination of the free-energy functional of the spin system based on the symmetry properties of a bulk crystal, without the need for knowing the atomic-scale pattern of the interactions.

### 2.2.2 Micromagnetic model of the interactions

In the continuous-field micromagnetic model, the localized spins are replaced by the local magnetization, introduced as $M = \frac{1}{v} g \mu_B \int dr \sum S_i \delta(r - R_i)$, where $g$ is the Landé factor, $\mu_B$ is the Bohr-magneton and the volume of the averaging, $v$, is small relative to the characteristic length scale of the spin modulation, i.e. $a < v^{1/3} < \lambda$. The continuous model follows from the atomic-scale description in Eq. 2.4 by the spatial expansion of the magnetization up to the linear order, which yields the following energy density functional associated to the Heisenberg exchange [75]:

$$w_{ex}(r) = -AM^2(r) + \frac{1}{2} \sum_{\mu \nu} J_{\mu \nu}(r) \frac{\partial M(r)}{\partial r_\mu} \frac{\partial M(r)}{\partial r_\nu},$$

where $J_{\mu \nu} = \frac{1}{(g\mu_B)^2} \int dr' \tilde{J}(r') r_\mu r_\nu$, and $A = \frac{1}{(g\mu_B)^2} \int dr' \tilde{J}(r')$. The local value of the spatial average of the exchange parameter is defined by $\tilde{J}(r) = \frac{1}{v} \int r_\mu \delta(r - (R_i - R_j)) dr$.

The first term in Eq. 2.5 is invariant with respect to the rotation of the magnetization due to the isotropy of the Heisenberg interaction assumed in Eq. 2.4. Exchange anisotropies can be introduced both in the interaction strength between the various spin components as well as in the spatial dependence of the exchange stiffness, $J(r)_{\mu \nu}$.
In a more phenomenological approach, the exchange energy density or Landau-functional is not derived from the microscopic model, rather it is introduced based on symmetry arguments. Namely, it is constructed as the sum of polynomials of the order parameter and its spatial derivatives that are invariant under the crystal symmetry operations. Generally, the lowest-order polynomials are considered in the expansion. Since in the present case we study slow modulations of the ferromagnetic state, the point group symmetries of the crystal (in the non-magnetic state) have to be considered. For instance, in the simplest case of a crystal featuring a cubic symmetry, the energy density in Eq. 2.5 is extended with the following anisotropy terms [75]:

\[ w_{\text{anis}}^c = C \left( M_x^2 M_y^2 + M_y^2 M_z^2 + M_z^2 M_x^2 \right) + D(M_x^2 M_y^2 M_z^2) + \ldots, \]  

(2.6)

thus the energy functional acquires the form:

\[ w^c(r) = -A M^2(r) + \]
\[ + B \left\{ \left[ \nabla M_x(r) \right]^2 + \left[ \nabla M_y(r) \right]^2 + \left[ \nabla M_z(r) \right]^2 \right\} + \]
\[ + w_{\text{anis}}^c + \ldots \]  

(2.7)

Here, the first quadratic term is responsible for the magnetic phase transition in the Landau-theory, requiring that \( A = a(T_C - T) \) changes sign at the Curie-temperature. The second term is the exchange stiffness, following from \( J_{\mu\nu} = B \delta_{\mu\nu} \) in Eq. 2.5 due to the cubic symmetry. The term \( w_{\text{anis}}^c \) contains the lowest-order cubic magnetocrystalline anisotropies up to the sixth power of the magnetization components that are invariant under the cubic symmetries. These terms are responsible for the preferred direction of the magnetization in a cubic crystal. Considering only the fourth-order term, the ground-state magnetization is parallel to either the \( \langle 111 \rangle \) axis (\( C < 0 \)) or to the \( \langle 100 \rangle \) axis (\( C > 0 \)).

In crystals featuring uniaxial symmetry, the following anisotropy terms are used in the lowest order:

\[ w^u(r) = K_1(aM)^2 + K_2(aM)^4, \]  

(2.8)

where the vector \( a \) designates the axis of the uniaxial anisotropy. In the absence of the \( K_2 \) term, \( K_1 > 0 \) expresses an easy-plane, while \( K_1 < 0 \) represents an easy-axis anisotropy.
Additional anisotropy terms may be included to the expansion of the Landau energy density by taking the crystal symmetries into consideration. Most importantly in non-centrosymmetric crystals, antisymmetric combinations of the magnetization and its gradients arise in the expansion, generally referred to as Lifshitz-invariants \[76\]:

\[
\mathcal{L}_{ij}^k = M_i \frac{\partial M_j}{\partial x_k} - M_j \frac{\partial M_i}{\partial x_k}.
\] (2.9)

The antisymmetric terms in Eq. 2.9 are connected to the Dzyaloshinsky-Moriya interaction \[73\] and are of the first order in the spin-orbit coupling \[77\]. Different crystal classes are described by different combinations of the Lifshitz-invariants, as determined by the crystal symmetry. In case of the most common skyrmion host materials, the cubic helimagnets, such as the \(B20\)-compounds and \(Cu_2OSeO_3\) (\(P2_13\)), as well as \(\beta\)-manganites (\(P4_132\)), belonging to the \(T\) and \(O\) crystal classes, respectively, the DMI manifests in the following form \[78\]:

\[
w^{O}_{DMI} = D(\mathcal{L}_{yx}^z + \mathcal{L}_{xz}^y + \mathcal{L}_{zy}^x) = DM(\nabla \times M).
\] (2.10)

On the other hand, lacunar spinel compounds (\(R3m\)) are characterized by the uniaxial \(C_{3v}\) symmetry, thereby the allowed antisymmetric terms in the Landau-functional are expressed as follows \[28\]:

\[
w^{C_{3v}}_{DMI} = D(\mathcal{L}_{zx}^z + \mathcal{L}_{zy}^y) = D \left( M_z \frac{\partial M_x}{\partial x} - M_x \frac{\partial M_z}{\partial x} + M_z \frac{\partial M_y}{\partial y} - M_y \frac{\partial M_z}{\partial y} \right),
\] (2.11)

where the \(z\) axis was chosen parallel to the axis of three-fold rotation. The difference in the form of the DMI in Eqs. 2.10 and 2.11 has a fundamental impact on the magnetic structures arising in the two types of materials, as will be demonstrated in the following.

### 2.2.3 Modulated magnetic structures in cubic and polar magnets

For the comparison of the magnetic structures in the \(T\) and \(C_{3v}\) crystal classes, let us consider the following Landau-functional:

\[
w = B \left\{ [\nabla M_x(r)]^2 + [\nabla M_y(r)]^2 + [\nabla M_z(r)]^2 \right\} + w_{DMI} + w_{anis} - \mu_0 MH,
\] (2.12)
where $w_{DMI}$ takes the form of Eq. 2.10 and Eq. 2.11, while $w_{anis}$ is described by Eq. 2.6 and Eq. 2.8 in case of the cubic helimagnets and the polar lacunar spinels, respectively. The Zeeman interaction in the presence of an external field is included as the last term.

One-dimensional spin modulations

In case of the cubic helimagnets, in the absence of an external field the ground-state solution to the energy functional, Eq. 2.12, is a spin helix with a single $q$-vector, where the spins rotate in the plane perpendicular plane to $q$ [78]:

\[
M = M_s [n_1 \cos(qr) + n_2 \sin(qr)],
\]

(2.13)

where $n_1 \perp n_2 \perp q$ and $|q| = D/2B$.

The sense of the rotation of the spins is determined by the sign of $D$ in 2.10, fixed by the handedness of the chiral crystal. In the absence of magneto-crystalline anisotropies, the energy of the spin helices is degenerate for all the directions of the $q$-vector over the unit sphere [see Fig. 2.2 (a)]. In the presence of an external magnetic field a single helical state with propagation direction $q \parallel H$ is selected as the minimal-energy solution, since the largest susceptibility of the spin-helix is along the direction normal to the rotation plane of the spins. The spins are continuously tilted towards the magnetic field, tracing out a conical path along the propagation direction parallel to the field [see Fig. 2.2 (b)]. Note that the $P2_13$ symmetry of the cubic helimagnets allows for an additional exchange anisotropy term, in addition to the fourth- or sixth-order magneto-crystalline anisotropy terms listed in Eq. 2.6, fixing the preferred propagation direction of the helices along either the $\langle 111 \rangle$ (e.g. in MnSi [78]), or the $\langle 100 \rangle$ axes (e.g. in Cu$_2$OSeO$_3$ [48]) in zero field. Therefore, the flipping of the helical states to the conical state occurs in finite magnetic fields, when the weak exchange anisotropy is overcome by the Zeeman energy [79, 80]. The field-induced reorientation of the helices may be partially discontinuous, depending on the relative orientation of the applied field and the cubic easy-axes [80]. The longitudinal conical state finally transforms into a field-polarized ferromagnetic state in a second-order transition at the critical field of the saturation [81].

In lacunar spinels featuring a crystal symmetry of $C_{3v}$, the structure of the spiral modulations is fundamentally different. On one hand, the zero-field ground state of Eq. 2.12 also takes the form of Eq. 2.13. However, due to the different combinations of the Lifshitz-invariants, the spins now rotate in the plane containing the propagation direction, $n_1 \perp n_2 \parallel q$, corresponding to a cycloidal or Néel-type modulation. Even more importantly, due to the lower
Figure 2.2: *Spiral spin modulations in cubic helimagnets (a),(b) and in lacunar spinels (c),(d) with a polar rhombohedral crystal symmetry. In the former case, the spins are arranged in helices, whereas in the latter, the spins trace out a cycloidal path. The blue arrows pointing towards the surface of the sphere and the edge of the circle in panels (a) and (c) represent the continuous degeneracy of the propagation vectors in the absence of a magnetic field and magnetocrystalline anisotropies. The green arrows in panels (b) and (d) indicate the direction of the applied magnetic field, and the red arrows show the corresponding ground-state q-vectors.*

symmetry of the polar magnets the propagation directions of the magnetic modulations are confined by the DMI to the plane perpendicular to the polar
axis, i.e. $q \perp C_3$ axis [26], as shown in Fig. 2.2 (c). As a consequence, for magnetic fields applied along the polar axis the longitudinal conical state cannot emerge due to the DMI term, and therefore, the cycloidal states become more robust against external fields. Note that the isotropy of the plane is not affected by uniaxial magnetic anisotropies, therefore all cycloidal modulations are expected to be degenerate irrespective of the direction of the $q$-vectors within the plane perpendicular to the polar axis. The orientation of the modulation wavevectors will be experimentally analyzed in section 6.1.1 for GaV$_4$S$_8$ and in section 8.2 for GaMo$_4$S$_8$ via small-angle neutron scattering. It turns out that in the latter case, additional cubic anisotropic terms must be assumed in order to explain the zero-field distribution of the $q$-vectors.

Magnetic fields oblique to the polar axis may introduce an in-plane anisotropy through the susceptibility anisotropy of the spin cycloids, redistributing the propagation wavevectors within the plane. As a result, a transverse conical state is established [see Fig. 2.2 (d)]. Experimental evidence of this effect will be provided for GaV$_4$S$_8$ in section 6.1.3.

**Two-dimensional vortex state, the skyrmion lattice**

The skyrmion lattice phase (SkL) was first predicted theoretically by Bogdanov [28] to emerge in non-centrosymmetric magnets upon the application of an external magnetic field parallel to the unique axis. The SkL consists of the coherent superposition of three spiral states with propagation directions perpendicular to the magnetic field [29]:

$$M(r) = M_0 + \sum_{i=1}^{3} [n_{i1} \cos(q_i r) + n_{i2} \sin(q_i r) + \text{higher harmonics}] , \quad (2.14)$$

where $M_0$ is the uniform magnetization induced by the field, while the spin rotation planes of the three spin spirals are spanned by $n_{i1}$ and $n_{i2}$ with the corresponding propagation vectors denoted as $q_i$. For the Néel-type SkL $n_{i1} \perp n_{i2} \parallel q_i$, while all the three vectors are mutually perpendicular to each other for the Bloch-type SkL. The uniform component of the magnetization is created by the field-induced anharmonicity in the path traced by the spins along the spiral, represented by the appearance of higher harmonics in the magnetization. The three in-plane propagation wavevectors span an angle of 120° with one another, i.e. $\sum_{i=1}^{3} q_i = 0$, establishing a 2-dimensional hexagonal lattice of the magnetization, similarly to the Abrikosov-phase in type-II superconductors. There is a direct analogy between the two systems,
since the vortex solution arises in both as a result of the destabilization of the uniform state against the formation of domain walls. Calculation of the skyrmion number for a single unit cell results in \( N_{sk} = -1 \), indicating that the SkL phase is essentially a triangular lattice of individual skyrmions [29]. In the direction normal to the skyrmion lattice, the magnetization pattern over each atomic layer is phase-locked, i.e. skyrmion tubes with finite correlation length are formed, similarly to the vortex tubes in superconductors [see Fig 2.3 (c)].

In the continuous mean-field theory, employing Eq. 2.12, the skyrmion lattice represents only a metastable solution in cubic helimagnets, while the largest part of the magnetic phase diagram, underlying the field polarized ferromagnetic state, is occupied by the longitudinal conical state realizing a global energy minimum [28]. Nevertheless, as has been demonstrated by Mühlbauer et al. [29], by adding Gaussian fluctuations to the model, the SkL is thermally stabilized in the close vicinity of the Curie-temperature. They demonstrated that the small phase pocket near \( T_C \) in MnSi, previously termed as the 'A-phase', is indeed a Bloch-type SkL phase. Due to the DMI pattern, the spins rotate in tangential planes, perpendicular to the radial directions, thus a Bloch-type SkL is established [see Fig 2.3 (a)]. Because of the high cubic symmetry, the three helical wavevectors constituting the SkL always align in the plane normal to the magnetic field direction.

The magnetic phase diagram featuring a SkL phase pocket embedded in the conical state near \( T_C \), is generic to all cubic helimagnets, irrespective of the Curie-temperature (ranging from 30 K to 500 K), and whether the material is metallic (MnSi, FeGe, MnSi, etc.) or insulating (Cu$_2$OSeO$_3$). This indicates that the physics of the skyrmion formation is captured by

Figure 2.3: Magnetization pattern of a single Bloch-type skyrmion (a), a Néel-type skyrmion (b) and a Bloch-type skyrmion lattice (c). Images adapted from [26] and [24]. Reprinted with permission from Springer Nature and AAAS.
Eq. 2.12 including the effects of the thermal fluctuations. Higher-order anisotropies do not play an important role in the stability of the SkL but may determine the orientation of the $q$-vectors.

Since the longitudinal conical state is absent in polar magnets, the SkL solution can be stabilized by axial magnetic fields even in the absence of thermal fluctuations [28]. Indeed, the lacunar spinel $\text{GaV}_4\text{S}_8$, characterized by a non-chiral but polar symmetry, was demonstrated by Kézsmárki et al. to host the Néel-type SkL [Fig 2.3 (b)] in a relatively broad temperature range below its Curie-temperature, $T_C = 13$ K [26]. Remarkably, the orientation of the SkL is determined by the DMI, confining the cycloidal wavevectors to the plane normal to the polar axis. This feature provides robustness to the SkL against oblique magnetic fields.

2.3 An overview of skyrmion-host materials

The emergence of the SkL phase has been identified in several non-centrosymmetric magnets. The non-centrosymmetric bulk skyrmion host materials and their most important properties are presented in Table 2.1, based on the collection by J.S. White [84] and the review paper of Kanazawa et al. [17]. Most importantly, the Curie-temperature of these materials varies on a large scale, ranging from 13 K up to over 500 K. The skyrmion lattice phase arises near and above room temperature in FeGe and some of the Co-Zn-Mn alloys, promising for their application under ambient circumstances. The length scale of the magnetic modulations and the lattice constant of the SkL ranges from 10 nm up to hundreds of nanometers. In metallic compounds, the topological nature of the skyrmions gives rise to emergent phenomena, such as the topological Hall-effect [51], moreover, the skyrmions can be manipulated by electric currents owing to their interaction with the conduction electrons [13]. On the other hand, insulating skyrmion host materials offer the manipulation of the skyrmions by electric fields [59]. Furthermore, the magnetoelectric nature of the skyrmions in $\text{Cu}_2\text{OSeO}_3$ [61] as well as in the lacunar spinels [27, 85] results in the nonreciprocity of the spin-wave propagation [86], making them potential candidates for magnonic devices with diode functionalities in the GHz range. Lacunar spinel compounds featuring a polar crystal symmetry represent a unique class of skyrmion host materials, exhibiting Néel-type skyrmion tubes oriented along the polar axis [26]. Recently, a condensed lattice phase of antiskyrmions has been discovered in the tetragonal Heusler compound, $\text{Mn}_{1.4}\text{Pt}_{0.9}\text{Pd}_{0.1}\text{Sn}$, appearing in a wide temperature range of 100-400 K.
<table>
<thead>
<tr>
<th>Material</th>
<th>Crys. Class</th>
<th>SG</th>
<th>Skyrm. Type</th>
<th>Tc (K)</th>
<th>λ (nm)</th>
<th>Conductivity</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnSi</td>
<td>T</td>
<td>P2,3</td>
<td>Bloch</td>
<td>30</td>
<td>18</td>
<td>Metal</td>
<td>Mühlbauer et al., Science 323, 915 (2009)</td>
</tr>
<tr>
<td>FeGe</td>
<td>T</td>
<td>P2,3</td>
<td>Bloch</td>
<td>279</td>
<td>70</td>
<td>Metal</td>
<td>Yu et al., Nat. Mater. 10, 106 (2010)</td>
</tr>
<tr>
<td>MnGe</td>
<td>T</td>
<td>P2,3</td>
<td>Hedgehog</td>
<td>170</td>
<td>3</td>
<td>Metal</td>
<td>Kanazawa et al., PRB 86, 234435, (2012)</td>
</tr>
<tr>
<td>Fe1-xCoSi</td>
<td>T</td>
<td>P2,3</td>
<td>Bloch</td>
<td>&lt; 36</td>
<td>40-230</td>
<td>Metal*</td>
<td>Münzer et al., PRB 81, 041203(R) (2010)</td>
</tr>
<tr>
<td>Mn1-xFeSi</td>
<td>T</td>
<td>P2,3</td>
<td>Bloch</td>
<td>&lt; 17</td>
<td>10-12</td>
<td>Metal*</td>
<td>Gogolin et al., PRB 79, 205417 (2009)</td>
</tr>
<tr>
<td>Cu2OSeO3</td>
<td>T</td>
<td>P2,3</td>
<td>Bloch</td>
<td>58</td>
<td>60</td>
<td>Insulator</td>
<td>Seki et al., Science 336, 198 (2012)</td>
</tr>
<tr>
<td>(Fe,Co)2MoN</td>
<td>O</td>
<td>P4/32</td>
<td>Bloch</td>
<td>&lt; 36</td>
<td>110</td>
<td>Metal*</td>
<td>Li et al., Phys. Rev. B 93, 060409(R) (2016)</td>
</tr>
<tr>
<td>GaVSe</td>
<td>C3a</td>
<td>R3m</td>
<td>Néel</td>
<td>13</td>
<td>17</td>
<td>Semiconductor</td>
<td>Minamide et al., Nat. Mater. 14, 1118 (2015)</td>
</tr>
<tr>
<td>GaMoSe</td>
<td>C3a</td>
<td>R3m</td>
<td>Néel</td>
<td>19</td>
<td>10</td>
<td>Semiconductor</td>
<td>Fujima et al., PRB 95, 180410, (2017)</td>
</tr>
<tr>
<td>VOSeO3</td>
<td>C4v</td>
<td>P4cc</td>
<td>Néel</td>
<td>7.5</td>
<td>100-200</td>
<td>Insulator</td>
<td>Kuzumagi et al., PRL 119, 237201, (2017)</td>
</tr>
<tr>
<td>Mn1.4Pt0.9Pd0.1Sn</td>
<td>D3d</td>
<td>I42m</td>
<td>Antiskyrmion</td>
<td>400K</td>
<td>100</td>
<td>Metal</td>
<td>Nayak et al, Nature 548, 561–566 (2017)</td>
</tr>
</tbody>
</table>

Table 2.1: List of bulk skyrmion host materials and their basic properties. Collection based on the talk of J.S. White [84] and the review paper of Kanazawa et al. [17]. In doped B20 compounds, the conductivity depends on the doping, indicated by asterisks in the table.
Chapter 3

Structure and magnetism of lacunar spinel compounds

In this chapter, I introduce the structural and magnetic properties of the lacunar spinels, focusing on three specific compounds, GaV$_4$S$_8$, GaV$_4$Se$_8$ and GaMo$_4$S$_8$, being the main subjects of my studies.

3.1 Structure and pyroelectricity in lacunar spinels

The family of lacunar spinels is characterized by the chemical composition of AB$_4$X$_8$, where the A site can be occupied by Ga, Ge, Al or Zn, B sites can be occupied by transition metals V, Ti, Cr, Nb, Mo, Ta, W and X is a chalcogenide ligand such as S, Se or Te [119–126]. As compared to the regular spinel compounds, with the formula AB$_2$X$_4$, lacunar spinels lack a cationic A-site in every second unit cell. In a regular spinel structure, the B-site atoms would be arranged in a network of corner-sharing tetrahedrons, known as the pyrochlore lattice. However, due to the central cationic void in every second tetrahedron the lattice decomposes into smaller and larger B$_4$ tetrahedral clusters, hence forming a breathing pyrochlore lattice [127]. It is physically motivated to describe the structure as a rocksalt lattice of weakly linked [B$_4$X$_4$]$^{4+}$ cubane clusters and [AX$_4$]$^{4-}$ tetrahedra [123, 124], as shown in Fig. 3.1 (a). The electronic and the magnetic properties of the lacunar spinels are principally determined by the hopping and magnetic exchange between the neighboring metallically bonded B$_4$ clusters, hence in the following, the system will be simplified to an FCC lattice of B$_4$ tetrahedra 3.1 (b).

Hereafter in this chapter, the discussion of the structural and the pyroelec-
tric properties will be limited to the three specific lacunar spinel compounds GaV$_4$S$_8$, GaV$_4$Se$_8$ and GaMo$_4$S$_8$, being the primary subjects of my research.

At room temperature, lacunar spinels have a non-centrosymmetric, cubic structure, belonging to the space group F$ar{4}3m$. Due to the lack of an inversion center, there may be two inversion domains coexisting in a crystal. The unit cell of the FCC lattice of the B$_4$ clusters is presented in Fig. 3.2 (b). The 3d or 4d orbitals of the transitional metals in the V$_4$ and Mo$_4$ tetrahedra, respectively, form hybridized cluster orbitals with $a_1$, $e$ and $t_2$ symmetries in the $\Gamma$ point [124], constituting 12 electronic states. In an ideal ionization state, Ga$^{3+}$ and X$^{2-}$, the metallic B$_4$ cluster provides 13 electrons to covalent bonds within the cubane unit and between the cubane and the tetrahedral clusters. That leaves 7 and 11 electrons on the outer shell for the formation of metallic bonds in the V$_4$ and Mo$_4$ clusters, respectively. As a consequence, the highest-energy triply-degenerate $t_2$ state is occupied by an unpaired electron in the case of GaV$_4$S$_8$ and GaV$_4$Se$_8$ and an unpaired hole in GaMo$_4$S$_8$ [124], as depicted in Fig. 3.2 (a) and (c). In both cases, the highest-energy unfilled shell carries a net spin of $S=1/2$. This simple electronic configuration model is corroborated by spin-polarized band structure calculations, which
yield magnetic moments corresponding to one unpaired electron per V$_4$ and Mo$_4$ cluster [124].

The orbital degeneracy in GaV$_4$S$_8$, GaV$_4$Se$_8$ and GaMo$_4$S$_8$ is lifted via a cooperative Jahn-Teller distortion at $T_s = 42$ K, 42 K and 45 K respectively [125],[P3], through the deformation of the lattice along any of the four (111)-type body diagonals in the pseudocubic system. As a result, the crystal symmetry is reduced to polar rhombohedral, corresponding to the space group $R3m$ [124, 128]. Due to the different filling of the degenerate $t_2$ level in case of the V$_4$ and Mo$_4$ clusters, an opposite splitting of the energy states is favored in the two cases [see Figs. 3.2 (f) and (e)]. This is achieved by a rhombohedral elongation in the case of GaV$_4$S$_8$ and GaV$_4$Se$_8$, whereas a rhombohedral contraction takes place in GaMo$_4$S$_8$, as visualized by Figs. 3.2 (d) and (e). These findings are in accord with band structure and chemical bonding calculations as well as X-ray diffraction data [124].

In canonical Jahn-Teller materials with a centrosymmetric crystal structure, such as YTiO$_3$ and LaMnO$_3$, the distortion does not induce any electric polarization, whereas the tendency of ionic displacements generating ferroelectricity is inhibited [129]. In contrast, when the high-symmetry phase of a compound lacks the inversion symmetry, i.e. the material is piezoelectric [91], the Jahn-Teller distortion can give rise to a polar phase, where the pyroelectric order goes hand in hand with the ferroorbital ordering. Indeed, theoretical studies show that in strong contrast to perovskite oxides [129], such a development of pyroelectric polarization in non-centrosymmetric magnets is not suppressed by the partial occupancy of the d shells. Thus, the polar Jahn-Teller distortion provides a source of pyroelectricity that may coexist with an additional magnetic order, allowing for the emergence of magnetoelectric multiferroicity [130]. As a realization of the concept above, the Jahn-Teller transition in GaV$_4$S$_8$, GaV$_4$Se$_8$ and GaMo$_4$S$_8$ gives rise to sizable electric polarization of 0.6 $\mu$C/cm$^2$, 1 $\mu$C/cm$^2$ and 0.2 $\mu$C/cm$^2$, respectively, as detected by pyrocurrent measurements [27], [P3],[P6].

Infrared and Raman phonon spectroscopy [128] and dielectric spectroscopy [131] on GaV$_4$S$_8$ indicate the presence of orbital fluctuations in the high temperature phase at $T > T_s$, implying the presence of dynamical Jahn-Teller distortions even above $T_s$, where the average structure is cubic. The ferroorbital and ferroelastic ordering occurs at $T_s$ upon a disorder-to-order type transition with a first-order character [27, 132].

To minimize the electrical stray field energy, bulk pyroelectric crystals break up into domains [133]. In lacunar spinels the 4 symmetry is lost upon the Jahn-Teller transition and the $T_d$ point symmetry is reduced to its subgroup $C_{3v}$, therefore the formation of four degenerate structural domains is allowed. The polarization in each structural domain is aligned parallel to
one of the four $\langle 111 \rangle$ axes, i.e. the rhombohedral axis, which is the only remaining C$_3$ axis of the given domain. The local electric polarization in each B$_4$ tetrahedron must point along this axis. Since the inversion symmetry is already broken in the cubic F43m phase, antiparallel polarization domains cannot arise within a single inversion domain of the crystal. By convention, the polarization vector will be displayed pointing toward the unique corner located on the C$_3$ axis, as shown in Fig. 3.2 (d) and (e). Throughout this
thesis, the structural domains will be labeled by this direction of the local polarization, such as [111], [111], [111] and [111]. Although these domains represent only one of the two possible inversion domains, all arguments in this study can be equally applied to the other inversion domain by reversing the sign of the polarization vectors.

In a strict sense, those compounds are classified as ferroelectrics whose electric polarization can be flipped by an external electric field. Even though the remanent polarization cannot be reversed within a single rhombohedral domain, polarization reversal may be achieved by the field-induced change in the relative population of the four developing structural domains, selecting those with the largest projection of their polarization along the applied electric field. Indeed, the magnitude and the sign of the overall polarization in GaV₄Se₈ [P3] and GaMo₄S₈ [P6] have been demonstrated to be influenced by poling electric fields applied during the cooling process through the Jahn-Teller phase transition. Electric field strengths within the range of ±2 kV and ±10 kV were used for the two compounds, respectively. The poling experiments were performed by E. Ruff and K. Geirhos at the University of Augsburg. So far the domain population could not be altered below the temperature structural phase transition, due to leakage currents heating up the sample when applying larger electric fields. Therefore, the strict definition will be used throughout this thesis, referring to these lacunar spinels as pyroelectrics.

Pyroelectrics as well as ferroelectrics find numerous applications, among others, in heat sensors, non-linear electronic components, memory elements, electro-optical devices, piezoelectric transducers and actuators [134]. Furthermore, domain boundaries are interesting on their own due to their emergent functionalities [33, 135]. For instance, domain walls can host itinerant electrons, attracting a lot of attention recently for domain wall conductivity [136-140]. Particularly in GaV₄S₈, GaV₄Se₈ and GaMo₄S₈, the domain structure is expected to have a key impact on the magnetic properties of these materials. Most importantly, the rhombohedral axis in each pyroelectric domain determines the direction of the uniaxial magnetic anisotropy as well as the pattern of the DMI vectors. As a result, different magnetic phases may coexist in a multi-domain sample, depending on the strength and direction of the applied magnetic field with respect to the four polar axes. Moreover, as shown in section 2.2.3, the $C_{3v}$ symmetry gives rise to an orientational confinement of the skyrmion cores in each domain along the corresponding rhombohedral axis. Therefore the size of a rhombohedral domain sets an upper limit to the size of a consistent SkL in that domain. The experimental investigation of the domain structures arising upon the Jahn-Teller distortion in GaV₄S₈ and GaMo₄S₈ will be detailed in sections 5.3 and 8.1,
respectively.

3.2 Magnetic properties of lacunar spinels

According to temperature-dependent susceptibility measurements in lacunar spinels GaV$_4$S$_8$ [124, 150, 151] GaV$_4$Se$_8$ [P3] and GaMo$_4$S$_8$ [152], the high-temperature cubic phase is paramagnetic with a weak antiferromagnetic interaction between the S=1/2 cluster spins. The ferroorbital ordering at the Jahn-Teller temperature changes the character of the interaction to ferromagnetic. As a result, long-range magnetic ordering occurs at $T_C=13$ K, $18$ K and $20$ K in GaV$_4$S$_8$ [26, 124, 150], GaV$_4$Se$_8$ [P3] and GaMo$_4$S$_8$ [152-154], [P7], respectively. Since the orbitally-driven pyroelectricity sets in at higher temperature than the magnetic ordering, these compounds belong to the class of type-I multiferroics. In the following section, the magnetic phase diagram of GaV$_4$S$_8$, the first member of the lacunar spinel family studied by our group [26], will be introduced.

3.3 Magnetic phase diagram of GaV$_4$S$_8$

Earlier magnetization studies on single crystalline GaV$_4$S$_8$ samples performed by Nakamura et al. revealed the presence of low-field magnetization steps, associated with metamagnetic phase transitions below the ordering temperatures [99]. According to the unequivocal evidence collected by Kézsmárki et al. via magnetization, magnetic AFM and small-angle neutron scattering (SANS) experiments, these phases were identified with the cycloidal and the Néel-type skyrmion lattice phases [26]. Thereby, GaV$_4$S$_8$ has been demonstrated to be the first skyrmion host material with a non-chiral but polar symmetry, exhibiting a Néel-type skyrmion lattice phase as opposed to the Bloch-skyrmions in chiral helimagnets.

The magnetic phase diagram of GaV$_4$S$_8$ was explored based on magnetization measurements with the magnetic field applied along different high-symmetry crystallographic axes of the crystal, namely $H \parallel [111]$, [001] and [110], as displayed in Figs. 3.3 (a)-(c), respectively [26]. The critical fields of the phase transitions were identified as anomalies in the differential susceptibility curves.

As a result of the multi-domain nature of the lacunar spinel crystals, besides the strength of the applied field, the critical field values of the phase transitions depend on the relative direction of the field and the polar axes, specific to the different structural domains. The anomalies associated to the
critical fields of all the four coexisting rhombohedral domains are superimposed in the individual magnetization curves.

For instance in the $H \parallel [111]$ configuration [Fig. 3.3 (a)], the magnetic field is parallel to the rhombohedral axis in the unique [111] domain, whereas it encloses 70.9° with the rhombohedral axis of the other three domains. On the other hand, when $H \parallel [001]$ [Fig. 3.3 (b)], all the four polar axes span 54.7° with the direction of the magnetic field, thus they are indistinguishable by magnetization measurements, i.e. the magnetic phase transitions occur at the same critical fields in all the four domains. In the third configuration with $H \parallel [110]$ [Fig. 3.3 (c)], two of the rhombohedral axes span 35.3° with the direction of the magnetic field, while two others axes are perpendicular to the field.

![Figure 3.3: Relative orientations of the magnetic field and the four rhombohedral axes. The (111)-type rhombohedral axes are displayed as the body diagonals of the cube. The different coloring of the rhombohedral axes (blue and red) indicate the different angles spanned by the magnetic field and the polar axes. The angles spanned by the rhombohedral axes and the magnetic field are listed below the drawings using the respective colors.](image)

In all these configurations, the critical fields of the phase transitions in each specific domain may be uniquely characterized by the strength of the critical field $H_c$ and the angle $\alpha$ spanned by the magnetic field and the rhombohedral axis in that domain. Note that the in-plane component of the magnetic field normal to the rhombohedral axes are in all these cases equivalent directions within the domains characterized by the same $\alpha$ values.

Kézsmárki and colleagues performed SANS experiments with magnetic field scans along the same directions to identify the contributions of the different rhombohedral domains in the magnetization curve [26]. Their analysis of the rocking curves allowed for the separation of the SANS intensity
contributions coming from the different domains. Correlating the anomalies observed in the SANS intensity (domain selectively) and in the magnetization curves, they were able to associate the critical fields to the different types of domains [26].

Figures 3.4 (a)-(e) show the magnetic phase diagrams of GaV$_4$S$_8$ for various $\alpha$ angles spanned by the applied field and a the rhombohedral axis. Remarkably, the projections of the critical fields to the rhombohedral axes are nearly the same for each angle of the applied field, except for $\alpha$ close to $90^\circ$, where the SkL phase does not emerge. This is well demonstrated by the universal phase diagram, shown in Fig. 3.4 (f).

The magnetic phase diagram of GaV$_4$S$_8$ is fundamentally different from that in cubic helimagnets [79]. Owing to the specific combination of Lifshitz-invariants compatible with the $C_3v$ symmetry (see Eq. 2.11), a cycloidal spin structure (Cyc) emerges in zero magnetic field, which is transformed to a Néel-type skyrmion lattice (SkL) in moderate magnetic fields. Polarized neutron scattering experiments performed by S. Bordács and J.S. White [P5] provided firm evidence that the spiral magnetic ordering is indeed cycloidal, i.e. the magnetization rotates in the plane spanned by the rhombohedral axis and the modulation wavevector. Real-space imaging by mAFM as well as reciprocal-space SANS studies showed that the SkL is confined within the plane perpendicular to the rhombohedral axis, irrespective of the direction of the magnetic fields [26]. This lies in contrast with the cubic magnets, where the skyrmion cores align towards the magnetic field direction [79]. Stronger magnetic fields drive the modulated phases to a field-polarized ferromagnetic (FM) state. Due to the absence of the longitudinal conical state, the SkL phase extends to a relatively broader range of temperatures below the Curie-temperature, compared to that observed in cubic helimagnets, where the SkL phase is stabilized by thermal fluctuations close to $T_C$. On the other hand, uniquely in GaV$_4$S$_8$, the modulated phases are replaced by a ferromagnetic order (FM) below $T_{FM} = 5$K even in the absence of a magnetic field. The FM ground state is the consequence of the strong easy-axis anisotropy in GaV$_4$S$_8$ [82, 83]. In magnetic fields normal to the polar axis ($\alpha = 90^\circ$) a transverse conical state is established, persisting up to 200-900 mT, depending on the temperature, above which a field-polarized state sets in with the magnetization co-aligned with the field. Note that the FM state at low temperatures in zero or low magnetic fields represents a ferromagnetic ordering in each domain along the corresponding polar axis, equivalent to the magnetic easy axis. The field-polarized state emerges only in larger magnetic fields, not indicated in panels (a)-(d).

In addition to the spontaneous polarization induced by the orbital ordering, it has been shown in GaV$_4$S$_8$ [27] and GaV$_4$Se$_8$ [85], [P3,P4] that the
Figure 3.4: Panels (a)-(e): Magnetic phase diagram of GaV$_4$S$_8$ for various $\alpha$ angles enclosed by the applied field and the rhombohedral axis. Panel (f) displays the critical fields for $\mathbf{B} \parallel [111]$, $\mathbf{B} \parallel [110]$, and $\mathbf{B} \parallel [001]$, projected to the rhombohedral axes, revealing a unique phase diagram. This picture breaks down for angles close to 90°, where the SkL phase does not emerge.
emerging Cyc, SkL and FM phases carry an excess magnetoelectric polarization, generated by an anisotropic exchange striction mechanism. This excess polarization enables the exploration of the magnetic phase diagram through magnetocurrent and pyrocurrent measurements as well. Moreover, the multiferroic nature of the magnetic skyrmions may enable their manipulation via electric fields instead of electric currents, further reducing the energy cost of the storage and transport of the information encoded in skyrmions.
Chapter 4

Experimental tools to study mesoscale structures

In this chapter, I briefly introduce the measurement techniques employed in my research for the study of the structural, and magnetic properties of the lacunar spinel compounds. Piezoresponse force microscopy was utilized for the imaging of ferroelastic and pyroelectric domains. The magnetic structures and the phase diagram was investigated by bulk magnetization measurements together with SANS experiments. In case of GaV$_4$S$_8$ complementary magnetic AFM measurements were performed for the real-space visualization of the spin textures. The magnetoelectric polarization was studied in GaV$_4$Se$_8$ via pyrocurent and magnetocurrent measurements.

4.1 Scanning Probe Microscopy

Scanning probe microscopy (SPM) broadly refers to the class of measurement techniques, where the surface of a sample is scanned over by an atomically sharp tip mounted onto the end of a cantilever [87]. The imaging is performed through the monitoring of the interactions arising between the sample and the tip, where the lateral resolution of the imaging can reach the sub-nanometer level.

The real-space imaging experiments using SPM in GaV$_4$S$_8$ [P1] were performed in Dresden in collaboration with researchers of the Institute of Applied Physics at the Technical University of Dresden and Helmholtz-Zentrum Dresden-Rossendorf (HZDR). The laboratory at HZDR features a custom-made low-temperature SPM microscope (attocube-systems$^{TM}$) with an interferometric cantilever detection. A similar system is located at TU Dresden, where previous real-space magnetic imaging studies were performed on
GaV\textsubscript{4}S\textsubscript{8} along with ongoing experiments on GaMo\textsubscript{4}S\textsubscript{8} and GaV\textsubscript{4}Se\textsubscript{8}. In the following, the specific features of these systems will be described.

4.1.1 Atomic Force Microscopy

Scanning-probe measurements in which the sample surface topography is mapped through the van der Waals interactions between the sample and the tip are termed as atomic force microscopy (AFM). In our measurements, two complementary modes of operation were used: the contact and non-contact modes. In contact mode, the tip is brought in contact with the sample surface, i.e. in the distance regime, where forces between the tip and the surface become repulsive [88]. The deflection of the tip along the z direction, normal to the surface, is monitored by a laser interferometer as the sample is moved laterally by a piezo tube scanner under the tip, thus recovering the \( h(x, y) \) topography map of the scanned surface area.

In non-contact mode methodologies the tip is lifted from the sample to distances where it is sensitive only to long-ranged intermolecular interactions with the surface [88]. The cantilever is resonated via a piezo oscillator at its eigenfrequency, which is affected by the tip-surface interaction. The drive frequency is then tuned via a phase-locked loop to keep the oscillation on resonance, while the shift of the drive frequency, \( \Delta f(x, y) \) is recorded. At the same time, the oscillation amplitude of the cantilever \( A \) is kept constant, by adjusting the excitation amplitude of the piezo drive \( A_{\text{exc}} \). The dissipated power, \( P(x, y) \) is monitored by calculating:

\[
P(x, y) = \frac{\pi k f R_0 A}{Q_{\text{eff}}} A_{\text{exc}},
\]

where \( k \) is the spring constant of the cantilever, \( f \) is the resonance frequency, \( Q_{\text{eff}} \) is the effective quality factor and the \( R_0 \) is the signal-to-drive ratio far away from the sample [26].

AFM instruments are often equipped with further functionalities, making them sensitive to other force fields, thus enabling them to map the electric charge distribution, piezoelectric constant, electric polarization or the magnetization patterns over a sample surface. Specifically, magnetic AFM (mAFM) and piezoresponse force microscopy (PFM) were used to explore the magnetic and pyroelectric structures in lacunar spinels, respectively [P1]. These techniques are described in details below.
4.1.2 Magnetic Force Microscopy

In order to map the magnetic structures on the sample surface, a magnetized tip is utilized in non-contact mode and the shift in the resonance frequency of the cantilever, \( \Delta f(x, y) \), is monitored. Owing to the long-range of the magnetic dipolar interaction, the magnetic pattern over the surface can be measured in a distance where van der Waals forces are negligible, thus excluding the interplay of topographic features. This method is referred to as magnetic force microscopy (MFM), which has been applied to visualize magnetic skyrmions and their evolution under various fields e.g. in \( \text{Fe}_{1-x}\text{Co}_x\text{Si} \) [24]. The magnetic structures were also investigated in \( \text{GaV}_4\text{S}_8 \), however their signature appeared in the dissipation channel, \( P(x, y) \) in the non-contact mode AFM rather than in the frequency shift [26]. The imaging based on the dissipation caused by the magnetic interactions in the non-contact AFM signal will be referred to as magnetic AFM (mAFM).

4.1.3 Piezoresponse Force Microscopy

In piezoelectric materials an electric polarization is induced by applying mechanical stress, or conversely, mechanical deformation is induced by applying an electric field. This latter is termed the converse piezoelectric effect, which is probed by PFM [89, 90].

In PFM measurements a conducting tip is brought in contact with the sample. While a standard contact-mode AFM scan is performed, an ac modulating voltage is applied between the tip and a bottom electrode below the sample. As a response to the oscillating electric field, the sample surface is periodically distorted owing to the converse piezoelectric effect. The out-of-plane component of the induced surface distortion is measured through the interferometric monitoring of the deflection of the tip. The PFM signal is separated from the topographic AFM by lock-in demodulation, obtaining the spatial dependence of the voltage-driven ac-deformation perpendicular to the surface, i.e. \( \varepsilon_{zz}(x, y) \), in a phase sensitive manner. A schematic image of the measurement setup is presented in Fig. 4.1. From the spatial variations in the magnitude and phase of the measured PFM signal, the spatial dependence of the out-of-plane component of the converse piezoelectric tensor can be determined over the scanned surface:

\[
\varepsilon_{zz} = d_{33}E_z,
\]

where \( d_{33} \) is the \( d_{zzz} \) component of the converse piezoelectric tensor in the Voigt-notation and \( E_z \) is the electric field component normal to the surface, close to the apex of the tip. In practice, the electric field is not exactly
Figure 4.1: A schematic layout of the PFM setup. An idealized measurement on a ferroelectric sample with opposite polarization domains is shown in the graphs at the bottom. The amplitude of the piezoelectric deformation is the same, however its phase with respect to the ac electric field varies by $\pi$ from domain to domain, as $d_{33}(P) = -d_{33}(-P)$.

vertical and other off-diagonal elements of the piezoresponse tensor, $d_{33x}$ and $d_{33y}$ may contribute to the vertical displacement of the tip as well.

Piezoelectricity is allowed by symmetry in crystals lacking an inversion center. There are 20 piezoelectric crystal classes [91], out of which 10 classes are also polar [92], in which a spontaneous pyroelectric polarization may emerge. Pyroelectric crystals wherein the electric polarization can be flipped by an external field are characterized as ferroelectrics. PFM is most typically applied for the nanometric mapping of the domain structure in single crystalline ferroelectrics such as BiFeO$_3$ [93, 94] and BaTiO$_3$ [95, 96] as well as in piezoceramics like lead zirconate titanate (PZT) [97, 98].

Ferroelectric domains with antiparallel electric polarization are connected by the space-inversion operation. Following Neumann’s principle, the piezoresponse tensor components probed by PFM have an opposite sign in the two domains: $d_{33}(P) = -d_{33}(-P)$. Consequently, in a PFM measurement the two type of domains are deformed with the same magnitude but in opposite directions, resulting in a $180^\circ$ phase shift in the detected signal (see Fig.4.1).

In my work, I employed PFM to explore and characterize the structural domain patterns arising upon the ferroelastic and pyroelectric phase transi-
tion in GaV$_4$S$_8$ [P1]. Commercial platinum-iridium coated silicon tips with a tip radius of about 30 nm were used for the experiments. The applied ac voltage was ±5V at a frequency of 22.3kHz.

4.1.4 Kelvin Probe Force Microscopy

The SPM instruments in the laboratories at TU Dresden and HZDR allow for the local measurement of the work function of the sample, via monitoring the contact potential difference, $U_{CPD}$ arising between the sample and the tip in a non-contact mode AFM measurement. This functionality is referred to as Kelvin probe force microscopy (KPFM), which is often employed to map the spatial variation of the surface potential e.g. due to charged domain walls [P6]. For the sensitive measurement of the surface potential of the sample, the voltage applied between the sample and the tip is modulated with a frequency of $f_{mod}$ and an amplitude of $u_{mod}$. The electrostatic force arising between the sample and the tip reads as:

$$F_{el} = \frac{1}{2} \frac{\partial C}{\partial z} \left[ U_{CPD} - U_{dc} + u_{mod} \sin (2\pi f_{mod} t) \right]^2,$$

(4.3)

where $\partial C/\partial z$ is the partial derivative of the sample-tip capacitance, with respect to their distance and $U_{dc}$ is an additional bias voltage applied between the sample and the tip. Via the lock-in detection of the force acting on the AFM tip at the modulation frequency allows for the measurement of the contact potential difference, whereas the second harmonic signal provides information on the spatial variation of the local capacitance:

$$F_{1f} = \frac{\partial C}{\partial d} (U_{CPD} - U_{dc})u_{mod} \sin (2\pi f_{mod} t)$$

(4.4a)

$$F_{2f} = \frac{1}{4} \frac{\partial C}{\partial d^2} u_{mod}^2 \cos (2\pi 2f_{mod} t)$$

(4.4b)

Note that in PFM mode, where the modulation scheme is applied to measure the piezoresponse of the sample, an uniform baseline signal originating from the contact potential difference between the sample and the tip can be eliminated by an appropriate bias voltage, $U_{dc} = U_{CPD}$, according to Eq. 4.4a.
4.2 Magnetization and ac susceptibility measurements

The measurement of static magnetization and/or magnetic susceptibility has become a primary methodology to reveal the phase transitions between the modulated magnetic states in non-centrosymmetric magnets [26, 47, 48, 79, 99, 100]. Metamagnetic transitions are typically observed as anomalies in the magnetization as the magnetic field or the temperature is varied. The magnetic phase diagram over the magnetic-field versus temperature plane is mapped by measuring the magnetization of the sample as a function of the magnetic field at various temperatures, or conversely, against the temperature in various external magnetic fields. The critical magnetic fields and temperatures associated to phase transitions are indicated by steps or cusps in the magnetization. Magnetization measurements offer a fast and straightforward means of locating the magnetic phase boundaries, nevertheless, this methodology alone does not provide any information on the nature and structure of the neighboring phases.

The magnetization and susceptibility measurements on the lacunar spinel crystals [P2] were performed by a 5 T Magnetic Property Measurement System (MPMS) manufactured by Quantum Design in the Wigner Research Centre for Physics, Institute for Solid State Physics and Optics with the technical guidance of Dr. L.F. Kiss. In this system, the magnetic field is generated by a 5 T superconducting magnet. The temperature of the sample space can be controlled in the range of 2 K to 400 K to perform magnetization and susceptibility measurements as the function of the temperature.

4.2.1 Static magnetization and susceptibility measurements

Magnetization curves, \( M(H) \) are obtained by recording the static magnetization upon the stepwise variation of the applied magnetic field. A longitudinal pickup coil was used in my experiments, which is sensitive only to the longitudinal magnetic moment, i.e. the magnetization component parallel to the applied field. The static susceptibility is calculated as:

\[
\chi_{dc} = \frac{\partial M}{\partial H} \approx \frac{\Delta M}{\Delta H} \tag{4.5}
\]

where \( M \) denotes the longitudinal component of the volume magnetization density, and its derivative with respect to the magnetic field is approximated with numerical differentiation.
4.2.2 ac-susceptibility measurements

The MPMS instrument is equipped with an ac modulation coil located around the sample, enabling the application of a small modulation field of $\mu_0 H_\omega = 0.1 - 0.5 \text{mT}$ in addition to the static field generated by the superconducting magnet. Applicable modulation frequencies range from $f = 0.1 \text{Hz}$ to $f = 1 \text{kHz}$. The sample position is fixed at the center height of the detection coil. The SQUID output is measured phase sensitively with regard to the ac modulation signal by a lock-in amplifier. The real and imaginary parts of the ac-susceptibility, $\chi'(\omega)$ and $\chi''(\omega)$, are respectively obtained by normalizing the in-phase ($M'$) and out-of-phase components ($M''$) of the magnetization with the drive amplitude, $H_\omega$:

$$
\chi(\omega) = \chi'(\omega) - i\chi''(\omega) = \frac{M'(\omega)}{H_\omega} - i\frac{M''(\omega)}{H_\omega}.
$$

(4.6)

Ac-susceptibility measurements provide insight into the frequency dependence of slow magnetic relaxational processes \[103\], emerging in systems with a large number of correlated spins, such as superparamagnetic nanoparticles \[104\] and spin glasses \[105\]. This technique has been frequently used to establish magnetic phase boundaries in skyrmionic systems as well \[47, 100, 106\]. Moreover, a frequency dependence of the ac susceptibility in such systems was observed, suggesting the emergence of slow relaxational processes associated to the rearrangement of modulated magnetic structures \[79, 100, 107-110\]. In my study, ac-susceptibility measurements were performed to investigate the slow relaxation dynamics emerging near the phase transitions between the complex modulated magnetic phases in GaV$_4$S$_8$ \[P2\], as discussed in Section 6.2.

4.3 Polarization measurements

Lacunar spinels belong to the group of type-I multiferroics, that is they exhibit a magnetic order within the pre-existing pyroelectric phase, where the electric and magnetic degrees of freedom are interconnected. Therefore the polarization induced upon the structural as well as the magnetic phase transitions can be measured by pyrocurrent and magnetocurrent measurements. Moreover, these measurements allow for the determination of the critical temperatures and critical magnetic fields of these phase transitions \[27\].

In polarization measurements the temperature or the magnetic field is changed over time, inducing a change in the electric polarization $P$ in the
material, which generates a displacement current in the sample:

\[ j_d = \frac{\partial P}{\partial t}. \]  

(4.7)

This current is measured through an electric connection between two parallel faces of the sample. The normal component of the polarization with respect to the sample surface is obtained by integrating the current over time:

\[ P_{\perp}(t) = P_{\perp}^0 + \int_{t_0}^{t} j_d(t') A \, dt', \]  

(4.8)

where the two parallel and flat crystal surfaces have a surface area of \( A \).

I performed polarization measurements on GaV₄Se₈ in the Solid State Physics Laboratory at BME Department of Physics. The sample was mounted onto a temperature-controlled sample holder and placed into a helium-cooled Oxford cryostat, equipped by a 17 T superconducting magnet. Electric currents below the picoampere range were measured by a Femto DLPCA-200 current amplifier connected to a Keithley 2001 voltmeter. I used an n-doped Si platelet as a Hall-sensor placed next to the sample to access the magnetic field during field-sweeps to account for the demagnetizing fields of eddy currents induced in the sample tube. The calibration of the Hall-sensor was performed in static magnetic fields prior to field-sweeps at each temperature. The measurement control, data acquisition, noise filtering of the sub-picometer current signals and the on-line evaluation of the polarization was performed by a custom-designed measurement software.

4.4 Small-angle Neutron Scattering

As a complementary tool to real-space microscopic techniques, periodic magnetic structures with wavelengths in the nanometer regime can be investigated by the means of SANS. Contrary to surface scanning microscopies, SANS is a bulk sensitive technique, probing the magnetic structures in the reciprocal space, i.e. the Fourier-transform of the spin pair-correlation function is measured [75]. SANS is a powerful technique, widely employed to investigate magnetic structures ranging from superconducting vortices [111, 112] to incommensurate helical spin structures [113] and most recently, skyrmionic structures [26, 29, 45, 48]. In the following, I briefly review the basic theory of unpolarized magnetic SANS and its experimental realization. In this discussion, I shall focus on the magnetic interaction and exclude nuclear scattering, which may have an equally large contribution to the scattering cross section. Experimentally, the structural scattering peaks were eliminated in
our experiments by subtracting the background measured in the isostructural paramagnetic phase.

In elastic neutron scattering the differential cross section is given by [75]:

\[
\left( \frac{d\sigma}{d\Omega} \right)_{el} = \left( \frac{m_n}{2\pi\hbar^2} \right)^2 |\langle k'\lambda'_n\lambda'_e|V(r)|k\lambda_n\lambda_e\rangle|^2, \tag{4.9}
\]

where \(m_n\) denotes the mass of the neutron, and the matrix element describes the scattering of the neutron beam on the potential \(V(r)\) with wavevectors \(k\) and \(k'\) in the incident and final state, respectively. The initial spin states of the neutron and the electron system are denoted with \(\lambda_n\) and \(\lambda_e\), whereas their final states are labeled by \(\lambda'_n\) and \(\lambda'_e\), respectively. Expressing the scattering matrix element explicitly using the magnetic potential of a neutron carrying \(\mu_n\) magnetic moment yields:

\[
\langle k'|V(r)|k \rangle = \int d^3r V(r) e^{i(k-k')r} = -\mu_n \int d^3r B(r) e^{iqr}, \tag{4.10}
\]

where \(q = k - k'\) is the momentum transfer vector, and \(\mu_n = -\gamma e\hbar\sigma\). Here, \(\sigma\) is the Pauli spin operator and \(\gamma = 1.913\). The \(B(r)\) magnetic field of the electron system described by a continuous magnetization density, \(M(r)\), reads as [114]:

\[
B(r) = \frac{\mu_0}{4\pi} \nabla \times \int d^3r' M'(r') \frac{r - r'}{|r - r'|^3}. \tag{4.11}
\]

The Fourier transform in Eq. 4.10 leads to:

\[
\langle k'|V(r)|k \rangle = -\mu_0 \mu_n \frac{q \times [M(q) \times q]}{q^2} = \mu_0 \gamma \frac{e\hbar}{2m_n} \sigma M^\perp(q), \tag{4.12}
\]

where \(\mu_0\) is the vacuum permeability, \(e\) is the electron charge, \(M(q) = \int d^3r M(r)e^{iqr}\) is the Fourier transform of the magnetization density, and \(M^\perp(q)\) is its component normal to the momentum transfer vector, \(q\). This result shows that due to the anisotropic nature of the dipolar interaction, magnetic neutron scattering is only sensitive to spatial modulations in the magnetization components perpendicular to their corresponding \(q\) wavevectors. In order to calculate the differential cross section of the unpolarized SANS performed in my experiments, the matrix element in 4.10 has to be summed over the final states of the electronic and neutron spins, and averaged over their initial spin states. For the detailed calculation I refer to
The following textbooks: [75, 115]. The elastic scattering cross section for unpolarized neutrons reads as:

$$\left( \frac{d\sigma}{d\Omega} \right)_{el} = \left( \frac{\mu_0 \gamma e}{4\pi \hbar} \right)^2 |M_{\perp}(q)|^2.$$  \hspace{1cm} \text{(4.13)}

### 4.4.1 Sample rocking

In an elastic scattering experiment the well-known Ewald’s construction [75, 116] can be used to determine the orientation of the sample when the Bragg condition is satisfied, i.e. when the scattering vector \( q = k - k' \). Figure 4.2 (a) presents a case, where the magnetic modulation vectors in the sample, \( q_1 \) and \( q_2 \), are located in a plane perpendicular to the incoming neutron beam. If an infinite correlation length is assumed, scattering with the moment transfer vectors \( q_1 \) and \( q_2 \) is strictly forbidden by the conservation of energy. Even in a real sample, where the finite correlation lengths lead to a broadening of the Bragg peaks, the scattered intensity decreases for a normal incidence of the neutron beam to the moment transfer vectors. Therefore, in typical SANS experiments the sample is rotated step-by-step around the vertical \((y)\) and the horizontal \((x)\) axes, and in each step the intensity is collected. This method is called sample rocking and the intensity of the scattered peaks as a function of the rocking angle is referred to as a rocking curve. The 'TILT' or 'PHI' angles refer to the azimuthal rocking angle of the sample (Fig. 4.2 (b)), depending on the neutron facility, whereas 'SAN' refers to the polar rocking angle (Fig. 4.2 (c)).

### 4.4.2 The SANS instrument

The SANS experiments on lacunar spinel crystals were performed at Institute Laue-Langevin (ILL) using the D33 and D11 instruments [P5], the Swiss Spallation Neutron Source (SINQ) facility at Paul-Scherrer Institute (PSI) [P4,P5], and the High-Flux Isotope Reactor (HFIR) at Oak-Ridge National Laboratory (ORNL) using the General-Purpose Small-Angle Neutron Scattering Diffractometer (GP-SANS) [P7]. In the following, the general setup of a SANS experiment is discussed on the example of the D11 instrument. A schematic layout of the D11 instrument is presented in Fig. 4.3 (a) [117]. Neutrons are produced from the fission of uranium in a high-flux research reactor. In the cold deuterium source, the neutrons are thermalized to \( \sim 20 \) K in order to have high-flux at long wavelengths, with a Maxwell-Boltzmann distribution around \( \sim 6.9 \) Å, necessary for SANS experiments. A monochromatic beam for neutron diffraction experiments is selected from the wider
Figure 4.2: Ewald’s sphere and sample rocking in elastic neutron scattering experiments. Figure (a) presents the Ewald sphere, i.e. the set of possible scattering wavevectors that fulfill the conservation of energy. If the modulation wavevectors in the sample do not match the Ewald sphere, no scattered intensity is observed on the detector. Figure (b): matching of $\mathbf{q}_1$ wave vector to the Ewald sphere by sample rocking around the y-axis (SAN-rocking). Figure (c): matching of $\mathbf{q}_2$ wave vector to the Ewald sphere by sample rocking around the x-axis (PHI- or TILT-rocking).
spectrum by a rotating velocity selector. Preferentially, $\lambda_n \approx 4-6\,\text{Å}$ is used with $\delta\lambda/\lambda = 10\%$ precision close to the maximum of the Maxwell-Boltzmann distribution of the neutron energies. The beam is guided through a set of collimators and diaphragms before hitting the sample in order to reduce the divergence of the beam, $\delta\theta$, on the expense of the beam intensity. Since the periodicities of the magnetic structures of our interest are in the $\lambda_s \approx 10^{-20}\,\text{nm}$ range corresponding to $|q| = 0.03 - 0.06\,\text{Å}^{-1}$ [26], the scattering angles are expected to be small ($\theta \approx |q|/k \approx 2^\circ$).

The scattered intensity is measured by a 96 cm x 96 cm $^3$He gas pixel detector with a resolution of 128x128 pixels, which can be displaced from 1.2 m to 40 m from the sample, allowing for the measurement of momentum transfer vectors within the range of $7 \cdot 10^{-3} - 0.7\,\text{Å}^{-1}$. As a rule of thumb, the collimation length is selected to be equal to the sample-detector distance for an optimal tradeoff between the flux and resolution [117]. The $q$-resolution of the instrument is determined by the spectral linewidth of the neutrons and the angular divergence of the beam, as follows:

$$\frac{\Delta q}{q} = \left[ \left( \frac{\Delta \lambda}{\lambda} \right)^2 + \left( \frac{\Delta \theta}{\theta} \right)^2 \right]^{1/2}$$

Figure 4.3: Panel (a): layout of the D11 SANS instrument at ILL [117]. Panel (b): a photo of the sample cryostat taken at the D33 instrument at ILL.

The sample mounted at the end of the sample stick is inserted into the cryostat equipped with a 2.5 T horizontal-axis superconducting Helmholtz-magnet, as shown in Fig. 4.3 (b). The magnetic field can be set either parallel or perpendicular to the incoming neutron beam. The sapphire windows of the cryostat provide neutron access to the sample within a $10^\circ$ cone. The cryostat is fixed on the top of a goniometer, allowing for the polar and azimuthal rocking of the sample together with the whole cryostat-magnet system. The
side windows on the cryostat enable the magnet to be rotated by 90° with respect to the neutron beam. The sample stick can be rotated by a motorized rotation stage in the full 360° range around the vertical axis, independently from the magnet. This rotation angle is referred to as DOM/ROT/OMEGA angle in the different facilities.

The specifications of the SANS instruments used throughout my research are summarized in Table 4.1.

<table>
<thead>
<tr>
<th>Facility</th>
<th>Neutron wavelength [Å]</th>
<th>Detector distance [m]</th>
<th>Detector size [cm x cm]</th>
<th>Detector resolution [px]</th>
<th>Momentum transfer range [Å⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ILL D11</td>
<td>4.5-40</td>
<td>1.2-40</td>
<td>98x98</td>
<td>128x128</td>
<td>3·10⁻⁴–1</td>
</tr>
<tr>
<td>ILL D33</td>
<td>4.5-40</td>
<td>1.2-12.8</td>
<td>64x64</td>
<td>128x128</td>
<td>7·10⁻³–0.7</td>
</tr>
<tr>
<td>PSI</td>
<td>4.5-40</td>
<td>1.4-20</td>
<td>96x96</td>
<td>128x128</td>
<td>6·10⁻⁴–0.54</td>
</tr>
<tr>
<td>ORNL GP-SANS</td>
<td>4-20</td>
<td>1-20</td>
<td>100x100</td>
<td>192x250</td>
<td>7·10⁻⁴–1</td>
</tr>
</tbody>
</table>

Table 4.1: Specifications of the SANS instruments used in the investigations of magnetic structures in lacunar spinels.

During my studies, I performed SANS experiments to gain a deeper understanding of the reciprocal-space structure of the cycloidal modulations in GaV₄S₈ and to investigate their redistribution under in-plane magnetic fields [P5]. Furthermore, I analyzed SANS data on GaV₄Se₈ to identify the magnetic phases associated to the phase diagram determined by magnetization measurements [P4]. Finally, I performed experiments on GaMo₄S₈ to study the structure of the magnetic modulations in this material [P7].
Chapter 5

Structural phase transition and the pyroelectric domain structure in lacunar spinels

In this chapter, I investigate the structural properties of GaV$_4$S$_8$. As suggested in section 3.1, the characteristic size and arrangement of the rhombohedral structural domains may have a significant impact on the modulated magnetic textures in lacunar spinel crystals, owing to their anisotropic nature. In order to explore the pyroelectric and ferroelastic domain structure arising upon the Jahn-Teller transition in GaV$_4$S$_8$, I performed contact-AFM and PFM measurements with the cryo-AFM setup developed and operated by our collaborators at Helmholtz-Zentrum Dresden [96, 118],[P8]. The AFM and PFM measurement methodology is described in Section 4.1.3. The out-of-plane PFM measurements were carried out on as-grown (100) and (111) surfaces of GaV$_4$S$_8$ crystals.

This chapter is organized as follows. First I briefly review the theory of pyroelectric domain formation and the emergence of lamellar domain patterns in pyro- and ferroelectrics, drawing conclusions for the particular case of the lacunar spinels. Then, I examine the symmetry-allowed piezoelectric tensor elements in the different polar domains of the lacunar spinel crystals, probed by the PFM measurements in order to predict their PFM contrast. Finally, I present my AFM and PFM measurements on GaV$_4$S$_8$ and discuss the results in light of the above theoretical considerations.
5.1 Formation of lamellar pyroelectric domain patterns

5.1.1 Compatibility conditions

In a pyroelectric crystal the energy minimum is realized as an equilibrium between the cost of domain wall formation and the gain through the reduction in the stray field with increasing number of domains coexisting in the material [133, 141]. The energy of the domain walls is minimized if their mechanical continuity and and electric neutrality is ensured. These requirements are formulated as a set of so-called compatibility equations [133].

Mechanical compatibility requires a stress-free domain boundary between the two regions with different distortion directions. Let the unit vectors $e_1$ and $e_2$ point along the axes of the different uniaxial distortions in two neighboring domains. The possible stress-free boundaries between the two distorted lattices are characterized by the surface normal vectors given by [141]:

$$n_{1,2} = \frac{e_1 \pm e_2}{\sqrt{2}}.$$  \hspace{1cm} (5.1)

The electric compatibility condition requires the surface boundary between the two pyroelectric domains to remain uncharged, i.e. $\nabla \cdot P = 0$ for any point of the boundary. This condition is satisfied if $(P_2 - P_1)n = 0$, that is the component of the polarization normal to the domain boundary is continuous through the domain wall. The electric compatibility condition selects either $n_1$ or $n_2$ (given in Eq. 5.1) as the energetically optimal solution, depending on the sign of the polarization vector along the direction of the distortion. The minimum-energy solutions between two pyroelectric domains in a polar rhombohedral crystal are schematically shown in Figs. 5.1 (a) and (b). The pyroelectric domain boundaries are generally characterized by the angle spanned by the two polarization vectors in the neighboring domains. According to the solutions of the compatibility equations, in a polar rhombohedral crystal, $109^\circ$ polarization domains are separated by domain walls that are normal to the $\langle 100 \rangle$-type directions, whereas $71^\circ$ domain walls are expected to be normal to the $\langle 110 \rangle$-type vectors in the cubic setting. Note that $71^\circ$ polarization domains belong to the two different inversion domains of the lacunar spinel structure, therefore they are not expected to emerge in an inversion mono-domain region of the sample. For the same reason, the emergence of $180^\circ$ domain boundaries is excluded as well. Conclusively, the stress-free and uncharged polar domain walls emerging upon the structural phase transition in inversion mono-domain regions of the lacunar spinel.
crystals are necessarily \{100\}-type planes.

![Figure 5.1: Mechanical and electric compatibility in a polar rhombohedral crystal. Both compatibility criteria are satisfied for domain walls with \(n_1 \parallel \langle 100 \rangle\)-type normal vectors between 109° polarization domains, as shown in panel (a), and \(n_2 \parallel \langle 110 \rangle\) normal vector between 71° polarization domains, as depicted in panel (b). Note that such neighboring domains, whose polarizations span 71°, belong to the two different inversion domains of the lacunar spinel structure, therefore these type of domain walls are not expected to emerge in an inversion mono-domain sample region.](image)

5.1.2 Formation of lamellar domain patterns

Owing to the orientational confinement of the compatible pyroelectric domain walls, the arising pyroelectric domains often organize into a lamellar structure constituted by pairs of alternating domains with parallel boundaries [141, 142]. Such a lamellar pattern is presented in Fig. 5.2 (b). The (111) section of the domain pattern is also shown in the figure. Note that the apparent distance between the domain walls in the (111) cross section is larger by a factor of \(\sqrt{6}/2\) than the actual width of the domains with (100)-type boundaries.

In real pyro- and ferroelectrics, the domain growth may give rise to secondary domain boundaries, where two sets of alternating domain pairs intersect. Figure 5.2 (c) demonstrates the only fully (microscopically) compatible
configuration for each boundary within a secondary domain structure. As a consequence, a single secondary interface between a pair of alternating domains and a uniform rhombohedral domain cannot be fully compatible. However, in a real crystal the multigrain formation of the structural domains may lead to the emergence of locally incompatible domain walls, where the compatibility is satisfied only on average along the larger secondary (or higher-order) domain boundaries ensuring that the electrostatic and elastic energy is reduced in a larger, macroscopic scale [141].

![Figure 5.2: Possible lamellar pyroelectric domain structures in lacunar spinels. Panel (a): The four possible polarization directions, represented by different colors. Panel (b): A pair of alternating domains with polarizations of \([1\bar{1}1]\) and \([\bar{1}1\bar{1}]\). These two domains are separated by compatible domain walls normal to the \([100]\) direction. The figure also shows the \((111)\) section of the same pattern and the corresponding in-plane directions for comparison with PFM measurements on the \((111)\) surface. Note that the apparent width of the domains is increased by a factor of \(\sqrt{6}/2\) in the \((111)\) cross section as compared to the real distance between the parallel \((001)\)-type surfaces. Panel (c): The unique compatible configuration of a secondary domain wall comprising all the four rhombohedral domains.](image)
5.2 PFM contrast between the rhombohedral domains

The contrast between the polar domains observable by PFM measurements performed on the (100) as well as the (111) surface can be predicted on a symmetry basis, both in the high-temperature cubic phase and the low-temperature rhombohedral phase of lacunar spinels. The summary of my symmetry analysis is given below, while the details of the calculation are included in the Appendix A.2. The probed surface in the cubic setting is indicated in the superscript of the converse piezoresponse tensor components. The probed element of the tensor is denoted by the first subscript. The second subscript 'c' and 'r' stands for the cubic, and rhombohedral phases of the compound, respectively:

- \( T > T_s \), Cubic phase, PFM on the (001) surface: \( d_{zzz}^{(001)} = 0 \), no contrast
- \( T > T_s \), Cubic phase, PFM on the (111) surface:
  \[ d_{zzz,c}^{(111)} = d_{xyz,c}^{(001)} = \begin{cases} d & \text{for the inversion domain A} \\ -d & \text{for the inversion domain B.} \end{cases} \] (5.2)
- \( T < T_s \), Rhombohedral phase, PFM on the (100) surface within a single inversion domain, A:
  \[ d_{zzz,r}^{(001)} = \begin{cases} d_1 & \text{for domains [111] and [\overline{1}\overline{1}\overline{1}]} \\ -d_1 & \text{for domains [1\overline{1}\overline{1}] and [\overline{1}\overline{1}\overline{1}]} \end{cases} \] (5.3)
- \( T < T_s \), Rhombohedral phase, PFM on the (111) surface within a single inversion domain, A:
  \[ d_{zzz,r}^{(111)} = \begin{cases} \sqrt{3}/3 \left[ 2d_0 + (d_1 + 2d_2 + 4d_3) \right] , & \text{for domain [111]} \\ \sqrt{3}/3 \left[ 2d_0 - 1/3(d_1 - 2d_2 - 4d_3) \right] , & \text{for domains [1\overline{1}\overline{1}], [\overline{1}1\overline{1}], [\overline{1}\overline{1}\overline{1}]} \end{cases} \] (5.4)

Here, the symmetry-allowed components of the converse piezoresponse tensor are denoted as \( d \), and \( \{d_0, d_1, d_2, d_3\} \) in the cubic and rhombohedral phases of the crystal, respectively. For details, see the Appendix A.2. Note that while on the (100) surface the PFM signal of the two sets of domains is symmetric to zero (Eq. 5.3), on the (111) plane the PFM signal, after
subtracting the common $2\sqrt{3}/3 \cdot d_0$ value, has a ratio of 3:-1 for the unique [111] domain and the three other domains. The negative sign in both cases represents a $180^\circ$ phase shift between the PFM response of the two sets of domains. It can be easily seen that for any pair of domains, the PFM contrast is proportional to the ratio of the electric polarization components in the two domains normal to the probed surface.

5.3 Mapping of the pyroelectric domain structure

The pyroelectric and ferroelastic domain structure of GaV$_4$S$_8$ was investigated using the as-grown (100) and (111) surfaces of single crystalline samples, shown in Fig. 5.3 (b)-(d). The GaV$_4$S$_8$ single crystals were grown via the chemical vapour transport method as reported in [26]. The typical dimensions of the cuboid-shaped crystals are 1-2mm. The high quality of the samples has been confirmed by X-ray diffraction and specific heat measurements. The high-symmetry directions within scanned surfaces were determined by visual inspection of the as-grown surfaces reflecting the symmetries of the crystal structure. I performed the PFM experiments at the HZDR institute in Dresden, together with S. Bordács and J. Döring, who operated the cryo-AFM instrument.

![Figure 5.3: GaV$_4$S$_8$ samples used for the PFM studies. The coordinate system determined by the antilever is shown in panel (a). Panels (b)-(d): Optical micrographs of the three different GaV$_4$S$_8$ single crystals used in the PFM study, i.e. #1 and #3 with (001) surfaces, and #2 with a well-developed (111) crystallographic surface. The typical dimensions of the cuboid-shaped crystals are approximately 1-2mm. The high-symmetry directions within the as-grown surfaces are indicated with reference to the x and y PFM scanning directions.](image-url)
Figures 5.4 and 5.5 show all the measurements where PFM contrast has been observed in the rhombohedral phase of GaV$_4$S$_8$. All images display the raw PFM amplitude data without any baseline correction. As expected, the contrast in the PFM emerges below the Jahn-Teller transition temperature, $T_S = 42$ K. The stripe patterns observed by the PFM correspond to a lamellar structure of the pyroelectric domains, in agreement with the theoretical expectations described in Section 5.1. The typical domain width has been determined by the 2d Fourier-transformation performed on the real-space PFM images, as $w_i = 2\pi/|k_i|$, where $|k_i|$ represents the locations of the dominant peaks in the Fourier-space image. In case of measurements on the (111) surface, the measured periodicities in the PFM image have been scaled down by a factor of $\sqrt{6}/2$ to obtain the actual domain spacings [see Fig. 5.2 (b)]. The typical domain widths range from 150 nm to 800 nm.

Static voltages up to $\pm 10$ V applied between the sample and the tip did not indicate any local polarization switching. Even though the ordered magnetic states were shown to carry sizable magnetoelectric polarization [27], the lateral resolution of the PFM measurement, approximately 50 nm, is not sufficient to resolve the polarization pattern accompanying the nanometric magnetic modulations.

### 5.3.1 Identification of the polar domains and the orientation of the domain walls

Owing to the non-centrosymmetric crystal structure of GaV$_4$S$_8$, inversion domains could coexist in the material even above the Jahn-Teller transition. However, PFM imaging on the {001}-type planes is not appropriate to detect inversion domains, as $d_{zzz,c}^{(001)} \neq 0$. This in accord with the structureless PFM images in Figs. 5.4 obtained at 50 K.

On the other hand, the $d_{zzz,c}^{(111)}$ component of the converse piezoelectric tensor is allowed by the F$\bar{4}$3m symmetry, having opposite signs for the two inversion domains, according to Eq. 5.2. Therefore, PFM measurements on the (111) plane could reveal the contrast between the two inversion domains above $T_S=42$ K. The vanishing PFM contrast in the high-temperature phase, however, suggests that the rhombohedral domains observed below $T_S$ belong to the same inversion domain. Indeed, none of the high-temperature measurements on the (111) surface revealed any sign of inversion domain boundaries (see Figs. 5.5). Hence, it is reasonable to assume that the domain size of a pure inversion domain is large as compared to the scanned area, possibly extending over the whole crystal.

All PFM images taken both on the (001) and the (111) planes of GaV$_4$S$_8$
<table>
<thead>
<tr>
<th>Sample Orientation</th>
<th>PFM amplitude</th>
<th>PFM amplitude</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rhombohedral Phase $T&lt;T_s$</td>
<td>Cubic Phase $T&gt;T_s$</td>
</tr>
<tr>
<td>Sample #1 (001)</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>$w=0.67 \mu m$</td>
<td>$w=0.70 \mu m$</td>
</tr>
<tr>
<td></td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>$w=0.65 \mu m$</td>
<td>$w=0.67 \mu m$</td>
</tr>
<tr>
<td>Sample #3 (001)</td>
<td><img src="image5" alt="Image" /></td>
<td><img src="image6" alt="Image" /></td>
</tr>
<tr>
<td></td>
<td>$w=0.43 \mu m$</td>
<td>$w=0.49 \mu m$</td>
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<tr>
<td></td>
<td><img src="image7" alt="Image" /></td>
<td><img src="image8" alt="Image" /></td>
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<tr>
<td></td>
<td>$w=0.49 \mu m$</td>
<td>$w=0.49 \mu m$</td>
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</table>

**Figure 5.4:** Collection of all PFM amplitude images measured on the (001) surface of GaV₄S₈ samples #1 and #3. Images in the same row correspond to subsequent PFM measurements over the same surface area of the crystal. Red rectangles represent the scanned area of the subsequent PFM image. PFM images in the cubic phase of the crystal are displayed in the right column. Typical values of the domain width, determined by the 2d-Fourier transformation of the PFM amplitude, are listed below the images.

reveal lamellar domain structures below the temperature of the structural transition. In case of the (001) surface of Sample #1 and Sample #3 (Fig. 5.4), the normal vectors of the observed domain walls correspond to a $\langle 10\xi \rangle$-type pseudocubic direction of the crystal, where the $\xi$ out-of-plane compo-
<table>
<thead>
<tr>
<th>Sample Orientation</th>
<th>PFM amplitude Rhombohedral Phase $T&lt;T_s$</th>
<th>PFM amplitude Cubic Phase $T&gt;T_s$</th>
</tr>
</thead>
</table>
| Sample #2<br>(111)<br>
Y [112]<br>[101]<br>X [110] | ![Image](image1.png)<br>$w_1 \approx 0.45 \mu m$
$w_2 \approx 0.21 \mu m$
$w_3 \approx 0.13 \mu m$ | ![Image](image2.png)<br>$w_1 \approx 0.45 \mu m$
$w_2 \approx 0.21 \mu m$
$w_3 \approx 0.13 \mu m$ |
| ![Image](image3.png)<br>$w_1 \approx 0.68 \mu m$
$w_2 \approx 0.45 \mu m$ | ![Image](image4.png)<br>$w \approx 0.8 \mu m$ |
| ![Image](image5.png)<br>$w_1 \approx 0.81 \mu m$
$w_2 \approx 0.22 \mu m$ | ![Image](image6.png)<br>$w_1 \approx 0.62 \mu m$
$w_2 \approx 0.14 \mu m$
$w_3 \approx 0.13 \mu m$
$w \approx 0.55 \mu m$ |

Figure 5.5: Collection of all PFM amplitude images measured on the (111) surface of GaV$_4$S$_8$ sample #2. Typical values of the domain widths, determined by the 2d-Fourier transformation of the PFM amplitude, are listed below the images. Note that the distances observed in the (111) surface are scaled down by a factor of $\sqrt{6}/2$ to obtain the width of the domains.
nent cannot be unambiguously determined from the measurement on this single surface. The case of $\xi = 0$, corresponding to $\{100\}$-type domain walls separating $109^\circ$ polarization domains, is consistent with the compatibility criteria. In this case, the alternation of $[111]$- and $[\bar{1}1\bar{1}]$-type or $[\bar{1}1\bar{1}]$- and $[\bar{1}1\bar{1}]$-type domains (the former shown in Fig. 5.2 (b)) can be attributed to the observed lamellar domain structures. The two domains in any of the above pairs produce a PFM contrast on the $(001)$ surface, according to Eq. 5.3. The measurement of the out-of-plane deformation does not allow for any further distinction between these two possible domain pairs.

In the PFM measurements on Sample #2, stripes parallel with the $\langle 1\bar{1}0 \rangle$-type edges of the triangle-shaped $(111)$ surface have been evidenced (Fig. 5.5). Such patterns can be interpreted as compatible domain walls parallel to the $(001)$ plane, intersected by the $(111)$ surface [as seen in Fig. 5.2 (b)]. The only pair of compatible domains providing PFM contrast on the $(111)$ plane is $[111]$ and $[\bar{1}1\bar{1}]$, as shown by Eq. 5.4.

Note that $\{110\}$-type domain walls, corresponding to $\xi = 1$, could also account for similar patterns both in the $(001)$ and $(111)$ planes. Although such domain walls would be mechanically compatible, assuming a single inversion domain, the polarization vectors in the $109^\circ$-domains would be arranged in a head-to-head or tail-to-tail configuration with respect to these walls, resulting in a surface charge over the domain walls. Considering the additional energy of the charged domain walls, this possibility is unlikely. Moreover, the lamellar structure of these rhombohedral domains indicates their formation upon the pyroelectric phase transition, and not during the crystal growth. This is in accord with the assumption that they belong to a single inversion domain. The present PFM experiments thus confirm that the primary structural domain walls in GaV$_4$S$_8$ are parallel to $\{100\}$-type planes, satisfying both the mechanical and electric compatibility criteria.

5.3.2 Incompatible domain walls

In some cases, a deviation from the planar $\{001\}$-type domain walls can be observed in Figs. 5.4 and 5.5. These irregular domain walls are typically found at secondary interfaces.

Figure 5.6 (a) reveals the boundary between an alternating lamellar structure and a uniform domain observed on the $(100)$ surface of Sample #1. Compatibility cannot hold between both domains of the alternating structure and the uniform domain along the same surface [see Fig. 5.2 (c)]. The formation of the observed needle-like domain endings is the consequence of mechanical stress and electrostatic repulsion induced at the incompatible domain walls [143].
Additionally, more complex domain patterns may arise as a manifestation of adjoining lamellae, as seen on the (111) surface of Sample #2 displayed in Fig. 5.6 (b). The domain walls that are not parallel to the {001}-type planes are likely to be charged. Indeed, recent PFM and KPFM measurements on GaMo$_4$S$_8$ imply that charged domain walls typically emerge in these materials at secondary interfaces, while the primary domain walls with larger surface areas are in general electrically neutral [P6].

![Figure 5.6: Panel (a): Transition of alternating domain pairs into a uniform domain in Sample #3. Panel (b): junction of two different lamellar structures observed in Sample #2. The matching of incompatible domains results in the deformation of the domain walls, producing needle-like endings, or irregular domain wall inclinations.](image)

5.3.3 Quantitative analysis of the piezoresponse

AFM and PFM imaging on the (001) surface

Typical AFM and PFM amplitude and phase micrographs recorded at the same position on the (001) plane of Sample #1 are shown in Figs. 5.7 (a)-(c) and (d)-(f) at $T = 50$ K and $T = 10$ K, respectively. The size of the scanned area is approximately $10 \mu m \times 10 \mu m$. The difference in the length scales at the two temperatures are due to the temperature-dependent response of the piezo actuator, which was calibrated at $T = 50$ K.

PFM images taken at $T = 10$ K, below the Jahn-Teller transition, reveal the presence of stripe domains, that were analyzed using both the amplitude and phase dependence of the PFM signal [see Figs. 5.7 (e) and (f), respectively]. The width of the pyroelectric domains ranges from 200 - 300 nm in
Figure 5.7: Simultaneous measurements of the AFM topography, PFM amplitude and PFM phase, performed above [panels (a)-(c)] and below [panels (d)-(f)] the temperature of the structural phase transition. All images stem from the same surface area on the (001) surface of Sample #1, as clearly seen from the topographic AFM pictures (a) and (d). The crystallographic directions are indicated in panel (f) according to Fig. 5.3 (b). The yellow dashed rectangle in panel (d) marks the area of the measurements presented in Fig 5.8.

The scanned region of the sample. Irregularities in the alternating domain structure are observed close to the center of the image due to a topographic defect.

The topography images of the scanned areas obtained from the dc component of the AFM signal were acquired together with the modulated PFM signals both at $T = 50\, \text{K}$ and $T = 10\, \text{K}$, as shown in Figs. 5.7 (a) and (d), respectively. Besides the contrast observed in the PFM images, the topography image also reveals the presence of structural domains in the rhombohedral phase due to the different surface inclinations of the lattice in adjacent domains [see Appendix A.1 for details]. The faint contrast seen in Fig. 5.7 (d) appears more pronounced in an area without any topographic defects as in Fig. 5.8 (a) and (d).

The Jahn-Teller distortion leads to the appearance of a piezo-response, as expressed by the finite $d_{zzz,r}^{(001)} = \pm d_1$ component in Eq. 5.3. Whereas the magnitude of this element is equal in all rhombohedral domains, its sign is determined by the sign of the out-of-plane component of the strain. The
four domains can be divided into two pairs with an opposite out-of-plane distortion: [111],[I11] and [111],[I11]. In the PFM phase signal, $\Theta$, a 180° contrast is expected between these pairs, whereas, the PFM amplitude, $V_R$ is expected to be equal for all domains. The capacitive force arising between the tip and the sample surface [144], however, results in an appreciable background signal (see the Appendix A.3) affecting both the relative phase and amplitude of the PFM signals [145].

Figures 5.8 (a)-(c) display the AFM topography along with the PFM phase and amplitude images recorded at $T = 10$K in the area indicated by the yellow dashed rectangle in Fig. 5.7 (d). The PFM amplitude and phase maps are displayed background-corrected according to Eq.A.12 [for a detailed description of the background correction, see the Appendix A.3]. Figures 5.8 (d)-(f) demonstrate the profiles of the three channels along the same line perpendicular to the domain boundaries, as marked by white bars in each figure. The alternating domain structure along the profile can be easily traced both in the AFM topography and the PFM channels. The pyroelectric-ferroelastic domain boundaries are manifested by the reversal of the inclination angle in the topographic profile and by the 180° phase shift of the PFM signal and the minimum in its magnitude. Correspondingly, the alternating yellow-red backgrounds of the line profiles indicate domains distinguishable by the AFM topography and the PFM measurements. Panel (g) shows the polarization directions in the four rhombohedral domains in a single inversion domain of the crystal. Red and yellow colors represent the different sign of the out-of-plane PFM signal observable on the (001) surface. Panel (h) shows one of the two possible compatible solutions for the observed alternating structure along the line profile. The top image shows the in-plane and out-of-plane polarization vectors with reference to the scanning directions and the alternating electric field applied by the PFM tip, denoted by $E^\omega$. The bottom image illustrates the three-dimensional structure of this solution with the color coding corresponding to panels (d)-(g).

The measured piezo-response falls within the range of 20-40 $\mu$V, corresponding to displacements of 6-12 pm as determined from the calibration of the $z$-displacement of the AFM tip. The driving voltage was 10 V$_{pp}$, therefore the magnitude of the $d_{zzz,z}$-element is estimated to be in the range of 1-2 pm/V.

The total inclination angle between the surfaces inferred from the AFM topography profile, indicated by dashed blue arcs in Fig 5.8 (d), yields a value of approximately $\gamma_{meas}^{(001)} = 0.58^\circ \pm 0.08^\circ$. This value is in good agreement with the rhombohedral angle of 59.66°, as measured by X-ray diffraction at 20 K [124], which corresponds to the theoretical value of $\gamma^{(001)} = 0.58^\circ$, according
Figure 5.8: AFM topography (a), PFM phase (b) and amplitude (c) images taken on the (001) surface of Sample #1 at $T = 10\, K$ over the area marked by a yellow dashed rectangle in Fig. 5.7 (d). Panels (d)-(f): Corresponding signal profiles along the same line indicated by white bars in panels (a)-(c). A possible lamellar domain structure associated to the observed PFM contrast is sketched in panels (g) and (h).
to Eq.A.5 [see Appendix A.1 for details].

**AFM and PFM imaging on the (111) surface**

Figures 5.9 (a)-(c) display the AFM topography, PFM amplitude and PFM phase images, respectively, measured at $T = 50$ K. Figures 5.9 (d)-(f) show the micrographs captured over the same area with the sample cooled to $T = 30$ K.

Figures 5.10 (a)-(c) show the AFM topography image along with the PFM amplitude and phase channels background-corrected according to Eq.A.12 adapted to the case of the (111) surface (see the Appendix A.3 for details). The scans were recorded at $T = 30$ K on the area marked by the yellow dashed rectangle in Fig. 5.9 (d). Figures 5.10 (d)-(f) display the profiles along the white lines parallel to the [112] direction, as indicated in the images in the left panels. The domain boundaries are clearly visible in all three channels. Panel (g) shows the polarization directions in the four rhombohedral domains in a single inversion domain of the crystal. Red and yellow colors represent the different sign and magnitude of the out-of-plane PFM signal observable on the (111) surface.

PFM measurements on the (111) plane in the rhombohedral phase are sensitive to the contrast in the converse piezoelectric constants between the unique [111] domain and the three other domains [111], [111], [111], whose $d_{zzz,r}^{[111]}$ elements are equivalent, according to Eq.5.4. Panel (h) shows the only compatible solution that yields any PFM contrast, as observed along the line profile. The top image shows the in-plane and out-of-plane polarization vectors with reference to the scanning directions. The bottom image displays the three-dimensional structure of this solution with the color coding corresponding to panels (d)-(g).

The contrast, expected theoretically between the piezoresponse of the two distinguishable domain types, yields a ratio of $3 : -1$, where the negative sign indicates a $180^\circ$ shift in the PFM phase. The magnitude of the piezoelectric vibrations measured on the (111) plane is $\sim 80 \text{ - } 100 \, \mu V$ for domain [111] and $\sim 30 \text{ - } 40 \, \mu V$ for the other three domains. The corresponding value of $d_{zzz,r}^{[111]}$ is $2.5 \text{ - } 3 \, \text{pm/V}$. This tensor element involves contributions from $d_{zzz}^{(001)}$, $d_{xxy}^{(001)}$ and $d_{xzx}^{(001)}$ (See Eq.5.4), which accounts for the enhancement in the PFM signal with respect to that observed on the (001) surface.

The inclination of the (111) surface between the (111) domain and any of the three other domains is expected to be $\gamma^{[111]} = 0.55^\circ$ from the degree of rhombohedral distortion determined by X-ray diffraction [124] using Eq. A.5. The opposing surface inclination in the alternating domains is clearly
Figure 5.9: Simultaneous measurements of the AFM topography, PFM amplitude and PFM phase performed above (a)-(c) and below (d)-(f) the temperature of the structural phase transition. All images stem from the same surface area on the (111) surface of Sample #2. The crystallographic directions are indicated in panel (f) according to Fig. 5.3 (c). The yellow dashed rectangle in panel (d) marks the area of measurements presented in Fig. 5.10.

discernable from the AFM topography images, as seen in Figs. 5.9 (d) and 5.10 (a) and (d), though the measured angle, $\gamma_{\text{meas}}^{(111)} = 0.38^\circ \pm 0.05^\circ$, is somewhat lower than the predicted value [see the Appendix A.1 for details].

5.4 Conclusion

I have detected pyroelectric and ferroelastic domains in the rhombohedral phase of GaV$_4$S$_8$ via simultaneous out-of-plane PFM and AFM topographic measurements. Lamellar domain structures have been visualized and identified as alternating pairs of structural domains, belonging to a single inversion domain of the crystal. The magnitude of the piezoresponse measured on the (001) and (111) surfaces of the crystals ranges within $\sim$1-5 pm/V. Based on the mechanical and electric compatibility criteria, I have shown that the primary domain walls are parallel with \{100\}-type planes. The collection of PFM images supports that the compatibility criteria of non-charged domain walls are generally satisfied and also indicates the lack of inversion domains in the scanned regions of the crystals studied here. Notably, local incom-
Figure 5.10: AFM topography (a), PFM phase (b) and amplitude (c) images taken on the (111) surface of Sample #2 at $T = 30$ K over the area marked by a yellow dashed rectangle in Fig. 5.9 (d). Panels (d)-(f): Corresponding signal profiles along the same line indicated by white bars in panels (a)-(c). The only possible lamellar domain structure associated to the observed PFM contrast is sketched in panels (g) and (h).
patibilities have been encountered at the endings of the lamellar patterns, claiming for charged domain walls and polytype domain structures.

The typical thickness of the observed lamella-like domains is in the range of 150-800 nm. According to small-angle neutron scattering experiments reported in [26], the correlation lengths both within the plane of the SkL and parallel to the axis of the skyrmion tubes exceed 100 nm but remain well below 800 nm. Since skyrmion cores are oriented along the polar axes of the pyroelectric domains, the size of a consistent skyrmion lattice and the two correlation lengths are limited by the size of the lamellar domains, as also demonstrated by mAFM measurements [P1].

Since the thickness of the observed structural domains is still larger than lattice constant of the SkL found to be $\sim$20 nm in this material [26], the SkL state is likely to be robust within the domains and only destabilized near the domain boundaries due to discontinuity in the DM interactions and axial anisotropy. Recently, intensive research is focused on the formation and stability of skyrmions in confined geometries, such as nanowires and nanodisks [35, 146-149] for potential memory applications. The engineering of the structural domain patterns in polar skyrmion host compounds may provide a new route to create geometrical confinement for skyrmions in bulk 3d materials as well.
Chapter 6

Modulated magnetic phases in GaV$_4$S$_8$

In section 3.3, I presented the magnetic phase diagram of GaV$_4$S$_8$, established by recent magnetization, mAFM and SANS experiments [26]. In this chapter, I extend the analysis of the magnetic phases in this compound by investigating the structure and the low-frequency magnetization dynamics of the modulated magnetic textures, based on SANS and ac susceptibility measurements, respectively.

6.1 Investigation of the cycloidal state by SANS

The Landau-functional of the form of Eq. 2.12, introduced in section 2.2.3 for lacunar spinels, predicts that the cycloidal wavevectors are constrained to the plane perpendicular to the rhombohedral axis, as required by the Lifshitz-invariants allowed by the $C_{3v}$ symmetry. We carried out zero-field SANS measurements on GaV$_4$S$_8$ upon the wide-angle rotation of the sample, in order to explore the three-dimensional distribution of the cycloidal wavevectors. The obtained $q$-vector distribution will be examined through the predictions of the Landau-model. Following this analysis, I investigate the effect of magnetic fields applied within the plane perpendicular to the polar axis on the distribution of the $q$-vectors based on our SANS measurements. Finally, I discuss the characteristics of the zero-field phase transitions through the PM-Cyc and Cyc-FM phase boundaries, via temperature-dependent SANS experiments performed in zero field.
6.1.1 Reciprocal-space tomography of the zero-field cycloidal states

SANS measurements with the wide-angle rotation (DOM angle) of the sample were carried out at the Paul Scherrer Institute using a 25 mg single crystal of GaV$_4$S$_8$. The experiments were performed by S. Bordács and J.S. White, and I analyzed the data for the reconstruction of the tomographic images. The sample was mounted on the sample stick with its [110] direction co-aligned with the axis of the stick. Thereby, the high-symmetry crystallographic planes, (111), (110), (11$ar{2}$) and (001), were brought perpendicular to the incident neutron beam and imaged during a half revolution of the sample, as shown in Fig. 6.1. Indeed, upon the half revolution of the sample, the full volume of the scattered intensity can be recovered.

The neutron wavelength of $\lambda_n = 6$ Å was selected with the detector distance as well as the collimator length set to $d=8$ m. The sample was cooled down to $T = 10$ K in zero field. Thereafter, it was rotated in 1° steps followed by the SANS data acquisition of 60 s. The same measurements were repeated at $T = 20$ K, in the paramagnetic phase of GaV$_4$S$_8$, which were subtracted as a background from the low-temperature measurements.

![Figure 6.1: SANS imaging upon the wide-angle rotation of the sample. The rotation of the sample around the [110] axis allows for the SANS imaging of the full three dimensional structure of the q-states.](image)

Figure 6.2 shows the background-corrected SANS intensity maps averaged over a 10° moving window. In most of the SANS images with an arbitrary orientation six Bragg-spots are visible. This is, however, not the signature of the phase-locked triple-$q$ structure of a skyrmion lattice, since only cycloidal modulations emerge in zero field [26]. Instead, the spots are associated to cycloidal modulations in different rhombohedral domains the sample. The full three-dimensional distribution of the magnetic propagation vectors was
Figure 6.2: SANS images measured upon the wide-angle rotation of GaV$_4$S$_8$. The images show the SANS intensities averaged over a 10° moving window in consecutive rotation steps of 10°. The corresponding rotation angles are indicated in the top left corner of each frame. The vertical rotation axis is parallel to the [110] crystallographic axis, as indicated in the first image. Images where the neutron beam is approximately perpendicular to a high-symmetry planes of the cubic setting are highlighted by red frames.

reconstructed using the full set of SANS images. Figure 6.3 (a) displays a perspective view of the tomographic image of the modulation wavevectors with scattered intensities exceeding a distinct threshold value. The reciprocal-space distribution of the $q$-vectors can be decomposed to four intersecting rings with a fixed radius, lying within the four \{111\}-type planes, as shown in Figs. 6.3 (b) and (c).

Each ring represents the scattering of one of the four polar domains that form below $T_S$, featuring magnetic propagation vectors, $q$, confined to the plane normal to the associated rhombohedral axis, as shown in Fig. 6.3 (c), in accordance with the zero-field solution of the Landau-functional in Eq. 2.12. The length of the modulation vectors is fixed by the relative strength of the Dzyaloshinsky-Moriya interaction (DMI) and the symmetric exchange, i.e. $|q| \propto D/J$. The total scattering intensities are roughly the same within each ring, indicating a nearly equal population of the rhombohedral domains in the bulk sample. Remarkably, the cycloidal wavevectors are distributed evenly over the rings in each \{111\}-type plane, suggesting that the in-plane magnetic anisotropy is relatively weak in GaV$_4$S$_8$. This partial order lies in stark contrast with $B20$ helimagnets, where the cubic anisotropy selects specific wavevectors at all temperatures in zero field [29, 79, 80]. The order seen in GaV$_4$S$_8$ is more reminiscent of liquid crystals, but instead of fluctuations of molecular orientations in real space, here the orientational disorder
Figure 6.3: Panel (a): Three-dimensional distribution of the modulation wavevectors in GaV₄S₈ as recovered by SANS tomography. Panel (b): Graphical representation of the reciprocal-space structure as four intersecting rings. Each ring corresponds to the manifold of the modulation wavevectors in a single rhombohedral domain, lying within the plane normal to the corresponding rhombohedral axis as visualized in panel (c).

is reflected by a broad \( q \) distribution. While the role of pinning is clear from these data, we cannot conclude about the spatial variations of the wavevectors, namely if their broad distribution is related to the rhombohedral domain walls or their variation occurs on the sub-domain scale.

Figure 6.4 displays the SANS images recorded in the major crystal planes together with the 3d tomography images. The Bragg-condition holds for the modulation vectors lying approximately within the plane normal to the neutron beam, given by the intersection of the full 3d structure and the image plane. For instance, the ring seen in the scattered intensity in the first SANS image in Panel (a) corresponds to modulation vectors in the unique \([111]\) domain [displayed in blue color in Panel (c)]. The six spots superimposed on the ring intensity originate from those \( q \)-vectors within the three other structural domains which lie close to the \((111)\) plane. Similarly, in the \((110)\) plane shown in Panel (d), the top and bottom peaks correspond to two domains wherein the polar axis spans 35.2° with the axis of the neutron beam, whereas the other four spots to the side correspond to the two domains with their rhombohedral axis orthogonal to the neutron beam. This assignment of different regions of the scattering pattern to the different polar domains allows for the domain-specific analysis of the magnetic correlations. In particular, by tracking the anomalies in the SANS intensity or the modulus of the \( q \)-vectors at specific regions of the SANS pattern, the phase transitions in the different domains can be distinguished. This provides a complementary
method to bulk magnetization measurements to separate the critical fields of the magnetic phase transitions with respect to the angle enclosed by the magnetic field and the rhombohedral axis. This method will be employed in sections 7.2.2 and 8.3 to assign the critical fields determined by magnetization measurements to magnetic phase transitions within each rhombohedral domain in GaV$_4$Se$_8$ and GaMo$_4$S$_8$, respectively.

6.1.2 Correlation length of the magnetic modulations

In addition to the previous domain-specific separation of the regions of the SANS pattern, the analysis of rocking curves provides another means to separate the contributions from the different domains even at overlapping regions such as the (110)-type spots in the (111) plane [see Fig. 6.4 (a)]. By rocking the sample around the horizontal [110] axis within the range
of $\pm 10^\circ$, the ring lying within the (111) plane – associated to the unique domain – is rotated out of the plane perpendicular to the neutron beam i.e. the surface of the Ewald-sphere. On the other hand, the three out-of-plane $q$-rings are still intersected by the Ewald-sphere after the rotation of the sample. Therefore, the $I(\phi)$ rocking intensity, features two distinct components, where $\phi$ denotes the rocking angle. The peak in the rocking curve corresponds to modulations within the unique rhombohedral domain, whereas the flat baseline is associated to one of the other three domains. This method was used to distinguish the phase boundaries in the $\mathbf{H} \parallel [111]$ configuration in Ref. [26].

The full width of half maximum (FWHM) of the rocking peaks associated to the $q$-vectors within the (111) plane is inversely proportional to the magnetic correlation length along the [111] rhombohedral axis. The FWHM of the $q$ distribution perpendicular to the plane of the modulation vectors, i.e. along the polar axis is given by the FWHM of the rocking peak as $\delta q_\perp = \frac{|q| \sin \delta \phi}{\delta q_\parallel}$. Thereby, the out-of-plane correlation length is $\xi_\perp = \frac{2}{\delta q_\perp} \approx \frac{2}{|q| \sin \delta \phi}$. The out-of-plane correlation length was found to be $\xi_\perp = 170$ nm, which is comparable to that reported for the high-purity MnSi samples [29], indicating well-developed magnetic order along the rhombohedral axis. Note that the in-plane broadening of the $q$ rings is partially caused by the divergence of the neutron beam, limiting the lateral resolution of the instrument [26]. The in-plane radial correlation length of the ring appearing in the (111) plane is estimated to be $\xi_q \approx 40$ nm as determined from the $I$ vs $|q|$ plot after the deconvolution of the instrumental broadening [P5].

### 6.1.3 Field-induced rearrangement of the cycloidal domains

In zero magnetic field, SANS tomography revealed a uniform distribution of the cycloidal wavevectors over rings within the planes normal to the four rhombohedral axes. We performed additional measurements to study the response of the cycloidal states in GaV$_4$S$_8$ to in-plane magnetic fields. Magnetization measurements discussed in Section 3.3 indicate that the cycloidal phase persists up to magnetic fields of hundreds of mT when the field is applied normal to the polar axis. The SANS experiments were performed by S. Bordács and me at the ILL using the D33 instrument. A neutron wavelength of $\lambda = 4.6$ Å and a detector distance as well as a collimator length of $d = 5.3$ m were selected. The sample was rocked around the vertical [110] axis (SAN rocking) and the horizontal [112] axis (PHI rocking) within the range of $\pm 4^\circ$ and $\pm 3^\circ$, respectively, in $0.5^\circ$ steps with an acquisition time of
The SANS images are obtained by averaging the scattered data over all the SAN and PHI rocking angles.

Figs. 6.5 (a)-(c) show unpolarized SANS data obtained at \( T = 11 \text{K} \) with the incident neutron beam parallel to the [111] axis and a transverse field applied along \( B \parallel [112] \), i.e. normal to the polar axis of the [111] domain (\( \alpha = 90^\circ \)). After zero-field cooling, an isotropic ring of the scattered intensity is observed, originating from the [111] domain, along with six spots at locations #1-#4, #2-#5 and #3-#6 due to scattering on magnetic structures within the three remaining polar domains, [\( \bar{1}11 \)], [\( \bar{1}11 \)] and [\( 11\bar{1} \)]. The \( \alpha \) angles spanned by the field and these three polar axes are 19.5\( ^\circ \), 61.9\( ^\circ \) and 61.9\( ^\circ \), respectively. In these domains, the parallel component of the field along the respective rhombohedral axes drives the Cyc-SkL and SkL-FM phase transitions, as indicated in Fig. 6.5(d).

In contrast, in the [111] domain, the cycloidal order is maintained, and the increasing field gives rise to a gradual redistribution of the propagation wavevectors to the spots #1-#4 [Figs. 6.5(b) and (c)], i.e. to the direction normal to the field. This provides further evidence that a cycloidal order is realized in \( \text{GaV}_4\text{S}_8 \), since the susceptibility of a cycloid is generally enhanced normal to the cycloidal plane. Under an in-plane plane magnetic field, the orientationally disordered cycloidal state [Fig. 6.5(e)] transforms smoothly into a mono-domain transverse conical state with \( q \) normal to \( B \) [Fig. 6.5(f)]. Here the cone axis is parallel to \( B \), and the cone angle closes at \( \sim 0.45 \text{T} \) [Fig. 6.5(d)]. Combining these data with previous experimental [26] and theoretical [83] results shows that in \( \text{GaV}_4\text{S}_8 \) the transverse conical state exists only when \( B \) lies close (\( \lesssim 19^\circ \)) to the rhombohedral plane within which \( q \) is confined. This is in contrast to cubic helimagnets where \( B, q \) and the cone axis are all parallel with each other, and this longitudinal conical phase covers the major part of the phase diagram for any field direction [29, 79].

### 6.1.4 Temperature-induced phase transition in zero field

Besides the absence of the longitudinal conical state in lacunar spinels another major difference between the magnetic phase diagram of \( \text{GaV}_4\text{S}_8 \) and the \( B20 \) compounds is that in \( \text{GaV}_4\text{S}_8 \) the modulated states transform to a ferromagnetic state at low temperatures even in zero magnetic field, where this transition occurs at \( T_{FM} = 5 \text{K} \). In the following, I present our SANS experiments carried out in zero field upon the cooling \( \text{GaV}_4\text{S}_8 \) through the paramagnetic-Cyc and the Cyc-FM phase boundaries. The neutron wavelength was \( \lambda = 6 \text{Å} \) and the detector was moved to \( d = 10.5 \text{m} \). Rocking in SAN and PHI was performed following the same procedure as in the previous
Figure 6.5: SANS patterns measured at 11 K in the (111) plane at (a) 0 mT, (b) 70 mT, and (c) 200 mT, when $B_{||}[11\overline{2}]$. (d) Field dependence of the SANS intensity for the positions labeled in panel a). Phase diagrams for each polar domain are shown according to the orientation of the rhombohedral axis, with the dashed lines denoting phase boundaries discussed in Ref. [26]. Visual representation of the orientationally disordered cycloidal state in zero field (e) and the transverse conical state with $q \perp B$ (f) in moderate magnetic fields. Figures reproduced from [P4] and [P5]. Copyright (2018) by the American Physical Society.

experiments. I performed additional temperature-dependent magnetization measurements on GaV$_4$S$_8$ in zero field at the Wigner Research Centre for Physics.

Fig. 6.6 shows unpolarized SANS images obtained on the (111) plane of GaV$_4$S$_8$ summarizing the temperature dependence of the cycloidal order in zero field. The smooth increase of SANS intensity at finite $|q|$ upon cooling below $T_C=13$ K [Fig. 6.6(f)] implies a continuous transition between the paramagnetic and cycloidal states. Fig. 6.6(e) reveals an 50% reduction in the length of the modulation wavevectors, $|q|$, upon cooling from $T_C = 13$ K to $T_{FM} = 5$ K. At the same time, the SANS intensity peaks at $T = 6$ K.
with $|q| = 0.04 \text{ Å}^{-1}$. In the low-temperature range where $|q|$ is still finite, the intensity drops sharply to zero [Fig. 6.6(f)] and simultaneously a tail of low-$q$ scattering develops indicating the growth of FM correlations [Fig. 6.6(d)]. This phase coexistence, sharp change in SANS intensity, and hysteresis in the temperature dependence of the magnetization [Fig. 6.6(g)], indicate the Cyc-FM transition to be of first-order, consistent with recent specific heat data [151]. In contrast however, Fig. 6.6(a) shows that close to $T_{FM}$ the radial intensity distribution has significantly broadened in $|q|$, and the intensity ring is transformed into a disk-like profile in the (111) plane with a sharp cut off at the high-$q$ end [Fig. 6.6(e)]. In the other three polar domains, the intensity disks appear as a six-spoked asterix when imaged on the (111) plane. These data show the length of $|q|$ to vary strongly, or even fluctuate, upon approaching $T_{FM}$. This could indicate the transition at $T_{FM}$ to be continuous in theory, but hysteresis effects emerge due to slow dynamics when the rearrangements of large structures are involved, as also evidenced by ac susceptibility measurements [P2].

Nevertheless, in comparison with the general phase diagram of the $B20$ helimagnets, the results for GaV$_4$S$_8$ stand out as rather unusual. At such low temperatures as the $T_{FM}$ in GaV$_4$S$_8$, it is unlikely that the microscopic couplings such as the symmetric exchange or DMIs vary sufficiently to drive the Cyc-FM transition. A more plausible scenario is that thermal fluctuations are crucial for stabilizing the long-wavelength modulated states close to $T_C$, and when they are suppressed at low temperatures, the system transforms to a FM state expected in accord with the strong easy-axis magnetic anisotropy [26]. Whereas the uniaxial FM order represents a low-entropy ground state of the system, the entropy gain due to the energetically degenerate phase degree of freedom of the spin cycloids favors the cycloidal state at higher temperatures.

Similar behaviour has been discussed in the context of the spiral-FM transition in the elemental rare-earths like Dy and Tb, wherein the effective anisotropy becomes more influential as fluctuations are suppressed at low temperatures [155]. In those systems the strong axial anisotropy leads to a larger periodicity in real-space with increased anharmonicity, and close to transition the spiral transforms to a soliton lattice with periodically arranged FM domain walls. Such a state in GaV$_4$S$_8$ may explain the unusual temperature dependence of the SANS data shown in Figs. 6.6(a)-(c). Indeed, the reduction of $|q|$ by 50% on cooling from $T_C$ to $T_{FM}$ [Fig. 6.6(e)] supports this picture, although close to $T_{FM}$ the signal expected at higher harmonics of $q$ due to soliton lattice formation lies below the detectable limit. Nevertheless, the proposed interplay between the easy-axis anisotropy and thermal fluctuations likely governs the fine structure of the phase diagram in GaV$_4$S$_8$. 

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Figure 6.6: Temperature evolution of the SANS intensity on the (111) plane in GaV$_4$S$_8$ in zero field, as shown in (a)-(c) in the vicinity of the Cyc-FM transition. (d) Temperature dependence of the $|q|$-dependent, azimuthally-averaged SANS intensity on the detector plane. (e) Temperature dependence of the cycloid scattering vector and (f) its intensity. (g) Temperature dependence of the magnetization measured in 10 mT. Figure reproduced from [P5]. Copyright (2018) by the American Physical Society.

6.2 Magnetization dynamics near the magnetic phase boundaries of GaV$_4$S$_8$

The magnetic phase diagram of GaV$_4$S$_8$ was established by the analysis of the anomalies of the derivative of the static magnetization curves, i.e., by the dc differential susceptibility, as described in Section 3.3 [26]. This is a widely-used methodology to reveal phase transitions between the modulated magnetic states in non-centrosymmetric magnets [26, 47, 48, 79, 99]. Beyond the determination of the phase diagram via dc susceptibility measurements, recently, several works have been devoted to analyzing the dynamic response of the modulated spin structures via ac susceptibility measurements [79, 100, 107-110]. The dynamic features arising in the ac susceptibility response in
the vicinity of the magnetic phase transitions in various compounds of the B20 family as well as in CuO$_2$SeO$_3$ show distinct similarities associated to the slow relaxation processes involved in the reorientation of large magnetic volumes upon the phase transitions [100, 107, 109, 110].

The magnetic modulations in GaV$_4$S$_8$ are governed by the same magnetic interactions as in cubic helimagnets, i.e. the Heisenberg exchange and the DMI, however, there is an additional easy-axis-type uniaxial magnetic anisotropy present in this material [82][P5]. Moreover, as the result of the polar rhombohedral symmetry of the compound, the symmetry of the modulations [P5], the distribution of the modulation vectors [Section 6.1.1] and the magnetic phase diagram [Section 3.3] of GaV$_4$S$_8$ is essentially different from those in cubic helimagnets. Therefore, it is intriguing to investigate the dynamical properties of the magnetic phase transitions in GaV$_4$S$_8$ in order to underpin the features generic to all skyrmion host compounds and to explore the material dependent differences. Notably, the Cyc-FM transition in GaV$_4$S$_8$ [Section 6.1.4] is not present in cubic magnets, hence it is interesting to study the underlying dynamics.

In order to reveal the dynamic response of the modulated magnetic states in GaV$_4$S$_8$, I performed ac susceptibility measurements and analyzed the results in terms of the Cole-Cole relaxation model. In the following section I introduce the Cole-Cole formalism to describe the dynamical response of systems characterized by a distribution of relaxation times. Thereafter, I present and discuss the experimental results.

6.2.1 Cole-Cole relaxation model

The modulated magnetic structures in skyrmion host compounds are generally characterized by a long correlation length, forming coherent magnetic regions with typical dimensions of hundreds of nanometers [26, 29]. The ac susceptibility of correlated spin structures consisting of clusters and/or domains of various volumes is broadly treated within the framework of the Cole-Cole relaxation model. This phenomenological model has been effectively applied to various systems [103] comprising large magnetic volumes, such as spin glasses [105], superparamagnetic nanoparticles [104], and more recently it has been proposed for the description of the relaxation processes at the phase transitions between modulated magnetic states in chiral helimagnets, Fe$_{1-x}$Co$_x$Si [109] and Cu$_2$OSeO$_3$ [107, 110].

The dynamic response of the magnetic system in the Cole-Cole model is formulated as an extension of the Debye-relaxation by introducing a distribution of relaxation times, while keeping the exponential time dependence of the relaxation [103, 156]:
\[
\chi(\omega) = \chi_\infty + (\chi_0 - \chi_\infty) \frac{1}{1 + (i\omega\tau_c)^{1-\alpha}}, \quad (6.1)
\]

where \(\tau_c\) represents the central value of the relaxation times and the \(\alpha\) parameter is connected to the width of their distribution. The response of the magnetic system is separated into two components according to their characteristic time scales as compared to the studied frequency range. The fast response of the spins occurring at frequencies much larger than our experimental window \((1/\tau \gg 1\text{kHz})\) are referred to as adiabatic, approximated by a frequency-independent and purely real quantity, \(\chi_\infty\), in the frequency range covered by this study. The slow relaxation processes responsible for the frequency dependence of the susceptibility in the low-frequency range of the experiments is described by the second term in Eq. 6.1. The static limit of the ac susceptibility is denoted as \(\chi_0\). The distribution of the relaxation times, \(g(\ln(\tau))\), is expressed by the \(\tau_c\) and \(\alpha\) parameters as follows [156]:

\[
g(\ln \tau) = \frac{1}{2\pi} \left( \frac{\sin \alpha \pi}{\cosh ([1-\alpha] \ln (\tau/\tau_c) - \cos \alpha \pi)} \right), \quad (6.2)
\]

The distribution is symmetric on the logarithmic scale with the central value of \(\tau_c\). The zero value of \(\alpha\) represents a single Debye-relaxation process, while values close to unity lead to an infinitely broad distribution of relaxation times.

Owing to the phase sensitivity of the ac susceptibility measurements, both the real and imaginary components of the susceptibility, \(\chi'\)(\(\omega\)) and \(\chi''\)(\(\omega\)), can be recovered. The frequency dependence of the two components, expressed from Eq.6.1, reads as:

\[
\chi'(\omega) = \chi_\infty + (\chi_0 - \chi_\infty) \frac{\omega \tau_c^{\alpha-1} + \sin \left( \frac{\alpha \pi}{2} \right)}{\omega \tau_c^{\alpha-1} + \omega \tau_c^{1-\alpha} + 2 \sin \left( \frac{\alpha \pi}{2} \right)}, \quad (6.3)
\]

\[
\chi''(\omega) = (\chi_0 - \chi_\infty) \frac{\cos \left( \frac{\alpha \pi}{2} \right)}{\omega \tau_c^{\alpha-1} + \omega \tau_c^{1-\alpha} + 2 \sin \left( \frac{\alpha \pi}{2} \right)}. \quad (6.4)
\]

### 6.2.2 ac susceptibility measurements

A cuboid-shaped sample with a mass of 23.4 mg was selected for the ac susceptibility measurements. A 5T Quantum Design MPMS SQUID magnetometer was used for the static and ac susceptibility measurements located at the Department of Experimental Solid State Physics at Wigner Research Centre for Physics. Both the static magnetic field and the ac modulation
field were normal to the (111) plane of the GaV$_4$S$_8$ crystal and the longitudinal magnetic moment was measured in a phase sensitive manner. The field dependence of the ac susceptibility was measured in the 0-80 mT range with a modulation amplitude of $\mu_0H_0=0.3$ mT. In order to probe the dynamics of the magnetically ordered spin system in the low-frequency regime, the drive frequency of the modulating coil was varied between $f=0.1$ Hz and 1 kHz. The in-phase and out-of-phase components of the oscillating magnetization were measured and normalized by the drive amplitude, $H_0$, to obtain the real and imaginary parts of the ac-susceptibility, respectively. The dc magnetization was measured in a subsequent run after the ac susceptibility measurements. The static differential susceptibility, $\partial m/\partial H$, was obtained from the measured dc magnetization curves by numerical derivation. The typical duration of the static measurements was 100 s per data point, which involved the ramping of the magnetic field and performing the measurement by the reciprocating sample option (RSO).

The magnetic-field dependence of the ac susceptibility was recorded at various temperatures within the magnetically ordered phases of GaV$_4$S$_8$, i.e. between $T=6.5$ K and $T=12$ K with magnetic fields applied parallel to the crystallographic [111] axis. The real and imaginary parts of the susceptibility are shown in Figs. 6.7 (a) and (b), respectively.

### 6.2.3 Magnetic phase diagram established by dc and ac susceptibility measurements

The field-driven phase transitions are associated with anomalies in the static susceptibility [26, 79]. The susceptibility measurements presented in Fig. 6.7 reveal distinct peaks near the critical fields of the phase transitions between the Cyc, SkL and FM states, following a clear temperature dependence, and resulting essentially in the same phase diagram as established by Kézsmárki et al. via earlier static magnetization measurements [26]. The three states adjoin at the triple point located at $T=9.5$ K and $\mu_0H=32$ mT.

Despite the coexistence of structural domains in the compound, within the studied field range, phase transitions are attributed to the unique structural domain wherein the rhombohedral axis is parallel to the field, i.e. points along the [111] direction. In the other three domains with their rhombohedral axes along [111], [111] and [111] the susceptibility peaks corresponding to the Cyc-FM phase transition are dominated by the peaks of the unique domain and are not visible on the scale of the graphs. At higher temperatures, the Cyc phase persists up to fields higher than $\mu_0H=80$ mT in these domains [26], showing no anomalies in the studied field range. Therefore the phase
Figure 6.7: Static and dynamic susceptibility of GaV$_4$S$_8$, plotted against the external magnetic field. Panel (a): Static susceptibility, $\partial m/\partial H$, plotted in gray, along with the real component of the ac susceptibility, $\chi'(H)$. Panel (b): Imaginary component of the ac susceptibility, $\chi''(H)$. Different colors represent data measured at various ac frequencies in the $f=0.1$ Hz-1 kHz range. Measured data are shifted proportionally to the sample temperature, which is indicated on the left side of each curve. The continuous lines connecting the dots are guides to the eye. The magnetic phases separated by the susceptibility peaks in the $H$-$T$ plane are indicated in the graphs. The paramagnetic state above $T_C=13$ K is denoted as PM. Figure reproduced from [P2]. Copyright (2017) by the American Physical Society.

transitions occurring in the non-unique structural domains will be ignored in the following analysis.

The susceptibility peaks observed in Fig. 6.7 are not sharp but extend over relatively wide regions of magnetic fields. These regions are presumably characterized by the coexistence of the magnetic phases [79, 100], as has been observed in various skyrmion host compounds in real space via magnetic force microscopy [24] and Lorentz TEM imaging [30, 34, 43, 157]. In the case of GaV$_4$S$_8$, the lamellar structure of the ferroelastic domains with a typical thickness in the micrometer range [P1] may introduce significant disorder in the vicinity of domain boundaries and may also enhance demagnetizing fields in the sample. However, the relatively wide susceptibility peaks as compared
to the values of the critical magnetic fields suggest that disorder is likely to play the key role in the broadening of phase transitions.

Figure 6.8: Panel (a): Magnetization curve $m(H)$ (right axis, gray curve), along with the static susceptibility $\partial m/\partial H$ and the ac susceptibility data measured with the highest modulation frequency, $f=1$ kHz at $T=11$ K (left axis, black and red curves, respectively). Panel (b): Imaginary component of the ac susceptibility at the same temperature and modulation frequency. The inset compares the adiabatic susceptibility, $\chi_{\infty}$, in the Cyc and SkL phases at various temperatures, obtained from the dc susceptibility curves as indicated by the black arrows in Panel (a). The symbols signaling the main features of the susceptibility curves are the same as those used in Fig. 6.9. Figure reproduced from [P2]. Copyright (2017) by the American Physical Society.

Figure 6.8 (a) shows the dc magnetization along with the calculated static
susceptibility $\left( \frac{\partial m}{\partial H} \right)$ and the real part of the ac susceptibility measured with the highest modulation frequency, $f=1\,\text{kHz}$ at $T=11\,\text{K}$, where all three magnetic phases are present. Magnetization measurements in increasing and decreasing fields did not reveal any hysteresis.

The regions within the Cyc, SkL and FM phases are characterized by the static susceptibility values fully tracked by the ac susceptibility, even at $f=1\,\text{kHz}$. The frequency independence of the susceptibility in the phase-pure regions may be caused either by the vanishing of the low-frequency relaxation processes, i.e. $(\chi_0 - \chi_\infty) = 0$ in Eqs. 6.3 and 6.4, or by the increase of their characteristic frequency above the experimental window, $1/\tau_c \gg 1\,\text{kHz}$. The former scenario is confirmed by fitting Eqs. 6.3 and 6.4 to the experimental data, as will be discussed in Section 6.2.5. Therefore, the measured static susceptibility inside the phases corresponds to the adiabatic values, as $\chi_0 = \chi_\infty$. Remarkably, the susceptibility is enhanced in the SkL phase as compared to the Cyc phase, in contrast to the $B_{20}$ compounds, where the SkL phase is typically seen as a dip in the susceptibility of the embedding conical state [79]. In this longitudinal conical state, the magnetic field is roughly perpendicular to the rotation plane of the spins, while in the present case the magnetic field is applied within the spin rotation plane of the cycloids. Correspondingly, a lower susceptibility is expected in the latter case. The inset of Fig. 6.8 (b) shows the values of the susceptibility as a function of temperature in the magnetic field regions of the pure Cyc and SkL phases, as indicated by black arrows in Fig. 6.8 (a) at $T=11\,\text{K}$. The adiabatic susceptibility increases towards lower temperatures, but remains larger in the SkL phase than in the Cyc phase at all temperatures. In the FM state the susceptibility is nearly zero, with contributions from the persisting Cyc phase in the three non-unique domains and the unsaturated moments in the FM state in the unique domain.

Figure 6.8 (b) displays the imaginary component of the ac susceptibility, measured at $T=11\,\text{K}$ with $f=1\,\text{kHz}$ modulation frequency. The two peaks located at the Cyc-SkL and SkL-FM phase transitions are attributed to dissipative processes occurring at low frequencies, which will be discussed in detail in Section 6.2.4.

The magnetic phase diagram is displayed in Fig. 6.9, based on the main features of the static and ac susceptibility data measured with the highest modulation frequency, $f=1\,\text{kHz}$. The phase diagram indicates the main features of the susceptibility curves, with the same symbols as used in Fig. 6.8: $B_{\text{Cyc}}^c(\text{+})$ and $B_{\text{SkL}}^c(\text{+})$ correspond to the higher-field boundaries of the Cyc and SkL phases, respectively, while $B_{\text{SkL}}^c(\text{−})$ and $B_{\text{FM}}^c(\text{−})$ are the lower-field boundaries of the SkL and FM phases, respectively. The position of the maximum values in the static susceptibility, associated with the critical fields
Figure 6.9: Magnetic phase diagram of GaV$_4$S$_8$ established by static magnetization and ac susceptibility measured at $f=1$ kHz. Upward and downward pointing triangles represent the beginning and the end of the peaks in the static susceptibility, separating the pure Cyc, SkL and FM phases from the regions of phase coexistence, indicated by pale shadowing. Full circles represent the location of the peaks in the static susceptibility, associated to the phase boundaries in earlier reports [26, 27, 151]. Red and blue stars display the location of the maxima in the real and imaginary parts of the ac susceptibility using a modulation frequency of $f=1$ kHz. Figure reproduced from [P2]. Copyright (2017) by the American Physical Society.

of the phase transitions in previous studies [26, 27, 151], are also indicated in the phase diagram, along with the location of the peaks in the real and imaginary components of the ac susceptibility. The critical fields determined from the ac susceptibility curves agree well with those obtained from the static susceptibility, however the position of the ac susceptibility peaks is clearly frequency dependent – see e.g. the susceptibility curves measured at $T=10.5$ K in Fig. 6.7 (b).

6.2.4 Slow relaxation phenomena at the magnetic phase boundaries

It is clearly seen in Figs. 6.7 (a) and (b) that away from the phase transitions, the ac susceptibility is frequency-independent and purely real, with
values identical to the static susceptibility. In these regions, the characteristic relaxation times are much shorter than 1 ms, the time period of the highest-frequency modulation in our experiments, i.e. the measured frequency-independent susceptibility values correspond to $\chi_\infty$. On the other hand, in the field range of the phase transitions, the real component of the ac susceptibility falls behind the static values, accompanied with a peak in the imaginary component, both exhibiting strong frequency dependence. These features indicate slow relaxation processes with characteristic frequencies close to or below the range of $f=0.1$ Hz-1000 Hz, used in the experiment. Such behavior was also reported in cubic helimagnets of the $B_20$ family [47, 100, 106, 109] and in Cu$_2$OSeO$_3$ [107, 110] in the vicinity of the magnetic phase transitions. The dynamics governing the Cyc-SkL phase transition is expected to be rather similar to the conical-SkL transition observed in chiral magnets. There, the phase coexistence region is characterized by the nucleation of the skyrmions through the emergence of topological point defects, monopoles and antimonopoles, as the helical states are unzipped [24, 34]. The excitation of these defects over pinning barriers might lead to the observed frequency dependence of the susceptibility [107]. Moreover, the emerging SkL, coexisting with the helical states, is prone to develop lattice defects such as irregular coordination or edge dislocations, eventually relaxing to the equilibrium single domain SkL state in the pure SkL phase [34, 157]. The ac-field-induced relaxation of the defects in the SkL may also be responsible for the slow dynamics seen in the ac susceptibility measurements.

However, due to the absence of the longitudinal conical state in GaV$_4$S$_8$, the Cyc-FM and the SkL-FM transitions are unique in this material, featuring different dynamical processes than those present in the cubic helimagnets, which is also reflected in the real and imaginary susceptibility components at the phase transitions. The main differences between the ac magnetic response of the two types of materials are listed below:

1. In cubic helimagnets the zero-field multi-domain helical state is rearranged by the external magnetic field and a longitudinal conical state with the modulation vector parallel to the field is established [30, 48, 78-80, 100, 158, 159]. Ac susceptibility measurements in FeGe [106], MnSi [80, 100], Cu$_2$OSeO$_3$ [107, 110] and Fe$_{1-x}$Co$_x$Si [109] revealed a frequency-dependent peak in the susceptibility accompanied with a finite dissipation emerging over this transition. These features of the ac susceptibility indicate that the rearrangement of the large magnetic spirals occurs on extended time scales.

In GaV$_4$S$_8$, on the other hand, the zero-field state is cycloidal with the modulation vectors confined to the plane perpendicular to the
rhombohedral axis in each domain. As demonstrated by the SANS measurements discussed in section 6.1.1, the $q$-vectors are distributed evenly over rings within the \{111\}-type planes, indicating a negligible (or weak) in-plane anisotropy and the presence of pinning \[P5\]. The external field applied in the [111] direction does not break the isotropy of the (111) plane, therefore the modulation directions in the unique domain remain unaffected by the field, which is in accord with the absence of dissipation within the pure Cyc phase. Note that a field-induced redistribution of the cycloidally modulated states may take place in the three other polar domains, as seen previously for magnetic fields applied normal to the rhombohedral axis \[see Section 6.1.3\]. Here the magnetic field spans 71° with the rhombohedral axes, therefore in the three equivalent domains the redistribution of the cycloidal states is likely to begin at the studied field range of $\mu_0H = 70$ mT. However, the small increase in the susceptibility obtained by the gradual rotation of the cycloidal planes perpendicular to the applied field remains below the limit of our detection.

2. In the bulk chiral magnets, the FM state is achieved through the longitudinal conical state by the continuous closing of the conical angle \[79\]. The fact that ac susceptibility measurements do not reveal dissipation and frequency-dependent susceptibility at the conical-FM phase boundary \[79\] indicates that this process occurs on time scales much faster than those of the ac modulations. Oppositely, in GaV$_4$S$_8$, the FM state is achieved by the expansion of the cycloidal pitch and the increasing anharmonicity of the modulation \[158\], similarly to monoaaxial chiral magnets \[160\]. In addition, structural disorder may introduce pinning along with a spatial variation of the modulation wavelength. According to earlier SANS measurements, the modulation wavelength indeed shows significant increase in the vicinity of the FM state \[26\]. Moreover, the SANS measurements presented in Section 6.1.4 reveal strong fluctuations in the cycloidal wavelength along the temperature-driven phase transition from the Cyc to the zero-field FM below 6 K, supporting this scenario \[P5\].

The spatial variation in the length or orientation of the cycloidal wave vector is expected to result in the formation of topological defects, such as edge disclinations \[34, 43, 80, 161\]. The slow relaxation observed in the ac susceptibility measurements at the Cyc-FM boundary are probably associated to the field-induced motion of such defects along the phase fronts of the spin-cycloids, involving the collective excitation
of a large number of spins over pinning barriers.

3. In bulk chiral magnets, the SkL phase is embedded in the conical phase. However, a phase coexistence between the SkL and the FM states has been observed in thin films of cubic helimagnets, where the conical state is suppressed by the geometrical confinement [34]. In elevated magnetic fields a glassy state of skyrmions is realized, exhibiting large fluctuations in the SkL orientation and lattice constant [34, 162]. Relaxation processes involving the rearrangement of such SkL clusters may govern the slow dynamics at the SkL-FM phase transition in GaV$_4$S$_8$.

6.2.5 Temperature and magnetic-field dependence of the relaxation processes

Fitting the frequency dependence of the susceptibility

The frequency dependence of the peaks in both susceptibility components [Fig. 6.7 (a) and (b)] shows a strong variation with the temperature. Concerning the Cyc-FM phase boundary, at $T = 7\, \text{K}$ the dissipation is the largest for the smallest modulation frequency, whereas at $T = 9\, \text{K}$ it becomes almost frequency independent. Above the triple point between $T = 10\, \text{K}$ and $T = 11\, \text{K}$, a reversal can be seen in the hierarchy of the frequencies in the dissipation peaks at both the Cyc-SkL and SkL-FM phase boundaries, indicating that the characteristic frequencies of the relaxation processes pass through the measurement window. Additionally, the peaks in the imaginary part of the susceptibility are shifted in magnetic field with the change of the drive frequency, which is most prominent at $T = 10.5\, \text{K}$. In order to systematically investigate the behavior of the relaxation as the function of the temperature and magnetic field, I analyzed the frequency dependence of the real and imaginary components of the susceptibility at all measured (H,T) points in the vicinity of the magnetic phase boundaries.

Figure 6.10 shows the frequency dependence of $\chi'$ and $\chi''$ in various magnetic fields. Three representative temperatures are selected above the triple point, where the peak in the imaginary part of the susceptibility passes through the experimental window, indicating that the inverse relaxation times go through the range of the measurement frequencies. The color coding of the measured values represents the different ac frequencies in accordance with Fig. 6.7. The color bars next to the right axes represent the range of magnetic fields corresponding to the Cyc-SkL and SkL-FM phase transitions with color gradients corresponding to Fig. 6.9. Figure 6.10 shows only the data measured in representative magnetic field regions near the
Cyc-SkL and SkL-FM phase transitions. The frequency dependence of the complex susceptibility can be fitted well by the Cole-Cole relaxation model (Eqs. 6.3 and 6.4) using the same set of parameters for the real and imaginary components. The shifting of the peak in $\chi''$ towards lower frequencies with decreasing temperature is well traced by the fitted curves for both the Cyc-SkL and the SkL-FM transitions, implying an overall slowing down of the relaxation.

Figure 6.11 (a) presents the fitted magnitudes, $(\chi_0 - \chi_\infty)$, of the low-frequency relaxation processes at all temperatures as a function of the magnetic field. According to the fitting, the magnitude of these processes vanishes smoothly upon entering into the pure phases, while the associated relaxation time scales remain accessible by our measurements (as seen e.g. in Figs. 6.10 (b), (d) and (f)). This indicates that the slow relaxation phenomena arise only in the range of the phase coexistence, and the magnitude of the frequency-dependent susceptibility is probably connected to the density of magnetic defects, vanishing in the pure phases. It further confirms, that the frequency-independent susceptibility measured inside the phases can be regarded as adiabatic, $\chi_0 = \chi_\infty$, as previously assumed in Fig. 6.8.

Using the $\tau_c$ and $\alpha$ parameters retrieved from the Cole-Cole fits, the distribution of the relaxation times, $g(\ln \tau)$ was calculated for each (H,T) point, according to Eq. 6.2. Figures 6.11 (b), (c) and (d) display the calculated distributions of the relaxation times for the Cyc-SkL, SkL-FM and Cyc-FM phase transitions, respectively. For each transition, the characteristic time scales fall below $\tau \ll 1$ ms at the high-temperature end of the phase boundary, exhibiting a dramatic increase towards lower temperatures, reaching values $\tau \gg 10$ s at the low-temperature part of the phase boundaries. Similar tendencies have been identified in Cu$_2$OSeO$_3$ [107, 110].

**Temperature dependence of the relaxation times**

Figure 6.12 shows the temperature dependence of the fitted relaxation times averaged over the range of magnetic fields near the phase transitions as $\log (\tau_{av}) = \sum_i^N \log (\tau(H_i))/N$. The sum runs over the values of relaxation times, $\tau(H_i)$, which are determined by fitting at each field, $H_i$, where the susceptibility shows observable frequency dependence in the vicinity of the phase boundaries. The error bars assigned to the data are calculated as the standard deviation of the $\log (\tau(H_i))$ values. The rapid drop in the relaxation times with increasing temperatures is clearly seen for each phase boundary. The discontinuous jump in the relaxation time at the triple point marks an abrupt change in the relaxation processes between the Cyc-FM and the Cyc-SkL phase.
Figure 6.10: Frequency dependence of the real (left column) and imaginary components (right column) of the susceptibility in various magnetic fields above the temperature of the triple point, at $T=11K$ (top), $T=10.75K$ (middle) and $T=10.5K$ (bottom row). Solid lines are fitted curves according to Eqs. 6.3 and 6.4. Figure reproduced from [P2]. Copyright (2017) by the American Physical Society.
Figure 6.11: Panel (a): Fitted magnitude of the low-frequency susceptibility, $(\chi_0 - \chi_\infty)$, as a function of the magnetic field at various temperatures. The fitted values are scaled to a common range using the factors indicated at three temperatures. Panels (b)-(f): Distribution of relaxation times, $g(\ln (\tau))$, plotted as a function of the temperature and magnetic field. The distributions were calculated according to Eq. 6.2 with the $\tau_c$ and $\alpha$ parameters obtained from the fits to the frequency dependence of the complex susceptibility. Panels (b),(c) and (d) show the relaxation times in the ranges of magnetic fields corresponding to the Cyc-SkL, SkL-FM and Cyc-FM transitions, respectively. The distribution curves are shifted proportionally with the temperature along the z axis, which is also indicated in the right side of the graphs. The curves are colored according to a color map representing decreasing temperatures ranging from $T=12 K$ (red) to $T=6.5 K$ (blue). Figure reproduced from [P2]. Copyright (2017) by the American Physical Society.

The exponential character of the temperature dependence of the relaxation times suggests a thermally activated behavior possibly related to the pinning barriers of the topological defects, $\Delta E$. The energy barriers over the Cyc-SkL and SkL-FM phase transitions were estimated by linear fits to the Arrhenius-plots, i.e. $\ln (\tau_{av})$ against $1/T$, as presented in the inset of Fig. 6.12. The fitted values yield average activation energies of $\Delta E_{\text{Cyc-SkL}} = 1300 K \pm 150 K$ and $\Delta E_{\text{SkL-FM}} = 1100 K \pm 35 K$ at the Cyc-SkL and the SkL-FM boundaries, respectively, where the values of the uncertainty are estimated from the linear fits, taking the error bars of the data points into consideration. These large values imply the reorientation dynamics of sizable magnetic regions instead of individual spins. Since the susceptibility at the Cyc-FM boundary could not be accurately fitted (as dis-
cussed later), the relaxation times for this transition have not been analyzed quantitatively.

**Figure 6.12:** Temperature dependence of the logarithmic average of the relaxation times obtained from the Cole-Cole fits, where the averaging was performed over the fitted values in the magnetic field region close to the phase transitions. The green, red and blue circles correspond to the average relaxation times at the Cyc-FM, Cyc-SkL and SkL-FM transitions. The error bars represent the standard deviation of the relaxation times on the logarithmic scale. The lines connecting the data points are guides to the eye. The dashed horizontal lines represent the measurement window defined by the inverse of the highest (1 kHz) and lowest (0.1 Hz) ac frequencies. The inset presents ln(\(\tau_{av}\)) as the function of 1/T along the Cyc-SkL and SkL-FM phase boundaries. Relaxation time values close to the experimental window are plotted, as indicated by the black dotted frame. Figure reproduced from [P2]. Copyright (2017) by the American Physical Society.

**Frequency dependence of the susceptibility at the Cyc-FM transition**

In contrast to the other two phase boundaries, the Cole-Cole model fails to fit the frequency dependence of the complex susceptibility for the Cyc-FM transition, as demonstrated in Fig. 6.13 for two selected temperatures below the triple point. Even though the real and the imaginary components can
be fitted separately with two different sets of parameters (see dashed gray curves in Fig. 6.13), the resulting parameters convey no physical meaning, as the Kramers-Kronig relation does not hold between the two components of the response function. The large difference between the static susceptibility values and the real part of the ac susceptibility measured even at the lowest frequency of \( f = 0.1 \) Hz, as seen in Fig. 6.7 (a), suggests that dynamic processes exist with characteristic relaxation times far beyond 10s.

The Cole-Cole model assumes a symmetric distribution of relaxation times on the logarithmic scale \([156]\), which may not apply for more complex processes involved in the magnetic phase transitions in \( \text{GaV}_4\text{S}_8 \). A generalization of the Cole-Cole function was provided by Havriliak and Negami \([163]\) allowing for an asymmetric distribution of relaxation times \([164]\). Applying the Havriliak-Negami model to our data, however, yielded the same parameters as the Cole-Cole fits returning the same symmetric distribution of relaxation times, hence did not improve the fit.

Only a few recent studies made an attempt to quantitatively describe the relaxation processes at the magnetic phase boundaries in cubic skyrmion host compounds, each within the framework of the Cole-Cole model \([107, 109, 110]\). However, in most of these studies the real and imaginary components of the ac susceptibility were handled separately, which may lead to unphysical parameters, as seen for the Cyc-FM transition in \( \text{GaV}_4\text{S}_8 \) (Fig. 6.13). Qian et al. correlated the Cole-Cole fits to the real and the imaginary parts of the susceptibility in \( \text{Cu}_2\text{OSeO}_3 \), finding good agreement in case of the conical-to-skyrmion and skyrmion-to-conical transitions, whereas a discrepancy was reported at the helical-to-conical transition. The authors attributed this difference to additional relaxation processes present at extremely low frequencies. Bannenberg et al. \([109]\) also identified a low-frequency contribution to the dissipation in \( \text{Fe}_{1-x}\text{Co}_x\text{Si} \) both at the conical-to-skyrmion and the skyrmion-to-conical transitions, which could not be described by the Cole-Cole model.

### 6.3 Conclusion

In this chapter the unique features of the modulated magnetic structures in \( \text{GaV}_4\text{S}_8 \) were demonstrated. The difference between the magnetic structures and phase diagrams of \( \text{GaV}_4\text{S}_8 \) and the \( B20 \) compounds was discussed on the basis of SANS and ac susceptibility measurements. In section 6.2, I presented a comprehensive analysis of the relaxation dynamics in \( \text{GaV}_4\text{S}_8 \), based on ac susceptibility measurements \([P2]\). Apart from the direct transition between the Cyc and FM states in \( \text{GaV}_4\text{S}_8 \), which does not emerge in the chiral
Figure 6.13: Frequency dependence of the real (left column) and imaginary components (right column) of the susceptibility in various magnetic fields below the temperature of the triple point at $T=9\,K$ (top), $T=8\,K$ (bottom row). Measured values are shifted vertically in proportion to the magnetic field. Solid lines are fitted curves according to Eqs. 6.3 and 6.4. Gray dashed lines are separate fits to the real [(a) and (c)] and the imaginary components [(b) and (d)] of the susceptibility. Figure reproduced from [P2]. Copyright (2017) by the American Physical Society.
helimagnets, similar features have been identified in the dynamical processes arising in the polar and chiral magnets. The underlying reason is presumably the slow magnetic response of the topological defects at the phase-coexistence regions to the ac magnetic field. Through the analysis of the frequency dependence of the complex susceptibility, I estimated the average relaxation times of these magnetic structures, ranging from below 1 ms to time scales over the minute range.

To develop a more general picture about the nature of modulated magnetic states in polar magnets with axial symmetry, it may be instructive to study the magnetic properties of other lacunar spinels such as GaV$_4$Se$_8$ and GaMo$_4$S$_8$, which undergo the same cubic-to-rhombohedral phase transition, while on the other hand, the strength of the relevant magnetic interactions may be significantly different. Understanding the differences in the magnetic structures in these three compounds may help in underpinning the key properties that influence the magnetic structures for a potential engineering of the magnetic phase diagram by chemical substitution or mechanical pressure. This will be the goal of the following chapters.
Chapter 7

Pyroelectric and magnetic properties of GaV$_4$Se$_8$

GaV$_4$Se$_8$ is a compound closely related to GaV$_4$S$_8$, crystallizing in the same lacunar spinel structure. Due to the identical valency of the selenium and sulfur ligands, a similar electronic structure develops in the two compounds. In particular, the Jahn-Teller instability in GaV$_4$Se$_8$ is expected to induce a pyroelectric and ferroelastic phase transition, similarly to GaV$_4$S$_8$.

In this chapter, I introduce the results of my pyroelectric polarization measurements [P3], demonstrating the onset of a cooperative Jahn-Teller transition at $T_S = 42$ K, giving rise to a sizable electric polarization. The pyroccurrent measurements also indicate the development of a magnetic order at $T_C = 19$ K, inducing additional magnetoelectric contributions to the electric polarization.

Following the polarization measurements, I will investigate the magnetic phase diagram in GaV$_4$Se$_8$, via a comparative set of magnetization measurements performed by our colleagues at Augsburg University and SANS experiments conducted by our group [P4]. As a result, I can assign the critical fields obtained from the magnetization data to the phase transitions within the specific rhombohedral domains, characterized by the angle of the magnetic field and the polar axis. This analysis relies to a great extent on the knowledge based on previous SANS results obtained on the prototype compound, GaV$_4$S$_8$ [P5].

Finally, my magnetocurrent measurements will be presented, revealing magnetically induced electric polarization with a magnitude specific to the underlying magnetic structure. The anomalies in the magnetocurrent reflect the transitions between magnetic phases, allowing for the mapping of the magnetic phase diagram via polarization measurements. The phase diagram obtained from the polarization measurements will be compared to that based
7.1 Pyroelectric and magnetoelectric polarization in GaV$_4$Se$_8$

Two single crystalline samples of GaV$_4$Se$_8$ were used for the polarization experiments performed at the BME Solid State Physics Laboratory. The single crystals were grown by V. Tsukan via the chemical-transport reaction method using polycrystalline powder as starting material and iodine as transport agent [P3]. Both samples were polished to a thickness of 150-200 µm and the two parallel (111) surfaces with approximately 1 mm$^2$ surface area were contacted by silver paste.

The samples were cooled down in zero field to 4.2 K, while the pyrocurrent was monitored by a Femto current amplifier using an amplification of $10^9$, with a sampling rate of 10 sample/s [see Section 4.3 for more details]. Figure 7.1 displays the results of consecutive zero-field cooling and heating cycles on sample #1. A cooling/heating rate of 1 K/min was applied in the vicinity of the pyroelectric phase transition [Fig. 7.1 (a)], while a higher rate of 20 K/min was used at lower temperatures to enhance sensitivity [Fig. 7.1 (b)].

Upon cooling, the ferroelastic-pyroelectric phase transition was observed between $T^\downarrow_S=45-46$ K, whereas the temperature range of the phase transition shifts to $T^\uparrow_S=46-47$ K upon heating. The deviation of these phase transition temperatures from $T_S=42$ K obtained in independent measurements by our colleagues in Augsburg and published in [P3] and [P4], as well as $T_S=41$ K reported by Fujima et al. in [85], is possibly due to the improper calibration of the temperature sensor used in my experiments. Nevertheless, the measured transition temperatures reproduce with a high accuracy irrespective of the cooling and heating rates, therefore in the following, I report the results of my measurements.

The sharp peaks in the pyrocurrent are associated to an electric Barkhausen-noise as a signature of the abrupt formation of polarization domains [165]. Consecutive cooling cycles show minor variation in the fine structure of the pyrocurrent, resulting in slight differences in the overall magnitude of the pyroelectric polarization. Variations in the cooling and heating rates and do not affect the character of the curves, and the hysteresis in temperature also persists at lower rates, such as 0.1 K/min (not shown here). This excludes the possibility of a lag between the temperature of the sample and the thermometer, and confirms the emergence of an intrinsic thermal hysteresis.
Figure 7.1: Temperature-dependent polarization measurements on GaV₄Se₈. Panel (a): Pyrocurrent measured over two consecutive cycles of zero-field cooling and heating through the structural-pyroelectric phase transition, $T_S \approx 45 - 47$ K. Panel (b) displays the pyrocurrent measured over the same cycles at lower temperatures near the magnetic phase transition, $T_C \approx 19$ K. The overall polarization as a function of the temperature is plotted in Panel (c). The magnetoelectric contribution is magnified in the inset.

attributed to the first-order nature of the structural phase transition.

The temporal integration of the pyrocurrent yields the polarization developing upon the Jahn-Teller transition, as plotted in Fig. 7.1 (c). A baseline with an exponentially decaying character in temperature has been subtracted from the pyrocurrent curves prior to the integration in order to exclude contributions related to the temperature dependent current contribution induced by the Seebeck effect due to the temperature dependence of the sample resistance. The structural phase transition gives rise to a sizable polarization of $\sim 0.43 \mu C/cm^2$ in the sample. Subsequent cooling and heating runs reveal a $\sim 20\%$ variation in the measured polarization, probably due to leakage currents through the sample. Consecutive cooling cycles using the same cooling rates reveal only a $\sim 2\%$ difference in the measured polarization values.

Note that the polarization experiments were performed without the ap-
plication of an external field, suggesting an imbalance in the spontaneously developing population of the four polar domains. This might be a result of the discharging of the (111) surfaces through the electric contacts, or due to a mechanical stress exerted by the contraction of silver paste upon cooling. The same effect has been observed in GaV$_4$S$_8$, featuring a similar magnitude of the pyroelectric polarization upon zero-field cooling [27].

Pyrocurent measurements performed after an electric field poling by E. Ru and colleagues on another sample of GaV$_4$Se$_8$ indicated significant electric-field effect on the magnitude of the polarization [P3], although polarization switching in the low-temperature phase could not be achieved due to a small conductivity of the material. The magnitude of the polarization in those experiments was found to be larger by a factor of 2, which also suggests a variation in the domain population depending on the specimen or the electric contacts applied on the sample.

At $T_C \approx 19$ K, magnetic ordering sets in, reflected by a discernible peak in the pyrocurent [Fig. 7.1 (b)] due to the additional magnetoelectric polarization [Fig. 7.1 (c) inset] previously attributed to anisotropic exchange striction in GaV$_4$S$_8$ [27]. The magnitude of the magnetoelectric contribution in sample #1 is $\approx 0.01 \mu C/cm^2$. A similar magnitude was reported in GaV$_4$S$_8$ [27] as well as in the other samples of GaV$_4$Se$_8$ [P3].

Figure 7.2 compares the temperature dependence of the polarization observed in sample #1 and sample #2. The pyroelectric polarization developing at the Jahn-Teller transition in sample #1 [panel (a)] is approximately five times larger than in sample #2 [panel (b)], probably due to a different population of the four polar domains. However, the magnetoelectric contribution to the polarization is only twice as large as in sample #2 [see insets]. Note that due to the multi-domain nature of the lacunar spinel crystals, the out-of-plane component of the magnetoelectric polarization may not be proportional to the same component of the pyroelectric polarization for various relative domain populations, as would expected for a single-domain sample based on a magnetostrictive polarization model [27]. Moreover, these results are only quantitative within $\sim 20\%$, due to the large variance of the pyroelectric polarization upon consecutive cooling cycles, the relatively large baseline thermocurrent, possible leakage currents within the sample and the rough estimate of the contacted surface of the crystals. Nevertheless, the data presented here provides solid evidence on the first-order pyroelectric phase transition at $T_2 \approx 45 - 47$ K giving rise to a sizable polarization, and the onset of magnetic phases below $T_C \approx 19$ K yielding an additional magnetoelectric polarization of 2 – 5% of the pyroelectric contribution. The magnetoelectric polarization may be used to determine the magnetic phase boundaries as will be discussed in Section 7.3.
Figure 7.2: Comparison of the polarization measurements in GaV$_4$Se$_8$ sample #1 (a) and sample #2 (b). The magnetoelectric component arising below $T_C \approx 19$ K is magnified in the insets of both panels.

7.2 Magnetic phases studied by SANS measurements

Magnetization measurements performed by S. Widmann and V. Tsurkan on GaV$_4$Se$_8$ revealed modulated magnetic phases below $T_C = 19$ K extending down to the lowest temperatures [P4] [166]. In this section, I present our complementary SANS measurements in order to identify the critical fields detected by magnetization measurements to the phase transitions separately in the four polar domains. This analysis relies on the reciprocal-space distribution of the magnetic wavevectors, already discussed for GaV$_4$S$_8$ in section 6.1.1. The similar SANS patterns obtained for GaV$_4$Se$_8$ allows for the adaptation of the acquired knowledge from its sister compound to the present case.

Small-angle neutron scattering experiments were performed on a single crystalline sample of GaV$_4$Se$_8$ by J. White, S. Bordács and B.Gy. Szigeti using the D33 and D11 beamlines at Institute Laue-Langevin. Here, I present my analysis of the results.
7.2.1 Field-induced phase transitions

Figures 7.3 (a)-(c) display the SANS images as the function of magnetic field after zero-field cooling to \( T = 12 \) K in three different measurement configurations with the incident beam, \( k_{in} \), perpendicular to the (001), (111) and (110) crystallographic planes, respectively. Additional measurements were carried out with neutron beams normal to the (111) plane at \( T = 1.5 \) K, where the magnetization measurements indicate the emergence of additional magnetic phases. In each setting the magnetic field was applied parallel to the neutron beam. Following each field scan, the sample was warmed up to the paramagnetic phase \( (T = 25 \) K) and cooled back in zero field. Note that in case of the (110) configuration, the measurement was performed in a different setting, where the sample was mounted with its \([1\bar{1}0]\) direction pointing in the vertical direction [see the second image in panel (c)], instead of the \([1\bar{1}0]\) direction in the other cases.

The scattering patterns observed in the three configurations are similar to the ones obtained in GaV\(_4\)S\(_8\) [26], [P5]. In zero field, a ring of scattered intensity is clearly discernible in the \( k_{in} \parallel [111] \) configuration [see the first image in Fig. 7.3 (b)]. In analogy to GaV\(_4\)S\(_8\), this ring can be attributed to the cycloidal states arising in the unique [111] polar domain. Similarly in GaV\(_4\)Se\(_8\), the magnetic \( q \)-vectors exhibit a high degree of orientational disorder within the plane normal to the polar axis. A faint intensity within the ring persists up to 400 mT, i.e. the close vicinity of the FM state.

The six Bragg-spots in the same image originate from cycloidal states present in the other three domains, with wavevectors confined within the three intersecting \{111\}-type planes, as visualized previously for GaV\(_4\)S\(_8\) in Fig. 6.4 (a). The intersection of the four-ring structure with the (001) plane results in four spots [panel (a)], while the scattering on the (110) plane reveals six spots [panel (c)], as previously seen in GaV\(_4\)S\(_8\) in Fig. 6.4 (b) and (d), respectively.

The wavelength of the magnetic modulations is \( \lambda_{Cyc} = 2\pi/q \approx 19.4 \) nm in zero field, featuring a significant increase in large magnetic fields, particularly in the \( H \parallel [111] \) configuration.

In each configuration, the intensity imaged in the detector plane increases in moderate magnetic fields of around \( \approx 70-100 \) mT, due to the redistribution of the modulation vectors governed by the magnetic anisotropy of the cycloidal structures, as observed in GaV\(_4\)S\(_8\) [see Fig. 6.5]. Since the plane perpendicular to the neutron beam, lying close to the surface of the Ewald’s sphere, is also perpendicular to the magnetic field, the \( q \)-vectors are redistributed by the field into the plane that is imaged by SANS, giving rise to an increase in the scattered intensities. Finally, in higher magnetic fields,
Figure 7.3: SANS images of GaV$_4$Se$_8$ recorded at $T=12\,K$ in various magnetic fields. Panels (a), (b) and (c) show scattering patterns with the neutron beam and the magnetic field normal to the (001), (111) and (110) surfaces of the crystal, respectively. The high-symmetry crystallographic directions are marked in the images of the second column.

the modulations vanish, as the magnetic structures transform into a field-polarized ferromagnetic state.

In order to trace the field-driven magnetic phase transitions through the SANS data, the total scattered intensity ($I$) and the central length of the modulation vectors ($|q|$) were analyzed as the function of the magnetic field. For this analysis, the radial intensity ($I$ vs $|q|$) was evaluated for each magnetic field, and the peaks were fitted with a Gaussian curve. The central value of the fitted Gaussian peak represents $|q|$, while the area under the curve yields the total intensity, $I$ at each magnetic field.

The differential susceptibility curves in comparison with the field-evolution of the SANS intensity and the length of the modulation vectors are plotted in the different measurement settings in Figs. 7.4-7.6. For the domain-selective
assignment of the magnetic phase transitions, the scattering contributions from the different polar domains were separately analyzed within the corresponding regions of the SANS pattern.

Figure 7.4 (a) shows the regions where the scattered intensity in the (111) plane originates exclusively from the unique [111] polar domain, visualized by a red ring in the 3d model image beside the SANS image. The polar axis of this domain is parallel with the applied magnetic field, i.e. their respective angle is \( \alpha = 0^\circ \). The SANS intensity and the length of the modulation vectors in panels (c) and (d) were evaluated in the masked areas marked by black boxes in panel (a) and compared with the anomalies in the magnetization and the dc susceptibility curves plotted in panel (b). It is clearly seen that the first and the third anomalies in the susceptibility are reflected in the SANS intensity and the \( q \)-modulus within the unique polar domain. Thus, the critical fields associated to these two anomalies are attributed to the Cyc-to-SkL and SkL-to-FM phase transitions in the unique [111] (\( \alpha = 0^\circ \)) domain.

Conversely, Figs. 7.4 (g) and (h) show the magnetic-field evolution of the SANS intensity and the length of the modulation vectors at \( T = 12 \) K, evaluated in the red trapezoidal regions shown in panel (e). Note that these regions carry the superposed contribution of the unique [111] domain (red ring), and one of the three other domains with their polar axis spanning \( \alpha = 70.5^\circ \) with the direction of the magnetic field. However, the second anomaly of the dc susceptibility is clearly reflected in the SANS intensity [panel (g)], whereas it has no sign in the regions associated to the unique domain [panel (c)]. Therefore the critical field near 150 mT is attributed to a direct phase transition from the Cyc state to the FM state in the three equivalent domains, driven by the oblique magnetic field applied in 70.5° with respect to the polar axis. The broad peak in the SANS intensity below the phase transition originates from the redistribution of the cycloidal wavevectors within the three domains to the (111) plane, governed by the magnetic anisotropy of the spin cycloids.

Figures 7.4 (i)-(k) and (l)-(n) present the same comparison of the magnetization and SANS measurements at \( T = 1.5 \) K. Remarkably, an additional anomaly arises in the dc susceptibility curve [panel (i)] close to \( \mu_0 H = 270 \) mT, which is also reflected in the SANS intensity and the \( q \)-vector modulus in the unique [111] domain [panels (j) and (k)]. Therefore, these data indicate the emergence of a possibly new magnetic phase at low temperatures, present for fields applied nearly parallel to the rhombohedral axis. Magnetization measurements up to 11 K (not shown here) suggest that even more additional phases may emerge below \( T = 12 \) K [P4]. The structure and origin of these phases are not yet known and is currently subject to further
Figure 7.4: Magnetic-field dependence of the SANS intensity and the modulus of the $q$-vectors compared to magnetization and dc susceptibility curves measured with $\mu_0 H \parallel \textbf{k}_m \parallel [111]$. Panels (a) and (e) indicate the sector masks in which the SANS data were evaluated in order to separate the contributions of magnetic structures within the unique [111] polar domain [(c)-(d) at $T=12$K and (i)-(k) at $T=1.5$K] from those primarily originating from the three other domains [(f)-(h) at $T=12$K and (l)-(n) at $T=1.5$K]. The magnetic phase boundaries are marked with vertical dashed lines, and a different background coloring for each phase. The parameter $\alpha$ denotes the angle enclosed by the direction of the magnetic field and the polar axis.
scanning probe experiments aiming for their real-space imaging.

Figure 7.5: Magnetic-field dependence of the SANS intensity and the modulus of the $q$-vectors compared to magnetization and dc susceptibility curves $\mu_0H \parallel k_{in} \parallel [110]$. Panels (a) and (e) indicate the sector masks in which the SANS data were evaluated, separating the contributions of magnetic structures within the [111] and [111] polar domains (c)-(d) from those in the [111] and [111] domains (g)-(h). The magnetic phase boundaries are marked with vertical dashed lines, and a different background coloring in each phase. The parameter $\alpha$ denotes the angle enclosed by the direction of the magnetic field and the polar axis.

The same analysis is performed in the $\mu_0H \parallel k_{in} \parallel [110]$ configuration, as displayed in Figure 7.5. Note that the in-plane alignment of the sample is different from that in the (111) case, as here the vertical direction is parallel to the [112] axis of the sample. The two Bragg spots lying along the [110] direction, marked by the black sectors in panel (a) correspond to the polar domains [111] (red ring) and [111] (blue ring), both characterized by an angle of $\alpha = 35.3^\circ$, whereas the red regions marked in panel (e) carry con-
Figure 7.6: Magnetic-field dependence of the SANS intensity and the modulus of the \( q \) vectors compared to magnetization and dc susceptibility curves for \( \mu_0 H \parallel k_{in} \parallel [100] \). The SANS data were evaluated within the sector masks presented in panel (a). In this setting, all four rhombohedral domains are identically characterized by the \( \alpha = 54.7^\circ \), enclosed by the direction of the magnetic field and the polar axis. The Cyc-SkL and SkL-FM phase boundaries are marked by vertical dashed lines and different background coloring. Panel (e) (Reproduced from [P4]): Stability ranges of the magnetic phases at \( T = 12 \, \text{K} \) as the function of the parallel and perpendicular components of the magnetic field with respect to the polar axis. Black squares and dots represent the critical fields of the phase boundaries observed in magnetization measurements, while black crosses mark the anomalies in the SANS intensity.

Contributions from the magnetic structures within the \([1\bar{1}1]\) and \([\bar{1}1\bar{1}]\) domains (represented by the green and yellow rings, respectively). Within these last two domains, the magnetic field is normal to the polar axes, i.e. \( \alpha = 90^\circ \). Three anomalies are observed in the susceptibility curve at \( T=12 \, \text{K} \). In the \( 90^\circ \) domains a continuous transformation from the Cyc state to the field-
polarized state is expected, through the gradual closing of the angle in the transverse conical structure [see 6.5 (f)]. This transition is unambiguously reflected by the vanishing of the SANS intensity in the regions marked by the red sectors at $\mu_0H \approx 150\text{mT}$, as seen in Fig. 7.5 (g). The other two anomalies observed in the magnetization curves correspond to phase transitions in the domains with $\alpha = 35.3^\circ$. Correspondingly, the highest critical field near 200 mT is attributed to the vanishing of the SkL modulations in the 35.3° domains [panels (c)-(d)], whereas the lowest critical field close to 80 mT indicates the Cyc-to-SkL transition. However, this latter phase transition does not appear markedly in the SANS data, or is obscured by the gradual increase of the SANS intensity due to the field-induced redistribution of the cycloidal wavevectors in a similar fashion as observed for in the SANS intensity within the (111) plane [Fig. 7.4 (g)].

Finally, results obtained in the $\mu_0H \parallel k \parallel [100]$ setting are summarized in Figs. 7.6 (a)-(d). In this configuration, each rhombohedral domain is equivalent, characterized by an angle of $\alpha = 54.7^\circ$ spanned by the magnetic field and the hard magnetic axis. The two anomalies observed in the magnetization data are also traceable in the SANS intensity, revealing the Cyc-SkL and SkL-FM phase transitions.

The information obtained by the analysis of the SANS data as compared to the magnetization curves in the different measurement configurations is summarized in Fig. 7.6 (e), where the stability ranges of the magnetic phases at $T=12\text{K}$ are plotted as the function of the parallel and perpendicular components of the magnetic field with respect to the polar axis. The magnetization measurements with $\mu_0H \parallel [112]$ exhibiting $\alpha$ angles of $19.5^\circ$, $61.9^\circ$ and $90^\circ$ were not shown here [P4].

### 7.2.2 Magnetic phase diagram of GaV$_4$Se$_8$

The magnetization data obtained over the full temperature range within the magnetic phases of GaV$_4$Se$_8$ [166],[P4] along with the assessment of the magnetic phase boundaries according to the SANS results at $T = 12\text{K}$ and $T = 1.5\text{K}$ allows for the reconstruction of the magnetic phase diagram over the whole range of temperatures for a single polar domain as a function of the strength and the orientation of the magnetic field.

Figure 7.7 displays the magnetic phase diagram for a single structural domain of GaV$_4$Se$_8$ for five different directions of the applied magnetic field. The critical fields of the phase transitions were obtained from magnetization measurements [166],[P4] in three different configurations: $H \parallel [111],[110]$ and [100], displayed in the first, second and third rows in Fig. 7.7, respectively. The transition line between the magnetic and paramagnetic phases was de-
determined by temperature-dependent magnetization measurements. In finite magnetic fields, this boundary is indicated by a broad feature in the $m(T)$ curve, suggesting a crossover character of the phase transition.

Figure 7.7: Magnetic phase diagram of a single domain of GaV$_4$Se$_8$ for various orientations of the applied magnetic field with respect to the polar axis, denoted by the angle $\alpha$. The anomalies in the magnetic-field and temperature-dependent dc susceptibility curves are indicated by full and open circles, respectively. The connecting lines are guides to the eye. The phase boundaries established by anomalies in the SANS intensities are denoted by black crosses. The Cyc and SkL modulated phases are the most robust for magnetic field directions close to the polar axis. Note that the y scale is different in case of the graphs in the top row. Additional phases denoted by question marks emerge below $T = 12$ K in magnetic fields applied parallel to the rhombohedral axis. Figure reproduced from [P4].
Most interestingly, the magnetic phase diagram of GaV₄Se₈ reveals the Cyc and SkL phases to extend down to the lowest temperature of the SANS experiments, \( T = 1.5 \) K. This lies in strong contrast with cubic helimagnets as well as GaV₄S₈, where the SkL state is observed only in the close vicinity of the Curie-temperature [26, 79]. In cubic helimagnets, the conical state represents a minimal-energy solution, suppressing the SkL, whereas in GaV₄S₈ the strong uniaxial anisotropy favors a ferromagnetic ground state. In contrast, the weaker easy-plane anisotropy in GaV₄Se₈ [P4] favors the modulated states over the uniformly magnetized ferromagnetic state even at low temperatures, likely down to zero Kelvin [83].

Another striking difference between the magnetic phase diagram of GaV₄S₈ and GaV₄Se₈ is the stability range of the SkL in oblique magnetic fields. In GaV₄S₈, the magnetic phase diagram is only weakly dependent of the perpendicular component of the magnetic field with respect to the polar axis, up to large \( \alpha \) angles, as demonstrated by Fig. 3.4 (f). However, in GaV₄Se₈, the magnetic-field range of the SkL phase is quickly suppressed as the angle of the magnetic field is increased. The SkL phase vanishes completely for angles greater than 61.9° [see Fig. 7.6 (f)], while it is stable at least up to \( \alpha = 71° \) in GaV₄S₈. On the contrary, in GaV₄Se₈, the stability range of the modulated phases are more extended for magnetic fields parallel to the polar axis. These features are well reproduced by Monte-Carlo simulations minimizing the Ginzburg-Landau energy density in the presence of an axial anisotropy [see Eq. 2.12], performed by A. Leonov [83],[P4]. The theoretical analysis of the phase diagram indeed confirms that easy-axis anisotropies enhance the robustness of the Cyc and SkL phases against oblique magnetic fields, while suppressing their stability range for fields applied parallel to the easy-axis. Conversely an easy-plane anisotropy stabilizes the modulated phases against fields applied along the polar (hard) axis, whereas suppressing them for oblique fields [83].

Finally, I briefly discuss our findings concerning the additional phases emerging for \( \alpha = 0° \) below 12 K. Apparently, these phases emerge only in magnetic fields applied at small angles with respect to the polar axis. Specifically, they emerge for \( \alpha = 0° \) and already absent for \( \alpha = 35.3° \). In the SANS images the hexagonal pattern of spots as well as the ring structure exclude the emergence of a square lattice of skyrmions, as proposed for polar materials with easy-plane type axial anisotropy [167–169]. On the basis of systematic Monte-Carlo studies, J. Rowland et. al proposed the emergence of an elliptical cone phase [168], which may be one of the extra phases observed in GaV₄Se₈. Fractionalization of skyrmions and emergence of additional exotic phases were also predicted for systems with axial anisotropy [169, 170]. The additional phases may also correspond to i) other distorted forms of...
the cycloidal state due the presence of lamella-like rhombohedral domain structures with typical thickness on the sub-micrometer scale or ii) further modulations developing along the polar axis due to frustrated exchange interactions. Ongoing research, including scanning probe microscopy, is being performed on GaV$_4$Se$_8$ in order to resolve the detailed microscopic properties of these phases.

7.3 Magnetoelectric polarization measurements in GaV$_4$Se$_8$

Similarly to susceptibility curves [79], anomalies in the pyrocurrent as the function of temperature and magnetic field can also reveal the transitions between the modulated magnetic phases [27]. I performed pyrocurrent and magnetocurrent measurements within the magnetic phases of GaV$_4$Se$_8$ in order to characterize the magnetoelectric response of the material as well as to explore the magnetic phase diagram via the polarization experiments.

7.3.1 Magnetic phase diagram via polarization measurements

Figure 7.8 shows the polarization measurements performed on the samples #1 and #2 presented in Section 7.1, compared with the static magnetization data obtained by S. Widmann and V. Tsurkan at the University of Augsburg on a different specimen, denoted as sample #3. The magnetizing field was applied perpendicular to the (111) surface of the crystal. The peaks in the susceptibility as well as the steps in the magnetization curves indicate magnetic phase transitions emerging either in the unique [111] domain or within the three equivalent domains whose polar axes spans $71^\circ$ with the magnetic field, as shown previously in Fig.3.3. In this configuration, the unique domain features transitions between the Cyc, SkL and FM phases, while the Cyc phase extends to higher fields in the three other polar domains, followed by a direct transition to the ferromagnetic phase, as assessed using the SANS data in Section 7.2.1.

The magnetocurrent was measured on both GaV$_4$Se$_8$ samples in increasing and decreasing magnetic fields at various temperatures with a sweeping rate of 1T/min. The measurement performed at $T=10$ K on sample #1 and sample#2 are shown in Figs. 7.8 (b) and (c), respectively. The presented magnetocurrent curves were obtained by averaging over ten field cycles followed by the removal of a constant baseline due to inductive currents. The
Figure 7.8: Comparison of magnetization and polarization measurements in GaV₄Se₈. Panels (a) and (d) display the dc susceptibility and the magnetization curves measured on a different sample at T=10.5 K. Panels (b) and (c) show magnetocurrent measurements in samples #1 and #2, respectively, in increasing (red curves) and decreasing fields (blue curves). The magnetically induced polarization ΔP was obtained as the temporal integral of the magnetocurrent curves.
magnetically induced polarization within the two samples were obtained by temporal integration of the corresponding magnetocurrent curves.

In case of sample #1 [Fig. 7.8 (b)], two peaks are discernible in the magnetocurrent both in increasing (red) and decreasing fields (blue), indicated by red and blue dashed lines. The low-field peak, located at 0.1 T and 0.15 T in increasing and decreasing fields, respectively, is approximately an order of magnitude smaller than the second one located at 0.3 T and 0.4 T. The negative sign of the magnetocurrent peaks in increasing fields implies that the polarization in the SkL and FM phases is reduced as compared to the zero-field Cyc phase. The two magnetocurrent peaks lie close to the critical fields of the Cyc-SkL and SkL-FM phase transitions, as established by magnetization and SANS measurements in Section 7.2.1. Therefore, these peaks are attributed to a change in the polarization at the phase transition between the Cyc and SkL states and between the SkL and FM states in the unique [111] rhombohedral domain. The change in the magnetoelectric polarization at the two phase boundaries are approximately $\Delta P_{\text{Cyc-SkL}} \approx -0.5 \mu C/m^2$ and $\Delta P_{\text{SkL-FM}} \approx -6 \mu C/m^2$. Notably, there is a significant hysteresis in the position of the peaks, which is independent of the sweeping rate, suggesting a bistability of the modulated phases in a broad magnetic field region of 50-100 mT. The polarization contribution in the three other structural domains is not detected in this specimen suggesting a relatively small population of those domains in this sample.

Figure 7.9 (c) shows the magnetocurrent in sample #2 measured at $T=10$ K with the same field sweep rates. The anomalies observed in sample #1 are absent from the magnetocurrent curves in this sample, whereas another broad feature appears between 100-200 mT. The location of the peak lies close to the critical field associated to the Cyc-FM phase transition in the three rhombohedral domains wherein the polar axis spans 71° with the applied field. Sample #2 therefore appears to contain a larger proportion of the other three domains and a negligible proportion of [111] domain. Note that the sign of the magnetically induced polarization is also different as compared to sample #1. Indeed, due to the 71° angle between the applied field and the polar axis in these domains, a combination of the magnetoelectric tensor elements is probed by the polarization measurement. Furthermore, since the electric contacts are applied to the (111) surfaces of the crystal, only the projection of the induced polarization along the [111] axis is measured. This component measures approximately $\Delta P_{\text{Cyc-FM}} \approx 1.5 \mu C/m^2$.

Since samples #1 and #2 provide complementary information on the phase transitions in the [111] and the three other polar domains, respectively, the whole magnetic phase diagram for the $\mu_0 H \parallel [111]$ configuration may be explored by the magnetoelectric results obtained on these two samples.
Figure 7.9: Temperature and magnetic-field dependence of the displacement current in GaV₄Se₈. Panel (a): Pyrocurrent curves measured in various magnetic fields. The curves are shifted proportional to the magnetic field, as indicated in the right axis of the graph. Panels (b) and (c): Magnetocurrent measurements on sample #1 and sample #2, respectively. The curves are shifted proportionally to the sample temperature. Red curves were measured in increasing fields, while blue curves correspond to measurements in decreasing fields.

The phase boundary between the paramagnetic and magnetically ordered phases was explored by pyrocurrent measurements performed in various magnetic fields using a cooling rate of 20 K/min, as shown in Figure 7.9 (a). The transition is marked by a peak in the pyrocurrent curves with a maximum at \( \approx 19 \) K. The magnetic ordering temperature seems to be weakly affected by the applied magnetic fields. The features of the pyrocurrent curves are smeared in higher magnetic fields, indicating a crossover rather than a phase transition.

Magnetocurrent curves obtained on samples #1 and #2 at various temperatures are plotted in Figs. 7.9 (b) and (c), respectively. Following the temperature dependence of the magnetocurrent peaks, the magnetic phase boundaries are mapped over the H-T plane. Remarkably, a hysteresis is ob-
served for both peaks in sample #1 [panel (b)] below $T < 15$ K, with a gradual increase towards lower temperatures.

Figure 7.10 shows the temperature dependence of the critical fields established by the magnetoelectric polarization measurements plotted together with the phase diagram based on the magnetization measurements in the $H \parallel [111]$ configuration. The phase boundaries obtained by the polarization measurements in sample #1 are plotted together with the phase diagram corresponding to the unique [111] domain [panel (a)], whereas results on sample #2 are plotted over the phase diagram corresponding to the three other domains [panel (b)]. There is a good agreement between the phase diagrams obtained by magnetization and magnetoelectric polarization measurements. The temperature mismatch of $\sim 1$ K between the two measurements may originate from sample variation or the miscalibration of our temperature sensor. A variation in the critical fields may result from demagnetization effects due to the different sample geometries or due to slight misorientation of the samples. Note that the additional magnetic phases below $T = 12$ K were not observed in the polarization measurements, suggesting that the difference of the polarization between these states falls below the sensitivity of our measurement.

In conclusion, a sizable pyroelectric polarization in the range of $P_{FE} \simeq 0.4 \, \mu C/cm^2$ was demonstrated to arise in GaV$_4$Se$_8$ upon the Jahn-Teller phase transition. This value is of the same order of magnitude as that measured in GaV$_4$S$_8$ [27] and other samples of GaV$_4$Se$_8$ [85],[P3]. Further pyrocurrent and magnetocurrent measurements demonstrated that the magnetic phases give rise to additional magnetoelectric polarization contribution in the range of 2-5% of the pyroelectric polarization. The associated anomalies in the magnetocurrent curve are the signature of the magnetic phase transitions. The critical field values obtained in the magnetoelectric study agree well with those established by magnetization measurements.

My results are corroborated by the findings of Fujima et al. published in [85] shortly after my experiments were performed. They managed to achieve a better sensitivity in the magnetocurrent measurements by at least one order of magnitude in a similar experimental setup using a Keithley electrometer. Nevertheless, their results strongly resemble those in my experiments on sample #1. They observed the magnetically induced polarization with magnitudes of $\Delta P_{\text{Cyc-SKL}} \simeq -2 \mu C/m^2$ and $\Delta P_{\text{SKL-FM}} \simeq -10 \mu C/m^2$, however, the pyroelectric component developing upon the Jahn-Teller phase transition was not reported. They were also able to resolve the third anomaly in the magnetocurrent curves associated to the Cyc-FM phase transition arising in the three 71° domains. However, the detailed understanding of the magnetic phase diagram in the structural multi-domain GaV$_4$Se$_8$ was provided in [P4],
Figure 7.10: Magnetic phase diagrams of GaV$_4$Se$_8$ for $\alpha = 0^\circ$ and $\alpha = 71^\circ$ in panels (a) and (b) respectively. The phase boundaries determined by the magnetoelectric measurements are overlaid on the phase diagrams based on magnetization data. The red upward pointing triangles in panel (a) represent phase boundaries in sample #1 measured in increasing magnetic fields, while blue triangles pointing downwards were measured in decreasing fields. The black squares represent the PM-FM phase boundary determined from pyrocurrent measurements. The Cyc-FM phase boundary measured in sample #2 via polarization measurements in both increasing and decreasing magnetic fields are presented as black triangles. The connecting lines are guides to the eye.

based on the combination of magnetization and SANS data, as discussed in section 7.2.1.

7.4 Conclusion

In this chapter, I described the pyroelectric and magnetic properties of GaV$_4$Se$_8$, based on our electric polarization, magnetization and SANS measurements. The ferroelastic-pyroelectric phase transition was analyzed through my pyrocurrent measurements, and a sizable polarization was found [P3]. A comprehensive study of the magnetic phase diagram was provided, resolving the phase transitions as the function of the magnetic field direction, utilizing our SANS measurements to distinguish the contributions of the different coexisting structural domains in the bulk samples [P4]. Remarkably, in this compound, the modulated magnetic phases extend down to the lowest temperatures, owing to the easy-plane anisotropy, in contrast with GaV$_4$S$_8$, featuring a FM ground state, favored by the strong easy-axis anisotropy. As
a further consequence of the easy-plane anisotropy, the modulated magnetic structures are more robust against axial magnetic fields, but their stability is reduced in magnetic fields normal to the polar axis. Finally, the magneto-electric polarization induced by the magnetic textures was analyzed, based on my magnetocurrent measurements on two GaV$_4$Se$_8$ samples.
Chapter 8

Modulated magnetic phases in GaMo$_4$S$_8$

In this chapter, I investigate the modulated magnetic phases in GaMo$_4$S$_8$, the third lacunar spinel compound of our interest.

First, the structural and pyroelectric properties of the compound will be summarized based on the results of polarization and surface scanning probe experiments [P6] performed by our collaborators at the University of Augsburg and at the University of Dresden. Thereafter, the magnetic properties of GaMo$_4$S$_8$ will be presented through the analysis of static magnetization and small-angle neutron scattering (SANS) experiments [P7]. The magnetization experiments were performed at the Wigner Research Centre for Physics by me with the assistance of Dr. L.F. Kiss and L. Balogh. The SANS experiments were carried out at the Oak-Ridge National Laboratory using the GP-SANS instrument. The local group performing the experiments were Dávid Szaller, Lisa deBeer-Schmitt and me, and I analyzed the results. In the first part of the SANS study the distribution of the cycloidal wavevectors in the reciprocal space will be analyzed in zero field. Finally, the magnetic phase diagram of GaMo$_4$S$_8$ will be presented, deduced via the comparison of magnetization and SANS data.

8.1 Structure and polarization in GaMo$_4$S$_8$

8.1.1 GaMo$_4$S$_8$ samples

GaMo$_4$S$_8$ crystals were synthesized by H. Nakamura at Kyoto University via the flux method in a sealed molybdenum tube [171]. Characterization with X-ray and neutron diffraction confirmed the single-crystalline nature
of the samples. The chemical constituents of the crystals were identified as Ga, Mo and S by energy-dispersive spectroscopy performed by Prof. Nakamura, however, traces of parasitic glassy phases containing Si, Ca and K were found. These amorphous phases are separated macroscopically from the single-crystalline volumes [172].

8.1.2 Ferroelastic and pyroelectric domains in GaMo$_4$S$_8$

Scanning-probe microscopic (SPM) measurements were performed on the as-grown (111) surface of GaMo$_4$S$_8$ in order to explore the polar domain structures arising below the temperature of the Jahn-Teller transition [P6]. The measurements were carried out by E. Neuber and P. Milde at the Technical University of Dresden and I contributed to the interpretation of the results.

Figures 8.1 (a)-(d) show the AFM, KPFM, mAFM images obtained in non-contact scanning mode at $T = 7.8 \, \text{K}$ and the PFM image obtained subsequently in contact mode over the same surface region at $T = 11.1 \, \text{K}$. The images clearly demonstrate that similarly to GaV$_4$S$_8$ [P1], the GaMo$_4$S$_8$ sample also consists of pyroelectric domains, forming alternating lamellar structures, as shown schematically in Fig. 8.1 (e). The colored lines represent the domain walls resolved by the combination of the four scanning-probe measurements. The continuous lines indicate domain walls parallel to the $\langle 110 \rangle$-type directions on the (111) surface, i.e. $\{001\}$-type domain walls. The dotted lines correspond to domain walls whose intersection with the (111) plane is not parallel to the $\langle 110 \rangle$-type directions. For some of the domain walls the KPFM image reveals a negative (black) and positive (white) contrast in the electrostatic potential, corresponding to positive and negative surface charges, as indicated by the red and blue colors in panel (e), respectively.

Two regions of alternating domains can be discerned in the areas I and II, based on the AFM and PFM micrographs (a) and (d). The primary domain walls separating the individual structural domains are electrically neutral [see the KPFM image in panel (b)] and are parallel to the $\{001\}$-type planes, therefore they are both mechanically and electrically compatible.

The secondary domain boundaries between the regions IV&I and I&III are apparently also compatible, on the other hand, all the other secondary interfaces are either positively (I&II) or negatively charged (IV&V, II&III, III&V), with orientations different from $\{001\}$-type planes. Note that $\{110\}$-type domain walls intersecting the (111) surface along $\langle 112 \rangle$-type directions still represent mechanically compatible but charged domain walls. The actual orientation of an incompatible domain wall is determined by the relative magnitudes of the elastic and the electrostatic energy.
Figure 8.1: SPM images on the (111) surface of GaMo$_4$S$_8$. Panel (a)-(c): Topography, surface potential and dissipation channels of the non-contact mode AFM scan, respectively. Panel (d): In-phase (X) channel of the contact-mode PFM image captured over the same surface region. Panel (e): Schematic representation of the domain boundaries according to the SPM measurements. Domain boundaries parallel to the $\langle 1\bar{1}0 \rangle$-type directions are indicated by continuous lines, whereas other directions are shown by dashed lines. Negative, neutral and positive surface potentials along the domain walls, corresponding to the KPFM image in panel (b), are indicated by the blue, green and red lines, respectively. Panel (f): Assignment of the four rhombohedral domains according to the scanning probe measurements (a)-(d). The color code is visualized at the bottom by the four arrows representing the direction of the polarization in each domain. The black arrows indicate the direction of the average polarization in each secondary domain region, denoted by roman numbers. Figure reproduced with permission from [P6]. Copyright by IOP Publishing.
Figure 5.2 (c) shows the only possible fully compatible arrangement of the pyroelectric domains over a secondary domain boundary. Based on the combined information gathered from the four complementary channels of the scanning probe measurements, the pyroelectric domain pattern over the whole scanned area can be unambiguously determined, as displayed in Fig. 8.1 (f). Note that PFM only reveals contrast between the unique [111] polarization (colored green) and the other three domains (red, blue and yellow). Even though the areas III, IV and V appear as uniform in the PFM image, the compatibility of the interfaces IV&I and I&III, as suggested by the uniform KPFM signal along these boundaries, requires the presence of an alternating lamellar structure, according to the assignment in panel (f). Regions II and V were assigned in a way to satisfy the compatibility criteria along the primary domain walls, while accounting for the positive and negative surface charges due to the head-to-head and tail-to-tail arrangement of the average polarization (see black arrows) in the secondary domains, in accord with the sign of the surface potential revealed by the KPFM image.

The typical domain widths range from 10 nm to 100 nm with a peak in the distribution around $d \approx 25 \text{ nm}$, as found via the analysis of $\sim 1000$ structural domains [P6]. These domain widths are at least an order of magnitude smaller than those observed in GaV$_4$S$_8$ [P1]. So far, no magnetic structures could be visualized in GaMo$_4$S$_8$, probably since the small modulation lengths falls below the limits of the spatial resolution of the mAFM measurements. The modulation wavelength was found to be approximately $\lambda_{Cyc} \approx 10 \text{ nm}$ via SANS measurement (as will be shown in Section 8.4). Since the typical wavelength of the magnetic modulations lies in the range similar to the width of the structural lamellae, the magnetic textures might be significantly influenced by the geometrical confinement imposed by the narrow domains. As a result the magnetic properties may strongly depend on the pyroelectric domain structure developing upon the Jahn-Teller transition.

Polarization experiments carried out by K. Geirhos at the University of Augsburg demonstrated that the Jahn-Teller phase transition gives rise to an electric polarization of $P_{FE} \approx 0.2 \mu\text{C/cm}^2$, which can be reversed by the application of poling fields in the kilovolt range, demonstrating that the domain population can be influenced by external electric fields.
8.2 SANS tomography of magnetic modulations in zero field

In this section, I introduce the results of zero-field SANS experiments, providing insight into the distribution of the magnetic propagation vectors in the reciprocal space.

The SANS experiments were carried at the Oak Ridge National Laboratory with the GP SANS instrument on a single crystalline specimen of GaMo$_4$S$_8$ with a mass of $m = 112.5$ mg. The sample was mounted to the goniometer stick with its $[1\bar{1}0]$ cubic direction parallel to the vertical rotation axis. The reciprocal-space distribution of the zero-field magnetic modulation wavevectors was explored via the wide-angle rotation of the sample around the $[1\bar{1}0]$ axis, as done previously in the case of GaV$_4$S$_8$ [see section 6.1.1].

A neutron wavelength of 6 Å was used with the detector set to a distance of 5 m from the sample, employing a collimator of the same length. The sample was zero-field cooled to 2 K and rotated in $1^\circ$ steps, followed by a 120 s acquisition of the scattered intensity. The background signal was measured in the paramagnetic phase at $T = 25$ K following the same procedure.

Despite the larger mass and the longer acquisition time, the SANS images are characterized by a worse signal-to-noise ratio than those measured on GaV$_4$S$_8$ and GaV$_4$Se$_8$. Therefore, scattering images were averaged over a $10^\circ$ moving window in the rotation angle. Figures 8.2 (a)-(d) show the SANS images obtained on four high-symmetry planes, namely the (111), (110), (112) and (001) planes, respectively. A pixel-wise adaptive Wiener filter, assuming Gaussian noise, was applied for the visualization. The scattering on the (111) plane reveals six Bragg spots and a faint band of intensity between the spots. Remarkably, the Bragg spots are smeared out in an asymmetric, V-shaped fashion, stretching outside the perimeter of the band.

Six spots are discernible in the (110) plane as well, uniformly spanning a central angle of $\sim 60^\circ$. This lies in contrast with the case of GaV$_4$S$_8$ and GaV$_4$Se$_8$, where the spots corresponding to the $\alpha = 90^\circ$ domains enclose $55^\circ$ with the spots of the $\alpha = 35.3^\circ$ domains [c.f. Figs. 6.4 (b) and 7.3 (c)]. This suggests that the reciprocal-space distribution of the cycloidal wavevectors in GaMo$_4$S$_8$ deviates from the ring structure observed in GaV$_4$S$_8$.

In the (112) plane the azimuthal angle between the side spots is reduced to $\sim 40^\circ$, finally the two spots merge to a single one in the (001) plane. The anisotropic broadening of the peaks is also well seen in the (001) plane, where the spots are smeared along the (100)-type directions, with stronger streaks observed along the [100] than the [010] direction.

The length of the $q$-vectors is approximately $|q| \approx 0.6$ nm$^{-1}$, which shows
that the periodicity of the modulations is $\lambda = 2\pi/|q| \approx 10.5\text{nm}$. This modulation wavelength is roughly the half of that in GaV$_4$S$_8$ and GaV$_4$Se$_8$ suggesting a relatively stronger Dzyaloshinsky-Moriya interaction (DMI), as $\lambda \propto J/D$ and the Curie-temperature is close to that in GaV$_4$Se$_8$, implying a similar strength of the symmetric exchange, $J$, in the two compounds.

The 3d reciprocal-space tomographic image has been retrieved from the SANS images by the same method as done in the case of GaV$_4$S$_8$ [see 6.1]. In order to enhance the signal-to-noise ratio and to eliminate the asymmetries of the scattering pattern introduced by imbalances between the populations of the different types of structural domains, the 3d scattering pattern was sym-
metrized by applying all the symmetry operations of the high-temperature $T_d$ point group to the 3d pattern of scattered intensity and averaging the original and all the transformed scattering patterns.

Figures 8.2 (e)-(h) display the symmetrized tomographic image viewed from the different high-symmetry directions. The $q$-vectors are visualized above an arbitrary threshold in the scattering intensity, filtering out most of the diffuse background. Figure B.1 in the Appendix demonstrates the effect of the symmetrization and filtering by comparing the same tomographic data with and without symmetrization using various threshold intensities. It is well seen that besides equalizing the symmetrically equivalent spots for a better visualization, the symmetrization does not introduce any artifact in the scattering pattern. The threshold value of the 3d plots was chosen to display the strongest features clearly, therefore the weak stripes of intensity between the spots in the (001) plane are not displayed [see Fig. B.1 in the Appendix]. The smearing of the Bragg spots along the $\langle 100 \rangle$-type directions may originate from domain-boundary effects due to the narrow structural domains with $\{100\}$-type domain walls, deflecting the magnetic propagation vectors towards the $\langle 100 \rangle$ directions. According to the PFM measurements on GaMo$_4$S$_8$, the width of the structural domains, ranging from 10-100 nm, is comparable with the length-scale of the magnetic modulation wavelengths, therefore possible domain-boundary effects may have a significant influence on the SANS intensity. In the following analysis I neglect these supposedly domain-wall-induced contributions to the wavevector distribution and focus on those governed by the interactions in the bulk.

It is instructive to compare the reciprocal-space tomographic images in GaV$_4$S$_8$ and GaMo$_4$S$_8$, as shown in Figs. 8.3 (a)-(c) and (d)-(f), respectively. Similarly to GaV$_4$S$_8$, the modulation wavevectors in GaMo$_4$S$_8$ are distributed over four rings, associated to the four rhombohedral domains. However, between the crossing of the rings along the $\langle 110 \rangle$ cubic directions, the $q$-vectors deflect out of the $\{111\}$-type planes in an alternating manner. This alternation obeys the three-fold rotational symmetry of the crystal structure. This feature is most prominently seen in 8.2 (f) and (g), highlighted by the schematic representation in Figs. 8.3 (e) and (f). The different colors of the rings represent the modulation vectors belonging to the four structural domains with their polar axes pointing towards the $\langle 111 \rangle$ directions. The same images are shown in Figs. 8.2 (i)-(l) from the same views as the tomographic images in panels (e)-(h).

The zero-field SANS tomography in GaV$_4$S$_8$ revealed a high degree of orientational freedom within the $\{111\}$-type planes, suggesting that the in-plane magnetic anisotropies are negligibly weak relatively to the Heisenberg exchange interaction and the DMI, thus, the $q$-vectors are subject of pinning.
Figure 8.3: A comparison of the reciprocal-space structure of the modulation wavevectors in GaV₄S₈ and GaMo₄S₈. The first row contains the SANS tomographic image and its graphical representation in GaV₄S₈ in panels (a) and (b), respectively. The scattering pattern contains four rings of q-vectors, each corresponding to one type of rhombohedral domains. A single ring corresponding to the [111] polar domain is displayed in panel (c). Panels (d)-(f): Pattern of the wavevectors observed in GaMo₄S₈. The rings are deflected from the {111}-type planes in the segments between the ⟨110⟩ directions in an alternating manner.

On the other hand, the deviation of the q-vectors from the {111} planes in GaMo₄S₈ indicates the presence of stronger magnetic anisotropies, likely due to the relatively stronger coupling of the magnetic textures to the crystal lattice via the spin-orbit interaction. Indeed, stronger spin-orbit coupling is expected for the 4d shell of Mo as compared to the 3d shell of V.

For a phenomenological description of the distribution of the q-vectors, the following effective Landau potential is considered, containing the lowest-order polynomials compatible with the F̅43m space group symmetry of the high-temperature phase [173]:

\[ q_z (n_m - 1) q_z (n_m - 1) \]
\[ V(\hat{q}) = (\hat{n}\hat{q})^2 + \alpha \left( \hat{q}_x^4 + \hat{q}_y^4 + \hat{q}_z^4 \right) + ... \]  

(8.1)

where the unit vector \( \hat{n} \) represents any of the four \( \langle 111 \rangle \) polar axes for a single rhombohedral domain, \( \hat{q} \) is the normalized wavevector and the \( x, y, z \) components are defined in the cubic setting. Thereby, the length of the \( q \) vectors is assumed to be fixed by \( D/J \). The first term in Eq. 8.1 is of second order in spin-orbit coupling and favors the confinement of the \( q \)-vectors normal to the polar axes, \( \hat{n} \). The orientational degeneracy of the four \( \{111\} \)-type planes is broken by the second term, being of fourth order in spin-orbit coupling [29], whose strength is tuned by the empirical parameter, \( \alpha \). Note that the form of the potential is compatible both with the high-temperature cubic and the low-temperature rhombohedral symmetry of the lacunar spinel compounds. As it turns out, the cubic anisotropy term in Eq. 8.1 is sufficient for a qualitative description of the \( q \)-vector distribution without considering additional terms arising due to the rhombohedral distortion.

The minimal-energy solutions to Eq. 8.1 are sought by parametrizing \( \hat{q} \) in spherical coordinates on the surface of the unit sphere:

\[ \hat{q} = \hat{e}_1 \sin \Theta \cos \Phi + \hat{e}_2 \sin \Theta \sin \Phi + \hat{e}_3 \cos \Theta. \]  

(8.2)

It is practical to select an orthonormal coordinate system where the \( \hat{e}_3 \) unit vector points along the polar axis of the given rhombohedral domain. For instance in the case of the \( \{111\} \) polar domain, \( \hat{e}_1 = 1/\sqrt{2} [1\overline{1}0] \), \( \hat{e}_2 = 1/\sqrt{6} [11\overline{2}] \), and \( \hat{e}_3 = 1/\sqrt{3}[1,1,1] \) are chosen. The \( q \)-vectors are parametrized in a similar fashion for the other three domains as well. In this setting, the first term in Eq. 8.1 is minimized by \( \Theta = \pi/2 \) for all \( \phi \in [0, 2\pi] \), describing a circle in the plane perpendicular to the polar axis. The minimal-energy solutions for small values of \( \alpha \) are found perturbatively by expanding the potential in \( \Theta \) around \( \pi/2 \) up to the second order. Minimizing the potential with respect to \( \Theta \) yields the following parametric space curve for the \( q \)-vectors of the lowest-energy cycloidal states:

\[ \Theta = \frac{\pi}{2} + \frac{\sqrt{2}}{3} \frac{\alpha}{1 + \alpha} \sin (3\Phi). \]  

(8.3)

Figure 8.4 (a) and (b) show the perturbative solutions of the potential according to Eq. 8.3 for \( \alpha = \pm 0.2 \), respectively. In both cases, the curve described in Eq. 8.3 contains the \( \langle 110 \rangle \)-type \( q \)-vectors within the \( \langle 111 \rangle \) plane, whereas the curve is deflected the most out of the \( \langle 111 \rangle \) plane for the \( \langle 112 \rangle \)-type directions in an alternating manner. The sign of the deflection is opposite for the opposite signs of \( \alpha \).
Figure 8.4: Perturbative and numerical solutions minimizing the potential in Eq.8.1 for \( \hat{n} = 1/\sqrt{3}[111] \) with the anisotropy parameter, \( \alpha = 0.2 \) and -0.2 in panel (a) and (b), respectively. The black regions represent the 5%-vicinity of the energy minima obtained by the numerical minimization of the potential. The continuous curve displays the minimal-energy solution determined perturbatively according to Eq.8.3. The \( \langle 110 \rangle \)-type wavevectors are indicated by arrows. The colormap encodes the value of the energy functional in Eq.8.1 for the \( q \)-states of the perturbative solution.

The color coding represents the value of the effective potential at each \( \hat{q} \) point of the curves, according to Eq.8.1. The small modulation in the energy of the perturbative solutions implies that the exact minimal-energy solutions of the model are given by \( \Phi = \pi/6 + m\pi/3 \), i.e. the deflected \( \langle 112 \rangle \)-type \( q \)-vectors, whereas the \( \langle 110 \rangle \) states represent higher-energy solutions. This small variation of the potential around the curves was neglected in the second-order approximation.

The black shaded region in Fig. 8.4 corresponds to the solutions obtained by numerically minimizing the \( V(\hat{Q}) \) potential among all the \( q \)-states on the unit sphere, within a range of 5% around the minimal energy. Indeed, the numerically obtained solutions agree well with the minimal-energy regions of the perturbative solution.

The distribution of the \( q \)-states according to Eq.8.3 was fitted to the tomographic SANS data by minimizing the sum of the least-square distances of the experimental \( q \)-vectors from the curves described by the model, parametrized by \( \alpha \) and the modulus of the wavevectors, \( |q| \). The least-square distances were weighted by the SANS intensity corresponding to the given \( q \)-vectors. Minimizing the weighted least-square error yielded the fitting parameters of \( |q| = 0.64 \text{nm}^{-1} \) \( (\lambda = 9.81 \text{nm}) \) and \( \alpha = -0.14 \).

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Figure 8.5: Result of the least-square fitting of the perturbative solution of Eq. 8.3 to the experimental SANS tomography data.

Figure 8.5 shows the fitted manifold of the cycloidal wavevectors, represented by the four colors associated to the four polar domains. The fitted rings are plotted over the tomographic SANS data. There is a good agreement between the model curves and the 3d SANS pattern, underpinning the importance of the fourth-order anisotropy terms in the distribution of the cycloidal wavevectors in GaMo$_4$S$_8$ as opposed to those in GaV$_4$S$_8$. These results together with the short modulation wavelength observed by SANS indicate a significantly stronger spin-orbit coupling in GaMo$_4$S$_8$ as compared to GaV$_4$S$_8$.

8.3 Magnetization measurements on GaMo$_4$S$_8$

I performed static magnetization measurements on GaMo$_4$S$_8$ at the Wigner Research Centre for Physics, using the MPMS SQUID in the laboratory of Dr. L.F. Kiss. The mass of the crystal was $m = 75.4\, \text{mg}$, from the same batch as the one used for the SANS measurements. For the comparison of these magnetization curves and the corresponding phase diagrams with those obtained on crystals from two other batches by Y. Tabata and H. Nakamura at Kyoto University [172] and by S. Widmann at the University of Augsburg [174] please refer to Fig. C.1 in the Appendix. Notably, there is a sample variance in the strength, the shape and even the number of the anomalies in the field dependent susceptibility curves.

Magnetization measurements were carried out in three different configurations, with the magnetic field applied along the [111], [001] and [110] cubic directions of the crystal. The hysteresis of the magnetization in increasing and decreasing fields in the range of $\mu_0 H = 0 - 5\, \text{T}$ was measured at $T = 5\, \text{K}$ after zero-field cooling, as shown in Figs 8.6 (a)-(c). The differential susceptibility curves obtained as the numerical derivative of the magnetization are
displayed in panels (d)-(f). Hysteresis is found particularly at low magnetic fields. The saturation magnetization falls $\sim 40\%$ below $1\mu_B$ per formula unit expected for an $S=1/2$ system, which might be due to a significant amount of non-magnetic secondary phase present within the crystal. The real value of the saturation moment was determined to be $1.05\mu_B$ by Nakamura and colleagues, using a small but high-quality crystal.

![Graphs showing magnetization and susceptibility curves](image)

**Figure 8.6:** Static magnetization measurements on GaMo$_4$S$_8$ with increasing (red) and decreasing (blue) magnetic fields applied along the [111], [001] and [110] cubic directions of the crystal. For the three orientations of the field, the magnetization curves are plotted in panels (a)-(c), respectively. The corresponding differential susceptibility curves, $\partial m/\partial H$ are displayed in panels (d)-(f).

In order to explore the magnetic phase diagram, the magnetization was measured in increasing fields at various temperatures below the Curie-temperature, $T_C = 19\, \text{K}$. Figures 8.7 (a),(b) and (c) show the differential susceptibility curves measured with magnetic fields applied along the [111], [001] and [110] directions, respectively. Multiple anomalies are discernible in the field-dependent magnetization and susceptibility curves, as signatures of metamagnetic phase transitions. The anomalies observed at the lowest sample temperature, $T = 5\, \text{K}$, are indicated by black arrows in the figures. Remarkably, more anomalies are found in the susceptibility curves of GaMo$_4$S$_8$ than in case of GaV$_4$S$_8$ and GaV$_4$Se$_8$, which may indicate the emergence of additional magnetic phases. In particular, five anomalies are discerned.
in the $H \parallel [001]$ configuration, where all the four polar domains are magnetically equivalent [see Fig. 3.3 (b)], therefore all the intermediate magnetic phases are expected to simultaneously emerge in each domain. The modulated magnetic states are extremely robust against the external magnetic fields, extending up to 1-2 T, depending on the field orientation. Since $H_{FM} \propto D^2/J$, this finding corroborates the SANS data evidencing a relatively strong Dzyaloshinsky-Moriya interaction in GaMo$_4$S$_8$ as compared to its sister compounds. The magnetization measurements performed in Kyoto and Augsburg indicate that the modulated states extend down below 2 K [see Figs. C.1 and C.2 in the Appendix].

Figure 8.7: Static susceptibility measurements on GaMo$_4$S$_8$ with the magnetic field applied parallel to the [111], [001] and [110] directions of the crystal, as respectively shown in panels (a), (b) and (c). The susceptibility curves measured at various temperatures are shifted proportionally to the temperature. The black arrows indicate the anomalies in the susceptibility, associated to magnetic phase transitions, at $T = 5 K$.

Figure 8.8 displays the magnetic phase diagrams of GaMo$_4$S$_8$ constructed by reading off the temperature evolution of the critical fields, corresponding to anomalies in the field dependent susceptibility curves. While a cycloidal
Figure 8.8: Magnetic phase diagrams of GaMo$_4$S$_8$ as obtained by static susceptibility measurements for field directions parallel to the [111], [001] and [110] crystallographic directions, displayed in panels (a), (b) and (c), respectively. The black symbols indicate the anomalies observed in the static susceptibility curves. The connecting lines are guides to the eye. The anomalies that appear weaker in the differential susceptibility curves are indicated by smaller dots connected by dashed lines.

(Cyc), as well as a skyrmion lattice (SkL) phase are likely to emerge below the critical field of the field-polarized ferromagnetic (FM) state, the real-space structure of the intermediate phases and the nature of the phase transitions between them are yet unknown.

The differential susceptibility curves reflect the phase transitions in all the coexisting structural domains occurring at different critical fields depending on the relative orientation of the polar axis and the direction of the external field. In order to separate the contributions of each polar domains in the magnetization, complementary magnetic-field dependent SANS experiments were performed.

8.4 Analysis of the magnetic phase diagram of GaMo$_4$S$_8$ by SANS

8.4.1 Field-dependent SANS measurements

SANS data was collected after zero-field cooling in increasing magnetic fields up to $\mu_0 H = 2$ T with 0.1 T steps. In each magnetic field the sample was rocked around the vertical and horizontal axes in 1° steps within the range of $\pm 10°$ and $\pm 5°$, respectively. The SANS images were averaged over all rocking angles. The zero-field paramagnetic background obtained at $T = 25$ K, following the same procedure, was subtracted from each image.

Figures 8.9 (a)-(d) display the SANS images with the incident beam $k_{in} ||
[111], [111], [001] and [110] at three representative magnetic field values applied along $\mathbf{H} \parallel [111]$, [112], [001] and [110], respectively. The sample temperature was $T = 10$ K and $\lambda = 6 \text{ Å}$ neutron wavelength was used with the detector set to a distance of $d = 5$ m using the same collimation length for the data shown in panels (a)-(c). The $\mathbf{H} \parallel [110]$ experiments, shown in panel (d), were done at $T = 1.7$ K with $\lambda = 4.5 \text{ Å}$ and $d = 6$ m settings.

Figure 8.9: Magnetic-field dependence of the SANS patterns in various orientations of the sample and the magnetic field with respect to the neutron beam. Panel (a): $\mathbf{k}_{\text{in}} \parallel \mathbf{H} \parallel [111]$. Panel (b): $\mathbf{k}_{\text{in}} \parallel [111], \mathbf{H} \parallel [112]$. Panel (c): $\mathbf{k}_{\text{in}} \parallel \mathbf{H} \parallel [001]$. Panel (d): $\mathbf{k}_{\text{in}} \parallel \mathbf{H} \parallel [110]$. The main crystallographic directions and the direction of the magnetic field are indicated by white arrows. The white bar in the second column of the images indicates $|q| = 0.4 \text{ nm}^{-1}$. 

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The field dependence of the SANS images reveals two effects occurring simultaneously. On one hand the intensities of the Bragg spots seem to increase at the expense of the smeared regions, suggesting that the modulation vectors are redistributed by the field, confining them to the direction perpendicular to the field. This effect is clearly seen in panel (b), where the cycloidal wavevectors are concentrated to the \( \pm [110] \) directions in response to the perpendicular field along [112]. The same effect was observed in GaV\(_4\)S\(_8\) [P5](see Fig. 6.5) and in GaV\(_4\)Se\(_8\) [P4]. The turning of the spin rotation plane of the cycloids perpendicular to the magnetic field is governed by the gain in the Zeeman energy of the spins exhibiting the largest susceptibility along the direction normal to the cycloidal plane. Moreover, in panels (a)-(c) one can also trace that the \( q \)-vectors become concentrated along the \( \langle 110 \rangle \)-type directions and the intermediate ring structure fades out with increasing magnetic field.

On the other hand, the increase of the magnetic field gives rise to magnetic phase transitions, which may be seen as anomalies in the SANS intensity. Moreover, the vanishing of the scattering intensity at different regions of the SANS pattern indicates the transition to the ferromagnetic state in some of the structural domains. For instance, the third image in Fig. 8.9 (d) shows that the top and bottom Bragg spots vanish in \( \mu_0 H = 1.4 \) T, whereas the peaks in the left and right sides persist up to larger fields. The spatial separation of the scattering contributions of the magnetic structures in the four different polar domains allows for the selective analysis of the phase transitions with respect to the angle between the applied magnetic field and the polar axis of the given domain, as previously done in GaV\(_4\)Se\(_8\) [see section 7.2.1]. In the following, I attempt to separate the critical fields of the magnetic phase transitions by correlating the anomalies in the differential susceptibility curves with those in the SANS intensity within the regions corresponding to specific polar domains, following the same procedure as in the case of GaV\(_4\)Se\(_8\) [see section 7.2.1]. Even though there is a slight difference in the sample temperatures in the two sets of measurements, the magnetization data suggests that the temperature dependence of the critical fields is considerably weak, particularly at lower temperatures, as discerned in the phase diagrams in Fig. 8.8.

8.4.2 Domain-selective analysis of the critical fields by SANS

In the \( H \parallel [001] \) configuration, as it is the case e.g. in Fig. 8.9 (c), each polar domain is magnetically equivalent, characterized by the angle \( \alpha = 54.7^\circ \)
enclosed by the magnetic field and the four polar axes. Figure 8.10 gives a comparison of the field-dependent differential susceptibility measured at $T = 11\, \text{K}$ with the magnetic-field evolution of the SANS intensity and the average length of the $q$-vectors within the four Bragg peaks at $T = 10\, \text{K}$, obtained from the Gaussian fitting of the radial distribution of SANS intensities.

Figure 8.10: Comparison of the magnetic-field dependence of the static magnetic susceptibility (c) with the SANS intensity (d) and the modulus of the $q$-vectors (e), in the $\mathbf{H} \parallel [001]$ configuration, where the magnetic field uniformly spans 54.7° with the polar axes in each domain. The SANS intensity as the function of $|q|$ was extracted from the masked regions indicated in panel (a). The intensity $I$ and the location $|q|$ of the Bragg peaks was retrieved from the $I$ vs $|q|$ plots by Gaussian fitting at each magnetic field. A graphical model of the distribution of the wavevectors in zero field is shown in panel (b) for reference. The dashed lines in Figs. (c)-(e) represent the critical fields associated to the anomalies in the susceptibility curves.

The anomalies observed in the magnetization are also reflected by the SANS data, however, the features appear smeared out due to the field-induced redistribution of the $q$-vectors. The gradual change in the average length of the $q$-vectors around 0.5 T is partially attributed to the fact that the smearing of the Bragg spots vanishes and the intensity is concentrated in
well-defined spots [see Fig. 8.9 (c)]. Note that in larger fields, additional scattered intensity emerges along the two diagonal lines, i.e. the [100] and [010] directions. These are not caused by the magnetic modulations within the domains but by the modulation in the average magnetization from domain to domain through the lamellar rhombohedral domain structure, stacked along any of the ⟨100⟩-type axes. Due to the finite size distribution, the corresponding scattering vectors are not concentrated in spots but appear in elongated areas of the reciprocal space along the ⟨100⟩-type directions. The reason why these scattering seemingly emerges in spots is because of the finite steps in the rocking. This magnetic contribution to the scattering from the submicron-sized structural domains is not subtracted with the background measured in the paramagnetic phase of the material, and becomes stronger with the increase of the magnetic field, persisting even in the ferromagnetic state until the magnetic moments on each rhombohedral domain become parallel to the applied field.

Figure 8.11 shows the same analysis in the $H \parallel [111]$ configuration. Here, the scattering of the unique [111] domain with $\alpha = 0^\circ$ and the three other domains with $\alpha = 70.5^\circ$ are separated as shown in panels (a) and (e), respectively. Note that the regions in panel (a) belong exclusively to the unique domain, while those in panel (e) carry contributions from both the unique domain and one of the other three domains. Two anomalies are identified in the SANS intensity coming from the unique domain, which are also reflected in the susceptibility curve by two peaks at the same locations. These critical fields are thus attributed to phase transitions in the $\alpha = 0^\circ$ domain. The vanishing of the SANS intensity in these regions in magnetic fields close to 1T suggest the onset of a field-polarized FM state in the unique domain.

By exclusion, the other four anomalies observed in the magnetization are attributed to the domains with $\alpha = 70.5^\circ$, featuring clear anomalies in the SANS intensity in the regions marked by panel (b). Note that this analysis excludes the possibility of the redistribution of the SANS intensity from the ring to the ⟨110⟩-type spots within the unique domain. Nevertheless, there is no way to separate the contribution of the two types of domains within those spots for two reasons: 1) the SANS intensities are too weak to quantitatively analyze the rocking curves. 2) in fields above 1T, the $q$-vectors are highly concentrated to the ⟨111⟩ plane in the three other domains as well, therefore the associated peaks start to show rocking.

Remarkably, there is an imbalance in the intensities in the ⟨110⟩-type directions in zero field [see panel (g)], which is equalized at the critical field of the first phase transition. This suggests that the population of the three polar domains are identical and the initial imbalance in the Bragg intensities is caused by the different angular distribution of the $q$-vectors around the
Figure 8.11: Comparison of the magnetic-field dependence of the static magnetic susceptibility with the SANS intensity and the modulus of the $q$-vectors, in the $\mathbf{H} \parallel [111]$ configuration. The magnetic field spans $0^\circ$ with the polar axis in the unique [111] domain, whereas the polar axes of the other three domains enclose $70.5^\circ$ with the field direction. The SANS data in panels (c)-(d), corresponding to the unique domain, and panels (g)-(h), corresponding to the other three domains, were extracted from the masked regions indicated in panels (a) and (e), respectively. A graphical model of the distribution of the wavevectors in zero field is shown for reference. The dashed lines represent the critical fields associated to the anomalies in the susceptibility curves.

Three rings corresponding to these three types of structural domains. If these intensities also originate from the unique domain the equalization would be indicative of the formation of the SkL state, requiring all three $q$-vectors equally populated.

Finally, the $\mathbf{H} \parallel [110]$ configuration is analyzed in Fig.8.12. In this setting, the contributions of the magnetic structures within the two differently oriented polar domains are clearly separated in the SANS pattern. The top and bottom peaks in panel (a) correspond to the two domains with $\alpha = 35.3^\circ$, 

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whereas the four peaks at the left and right side in panel (e) are associated
to the two other domains with $\alpha = 90^\circ$. Panel (g) shows that the modulated
magnetic structures persist up to 2.2 T in the setting where the magnetic
field is applied perpendicular to the polar axis, whereas the field-polarized
state sets in at $\sim 1.2$ T for the domains with $\alpha = 35.3^\circ$. The anomaly seen
in the susceptibility at 0.6 T is reflected in the SANS data associated to the
$\alpha = 90^\circ$ domains [panels (g),(h)], manifesting as turning points in the inten-
sity and the length of the $q$-vectors preceding a steep increase in both.
The three other anomalies in the magnetization are clearly discernible in the
SANS data in the top and bottom peaks, and thus are attributed to phase
transitions in the $\alpha = 35.3^\circ$ polar domains [see panels (c) and (d)].

In the $\alpha = 90^\circ$ configuration, the transverse magnetic field gives rise to a
redistribution of the cycloidal propagation vectors to the plane perpendicular
to the magnetic field, as directly observed by SANS in GaV$_4$S$_8$ [Fig.6.5], and
GaV$_4$Se$_8$ [P4] as well as in GaMo$_4$S$_8$ [Fig.8.2 (b)]. In the present setting, the
wavevectors concentrate to the $\langle 112 \rangle$-type directions, captured by the red
sectors in panel (e), resulting in an increase of the SANS intensity in these
spots. Whereas this redistribution is expected to be continuous in a perfectly
ordered system, no significant change can be discerned in the intensity up
to the first critical field at 0.6 T followed by a steep change in the intensity
and the length of the $q$-vectors in higher fields. This may be the signature
of a pinning of the cycloidal states in low magnetic fields, explaining the
anomalous increase in the magnetization at the depinning field. The gradual
decrease of the SANS intensity above 1.2 T is due to the continuous closing of
the conical angle in the transverse conical state towards the magnetic field.

Here, I note that the anomalies observed in the field dependence of the
susceptibility and the SANS intensity may originate not only from phase
transitions between different magnetic orders but also from avalanche-like
reorientation of the $q$-vectors, governed mainly by the anisotropic suscept-
ibility of the cycloids, the magnetic anisotropy within the rhombohedral
plane and the strength of magnetic pinning. However, based on the present
experimental data set, there is no way to distinguish such sudden $q$-vector
reorientations from true meta-magnetic transitions, therefore, in the follow-
ing we disregard the $q$-vector reorientations when constructing the magnetic
phase diagrams of GaMo$_4$S$_8$, based on the magnetization and SANS data.
To settle this issue, the ultimate experiment would be to perform SANS to-
moscopy in finite magnetic fields, which is not straightforward at all due to
technical and sample limitations.
Figure 8.12: Comparison of the magnetic-field dependence of the static magnetic susceptibility with the SANS intensity and the modulus of the q-vectors, in the $H \parallel [110]$ configuration. The scattering contributions of the two pairs of polar domains characterized by the angles $\alpha = 35.3^\circ$ and $\alpha = 90^\circ$ are located in the regions indicated by panels (a) and (e), respectively. A graphical model of the distribution of the wavevectors in zero field is shown for reference. The dashed lines represent the critical fields associated to the anomalies in the susceptibility curves.

8.4.3 Magnetic phase diagram corresponding to a monodomain GaMo$_4$S$_8$ crystal

On the grounds of the analysis of the SANS data presented above, the critical fields observed in a bulk multi-domain GaMo$_4$S$_8$ crystal can be separated with respect to the angle $\alpha$ between the applied field and the polar axis of the domains. Figures 8.13 (a) and (b) show the assignment of the anomalies in the differential susceptibility curves to different values of $\alpha$ based on the SANS data at $T = 5 K$ and $T = 11 K$, respectively. The critical fields are plotted as the function of $\alpha$ in the polar graphs in panels (c) and (d).
Full circles represent critical fields corresponding to a given $\alpha$, whereas open circles indicate critical fields emerging in the same measurement configuration but belonging to another value of $\alpha$.

The angle-dependent magnetic phase boundaries have been drawn at the lowest and the highest critical fields, indicating the upper field range of the cycloidal phase and the onset of the field-polarized ferromagnetic state. The evolution of the intermediate phase boundaries with the angle $\alpha$ cannot be unambiguously determined. However, the stability range of the modulated structures is apparently larger for oblique magnetic fields than for those parallel with the polar axis. In this sense, GaMo$_4$S$_8$ shows stronger resemblance to GaV$_4$S$_8$, featuring an easy-axis magnetic anisotropy, than to GaV$_4$Se$_8$, characterized by an easy-plane anisotropy. Nevertheless, the SANS tomography in GaMo$_4$S$_8$ indicates that besides the uniaxial anisotropy, cubic magnetocrystalline anisotropy terms may be relevant as well. Therefore, further ESR measurements are needed to establish the nature of the magnetic anisotropy.

Following the temperature evolution of the critical fields, the magnetic phase diagram of a single polar domain of GaMo$_4$S$_8$ is displayed in Fig. 8.14, for various values of $\alpha$. Remarkably, the number of the intermediate modulated phases is apparently larger for oblique angles between $0^\circ$ and $90^\circ$.

A qualitative understanding of the intrinsic phases in the phase diagram could be acquired by Monte Carlo simulations, employing Eq. 2.12 taking the magnetic anisotropy of the cycloidal states into consideration. Additional magnetic phases may emerge due to extrinsic features such as the lamellar structural domains with periodicities close to that of the magnetic modulations. As mentioned above, disorder-induced pinning may also give rise to avalanche-like reorientations of the $q$-vectors, also showing up as anomalies in the susceptibility curves.

The strength of the disorder in both cases depend greatly on the sample quality and therefore the resulting magnetic phases are expected to show substantial sample variance. Indeed, magnetization measurements performed on GaMo$_4$S$_8$ crystals originating from three different batches are significantly different [see Fig.C.1 in the Appendix]. On the other hand, the phase diagrams recovered from the susceptibility data of the three crystals are reasonably similar [see Fig.C.2 in the Appendix], even though the features in the susceptibility curves associated to the critical fields are expressed in a strikingly different manner.
Figure 8.13: Polar magnetic phase diagrams of GaMo₄S₈ at T = 5K (c) and T = 11 K (d), based on the anomalies in the static susceptibility curves (a) and (b), respectively. Black, red and blue colors represent the measurement configurations with the magnetic field parallel to the [111], [110] and [001] axes, respectively. The critical fields are sorted with respect to the polar angles based on the domain-selective analysis of the SANS data. Full circles indicate critical fields at a single field orientation for domains characterized with the given angle, while empty circles represent critical fields measured in the same field configuration but associated to another angle. The lines connecting the lowest and highest critical fields are guides to the eye.
Figure 8.14: Magnetic phase diagrams of a single polar domain of GaMo$_4$S$_8$ as the function of the relative angle, $\alpha$, between the magnetic field and the polar axis. Black symbols represent the anomalies observed in the static susceptibility curves. The size of the symbols indicate the strength of the observed features in the susceptibility data.

8.5 Conclusion

In this chapter, I presented a comprehensive study of the magnetic properties of the lacunar spinel GaMo$_4$S$_8$. Field-dependent magnetization mea-
surements revealed a rich phase diagram of modulated magnetic structures below $T_C = 19$ K, as also confirmed by SANS. Based on the SANS data, the modulation wavelength is $\lambda \approx 10$ nm in the absence of external fields, being twice shorter than that in the other two lacunar spinel compounds studied in this thesis. I carried out SANS measurements upon the wide-angle rotation of the crystal and retrieved the reciprocal-space structure of the zero-field magnetic propagation vectors. The tomographic data indicate that similarly to the GaV$_4$S$_8$, the cycloidal wavevectors populate four rings corresponding to an orientationally disordered state of the cycloidal $q$-vectors within the four structural domains. However, the ring segments between the $\langle 110 \rangle$-type directions deflect out of the $\{111\}$-type planes in an alternating manner, reflecting a threefold rotation symmetry around the polar axes. This structure was well reproduced using an effective potential, assuming the interplay of the DMI and a cubic anisotropy. The strength of the latter is described by the dimensionless parameter, $\alpha = -0.14$, as obtained by the fitting. Finally, the combination of the magnetization and field-dependent SANS data was employed to construct the magnetic phase diagram of a polar mono-domain GaMo$_4$S$_8$ crystal. The modulated phases are extremely robust against both the temperature and applied fields, extending down below 2 K and persisting up to 1.1 T and 1.9 T in fields parallel and perpendicular to the polar axis, respectively. The high critical fields along with the short periodicities of the magnetic textures and the relevance of higher-order anisotropies in the distribution of the magnetic propagation vectors equivocally indicate a relatively strong DMI in this material. The enhanced DMI, as compared to GaV$_4$S$_8$ and GaV$_4$Se$_8$, is likely due to 4d Mo electrons, governing the magnetic properties. The abundance of additional magnetic phases might be an intrinsic feature of GaMo$_4$S$_8$ due to the competition of the Heisenberg-exchange, the DMI, the Zeeman-interaction and the magnetic anisotropy of the magnetic states. Alternatively, a fragmentation of the magnetic phases could be introduced due to disorder and geometrical confinement of the spin textures by the small structural domains or the amorphous phases in the crystals. For a more detailed understanding, Monte Carlo simulations will be performed and the magnetization measurements should be repeated using single-crystalline specimens with a better quality, when available.
Chapter 9

Summary

During my Ph.D. work I studied the structural, pyroelectric and magnetic properties of three compounds, \( \text{GaV}_4\text{S}_8 \), \( \text{GaV}_4\text{Se}_8 \) and \( \text{GaMo}_4\text{S}_8 \), belonging to the lacunar spinel family. This is a new class of polar, magnetic semiconductors, where the Néel-type skyrmion lattice state has been first observed. Using a combination of various experimental techniques, including scanning probe microscopy, static and dynamic susceptibility, electric polarization and small-angle neutron scattering measurements, I have investigated the ferroelastic and pyroelectric domain structure as well as the static and dynamic properties of the non-collinear magnetic structures in this group of materials, namely the cycloidally modulated states and Néel-type skyrmion lattice. I highlighted the similarities and differences between these magnetic patterns and those formerly observed in the cubic helimagnets, the prototypical compounds hosting Bloch-type skyrmions.

The major achievements of my Ph.D. work are summarized in the following thesis points:

1. I investigated the ferroelastic and pyroelectric domain structure of \( \text{GaV}_4\text{S}_8 \) by PFM measurements on the (001) and (111) surfaces [P1]. The measurements were carried out at the Helmholtz Zentrum Dresden using a cryo-AFM setup operated by J. Döring. The PFM micrographs revealed a lamellar domain pattern, arising upon the Jahn-Teller distortion. I determined the possible configurations of the pyroelectric polarization within the structural domains by the analysis of the mechanical and electric compatibility criteria. I found that in general, the primary domain boundaries are electrically neutral and stress-free in this compound. However, incompatibilities are likely to arise at secondary domain boundaries, possibly giving rise to surface charges at the domain walls. I determined the magnitude of the out-of-plane con-
verse piezoresponse components probed by the PFM, being within the range of 1-5 pm/V.

2. I studied the properties of the cycloidal modulations in GaV$_4$S$_8$ by SANS experiments [P5]. The measurements were performed at the Paul Scherrer Institute by J.S. White and S. Bordács, and at the Institute Laue-Langevin by S. Bordács and myself. As a result, the following points have been established:

- I reconstructed the three-dimensional reciprocal-space distribution of the modulation wavevectors via SANS imaging upon the wide-angle rotation of the sample. This provides experimental evidence that the $q$-vectors are distributed over four rings lying within the four \{111\}-type crystallographic planes, corresponding to the planes normal to the rhombohedral axes of the four coexisting polar domains. The confinement of the modulation vectors to these planes are the consequence of the specific DMI pattern imposed by the $C_{3v}$ point group symmetry of the compound. The uniform distribution of the $q$-vectors over the rings indicates the weakness of the magnetic anisotropies in the plane normal to the polar axes.

- Our SANS experiments demonstrate that the cycloidal wavevectors are redistributed within the \{111\}-type planes by an in-plane magnetic field, owing to the magnetic anisotropy of the spin cycloids.

- I analyzed the temperature dependence of the zero-field SANS measurements confirming the second-order nature of the phase transition from the paramagnetic to the Cyc phase as well as the first order characteristics of the Cyc to FM phase transition. The Cyc-FM phase transition is characterized by a broad distribution of the length of the $q$-vectors below a sharp cutoff, indicative of a non-uniform FM state with solitonic-like defects and or fragments of highly anharmonic cycloidal modulations.

3. I studied the low-frequency relaxation of the magnetic structures in GaV$_4$S$_8$ via ac susceptibility measurements, performed at the Wigner Research Centre for Physics, with the assistance of L.F. Kiss [P2]. Through the analysis of the frequency dependence of the complex susceptibility, I estimated the average relaxation times of these magnetic structures, ranging from less than 1 ms to time scales over the minute range in the vicinity of the magnetic phase transitions. These results
indicate the emergence of slow dynamics related to the excitation of magnetic defects in the phase-coexistence regions between the Cyc, SkL and FM phases.

4. I studied the pyroelectric and magnetoelectric polarization and the magnetic modulations in the lacunar spinel GaV$_4$Se$_8$. My work covers the following two topics:

- I investigated the pyroelectric and magnetoelectric polarization arising in GaV$_4$Se$_8$ via pyrocurrent [P3] and magnetocurrent measurements. I performed the experiments at the BME Solid state physics laboratory with the technical assistance of M. Csontos, using a custom-developed measurement system and data acquisition software. I explored the magnetic phase diagram of the compound by the magnetoelectric measurements, which is in good agreement with the phase diagram obtained from magnetization data [P4].

- I analyzed the field-dependent SANS data obtained by J.S. White, S. Bordács and B.Gy. Szigeti at the Institute Laue-Langevin, in order to assign the magnetic phase boundaries specifically to each polar domain [P4]. By comparing the magnetic-field evolution of the SANS intensity in specific regions of the scattering pattern with the anomalies in the differential susceptibility, I determined the phase diagram of a single polar domain of GaV$_4$Se$_8$ for various directions of the applied magnetic fields.

5. I analyzed the pyroelectric [P6] and magnetic properties [P7] of GaMo$_4$S$_8$ based on SPM, differential susceptibility and SANS measurements. The SPM measurements were performed by E. Neuber, P. Milde at TU Dresden, and I was involved in the assessment of the observed domain structures. I performed the magnetization measurements at the Wigner Research Centre for Physics and constructed the magnetic phase diagrams of the compound based on the anomalies in the differential susceptibility. The SANS experiments were carried out at the Oak-Ridge National Laboratory by D. Szaller, L. DeBeer-Schmitt and myself. I determined the 3d distribution of the cycloidal wavevectors, revealing a similar four-ring structure as in GaV$_4$S$_8$, but with the deflection of the $q$-vectors out of the \{111\}-type planes. I used a qualitative model to fit this distribution, underlining the importance of cubic anisotropies in the molybdenum compound, due to the stronger spin-orbit coupling, as compared to GaV$_4$S$_8$. The magnetization data revealed even more robust modulated phases than those in GaV$_4$Se$_8$, extending up to mag-
netic fields of 1-2 T, indicating a strong DMI in this material. By comparing the differential susceptibility and the magnetic-field dependence of the SANS intensity, I constructed the hypothetical magnetic phase diagram of a structurally mono-domain GaMo$_4$S$_8$ crystal. Several additional magnetic phases were observed, whose origin is yet unclear and will be subject to future studies.
List of publications

Publications related to thesis points


Further publications


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Appendices
Appendix A

Ferroelastic and pyroelectric properties of lacunar spinels

A.1 Surface inclination between the rhombohedral domains

As a result of the rhombohedral distortion in each domain, the lattice planes originally parallel to (100) and (111) in the cubic phase become slightly distorted. Consequently, the surface planes of the neighboring rhombohedral domains no longer remain coplanar. Macroscopically, this manifests in an inclination between the surface planes of the crystal, which is detected in the AFM topography as a saw-tooth or rooftop pattern throughout the lamellar domain structure.

Here, I calculate the inclination angles between the distorted (100) and (111) surfaces of two adjoining compatible rhombohedral domains in Ga$_4$V$_4$S$_8$. Pocha et al. [124] report a rhombohedral angle in Ga$_4$V$_4$S$_8$ of 59.66° at 20 K, based on X-ray scattering data. Figure A.1 (a) displays a rhombohedrally distorted cube along the [111]-direction in the Cartesian coordinate system, representing a [111]-type rhombohedral domain. In Fig. A.1 (b) the same [111]-domain is presented together with a [111]-type domain. Mechanical and electric compatibility requires that these two domains are separated by a (001) domain wall [142], i.e. the (x,y)-plane of our coordinate system.

As a result of the distortion, the edges of the two rhombohedra, $\{e_1, e_2, e_3\}$ deviate from the cubic coordinate system, $\{x, y, z\}$. In order to ensure the continuity of the lattice on the two sides, the corners $\{A, B, F, E\}$ and $\{A, B', F', E'\}$ must be matched pairwise. This is achieved by rotating the bases of the rhombohedrons into the $(x,y)$-plane. For this purpose, let us express the $\{e_1,...,e_3\}$ vectors in terms of the rhombohedral angle and the
Figure A.1: Panel (a) shows a rhombohedrally distorted cube along the [111]-axis, representing a [111]-domain in GaV₄S₈. Panel (b) displays two cubes distorted along [111] and [111] visualized in the (x,z)-plane. Mechanical and electric compatibility holds for an interface with (001)-normal, i.e. the (x,y)-plane. The orthogonal transformations described in the text match the A,B,F,E corners of the top cube with the A,B’,F’,E’ corners of the bottom cube, by rotating them into the (x,y)-plane.
axes of the distortions.

The axis of the rhombohedral stretching and the plane perpendicular to this axis [red triangle in Fig. A.1 (a)] constitute the two eigenspaces of the distortion. Therefore, the [111] eigenvector and the three ⟨112⟩-type directions in the two-dimensional eigenspace of the distortion [indicated by black arrows starting from point O in Fig. A.1 (a)] are invariant directions of the distortion. The \{\mathbf{r}_1, \ldots, \mathbf{r}_6\} base vectors in the rhombohedral system are expressed as a function of these invariant directions as:

\[
\begin{align*}
\mathbf{r}_1 &= c_{\text{hex}} \frac{1}{3 \sqrt{3}} \cdot [111] + \frac{2 \sqrt{3}}{3} \frac{a_{\text{hex}}}{2} \frac{1}{\sqrt{6}} \cdot [112] \\
\mathbf{r}_2 &= c_{\text{hex}} \frac{1}{3 \sqrt{3}} \cdot [111] + \frac{2 \sqrt{3}}{3} \frac{a_{\text{hex}}}{2} \frac{1}{\sqrt{6}} \cdot [211] \\
\mathbf{r}_3 &= c_{\text{hex}} \frac{1}{3 \sqrt{3}} \cdot [111] + \frac{2 \sqrt{3}}{3} \frac{a_{\text{hex}}}{2} \frac{1}{\sqrt{6}} \cdot [121] \\
\mathbf{r}_4 &= c_{\text{hex}} \frac{1}{3 \sqrt{3}} \cdot [11\bar{1}] + \frac{2 \sqrt{3}}{3} \frac{a_{\text{hex}}}{2} \frac{1}{\sqrt{6}} \cdot [112] \\
\mathbf{r}_5 &= c_{\text{hex}} \frac{1}{3 \sqrt{3}} \cdot [11\bar{1}] + \frac{2 \sqrt{3}}{3} \frac{a_{\text{hex}}}{2} \frac{1}{\sqrt{6}} \cdot [21\bar{1}] \\
\mathbf{r}_6 &= c_{\text{hex}} \frac{1}{3 \sqrt{3}} \cdot [11\bar{1}] + \frac{2 \sqrt{3}}{3} \frac{a_{\text{hex}}}{2} \frac{1}{\sqrt{6}} \cdot [12\bar{1}],
\end{align*}
\]

where \(a_{\text{hex}}\) and \(c_{\text{hex}}\) are the lengths of the base vectors in the equivalent hexagonal crystal system: \(a_{\text{hex}} = 2 \sin (\alpha_{\text{RH}}/2)\) and \(c_{\text{hex}} = 3 \sqrt{4/3} \cos^2 (\alpha_{\text{RH}}/2) - 1/3\), \(\alpha_{\text{RH}}\) is the rhombohedral angle known from x-ray diffraction data. The unit vectors pointing along the three edges of the rhombohedrons read as:

\[
\begin{align*}
\mathbf{e}_1 &= (\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{r}_3) / ||\mathbf{r}_1 - \mathbf{r}_2 + \mathbf{r}_3|| \\
\mathbf{e}_2 &= (\mathbf{r}_1 + \mathbf{r}_2 - \mathbf{r}_3) / ||\mathbf{r}_1 + \mathbf{r}_2 - \mathbf{r}_3|| \\
\mathbf{e}_3 &= (-\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3) / ||-\mathbf{r}_1 + \mathbf{r}_2 + \mathbf{r}_3|| \\
\mathbf{e}_4 &= (\mathbf{r}_4 - \mathbf{r}_5 + \mathbf{r}_6) / ||\mathbf{r}_4 - \mathbf{r}_5 + \mathbf{r}_6|| \\
\mathbf{e}_5 &= (\mathbf{r}_4 + \mathbf{r}_5 - \mathbf{r}_6) / ||\mathbf{r}_4 + \mathbf{r}_5 - \mathbf{r}_6|| \\
\mathbf{e}_6 &= (-\mathbf{r}_4 + \mathbf{r}_5 + \mathbf{r}_6) / ||-\mathbf{r}_4 + \mathbf{r}_5 + \mathbf{r}_6||
\end{align*}
\]

Now, let us define two rotation matrices to align \(\mathbf{e}_1\) and \(\mathbf{e}_4\) with \(x\), \(\mathbf{e}_1 \times \mathbf{e}_2\) and \(\mathbf{e}_4 \times \mathbf{e}_5\) with \(z\), and the cross-product of the first two vectors in both domains with \(y\):
\[ R_1 = \begin{bmatrix} e_1, & \left(\frac{(e_1 \times e_2) \times e_1}{\| (e_1 \times e_2) \times e_1 \|}, \frac{e_1 \times e_2}{\| e_1 \times e_2 \|} \right) \end{bmatrix}^T, \]
\[ R_2 = \begin{bmatrix} e_4, & \left(\frac{(e_4 \times e_5) \times e_4}{\| (e_4 \times e_5) \times e_4 \|}, \frac{e_5 \times e_6}{\| e_5 \times e_6 \|} \right) \end{bmatrix}^T. \] (A.3)

The (010) and (111) surface normals are expressed in the coordinate system of the two distorted rhombohedrons:

\[ n_{[111]}^{(010)} = \frac{e_1 \times e_3}{\| e_1 \times e_3 \|}, \]
\[ n_{[111]}^{(111)} = \frac{1}{\sqrt{3}}[111], \]
\[ n_{[11]}^{[11]} = \frac{e_4 \times e_6}{\| e_4 \times e_6 \|}, \]
\[ n_{[11]}^{[11]} = \frac{(e_5 + e_6) \times (e_5 - e_4)}{\| (e_5 + e_6) \times (e_5 - e_4) \|}, \] (A.4)

where the lower indices in round parentheses refer to the surfaces in the neighboring domains and the upper indices in squared parentheses denote the axis of distortion in the given domain.

Finally, the normal vectors of the neighboring surfaces are transformed to the Cartesian coordinate system to calculate the inclination angles:

\[ \gamma_{[010]} = \arccos (R_1 n_{[11]}^{[11]} \cdot R_2 n_{[010]}^{[11]}), \]
\[ \gamma_{[111]} = \arccos (R_1 n_{[11]}^{[11]} \cdot R_2 n_{[111]}^{[11]}). \] (A.5)

Substituting \( \alpha_{RH} = 59.66^\circ \) into the above calculation yields \( \gamma_{[010]} = 0.5844^\circ \) and \( \gamma_{[111]} = 0.5515^\circ \). This result shows that a surface inclination of approximately 0.6° is expected to emerge in the topography between different rhombohedral domains on both the (001) and the (111) surfaces.

It is important to note that such changes in the slope of the surface only emerge between rhombohedral domains that have a different magnitude of the out-of-plane strain with respect to the observed surface. This means that the (111) lattice planes of the \([111]\), \([111]\) and \([111]\) rhombohedral domains remain coplanar and thus are indistinguishable by AFM measurements, even though domain walls between pairs of such domains might cross the (111) plane. According to the same argument, the domain pairs of [111] with [111] and [111] with [111] exhibit the same magnitude of out-of-plane deformation.
in the [001] direction. Nevertheless, the compatible domain walls between these domain pairs are parallel to the (001) planes, therefore they are not expected to be visualized at the same time by an AFM scan on the (001) surface.

A.2 Piezoresponse in the paraelectric and pyroelectric phases of lacunar spinels

In this section, I apply symmetry considerations to obtain the finite elements of the piezoresponse tensor in lacunar spinels, in order to determine the expected PFM contrast between the structural domains of GaV₄S₈ in its cubic and rhombohedral phase.

A.2.1 PFM contrast in the cubic phase

Neumann’s principle is applied to obtain the structure of the converse piezoelectric tensor for the two inversion domains of the crystal in the high-temperature cubic phase, as presented in Eqs. A.7. The base vectors of the coordinate system, \{eₓ,eᵧ,eﺯ\}, point along the cubic [100], [010] and [001] directions, respectively. The converse piezoelectric tensor is a rank-3 polar tensor expressing the connection between the strain tensor \(S_{ij}\) and the electric field strength \(E_k\), as written in the Einstein-notation:

\[
S_{ij} = d_{kij}E_k. \tag{A.6}
\]

In the cubic phase, the \(C_2\) rotations around \(x,y,z\) axes eliminate all \(d_{iii}\) and \(d_{ijj}\)-type components, leaving only those \(d_{ijk}\) elements intact, where \(i \neq j \neq k\). Furthermore, the \(C_3\) rotations around the \((111)\) axes require that \(d_{xyz}=d_{yzx}=d_{zxy}\). Due to the symmetric property of the strain tensor, the piezoresponse tensor is also symmetric in its second and third indices. Therefore it is customary to present the piezoelectric and the converse piezoelectric tensors as 6-by-3 rank-2 tensors using the following relabeling of the symmetric indices (Voigt-notation): \(xx \rightarrow 1, yy \rightarrow 2, zz \rightarrow 3, xz \rightarrow 4, yz \rightarrow 5\) and \(xy \rightarrow 6\). The (converse) piezoresponse tensor in the cubic phase of the lacunar spinels takes the following form:
\[
\begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & d & 0 \\
d & 0 & 0 \\
0 & 0 & d
\end{pmatrix}, \quad \begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & -d & 0 \\
-d & 0 & 0 \\
0 & 0 & -d
\end{pmatrix}, \quad (A.7)
\]

where in the upper index the [001] direction refers to that of the z direction determined by the applied electric field, A and B indices denote the two inversion domains and the label 'c' refers to the cubic phase of the compound.

The non-centrosymmetric structure of GaV₄S₈ is responsible for the finite piezo-response, represented by the non-vanishing tensor elements with magnitudes of \(d\) and \(-d\) in the A and B domains, respectively.

The out-of-plane PFM measurement probes the \(d_{zzz}\) element of the inverse piezoelectric tensor, where the z-direction is normal to the scanned surface. When \(z = [001]\), that is when the (001) surface is scanned, the piezo-response vanishes, i.e. \(d_{zzz,001} = 0\).

In order to obtain the magnitude of the piezo-response probed by PFM measurements on the (111) surface of the crystal, i.e. for \(z = [111]\), the \(d_{zzz}\) tensor element is expressed in the coordinate system of the PFM tip, defined by: \(e_x' = 1/\sqrt{2}(10\bar{1})\), \(e_y' = 1/\sqrt{6}(1\bar{2}1)\) and \(e_z' = 1/\sqrt{3}(111)\). Note that the new \(e_z'\) base vector is normal to the scanned (111) plane, whereas \(e_x'\) and \(e_y'\) orthogonal base vectors may be chosen arbitrarily within the (111)-plane without affecting the \(d_{zzz}\)-component. The transformation yields:

\[
d_{[111]zzz, c} = d_{[001]xyz, c} = \begin{cases} 
d & \text{for domain A} \\
-d & \text{for domain B.}
\end{cases} \quad (A.8)
\]

Hence, inversion domain boundaries may be visualized by PFM measurements on the (111) surface in the cubic phase of the compound. Nevertheless, as presented in Section 5.3, no PFM images reveal any contrast above the structural phase transition temperature, suggesting that the scanned surface areas belong to the same inversion domain.

**A.2.2 PFM contrast in the rhombohedral phase**

Below the temperature of the Jahn-Teller transition, the crystal symmetry is reduced to \(C_{3v}\). Remarkably, the \(C_2\) symmetries are lost, which allows for any elements of the converse piezoelectric tensor to be finite. The remaining symmetries in the rhombohedral phase dictate that there are four
independent elements of the piezoresponse tensor, denoted as $d_0, d_1, d_2$ and $d_3$. The form of the tensor in the four different rhombohedral domains is presented in Eqs. A.9 in the Cartesian coordinate system. Again, the upper index denotes the direction of the $z$-axis, while the direction in the bottom index refers to the rhombohedral axis, labeling the given rhombohedral domain. The ‘r’ label refers to the rhombohedral phase of the material. Here, rhombohedral domains originating from a single inversion domain (A) are considered. The corresponding piezoelectric tensors in B crystal domain can be obtained by an overall sign reversal. Also note that the tensors in the different rhombohedral domains are connected by $C_2$ rotations around the cubic $x,y$ and $z$ axes.

\[
\begin{align*}
    d_{[001]}^{[001]}(r) &= \begin{pmatrix} d_1 & d_2 & d_2 \\ d_2 & d_1 & d_2 \\ d_2 & d_2 & d_1 \\ d_3 & d_0 & d_3 \\ d_0 & d_3 & d_3 \\ d_3 & d_3 & d_0 \end{pmatrix} , \\
    d_{[111]}^{[001]}(r) &= \begin{pmatrix} d_1 & -d_2 & d_2 \\ -d_2 & d_1 & d_2 \\ -d_2 & -d_2 & d_1 \\ d_3 & d_0 & -d_3 \\ d_0 & d_3 & -d_3 \\ -d_3 & -d_3 & d_0 \end{pmatrix} , \\
    d_{[111]}^{[001]}(r) &= \begin{pmatrix} -d_1 & d_2 & -d_2 \\ -d_2 & d_1 & -d_2 \\ -d_2 & -d_2 & d_1 \\ d_3 & d_0 & d_3 \\ d_0 & d_3 & d_3 \\ d_3 & d_3 & d_0 \end{pmatrix} , \\
    d_{[111]}^{[001]}(r) &= \begin{pmatrix} d_1 & -d_2 & -d_2 \\ d_2 & -d_1 & -d_2 \\ d_2 & -d_2 & -d_1 \\ -d_3 & d_0 & d_3 \\ -d_3 & -d_3 & d_0 \\ -d_3 & -d_3 & d_0 \end{pmatrix} .
\end{align*}
\] (A.9)

In case of PFM measurements on the (001) plane, the probed tensor component reads:

\[
    d_{zzz}^{[001]}(r) = \begin{cases} \\
    d_1 & \text{for domains } [111] \text{ and } [\bar{1}\bar{1}1] \\
    -d_1 & \text{for domains } [\bar{1}11] \text{ and } [1\bar{1}1] \\
\end{cases}
\] (A.10)

Apparently, the structural distortion gives rise to a finite piezo-response in each structural domain, however, PFM contrast appears only between those with an opposite $z$-component in their distortion direction. Indeed, the domains within both groups can be interchanged by a twofold rotation around the $z$-axis, leaving the $d_{zzz}$ tensor element invariant, while point group transformations that interchange the two pairs of domains reverse the sign of $d_{zzz}$.

The $d_{zzz}^{[111]}(r)$ tensor element probed in (111) plane PFM measurements are
expressed for the four domains via the base transformation from \( \{e_x, e_y, e_z\} \) to \( \{e'_x, e'_y, e'_z\} \) as done previously in the cubic case:

\[
\begin{align*}
    d^{[111]}_{zzz,r} &= \begin{cases}
    2\sqrt{3}/3 \cdot d_0 + \sqrt{3}/3 \cdot d_1 + 2\sqrt{3}/3 \cdot d_2 + 4\sqrt{3}/3 \cdot d_3, \\
    2\sqrt{3}/3 \cdot d_0 - \sqrt{3}/9 \cdot d_1 - 2\sqrt{3}/9 \cdot d_2 - 4\sqrt{3}/9 \cdot d_3,
    \end{cases} \\
    \text{for domains } [111], [\bar{1}11], [\bar{1}11], [1\bar{1}1].
\end{align*}
\]  

Remarkably, the magnitude of the probed piezo-response of the unique [111]-domain and the three other domains is not symmetric to zero, as opposed to PFM measurements in the (001) plane. Instead, the contrast is distributed around a constant baseline, \( 2\sqrt{3}/3d_0 \), with a ratio of 3:1 for the unique [111]-domain selected by the direction of the electric field and the other three domains, respectively. Note that the out-of-plane PFM measurement is unable to reveal any contrast between the three domains with an identical out-of-plane component in their rhombohedral axes.

In the inversion domains, the sign of the probed tensor element is reversed, including that of the baseline term. Therefore, the presence of inversion domains must be reflected in the PFM contrast measured on a (111) surface in the rhombohedral phase, which does not vanish above the structural phase transition. Nevertheless, such inversion domains have not been evidenced throughout my measurements.

### A.3 Complex background subtraction in a real PFM measurement

According to the previous considerations, structural domains with an opposite sign of their out-of-plane deformation direction feature a 180° phase contrast, whereas the amplitude of the PFM signal is proportional to the magnitude of the out-of-plane distortion [175, 176]. However, besides the intrinsic PFM signal, capacitive forces arising between the tip and the sample surface [144] lead to an oscillation of the tip as well, manifesting as a background signal with an arbitrary phase with respect to the intrinsic PFM response. The parasitic baseline signal is typically commensurate with the piezo-response of the sample [144, 145, 177, 178]. Hence, both the PFM amplitude and the phase contrast between the domains may be shifted significantly. The magnitude of the surface vibrations (\( V_R \)) originating exclusively from the converse piezoelectric effect can be estimated from the demodulated
PFM amplitude and phase maps via background subtraction in the complex plane [145].

In case of measurements performed on the (001) surface, the magnitude of the piezo-response is equal in all the four domains (see Eq. A.10), implying that the intrinsic complex PFM signal must be symmetric to zero. Hence, the complex components of the baseline, $V_{X0}$ and $V_{Y0}$, are determined as the spatial average values of the measured in-phase ($V_X$) and out-of-phase component ($V_Y$) of the PFM signal: $V_{X0} = \bar{V}_X$ and $V_{Y0} = \bar{V}_Y$. After subtracting the baseline, the background-corrected signal becomes symmetric to the origin of the complex plane. The magnitude and the phase of the surface piezoelectric vibration thus can be expressed as [145):

$$V_R = \sqrt{(V_X - V_{X0})^2 + (V_Y - V_{Y0})^2},$$
$$\Theta = \arg((V_X - V_{X0}) + i(V_Y - V_{Y0})).$$  \hspace{1cm} (A.12)

In case of experiments performed on the (111) surfaces, the magnitude of the probed piezo-response component of the [111]-domain is expected to be three times larger as compared to the other three domains (see A.11). Therefore, the baseline correction in Eq. A.12 is employed using the modified $V_{X0} = \frac{V_{X+} + 3V_{X-}}{4}$ and $V_{Y0} = \frac{V_{Y+} + 3V_{Y-}}{4}$ complex background components, where $V_{X,Y+}$ and $V_{X,Y-}$ are the average of the maximal and minimal amplitudes in the X and Y channels, respectively.
Appendix B

The effects of symmetrization and smoothing on the reciprocal-space tomographic image of the cycloidal states in GaMo$_4$S$_8$

Figure B.1 compares the tomographic images reconstructed from the wide-angle SANS rotation of the GaMo$_4$S$_8$ sample in zero field. Apparently, the symmetrization (c) and (d) does not introduce artificial features to the images. A lower threshold intensity used for row (c) results in broader rings and also visualizes the streaks observed in the \{100\}-type planes along the \langle 100 \rangle-type directions. Such modulations may be introduced due to the boundary effects of the structural domain walls lying in the \{100\}-type planes on the magnetic patterns.
Figure B.1: SANS reciprocal-space tomography images of the cycloidal states of GaMo$_4$S$_8$ using different noise filtering methods. Panel (a) shows the original image with a threshold intensity of 3.6 in arbitrary units. In the second row (b), the same data is displayed using a strong Gaussian convolutional filtering with a radius of $r = 0.31\text{ nm}^{-1}$ and a FWHM of $\sigma = 0.03\text{ nm}^{-1}$. The effect of the symmetrization of the reciprocal-space volume of the scattered intensity is demonstrated in rows (c) and (d) with the visualization thresholds of 2 and 3.6 units, respectively. The deflection of the rings from the \{111\}-type planes is seen already on the raw data (a), therefore it is not an effect of the symmetrization. The choice of the intensity threshold affects the signal-to-noise ratio and the visualization of the streaks within the \{100\}-type planes along the \langle 100 \rangle-type directions [c.f. rows (c) and (d)].
Appendix C

Comparison of magnetization measurements on different samples of GaMo$_4$S$_8$

Static magnetization measurements were carried out on samples from three different batches of GaMo$_4$S$_8$ crystals by Y. Tabata and H. Nakamura at the Kyoto University, by S. Widmann at the University of Augsburg and by me at the Wigner Research Centre for Physics, using the MPMS SQUID in the laboratory of L.F. Kiss.

Figure C.1 shows the dc susceptibility curves, $\partial m/\partial H$ compared for the three different crystal batches in three configurations of the magnetic field, applied parallel to [100] (a)-(b), [111] (c)-(d) and [110] (e)-(f). Measurements with sample temperatures of $T=5$ K and $T=10$ K are presented. In Budapest, no measurements were performed at $T=10$ K, therefore the measurements at the closest temperature, $T=11$ K are displayed for comparison. Note that the temperature dependence of the critical fields is weak at these temperature ranges. The black arrows mark the anomalies in the dc susceptibility associated to the critical fields of the magnetic phase transitions. Interestingly, the features in the susceptibility are expressed with different relative magnitudes in the three crystals, which is possibly related to the variance in the volume fractions of the structural domains in the different samples. Small shifts of the critical fields may be caused by demagnetization effects or a sample misalignment.

The magnetic phase diagrams of the three samples with the three field orientations of $\mathbf{H} \parallel [111], [001]$ and [110] are compared in Figs. C.2 (a)-(c), respectively. Note that there was no measurement performed in the [110] configuration in Augsburg. The background associated to the phases is colored according to the measurements in Kyoto (black symbols) [172],
Figure C.1: Static susceptibility measurements on GaMo$_4$S$_8$ crystals from three different batches, measured at different locations as shown in the legend. The measurements were performed in three different configurations, with the applied field parallel to [100] (a)-(b), [111] (c)-(d) and [110] (e)-(f) at various temperatures. The measurements at $T=5$ K and $T=10$ K are shown in the first and second column, respectively. Note that in Budapest, the closest sample temperature of the magnetization measurement was $T=11$ K, which is presented together with the two other curves measured at $T=10$ K for comparison. The black arrows indicate anomalies in the susceptibility curves, associated to the critical fields of the magnetic phase transitions. Magnetization data obtained from S. Widmann and H. Nakamura are presented with permission.
Figure C.2: Comparison of the magnetic phase diagrams of GaMo$_4$S$_8$ based on magnetization measurements on three different batches of single-crystalline samples. Panels (a)-(c) display the phase diagrams in the $\mathbf{H} \parallel \{111\}, \{001\}$ and $\{110\}$ configurations, respectively. The coloring of the phases is based on the magnetization data measured in Kyoto (black dots) [172]. The green and red dots represent the measurement data obtained in Augsburg [174] and Budapest [P7].

while the critical fields established by the measurements in Budapest and Augsburg [174] are indicated by red and green dots, respectively. Despite the striking differences in the shape of the features of the susceptibility curves, the location of the anomalies exhibits reasonably good agreement between the three samples. However, some of the anomalies are present only in one or two of the crystals, introducing additional phase boundaries in some of the samples.

Additional magnetic phases might emerge due to the geometrical confinement imposed by the small structural domains with the width scale comparable to the periodicity of the magnetic textures. Pinning due to crystal defects or the structural domains may also introduce additional features as the magnetic structures are depinned and redistributed by the external field. The size distribution of the polar domains and the crystal quality could exhibit significant sample variance, which may account for the observed differences in the susceptibility curves and the magnetic phase diagrams of the samples.
Bibliography


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